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Progress Reports: Advanced Battery Materials Research (BMR) Program & Battery500 Consortium

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A MESSAGE FROM THE MANAGERS: ADVANCED BATTERY MATERIALS RESEARCH AND BATTERY500 CONSORTIUM

It is with great sadness that we report on the loss of our colleague, Dr. Peter Faguy. He passed away on August 12, 2022. Peter joined the Department of Energy (DOE) in 2010 where he was manager of the Applied Battery Research Program, in DOE's Office of Energy Efficiency and Renewable Energy (EERE). His translational R&D portfolio was distributed over several National Laboratories (Argonne, Brookhaven, Lawrence Berkeley, Oak Ridge, National Renewable Energy, Pacific Northwest, SLAC National Accelerator), academia, and industry. He oversaw numerous projects aimed at screening novel materials, developing new processing capabilities, and solving barriers associated with the commercialization of affordable, high-performance batteries for electric vehicles. Peter successfully led these efforts by



building a diverse and inclusive Team of scientists and engineers. Peter's legacy is strong and will continue to guide us as we face new material and cell manufacturing challenges. We will stay focused on his mission to advance battery technologies that will enable an affordable, secure, and clean energy source to move people and goods across America.

A few notable achievements from BMR investigators from April 1, 2022, through June 30, 2022, are summarized below:

- S. Martin's Iowa State University team demonstrated more than 10 hours of room-temperature cycling of their 190-μm-thick glass electrolytes in lithium symmetric cells at current densities of up to 2.5 mA/cm².
- Solid Power (P. Zhang's group) performed calendar life studies on full-cell LiNi_{0.6}Mn_{0.2}Co_{0.2} (NMC-622) / solid-state electrolyte (SSE) / Li-metal batteries, showing capacity retention of 87%. The projected specific energy density of their current cells is 350 Wh/kg and 810 Wh/L.
- D. Lu's group at Pacific Northwest National Laboratory (PNNL) identified a reversible surface coating strategy for enhancing the moisture stability of sulfide-based SSEs using amphipathic organic molecules. Clear suppression of H₂S release was observed when electrolytes were coated with 1-bromopentane, suggesting that the hydrophobic long-chain alkyl tail can effectively repel water molecules.
- The Stanford University / SLAC National Accelerator Laboratory team (Y. Cui / W. Chueh / M. Toney) successfully developed an *operando* electrochemical platform to investigate the mechanical effects on lithium metal intrusion behavior. Along with electrochemical modeling, their study identified two lithium growth modes of pre-intrusion and post-intrusion on a Li₇La₃Zr₂O₁₂ solid electrolyte.
- B. Narayanan's group at University of Louisville has used molecular dynamics to understand the reaction at the Li/Li₇PS₆ and S₈/Li₇PS₆ interfaces. Simulations suggest that Li₇PS₆ undergoes reductive decomposition through the progressive breakdown of the PS₄³⁻ motifs present in the electrolyte. These products bind with lithium atoms to form a solid electrolyte interphase (SEI). Growth of the SEI occurs by formation of bonds between lithium and the P/S atoms from the electrolyte.
- The PNNL team led by P. M. L. Le has developed ether-based electrolytes containing glymes to stabilize the sodium metal during the plating/stripping process. One formulation was found to yield a high Coulombic efficiency (> 99.5%) in Na||Cu half-cells.

A few notable achievements from the Battery500 Team this quarter include:

- The Pennsylvania State University team has developed an electrolyte that has demonstrated promising results in a lithium || LiNi_{0.8}Mn_{0.1}Co_{0.1} (NMC-811) pouch cell. The cell consisting of a high areal capacity (4.0 mAh cm⁻²) cathode, 50-µm-thin lithium anode, and lean electrolyte (3.0 g/Ah), displayed a high gravimetric energy density of 366 Wh/kg and an unprecedented cycling stability with 80% capacity retention after 335 cycles.
- The University of Pittsburgh, Pennsylvania, team employed computational approaches to identify functional electrocatalysts for use in a Li-S cathode. The activation barrier for the conversion of Li_2S_2 to Li_2S was lowered from an average value of ~ 1 eV to ~ 0.6 eV, with the best system demonstrating a value of ~ 0.3 eV.
- The PNNL team successfully developed a prototype 400 Wh/kg Li-metal pouch cell and demonstrated 284 stable cycles with 80% capacity retention, thereby meeting/exceeding the Battery500 Consortium's FY 2022 milestone.
- The Brookhaven National Laboratory and PNNL teams have shown that the degradation of NMC cathodes cycling at high voltage can be solved by a simple interphase engineering approach that uses an ionic additive (LiPO₂F₂) in the electrolyte. A high discharge capacity of 228 mAh/g (97.64%) even after 200 cycles at 4.8 V was obtained, opening a new approach to improve high-voltage performance of NMC cathodes.

Sincerely,

Tien Q. Duong

Tien Q. Duong Manager, Advanced Battery Materials Research Program & Battery500 Consortium Batteries & Electrification R&D Office of Energy Efficiency and Renewable Energy U.S. Department of Energy

Simon Thompson

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TASK 1 – Solid-State Electrolytes Team Lead: Andrew Westover, Oak Ridge National Laboratory

Summary and Highlights

The U. S. Department of Energy (DOE) has made a clear goal of realizing next-generation batteries with an energy density greater than 500 Wh/kg, that can cycle for more than 300 cycles, and that can demonstrate high-rate capabilities. To achieve this step-change in battery performance, a significant change in the battery chemistry and cell design is needed. This task focuses on developing solid-state electrolytes (SSEs) that enable Li-metal anodes and high-energy cathodes to achieve just such a step change. This task includes 12 projects centered in DOE national laboratories and 13 in companies and universities. These projects span the gamut of different materials for SSEs, interfacial design strategies to enable Li-metal anodes, and high-energy cathodes. Together, they can significantly impact the successful realization of the DOE battery performance targets.

In summary, the projects focus on research and development of a range of solid electrolytes (SEs), including:

- sulfur ceramics and glasses (1.1 1.9),
- oxide ceramics (1.10 1.13),
- halides and anti-perovskites (1.13 1.15),
- polymers (1.16 1.18),
- composites (1.19 1.22),
- multiple electrolytes / full cells (1.23 1.24), and
- Li-metal SSE interface (1.25).

These projects encompass common research themes essential to achieving high-energy solid-state batteries (SSBs), including:

- engineering high ionic conductivity > 1 mS/cm,
- developing electrolytes that are stable with various high-energy cathodes, including layered oxide cathodes, high-voltage spinels, and conversion cathodes such as sulfur and FeF₃,
- developing electrolytes or interfaces that are stable with lithium metal,
- developing thin SEs 20-100 μm thick, and
- understanding the mechanics of SSBs.

Highlights

The highlights for this quarter are as follows:

- J. Connell's group at Argonne National Laboratory (ANL) demonstrated the ability to use atomic layer deposition (ALD) to coat sulfide SEs and improve their stability with lithium metal.
- G. Xu's ANL team developed design and synthesis criteria for oxygen and bromine co-doped sulfide-based argyrodite SEs.
- Y. Cui's group at Stanford University determined that the Li₁₀B₁₀S₂₀ has a theoretical conductivity of up to 74 mS/cm and showed an experimental stability window of 1.3-3.0 V versus Li/Li⁺.
- J. Nanda's Oak Ridge National Laboratory (ORNL) team explored the interface between argyrodite SEs and Ni-Mn-C (NMC) cathodes using Raman identifying interfacial species including Li₄P₂S₆ or Li₇P₃S₁₁.

- D. Lu's group at Pacific Northwest National Laboratory (PNNL) used density functional theory (DFT) to estimate the stability of 1-bromopentane coated Li₇P₂S₈Br_{0.5}I_{0.5}. The DFT and corresponding impedance measurements both show improved moisture stability for the 1-bromopentane-coated Li₇P₂S₈Br_{0.5}I_{0.5}.
- S. Martin's Iowa State University team demonstrated more than 10 hours of room-temperature cycling of their 190-µm-thick glass electrolytes at current densities of up to 2.5 mA/cm². They also identified glasses with the best combined viscosity and glass transition temperature for glass drawing.
- P. Zhang's group at Solid Power performed calendar life studies on their full-cell LiNi_{0.6}Mn_{0.2}Co_{0.2} (NMC-622) / SSE / Li-metal batteries, showing a capacity retention of 87%. They also projected the specific energy density of their current cells at 350 Wh/kg and 810 Wh/L.
- D. Wang's Pennsylvania State University team explored the effect of sulfur loading between 2.5 mg/cm² and 6 mg/cm². They found that the higher sulfur loading leads to larger internal resistance, informing requirements for full-cell battery design. Two of their alloy anodes also showed > 100 cycles at 60°C and a 0.1C charge rate.
- T. Yersak's General Motors group demonstrated a LiSiPS glass electrolyte able to cycle at 2 mA/cm² and 2 mAh/cm² for almost 100 cycles. They also demonstrated the ability to modify this structure to make thin reinforced glass electrolyte membranes 110 μm thick by adding a small amount of oxide into the glass.
- J. Ye's team at Lawrence Livermore National Laboratory found that zwitterionic polymer electrolyte Li₇La₃Zr₂O₁₂ (LLZO) composites had significantly improved ionic conductivity compared to poly(ethylene oxide) (PEO)-based electrolytes. They also successfully printed three-dimensional (3D) cathodes based on single-crystal NMC.
- J. Sakamoto's University of Michigan group developed a model to inform "Li free" anode formation in LLZO/Li-metal cells. They found that the stack pressure, interfacial toughness (resistance to fracture or delamination), current collector, and cell geometry all affect plating uniformity.
- E. Wachsman's team at University of Maryland used X-ray diffraction measurements after co-sintering NMC cathodes and LLZO electrolytes in argon and O₂ to show that NMC with higher nickel content is less stable with LLZO, necessitating better stabilization of the high nickel NMC cathodes. They also show ALD coating of Li₂SiO₃ as a potential method to stabilize the high nickel NMC cathodes.
- Z. Chen and T. Li's ANL group found that the best ionic conductivity in their antiperovskite phases was found with the Li₂HOCl_{0.75}Br_{0.25} composition. They also found that exposure to moisture destabilizes the higher ionic conductivity cubic phase.
- J. Nanda's team at ORNL compared the ionic conductivity of different synthesis methods, finding that planetary milling, solution synthesis in water with excess InCl₃ and solution synthesis in ethanol all produced Li₃InCl₆ with room-temperature ionic conductivities of ~ 10⁻³ S/cm.
- D. Qu's University of Wisconsin, Madison, group demonstrated that a full-cell Li-S/SSE/Si cell has good cycling performance with a sulfur loading of 3 mg/cm², showing 500 cycles with less than 20% capacity loss.
- N. Balsara's team at University of California, Berkeley, (UCB) found that multiple poly(pentylene malonate) / lithium bis(trifluoromethanesulfonyl)imide (PPM/LiTFSI) electrolytes have a current fraction greater than 0.5 compared to 0.1 for PEO/LiTFSI electrolytes, suggesting their electrochemical properties may exceed that of PEO-based electrolytes.
- Z. Bao and Y. Cui's Stanford group compared the Coulombic efficiency of hybrid liquid-polymer electrolyte systems. Stanford's SP² electrolyte significantly improved the efficiency in both 1,3-dioxolane / 1,2-dimethoxyethane (DOL/DME) and fluorinated 1,4-dimethoxylbutane (FDMB) based electrolytes, whereas the modified SP²_{Alkyl} polymer with electrolyte affinity only improved performance in the standard DOL/DME electrolyte.

- L. Madsen's team at Virginia Polytechnic Institute and State University performed cycling tests at 23°C of their molecular ionic composites (MIC) with various additives. The most successful was fluoroethylene carbonate, which enabled a room-temperature current density up to 0.35 mA/cm². They also used X-ray absorption and extended X-ray absorption fine structure to demonstrate that the MICs are stable with standard NMC cathodes.
- S. Tepavcevic's ANL group focused on the synthesis of Ga-doped and Al-doped electrospun fibers this quarter. They successfully synthesized undoped, Al-doped, and Ga-doped LLZO nanofibers with a cubic structure. They also performed DFT simulations of the Al-doped and Ga-doped structures and found that gallium is reduced at the LLZO/Ga interface to form a resistive Ga-Li alloy that limits performance.
- X. C. Chen's team at ORNL showed that the mixture of 60% perfluoropolyether (PFPE) 40% PEO has an excellent balance between ionic conductivity and oxidative stability. The ionic conductivity is slightly lower than pure PEO, but with significantly improved oxidative stability highlighting its potential as a catholyte. They also demonstrated that the trilayer composite significantly improves the cycling voltage profile of Li/SSE/Li cells.
- B. McCloskey's UCB group focused on plasticizing their poly((trifluoromethane)sulfonimide lithium methacrylate) (PLiMTFSI) electrolytes this quarter. They successfully incorporated two different polymer plasticizers that improved processability with modest impact on ionic conductivity.
- E. Hu's Brookhaven National Laboratory team synthesized argyrodite sulfide SE powders for future use in their composites with ionic conductivities of 8 mS/cm.
- G. Cedar's team at UCB demonstrated the ability to make 10- μ m-thick Ag-C buffer layers in their first task. Their second task showed that they can successfully synthesize core-shell carbon-cathode composites. In this way, they can successfully protect the SE from the carbon while maintaining the active area. Their third task performed tape casting of LLZO, resulting in 75- μ m-thick LLZO films that are 97% dense with an ionic conductivity of 5 × 10⁻⁴ S/cm. Their fourth task developed methods to solution process PEO-sulfide SE composites, successfully demonstrating the synthesis of Li-P-S-Cl PEO composites with a conductivity of 0.04 mS/cm using ethanol as a precursor.
- A. Burrell's National Renewable Energy Laboratory group developed a new BH_4 -doped $Li_6PS_5Cl_{1-x}(BH_4)_x$ (x = 0-0.5) SE. The properties of the material will be explored next quarter. The team also built a load frame for applying pressure to full pouch cells during cycling. Finally, the team is also working on 3D patterning of cathodes to optimize surface area and improve ion conduction in thick cathodes. They demonstrated the use of laser ablation to make the patterned 3D cathode that can be integrated with a full-cell slurry casting process.
- A. Westover's ORNL team followed up their last quarter's work by performing both nanoindentation and electrochemical testing of different lithium sources. For the mechanics, nanoindentation shows that the thickness of the surface layers does not significantly affect the ability of lithium to relieve stress. On the other hand, electrochemical tests using liquid electrolytes show that the thickness and chemistry of the surface layer significantly impact the interfacial resistance and uniformity of the lithium plating and stripping.

Task 1.1 – Multifunctional Gradient Coatings for Scalable, High-Energy-Density Sulfide-Based Solid-State Batteries (Justin Connell, Argonne National Laboratory)

Project Objective. This task seeks to develop scalable approaches to synthesize gradient-coated sulfide solid-state-electrolyte (SSE) particles to improve their air/moisture tolerance and provide chemical compatibility with Li-metal anodes and high-voltage oxide cathodes. The compositional gradient is targeted to provide the additional advantage of lower interfacial impedance due to mitigation of detrimental, spontaneously formed space-charge layers and/or elemental interdiffusion at the sulfide SSE-oxide cathode interface.

Impact. Development of coated SSE materials that provide stable, low-impedance interfaces with both anode and cathode will enable high-energy-density, all-solid-state full cells with improved cyclability at high rates relative to benchmarked, uncoated materials. Coating the SSE directly will also remove the need for separate anode and cathode coatings, significantly reducing the cost and complexity associated with materials processing while maintaining compatibility with roll-to-roll manufacturing.

Approach. The team will leverage a surface science-based, integrated experimental-theoretical approach to synthesize gradient-coated SSE powders, characterize the structure, composition, and intrinsic stability of coated SSEs in contact with reactive electrodes, and directly correlate this understanding with their electrochemical performance. Gradient coatings will be developed using atomic layer deposition (ALD) and/or physical mixing methodologies viable at the kg/ton scale, ensuring technical and commercial relevance of the final, optimized coating process. Well characterized, model surfaces will be used to understand the electronic structure and chemical stability of the gradient coatings as a function of gradient composition and thickness to understand the effect of space-charge layers and chemical reactions on interface resistance. They will accelerate development and optimization of the gradient coatings for improved performance in full cells by establishing a tight feedback loop between materials synthesis and experimental/computational characterization of interfacial (electro)chemistry.

Out-Year Goals. The out-year goals are to demonstrate high-energy-density, low-impedance full cells assembled from fully optimized, gradient-coated SSE powders, high-energy-density cathodes, and Li-metal anodes. The team will also significantly improve the ability to manipulate the formation of space-charge layers at sulfide SSE-oxide cathode interfaces based on mechanistic understanding of the extent to which they can be mitigated to reduce overall cell impedance.

Collaborations. This project funds work within multiple divisions and directorates at Argonne National Laboratory and includes in-kind contributions from Solid Power.

Milestones

- 1. Baseline Li||Li symmetric cell testing and characterization of uncoated argyrodite SSEs. (Q2, FY 2022; Completed)
- 2. Chemical stability characterization of gradient coatings for argyrodite SSEs. (Q3, FY 2022; Completed)
- 3. Computational assessment of electronic structure of candidate gradient coating chemistries. (Q4, FY 2022; In progress)
- 4. Identification of multiple gradient coating chemistries that deliver > 50% reduction in weight gain during humidified air exposure. (Q1, FY 2023; In progress)

Progress Report

Among the various classes of SSEs that have been investigated to date, sulfide-based SSEs deliver the highest Li-ion conductivities ($\geq 10 \text{ mS/cm}$ in some cases) compared to polymer and oxide SSEs across a wide range of temperatures with favorable mechanical properties and low temperature processability. Argyrodite-based SSEs, with the general formula Li_{7-y}PS_{6-y}X_y (LPSX; X = Cl, Br, I), have emerged as one of the most promising families of sulfide-based materials due to the wide range of compositional control and structural (dis)order achievable depending on the nature and chemistry of the halide dopant. Having established performance baselines for Li-Li symmetric cells with uncoated LPSCl, the team turns their attention to the chemical stability of these materials to ALD coating and contact with lithium metal.

To analyze the stability of LPSCl to coating via ALD, pressed SSE pellets were prepared and inserted into the ALD reactor alongside powders (LPSCl materials were used as received from Ampcera). This provides extended surfaces for X-ray photoelectron spectroscopy (XPS) analysis while ensuring that surface characterization is done on the exact same reaction conditions for coating powders used in subsequent electrochemical characterization. ALD Al₂O₃ coatings were applied at 150°C, with each ALD cycle consisting of alternating half-cycles of trimethylaluminum (TMA) followed by H₂O exposure. The intensity of the aluminum 2p and oxygen 1s signals increases with increasing ALD cycles (Figure 1), consistent with the deposition of Al₂O₃ and a small fraction of Li_xAlO_y onto the SSE. Analysis of the sulfur 2p, phosphorus 2p, and chlorine 2p core levels further reveals that the LPSCl materials are surprisingly robust to the ALD coating chemistry (Figure 1). Specifically, the only chemical reactivity observed on ALD-coated SSEs relative to uncoated materials was found in the sulfur 2p core level, where a small fraction of Li₂S formation is observed ($\leq 10\%$ of the total signal after 10 ALD cycles). No other changes in chemistry are observed in the phosphorus or chlorine core levels after ALD coating, indicating the small amount of reactivity observed is confined to sulfur species in LPSCl. This result is particularly surprising given that each ALD cycle contains one half cycle of H₂O exposure to complete the ALD reaction and form Al₂O₃. Despite the exposure of the surface to pure



Figure 1. Sulfur 2p, phosphorus 2p, chlorine 2p, aluminum 2p, and oxygen 1s core level spectra for Ampcera LPSCI solid-state electrolyte with varying numbers of atomic layer deposition Al₂O₃ coating cycles. Intensities of the sulfur 2p, phosphorus 2p, and chlorine 2p spectra are normalized for comparison.

H₂O at 150°C, there is no evidence of oxidation, for example, SO_3^{2-} formation, which would be observed at $\sim 167 \text{ eV}$ in the sulfur 2p core level spectrum. Identical reactivity is observed on material sourced from NEI. indicating this result is not material specific. The team speculates that the exposure of the SSE surface to TMA, which is highly reducing, leads to the formation of a thin layer of Li₂S that passivates the surface to further reaction with TMA and H₂O. Regardless of the mechanism, however, results are unambiguous that ALD coating of sulfide SSEs is feasible, and leads to negligible reactivity to the underlying material.



Figure 2. Sulfur 2p core level spectra of uncoated LPSCI (left) and LPSCI coated with 10 atomic layer deposition cycles (right) before and after Li-metal deposition.

Not only is LPSCl robust to the ALD coating chemistry, but coating of the SSE with ~ 1 nm ALD Al_2O_3 (10 cycles) results in significantly more stable interfaces with lithium metal. Approximately 10 nm of lithium metal was deposited onto the same SSE pellets analyzed in Figure 1, and utilizing the team's unique, air-free ultrahigh vacuum transfer line, they were able to use XPS to directly measure the reactivity of coated and uncoated materials at the pristine Li-SSE interface. Analysis of the sulfur 2p (Figure 2) and phosphorus 2p (Figure 3) core levels of coated and uncoated material before and after lithium deposition reveals significantly



Figure 3. Phosphorus 2p core level spectra of uncoated LPSCI (left) and LPSCI coated with 10 atomic layer deposition cycles (right) before and after Li-metal deposition.

less reduction of LPSCl that was coated by 10 cycles of ALD Al₂O₃. For both materials, sulfur 2p core level spectra reveal the reduction of PS_4^{2-} species to Li₂S; however, the relative fraction of Li2S formed coated material is on significantly lower: ~ 61% versus 81% of the total signal for coated and uncoated material, respectively. This difference is even more significant considering that $\sim 10\%$ of the SSE coated was already converted to Li₂S during the ALD coating process. Analysis of the phosphorus 2p core-level spectra reveals that phosphorus species are even more protected from reduction by lithium metal

than sulfur species. Specifically, ~ 78% of the phosphorus species on uncoated material is reduced, whereas only 53% of the coated material is reduced by contact with lithium. Furthermore, the majority of the species formed on uncoated LPSCl are assigned to fully reduced Li_3P , whereas a more or less equal fraction of Li_3P and less reduced Li_xP and $Li_{(x-1)}P$ species are observed on ALD-coated SSE, indicating a greater degree of

protection. Taken together, these results indicate the significant promise of the team's ALD coating strategy. Not only are sulfide SSEs surprisingly robust to the ALD coating chemistry, even after direct exposure to TMA and H₂O vapors, but they also provide a significant benefit to materials stability against the highly reducing Li-metal anode. The team anticipates that a wide spectrum of ALD coating chemistries will provide similar benefits to materials stability against reactive electrodes while preserving the underlying SSE chemistry. With these results in mind, they will continue developing additional ALD coating chemistries through a combination of computational assessment and experimental validation of materials stability, electronic structure, and electrochemical performance.

Patents/Publications/Presentations

Patent

 Connell, J. G., and J. W. Elam, Z. D. Hood, and A. U. Mane. "Multifunctional Coatings for Solid-State Electrolyte Powders." ANL-IN-22-023.

Task 1.2 – Electrolytes for High-Energy, All-Solid-State, Lithium-Metal Batteries (Guiliang Xu, Argonne National Laboratory)

Project Objective. The project objective is to develop ultrathin (< $30 \mu m$) sulfide solid-state electrolytes (SSEs) with high room-temperature ionic conductivity (> 0.01 S/cm) and high chemical/mechanical/ electrochemical stability, and further integrate them with lithium metal and high-loading Se-doped sulfur cathodes through rational interface engineering to develop all-solid-state Li-S batteries with high energy density and long cycle life.

Impact. The project is related to development and mass production of high-performance sulfide SSEs for high-energy all-solid-state Li-S pouch cells. The project's success in meeting or exceeding U. S. Department of Energy targets can promote practical implementation of Li-S battery in electric vehicles, electric aviation, and grid energy storage, and hence significantly reduce oil dependence and emissions of carbon dioxide. It can also mitigate the domestic supply challenge on the critical raw battery materials (for example, nickel and cobalt).

Approach. The thickness and chemical/interfacial stability of sulfide SSEs are the critical challenges for energy density, cycle life, and mass production of all-solid-state Li-S pouch cells. The team will combine innovative material design, electrode architecture fabrication, and advanced diagnostics tools to address these challenges. Specifically, the approaches include: (1) improving air stability and ionic conductivity of sulfides through synthetic control and cation/anion doping, and (2) fabrication of flexible thick SeS cathode supported thin sulfide electrolytes to ensure intimate contact and increase energy density, (3) stabilizing Li-metal/sulfide electrolytes interface via interlayer and additives design to increase critical current density of lithium stripping/plating, (4) advanced Li-S pouch-cell design, and (5) multiscale advanced diagnostic such as *in situ* X-ray diffraction (XRD), X-ray absorption spectroscopy, X-ray imaging, and focused ion beam – scanning electron microscopy to understand and overcome the degradation pathways.

Out-Year Goals. The out-year goals are to scale up the optimal sulfide SSEs to develop Ah-level all-solid-state Li-S pouch cells that can reach a cell energy density of > 500 Wh/kg with 80% capacity retention for > 300 cycles at a current density of > 1 mA/cm².

Collaborations. The team is closely collaborating with top scientists at University of Chicago (X. Huang) and at Advanced Photon Source (C. Sun, W. Xu, D. Zhang, and J. Deng) and Center for Nanoscale Materials (Y. Liu and M. Chan) of Argonne National Laboratory for *in situ* diagnostics on the synthesis and aging mechanism of the proposed sulfide SSEs.

Milestones

- 1. Set up a dedicated lab for synthesis, processing, and characterization of sulfide SSEs. (Q1, FY 2022; Completed)
- 2. Reveal the formation and degradation mechanism of sulfide SSE. (Q2, FY 2022; Completed)
- 3. Complete composition tuning of sulfide SSE. (Q3, FY 2022; Completed)
- 4. Develop doped sulfide SSE with high room-temperature ionic conductivity (> 1 mS/cm) and air stability. (Q4, FY 2022; In progress)
Last quarter, the team used *in situ* XRD to investigate the formation mechanism of Li_6PS_5Br and $Li_6PS_5O_{0.2}Br$ during heating/holding/rapid cooling. This quarter, they used *in situ* XRD to monitor the phase transition during synthesis of O-/Br co-substituted argyrodite electrolytes— $Li_{5.5}PS_{4.3}O_{0.2}Br_{1.5}$, aiming to simultaneously improve the air stability and ionic conductivity.

Figure 4a shows the *in situ* XRD patterns during heating a ball-milled mixture of $Li_2S/P_2S_5/P_2O_5/LiBr$ from room temperature to 600°C to form $Li_{5.5}PS_{4.3}O_{0.2}Br_{1.5}$. The results show that in addition to the cubic structure argyrodite solid electrolytes (SEs), there is significant residue of LiBr in the final product, even when the temperature reached 600°C, indicating that bromine has not been successfully incorporated into the 4a sites. This could be due to the larger ionic radii of Br⁻ (182 pm) than S²⁻ (170 pm). The results also indicate that higher temperature might be necessary to substitute more bromine in the Li_6PS_5Br .

Figure 4b shows the selected XRD patterns during cooling from 600°C to 50°C, with a cooling rate of 30°C/min. Strikingly, in addition to the peak shift to higher 2-theta



Figure 4. *In situ* X-ray diffraction patterns during (a) heating (25° C to 600° C) and (b) rapid cooling (30° C/min) of a ball-milled mixture of Li₂S/P₂S₅/P₂O₅/LiBr to form Li_{5.5}PS_{4.3}O_{0.2}Br_{1.5}.

degree due to lattice contraction, the team observes an obvious series of new peaks, as marked at 8.50° , 12.07° , 12.78° , and 14.26° , indicating formation of new phases during rapid cooling. This differs from results in Li₆PS₅Br and Li₆PS_{4.8}O_{0.2}Br, in which rapid cooling does not induce formation of new phases. The reason is unclear; however, results show control of the cooling process would be critical to tailor the phase structure of the final products.

To obtain local structure changes such as lattice parameter, cell volume, phase fraction, microstrain and site disorder as function of temperature, O-content, and Br-content, the team performed Rietveld refinement on all in situ XRD (>400)patterns during synthesis of Li₆PS₅Br, $Li_6PS_{4.8}O_{0.2}Br$, and Li_{5.5}PS_{4.3}O_{0.2}Br_{1.5}. Figure 5 shows the representative weighted-profile **R**-factor (R_{wp}) value of Rietveld refinement results and



Figure 5. (a) Representative weighted-profile R-factor (R_{wp}) value of Rietveld refinement results and (b-f) selected refined *in situ* X-ray diffraction patterns at different temperatures during synthesis of Li₆PS₅Br. R_{wp} represents the weighted profile residual, which is an indicator of refinement results.

selected refined XRD patterns at different temperatures. As shown, the R_{wp} values of all refined 116 patterns are below 7%, indicating a good fitting result. The refined XRD patterns also exhibit a good match between experimental and calculated results.



Figure 6. (a) Lattice parameter *a*, (b) phase fraction of Li_6PS_5Br , and (c) percentage of site disorder as a function of temperature during synthesis of Li_6PS_5Br . (d) Lattice parameter *a*, (e) phase fraction of $Li_6PS_{4.8}O_{0.2}Br$, and (f) percentage of site disorder as a function of temperature during synthesis of $Li_6PS_{4.8}O_{0.2}Br$. (g) Lattice parameter *a*, (h) phase fraction of $Li_{5.5}PS_{4.3}O_{0.2}Br_{1.5}$, and (i) percentage of site disorder as a function of temperature during synthesis of $Li_{5.5}PS_{4.3}O_{0.2}Br_{1.5}$, and (i) percentage of site disorder as a function of temperature during synthesis of $Li_{5.5}PS_{4.3}O_{0.2}Br_{1.5}$. Note: Black line represents the parameter in the left y-axis, while blue line corresponds to the change in temperature in the right y-axis.

Figure 6 shows the lattice parameter, phase fraction, and percentage of site disorder during synthesis of Li_6PS_5Br , $Li_6PS_{4.8}O_{0.2}Br$, and $Li_{5.5}PS_{4.3}O_{0.2}Br_{1.5}$. During heating, the lattice parameter exhibits a gradual increase in all three samples due to thermal expansion and undergoes a sudden decrease during rapid cooling due to thermal contraction. It is also noticed that high-temperature holding could lead to a decrease of lattice constant, which is due to gradual incorporation of oxygen sites in the case of $Li_6PS_{4.8}O_{0.2}Br$ due to smaller ionic radii of O^{2-} (126 pm) than S^{2-} (170 pm). It is also noticed that compared to bromine substitution, oxygen substitution led to a more distinct lattice contraction, indicating chemical bonding between isovalent chalcogen is stronger than the change between halogen elements, leading to better structural stability.

Regarding phase fraction, the team can see that without oxygen or bromine substitution, they could form almost pure $\text{Li}_6\text{PS}_5\text{Br}$ with a percentage of ~ 100% when the temperature reaches 600°C. Oxygen substitution would compete with incorporation of sulfur site, leading to ~ 2 wt% Li₂S in the final product, even after high-temperature holding for 8 hours. In the case of high bromine content, a high amount of ~ 10-12 wt% LiBr residue was observed when the temperature was below 550°C, which was decreased to 8 wt% at a higher temperature of 600°C, indicating a higher calcination temperature might be necessary to achieve high Br-content substitution.

Site disorder is a key factor that can significantly affect the transport of Li⁺, particularly the shorter intercage jump that is the limiting step. Through Rietveld refinement, the team could see slow heating could lead to gradual decrease of site disorder, while rapid cooling caused significant increase of site disorder. This result provided evidence for synthetic control to tailor the site disorder in the argyrodite sulfide SEs. In general, the oxygen substitution at sulfur sites reduces the site disorder because the ionic radii of O²⁻ (126 pm) is much smaller than Br^{2-} (182 pm), which prevents the exchange between bromine and sulfur. In turn, more bromine content would promote site disorder and hence increase ionic conductivity. These findings have provided the team with a valuable guideline to synthesize different structured Br-based sulfide electrolytes.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 1.3 – Thioborate Solid-State Electrolytes for Practical All-Solid-State Batteries (Yi Cui, Stanford University)

Project Objective. This project aims to develop novel lithium thioborates (Li-B-S, LBS) as a new class of solid-state electrolytes (SSEs) to realize high-performance all-solid-state batteries (ASSBs), with a particular focus on addressing the technical challenges in electrolyte synthesis, cell integration, failure diagnostics, and scale-up. The approach will be technologically transformative to the current solutions for ASSB development. For the final deliverables, ASSBs with the ability to reach an energy density of 500 Wh/kg and maintain 80% capacity for at least 300 cycles will be demonstrated.

Impact. The project approaches provide new directions toward developing high-conductivity and electrochemically stable sulfur-based electrolytes for ASSBs. Such high-performance electrolytes can enable the practical realization of ASSBs with a high energy density and improved safety.

Approach. The long-term project has a multistep approach toward integration of LBS with high-voltage cathodes, with steps 1-3 as the focus for this year:

- 1. Fabricate undoped LBS powders using an all-solid-state synthesis method to achieve high ionic conductivity, low electronic conductivity, and a wide operational voltage window.
- 2. Integrate LBS SSEs into symmetric Li/LBS/Li cells and into full batteries using high-voltage cathodes including lithium Ni-Mn-Co (NMC) oxide.
- 3. Study atomic, particle, and cell-scale Li-metal-SSE interface development and dendrite growth mechanisms in SSEs using advanced characterization tools. Use knowledge to better develop SSEs and modify interfaces for stable cycling in full cells.
- 4. Fabricate doped LBS powders and develop particle/surface modifications to increase ionic conductivity as well as stability in full batteries and in air for glovebox-free synthesis.
- 5. Use density functional theory to guide development of new doped LBS materials and to explore interactions at solid-solid interfaces.

Out-Year Goals. In the following year, the team will develop solid-state reaction methods to synthesize undoped LBS powders and construct Li/LBS/Li symmetric cells to test the electrochemical performance of synthesized LBS. Meanwhile, the team will utilize advanced characterization tools [for example, cryogenic electron microscopy (cryo-EM), X-ray computed tomography (CT), etc.] to resolve the nanostructure of Li/LBS interphase and investigate the electrochemical stability between LBS and lithium metal.

Collaborations. The Y. Cui group is collaborating with W. Chueh's group (advanced characterization) and E. Reed's group (crystal structure computation) at Stanford University as well as with Y. Liu (advanced characterization) at SLAC National Accelerator Laboratory.

- 1. Develop solid-state reaction methods to synthesize undoped LBS powders with high ionic conductivity. (Q1, FY 2022; Completed)
- 2. Construct Li/LBS/Li symmetric cells for electrochemical characterizations. (Q2, FY 2022; Completed)
- 3. Study the evolution of Li/LBS interphase. (Q3, FY 2022; Completed)
- 4. Resolve the nanostructure of Li/LBS interphase using advanced characterizations (for example, cryo-EM, CT, etc.). Achieve ionic conductivity of LBS SSE of 1.0×10^{-3} S cm⁻¹. (Q4, FY 2022; In progress)

In a collaboration with the Reed group at Stanford, the team discovered that the theoretical ionic conductivity of LBS SSEs can reach 74 mS cm⁻¹. Motivated by these calculations and by the possibility of discovering a new class of SSEs made from earth-abundant elements, they are working to develop LBS SSEs with high ionic conductivity and high stability for application in full batteries. They have synthesized high-purity $Li_{10}B_{10}S_{20}$ SSE with total resistance of 220 Ω and ionic conductivity of 0.34 mS cm⁻¹ (Figure 7a) under 360 MPa pressure with stainless-steel electrodes. In Li-Li₁₀B₁₀S₂₀-SS asymmetric cells, they measured the voltage stability window to be 1.3-3.0 V versus Li/Li⁺ when measured at room temperature, with a scan rate of 0.1 mV/s.





Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 1.4 – Substituted Argyrodite Solid Electrolytes and High-Capacity Conversion Cathodes for All-Solid-State Batteries (Jagjit Nanda, SLAC Stanford Battery Research Center)

Project Objective. The project aims at synthesis and fabrication of Li-ion conducting argyrodite solid electrolytes (SEs) with nominal composition Li_6PS_5X , where X = chlorine and/or bromine. The team will combine alternating current impedance with complementary *in situ* spectroscopy and microscopy to identify buried interfacial side-reaction products and quantify the voltage losses associated with these side reactions. Specifically, they plan to investigate the interfacial reaction between various Li_6PS_5X SE and Li-ion cathodes belonging to different structural families [transition metal-based sulfides and fluorides (for example, FeS₂ and FeF₂) and high-voltage layered oxides (for example, $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$, NMC-811)]. New dopants such as niobium and partial substitution of sulfur with oxygen will be explored to improve stability of argyrodite SEs against lithium metal and high-voltage cathodes.

Impact. The proposed work addresses key technical barriers to achieve Li-metal SSBs with energy densities of > 450 Wh/kg and 1,000 Wh/L, which are critical for next-generation electric vehicles. Integrating new sulfide SEs prepared through scalable, low-cost solvent-mediated routes with high capacity, earth abundant conversion cathodes (for example, sulfur, FeF₃, and FeS₂) will lower solid-state battery (SSB) cost to \$80/kWh and eliminate use of critical materials such as cobalt and nickel.

Approach. Scalable solution-based processing routes will be developed to produce freestanding sulfide/binder solid-state separators with thicknesses < 50 μ m and area specific resistance < 50 Ω cm². These ultrathin separators will be integrated with Li-metal anodes and high areal capacity conversion cathodes (for example, sulfur, FeS₂, and FeF₃) to demonstrate lab-scale prototype SSBs. As a cross-cut activity, various *in situ* and *ex situ* passivation methods will be combined with enabling characterization techniques to facilitate Li⁺ transport across electrode/SE interfaces.

Out-Year Goals. Optimize SSB performance by: (1) varying cathode composition, particle size, and porosity, (2) applying halide-rich and carbon layers at electrode/electrolyte interfaces, and (3) evaluating how stack pressure (0.1-10 MPa) and temperature (25-75°C) impact performance. Targets: room-temperature cycling with areal capacities > 5 mAh/cm², current densities > 2 mA/cm², stack pressures < 1 MPa, and < 20% capacity fade over 300 cycles.

Collaborations. D. Hallinan and his group are funded collaborators to develop the binder system for sulfide SEs and evaluate compatibility with cathode and Li-metal. P. Jena from Virginia Commonwealth University will be an unfunded collaborator on density functional theory modeling of bulk Li-ion transport and *ab initio* molecular dynamics at SE interfaces.

- 1. Produce Li_6PS_5X (X = Cl, Br, I) SEs using solvent-mediated routes with ionic conductivity $\geq 1 \times 10^{-3}$ S/cm⁻¹ at room temperature. (Q1, FY 2022; Completed)
- 2. Optimize synthesis and annealing conditions to obtain phase-pure SE Li₆PS₅X powders. Evaluate structure using X-ray diffraction, Raman, and neutron scattering. (Q2, FY 2022; Completed)
- 3. Compare the structure and Li⁺ conductivity of Li₆PS₅X prepared through solvent-mediated versus mechano-chemical and solid-state routes. (Q3, FY 2022; Completed)
- 4. Integrate SSB using Li₆PS₅X SE with a working cathode and thin Li-metal anode for testing and capacity optimization. (Q4, FY 2022; In progress)

This quarter's activities explored interfacial stability between a high-voltage Li-ion cathode (LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂, NMC) and model sulfide SE (β -Li₃PS₄). To monitor the interfacial chemistry during

SSB cycling, the team designed a hermetically sealed *in situ* Raman cell (Figure 8) comprised of a mechanical clamp, stainless-steel current collectors, and a G10 composite tube. Using this design, a Li/ β -Li₃PS₄/NMC full cell was fabricated and tested under a stack pressure of ~ 50 MPa. Raman mapping frames were collected at different states of charge (SOCs) to monitor the NMC/SE interfacial chemistry.

An optical micrograph of the NMC/SE interface is shown in Figure 9a. Raman measurements were collected over an area of $60 \,\mu\text{m}^2 \times 120 \,\mu\text{m}^2$ with a step size of 1 µm, and each resultant map contains 7,200 spectra. Α typical spectrum of the bulk sulfide SE is shown in Figure 9b, and the peak centered at 425 cm⁻² is assigned to P-S stretching of the PS_4^{3-} tetrahedra. Figure 9c shows a corresponding Raman mapping frame that was obtained by scaling the intensity of the 425 cm⁻² peak to represent the PS_4^{3-} distribution within the scanned area. Notably, Raman maps based on a single peak intensity do not provide information about multiple phases that are present at the NMC/SE interface.

To provide detailed chemical information at the NMC/SE interface, an unsupervised machine learning method (K-means clustering) was used to process each Raman mapping frame. The basic idea of a K-means clustering algorithm is to partition the total number of Raman spectra (7,200 in this case) into a mapping frame into K groups, where each group contains Raman



Figure 8. (left) Image of in-house developed Raman cell. (middle) Schematic illustration of Raman mapping at the NMC cathode / solid-state electrolyte interface. (right) An *in situ* Raman experiment setup.



Figure 9. (a) Optical microscope image of the NMC / solid-state electrolyte (SSE) interface. (b) Raman spectrum taken from the bulk SSE. (c) Raman mapping based on scaling single-peak intensity of the P-S stretching mode centered at 425 cm⁻¹.



Figure 10. (a) Raman mapping of the NMC / solid-state electrolyte (SSE) interface after K-means clustering analysis. (b) Comparison of centroid spectra taken at the NMC/SSE interface at different states of charge. (c) Magnified view of the P-S stretching mode in (b).

spectra of a certain level of similarity. Different groups are color coded, and the spatial distribution of these groups can be represented through a map, as shown in Figure 10a. The average spectrum (so called centroid spectrum) of each group can be used as the characteristic spectrum of that group. Figure 10b compares the average Raman spectra of the NMC/SE interface at different SOCs. These results indicate that sulfur and polysulfidophosphates (Li₃PS_{4+n}) are the oxidative byproducts after charging the Li/SE/NMC full cell to 4.2 V. After the 1st charge/discharge cycle, the P-S stretching mode red shifts to a lower frequency (Figure 10c), indicating generation of other sulfide compounds, such as Li₄P₂S₆ (with generation of sulfur) or Li₇P₃S₁₁.

Notably, discharging the cell to 2.7 V did not restore the original NMC/SE interfacial chemistry, confirming the presence of irreversible side reactions as detailed by the team's previous electrochemical investigations.

In summary, an *in situ* Raman cell was designed to explore the electrode/electrolyte interfacial structure and chemistry at different SOCs for SSBs containing sulfide SEs. These initial studies focused on a model sulfide material (β -Li₃PS₄), and ongoing efforts are focused on using this capability to evaluate alternative SE chemistries, including argyrodite Li₆PS₅X.

Patents/Publications/Presentations

Publication

 Yang, G., Y. Zhang, E. Self, T. Brahmbhatt, J. C. Bilheux, H. Bilheux, and J. Nanda. "Initial Capacity Loss Mechanism of All-Solid-State Lithium Sulfide Battery Unraveled by *In Situ* Neutron Tomography." IOP Publishing, *Electrochemical Society Meeting Abstracts* 2 (2022): 205.

Presentation

 TechConnect World Innovation Conference & Expo (June 13, 2022): "All-Solid-State Batteries Containing Lithium Thiophosphate Separators"; E. C. Self, F. M Delnick, G. Yang, T. Brahmbhatt, W-Y. Tsai, and J. Nanda. Task 1.5 – Stable Solid-State Electrolyte and Interface for High-Energy, All-Solid-State, Lithium-Sulfur Battery (Dongping Lu, Pacific Northwest National Laboratory)

Project Objective. The project objective is to address material and interfacial barriers of sulfide-based solid-state electrolyte (S-SSE) for deep cycling of Li-metal anode in all-solid-state lithium batteries (ASSLBs). All proposed work will be focused on development of highly conductive sulfide Li⁺ conductors with extremely low Li/SSE interfacial resistance and ultrathin multifunctional interlayer to enable deep and stable lithium cycling. The solid electrolytes (SEs) and interlayer assembly achieved in the project will be tested at practical conditions and validated in realistic Li-S pouch cells.

Impact. ASSLBs have the potential to achieve higher energy and power densities, extending the range of electric vehicles (EVs) and reducing charging time simultaneously. The success of the project would advance the research and deployment of superionic SEs and protective Li-compatible interlayers to support the U. S. Department of Energy Vehicle Technologies Office (VTO) target of developing next-generation ASSLBs for EVs, accelerating market acceptance of long-range EVs required by the EV Everywhere Grand Challenge.

Approach. The project proposes the following approach: (1) to develop Li-compatible superionic S-SSEs and effective coating approaches, (2) to stabilize Li/SSE interface by employing a multifunctional interlayer, (3) to enable robust Li^+/e^- mixed conduction network for a high-loading sulfur cathode, (4) to develop dry processing for SSE film, cathode, and interlayer fabrication, and (5) to advance the mechanism study of the sulfur cathode, lithium anode, and interfaces by multiscale characterization and multiscale modeling.

Out-Year Goals. This project has the following out-year goals:

- Development of Li-metal-compatible S-SSEs with Li/SSE interfacial resistance $< 5 \Omega \text{ cm}^2$ and room-temperature Li⁺ conductivity > 5 mS/cm.
- Operation of lithium anode at critical current density (CCD) > 1 mA/cm², and lithium cycling for at least 400 cycles.
- Ultrathin multifunctional interlayer to enable deep lithium cycling > 4 mAh/cm² to couple high areal-capacity cathode.
- Dry processing of an SSE/interlayer assembly with an overall ionic conductivity > 1 mS/cm.
- Validation of the S-SSE, high-areal capacity cathode, and bilayer assembly in a realistic Li-S pouch cell.

Collaborations. This project engages in collaboration with the following: D. Y. Qu (University of Wisconsin, Madison, or UWM), Z. K. Liu (Pennsylvania State University), C. M. Wang and J. Bao (Pacific Northwest National Laboratory, H. Du (Ampcera Inc.), and Z. Liu (Thermo Fisher Scientific).

- 1. Synthesis of lithium halides doped S-SSE to realize low Li/SSE areal interfacial resistance (AIR, $< 5 \Omega \text{ cm}^2$) and high room-temperature Li⁺ conductivity ($\sigma \sim 6 \text{ mS/cm}$). (Q1, FY 2022; Completed)
- 2. Development of surface treatment approach to improve moisture stability of S-SSE. (Q2, FY 2022; Completed)
- 3. Optimization, characterization, and simulation of Li/SSE interface and its dynamics. (Q3, FY 2022; Completed)
- Optimization of external pressure to improve CCD (> 1 mA/cm²) and Li/SSE/Li cycle life (> 400 cycles). (Q4, FY 2022; In progress)

Last quarter, the team introduced amphipathic organic layer (1-bromopentane, 1BR) onto the S-SSE surface [for example, Li₇P₂S₈Br_{0.5}I_{0.5} (LPSBI)] to enhance its moisture stability. Clear suppression of H₂S release was observed on 1BR coating, suggesting that the hydrophobic long-chain alkyl tail can effectively repel water molecules. This quarter, they investigated the functional mechanism of amphipathic coating for the enhanced moisture stability and its impact on Li/SSE interface. For dry processing of solid-state cell, the UWM team has started screening study of compatible binders for both cathode and solid electrolyte membrane film.



Figure 11. Adsorption of (a) H_2O or (b) 1-bromopentane (1BR) on the stable surface of Li₇P₂S₈Br_{0.5}I_{0.5} (LPSBI). Adsorption of 1BR on LPBSI with $E_{ad} = -0.9 \pm 0.7$ eV / adsorbate-atom is favorable compared to H₂O on LPSBI with $E_{ad} = -0.1 \pm 0.8$ eV/adsorbate-atom.

The mechanism of improved moisture stability due to the introduced 1BR coating was studied by examining the adsorption energy of adsorbate (H₂O versus 1BR molecule) on the LPSBI surface through first-principles calculations based on density functional theory.

$$E_{\rm ad} = E_{\rm adsorbate/LPSBI} - E_{\rm adsorbate} - E_{\rm LPSBI} (1),$$

where $E_{adsorbate/LPSBI}$ is the total energy of the adsorbed H₂O or 1BR on the surface of LPSBI, $E_{adsorbate}$ is the total energy of an isolated H₂O or 1BR molecule, and E_{LPSBI} is the total energy of the relaxed bare LPSBI slab. Equation (1) indicates that a negative adsorption energy (E_{ad}) corresponds to a favorable adsorption process (that is, a strong bonding of adsorbate with respect to 1BR), and vice versa. Figure 11 illustrates the adsorptions of H₂O and 1BR, respectively, on

the surface of LPSBI after structural relaxations by first-principles calculations. It is indicated that the atom oxygen in H₂O is connected to Li⁺ with a bond length of 2.05 Å, while oxygen is far from the other ions (P⁵⁺, S²⁻, Br⁻, and I⁻) on the surface of LPSBI (> 3.2 Å). For 1BR, the atom bromine does not have a distinct bonding preference associated with the ions on the surface of LPSBI, as suggested by its long bond lengths

(> 4.2 Å) with respect to the ions of sulfur, lithium, and phosphorus. The longer bond length of 1BR with respect to LPSBI compared with that of H₂O is due mainly to the larger 1BR molecule and bromine ion (for example, the atomic radius is 120 pm for bromine, while it is 66 pm for oxygen). However, when extracting the absorption energy, the adsorption of 1BR on LPBSI is very favorable (that is, showing a stronger bonding) compared to that of H₂O on LPSBI. The adsorption of 1BR on LPBSI has an $E_{ad} = -0.9 \pm 0.7 \text{ eV}$ (per adsorbate-atom), which is much lower that of H₂O ($E_{ad} = -0.1 \pm 0.8$ eV). This suggests that the 1BR coating is more easily formed thermodynamically on the surface of LPSBI than the adsorption of H₂O, and in turn, provides protection against H₂O vapor attacking, as verified by the present experiments.

The Li/LPSBI interfacial behaviors with/without

1BR coating were studied at different conditions. Figure 12 compares time-dependent electrochemical impedance spectroscopy (EIS) spectra of the LPSBI with/without coating and before/after air exposure (dry room, 0.5% relative humidity). All the LPSBI pellets were pressed under 350 MPa with 700 µm in thickness



spectroscopy of Li/SSE/Li cells. (a) Li/LPSBI/Li, (b) Li/LPSBI-0.5%/Li, (c) Li/LPSBI-Bromo/Li, and (d) Li/LPSBI-Bromo-0.5%/Li.

for EIS measurement. Figure 12a shows that the AIR of pristine LPSBI/Li only increased by 2 Ω after contacting with lithium for 15 hours. With 1BR on the surface, areal resistance increased by 8 Ω after 15 hours (Figure 12c), which is comparable with the pristine LPSBI. After air exposure in dry room, the interfacial resistance for LPSBI-0.5%/Li increased by 50 Ω (Figure 12b), indicating that water reaction products on the surface of LPSBI are not stable with lithium metal and even deteriorate the interfacial stability. In contrast, LPSBI-Bromo-0.5%/Li showed only 12 Ω increasing in interfacial resistance (Figure 12b), similar to LPSBI-Bromo, indicating a good protection effect from 1BR against moisture.

Patents/Publications/Presentations

Publication

 Yu, Z., S-L. Shang, K. Ahn, D. T. Marty, R. Feng, M. H. Engelhard, Z-K. Liu, and D. Lu. "Enhancing Moisture Stability of Sulfide Solid-State Electrolytes by Reversible Amphipathic Molecular Coating." ACS Applied Materials & Interfaces 14, no. 28 (2022): 32035–32042.

Presentation

 VTO Annual Merit Review, Washington, D. C. (June 21–23, 2022): "Scaling-Up and Roll-to-Roll Processing of Highly Conductive Sulfide Solid-State Electrolytes"; D. Lu. Task 1.6 – Development of Thin, Robust, Lithium-Impenetrable, High-Conductivity, Electrochemically Stable, Scalable, and Low-Cost Glassy Solid Electrolytes for Solid-State Lithium Batteries (Steve Martin, Iowa State University of Science and Technology)

Project Objective. The project objective is to develop new Li⁺-conducting mixed oxy-sulfide nitride (MOSN) glassy solid electrolytes (GSEs) that are impermeable to lithium dendrites, have high conductivities, are scalable through low-cost glass manufacturing, are chemically and electrochemically stable, and will enable low-cost, high-energy-density solid-state lithium batteries (SSLBs). The SSLBs constructed from these new GSEs will meet and exceed all program objectives: usable specific energy @ C/3 \geq 350 Wh/kg, calendar life of 15 years, cycle life (C/3 deep discharge with < 20% energy fade) of 1000, and cost \leq \$100/kWh.

Project Impact. This project will enable the team to demonstrate the following: (1) thin MOSN GSE films yield superior performance in a much safer, lower-cost, and Li-dendrite impenetrable form, and (2) high rate and long cycle life can be achieved in SSLBs using thin-film MOSN GSEs. The new GSEs in SSLBs are anticipated to increase energy density (anode basis) from ~ 300 mAh/g to ~ 4,000 mAh/g, enabling replacement of internal combustion engines in both light-duty and heavy-duty vehicles. Each 20% reduction in the ~ 1.6 billion l of gasoline used per day in the United States would reduce CO₂ emissions by ~ 4 billion kg or 2×10^{12} 1 of CO₂ per day. The team will also increase scientific and engineering knowledge of thin-film GSEs in SSLBs.

Approach. The MOSN mixed glass former (MGF) glasses used for the GSEs in this project were developed in previous work to have the necessary thermal stability and high ionic conductivity for successful use as a drawn-film electrolyte. In this project, the glass chemistry will be tuned for even more desirable properties, by investigating structure-property relationships and testing variations in glass chemistry.

Out-Year Goals. Work will progress toward developing a glass capable of being drawn to 100-µm thickness, while having high conductivity and electrochemical stability and good cycling ability.

Collaborations. The team is collaborating with S. Kalnaus and G. Veith (Oak Ridge National Laboratory) on the physical and mechanical properties of oxy-nitride glasses and with Y. Cui (Stanford University) and A. Sendek (Avionics) on new classes of polycrystalline lithium thioborate SE. The team is also collaborating with T. Versak (General Motors) on testing of the GSEs in their solid-state cells.

- 1. Accomplish: Large MOSN MGF GSE preforms $(10 \text{ cm} \times 0.5 \text{ cm} \times 30 \text{ cm})$ demonstrate < 1 vol% crystallization at 90°C above the glass transition temperature (Tg). (Q1, FY 2022; Completed)
- 2. Accomplish: Optimize draw conditions for MOSN GSE to achieve $5 \text{ m} \times 5 \text{ cm} \times < 50 \mu \text{m}$ thin films. (Q2, FY 2022; In progress)
- 3. Accomplish: Fabricate MOSN MGF Li|GSE|Li cells in intermediate area format, ~ 2 cm². (Q3, FY 2022; In progress)
- 4. *Go/No-Go Decision*: Fabricate MOSN MGF GSE cells in large format ~ 5 cm². Cells achieve targeted performance metrics. Analysis indicates technical approach capable of achieving performance targets. (Q4, FY 2022; In progress)

Development of Optimized High Li⁺ Conductivity MOSN MGF GSEs

Further work is being completed to determine the crystallization and viscosity behaviors of MOSN GSEs to expand on the initial crystallization onset measurements. Two new glasses were studied this quarter with compositions shown in Table 1. The crystallization behavior of each glass was determined using isothermal holds to model the time-temperature-transformation (TTT) behavior through the Johnson-Mehl-Avrami-Kohnogorov model.^[1] Figure 13a shows the TTT curve for pure sulfide, mixed-oxy sulfide (MOS), and MOSN glass compositions. The Mauro-Yue-Ellison-Gupta-Allan (MYEGA) model is then utilized to determine the viscosity behavior of each of these same glasses through simple differential scanning calorimetry measurements of the Tg using various heating rates.^[2] Figure 13b shows a comparison between the viscosity behaviors of a pure sulfide, MOS, and MOSN glass. Of the compositions tested, the MOS glass shows the most viable combined viscosity and crystallization properties for usage in thin-film processing, while the sulfide-based glass does not meet the minimum viscosity required for thin-film processing, ~ 10^{11} Pa-s. That is, Figure 13b shows that the sulfide glass crystallizes before, at a lower temperature, it can be heated hot enough to be drawn into a thin film. The MOSN glass can be heated into the low-temperature part of the draw temperature-viscosity range, but it crystallizes in the high-temperature part of the range. The MOS glass, green curve, on the other hand, can be heated up to, through, and even beyond the draw temperature-viscosity temperature range without crystallization. In this way, the MOSN GSE can be safely drawn into a thin film without crystallizing during the draw process. The team anticipates that the MOSN glass composition may have some electrochemical advantages over the simpler MOS glass; because it is "almost" stable against crystallization during the draw process, the team is continuing research to further compositionally refine this MOSN glass to determine if it can be developed to have thermal characteristics consistent with drawing into a thin film without crystallization.

Sample ID	Compositional Formula				
ISU-6 SULFIDE	$0.58 \text{ Li}_2\text{S} + 0.315 \text{ SiS}_2 + 0.105 \text{ LiPS}_3$				
ISU-6 MOS	$0.58 \text{ Li}_2\text{S} + 0.315 \text{ SiS}_2 + 0.105 \text{ LiPO}_3$				
ISU-6 MOSN	$0.58 \ Li_2S + 0.315 \ SiS_2 + 0.105 \ [0.75 \ LiPO_3 + 0.25 \ LiPO_{2.83}N_{0.314}]$				

Table 1. Chemical composition and naming scheme of various mixed oxy-sulfide nitride (MOSN) glasses.



Figure 13. (a) Modeled time-temperature-transformation (TTT) curves showing the 10% crystallization threshold for the pure sulfide, mixed-oxy sulfide (MOS), and mixed oxy-sulfide nitride (MOSN) glasses. (b) Modeled viscosity curves for the three-glass series. Cutoffs for the curves are at the 15-hour mark of each glass on the TTT curve.

Development of Micro-Sheet Glass Ribbon Processing Facility for GSEs

The micro-sheet glass ribbon processing facility located in a large glove box was replumbed this quarter to be able to switch between argon and nitrogen as the working gas. This will allow for easier transportation of fabricated thin films into argon glove boxes for battery testing without contamination of the argon glovebox with nitrogen. Valves were added to the line to be able to easily switch between argon and nitrogen gases.

Development of Processing Conditions for Micro-Sheet Ribbons of MOSN MGF GSEs

Work is being done to create a new preform using extremely high-quality glass. The previous preform has become too small to continue drawing into thin film and has started to show some small defects that are affecting the film drawing process. As such, an entirely new preform is being synthesized with a goal of more than 200 g of glass made through small batches (< 15 g). The previously drawn thin films have been found to be at thicknesses of ~ 180 μ m, with some sections ~ 150 μ m. Figure 14 shows a scanning electron microscopy (SEM) image showing the thickness measurement of a side-view of thin-film ISU-6.



Figure 14. Scanning electron microscopy image showing thickness measurement of drawn thin film ISU-6.

Fabrication and Testing of ASSLBs using GSEs in Large Area Planar Formats

Several thicknesses of thin-film ISU-6 glass have been successfully fabricated into symmetric lithium cells for electrochemical testing. These cells were left to sit while doing electrochemical impedance spectroscopy for 24 hours after fabrication. Following this, the cells were tested in a Novocontrol Dielectric 2 spectrometer equipped with a cryostat to determine temperature-dependent ionic conductivity. These results are compared to that of a polished and sputtered melt-quenched bulk disc in Figure 15a. The resistance values were also normalized to area specific resistance (ASR), and the expected ASR calculated from the bulk conductivity was compared to the experimental ASR in Figure 15b. From this, the film appears to exhibit a slightly lower conductivity than the bulk preform; however, more tests are being conducted to verify conductivity.



Figure 15. (a) Arrhenius plot showing the conductivity of various thin-film samples compared to the conductivity a bulk piece of glass. (b) Expected area specific resistance compared to experimental area specific resistance, showing that the thin films exhibit close to expected behavior.

Some of the symmetric cells tested for conductivity were then transferred to the team's BioLogic VMP-300 for galvanostatic cycling. The thinnest film currently tested is 190- μ m thick. Following 80 cycles at room temperature at 0.05 mA/cm², a critical current density (CCD) experiment was conducted to determine the CCD prior to shorting, with a constant charge of 100 μ Ah/cm². No shorting was observed through 2.5 mA/cm²; thus, the cell was cycled at 2.5 mA/cm² for 100 cycles, showing stable behavior, as can be seen in Figure 16. This is excellent behavior, and the team will be testing more cells soon to verify this result.



Figure 16. Cycling profile for 190-µm thin-film Li|GSE|Li symmetric cell at a constant current of 2.5 mA/cm² showing stable behavior.

Work has been done toward creating full cell Li-S batteries. Based on reports by S. Kinoshita et al., a new method to prepare the cathode composite has been tested.^[3] While Kinoshita utilizes sulfur as a raw material, the team has decided to begin with lithium sulfide, Li₂S, to move toward an anode-free cell design. As such, this new method involves planetary ball milling of a mixture of Li₂S and vapor-grown carbon fibers (VGCF) for 1 hour before adding in ISU-6 as the ionic conductor. The material mass ratios were 45 : 7.5 : 47.5 by Li₂S : VGCF : ISU-6. This was then milled for 1 hour, 5 hours, 10 hours, 15 hours, 20 hours, and 24 hours to determine how the powder changes during milling. X-ray diffraction (XRD) and SEM were conducted to characterize the powder mixtures prior to using them as a cathode. The SEM images from Figure 17a-d show that as the powder is milled for longer times, the overall powder particle size decreases. Furthermore, energy-dispersive X-ray spectroscopy show a well-mixed powder with no particles being distinctly Li₂S, carbon, or glass. This indicates that the utilization of the sulfur in the cathode should be high, which will be confirmed in future experiments. The XRD patterns in Figure 17e show the same peaks at different milling times, with only peaks for Li₂S present, which decrease in intensity and broaden, thus indicating that the Li₂S is becoming strained and potentially amorphous. Future work will contain the cycling behavior of this synthesized cathode.



Figure 17. Scanning electron microscopy images showing the planetary milled powder at milling time of 1 hour (a), 5 hours (b), 15 hours (c), and 24 hours (d). (e) X-ray diffraction pattern of cathode composite sample milled at 1-24 hours showing decreasing peak intensity with milling time.

To assess the performance of SSLBs fabricated with tape-cast electrodes (shown in previous reports) and GSEs, both the long cycling performance and rate capability of full cells were explored. SSLBs were fabricated in 2032 coin cells ~ 1 cm² in area using a Li-metal anode, a monolithic MOS GSE ~ 1 mm thick as a GSE, and a

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tape-cast cathode. A small amount $(0.5 \,\mu\text{L})$ of a solvate ionic liquid was placed at the cathode-GSE interface to improve Li⁺ transport across the otherwise poorly conducting solid-solid interface. Using this cell format, long-term cycling was conducted at a rate of C/50 and has completed 35 full cycles. As demonstrated in Figure 18a, this cell possesses capacities in the range of 90-100 mAh/g throughout its life and consistently achieves Coulombic efficiency > 98% each cycle. The cell's rate capability was tested at C/20, C/10, C/5, C/2, and C/20 for 3 cycles each, shown in Figure 18b. Even after cycling at C/2, the capacity of the cell increased on returning to a capacity higher than that of the original rate of C/20.



Figure 18. (a) Long-term cycling of full-cell solid-state lithium batteries. (b) Rate capability of full-cell solid-state lithium batteries.

Cyclic voltammetry (CV) was also performed on full cells of the same format. A scanning rate of 0.025 mV/s was used from 1.8-4.2 V versus Li/Li⁺. Figure 19 shows the CV of the full cell. An oxidation peak exists at 3.8 V as lithium is extracted from the Li₂S cathode, and a reduction peak at 3.0 V as the reaction is reversed and lithium is reinserted. Outside of these two characteristic redox peaks, no significant electrochemical side reactions were identified, demonstrating the electrochemical stability of this cell format.



Figure 19. Cyclic voltammetry of glassy solid electrolyte (GSE)-containing full-cell solid-state lithium battery.

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References

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- [3] Kinoshita, S., K. Okuda, N. Machida, M. Naito, and T. Sigematsu. "All-Solid-State Lithium Battery with Sulfur/Carbon Composites as Positive Electrode Materials." *Solid State Ionics* 256 (2014): 97–102.

Patents/Publications/Presentations

Presentations

- Glass and Optical Materials Division (GOMD) Annual Meeting, American Ceramic Society (ACerS), Baltimore, Maryland (May 2022): "Effects of Oxy-Silicate Dopants in Li₂S – SiS₂ Based Glassy Solid-State Electrolyte Systems"; J. Wheaton, S. Leland, and S. Martin.
- GOMD Annual Meeting, ACerS, Baltimore, Maryland (May 2022): "Preparation and Characterization of New Li-Si-P-S-O-N Glasses: Comparison of the Effects of Different Starting Materials"; V. Torres, P. Philipp, and S. Martin.

Task 1.7 – All-Solid-State Batteries Enabled by Multifunctional Electrolyte Materials (Pu Zhang, Solid Power Inc.)

Project Objective. The project objective is to develop Li-metal solid-state batteries enabled by multifunctional solid-state electrolytes (SSEs) for electric vehicle (EV) application. The ultimate goal is scalable production of large-format all-solid-state batteries (ASSBs) able to deliver \geq 350 Wh/kg specific energy, \geq 1000 cycle life, and \leq \$100/kWh cost.

Project Impact. The project is enabling scalable production of large-format ASSBs required by the vehicle market and is building domestic battery manufacturers as leaders in the global vehicle ASSB production. The proposed technology will address key limitations of state-of-the-art lithium batteries to meet U. S. Department of Energy EV battery targets and accelerate their adoption as large-format EV batteries for sustainable transportation technology.

Approach. The project will develop a high-performance Li-metal solid-state cell enabled by a multifunctional SSE. The new SSE will (1) have high conductivity (up to 10 mS/cm), (2) be stable against lithium metal and high-voltage cathodes (0-4.5 V), (3) promote uniform lithium plating (enabling > 2C charge rate), and (4) be compatible with large-scale manufacturing processes. The specific cell chemistry to be demonstrated will be the SSE with Li-metal anode and high-nickel-content Li-metal oxide cathode. The solid-state cell will be assembled by scalable roll-to-roll processes developed by Solid Power.

Out-Year Goals. In Year 1, a multifunctional SSE will be developed with lithium ionic conductivity of $\geq 3 \times 10^{-3}$ S/cm. A critical current density of ≥ 6 mA/cm² will be achieved in a symmetric lithium cell. The SSE design concept will be proven by demonstrating a cycle life of ≥ 200 in a full cell. In Year 2, SSE material will be optimized with lithium ionic conductivity of $\geq 5 \times 10^{-3}$ S/cm. Scalable cell assembly processes will be developed. A cycle life of ≥ 500 will be demonstrated in a full cell. In Year 3, large-format solid-state cells (> 2 Ah) will be assembled and tested to meet the final goal: ≥ 350 Wh/kg, ≥ 1000 cycles, and $\leq 100 /kWh cost.

Collaborations. The proposed team consists of Solid Power and a subcontractor, University of California, San Diego (UCSD). Solid Power (principal investigator, or PI: P. Zhang) will develop the multifunctional SSE and other cell components, assemble cells, and conduct cell tests. UCSD (PI: Y. S. Meng) will carry out material characterization by using advanced techniques such as X-ray photoelectron spectroscopy, cryogenic scanning transmission electron microscopy (cryo-STEM) imaging, cryo-STEM energy-dispersive X-ray spectroscopy, electron energy loss spectroscopy, and cryogenic focused ion beam milling. The UCSD team seeks to quantify the kinetics and evolution of each contributing factor and its impact on battery performance.

- 1. Charge rate \geq 2C. (Q1, FY 2022; Completed)
- 2. SSE film \geq 10 m and \leq 40 µm. (Q2, FY 2022; Completed)
- 3. Pouch cell \geq 2 Ah. (Q3, FY 2022; Completed)
- 4. Cycle life \geq 1000. (Q4, FY 2022; In progress)

Pouch Cell Calendar Life

The calendar life was evaluated in a 6 mAh lithium – Ni-Mn-Co (Li-NMC) pouch cell. The cell was formed at 2.5-4.2 V at C/10 and 45°C. It was then charged to 4.2 V at C/10 and 45°C (100% state of charge) and stored at 60°C for 30 days. After the storage, the cell was discharged to 2.5 V ("capacity retention"), recharged to 4.2 V, and discharged again to 2.5 V ("capacity recovery") at C/10 and 45°C. As shown in Figure 20, the cell capacity retention is 87% and recovery is 95%, when compared to the initial discharge capacity, after the storage. Both the capacity retention and recovery from the ASSB cell are better than the conventional Li-ion battery cell at the same testing conditions. The storage result confirms long-term stability of the solid-state electrolyte (SSE) and suggests the ASSB cell has a longer calendar life than the state-of-the-art Li-ion cell.



Figure 20. Calendar life of an NMC/Li-metal all-solid-state pouch cell at 60°C.

Pouch Cell Energy Projection

In this project, the team has demonstrated a multifunctional SSE separator at 40 μ m, LiNi_{0.6}Mn_{0.2}Co_{0.2} (NMC-622) cathode at 3.2 mAh/cm² loading, and stand-alone Li-metal anode at 35 μ m in a full pouch cell.

By applying the current cell parameters to an EV-relevant pouch cell at 100 Ah, the cell specific energy and energy density are projected be 350 Wh/kg and 810 Wh/L, respectively.

In future development beyond the project, the team plans to validate a $LiNi_{0.8}Mn_{0.1}Co_{0.1}$ (NMC-811) cathode in the ASSB cell. By applying the NMC-811 cathode, increasing the cathode loading to 3.5 mAh/cm², and reducing the separator thickness to 35 μ m. An EV cell with energy densities at 400 Wh/kg and 950 Wh/L is achievable.

The key cell design parameters and projected EV cell specific energy and energy density in the current generation and next-generation technologies are summarized in Table 2.

		Key Cell Desig	100 Ah EV Cell Energy Density (Projected)			
Timeline	Cathode Type	Cathode Loading (mAh/cm²)	Lithium Thickness (µm)	Separator Thickness (µm)	Specific Energy (Wh/kg)	Energy Density (Wh/L)
Current Project	NMC-622	3.2	35	40	350	810
Next Generation	NMC-811	3.5	35	35	410	950

Table 2. All-solid-state battery lithium pouch-cell design parameters and projected energy densities.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 1.8 – Developing Materials for High-Energy-Density Solid-State Lithium-Sulfur Batteries (Donghai Wang, Pennsylvania State University)

Project Objective. The project objectives are to develop materials involving advanced S-C composite materials, solid additives, and sulfide-based solid-state electrolytes (S-SSEs) and also to acquire knowledge for ASSLSBs. These batteries—with large areal sulfur loading (\geq 5 mg cm⁻²) and high sulfur content (\geq 50 wt% in cathode), and paired with lithium or Li-alloy anode—will deliver a high initial specific capacity > 1200 mAh g⁻¹ at high charge/discharge rate (> 0.3 C) for 500 cycles with over 80% capacity retention.

Project Impact. This project aims to develop new materials to enable ASSLSBs with high energy density, excellent cycling stability, and good rate performance, and thus to build knowledge for fabrication of prototype ASSLSBs. Specifically, the developed new materials will greatly increase the specific capacity of sulfur and sulfur utilization at high areal sulfur loading, alleviate the interfacial problem between S-C composite and SSE within sulfur cathode, boost Li-ion conductivity, and improve moisture stability of glass and glass-ceramic S-SSEs. Meeting the technical targets will potentially promote development of high-energy-density ASSLSBs and their practical application in EVs and plug-in hybrid EVs and will also reduce petroleum consumption in the transportation sector by helping battery-powered vehicles become more accepted by consumers as a reliable source of transportation.

Approach. The project goal will be accomplished through developing new materials, together with in-depth characterization of sulfur cathodes. Specifically, approaches to realize the project objectives include the following: (1) development of new carbon material with unique structure, high surface area, and large pore volume; (2) development of new S-C and S-C-M_xS_y materials (M = Li, Co, Ti, Mo, etc.) to facilitate electron/ion transport; (3) development of novel additives to tune interfacial behavior among components in the cathode; (4) development and optimization of new SSE through cation and anion doping with superior properties such as high ionic conductivity, good moisture, and stability; and (5) diagnostics, characterization, and cell tests on the developed new material or advanced sulfur cathode.

Out-Year Goals. The out-year goals are as follows: (1) develop and optimize sulfur cathode materials and synthesize new solid electrolytes (SEs; ionic conductivity > 5 mS cm⁻¹ at room temperature), and (2) conduct characterization and performance tests on both material and electrode levels. The final demonstration will be all-solid-state sulfur cathodes with > 1200 mAh g⁻¹ discharge capacity at 0.3 C discharge rate and 50 wt% sulfur content for 500 cycles at room temperature.

Collaborations. There are no active collaborations.

- 1. Demonstrate sulfur cathode with high areal sulfur loading ($\geq 5 \text{ mg cm}^{-2}$) and 50 wt% sulfur content over 1000 mAh g⁻¹ discharge capacity at 0.1 C rate at 25°C for 10 cycles. (Q1, FY 2022; In progress)
- 2. Demonstrate new SE with ionic conductivity > 3 mS cm⁻¹ at 25°C. (Q2, FY 2022; Completed)
- 3. Demonstrate sulfur cathode with high areal sulfur loading ($\geq 5 \text{ mg cm}^{-2}$) and above 50 wt% sulfur content over 1000 mAh g⁻¹ discharge capacity at 0.3 C rate at 25°C for 50 cycles. (Q3, FY 2022; In progress)
- 4. Demonstrate sulfur cathode with high sulfur content (> 50 wt%) and over 1200 mAh g⁻¹ at 0.3 C rate for 500 cycles (< 20% capacity decay) at room temperature, and new SEs with ionic conductivity > 5 mS cm⁻¹ at 25°C. (Q4, FY 2022; In progress)

This quarter, the team systematically investigated the fundamental reasons behind the unsatisfactory performance of sulfur cathodes with high areal sulfur loading at room temperature. Based on the acquired knowledge, generations of sulfur cathodes were developed, that is, PSU-1 and PSU-2. PSU-2 sulfur cathode showed superior rate performance and delivered a high discharge specific capacity of over 1200 mAh g⁻¹ at 0.5 C.

Development of Sulfur Cathode with Superior Performance at Room Temperature

The team investigated the performance of sulfur cathode under different testing conditions (such as temperatures, cathode sulfur loading, membrane thickness, cathode compositions, operation pressure, etc.). For example, they noticed that sulfur cathode performance would significantly deteriorate with lower 1st-cycle Coulombic efficiency and discharged capacities on increasing sulfur loading or decreasing temperatures (Figure 21). Through detailed analysis, the team discovered that the primary cause of this problem is the high internal resistance of the cell, particularly the sulfur cathode, at room temperature or high areal sulfur loading. Therefore, they reduced the membrane thickness, employed SEs with higher ionic conductivity, optimized cathode compositions, and developed new sulfur cathode materials to minimize internal resistance of the batteries.



Figure 21. 1st-cycle galvanostatic charge-discharge curves of sulfur cathodes evaluated (a) with different areal sulfur loading of 2.5-6.0 mg cm⁻² under 60°C and (b) with areal sulfur loading of \sim 2.685 mg cm⁻² at room temperature. The current rate is 0.1 C. Capacities are reported relative to the total amount of sulfur in the system.

Of particular note, the team developed two sulfur cathodes, that is, PSU-1 and PSU-2. The rate performance of the two cathodes with areal sulfur loading of 2-3 mg_{sulfur} cm⁻² is summarized in Figure 22. With enhanced ionic and electronic transport, PSU-1 delivered a good discharge specific capacity of over 1150 mAh g⁻¹ at 0.1 C. However, on increasing the current rate to 0.5 C, the discharge specific capacity of PSU-1 cathode dropped sharply to ~ 550 mAh g⁻¹, signaling that the electron/ion transport within the cathode still needs further optimization and improvement. By optimizing the cathode compositions, preparing procedures, and employing SEs with higher ionic conductivity, PSU-2 sulfur cathodes were successfully developed. Impressively, the PSU-2 cathode delivered a superior specific capacity of over 1200 mAh g⁻¹ at a high current rate of 0.5 C. They will then test the performance of sulfur cathodes with higher areal sulfur loading of > 5 mg_{sulfur} cm⁻² and anticipate that milestones will be fulfilled in future study.

Li-Alloy Anodes for ASSLSBs

The team utilized the high-energy ball-milling method to synthesize Li-alloy anodes for ASSLSBs. To achieve stable and long-term cycling performance, an anode material that is reversible for lithium stripping/plating and has low electrochemical potential versus lithium metal is of importance. They studied various types of lithium alloys and compared their open-circuit voltages, energy density, and electrochemical performance. After optimization of the composition and synthesis procedure, they found an alloy anode material that can cycle stably and deliver high discharge specific capacity of 1404.6 mAh g⁻¹ after 100 cycles as shown in Figure 23 (blue). The full cells were cycled under 0.1 C at 60°C, and the sulfur cathode loading was around 2.19 mg cm⁻². Other than that, the other two types of Li-alloy anode behaved differently. One possessed high



Figure 22. Rate performance of two developed sulfur cathodes, that is, PSU-1 and PSU-2. The areal sulfur loading of the cathodes is 2-3 mg_{sulfur} cm⁻². Cells were tested at room temperature.

discharge capacity of ~ 1400 mAh g⁻¹, but suffered from short-circuit after 20 cycles (red). The other (green) also had good reversibility and high discharge specific capacity of 1215.1 mAh g⁻¹ after 100 cycles. It shows that these types of Li-alloy anodes could be utilized for ASSLSBs and deliver high discharge specific capacities for a long period of time cycling. They are investigating the mechanism of the short-circuit behavior and trying to deeply understand the lithium stripping/plating process within the Li-alloy anodes to achieve an excellent electrochemical performance.





Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 1.9 – Hot Pressing of Reinforced Lithium-NMC All-Solid-State Batteries with Sulfide Glass Electrolyte (Thomas Yersak, General Motors, LLC)

Project Objective. The project objective is to research, develop, and test Li-NMC all-solid-state batteries (ASSBs) capable of achieving program performance metrics by implementing sulfide glass solid-state electrolytes (SSEs) and hot-press processing in a dry-room environment. The performance of ASSBs with sulfide SSEs is limited because they are essentially green tapes with up to 20% porosity. In composite cathodes, the porosity limits energy density and power, while porosity in the separator acts as a conduit for Li-metal deposits if cycling conditions (C-rate, operating temperature, and pressure) are not strictly controlled. The project goal is to demonstrate that the hot-pressing method and appropriately formulated sulfide glass SSEs can eliminate porosity to enable Li-NMC ASSBs with energy density of > 350 Wh/kg.

Project Impact. The hot-press processing method and appropriately formulated sulfide glass SSEs may enable Li-NMC ASSBs with improved energy density > 350 Wh/kg. The GM processing technology depends on heating a sulfide glass SSE above its transition temperature, at which point it can consolidate via viscoplastic flow. In the composite cathode, hot-pressing provides liquid-like contact between the NMC cathode and SSE to increase energy density and power by enabling thick composite cathodes with high active material loading. Furthermore, cathode-supported sulfide glass separators can be made dense and thin by hot-pressing. A dense separator enables the use of Li-metal anodes because lithium deposits may be more effectively blocked, preventing cell shorting.

Approach. The sulfide SSE used in the composite cathode, otherwise known as the catholyte, will dictate the processing specifications for ASSB hot-pressing. Thermal stability can be achieved by NMC passivation and proper catholyte formulation. This project will systematically evaluate different NMC coatings, catholyte formulations, and hot-press processing specifications (temperature, time, and pressure). The performance of hot-pressed ASSBs will be compared to green baseline ASSBs and hot-pressed control ASSBs consisting of the β -Li₃PS₄ and Li₆PS₅Cl model SSEs. Electron microscopy will be employed to understand interfacial phenomena and track composite cathode microstructure before and after hot-pressing.

Out-Year Goals. In the second year of this project, a sulfide glass SSE will be formulated specifically for use as the separator. The separator glass SSE formulation will be designed to achieve full densification under the hot-press processing specifications determined for the catholyte. Separator glass formulation design will also consider cathodic stability, moisture stability, and ionic conductivity. Once a system of separator glass SSE and catholyte has been determined, the third year of the project will demonstrate hot-pressed full cells at the coin-cell and single-layer pouch-cell levels, meeting program target performance metrics.

Collaborations. GM will lead this project with no subrecipients.

- 1. Report ionic conductivity of separators with multifunctional reinforcement. Decide whether to carry forward multifunctional reinforcement for the remainder of the project. (Q1, FY 2022; Completed)
- Demonstrate that H₂S generation of target separator glasses and catholytes can be cut by 50% in a -40°C dewpoint dry-room environment. Report functional characteristics of SSEs after exposure. (Q2, FY 2022; Completed)
- 3. Based on results collected during Budget Period 2, the best performing separator glasses will be carried forward for the remainder of the project. (Q3 FY 2022; Completed)
- 4. Retrofit glovebox: implement a simulated dry-room environment inside an inert glovebox by designing and installing custom equipment. (Q4, FY 2022; In progress)

This report describes progress toward achieving a SSE separator performance metric. Here, the team presents two datasets. In the first dataset, a melt cast LiPSiS glass wafer was combined with an ether-based liquid electrolyte (LE) to achieve a critical current density (CCD) of 3.0 mA/cm² at a stack pressure of only 0.1 Mpa.^[1] In the second dataset, third-party testing showed a cycle life of nearly 100 cycles at current density of 2 mA/cm² for a hot-pressed, reinforced LiPS pellet. Detailed descriptions for each dataset are provided below. The team concludes with a summary of the strategy they employed to reduce this technology to practice.

Dimethoxyethane (DME) and 1,3 dioxolane (DOL) are popular LE solvents for Li-metal batteries. The team therefore evaluated the solubility of $(\text{Li}_2\text{S})_{60}(\text{SiS}_2)_x(\text{P}_2\text{S}_5)_{40-x}$, $(0 \le x \le 40)$ sulfide glass SSEs in 1:1 (v/v) DME:DOL, and the data are provided in Figure 24.^[1] SiS₂-rich glasses within the compositional range of $x \ge 28$ were found to be insoluble in DME:DOL (Figure 24a). Insolubility of $x \ge 28$ compositions was confirmed with Raman spectroscopy (Figure 24b-c). Glass wafers with a composition of $(\text{Li}_2\text{S})_{60}(\text{SiS}_2)_{12}(\text{P}_2\text{S}_5)_{28}$ were prepared by melt casting, as previously described.^[2] Hybrid symmetric lithium test cells with a thin LE layer [0.6 M LiTFSI + 0.4 M LiNO₃ in 1:1 (v/v) DME:DOL] at the interface between Li-metal electrodes and an insoluble (Li₂S)₆₀(SiS₂)₂₈(P₂S₅)₁₂ glass wafer were tested. Hybrid test cells delivered a CCD of 3.0 mA/cm² at 25°C and 0.1 MPa, which is nearly double the CCD of comparable dry symmetric test cells cycled at 10× higher stack pressure (Figure 25).



Figure 24. (a) Solubility times series for $(Li_2S)_{60}(SiS_2)_x(P_2S_5)_{40-x}$ (x = 0, 4, 20, 28, 40) glasses soaked in 1:1 (v/v) DME:DOL. After 2 weeks, the x = 0, 4, and 20 sample solutions show signs of discoloration, which is attributed to dissolution of the glass. The x = 28 and 40 sample solutions remain clear over the course of the experiment. (b) Raman spectra of pristine DOL:DME solvent and solutions obtained by soaking $(Li_2S)_{60}(SiS_2)_x(P_2S_5)_{40-x}$ (x = 0, 4, 20, 28, 40) glasses in DME:DOL. The locations of structural unit vibrational modes are indicated with colored bars from left to right; namely, $P_2S_7^4$ (pink), $P_2S_6^4$ (blue), PS_4^3 (green), and S_8 (orange). Two vibrational modes of DME:DOL are also indicated (brown). (c) Summary of dissolved species as a function of glass composition.

LiPSiS melt-cast wafers are not practical for two reasons. First, sulfide glass melts are extremely volatile and corrosive and require process temperatures above 1000°C. Second, glass wafers are very brittle and easy to break. For these reasons, the team's previous work demonstrated that $(Li_2S)_{70}(P_2S_5)_{30}$ sulfide glass could be fully consolidated by hot pressing at 240°C and 370 MPa pressure.^[3] Several hot-pressed, reinforced SSE pellets with dimensions of ~ 25 mm in diameter and 1 mm in thickness were sent to a third party for testing, and the results are provided in Figure 26. The pellet was cycled under progressively higher current densities from 0.1 mA/cm² to 2.0 mA/cm². Nearly 100 hundred cycles were achieved with a current density of 2.0 mA/cm² and an areal capacity of 2.0 mA/cm².



Figure 25. Critical current density (CCD) of symmetric Li / solid-state electrolyte (SSE) / Li test cells with or without a liquid electrolyte (LE) interlayer and different stack pressures at 25°C. The SSE separators are $(Li_2S)_{60}(SiS_2)_{26}(P_2S_5)_{12}$ glass wafers of ~ 600 µm thickness. (a) A test cell with direct Li/SSE contact and 3 MPa stack pressure experiences shorting failure at a CCD of 1,800 µA cm⁻². (b) A hybrid test cell with LE Li/SSE interlayer and a 0.1 MPa stack pressure experiences shorting failure at a CCD of 3,000 µA cm⁻². Note: the test was paused for two days at 20 hours due to a planned facility power outage.

To translate this result to practice, the team considered two system changes. First, the sulfide glass composition was tuned for manufacturability by adding a P_2O_5 co-former. The P_2O_5 co-former slows down glass

crystallization kinetics by a factor of 10 to enable processing at low pressure and short time. With a $(Li_2S)_{70}(P_2S_5)_{25}(P_2O_5)_5$ glass composition, they fabricated a 40 cm⁻² stand-alone separator with non-woven aramid fiber reinforcement, a porosity of 8.6%, a thickness of ~ 110 µm thick, and an ionic conductivity of 0.75 mS cm⁻¹ (Figure 27). These separators will be used in future pouch-cell studies. Second, they evaluated use of solvate ionic liquids as an interfacial electrolyte since they are non-volatile and non-flammable interfacial LE. The team collected data that show 70Li₂S·(30-x)P₂S₅·xP₂O₅ (x = 0, 2, 5) glass electrolytes are insoluble in Li(G3)TFSI. G3 refers to triglyme.



Figure 26. Third-party validation of a 1-mm-thick hot-pressed LiPSO sulfide glass pellet reinforced with Kevlar fiber pulp.



Figure 27. Oxysulfide glass separator with 0.75 mS/cm ionic conductivity and 110 μm thickness.

References

- [1] Yersak, T. A., et al. *Materials Advances* 3.8 (2022): 3562–3570.
- [2] Yersak, T. A., et al. Journal of The Electrochemical Society 166.8 (2019): A1535.
- [3] Yersak, T. A., et al. ACS Applied Energy Materials 2.5 (2019): 3523–3531.

Patents/Publications/Presentations

Publication

 Yersak, T. A., et al. "Moisture Stability of Sulfide Solid-State Electrolytes." Frontiers in Energy Research (2022). doi: 10.3389/fenrg.2022.882508.

Task 1.10 – Three-Dimensional Printing of All-Solid-State Lithium Batteries (Jianchao Ye, Lawrence Livermore National Laboratory)

Project Objectives. The project has two primary objectives: (1) down select three-dimensional (3D) printing and post-processing approaches for solid-state electrolyte (SSE) / cathode integration, and (2) understand battery failure mechanisms via *ex situ* and *in situ* characterization.

Impact. The adoption of thin separator layer, thick cathode structure, and metallic lithium anode will lead to electric vehicle batteries with > 350 Wh/kg energy density for increased mileage per charge. The higher ionic conductivity with suppression of lithium dendrite growth will allow high critical current densities for fast charging applications. The improved electrode/electrolyte contact will increase battery cycle life for long-term service.

Approach. The technical approaches include advanced manufacturing based on 3D printing and related techniques, *ex situ / in situ* characterizations, and battery testing. Direct-ink writing 3D-printing techniques will be employed to fabricate thin-film SSEs (< 100 μ m), gradient SSEs, and 3D interfaces for battery performance evaluation. Three approaches, including sintering-free, hybrid, and co-sintering, will be investigated. The knowledge obtained from these approaches is transferable and complementary to each technique.

Out-Year Goals. The long-term vision of the team is to 3D-print all components of the all-solid-state lithium battery (ASSLB) to facilitate the scale-up of ASSLB manufacturing. In this project, the team will tackle the issues emerging from integrating solid electrolyte (SE) with electrodes. The project goal is to demonstrate a successful 3D-printing approach to integrate SSE into electrodes and show reasonable capacity retention (that is, > 80%) after 300 cycles at current density $\geq 1 \text{ mA/cm}^2$.

Collaborations. The team will work closely with a computational partner (Task 3.11 led by B. Wood) to better understand battery failure mechanisms and design new battery architectures and chemistries for performance improvement. The team is collaborating with Dr. S. Kim and Dr. G. Cheng from University of Illinois at Chicago on composite polymer electrolyte (CPE) development.

- 1. Determine the polymer / Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂ (LLZTO) interfacial chemistry effects on the total ionic conductivity and Li⁺ transference number. (Q2, FY 2022; Completed)
- 2. Improve conductivity and strength of CPEs. (Q3, FY 2022; In progress)
- 3. Obtain porous co-sintered LLZTO-SSE / Ni-Mn-Co (NMC) / C electrolyte/cathode bilayer structure. (Q4, FY 2022; On schedule)

Mechanical properties (Modulus E and hardness H) of poly(ethylene glycol) diacrylate (PEGDA) / poly(ethylene glycol) methyl ether acrylate (PEGMEA) / poly(ethylene oxide) (PEO) / lithium bis(trifluoro-methanesulfonyl)imide (LiTFSI) solid polymer electrolytes (SPEs) were measured using spherical indentation, as shown in Figure 28. The Young's modulus ranges from 290 kPa up to 10 MPa, while hardness ranges from 9 kPa to 300 kPa, depending on the composition of the SPEs. Both E and H increase with higher PEGDA content (Figure 28b/d), which forms 3D crosslink network. Increasing the ratio of PEO/PEGMEA can further improve E (Figure 28a), but shows little effects on H (Figure 28c), likely because the two are both with straight polymer chains. One composition used for further studies (PEGDA:PEGMEA:PEO = 1:8:1) shows E of ~ 2.58 MPa and H of ~ 156 kPa, which delivers an ionic conductivity of 10^{-5} S/cm at room temperature. Reducing PEGDA and PEO contents can increase the ionic conductivity up to 6 × 10^{-5} S/cm; however, E reduces



to 0.29 MPa, and H to 12 kPa.

Figure 28. Young's modulus (E) and hardness (H) measured using spherical indentation.

To further improve the ionic conductivity of polymer electrolytes (PEs), LLZTO "active" filler nanoparticles were introduced in the 1PEGDA-8PEGMEA-1PEO/LiTFSI matrix. A series of LLZTO contents from 7 wt% up to 31 wt% was prepared. The highest ionic conductivity of 6.6×10^{-5} S/cm was obtained for 7 wt% LLZTO (Figure 29a). Further increasing the LLZTO content, however, leads to the decrease of ionic conductivity. Detailed optimization of the LLZTO content can be conducted in the range below 13 wt% to pin down the peak conductivity. The highly conductive LLZTO particles seem to be not involved in the overall Li⁺ conduction. The addition of LLZTO particles helps to reduce the crystallinity of PEG polymers and thus improves the conductivity. However, further addition of the particles increases the interfacial area, and the impedance between LLZTO and PE could hinder the Li⁺ ion transport. Therefore, to improve the conductivity of high-LLZTO-content CPEs, one strategy is to form bicontinuous LLZTO/polymer networks, which is being explored in the sintering-refilling hybrid approach. Another strategy is to improve the Li⁺ ion transport between the LLZTO/polymer interface.



Figure 29. Conductivity of composite polymer electrolytes made from (a) PEG/LLZTO and (b) zPU/LLZTO recipes. (c) Cycling tests of Li|zPU/LLZTO|LFP solid-state batteries at 1C rate, room temperature.

To achieve that, the team is collaborating with researchers at University of Illinois at Chicago to develop zwitterionic polyurethane (zPU)/LLZTO CPE. The high surface energy of the zPU/LiTFSI PE improves the wetting with LLZTO particles. The high LiTFSI content (up to 80 wt%) increases the Li⁺ concentration in polymer matrix and facilitates the ion transport between zPU and LLZTO. As a result, as shown in Figure 29b, the Li⁺ conductivity of the CPE continuously increases from 1.5×10^{-4} S/cm to 2.2×10^{-4} S/cm (at room

temperature) with the increase of LLZTO content up to 30 wt%. The increasing trend can be fit using a Maxwell-Wagner-Sillars conductivity model. The Li-Fe-P (LFP) | zPU-LLZTO CPE|Li full cells also show improved capacity at 1C rate with the increase of LLZTO content (Figure 29c), likely attributed from the higher conductivity. There are significant capacity drops in the first 10-20 cycles for all the zPU cells, though the addition of LLZTO facilitates the stabilization. After ~ 50 cycles, cell capacity is very stable, with little decrease in the next 200 cycles. With such promising results, the team moves forward to introduce 3D-printed cathodes to integrate with the zPU/LLZTO CPE. Representative prints are shown in Figure 30. Liquid cells are under testing.



Figure 30. Direct ink writing printed single-crystal NMC-811 cathode. Nozzle diameter is 200 μ m, hatch spacing is 400 μ m, and mass loading is ~ 10 mg/cm².

Patents/Publications/Presentations

Presentation

 Materials Research Society Spring Meeting & Exhibit, Honolulu, Hawaii (May 2022): "Co-Sintered Solid Electrolyte/Cathode Interfaces in Solid-State Batteries"; M. Wood, L. Wan, A. Dive, and J. Ye. Task 1.11 – Physical and Mechano-Electrochemical Phenomena of Thin-Film Lithium-Ceramic Electrolyte Constructs (Jeff Sakamoto, University of Michigan)

Project Objective. While a small number of solid electrolytes (SEs) exhibit high ionic conductivity (~ 1 Ms cm at 298 K), few are stable against lithium metal. The garnet-type SE, based on the nominal formula Li₇La₃Zr₂O₁₂ (LLZO), is unique in that it is a fast ion conductor and—as demonstrated in the team's recent project (DE-EE-00006821)—is stable against lithium. Moreover, the team's former project successfully demonstrated a decrease in Li-LLZO interface resistance from 12,000 Ω cm² to 2 Ω cm² and stable cycling at 1 mA cm² for 100 cycles (± 15 µm of lithium per cycle). Although the past project demonstrated that LLZO is a viable SE for enabling batteries using metallic lithium, the studies used thick pellets (1 mm) and thick anodes (~ 500 µm). The goal of this project is to acquire a deep fundamental understanding of the physical and mechano-electrochemical phenomena that control the performance of cells consisting of thin LLZO (~ 10 µm), thin lithium anodes (~ 20 µm), and thin solid-state composite cathodes.

Project Impact. If successful, the project will gain knowledge to guide closely related commercialization efforts to scale up the production of LLZO-based solid-state batteries.

Approach. The team believes that to achieve a step increase in technology readiness level, the same performance characteristics previously shown should be demonstrated in technologically relevant cells, for example, thin LLZO and thin lithium.

Out-Year Goals. Out-year goals involve the following: custom thin-film composite (TFC) development, preliminary cycling studies, Vis cell development, lithium cycling, and polymer gel electrolyte (PGE) screening.

Collaborations. This project collaborates with N. Dasgupta and D. Siegel of University of Michigan, Mechanical Engineering.

- In thin lithium and thin LLZO TFC, determine the maximum plating critical current density (CCD^{plating}) and stripping critical current density (CCD^{stripping}) versus depth of discharge (DOD) at fixed lithium thickness (17 μm). (Q1, FY 2022; Completed)
- 2. Long-term cycling tests to demonstrate $\geq 80\%$ energy retention over 1000 cycles. (Q2, FY 2022; In progress)
- 3. In thin lithium and thin LLZO TFC, determine the max CCD^{plating} and CCD^{stripping} versus lithium thickness, DOD, stack press, and temperature. (Q3, FY 2022; Completed)
- 4. Optimize atomic layer deposition (ALD) coating technology to suppress reactions between the PGE and LLZO. (Q4, FY 2022; In progress)

Optimize ALD Coating Technology to Suppress Reactions Between the PGE and LLZO (Q4, FY 2022; In progress)

Because success was achieved in stabilizing the sulfur catholyte and LLZO interface, project resources were redirected from the study of ALD coatings to suppress reactions with LLZO and PGE to Li-LLZO-S cell cycling analysis. This work closely involves L. Nazar from the University of Waterloo, Canada.

In addition, a follow-on study was completed that relates to a second quarter milestone involving thin lithium anode formation. Recently, in situ anode formation has shown promise for overcoming these challenges, as well as enabling further increases in energy density. However, as lithium is plated out at the current collector/electrolyte interface in anode-free cells, mechanical evolve. which stresses strongly influence the uniformity of the resulting Li-metal anode. This work utilizes operando three-dimensional video microscopy to characterize electrode morphology during in situ anode formation LLZO SEs on garnet (Figure 31). morphological The evolution is linked with coupled electrochemical signatures, which are attributed to changes in hydrostatic stress at the Li/LLZO interface. The



Figure 31. Precision optical microscopy was used to analyze *in situ* lithium anode formation using the model copper foil LLZO solid-state electrolyte system.

team demonstrates the influence of stress on both the thermodynamic and kinetic behavior of the interface. A mechanistic framework is presented to provide insight into the parameters that control plating uniformity, which highlights the critical role of controlling stack pressure. The framework highlights the importance of tuning interfacial toughness, current collector properties, and cell geometry to optimize performance. Informed by these insights, the areal lithium coverage after 2 mAh/cm² of plating is increased from 50% to 95%. The mechanistic understanding in this study can be applied to optimize *in situ* anode formation in a range of material systems.

Patents/Publications/Presentations

Publication

 Kazyak, E., M. Wang, K. Lee, S. Yadavalli, A. J. Sanchez, M. D. Thouless, J. Sakamoto, and N. P. Dasgupta. "Understanding the Electro-Chemo-Mechanics of Li Plating in Anode-Free Solid-State Batteries with *Operando* 3-D Microscopy." *Matter* (2022). doi: 10.1016/j.matt.2022.07.020.

Presentations

- Materials Research Society (MRS) Spring Meeting & Exhibit, Honolulu, Hawaii (May 2022): "The Effect of Aspect Ratio on Creep Behavior of Lithium Metal in Relevant Solid-State Battery Configuration"; C. Haslam, J. Wolfenstine, and J. Sakamoto.
- MRS Spring Meeting & Exhibit, Honolulu, Hawaii (May 2022): "The Stripping Behavior of Thin Li on Li₇La₃Zr₂O₁₂ as a Function of Current Density and Thickness"; K. Lee, E. Kazyak, M. Wang, N. P. Dasgupta, and J. Sakamoto.
- MRS Spring Meeting & Exhibit, Honolulu, Hawaii (May 2022): "Understanding Coupled Electro-Chemo-Mechanics During *In Situ* Li Metal Anode Formation in Anode-Free Solid-State Batteries"; E. Kazyak, M. Wang, S. Yadavalli, K. Lee, A. Sanchez, M. D. Thouless, J. Sakamoto, and N. P. Dasgupta.
- MRS Spring Meeting & Exhibit, Honolulu, Hawaii (May 2022): "The Stability and Kinetics of the Li/Solid Electrolyte Interface"; J. Sakamoto, N. P. Dasgupta, and J. Janek. Invited.
- Electrochemical Society Meeting, Vancouver, British Columbia, Canada (May 29 June 2, 2022): "The Stability and Kinetics of the Li/Solid Electrolyte Interface"; J. Sakamoto, N. P. Dasgupta, and J. Janek. Invited.

Task 1.12 – Low Impedance Cathode/Electrolyte Interfaces for High-Energy-Density Solid-State Batteries (Eric Wachsman and Yifei Mo, University of Maryland)

Project Objective. The project objective is to research, develop, and test Li-metal-based batteries that implement solid Li-ion conductors equipped with Ni-Mn-Co (NMC) cathodes integrated into the Li-metal / Li-La-Zr (LLZ) tri-layer architecture. Specifically, the team will achieve the following: (1) identify and demonstrate interfacial layers to achieve low-impedance and stable NMC/LLZ interfaces; (2) develop novel processing techniques to fabricate NMC/LLZ composite cathodes with low interfacial resistance; and (3) enable high-performance all-solid-state batteries (ASSBs) with an energy density of 450 Wh/kg and 1400 Wh/L and negligible degradation for 500 cycles.

Project Impact. Instability or high resistance at the interface of high-energy cathode materials with Li-garnet solid electrolytes (SEs) limits the high-energy-density all-solid-state lithium batteries (ASSLBs). This project will lead to a fundamental understanding of solid-electrolyte/solid-cathode interfaces and a unique and transformative LLZ framework to enable high-energy-density, safe Li-metal batteries approaching ~ 400 Wh/kg.

Approach. In this new project, the team will build on their demonstrated expertise with garnet electrolytes and ASSB cells to accomplish the following: (1) engineer interfaces to overcome high NMC/LLZ interfacial impedance and interfacial degradation; (2) develop processing and fabrication techniques to achieve high-loading NMC/LLZ composite cathodes with low resistance and high cyclability; and (3) integrate the NMC/LLZ cathodes into all-solid-state Li-metal/LLZ cells to achieve high-energy-density batteries.

Out-Year Goals. The project will solve the current challenges of integrating garnet SE with a cathode to achieve a high-performance ASSB using a high-energy-density Li-metal anode. The resultant high energy density and stability using both high-energy-density Li-metal anodes and NMC cathodes will open new applications in portable electronics, electric vehicles, and beyond.

Collaborations. This project funds work at University of Maryland. The principal investigator (PI), E. Wachsman, will have management responsibility and will lead experimental efforts including garnet synthesis, interface processing, cell fabrication, and testing. The Co-PI, Y. Mo, will lead computational efforts on understanding stability between garnet and cathode and on identifying promising coating materials. In addition, Wachsman is actively collaborating with several universities and national laboratories through the U.S.–German cooperation on solid-state battery interfaces.

Milestones

- 1. Thermochemical stability between LLZ and interface-coated NMC experimentally determined. (Q3, FY 2022; In progress)
- 2. Experimental results compared with computational results, and model refined for side reactions and process optimization. (Q4, FY 2022; In progress)
- 3. Ten-times reduction in interfacial impedance between coated LLZ/NMC and uncoated LLZ/NMC interfaces demonstrated by co-sintering. (Q4, FY 2022; In progress)
- 4. Fabricate tri-layer cell with composite NMC-LLZ cathode layer and evaluate. (Q1, FY 2023; In progress)
- 5. Go/No-Go Decision: Demonstrate final cell with achieved performance. (Q2, FY 2023; In progress)

COVID-19 Impact. Progress on experimental results was impacted by COVID-19, which closed labs for several months; this resulted in a six-month no-cost extension reflected in the milestone dates above.

BMR Quarterly Report
Previous X-ray diffraction (XRD) results of sintered NMC/LLZ pellets suggested that NMCs with higher nickel content (for example, LiNi_{0.8}Mn_{0.1}Co_{0.1}, NMC-811) are more reactive toward garnet than those with lower amounts of nickel. NMC-811 / Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂ (LLZTO) pellets demonstrated near complete loss of peak intensity in XRD when sintered at 1000°C. Additionally, thermal gravimetric analysis (TGA) / differential scanning calorimetry (DSC) were performed on samples of the pristine NMCs in both argon and O₂ atmosphere, indicating NMC loses O₂ from the lattice at high temperatures to a greater degree the higher the nickel content of the NMC. Because of these results and computational results indicating that the reaction of NMC and LLZO is driven by lithium concentration gradients, the co-sintering XRD studies were expanded to include varying the co-sintering atmosphere between argon, air, and O₂, and varying the lithium content in LLZO from 10-40 mol% more than the stoichiometric amount.



Figure 32. X-ray diffraction and Rietveld refinement analysis of (a-b) NMC-811, (c-d) NMC-622, and (e-f) NMC-111 co-sintered in a 1:1 wt ratio with Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂ of varying amounts of excess lithium in both argon and O₂ atmospheres.

Figure 32 contains the summarized phase weight percentage results of the Rietveld refinement of the powder XRD spectra. The samples consisted of NMC and LLZO in a 1:1 weight ratio co-sintered at 900°C for 3 hours in argon and O_2 . The results for samples co-sintered in air are not included, as they show similar results to those processed in O_2 , except that the weight percent of NMC is slightly lower, which indicates an intermediate thermochemical stability between argon and O_2 of NMC. Across all NMC compositions, the wt% of NMC decreases with increasing lithium content of the LLZO, indicating either a loss of NMC crystallinity or formation of amorphous decomposition phases. For higher nickel-content NMCs, the increase in lithium content is also correlated with an increase in formation of a perovskite-like decomposition phase, La₂Li_{0.5}M_{0.5}O₄ (M = Ni, Mn, Co). It is unclear what the exact composition of the transition metal site is because all these compositions have very similar XRD patterns. Furthermore, more perovskite is formed when NMC-811 is co-sintered than NMC-622. This combined with previous TGA / DSC results seems to indicate that the lower the thermochemical stability of the pure NMC and higher lithium content in the LLZO leads to greater formation of the perovskite decomposition phase (NMC-811 demonstrated greater O_2 mass loss starting at lower temperatures than NMC-622). This trend holds true regardless of the co-sintering atmosphere.

Across all NMC compositions, the wt% of NMC is lower for samples sintered in argon than those sintered in O₂. This reinforces the importance of having high oxygen partial pressure to prevent O₂ loss from the NMC that leads to subsequent decomposition. This difference is smaller for NMC-111 and becomes greater for NMC-622 and greatest for NMC-811. It is notable that for NMC-811 co-sintered in argon, less than 10 wt% is still the NMC phase, as a high Ni-content lithiated spinel phase (Li_{0.5}Ni_{1.5}O₂) is detected instead. In O₂, the NMC-811 phase is largely preserved. Additionally, the weight fraction of the perovskite decomposition phase is higher for NMC-811 co-sintered in argon than in O₂. This suggests that stabilizing the NMC is of the utmost importance to prevent formation of decomposition products like La₂Li_{0.5}M_{0.5}O₄ (M = Ni, Mn, Co).



Figure 33. Results of electrochemical impedance spectroscopy experiments with pristine and Li₂SiO₃-coated NMC-622 co-sintered in O₂ at 1000°C summarized in a (a) Nyquist plot and (b) differential relaxation times analysis plot.

Figure 33 contains the summarized results from electrochemical impedance spectroscopy experiments of NMC-622 coated with Li₂SiO₃ via atomic layer deposition. It is observed that this interfacial coating reduced the area specific resistance by a factor of approximately 4, demonstrating the ability of this material to stabilize NMC-622 at high co-sintering temperatures. DSC/TGA further confirm that Li₂SiO₃ prevents O₂ loss until higher temperatures. XRD data on co-sintered pellets is forthcoming.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 1.13 – Development of All-Solid-State Battery Using Anti-Perovskite Electrolytes (Zonghai Chen and Tao Li, Argonne National Laboratory)

Project Objective. The objective of this project is to develop an optimized anti-perovskite electrolyte with a stabilized interface for scalable fabrication of liquid-free solid-state batteries.

Impact. The project will lead to impact on several areas: (1) establishing structure-property relationship of anti-perovskite electrolytes, (2) understanding and quantifying the interaction between the electrolytes and the environment, (3) understanding and mitigating the failure of all-solid-state batteries (ASSBs) at solid-solid interface, and (4) developing a scalable process for fabrication of ASSBs.

Approach. The project approach is multifold: (1) *chemistry design*: multiple doping at anion sites will be pursued to improve structural stability ionic conductivity and environmental compatibility; (2) *interfacial design*: surface coating will be deployed to improve the chemical and mechanical stability of solid/solid interface; and (3) *process development*: a scalable fabrication process based on melt-infiltration or dry lamination will be developed for the fabrication of ASSBs.

Out-Year Goals. The project has the following out-year goals:

- Developing high-performance anti-perovskite electrolytes.
- Accessing the air stability and proton mobility of anti-perovskite electrolytes.
- Stabilizing the solid/solid interface through interfacial engineering.
- Prototyping liquid-free cells using anti-perovskite electrolytes.

Collaborations. This project collaborates with Y. Z. Liu and W. Q. Xu (Argonne National Laboratory. ANL), X. H. Xiao (Brookhaven National Laboratory), and H. Meng (University of Arkansas).

- 1. Setting up high-throughput synthesis capability. (Q1, FY 2022; Completed)
- 2. Optimizing synthesis condition for anti-perovskite electrolytes. (Q2, FY 2022; Completed)
- 3. Investigating structural stability of doped electrolytes. (Q3, FY 2022; In progress, with completion expected in Q4)
- 4. Investigating transport properties of doped electrolytes. (Q4, FY 2022; In progress)

Last quarter, the team demonstrated that phase pure anti-perovskite electrolytes were able to be obtained after adopting tungsten crucibles, and the crystal structure of a series of synthesized electrolytes, $Li_2HOCl_{1-x}Br_x$ ($0 \le x \le 1$), was also characterized using high-energy X-ray diffraction (HEXRD). A cold press technique was used to prepare pellets out of the synthesized electrolytes. Figure 34 shows the measured Li-ion conductivity of the cold press samples at various temperatures. Worth mentioning is that Li₂HOCl exists as a tetragonal form at around room temperature, showing substantially lower Li-ion conductivity than others. When the temperature is higher than 40°C, Li₂HOCl converts its cubic form with a higher Li-ion conductivity. Overall, it is observed that partially replacing chlorine with bromine can improve the Li-ion conductivity, and the conductivity peaks at the



Figure 34. Measured Li-ion conductivity of protonated anti-perovskite electrolyte pellets prepared using cold press.

composition of $Li_2HOCl_{0.75}Br_{0.25}$. Nevertheless, the room-temperature conductivity for all these samples is still far below the expectation; more exploration on the material stoichiometry and material processing method will be conducted to further improve the room-temperature conductivity.

It is also anticipated that the synthesized anti-perovskite electrolytes are sensitive to moisture. Figure 35 compares X-ray diffraction patterns of Li_3OBr before and after aging in a glovebox for one month. Before aging, the material was dominated by a cubic structure, with a small amount of impurity phase. After aging, a clear growth of impurities phase was observed, even though the sample was stored inside the glovebox. Therefore, the team is interested to further study moisture sensitivity of the electrolytes, and to search for electrolyte candidates that can survive environment in a dry room.

Figure 36a shows the conceptual design of a simple sample holder to investigate the interaction between anti-perovskite electrolyte with the moisture in the air. In this design, an inert gas carrying a certain level of moisture will pass through the sample holder to provide a constant level of moisture in the sample holder.



Figure 35. Comparison of X-ray diffraction patterns of $L_{i3}OBr$ before and after aging in the glovebox for one month, showing the slow response of $L_{i3}OBr$ toward the environment.

CAPTON windows on both sides provide a good X-ray pathway to track the structure of the electrolyte material held inside the sample holder. Figure 36b shows an image of the implemented sample holder that is compatible with the working environment offered at sector 17BM of Advanced Photon Source at ANL. Controlling the moisture level at 40% humidity (~ 1070 Pa moisture partial pressure), the team was able to follow the conversion reaction from the cubic Li₃OBr to unidentified impurity phase using HEXRD. Using the ratio of peak intensity between cubic Li₃OBr and impurity phase as a quantitative indicator, the evolution from Li₃OBr to the impurities phase can be obtained, as shown in Figure 36c. Although a catastrophic decomposition was observed after exposing to high moisture level for about 3 hours, a continuous slow decomposition was also confirmed at

the very beginning of the experiment. In this project, the team will continue improving the design of the sample holder for better control of the moisture level, and the developed technique will be further used to study the moisture sensitivity of the developed electrolyte materials.



Figure 36. (a) Illustration of a sample environment to study the moisture sensitivity of electrolyte samples. (b) Image of the working sampler holder integrated in sector 17BM of Advanced Photon Source. (c) Evolution of Li₃OBr and its decomposition product during exposure to 40% humidity (~ 1070 Pa moisture partial pressure).

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 1.14 – Lithium Halide-Based Superionic Solid Electrolytes and High-Voltage Cathode Interface (Jagjit Nanda, SLAC Stanford Battery Research Center)

Project Objective. The project aims to develop low-temperature solution-based synthesis strategy for high ionic conducting halide-based solid electrolyte (SE) and to enable approaches to develop a scalable process for integrating halide-based SE within porous high-voltage Li-ion cathode matrix. Years 1 and 2 aim at developing low-cost, solution-based synthesis routes to produce a halide class of superionic conductor belonging to Li_3MX_6 (where = Sc, Y, La, Er, In, and X = Cl, Br, I) along with enabling electrochemical and structural characterization. Parallel efforts in years 2 and 3 target developing synthesis and processing methods where the high-voltage stable halide-based SEs can be readily infiltrated within the porous cathode structures such as NMC-622, high-voltage Mn-Ni spinel (LiMn_{1.5}Ni_{0.5}O₄), and recent fluorinated Mn-rich disorder rock salt cathodes. Years 3 and 4 focus on designing and fabricating thin halide SE separators with a thickness of 50 µm or lower and optimizing the cathode microstructure. Finally, years 4 and 5 will develop approaches for anode-free lithium plating and stripping on alloyed or engineered copper current collectors at relatively higher current densities aimed at improving the volumetric energy density of solid-state batteries (SSBs) with a high loading cathode and thin halide SE separator.

Impact. The proposed tasks and metrics aim at addressing the long-term Vehicle Technologies Office goal for developing SSBs at ambient temperature with energy density in the range of 500 Wh/Kg and 1000 Wh/L for electric drive vehicles. Advances in scalable processing of superionic SEs, stabilizing electrode-electrolyte interfaces, and promoting long cycle life are all needed to meet the energy density and cost targets for next-generation batteries for electric vehicles.

Approach. The project employs a multifaceted approach: (1) conduct solution-based synthesis of the metal halide superionic conductor as the platform to enable robust cathode-electrolyte interface processing for SSBs, (2) infiltrate pore structures using solution-based processing that deposits high-conductivity SEs within cathode pores, and (3) facilitate lithium transport and improve stability using cation doping (divalent to introduce lithium vacancies, and lanthanum to prevent indium redox).

Out-Year Goals. Demonstrate single-layer, pouch-cell SSB containing a thin halide SE separator coupled with high-voltage cathodes with 70% capacity retention over 300 cycles at 2 mA/cm^2 in an anode-free SSB configuration that can attain 1000 Wh/L in prototype cells.

Collaborations. Y. Yao and team at University of Houston (UH) are funded collaborators for halide-based SSB fabrication, testing, and interfacial studies. The project also involves unfunded collaboration with SLAC National Accelerator Laboratory for X-ray absorption spectroscopy and synchrotron X-ray diffraction (XRD) of SEs.

- 1. Produce gram-scale quantities of Li₃InCl₆SE using solvent-phase synthesis. (Q1, FY 2022; Completed)
- 2. Obtain phase-pure Li_3InCl_6 thin pellets with ~ 1 mS/cm⁻¹ conductivity. (Q2, FY 2022; Completed)
- 3. Utilize neutron diffraction, X-ray photoelectron spectroscopy, Raman, and electron microscopy to characterize Li₃InCl₆ SE. (Q3, FY 2022; Delayed until after the Q4 milestone)
- 4. Compare structure and Li^+ conductivity of Li_3InCl_6 prepared through solvent-mediated versus mechanochemical; > 5g batch with ionic conductivity in the range of 1 mS/cm⁻¹. (Q4, FY 2022; Initiated)

The team has switched the milestones for the third and fourth quarters. This milestone change is due to impurity issues observed in the XRD and in the parallel research that Y. Yao's group is conducting with the team's materials at UH. Basically, this report will cover the fourth quarter objective, with the third quarter milestone being targeted for the end of fourth quarter.

Since last quarter, the team has successfully scaled up the synthesis of Li_3InCl_6 in two solvent systems: ethanol and water (first and second quarter milestones). The time it now takes to synthesize > 10 g of Li_3InCl_6 is on the order of 3 hours, with the rate limiting step being removal of bulk solvent. They have reproduced this synthesis method and improved it. Previously, LiCl was the major impurity and was present in 0-5% by mass (estimated via XRD). The team found that synthesis from ethanol produced greater LiCl impurities and was less consistent. To probe this fact, they systematically increased the amount of $InCl_3$ from 0% excess to 20%. They found that 10% excess of $InCl_3$ was enough to force the reaction to completion. This systematic increase was also done for synthesizing from H₂O. The XRD showed little change, as synthesis from H₂O is robust, producing pure product with minimal art required. However, the ionic conductivity increased with the addition of 10% and 20% excess $InCl_3$. This is different from the ethanol-derived sample where the team sees a *decrease* in overall conductivity. This decrease seems to come from grain boundary (GB) issues.

Conclusion 1: 10% Excess of Rare Earth Improves Synthesis Purity and May Improve Overall Ionic Conductivity

The suggestion above is further supported by the results from the mechanical synthesis route. Here, they again systematically adjusted the amount of excess $InCl_3$ from 0% to 20%. They milled the precursors for 16 hours in a planetary mill. The milling was enough to obtain near phase pure product, though the XRD shows very broad diffraction peaks, suggesting the product is nanocrystalline or highly defective/disordered. The conductivity was found to be high, 0.25 mS cm⁻¹ at room temperature with energy of activation being 0.32 eV. Annealing at 150°C for 5 hours improved the ambient ionic conductivity, 0.40 mS cm⁻¹ with 0.30 eV. These results are in line with H₂O-based synthesis and therefore different from ethanol-based. This supports the idea that the Li₃InCl₆ synthesized from ethanol is different. Although this difference may only be surface level, this is the very region that results in GBs and impedes overall ion transport. Figure 37 summarizes the conductivity results under different synthesis conditions as described.

Conclusion 2: Mechanical and H₂O-based Synthesis have Minimal GB Resistance, while Ethanol-Based has Significantly More, Suggesting Surface Termination Difference



Figure 37. Arrhenius plot of overall conductivity of Li₃lnCl₆ as a function of different synthesis methods and Li₃lnCl₆ excess amounts.

The last report ended with a hypothesis that the excess $InCl_3$ fills in occupancies within the structure, which is a layered structure that houses lithium within the galleries. This means that the material becomes a more layered-like structure with increased $InCl_3$; therefore, the application of pressure (to make a device) may induce some anisotropic effects on conductivity. They conducted a pressure-resolved measurement, showing that the conductivity increases with pressure until ~ 33 MPA (Figure 38). After this, the conductivity decreases substantially. When the pressure is released back to the starting value, the conductivity slowly improves. This suggests that high pressure induces some change to the bulk material, either aligning it or chemically changing it. This is important information to know when the team begins making full-cell devices in years 3 and 4. They can now expect that while high pressures may improve cathode-electrolyte adhesion, they will affect bulk properties, perhaps negatively.



Figure 38. Nyquist plot (left) and Bode plot (right) showing pressure-induced effects of Li₃InCl₆ conductivity.

Conclusion 3: Excessive Pressure Induces Structural or Bulk Alignment Changes in Bulk Li₃InCl₆ that Result in Decreased Overall Conductivity (Increased GB Resistance)

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 1.15 – Developing an *In Situ* Formed Dynamic Protection Layer to Mitigate Lithium Interface Shifting: Preventing Dendrite Formation on Metallic Lithium Surface to Facilitate Long Cycle Life of Lithium Solid-State Batteries (Devang Qu, University of Wisconsin, Milwaukee)

Project Objective. The objective of this project is to research, develop, and test Li-metal-based batteries that implement solid Li-ion conductors equipped with a formed dynamic protection layer. The proposed project aims to enable safe, long-cycle lithium anodes to achieve cell performance targets of 400 Wh/Kg, over 100 cycles, with a 15-year shelf life, and < \$100/KWh cost.

Project Impact. Project efforts are to contribute an in-depth understanding of the lithium interface and dendrite growth prevention to the field of Li-metal batteries, which will pave the way for eventual development of high-energy-density, low-cost, and long-lasting lithium batteries. This advancement could be a crucial selling point for the greater adoption of electric vehicles. This project will make possible the translation of fundamental research into practical implementation of high-energy lithium anodes, enabling eventual achievement of cell performance targets.

Approach. The novelty of this approach is that the team intends to mitigate the dendrite problem by creating a dynamic protection layer during the interface shift to prevent dendrite formation throughout battery operation.

Out-Year Goals. The project has three *one-year* goals: (1) *in situ* diagnostic tools are verified; (2) thin solid-state electrolyte (SSE) and cathode are made; and (3) all-solid-state cells are made.

Collaborations. The principal investigator (PI) is the Johnson Control Endowed Chair Professor, who has close and frequent collaboration with Johnson Controls' scientists and engineers. The collaboration enables the team to validate the outcomes of fundamental research in pilot-scale cells. The PI also has been working closely with top scientists at Argonne National Laboratory, Brookhaven National Laboratory, Lawrence Berkeley National Laboratory, and Pacific Northwest National Laboratory, and with U. S. industrial collaborators, for example, General Motors, Millipore, and Clarios. In addition, the team works with international collaborators in China, Japan, and South Korea. These collaborations will be strengthened and expanded to give this project a vision with both today's state-of-the-art technology and tomorrow's technology in development, while incorporating feedback from material designers and synthesizers upstream, as well as from industrial end users downstream.

- 1. Coated lithium anode with dendrite suppression demonstrated. Demonstrate effectiveness of inorganic artificial protective layer. (Q1, FY 2022; Completed)
- 2. Lithium anode with suppressed dendrite growth demonstrated. Demonstrate effectiveness of artificial protective layer. (Q2, FY 2022; Completed)
- 3. Down select materials and cell fabrication method for final cell build. (Q3, FY 2022; Completed)
- 4. All-solid-state cell build and test. (Q4, FY 2022; In progress)
- 5. Dendrite suppression demonstrated; cell performance verified. (Q4, FY 2022; In progress)

Last quarter, the team reported an all-solid-state lithium battery made with polyimide-graphene cathode and lithium anode. The SSE in the full cell was manufactured with a dry process. The resulting electrolyte is a free-standing membrane with a high flexibility. The thickness of the finished solid-state membrane was $70 \,\mu m$.

From this quarter through next quarter, the team is working to determine the cathode material, anode material, and SSE processing method and to manufacture an all-solid-state Li-S pouch cell. This quarter, they report a full solid-state battery made with pure sulfur cathode and an "all-electrochem-active" Li_xSi anode.



Figure 39. (a) Cycling and (b-c) rate performance of Li-In | solid-state electrolyte (SSE) | S full cell at 60°C. (d) Cycling and (e-f) rate performance of μ -Li_xSi|SSE|S full cell at 60°C. (g) Cycling and (h-j) rate performance of μ -Li_xSi|SSE|S full cell at 25°C. Capacities are presented relative to the weight of sulfur.

Performance of the full cells was evaluated by pairing the sulfur cathode with a Li-In alloy anode, and a μ -Li_xSi alloy anode. As shown in Figure 39a-f, the μ -Li_xSi|SSE|S cell displayed a discharge voltage plateau of 1.8 V, which is roughly 280 mV higher than that compared with the Li-In|SSE|S cell (1.5 V). In long-term cycling tests, the Li-In|SSE|S cell (Figure 39a) showed a rapid capacity fading after 50 cycles and became

shorted at the 88th cycle, while the μ -Li_xSi|SSE|S cell (Figure 39d) showed stable cycling and retained 85.4% capacity after 200 cycles. Figure 39h-j shows the cyclic voltammetry and rate performance of the cell at 25°C. Under 1.2C, an accessible capacity of 866 mAh g⁻¹ was achieved, corresponding to 69% of the capacity under 0.05C (1249 mAh g⁻¹). All capacities are relative to the weight of sulfur.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 1.16 – Polyester-Based Block Copolymer Electrolytes for Lithium-Metal Batteries (Nitash Balsara, University of California, Berkeley)

Project Objective. The project objective is to design and synthesize polyester-based block copolymer electrolytes that can enable full-cell cycling at 1 mA/cm^2 or greater for 300 cycles. The cell comprises Li-metal anode, 4.5 V Ni-Mn-C (NMC) cathode, and thin separators (20-50 μ m) casted from the aforementioned block copolymer.

Impact. Polymer electrolytes offer increased stability in lithium batteries in comparison to more widely used liquid electrolytes. Block copolymer-based electrolytes containing both soft, ion-conducting domains and rigid, nonconducting domains offer the opportunity to tune both mechanical and electrical properties separately. Most block copolymer electrolytes studied thus far comprise poly(ethylene oxide) (PEO) as the conducting domain. The team hopes to develop polyester-based electrolytes that exhibit much higher transport properties and limiting currents than PEO-based electrolytes. An all-solid full cell with this new block copolymer electrolyte, a Li-metal anode, and an NMC cathode will have much higher energy density than current Li-ion technology.

Approach. The team will begin by synthesizing several series of polyester homopolymers and fully characterizing their blends with lithium salts as polymer electrolytes in Li-Li symmetric cells. Next, they will make block copolymer electrolytes based on the most promising candidate and measure the electrochemical and mechanical properties thoroughly. Finally, they will assemble full cells with the optimum block copolymer electrolytes together with lithium metal and a 4.5 V NMC cathode.

Out-Year Goals. In the first year, the team will establish an efficient synthesis and characterization platform for polyester electrolytes. Several polyesters will be synthesized, and electrolytes will be made by blending each polymer with lithium salt. Transport properties (such as conductivity and current fraction) and limiting current of resulting electrolytes will be measured in Li-Li symmetric cells. The highest performing polymer electrolyte will be used as the conducting phase in the block copolymer design in the second year.

Collaborations. There are no active collaborations this quarter.

- 1. Establish synthesis platform: synthesize at least two polyester electrolytes. (Q1, FY 2022; Completed)
- 2. Conductivity: measure conductivity of at least two electrolytes. (Q2, FY 2022; Completed)
- 3. Symmetric cell characterization: measure salt diffusion coefficient and current fraction of at least two electrolytes. (Q3, FY 2022; Completed)
- 4. Complete characterization: measure thermodynamic factor and thereby complete characterization of at least one polyester electrolyte. (Q4, FY 2022; In progress)

The third quarter milestone has been completed. The team measured the current fraction and salt diffusion coefficient of electrolytes using Li-Li symmetric cells based on polyester electrolytes they made during the previous two quarters.

They first examined the effect of polymer structure on the current fraction of polyester electrolytes. The structures of the four polyesters, poly(alkyl malonates), are shown in Figure 40a. They made four polymer electrolytes comprising 40 wt% of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt and 60 wt% of each polymer. The team defines salt concentration as r = [Li]/[O], where all the oxygen atoms in the polymer

are counted (a total of four in every repeating unit in Figure 40a). Due to the difference in molecular formula of these polymers, *r* falls between 0.07–0.11. The well-studied PEO/LiTFSI system exhibits a broad maximum in electrolyte efficacy in this range of *r* values.^[1] In Figure 40b, they show current fraction (ρ_+) values of these electrolytes measured in Li-polymer-Li symmetric cells at 90°C. They are delighted to observe very high current fraction values (~ 0.6) for all four polyester electrolytes. This is about six-fold of the current fraction of PEO/LiTFSI electrolyte (< 0.1). From the team's study on conductivity last quarter, they know that poly(pentylene malonate) (PPM) / LiTFSI has the best conductivity among the four polyester electrolytes. Thus, they are focusing on PPM/LiTFSI for the rest of the study.

The effect of salt concentration (*r*) on the current fraction (ρ_+) and electrolyte efficacy ($\kappa \rho_+$) of PPM/LiTFSI electrolytes is shown in Figure 41, which also shows values of the same parameters for PEO/LiTFSI electrolytes as reported in literature.^[1] The ρ_+ values of all PPM/LiTFSI electrolytes are all ~ 0.6 in the range 0.01 $\leq r \leq$ 0.15, while the ρ_+ values of PEO/LiTFSI decrease from 0.18 to 0.07 with increasing *r* from 0.01 to 0.14. The $\kappa \rho_+$ value of PPM/LiTFSI electrolytes is higher than PEO/LiTESI electrolytes across all salt



poly(alkyl malonates) synthesized for this project. (b) Current fraction of polymer electrolytes comprising 40 wt% of LiTFSI salt at 90°C. PEO stands for benchmark poly(ethylene oxide).

electrolytes is higher than PEO/LiTFSI electrolytes across all salt concentrations, with a maximum of 3×10^{-4} S/cm at r = 0.06. This is ~ 50% higher than the best efficacy of PEO/LiTFSI electrolyte observed at r = 0.08.



Figure 41. The effect of salt concentration r on (a) current fraction, ρ_+ , and (b) electrolyte efficacy, $\kappa \rho_+$, of PPM/LiTFSI (blue circles) and PEO/LiTFSI (black squares) electrolytes at 90°C. Data for PEO/LiTFSI electrolytes were taken from previous work.^[1] PPM data have been submitted for publication [Yu, X., et al. "A Practical Polymer Electrolyte for Lithium and Sodium Batteries: Poly(pentyl malonate)." Submitted to *ACS Energy Letters*].

The team further examined the effect of *r* on the salt diffusion coefficient (*D*) of PPM/LiTFSI electrolytes, as shown in Figure 42. The *D* values of all PPM/LiTFSI electrolytes are near 10^{-7} cm²/s, which is the same magnitude as PEO/LiTFSI electrolytes.

Next quarter, the team will carefully investigate the thermodynamic factor and thereby complete characterization of at least one polyester electrolyte.



Figure 42. The effect of salt concentration, r, on salt diffusion coefficient, D, of PPM/LiTFSI (blue circles) electrolytes at 90°C.

Reference

[1] Pesko, D. M., Z. G. Feng, S. Sawhney, J. Newman, V. Srinivasan, and N. P. Balsara. "Comparing Cycling Characteristics of Symmetric Lithium-Polymer-Lithium Cells with Theoretical Predictions." *Journal of the Electrochemical Society* 165 (2018): A3186–A3194.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 1.17 – Advanced Polymer Materials for Batteries (Zhenan Bao and Yi Cui, Stanford University)

Project Objective. This project will develop new polymer materials for batteries. The team will develop polymer coatings with specific mechanical properties that can accommodate the volume expansion and contraction of the Li-metal anode associated with deposition and stripping (charging and discharging).

Project Impact. The cycling stability and Coulombic efficiency (CE) of Li-metal electrodes will be increased by implementation of a polymer-based protective layer that functions as an artificial solid electrolyte interphase (SEI) with desired properties. The improved performance will enable further development toward practical utilization of Li-metal anodes with higher cycling efficiency and less susceptibility to dendrite-based failure.

Approach. The project uses soft polymer coatings with dynamic crosslinking to give the resulting polymers liquid-like rheological properties and stretchable and self-healing properties. In previous work, the team has shown that such coatings resulted in uniform deposition/stripping of lithium metal and improved cycling stability of Li-metal electrodes. To understand the design rules for effective polymer coatings, they chose a few representative polymers to systematically understand structure property relationships. Here, they investigate the correlation between surface energy of the polymer and exchange current for lithium deposition.

Out-Year Goals. Work will progress toward the correlation between dielectric constant and exchange current. These findings will enable further understanding and development of various polymer coatings for protecting Li-metal anodes.

Collaborations. The team is collaborating with J. Qin at Stanford University.

- 1. New lithium anode coating design. Design the polymer chemistry through density functional theory and contact angle measurement to find salt affinitive and solvent phobic moieties. (Q1, FY 2022; Completed)
- 2. Characterize selective transport of salt over solvents for this polymer. (Q2, FY 2022; Completed)
- 3. Characterize impact of polymeric coating on lithium deposition morphology and short-term CE. (Q3, FY 2022; Completed)
- 4. Coat thin Li-metal electrodes with the polymeric coating and achieve stable lithium cycling for \ge 200 cycles at 2.5 mAh/cm² capacity and C/3 D/5 current density in lean electrolyte condition. (Q4, FY 2022)

The ability of SP² polymer to improve SEI composition leads to upgrades in electrochemical performance in Li|Cu cycling. As shown in Figure 43a, the team compared CE for the two cases with and without SP² coating under a short-term of 10 cycles with 0.5 mA cm⁻¹ and 1 mAh cm⁻¹ cycling protocol.^[11] In 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) 1,3-dioxolane / 1,2-dimethoxyethane (DOL/DME) 1 wt% LiNO₃ electrolyte, CE increased from 98.3% to 99.5% with SP². The team also examined CE in carbonate (1 M LiPF₆ ethylene carbonate (EC) / diethyl carbonate (DC) with 10% fluoroethylene carbonate), as well as 1 M LiFSI in fluorinated 1,4-dimethoxylbutane (FDMB)^[2] electrolyte. In carbonate electrolyte, the CE increased from 96.0% to 97.0%. In FDMB electrolyte, since the baseline electrolytes already achieve high CE in this short-term cycling protocol, the team observed a small increase with the addition of SP² coating (99.4% to 99.5%). Figure 43b shows the individually plotted voltage profile of one set of cells for these CE measurements. They also paired the SP² coating with the state-of-the-art Li-metal electrolyte: 1.2 M LiFSI in 2-(2-(2,2-difluoroethoxy)ethoxy)-1,1,1-trifluoroethane (F5DEE),^[3] and CE increased from 99.5% to 99.6%. There is less room for CE improvement when the baseline CE is already high. However, in long-term tests, small increases of CE still translated to longer cell cycle life, as shown in the following section.

Previously, the team discussed the SP^2_{Alkyl} polymer, which has a lower salt-affinity compared to SP^2 , but still shows selective transport of salt over solvent. To examine the battery performance of SP^2_{Alkyl} , the team cycled SP^2_{Alkyl} coated Li|Cu cells with the short-term cycling protocol. For carbonate, SP^2_{Alkyl} improved performance (CE increased from 96.0% to 96.6%). However, in FDMB electrolyte, CE decreased from 99.4% to 98.9%, which they ascribed to insufficient ion transport at the interface. The SP^2_{Alkyl} coated electrode had higher overpotential (0.047 V) than the SP^2 coated one (0.037 V), and the standard deviation (STD) was doubled. Due to the lower salt affinity of SP^2_{Alkyl} , ion transport at the electrode interface was impeded. Especially in electrolytes with limited ionic conductivity, large deposition overpotential drives undesirable degradation (low CE) and reduced operational stability (high STD).^[3-4] Overall, the team found it is critical to maintain both solvent-phobicity and salt-affinity, and SP^2 showed superior cycling performance.

Since both the EC/DEC and FDMB electrolytes were cycled with Li|NMC configuration, the team characterized how SP² coating affects electrolyte stability with Li-metal anode through electrochemical impedance spectroscopy and long-term cycling in Li|Li symmetric cell. Figure 43b shows the interfacial impedance of SP² coated lithium in carbonate or FDMB electrolyte for different lengths of time. The uncoated ones were used as comparison. For both electrolytes, SP² layer was observed to suppress interfacial impedance increase. The team quantified the increase with this formula: $(I_{100} - I_0)/I_0$ (%). For the first 100 hrs, SP² reduced the impedance increase from 104% to 33% in carbonate electrolyte, and from 153% to 42% in FDMB electrolyte (Figure 43c). Since the polymer was coated on lithium surface with the tetrahydrofuran (THF) solvent, they also examined the influence of THF on interfacial impedance. They treated bare lithium metal with THF and tracked its impedance evolution in carbonate electrolyte. With or without THF treatment, lithium electrodes experienced a similar ~ 100% impedance increase, indicating that SP² polymer is the reason for reduced impedance growth.

The team also cycled Li|Li symmetric cells at 1 mA cm⁻¹ current density and 1 mAh cm⁻¹ capacity (Figure 43d). For the carbonate electrolyte, the addition of SP^2 coating resulted in a higher deposition overpotential, which was stable over cycles. For the uncoated lithium anode, the overpotential decreased between 25 and 40 cycles. This is due to increased surface area from irregular whisker-shaped lithium deposition,^[5] which was verified by scanning electron microscopy. The addition of SP^2 coating promoted homogeneous deposition, as opposed to whisker-shaped deposition. For the FDMB electrolyte, a layer of SP^2 polymer maintained a stable overpotential over time. Without the SP^2 coating, FDMB electrolyte continued to react with lithium metal and increased the deposition overpotential.^[2] In both cases, a layer of SP^2 coating limited the solvent breakdown at the lithium electrode and sustained stable operation.

To further understand the range of solvent-phobicity and salt-affinity requirements at the interface, the team assembled Li|Cu cells with a solvent-philic polymer coating (siloxane-glyme). In carbonate electrolyte, this coating had limited improvement on CE (96.0% to 96.1%). The lithium deposition morphology remained whisker-shaped. This confirms the importance of having solvent-phobicity at the electrode-electrolyte interface.



Figure 43. Electrochemical characterization of SP² with different electrolytes: (a) Coulombic efficiency measured of coated copper in Li]Cu geometry with 40 μ L of ether (1 M LiTFSI DOL/DME 1 wt% LiNO₃), carbonate (1 M LiPF₆ EC/DEC 10% FEC) or FDMB (1 M LiFSI FDMB) electrolyte. (b) Electrochemical impedance spectroscopy measurement over time with either SP² coated Li]Li symmetric cell in electrolytes. (c) Calculated impedance increase (%) over 100 hours. (d) Voltage curve of Li]Li symmetric cell with and without SP² coating. (e) Scanning electron microscopy top view image of deposited lithium on copper electrode in carbonate electrolyte, scale bar 10 μ m.

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Patents/Publications/Presentations

Publication

• Yu, Z., Z. Bao, et al. "A Solution-Processable High-Modulus Crystalline Artificial Solid Electrolyte Interphase for Practical Lithium Metal Batteries." *Advanced Energy Materials* (2022): 2201025.

Task 1.18 – Molecular Ionic Composites: A New Class of Polymer Electrolytes to Enable All-Solid-State and High-Voltage Lithium Batteries (Louis A. Madsen, Virginia Polytechnic Institute and State University)

Project Objective. Based on a newly discovered class of solid polymer electrolyte materials, that is, molecular ionic composites (MICs), the overall objective is to develop solid-state lithium conductors targeted for use in transportation applications. MICs form a mechanically stiff, electrochemically stable, and thermally stable matrix. Specific objectives include the following: (1) development of robust MIC electrolyte thin films (~ $20 \,\mu$ m) to serve as simultaneous nonflammable separators and dendrite-blocking Li⁺ conductors, (2) electrochemical quantification of key performance metrics including electrolyte stability, interfacial reactions, and suitability/compatibility with a range of electrode materials, and (3) comprehensive investigation of ion transport mechanisms and electrode-electrolyte interfacial reactivity under practical operating conditions using nuclear magnetic resonance (NMR) and synchrotron X-ray analyses.

Project Impact. Commercialization of Li-metal solid-state batteries (SSBs) is hampered by lack of a functional nonflammable solid electrolyte that can provide high ionic conductivity, wide electrochemical window, favorable mechanical properties to inhibit lithium dendritic growth, and low interfacial resistance. The tunable MIC materials platform has potential to fulfill these requirements with relatively simple fabrication techniques, and thus shows promise for enabling nonflammable SSBs that can be optimized for low cost and high energy density.

Approach. MICs rely on a unique polymer that is similar to Kevlar[®] in its strength, stiffness, and thermal stability, but with densely spaced ionic groups that serve to form an electrostatic network that permeates mobile ions in the MIC. The team can tailor the ion concentrations and types to yield MIC electrolyte films that are electrochemically compatible with Li-metal anode as well as a range of high-voltage layered cathodes. They are searching the composition space of lithium salts, electrochemically compatible ionic liquids, and polymer [poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide), or PBDT] molecular weight to determine best composition windows for MIC electrolytes. The team is also investigating best methods for casting thin films in terms of temperature, solvent/evaporation conditions, and control over the initial liquid crystalline gel formation point. Concurrently, they are testing MIC films in various electrochemical cells, quantifying transport and structural/morphology parameters with NMR and X-ray techniques, and measuring key mechanical (dynamic mechanical thermal analysis, stress-strain) and thermal (differential scanning calorimetry, thermal gravimetric analysis) properties.

Out-Year Goals. This year, the team will generate a predictive model to understand the relationship between the mobility of all ions and the MIC synthesis parameters. They will establish the testing protocol for NMR measurements under operating conditions. They will also study the surface chemistry of the MIC electrolyte before and after cycling. The team will identify methods to mitigate interfacial degradation. They will then test the final project electrolyte in full cell and develop specifications.

Collaborations. The team is collaborating with T. J. Dingemans' group at University of North Carolina, Chapel Hill, in which they are forming composites based on PBDT polymer and carbon materials such as graphene oxide and are beginning to develop charged rigid-rod polymers building on the PBDT structure. The team is exploring shear rheology and broadband dielectric spectroscopy collaboration with R. H. Colby at Pennsylvania State University. They are collaborating with D. Nordlund and Y. Liu at Stanford Linear Accelerator Center and S-M. Bak at Brookhaven National Laboratory to conduct synchrotron X-ray studies on MIC films.

Milestones

1. Multivariant analysis of experimental parameters and electrochemical properties. (Q1 FY 2022; Completed)

- 2. *In situ* experiments implementing NMR spectroscopy and diffusometry at different cell states of charge. (Q2, FY 2022; In progress)
- 3. Spectroscopic surface analysis of cathode, anode, and MIC electrolyte after various cycling history. (Q3, FY 2022; Completed)
- 4. Area specific resistance: MIC/Li $\leq 10 \ \Omega \ cm^2$ and cathode/MIC $\leq 50 \ \Omega \ cm^2$ / cells. (Q4, FY 2022; In progress)

The team has screened various types of additives to the MIC electrolytes to improve lithium symmetric cell performance at 23°C (Figure 44). Additives are incorporated into MIC electrolytes with the team's (now traditional) (trifluoromethanesulfonyl)imide (TFSI)-based compositions to aid in formation of stable solid electrolyte interphase films. Additives such as fluoroethylene carbonate (FEC), lithium difluoro(oxalate) borate (LiDFOB), and lithium bis(oxalate)borate (LiBOB) showed enhanced limiting current density compared to that of MIC membranes without additives.



Figure 44. Lithium symmetric cell performance with and without selected additives to aid in SEI formation. All plots are voltage profiles of symmetric cells cycled at 23°C with increasing steps of current density. The charge and discharge times are 0.5 hours, respectively, and the current density is stepped every 10 cycles. (a) 5 wt% of fluoroethylene carbonate (FEC), (b) lithium difluoro(oxalate)borate (LiDFOB), (c) lithium bis(oxalate)borate (LiBOB), and (d) without additives. The team observes significant gains (up to 2.3×) in limiting current for the FEC and LiDFOB additives. Goals are to explore a range of other additives, focusing on non-volatile compounds, spatial separation of additives near interfaces, and additives that can largely be consumed during dominant SEI formation.

This quarter, the team has also investigated how MIC electrolyte impacts the bulk properties of cathodes in batteries. They evaluate the bulk stability of LiNi_{0.8}Mn_{0.1}Co_{0.1} (NMC-811) cathodes by hard X-ray absorption spectroscopy (XAS). As nickel is the primary charge compensating element in Ni-rich layered oxides at 2.5-4.4 V, they mainly focus on evolution of nickel oxidation states. During the 1st cycle, the nickel K-edge exhibits a reversible energy shift on charging and discharging (Figure 45a). After 35 cycles, the pre-edge region feature is well-preserved and the edge position of the charged cathode shows a minor shift compared to the initially charged cathodes, suggesting that the bulk structural properties (for example, symmetry) of long-time cycled cathode is maintained. The extended X-ray absorption fine structure analysis in Figure 45b reveals that the interatomic distances of Ni-O and nickel - transition metal (Ni-TM) in charged materials remain unchanged after cycling, which is another positive indicator of structural stability. More detailed properties at the particle level are analyzed through transmission X-ray microscopy (TXM), which can pinpoint spatial redox reactions in a specific particle and provide information related to lithium diffusion pathways. The color code in the TXM images corresponds to different nickel oxidation states. Compared to the pristine particles (Figure 45c), a significant charge heterogeneity can be observed in the particles once they undergo initial charging (Figure 45d-f), which can be attributed to the non-uniform redox reactions caused by the local limitations of electronic and ionic transport. The charged particles also demonstrate a holistic core-shell structure, with a higher oxidation state at the subsurface region and a lower oxidation state in the bulk (Figure 45g). After prolonged cycling, the charge heterogeneity increases, with the appearance of some minor inactive domains (Figure 45e). Nevertheless, considering the consistency of hard XAS results for charged electrodes before and after long-time cycling, the bulk structure is stable in the MIC-based solid-state systems.



Figure 45. (a) X-ray absorption near-edge spectroscopy and (b) extended X-ray absorption fine structure results of pristine and charged NMC-811 cathodes. (c-e) Transmission X-ray microscopy results of (c) pristine cathode, (d) 2^{nd} charged cathode, and (e) 35^{th} charged cathode; scale bars are all $5 \,\mu$ m. (f) Histogram of nickel K-edge energy distribution, and (g) depth-dependent nickel K-edge energy variation in the 2^{nd} charged cathode.

Finally, the team is continuing advanced NMR analyses on MIC electrolytes, now on samples that have been long-term cycled and then removed intact from disassembled cells. They have investigated coin-cell crimping pressure over a range of 0.2 to 0.6 tons (employing a 0.9 cm² active cell area) to find the optimal cell performance in the range of 0.3 to 0.4 tons. After cell disassembly, MIC electrolytes are fully intact and can be peeled off the electrodes. The MIC electrolytes display a single component NMR diffusion signal curve, verifying that no heterogeneity (for example, cracking, surface modification, ion/salt loss) occurs during cell assembly/disassembly and cycling. Figure 46 shows a representative ¹H NMR Stejskal-Tanner (normalized NMR signal intensity) plot of a cycled cell at room temperature with a crimping pressure of 0.3 tons. Next, they will measure multinuclear diffusion and spectroscopy on NMC and Li-metal cells cycled until failure.



Figure 46. Proton (cation) nuclear magnetic resonance (NMR) diffusometry signal curve showing a diffusion coefficient $D = 1.95 \times 10^{-11}$ m²/s for a Li||Li cell charged/discharged for 100 cycles. Best fit to the data (black points) with a single diffusing component (red line) shows no significant heterogeneity introduced into the sample. The sample was sealed in glass under vacuum at room temperature after cell disassembly and cycling and measured at 25.3°C on the team's 400 MHz NMR spectrometer.

Patents/Publications/Presentations

Presentations

- Department of Chemistry, Clemson University, Clemson, South Carolina (April 7, 2022): "Novel Solid Electrolytes Based on a Highly Charged and Rigid Double Helical Polymer"; L. A. Madsen. Invited.
- Proctor and Gamble Corporation, Mason, Ohio (May 2, 2022): "Understanding Molecular Partitioning and Transport in Polymeric Systems"; L. A. Madsen. Invited.
- Center for Soft Matter and Biological Physics, Virginia Polytechnic Institute and State University, Blacksburg, Virginia (May 4, 2022) "Understanding a Double-Helix Ionic Polymer Composite Electrolyte"; L. A. Madsen. Invited.

Task 1.19 – Synthesis of Composite Electrolytes with Integrated Interface Design (Sanja Tepavcevic, Argonne National Laboratory)

Project Objective. This project aims to develop well-controlled, scalable $Li_7La_3Zr_2O_{12}$ (LLZO) nanofiber and composite polymer electrolyte (CPE) synthesis processes that will address the manufacturing challenges of current solid-state electrolytes (SSEs) and demonstrate the fabrication of large-area, thin CPE membranes with outstanding electro-chemomechanical properties.

Impact. The outcome of this proposal will be a transformative manufacturing solution that can create large-area, mechanically and (electro)chemically stable SSEs (0 V to 4.5 V versus Li/Li⁺) with Li⁺ conductivity of $\geq 10^{-3}$ S/cm at room temperature enabling ≥ 1 C charging rates.

Approach. To commercialize all-solid-state Li-ion battery technology, further advances will require the application of knowledge, concepts, and tools from several fields including materials science, physics, engineering, theory, and interfacial electrochemistry. The team's research philosophy is to establish a synthesis-material characterization-computation cycle that advances synthesis, chemistry, microstructure, interfaces, and transport in CPEs by a coordinated, interdisciplinary approach. The team's diverse expertise will allow them to understand, create, and rapidly scale up composite electrolytes to meet ambitious conductivity, energy, and power density targets.

Out-Year Goals. The innovative design and synthesis of integrated SSE interfaces include the following goals: (1) achieve high room-temperature conductivity by optimizing composite microstructures, synthetically modifying the LLZO-polymer interface, and reducing CPE membrane thicknesses down to 20 μ m; (2) create a stable and effective interface between the CPE and metallic lithium that yields low charge transfer resistance and enables high critical current density (> 3 mA/cm²); and (3) modify the CPE-cathode interface to enable the use of different cathodes [that is, lithium iron phosphate, LiCoO₂, and Ni-Mn-Co (NMC)] and achieve high energy and power density in batteries.

Collaborations. Computational researchers will further help the team to understand and design better all-solid-state batteries. They will work closely with L. A. Curtiss, P. Barai, K. Chavan, and V. Srinivasan (Argonne National Laboratory) to understand the molecular and mesoscopic characteristics and performance of the team's CPEs.

- 1. Achieve uniform distribution of LLZO nanofibers within CPEs. (Q1, FY 2022; Completed)
- 2. Vary LLZO doping (aluminum, germanium, undoped) to improve conductivity and strength. (Q2, FY 2022; Completed)
- 3. Optimize LLZO nanofibers loading and processing to demonstrate good percolation and maximize conductivity. (Q3, FY 2022; In progress)
- 4. Use computational methods at the continuum level to gain understanding of the improved conduction pathways and lithium deposition mechanisms. (Q4, FY 2022; In progress)

Impact of Aluminum and Gallium Dopants on Chemical Reactivity of LLZO with Metallic Lithium. Al^{3+} and Ga^{3+} dopants, when inserted into bulk LLZO, are directly substituting onto the lithium sublattice of interconnected tetrahedral and octahedral sites and show relatively little difference in formation energy with respect to defects on the lithium sublattice. This has led to the hypothesis that these two dopants are chemically similar in LLZO, making dopant selection a matter of preference and availability. To examine the above hypothesis, the team investigated phase transformation, dopant clustering, and diffusivity effects of Al³⁺ and Ga^{3+} doping. A series of modeling experiments has been initiated using density functional theory calculations as uniquely suitable for modeling the reduction of ionic species as they are moved closer to or further from the Li-metal interface. Example simulation cells of the Li/LLZO interfaces are shown in Figure 47a where dopants are on the tetrahedral sites. The oxidation/reduction potential of LLZO was assessed by looking at changes in the density of state (DOS) for electrons in the structures shown in Figure 47b. Substitution of $A1^{3+}/Ga^{3+}$ in the bulk of LLZO shows no changes in Fermi energy level or band gap width, indicating that the substitution of Al^{3+} for Ga^{3+} does not form electronically conducting states. However, when interfaced with lithium metal, the metallic lithium states fall between the valence and conduction bands of LLZO, shifting the DOS to the left and raising the Fermi energy closer to the conduction band of LLZO. While electrochemical impedance spectroscopy measurements with blocking electrodes showed that Al-doped LLZO can achieve an ionic conductivity of 6×10^4 S/cm (data not shown), Ga-doped LLZO pellets with the high purity cubic phase demonstrated a higher ionic conductivity of 2.3×10^{-3} S/cm (Figure 47c), being the highest among all the reported dopants. Despite the high conductivity of Ga-doped cubic LLZO, Figure 47d also shows that with prolonged contact between lithium and Ga-LLZO, interfacial resistance decreased, while charge transfer resistance continuously increased over time due to chemical reactions at the Li|Ga-LLZO interface. To investigate this interfacial reactivity, which is in the line with the team's previous experimental studies, a thin layer of lithium metal was deposited onto the Ga-LLZO surface by e-beam evaporation. X-ray photoelectron measurements of this sample revealed that Ga³⁺ was reduced to Ga⁰, which formed Ga-Li alloy at the interface (Figure 47e). Based on this observation, they believe that interfacial reactions with dopant atoms can dramatically impact the overall cell impedance and ultimate performance over time.



Figure 47. (a) Simulation cells showing three possible dopant locations in LLZO near the surface with the optimized dopant locations for Al³⁺ and Ga³⁺ in pink. (b) Density of states for doped and undoped bulk LLZO (left) and Li⁰|LLZO interface (right) shifted to the Fermi level at zero. (c) Electrochemical impedance spectroscopy (EIS) plots of Ga-LLZO with gold blocking electrodes. (d) ElS spectra and circuit of Ga-LLZO in a Li||Li symmetric cell at open circuit over several days. (e) X-ray photoelectron spectroscopy measurements of Ga-LLZO samples before and after lithium metal deposition.

Synthesis of Nanofibers Without and With Aluminum and Gallium Dopants. Gallium is the most attractive LLZO dopant, as it has the highest bulk ionic conductivity at room temperature. However, Ga³⁺ can be readily reduced when it is in contact with lithium metal, as shown in the theoretical studies above, limiting its use in Li-metal batteries. The team's LLZO polymer composites have the advantage of utilizing high conductivity Ga-doped LLZO for bulk Li⁺ transport while preventing its contact with the lithium electrode since the LLZO is physically separated from the electrode by the poly(ethylene oxide) – lithium bis(trifluoromethanesulfonyl)imide (PEO-LiTFSI) polymer phase.

They have investigated the synthesis of LLZO nanofibers without and with Al^{3+} or Ga^{3+} dopants. Figure 48a shows X-ray diffraction data for three nanofiber samples fabricated by annealing at 750°C for 2 hours. All LLZO phases are cubic, which is the necessary phase for fast Li⁺ conduction. Minor impurity phases like La₂Zr₂O₇ were observed in some samples, suggesting the request of further optimization of lithium content and/or precursor compositions of these samples. Figure 48b-c shows scanning transmission electron microscopy – high-angle annular dark field images and energy dispersive X-ray spectroscopy elemental mapping of Al-doped and Ga-doped LLZO nanofibers. Both aluminum and gallium dopants showed a homogeneous distribution within fibers, which is critical for obtaining a highly conductive Li⁺ transport network. Importantly, the team is able to generate cubic nanofibers with all dopants with both lab-scale and large roll-to-roll nanofiber fabrication equipment, showing this approach is scalable for generating Ga-doped LLZO nanofibers.



Figure 48. (a) X-ray diffraction of LLZO nanofiber without added dopants and with Al³⁺ and Ga³⁺ dopants, all showing cubic phase. Scanning transmission electron microscopy high-angle annular dark field images and energy dispersive X-ray spectroscopy elemental mapping of (b) Al-doped and (c) Ga-doped LLZO nanofibers showing uniform dopant distribution across multiple nanofibers.

CPE membranes made with the three different fibers (undoped, Al-doped, and Ga-doped) show identical flexibility and mechanical performance, indicating the dopant does not impact macroscale electrolyte properties. Preliminary measurements with composite electrolytes show no significant change in bulk ionic conductivity with changing dopant, as the PEO-LiTFSI matrix still dominates conductivity (~ 10^{-6} S/cm at 25° C and ~ 10^{-4} S/cm at 60° C). The team is collaborating with C. Chan at Arizona State University to determine the inherent conductivity of their LLZO nanofibers. Work next quarter will optimize LLZO loadings and other chemistries to improve percolation to unlock conductivity of LLZO nanofibers in these electrolytes.

Patents/Publications/Presentations

Presentation

 Vehicle Technologies Office Annual Merit Review, Washington, D. C. (June 21–23, 2022): "Synthesis of Composite Electrolytes with Integrated Interface Design"; S. Tepavcevic,^{*} M. Counihan, Y. Zhang, D. Powers, S. Hu, P. Barai, K. Chavan, J. Connell, L. A. Curtiss, and V. Srinivasan. Invited.

Task 1.20 – Polymer Electrolytes for Stable, Low-Impedance, Solid-State Battery Interfaces (X. Chelsea Chen, Oak Ridge National Laboratory)

Project Objective. The overall project objective is to develop stable polymer/cathode and polymer/anode interfaces with low interfacial impedance for integration of a thin solid composite electrolyte into a battery, to achieve chemical stability at the electrodes, high energy density (500 Wh/kg), high rate (1 mA/cm²), and long cycle life (80% capacity retention for 300 cycles), demonstrated in pouch cells.

Impact. Achieving stable, low-impedance interfaces at both the cathode and anode sides is critical to achieve high energy density with excellent safety, lifetime, and cycling efficiency. This project will identify key design strategies needed to prepare polymer electrolyte (PE) to achieve stable, low-impedance polymer/cathode and polymer/lithium interfaces and to develop processing procedure to integrate a thin composite electrolyte into a solid-state battery (SSB). Success will enable U. S. Department of Energy (DOE) technical targets: energy density of 500 Wh/kg with 80% capacity retention for at least 300 cycles.

Approach. The team's main design principle is to use an oxide ceramic as the main ion transporting phase in the electrolyte and a fluorinated polyether-based PE to form optimized interfaces as well as to provide flexibility to the electrolyte membrane. Compared with inorganic electrolytes, PEs are soft and flexible and capable of maintaining good contact at interfaces. However, several technical barriers remain. On the Li-metal side, the interface between PEs and thin-Li and Li-free anodes is still at an early stage of investigation. Interface optimization using thin-Li and Li-free designs is crucial to reaching the DOE 500 Wh/kg target. On the cathode side, studies on the polymer/cathode interface are scarce. The interface resistance between polymer (catholyte) and cathode active material (CAM) is not well understood. In addition, with a target voltage stability of 0-4.5 V versus Li/Li⁺, a polymer with oxidative stability up to 4.5 V is needed. Fluorinated polyethers have the potential to form stable and low impedance interfaces at both the cathode side and the anode side. By systematically examining the effects of fluorine content, polymer chain length and structure, and plasticization on the interfacial resistance with the cathode and the anode, a balance between the desolvation kinetics of Li⁺ and diffusion rate will be achieved to optimize the interface ion transport. A fundamental understanding of the origin of interfacial impedance with the cathode as well as Li-metal anode will be developed alongside the optimization process to generate design rules for polymers with optimized interfaces. The team will also develop a processing procedure to integrate a thin composite electrolyte that was previously developed into a full cell. The composite electrolyte features an interconnected ceramic structure with a thickness of 20 µm. It will be backfilled with the newly developed fluorinated PEs. The mechanical properties of the composite electrolytes will be optimized to accommodate roll-to-roll processing.

Out-Year Goals. In the second and third year of this project, the team will focus on optimizing the cathode/polymer as well as the Li-anode/polymer interface with maximized stability and minimized interfacial impedance. A fundamental understanding of parameters that determine the interfacial impedance and strategies to minimize the interfacial impedance will be developed. The fourth and fifth year of the project will be focused on integration of a thin composite electrolyte into a full cell to achieve high energy density, high rate, and long cycle life, as stated in the overall project objectives. Processing techniques and procedures for electrolyte integration will be investigated to achieve this goal.

Collaborations. Work is being conducted by B. Armstrong, S. Kalnaus, R. Sahore, X. Tang, A. Ullman, and X. C. Chen.

- 1. Synthesize fluoropolyether polymers with four fluorine concentrations. (Q1, FY 2022; Completed)
- 2. Quantify ionic conductivity, Li⁺ transference number, oxidative stability, thermal stability, glass transition temperature, and mechanical modulus as a function of fluorine concentration. (Q2, FY 2022; Completed)

- 3. Optimize conductivity of composite electrolyte with a three-dimensional (3D) interconnected structure (at least 5×10^{-5} S/cm at room temperature). Measure flexural strength of the composite electrolyte with three compositions. (Q3, FY 2022; Completed)
- 4. Quantify interfacial resistance and stability between the fluoropolyether polymers and lithium anode from two different sources. (Q4, FY 2022)
- 5. Build a prototype SSB in a pouch cell using the interconnected composite electrolyte as the electrolyte layer. (FY 2022 Annual Stretch Milestone)

Synthesis of Fluorinated Polyether-Containing PEs

This quarter, the team continued optimizing the conductivity of fluorinated polyether-containing PEs. They chose the membranes prepared using the acetonitrile/hexafluorobenzene (HFB) mixed solvents with the salt infused afterward as their system of study, as the other mixed solvent system, tetrahydrofuran (THF)/ n-methyl-2-pyrrolidone, produced membranes with large-scale phase separations (as reported last quarter). The salt was introduced into the membranes after membrane formation by soaking them in a Li-salt solution. The membranes were subsequently dried at 80°C in a vacuum oven to remove residual solvents. As reported last quarter, the conductivities of the dry poly(ethylene oxide) (PEO)/ perfluoropolyether (PFPE) mixed electrolytes were at least one order of magnitude lower than the dry PEO electrolyte membranes demonstrated steep overpotentials during Li//Li symmetric cell cycling and quickly reached the cut-off voltage; therefore, they could not be cycled. This quarter, the team explored plasticization of the electrolyte membranes to improve their ionic conductivity and also studied the electrochemical oxidative stability of the membranes in their plasticized state.

Ethylene carbonate (EC), dimethyl carbonate (DMC), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt were introduced into the PEs by thoroughly immersing the salt-free membranes in 1 M LiTFSI EC/DMC solution in a sealed container inside an Ar-filled glovebox for overnight. The swollen membranes were pat-dried and used for cell assembly without further drying. The ionic conductivities of all the plasticized membranes were 1-2 orders of magnitude higher compared to the dry membranes (Figure 49a). Room-temperature ionic conductivities of the plasticized PEO and 60PFPE (60:40 w/w PFPE:PEO) are in the range of 10^{-4} S/cm, which is relevant for electrochemical systems. Next, the team explored the electrochemical oxidative stability of these membranes. Figure 49b shows linear sweep voltammetry plots obtained in a Li/Mo cell configuration for the three plasticized electrolytes, by scanning from open circuit up to 7 V at a scan rate of 0.1 mV/s. They observed a spike in current for PEO starting from ~ 5.8 V. Taking a closer look reveals the reactions starting at ~ 3.6 V for PEO (Figure 49b, inset), whereas 60PFPE maintains a straight line within the whole test range, which indicates its superior oxidative stability. The team also performed step-wise potentiostatic holds to further study the oxidative stability of the membranes in Li/Mo cells. They increased voltage by 0.1 V for each step from open circuit to 6 V, held it for 1 hour at each step, and recorded the current response. The results shown in Figure 49c-d [open circuit voltage to 4.6 V in (c), and 4.7 - 6.0 V in (d)] indicate that in these tests, PEO is oxidatively stable up to only 5 V. Meanwhile, blending PFPE into PEO increased the oxidative stability to at least 6.0 V. Next quarter, the team will continue investigating performance of these membranes in full cells and also characterizing the structure and morphology of these membranes to gain insights on how to further improve the conductivity and electrochemical performance of these membranes.



Figure 49. (top left) lonic conductivity of PEO, 60PFPE, and PFPE electrolyte membranes in plasticized state. (top right) Linear sweep voltammetry from open circuit voltage (OCV) to 7 V at 0.1 mV/s for PEO, 60PFPE, and PFPE in Li/Mo cells at 30°C. (bottom) Potentiostatic holds for 1 hour at each voltage step from OCV to 6 V. Each step is 0.1 V in Li/Mo cells at 30°C. Black line is voltage. Blue is PEO current response, and red is 60PFPE current response.

3D-Interconnected Ceramic Based Composite Polymer Electrolytes (CPEs)

This quarter, the team continued the physical and electrochemical characterization of the trilayer structured 3D-interconnected ceramic-based trilayer CPE (Figure 50), developed last quarter. As a summary, it is a 145- μ m thick, 3D-interconnected LICGCTM ceramic based porous scaffold that is infiltrated completely with cross-linked polyethylene oxide (xPEO) / LiTFSI PE. Afterward, the two surfaces are spray coated with thin (<5 μ m) linear PEO/LiTFSI electrolyte layers. This membrane is robust enough to survive coin-cell crimping without fracturing for electrochemical evaluations, unlike previous iterations. At room temperature, its ionic conductivity is measured to be one order lower than the corresponding unfilled ceramic scaffold (Figure 50a). This is likely due to high interfacial impedance between linear PEO/LiTFSI and LICGCTM ceramic at the two surfaces (discussed later in Figure 51). The transference number of trilayer CPE is improved by roughly a factor of 3 (0.3 versus 0.1) compared to pure xPEO/LiTFSi (Figure 50b). Voltage profiles of Li//Li symmetric cell cycling showed lower and stable overpotentials, compared to the high and steep overpotentials of xPEO/LiTFSI electrolyte, likely stemming from their difference in transference numbers (Figure 50c). Long-term symmetric cell cycling at 0.2 mA/cm², 2.5 hours, and 70°C showed no dendrite formation for both trilayer CPE and the control xPEO/LiTFSI electrolyte (Figure 50d).



Figure 50. (a) Arrhenius plot of the ionic conductivity of the trilayer composite polymer electrolyte (CPE). (b) Current versus time obtained during the transference number measurement, comparing the steady-state current obtained during 10 hours of polarization, for the trilayer CPE and the pure xPEO/LiTFSI electrolytes. Note, one of the plots is shifted by an hour on the x-axis for ease of viewing the initial current values. (c) Voltage profiles of symmetric cells made with trilayer CPE and xPEO/LiTFSi electrolytes, cycled at 0.2 mA/cm², 2.5 hours each strip/plate, at 70°C. (d) Long-term cycling of the two symmetric cells shown in (c).

To investigate the role of surface linear PEO/LiTFSI layer in impacting the overall impedance of the trilayer CPE membrane, a control trilayer sample was prepared with a commercial, dense LiCGCTM plate (140- μ m thick) in the middle by spray coating its two surfaces with thin (< 5 μ m) linear PEO/LiTFSI PE (Figure 51a-b). The bulk conductivity of as-received dense LICGCTM plate is measured to be 2.9 × 10⁻⁴ S/cm. Despite its higher ionic conductivity compared to the unfilled LICGCTM scaffold (1.2 × 10⁻⁵ S/cm), its corresponding trilayer membrane showed similar or lower ionic conductivity at all temperatures measured (Figure 51c). A layer-by-layer breakdown of the total impedance of this trilayer was performed by individually fitting the two semicircles observed in electrochemical impedance spectroscopy (data not shown), and ascribing them to either dense ceramic plate or linear PEO/LiTFSI layer (Figure 51d). While the extracted impedance of the dense ceramic layer matches with what is expected, the extracted impedance of the linear PEO/LiTFSI layer is 1-2 orders lower than what is expected for this electrolyte, especially at high temperatures (70°C and above). Hence, it is reasonable to assume contribution from a highly resistive polymer/ceramic interface layer of unknown thickness contributing to the extra impedance in the trilayer. This result is overall consistent with the team's previous reports (X. Chen et. al, *ACS Energy Letters* 4 (2019): 1080–1085; M. Palmer et. al, *Energy Storage Materials* 26 (2020): 242–249).



Figure 51. (a-b) Cross-section scanning electron microscopy images of the trilayer membrane prepared with dense LICGC[™] plate in the middle. (c) Arrhenius plots of ionic conductivity of the two types of trilayer samples prepared with either LICGC[™] scaffold or dense plate. (d) lonic conductivity of the individual layers extracted from the impedance spectra for the dense LICGC[™] plate based trilayer sample shown in (c).

Patents/Publications/Presentations

Presentation

• Vehicle Technologies Office Annual Merit Review, Washington, D. C. (June 21–23, 2022): "Polymer Electrolytes for Stable Low Impedance Solid State Battery Interfaces"; R. Sahore on behalf of X. Chen.

Task 1.21 – Ion Conductive High Li⁺ Transference Number Polymer Composites for Solid-State Batteries (Bryan McCloskey, University of California, Berkeley)

Project Objective. This project seeks to develop polymer-inorganic composites that have an optimal combination of conductivity, processability, and low interfacial resistance at both a Li-metal anode and a porous $Li[Ni, Co, Mn]O_2$ (NMC) cathode. In an effort to enable Li-metal anodes, mechanically rigid solid-state Li^+ conductors, such as $Li_7La_3Zr_2O_{12}$ (LLZO), $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP), and $Li_2S-P_2S_5$ (LPS) glasses, have been employed due to their high Li^+ ion conductivity and, when engineered to eliminate interfacial defects, appropriate stiffness to suppress Li-metal dendrite formation. However, for these materials to result in batteries that compete against current commercial cells in terms of energy density and cost per kWh, they would need to be manufactured at no more than 50-µm thickness and cost no more than \$5 per square meter. These metrics are daunting for pure thin-film inorganic ion conductors, particularly when a porous, thick cathode also needs to be used to achieve competitive cell energy densities. To overcome these challenges, this project aims to develop polymer-inorganic composites, where high Li^+ transference number polymer electrolytes (PEs) serve as a binder for inorganic ion conducting particles.

Impact. By optimizing the composition of this composite electrolyte, the team aims to marry the processability and interfacial mechanical compliance of polymers with the impressive transport properties of inorganic composites, thereby enabling roll-to-roll manufacturing to allow thin ($< 50 \,\mu$ m) layers of high-conductivity solid-state conductors to be cost-effectively incorporated into batteries.

Approach. The project approach relies on the following key steps in FY 2022: (1) using monomers with (trifluoromethanesulfon)imide (TFSI) anions appended to them, synthesize and characterize polyanionic PEs with high Li⁺ transference number and conductivity; (2) through systematic material structure-property characterization, understand how to reduce interfacial ion transport impedance between inorganic ion conductors (specifically, thin-film inorganic conductors such as Li-La-Zr-Ta-O (LLZTO), LATP, and LPS) and high Li⁺ transference number PEs; and (3) characterize electrode-polymer and electrode-inorganic conductor interfacial resistances at a Li-metal anode.

Out-Year Goals. The overall project goal is to develop an optimized polymer-inorganic Li-ion conductor with superior conductivity (> 1 mS/cm), thin-film processability, and low electrode interfacial impedance. Of particular interest in the out years is development of a process to fabricate thick, porous, and electrochemically stable NMC cathodes using the polymer-inorganic composite as both the binder and electrolyte. The team aims to integrate the optimized high-loading cathode with a 25- μ m thin-film polymer-inorganic electrolyte to create an "anode-less" battery with 500 Wh/kg and 80% capacity retention after 300 cycles.

Collaborations. While this project has a single principal investigator (PI), B. McCloskey will leverage the collaborative battery research environment at Lawrence Berkeley National Laboratory (LBNL) and coordinate with other LBNL PIs in the BMR Program for materials and experimental development.

- 1. Establish polymer synthesis by making two neat TFSI-containing polymers. (Q1, FY 2022; Completed)
- 2. Measure conductivity of two polymers using Li-Li symmetric cells. (Q2, FY 2022; Completed)
- 3. Measure interfacial impedance evolution of polymer in a Li-Li cell. (Q3, FY 2022; Completed)
- 4. Synthesize a series of four copolymers with various ratios of TFSI monomer and a film-forming monomer. (Q4, FY 2022; In progress)

This quarter, the team refined their Reversible Addition-Fragmentation Chain Transfer polymerization methods of their model polyanion, poly((trifluoromethane)sulfonimide lithium methacrylate) (PLiMTFSI), ultimately allowing them to achieve 95% yield, as opposed to their previous method that gave a 60% yield. Molecular weight measured with gel permeation chromatography matched well with their previous synthesis technique. This gives the team confidence that they are able to precisely control the molecular weight in their refined synthesis procedure.

This quarter, to impart polymer mechanical properties that allow good film formation, the team incorporated two polymer plasticizers in film compositions that also contained PLiMTFSI. Glycerol carbonate methacrylate and acetonide-protected trimethylolpropane methacrylate allowed them to explore methods of creating flexible, free-standing films, whereas films prepared from PLiMTFSI by itself were brittle and difficult to handle, as was expected given its high ion content. While a reliable method to produce these free-standing films at a thickness of less than $100 \,\mu\text{m}$ is still ongoing, they were able to measure conductivity of various polymer/plasticizer combinations using stainless-steel symmetric cells. The conductivity values are given below in Figure 52, which shows that the plasticizer content had an impact on the conductivity of PLiMTFSI. While the plasticizers with good ion solvating properties, should provide improved ion conductivity. Conductivity measurements incorporating the team's Li₇La₃Zr₂O₁₂ (LLZO) ceramic will be targeted next quarter, in addition to measuring the interfacial impedance of their polymer-plasticizer-ceramic system. Additionally, moving their films to Li-Li symmetric cells from stainless-steel symmetric cells is a goal for next quarter.





In addition to polymer film synthesis and characterization, the team has initiated studies on the LLZO ceramic powder they have procured. Through an acid titration technique developed in the lab, they determined that their LLZO particles have significant amounts of lithium carbonate present, and through X-ray photoelectron spectroscopy verified that carbonate is present on the particle surface. Previous research shows that carbonate can have a significant impact on electrochemical performance and ion transport across interfaces, so the team investigated how they might be able to change the amount of carbonate on the surface. Exposing the LLZO particles to air for 12 hours resulted in more carbonate forming, suggesting that the particles' surface as received is not passivated, which suggests that the carbonate surface layer is not dense. Furthermore, a simple water washing procedure (exposure to air-free water for 5 minutes) resulted in approximately half of the carbonate being removed from the LLZO sample. These data are listed below in Table 3, and demonstrate that the team now has an additional, largely unstudied knob that they can turn to examine its impact on lithium transport properties.

Table 3. Lithium carbonate content of various Li7La3Zr2O12 (LLZO) sam	ples.
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LLZO Sample Type	Li ₂ CO ₃ wt%
As-received	5.56
Air-exposed	16.17
Washed	2.40

In short, this quarter the team has made significant progress in understanding the basic properties of the building blocks they are using in their composite electrolyte. Next quarter, they plan to produce free-standing polymer films that will allow them to begin using Li-Li symmetric cells. This will allow them to begin incorporating LLZO in with their PLiMTFSI electrolytes. Simultaneously, they hope to have a deeper understanding of where lithium carbonate is on LLZO particles as well as how to control the amount of carbonate on the ceramic.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 1.22 – Inorganic-Polymer-Composite Electrolyte with Architecture Design for Lithium-Metal Solid-State Batteries (Envuan Hu, Brookhaven National Laboratory)

Project Objective. This project targets the following goal: the composite electrolytes will be thin (< 100 µm) and have high Li-ion conductivity ($\geq 10^{-3}$ S/cm at room temperature), low interfacial impedance, and desirable mechanical properties. When used in the solid electrolyte (SE) Li-metal battery, a current density > 1 mA/cm² and an aerial capacity of 2-3 mAh/cm² can be achieved with more than 300 cycles. The constructed LiNi_xMn_yCo_{1-x-y}O₂ (NMC) / LiCoO₂ || composite electrolyte || Li-metal cell can be operated at up to 4.5 V versus Li⁺/Li. The SE will also be compatible with high loading cathodes in achieving high energy density at the coin or pouch-cell level.

Impact. The results of this project will lead to advancement of solid-state batteries (SSBs), a beyond Li-ion battery option with better safety characteristics and higher energy density. The project will also provide valuable knowledge to U. S. industries in scaling up SSB production for vehicle applications, thus providing solutions to the clean energy strategy.

Approach. The project approaches are as follows: (1) design and synthesize polymer with anion-tether strategy for high transference number, (2) through theories and experiments, design hierarchical inorganic electrolyte for suppressing lithium dendrite penetration, (3) optimize the composite electrolyte composition and structure, (4) use additives for Li-metal anode and NMC cathode protection, and (5) use synchrotron and cryogenic electron microscopy characterization to understand the bulk electrolyte and interphases.

Out-Year Goals. The out-year goals are to synthesize single ion conducting solid polymer electrolyte (SPE) with high transference number and conductivity; to design hierarchical inorganic electrolyte with high ionic conductivity and good mechanical/electrochemical stability; and to use synchrotron total scattering to study the structure of ceramic/polymer electrolyte.

Collaborations. The principal investigator (PI) will work closely with co-PIs H. Xin of University of California, Irvine, and X. Li of Harvard University.

- 1. Synthesize single ion conducting SPE with high transference number and conductivity. Achieve formulation optimization to achieve transference number > 0.5. (Q1, FY 2022; Completed)
- 2. Design hierarchical inorganic electrolyte with high ionic conductivity and good mechanical/electrochemical stability. Develop inorganic electrolytes (sulfides, halides) with ionic conductivity > 1 mS/cm and a hierarchy of voltage stability up to 4.5 V and down to near 0 V in cyclic voltammetry (CV) tests. (Q2, FY 2022; Completed).
- 3. Optimize composition for plastic hybrid electrolyte. Tune the SPE and inorganic electrolyte composition to enable compatibility. (Q3, FY 2022; delayed due to slow hiring process. Expected to be completed by September 2022.)
- 4. Use synchrotron total scattering to study the structure of ceramic/polymer electrolyte. Complete synchrotron pair distribution function analysis of the ceramic/polymer electrolyte. (Q4, FY 2022)

This quarter, the team designed a SE with the chemical composition of $Li_{5.5}PS_{4.5}Cl_{1.5}$ within the argyrodite phase through the chemical synthesis route optimized by X. Li's group at Harvard (Figure 53a). The electrolyte in the team's impedance measurement shows ionic conductivity of 8 mS/cm at room temperature (Figure 53b).



Figure 53. Powder X-ray diffraction (a) and impedance (b) at room temperature of as-synthesized Li_{5.5}PS_{4.5}Cl_{1.5}.

The CV test shows a wide voltage stability window. The decomposition current down to 0 V in direct contact with Li-metal anode (Figure 54a) is very small, with the same for the battery charged up to 6 V (Figure 54b) in SSBs. For the low-voltage region, cells were scanned from open circuit voltage (OCV) to 0.1 V and then back to 2.5 V. For the high-voltage region, cells were tested from OCV to 6 V and subsequently scanned back to 2.5 V. All cells were previously pressed at 125 Mpa, and external pressure of 38 MPa was applied during test.



Figure 54. Li_{5.5}PS_{4.5}Cl_{1.5} (LPSCI1.5) shows a voltage stability to lithium metal (a) and up to 6.0 V (b) in solid-state batteries in cyclic voltammetry tests. Li/LPSCI1.5/LPSCI1.5-C [cathode composition 0.9:0.1- LPSCI1.5:carbon black (w/w)] were collected on a Solartron 1455A with a voltage sweeping rate of 0.1 mV s⁻¹ from 0.1 V to 6 V.
Patents/Publications/Presentations

Publication

Lin, R., Y. He, C. Wang, P. Zou, E. Y. Hu, X-Q. Yang, K. Xu, and H. L. Xin. "Characterization of the Structure and Chemistry of the Solid–Electrolyte Interface by Cryo-EM Leads to High-Performance Solid-State Li-Metal Batteries." *Nature Nanotechnology* 17 (2022): 768. Task 1.23 – Solid-State Batteries with Long Cycle Life and High Energy Density through Materials Design and Integration (Gerbrand Ceder, University of California, Berkeley)

Project Objective. This project aims to create solid-state Li-metal batteries (SSLMBs) with high specific energy, high energy density, and long cycle life using scalable processing techniques. The team will achieve this by addressing fundamental challenges associated with (1) interfacial reactivity, (2) Li-metal plating, and (3) cathode loading. Addressing these challenges supports the broader Vehicle Technologies Office goal of solid-state batteries (SSBs) with increased cycle life and energy density.

Impact. Ultimately, this project will develop an understanding of how to prevent interfacial reactions, make uniform Li-metal plating, and increase cathode loading significantly. The knowledge obtained from this project will be used to design SSLMBs with high specific energy of 500 Wh/kg, 80% capacity retention for at least 300 cycles, and critical current density $> 1 \text{ mA/cm}^2$.

Approach. This project addresses several fundamental challenges and makes the SSLMB competitive, surpassing the specific energy, energy density, and cycle life of Li-ion batteries:

- Create homogeneous lithium deposition on the anode without penetration of lithium metal through the separator to achieve high cycle life and high safety. The team will achieve this with the use of an active buffer layer (ABL) that combines active and inactive components to homogenize lithium plating and to keep the lithium plating potential away from the solid electrolyte (SE) separator.
- Limit chemical reactivity and mechanical decohesion between the SE, carbon, and cathode material in the composite cathode so that high cycle life can be achieved. The team will limit chemical reactivity by protecting the carbon from the SE, by using novel cathode coatings designed to be stable to high voltage and that do not react with the SE, by using novel solid halide catholyte conductors, and by using inorganic/organic solid composite electrolytes in the cathode.
- Achieve high volumetric loading of the active cathode material in the composite cathode to achieve high energy density and high specific energy. The team will achieve high volumetric cathode loading by creating thin highly porous conductor scaffolds that are infiltrated with cathode, by tailored particle size distributions of deformable lightweight conductors, and by the use of organic/inorganic hybrids.
- Create inexpensive materials and processes to fabricate SSBs so that they can be cost-competitive with Li-ion batteries. The team will create solution-processable organic/inorganic hybrids to be used as separator and to blend in the composite cathode; they will use inexpensive, scalable ceramics processing techniques to create high loading composite cathodes.

Out-Year Goals. The ultimate project goal is to develop SSLMBs that achieve high specific energy of 500 Wh/kg, 80% of capacity retention after 300 cycles, and $> 1 \text{ mA/cm}^2$ of critical density.

Collaborations. The principal investigator's (PI's) team collaborates with the following co-PIs: H. Kim, V. Battaglia, G. Chen, M. M. Doeff, G. Liu, M. Scott, M. Tucker, and J. Urban, all at Lawrence Berkeley National Laboratory.

- 1. Demonstration of use of ABL in Li-metal cell with active component other than silver. (Project start in Q2, FY 2022; Completed)
- 2. Integration of LiNi_xMn_yCo_{1-x-y}O₂ (NMC) into three-dimensional (3D) carbon framework with cathode active material (CAM) loading > 80 wt%. (Q3, FY 2022; Completed)
- 3. Model studies to assess compatibility of cathode components. (Q4, FY 2022)

Task 1: Buffer Layers to Stabilize Lithium/SE Interface and Create Uniform Lithium Plating (H. Kim, G. Ceder, V. Battaglia, and M. Scott)

This task aims to develop ABLs to reduce interfacial resistance and stabilize interfaces at Li/SE, and to avoid dendritic lithium growth. Recent studies have shown that a AgC composite layer between the current collector and the SE can prevent dendrite formation in SSBs where lithium plating and stripping take place. The initial goal of this project is to understand the mechanism of lithium plating in the presence of such a buffer layer and to understand what causes more uniform, favorable lithium deposition. To understand the mechanism, it is important to reproduce some parts of the full cell. A major part is construction of the buffer layer itself, which consists of Ag-C composite. One major challenge has been to identify the percentage of binder that needs to be in the coating. Second, the buffer layer and current collector need to be combined with a compatible SE and a lithium source to make a cyclable cell.

The team has tested and optimized several important parameters, including (1) binder content, (2) mixing conditions, (3) drying conditions, (4) calendering conditions, and (5) surface roughness of the stainless-steel current collector. For example, different carbon and binder ratios were used with different mixing protocols to achieve a reasonable conductivity of the layer. Slurry was mixed using a rotor-stator homogenizer, high molecular weight polyvinylidene (di)fluoride, and n-methyl-2-pyrrolidone as the solvent. Surface resistance of the layer was relatively lower for higher binder contents versus the lower binder contents. This could be due to the porosity of the electrode decreasing with the introduction of higher amounts of binder. Higher binder contents reduce the overall conductivity of the system; therefore, lower amounts of binder were used. In the Ag-C composite, the team found that the percentage of carbon in the electrode coating determines the initial porosity of the coating. The higher the carbon content, the higher the porosity of the coating, which could cause higher interfacial resistance. Higher carbon content also causes the slurry to show more shear thinning properties. This would govern the determination of the



Figure 55. Image of final coating.

wet thickness of the cast that would give the correct dry thickness. The dry thickness of the final coating was 15 μ m prior to calendering. After the calendering, the coating layer becomes ~ 10 μ m (Figure 55). The team is also optimizing the electrochemical lithium plating test setup using a Ag-C ABL. In the team's model system, they used the following cell structure: lithium metal / Au-coated Li₇La₃Zr₂O₁₂ (LLZO) / Ag-C composite / stainless-steel current collector. Their initial attempts to plate lithium on the ABL side were unsuccessful. They will revise the cell design to overcome this issue.

To better understand the mechanisms of lithium plating under the ABL, the team has investigated the effects of carbon structure (glassy carbon versus graphitic carbon) and other potential metallic components (silver, tin, silicon, and magnesium nanoparticles). Last quarter, they reported that carbon structure plays a critical role to determine where Li-metal plating occurs (SE / buffer layer interface versus buffer layer / current collector interface). They are now testing several metallic components (silver, tin, silicon, and magnesium nanoparticles) to study what materials can replace expensive silver as a buffer layer, but also to understand what properties of metallic components govern Li-plating behaviors with aid by computations.

Task 2: Composite Cathode: High-Voltage Stability, Chemical and Mechanical Degradation Issue (G. Chen, H. Kim, J. Urban, G. Ceder, and M. Scott)

Currently, two main fundamental challenges limit the cyclability of composite cathodes: (1) chemical and electrochemical degradation at the cathode/SE and SE/carbon interfaces and (2) mechanical contact loss at the cathode/SE interface due to repeated expansion and contraction of the cathode particles. This quarter, they

evaluated the strategy of tailoring coatings to the chemistry of the cathode. The novel 3D composite developed in this task consists of 3D carbon frame as a core, which is coated with the cathode particles. The structure limits (or at least reduces) direct contact between carbon and SE and therefore minimizes the degradation of cathode composite. In addition, the soft and pliable carbon framework can accommodate the volume change of CAM, thus preventing mechanical contact loss at the cathode/SE interface.

Three routes were taken to synthesize the carbon/CAM composite: (1) directly deposit CAM particles outside the crystalline carbon framework surface and improve conductivity by thermal annealing or carbon nanotube integration, (2) synthesize 3D porous reduced graphene oxide (rGO) networks and then integrate them with the CAM particles, and (3) direct integration of CAM on two-dimensional rGO micro-flakes. The microstructures of the synthesized hybrids were evaluated by X-ray diffraction (XRD), Fourier transform infrared, and transmission electron microscope analysis. To achieve controlled uniform coatings in the first and second routes, they adopted a dual ligand modification method to deposit CAM around the carbon core with the assistant of poly(vinylpolypyrrolidone) (PVP) and polyethylenimine (PEI) polymers on the surface. While the former promoted the dispersion of particles, the amino groups in the latter can improve the binding. In the first route, they used molecular organic framework particles as an example to optimize the synthesis conditions. Covalent organic frameworks (COFs) were chosen as the carbon material due to their highly ordered structure, which can provide large surface area and one-dimensional (1D) channels to facilitate efficient ion transport. After thermal annealing under inert argon atmosphere, the inner COFs transform to porous carbon material with the structure retained. The reverse design was investigated first in which COFs were directly grown outside the particles only for demonstration. Based on experimental results, the thickness of COF shell can be tuned from ~ 10 nm to ~ 50 nm or more. The successful synthesis of the core / shell particle / carbon structures validates the potential of uniform deposition of CAM as a shell with the assistant of dual ligands.



Figure 56. Characterization of core-shell structures. X-ray diffraction and Fourier transform infrared show successful synthesis of the core-shell structures. Transmission electron microscopy confirms that shell thickness can be tunable.

The team also attempted to improve crystallinity of the COF shell to achieve the 1D ion transport channel as well as the use of other particles as core to demonstrate the generality of their method. Based on XRD results, both goals have been achieved. The team first modified the particles with PVP and PEI before directly dispersing the particles into the COF monomer solution with certain concentrations. After aging for 2 hours, a solvothermal method was applied to achieve the core/shell composite structure (Figure 56). Next, the team will prepare samples with particles as shell and with carbon as core by using the same method in the demonstration reactions.

In the third route, the team used graphite oxide (GtO), which is

obtained by oxidization from commercially available graphite, as a starting material. GtO is dispersed in deionized water and sonicated for 1.5 hours to exfoliate graphene layers. Commercially available NMC CAM is added to the exfoliated graphene oxide solution and homogeneously mixed. After the mixed solution is stirred for 20 hours at 90°C (oil bath) after adding urea (a reducing agent), the powder is filtered and dried. Figure 57a-d shows the morphologies of NMC before hybridization (Figure 57a-b) and after hybridization (Figure 57c-d).

Two main observations can be made: (1) rGO flakes are attached on large NMC particles, and (2) small NMC particles are decorated on rGO surface. XRD confirms that the crystallinity of NMC does not change after synthesis (Figure 57e). From the thermal gravimetric analysis (TGA), it is verified that the carbon content in the composite is ~ 9 wt%, as shown in Figure 57f. Synthesis conditions are being optimized by controlling several important parameters, including sonication time, CAM/graphene ratio, and CAM particle size.





New Li₃MX₆ halides containing rare earth (RE) elements are also being developed as high-voltage stable SEs. To date, a number of Li₃MCl₆ (M = Sc, In, Y, Er, Yb) chlorides have been reported to have a high ionic conductivity (up to $10^{-3} - 10^{-4}$ S·cm⁻¹) and a wide electrochemical stability window (up to 4.3 V versus Li/Li⁺). In the Li₃REX₆-family of compounds, it is fairly common for the halides to go through polymorphic transformations, especially under thermal treatments. For example, by means of solid-state reactions using relatively low annealing temperatures, metastable phases of Li₃RECl₆ (such as β-Li₃YCl₆ and trigonal Li₃YbCl₆) can be obtained, which were found to have higher ionic conductivities compared to their corresponding thermodynamically stable phases (α-Li₃YCl₆ and orthorhombic Li₃YbCl₆). The team aims to engineer new compositions and phases of Li₃REX₆ that may have better ionic transport properties, wider electrochemical stability windows, and/or better mechanical properties. Synthesis conditions will be optimized according to thermal analysis using variable-temperature XRD, TGA, and differential scanning calorimetry (DSC) measurements. Both variable-temperature XRD and DSC measurements can provide insights on phase transformations and may lead to discovery of new phases, especially high-temperature phases. By recognizing the heat effects in phase transitions (endothermic or exothermic), the energetic relationships between different phases can also be obtained.

Task 3: High-Loading Composite Cathodes (M. Tucker, M. Doeff, G. Chen, and G. Ceder)

In this task, tape casting is used to fabricate a thin (target thickness $20 \ \mu m$) LLZO electrolyte separator. Figure 58 shows the overall process to fabricate LLZO thin film. The tape casting and associated processes should be optimized to obtain high density, ionic conductivity, and mechanical properties of the prepared thin LLZO electrolyte. The team optimized variables such as lamination pressure, debinding time, and sintering time. First, the effect of lamination pressure on green body density and fabricated thin LLZO film was investigated. Lamination is a step to bind separate tape-casted LLZO sheets into one





sheet (green body) by exerting pressure at an elevated temperature (Figure 58, right). Lamination pressures between 4500 lb and 20000 lb for an area of 2.27 cm^2 were scanned. At a lamination pressure of 9000 lb at 90°C, the green density reached 2.07 g/cm³; it did not increase further with pressure. Thus, they decided to fix 9000 lb as an appropriate lamination pressure for the LLZO film fabrication.

Second, the effect of debinding time on densification of LLZO film was also investigated. Debinding involves the burning off of the binder and additives at a high temperature. If these are not fully removed



Figure 59. Debinding time versus green body weight. The inset pictures are fabricated LLZO film with different debinding times. The white area in the central area of the LLZO film has a relatively low density because of incomplete debinding.

through the debinding process, the residual hinders densification. Figure 59 shows the relationship between debinding time and the green body weight. The weight of the green body keeps decreasing even after 12 hours of debinding at 675°C. This result indicates that a longer debinding time is necessary. The team will work on finding an optimum time/temperature protocol.

Third, the sintering furniture is optimized to obtain a flat LLZO film. The sintering furniture includes graphite foils, dead weight, and a substrate. Graphite foil is used to prevent chemical reactions of LLZO with the substrate and dead weight during sintering. The dead weight is to prevent curving and/or twisting during sintering. Three kinds of dead weight (platinum mesh, alumina, graphite plate) were tested. The platinum mesh (0.53 g/cm^2) did not provide enough weight, so the sintered LLZO films were severely curved. The LLZO films were less curved when alumina (1.08 g/cm^2) was used, and were flattened with the graphite plate (4.85 g/cm^2). Thus, the optimum dead weight is in the range of $1.08 \text{ and } 4.85 \text{ g/cm}^2$. The team is planning to find the optimum dead weight next quarter.

Fourth, the microstructure of thin LLZO film was characterized using microdiffraction at Advanced Light Source beamline 12.3.2. Two areas (edge and central area) in the prepared LLZO film were characterized. The grain size, grain orientation, and strain distribution of the characterized areas are shown in Figure 60. The two areas have different grain sizes. In both areas, the grains have random directions. The strain seems to be concentrated along the grain boundary, something that needs to be investigated in more detail.

At the current state, the prepared thin LLZO electrolyte achieved a thickness of ~ 75 μ m, a density of ~ 97%, and ionic conductivity of ~ 5 \times 10⁻⁴ S/cm. Optimization is under way to achieve a thinner LLZO film with a higher density and ionic conductivity.

The team has started the investigation of the mechanical properties of the films. When the thickness of the LLZO film becomes thinner, it is more fragile. Thus, mechanical properties of the LLZO film need to be characterized and enhanced. Three-point bending and micro/nano indentation will be used to evaluate fracture strength, hardness, and fracture toughness. As a preliminary mechanical property testing, a thick LLZO pellet was fabricated and used for mechanical testing because it is easier to handle. As a preliminary test, micro indentation was conducted on a ~ 700- μ m thick LLZO pellet to evaluate hardness. The obtained hardness was 8.15 GPa, which is in the range of common LLZO pellets in the literature. The set-up for nano-indentation and 3-point bending testing is being improved. Next quarter, they will study and select a cathode material set consisting of CAM and secondary SE.



Figure 60. Picture of a fabricated LLZO film (left). Scanning electron microscopy image of two areas. Microdiffraction characterization (principal component analysis, grain orientation, and equivalent strain distribution) on the areas.

Task 4: Glass Composite SE by Low-Temperature Solution-Phase Synthesis (G. Liu)

This task aims to develop a sulfide glass separator that is both thin and resisting lithium dendrite penetration from the Li-metal anode side. Solution processable separators would be more easily integrated into SSBs through low-cost processing. In addition, solution processable SEs could be directly integrated with cathode materials to form a composite cathode through conventional slurry coating. The team's objective is therefore to develop the processes to synthesize hybrid SEs from inorganic conductors and polymer through solution-based processes, and which combine high ionic conductivities (> 10^{-3} S cm⁻¹) and high fracture toughness (> 10 Mpa m^{1/2}). They will initially focus on sulfide-based materials, but they will also consider other inorganic conductors later in the process. The sulfide coupled with a functional polymer network will be deposited through the solution-phase as a thin film onto a protected Li-metal surface. As the solvent evaporates, an intimate mixture of sulfide glass and polymer network is formed within a homogeneous film. Replicating the biomineralization processes that occur in natural structural materials, the polymer functional groups will strongly interact with the sulfide glass to form a material with high fracture toughness. The composition of the sulfide glass can also be modified using various dopants to tune the chemical and electrochemical properties of the solid-state electrolyte.



Figure 61. (a) Comparison of three possible methods for preparing the solid electrolyte-polymer composites. Note that the solution-precipitation method has an advantage of high mechanical strength owing to its smaller polymer-domain size and uniformly distributed microstructure. (b) Schematic showing the preparation process of the solution-precipitation method.

There are three methods that can mix functional polymers with solid-state ceramic materials: direct mechanical mixing, slurry dispersion, and solution precipitation, as shown in Figure 61. The morphology of the mixture is very different among the three methods. Mechanical mixing tends to yield the most inhomogeneous composite, since the particle size determines mixing uniformity. Slurry dispersion allows the polymer particles to dissolve in the slurry solvent; therefore, the polymers tend to coat the ceramic particles. In this case, the finer the ceramic particles, the better the dispersion. Solution precipitation dissolves both the polymer adhesive and ceramic particles in the solvents, and precipitates both polymer and ceramic out concurrently and instantaneously in nonsolvent. The mixture could form nanoscale or even molecular level mixture depending on the polymer and ceramic cluster interactions. This task mainly focuses on the developing, understanding, and controlling of the processes of the slurry dispersion and solution precipitation method. A novel solution-precipitation approach was employed to prepare LPSCl-polymer composites using poly(ethylene oxide) (PEO) and poly(phenylene oxide) (PPO) polymers. PEO can strongly interact with Li-ion through the oxygen elements in PEO. PPO also has oxygen elements, which can interact with Li-ion. PPO also has higher thermal stability. Ethanol (EtOH) is used as a solvent to dissolve the LPSCl solid form to a soluble cluster form. However, the overall liquid process time must be controlled to retain the cluster structure and subsequent argyrodite structure. Thus, the team first investigates the effect of dissolution time on the LPSCl structure properties, as shown in Figure 62. Scanning electron microscopy images (Figure 62a-c) show the decrease in the grain size of the SE with the dissolution time in EtOH, and it appears to form a more amorphous-like shape at a longer dissolution time (30 minutes). In addition, XRD results show a decrease in the signal for both cases compared to the pristine LPSCl, but the 30-minute sample shows the lowest intensity of XRD peaks among the samples (Figure 62d). A decrease in the ionic conductivity with the dissolution time is also observed (Figure 62e). The 30-minute sample shows a comparatively lower conductivity (0.01 mS/cm) than the 5-minute sample (0.04 mS/cm). These results suggest that the dissolution of LPSCI in EtOH will affect the overall crystal structure and ionic conductivity of the recovered precipitates, and those properties are strongly dependent on dissolution time. Thus, the solution-precipitation method requires the minimum exposure of LPSCl to EtOH to minimize depletion of the crystal structure of LPSCI and also additional heat treatment to recover some crystal structure and ionic conductivity of LPSCl.



Figure 62. Morphological and structural changes with dissolution time in ethanol (EtOH). (a-c) Scanning electron microscopy (SEM) images of (a) pristine LPSCI powder, LPSCI precipitate (b) after dissolution in EtOH for 5 minutes and (c) after dissolution for 30 minutes. Scale bars in SEM images are 10 μ m. (d) X-ray diffraction (XRD) results of LPSCI with a different dissolution time in EtOH. As the time increases, the intensities of the representative LPSCI peaks (denoted as a triangle) decrease. Please note that the sharp peak at ~ 13° and the bump peak at ~ 20° were from a different airtight XRD holder used in yellow and red patterns. (e) lonic conductivities of LPSCI with different dissolution times. Note that a shorter dissolution time of LPSCI is preferred to exhibit a higher conductivity.

Patents/Publications/Presentations

Publication

 Shen, H., K. Chen, J. Kou, Z. Jia, N. Tamura, W. Hua, W. Tang, H. Ehrenbert, and M. Doeff. "Spatiotemporal Mapping of Microscopic Strains and Defects to Reveal Li-Dendrite-Induced Failure in All-Solid-State Batteries." *Materials Today* (2022). doi: 10.1016/j.mattod.2022.06.005.

Task 1.24 – Low-Pressure All-Solid-State Cells (Anthony Burrell, National Renewable Energy Laboratory)

Project Objective. The goal of this project is to develop all-solid-state batteries (ASSBs) using four classes of solid-state electrolytes (SSEs), and/or electrode modifiers, that can be used to achieve the final 500 Wh/kg cell target. These materials will be down selected using full-cell testing and advanced characterization to achieve cell targets at cell pressures less than 100 psi.

Impact. Many factors limit ASSB performance, and this project seeks to address the interface stability of both the lithium interface and the high-voltage cathode. The combination of multiple ionic conductors coupled is specifically targeted to allow solution processing, and low-pressure cell outcome will enable lower cost deployment of solid-state cells in automotive applications.

Approach. To achieve the goal of low-pressure ASSBs, the team is utilizing three classes of solid ion conductors, sulfide materials, melt-processable lithium carboranes, and multinary metal halides. These materials can be chemically modified to optimize ionic conductivity and voltage stability in single conductor modes or in combinations to effect interface modification for full-cell development. Specifically, the use of flexible ionic conductors at the cathode interface will enable the mechanical effects of cathode expansion and contraction to be mitigated. In combination with the materials discovery work, the project has an extensive characterization team to help determine the impacts of interface, chemical, electrochemical, and mechanical factors on system performance. Full-cell assembly and development, targeting approaches that are readily scalable and compatible with roll-to-roll process, will drive the materials innovation and development.

Out-Year Goals. The out-year goal is demonstration of 2 Ah cells that achieve 500 Wh/kg and lifetimes exceeding 300 cycles at functional pressures below 100 psi.

Collaborations. There is a joint effort for this project between National Renewable Energy Laboratory, M. Toney at the University of Colorado, and A. Maughan at the Colorado School of Mines.

- 1. Prepare electrochemical cells using lithium carboranes. (Q1, FY 2022; Completed)
- 2. Prepare electrochemical cells using Li_yMCl_z. (Q2, FY 2022; Completed).
- 3. Prepare electrochemical cells using sulfur-polymer-coated cathodes. (Q3, FY 2022; Completed)
- 4. Demonstrate full-cell design that enables accurate, repeatable internal pressure control for ASSBs. (Q4, FY 2022; Completed)

New Materials

Work this quarter focused on the synthesis and characterization of borohydride substituted variants of the chloride argyrodite (Li₆PS₅Cl). Such materials have been previously reported, thorough interrogation of but а borohydride tetrahedra in the crystal structure (orientational disorder. dynamic reorientation, Li⁺ conduction pathways, etc.) has yet to be carried out. Initially, $Li_6PS_5Cl_{1-x}(BH_4)_x$ (x = 0-0.5) was synthesized via hand grinding followed by annealing at 550°C (Figure 63). X-ray diffraction (XRD) analysis of these samples revealed the presence of one or more unknown phases in addition to the desired argyrodite for



Figure 63. Powder X-ray diffraction patterns of hand ground and annealed borohydride argyrodites.

x = 0.1-0.5. To eliminate the unknown phase, a high-energy ball milling step was added prior to annealing, and $Li_6PS_5Cl_{1-x}(BH_4)_x$ (x = 0.0.3) was synthesized (Figure 64). While the intensities of the reflections attributed to the unknown phase appear to be lowered by ball milling, the unknown phase was not eliminated. It was speculated that the unknown phase could be due to decomposition of LiBH₄, so the annealing temperature was reduced. However, the unknown phase was still present in the XRD patterns collected, and signals attributed to precursors indicated that little argyrodite was formed. Next steps will focus on identifying and eliminating the unknown phase followed by in-depth investigation of borohydride dynamics in the argyrodite and the impact of borohydride substitution on the electrochemical stability of the argyrodite. The powder XRD data for these studies are shown in Figure 63 and Figure 64.



Figure 64. Powder X-ray diffraction patterns of ball-milled and annealed argyrodites.

Fabrication of Cells Using High-Volume Manufacturing Techniques

Argyrodite SSE is used as a baseline solid electrolyte (SE) material to develop slurry and tape-casting methods, composite cathodes and anodes, cell fabrication, and cell testing capability with controlled pressure. Composite cathodes containing > 60 wt% LiCoO₂ (LCO) and anodes containing > 60 wt% graphite were slurry coated onto aluminum and copper substrates, respectively. These films were each coated with a thin layer of argyrodite SSE and assembled into full-cell stacks in coin cells. The load frame is designed to apply pressures up to 20 MPa without shorting the cells (Figure 65). At present, the load frame does not have any load cells on it. The cell testing team developed appropriate components and procedures to enable electrical isolation and prevent misalignment during mechanical loading of cells. Cells fabricated using this method display steady voltage curves and reasonable capacity. Figure 66 illustrates cell potential for a solid-state graphite/LCO cell during initial constant current (CC) cycling at ~ C/20. The measured specific capacity was > 90 mAh/g LCO with modest voltage windows of 3.0-4.2 V. Thus, roughly 65% of the theoretical cathode capacity was accessed at an unknown/modest pressure. In the coming months, the team will add load cells to the load frames to explicitly measure force. This will allow for pressure dependent electrochemical measurements on tape-cast electrodes incorporating novel SE or interfacial materials. After demonstrating the ability to reliable make large area cells with a reasonable/repeatable capacity, the team will start to make cells using novel electrolyte materials from the materials development team to enable good cell performance at more modest pressures.



Figure 65. Cell testing hardware for solid-state electrolyte can be used to measure pressure real-time or used to calibrate individual spring stacks (top).



Figure 66. Representative cell potential for small area solid-state electrolyte graphite/LCO cell cycling at C/20 between 3.0 V and 4.2 V. The applied pressure is unknown; it will be measured in coming months.

Low Tortuosity Catholyte via Ultrafast Laser Patterning for Improved Solid-State Batteries (SSBs)

In fabricating SSBs, the SSE is usually formed first and then the composite cathode and the anode are added in subsequent steps. This approach results in an SSE/cathode interface susceptible to mechanical instability and high contact resistance that limits the allowable current density during battery operation. Furthermore, the planar interface limits how far lithium ions can diffuse away from the interface, which constrains the thickness of the cathode and limits overall energy density. The team proposes that microstructuring the cathode, via ultrafast laser ablation, will yield a much higher surface area that (1) greatly increases contact points between the SSE and cathode, and (2) allows both vertical and lateral Li-ion diffusion through lower-tortuosity pathways

into the cathode. Thev believe these improvements will be the key to achieving target current densities $> 1 \text{ mA/cm}^2$. Furthermore, reducing the diffusion barriers enables use of thicker cathode films that increase overall energy storage capacity, which is crucial to meet the energy density target of 500 Wh/kg. Figure 67 illustrates this concept. Microstructures with tunable micrometer dimensions will be created in the cathode using already established laser ablation capabilities at their facilities. The team's sulfide-based SSEs are amenable to filling in the cathode microstructures and creating greatly а enhanced interface.



Figure 67. A microstructured interface between the solid-state electrolyte and catholyte has many more less-tortuous pathways for ion conduction compared to a typical planar interface.

Sample Holder

Introduction of the sulfur-based SSE in the cathode, to form a "catholyte," requires moisture-free processing. To start, the team has constructed an air-free holder with 2-inch-diameter sapphire windows. The catholyte sample is mounted in the cell on the bottom window inside an argon-filled glovebox and then sealed by using a retaining ring to compress the windows onto an O-ring. Laser patterning is done through the top sapphire window. Figure 68a shows a catholyte sample of $LiNi_{0.8}Mn_{0.1}Co_{0.1}$ (NMC-811) / LPSCl composite film in the air-free holder.



Figure 68. (a) NMC-811/LPSCI catholyte sample in custom air-free holder with sapphire windows. (b) Scanning electron microscopy image of a laser ablated catholyte revealing the cross-hatch channel pattern made using ultrafast laser ablation, as well as energy dispersive spectroscopy of a region inside one of the channels.

Laser Ablation

Micrometer-sized channels were ablated using an ultrafast laser with ~ 600 fs pulse duration and near-infrared emission (1030 nm). The laser beam is steered across the sample using galvanometer-controlled mirrors. The depths of the channels are controlled by adjusting the power of the laser. Initially, the team tried a crosshatch of channels with 180 μ m spacing between channels. Scanning electron microscopy imaging confirms the patterning was successful (Figure 68b). In addition, energy dispersive spectroscopy was employed in a small

area inside one of the channels. The results show that some regions in the channel still contain some of the cathode based on the oxygen signature. In other areas, all of the material has been removed, exposing the aluminum current collector underneath based on the aluminum signature.

To test the effects of microstructures in the catholyte, the team will construct a symmetric cell with SE and measure the pressure-dependent electrochemical impedance spectroscopy. This will indicate whether the microstructures improve ionic resistance within the cathode and interfacial resistance between the cathode and SE. They will refine the laser ablation, for example, the size, shape, and density of microstructures, to determine more-optimal interfaces. In addition, a larger air-free holder will be designed and built to accommodate a much larger (> 4-inch diameter) sample of catholyte. This will facilitate slurry casting of the SSE onto the laser-patterned catholyte.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 1.25 – Precision Control of the Lithium Surface for Solid-State Batteries (Andrew Westover, Oak Ridge National Laboratory)

Project Objective. The overall goal of this project is to understand and engineer the surface and purity of thin Li-metal anodes to enable batteries with an energy density of 500 Wh/kg and a cycle life > 300 cycles.

Impact. The knowledge of lithium surface engineering and the implications for cell design of Li-metal-batteries will improve commercialization efforts for solid-state Li-metal batteries. There is very little standard knowledge about variations in the impurity level in different lithium sources, the surface chemistry of different lithium surfaces, and their impact on performance. Furthermore, the strategies developed to engineer the surface of the lithium metal for integration into Li-metal batteries will provide significant performance increases, ideally enabling successful commercialization.

Approach. This project is broken into two parts. First, the team is focused on thoroughly understanding the purity, mechanics, and surface chemistry of multiple lithium sources and how these parameters impact performance. Second, they will focus on intentional engineering of the lithium purity and surface chemistry to control the mechanical properties, electrochemical stability, and electrochemical performance. They will explore three approaches to engineer the surfaces: gas-phase passivation, deposition of thin metal coatings, and deposition of thin inorganic coatings. To test electrochemical performance, they will use standard ceramic and polymer electrolytes to demonstrate the impact of purity and surface chemistry. The program will also employ a range of standard and specialized characterization techniques, including a significant focus on understanding the mechanics of lithium metal using nanoindentation and adhesion measurements using surface probe microscopy.

Out-Year Goals. In FY 2023, the program plans to finish gaining a deep understanding of different lithium sources, purity, and surface conditions, and of how they affect performance in Li-metal cells with both ceramic and polymer electrolytes. In FY 2024 through FY 2027, the primary goal is to develop strategies to carefully control and engineer the surface of lithium metal to optimize performance, enabling batteries that can achieve 500 Wh/kg and cycle for more than 300 cycles at mid-to-high current densities.

Collaborations. The primary collaborator for this project is E. Herbert at Michigan Technological University, who is focused on mechanical measurements of Li-metal anodes and electrolytes in inert environments. The project also includes R. Sahore, S. Kalnaus, W-Y. Tsai, and R. Sacci of Oak Ridge National Laboratory (ORNL). The team anticipates the BMR program will also foster significant collaborations with other teams who have a complementary focus on lithium metal. H. Meyer from ORNL helped with the X-ray photoelectron spectroscopy (XPS) measurements and data analysis this quarter.

- 1. Obtain lithium sources. (Q1, FY 2022; Completed)
- 2. Conduct chemical characterization of lithium surfaces. (Q2, FY 2022; Completed).
- 3. Conduct nanoindentation of various lithium sources. (Q3, FY 2022; Completed)
- 4. Establish baseline electrochemical performance of multiple lithium sources. (Q4, FY 2022; In progress)

Building on last quarter, the team has performed nanoindentation and liquid-based lithium plating and stripping with the same lithium sources. The four commercial lithium sources are named Commercial Supplier 1-4. To give context to the nanoindentation results and the electrochemical testing, Table 4 shows a summary of the thickness of the surface layers measured by XPS in the prior quarter. The thicknesses are presented in etching time, as the exact etching rate was unknown.

Table 4. Summary of lithium surfaces from X-ray photoelectron spectroscopy data in terms of etching time in seconds.

Source	Outer later	Layer 2	Layer 3	Total
Supplier 1	Li ₂ CO ₃ - 160s	Li ₂ O – 1080 s	Mixed Li ₂ O/Li – 1780s	3020s
Supplier 2	Silicone - 60s	Li ₂ O – 180 s	Mixed Li ₂ O/Li – 1180s	1420s
Supplier 3	Organics - 20s	Li ₂ O/Li ₂ CO ₃ – 140 s	Mixed Li ₂ O/Li – 1200s	1360s
Supplier 4	Organics/Li ₂ CO ₃ - 40s	Li ₂ O – 880s	Mixed Li ₂ O/Li – 600s	1520s
Evaporated Li	Li ₂ CO ₃ - 5 s	Li ₂ 0 – 75s	Mixed Li ₂ O/Li – 380s	460s



Figure 69. Representative load-displacement curves obtained in metallic lithium from (a) commercial supplier 1 and (b) commercial supplier 2. The data were obtained using a diamond Berkovich indenter tip, a target strain rate 0.05 1/s, and a target depth of 800 nm.

Nanoindentation experiments have been performed on metallic lithium from Suppliers 1 and 2. Representative load-displacement curves obtained at a target strain rate of 0.05 1/s are shown in Figure 69a-b, respectively. The poor reproducibility from one test to the next and the stochastic nature of each test are wholly consistent with previously published^[1] load-displacement curves obtained at very similar strain rates in high-purity, evaporated lithium. Although not explicitly shown in Figure 69, the team notes the *in situ* surface detection was triggered at a contact stiffness of 40 N/m, and the point of contact between the indenter tip and the surface of the test specimen was accurately determined to within 5 nm or less. Among the more than 200 measurements performed in the two commercial sources, there was no significant experimental evidence of indenter tip contamination. In addition, nanoindentation results obtained in a fused silica reference block show no discernable change in the indenter tip geometry before and after the experiments performed in lithium.

Figure 70a shows the average elastic modulus measured as a continuous function of indentation depth. The scatter in the data reflects the variability and stochastic nature of the load-displacement curves shown in Figure 69. The measured modulus is well within the expected range of lithium, which is nominally 3 to 22 GPa depending on the crystallographic orientation. The average modulus shown in Figure 70a suggests both sources have very similar texture. The slight depth dependence observed in the modulus (from both suppliers) is unexpected, and its origin is under investigation. Among the experimental factors that could potentially cause



Figure 70. (a) The average elastic modulus of lithium obtained from the two commercial suppliers. (b) The average hardness of lithium obtained from the two commercial suppliers and an evaporated lithium deposited at Oak Ridge National Laboratory (data from the ORNL specimen were published in 2018).

or contribute to the observed depth dependence, the following have effectively been eliminated: thermal drift, a systematic error in the indenter tip area function, an error in the frame stiffness, the plasticity effect, the amplitude of the harmonic oscillation, and substrate effects. One possible explanation is a breakdown in the geometric self-similarity of the contact geometry brought about by the strong depth dependence observed in the measured hardness. Figure 70b shows the average hardness measured as a continuous function of depth. For the sake of clarity, the scatter bars have been omitted from the plot. For comparative purposes, the plot shows the average hardness measured at similar strain rates in an evaporated lithium deposited at ORNL. These data were published in 2018. In stark contrast to the measured elastic modulus shown in Figure 70a, Figure 70b shows the hardness exhibits a very strong depth dependence. This general observation is well-documented in evaporated lithium. The interesting observation here is that despite significant variations in the purity of the lithium surface, test specimens from Suppliers 1 and 2 exhibit similar behavior to that of the high-purity, evaporated lithium. That said, based on work characterizing the surface of the films, the team knows that Supplier 1 had a very thick surface layer that was characterized by ~ 50 nm of Li_2CO_3 followed by a distinct Li₂O layer. Supplier 2 on the other hand had a much thinner surface layer with an organic silicone layer followed by a mixed Li₂O/Li layer. The difference in the surface chemistry of the three different lithium sources may be part of the difference in the mechanics. More detailed analysis and understanding will be developed in the next few months.

In addition to the mechanical measurements, the team also compared the electrochemical performance of all five lithium sources characterized last quarter in liquid electrolytes (LEs). To perform the tests, Li//Li symmetric coin cells were made using one type of lithium metal as both the electrodes, with the diameter of

one electrode slightly larger than the other to ensure a well-defined active area (1/2" and 7/16"). Gen 2 [1.2 M LiPF₆ in ethylene carbonate (EC) / ethyl methyl carbonate (EMC) (3:7 by wt)] was used as the LE (25 μ L per cell), and Celgard[®] 2325 as the separator. After a 24-hour rest at room temperature, alternating current impedance was measured, followed by galvanostatic cycling at 0.2 mA/cm² for 2.5 hours at room temperature. The results are presented in Figure 71.



Figure 71. (a) Plating and stripping measurements in Gen 2 liquid electrolytes for the five lithium sources. (b) Zoomed-in plot of the first 50 hours of plating and stripping. (c) Zoomed-in plot of the last 50 hours of plating and stripping. (d) Nyquist plots for the symmetric lithium cells in liquid electrolyte for the five lithium sources after 10 plating and stripping cycles.

Figure 71a shows the full cycling set for all five lithium sources. Figure 71b-c shows zoomed-in plots of the first 8 cycles and last 8 cycles. Initially, there is a significant disparity in the lithium deposition overpotential with the lowest resistance for the evaporated lithium. From there, the overpotential of the lithium sources increases in the order of Supplier 3 < Supplier 1 < Supplier 2 < Supplier 4. After 8 cycles, the resistance level off a bit but have the same trends in overpotential. This matches with the total magnitude of the resistance measured in the electrochemical impedance spectroscopy (EIS) curves from 100kHz to 0.1 Hz in Figure 70d. The EIS curves also clearly show at least two semicircles consistent with the heterogenous surface layers demonstrated in the XPS data summarized in Table 4.

In addition to trends in overpotential, the commercial lithium sources, all of which were rolled, have irregular plating and stripping profiles. Literature works point to the fact that these irregularities correspond to non-homogenous lithium plating and stripping, and the formation of mossy lithium and dead lithium.^[2] After 200⁺ hours of plating and stripping, the plating and stripping profiles of all but the lithium from Supplier 2 have flat plating and stripping profiles with much lower resistance than the initial plating and stripping measurements.

The evaporated lithium still has the lowest resistance, but is followed closely by the lithium from Supplier 3. The final three Li-metal sources had very similar overpotentials, but while the deposition profiles for the lithium from Suppliers 1 and 4 have flat deposition profiles, the lithium from Supplier 2 had wide swings in the deposition overpotential that started to get worse with each cycle after ~ 150 hours of cycles. Notably, the lithium from Supplier 2 was the only lithium source that had a silicon signature in the XPS/infrared spectroscopy measurements presented last quarter. The best overpotential for the commercial lithium sources was for the lithium from Supplier 3. This lithium surface had a distinct signature of an organic passivation layer. Meanwhile, the surfaces of both lithium Suppliers 1 and 4 had distinct carbonate and distinct Li₂O surface layers. While the focus of this program will be on SEs, these data clearly show that the quality of the lithium surface has a real impact on the performance of Li-metal batteries utilizing thin lithium.

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Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

TASK 2 – DIAGNOSTICS

Team Lead: Guoying Chen, Lawrence Berkeley National Laboratory

Summary and Highlights

To meet the goals of the Vehicle Technologies Office programs on next-generation electric vehicles, low-cost and abuse-tolerant batteries with higher energy density, higher power density, better safety, and longer lifetimes are needed. In pursuit of these goals, high cell operating voltages and demanding cycling conditions are used, which leads to unprecedented chemical and mechanical instabilities in cell components. Successful implementation of promising electrode materials (such as silicon anode and high-voltage cathodes) and new cell chemistry (such as high-energy Li-metal cells combined with solid-state electrolytes, or SSEs) requires better understanding of fundamental processes, especially those at the interface/interphase of both anode and cathode. Identifying and understanding structure-property-electrochemical performance relationships in materials and various failure modes in cell chemistry are therefore more pressing than ever, not only in guiding battery development activities but also the scale-up efforts needed for commercialization.

Task 2 takes on these challenges by combining model systems, ex situ, in situ, and operando approaches, with an array of state-of-the-art analytical and computational tools. Numerous subtasks are tackling the chemical processes and reactions at the electrode/electrolyte interfaces in Li-metal batteries. Researchers at Lawrence Berkeley National Laboratory (LBNL) use surface- and bulk-sensitive techniques, including Fourier transform infrared (FTIR), attenuated total reflectance – FTIR, near-field infrared and Raman spectroscopy/microscopy, and scanning probe microscopy to characterize changes in materials and the physio-chemical phenomena occurring at the interface of Li-metal electrode. General Motors is developing in situ diagnostic techniques, including atomic force microscopy, nano-indentor, dilatometer, and stress-sensor, to be combined with atomic/continuum modeling schemes to investigate the coupled mechanical/chemical degradation of the solid electrolyte interphase layer as well as the microstructural evolution at the interface/interphase of Li-metal anode. Argonne National Laboratory aims to develop high-conductivity ceramic electrolytes through cation doping and to identify mechanistic barriers that limit chemical, mechanical, and electrochemical durability of solid/solid interfaces. University of Houston (UH) is developing multidimensional diagnostic tools, including focused ion beam - scanning electron microscopy, time-of-flight secondary ion mass spectrometry, and in situ scanning electron microcopy nanoindentation, to probe structural, chemical, and mechanical evolution at the interfaces of solid-state lithium batteries. At LBNL, model systems of electrode, SSE, and their interfaces with well-defined physical attributes are being developed and used for advanced diagnostic and mechanistic studies at both bulk and single-particle levels. These controlled studies remove the ambiguity in correlating a material's physical properties and reaction mechanisms to its performance and stability, which is critical for further optimization. Subtasks at Brookhaven National Laboratory (BNL) and Pacific Northwest National Laboratory (PNNL) focus on the understanding of fading mechanisms in electrode materials, with the help of synchrotronbased X-ray techniques (diffraction and hard/soft X-ray absorption) at BNL and high-resolution transmission electron microscopy / scanning transmission electron microscopy and related spectroscopy techniques at PNNL. The final subtask at Stanford / SLAC National Accelerator Laboratory (SLAC) develops and utilizes an integrated X-ray characterization toolkit to investigate and generate insights on solid-state batteries, by tracking the evolution of nanoscale chemistry as well as structure, microstructure, and transport properties. The diagnostics team not only produces a wealth of knowledge key to developing next-generation batteries, they also advance analytical techniques and instrumentation with a far-reaching effect on material and device development in various fields.

Highlights

The highlights for this quarter are as follows:

- The UH group (Y. Yao) developed a diagnostic approach to understand the chemo-mechanical behaviors of all-solid-state battery electrodes. The correlation between chemical evolution of a cathode active material and the mechanical properties of the composite cathode was illustrated.
- The Stanford/SLAC team (Y. Cui / W. Chueh / M. Toney) successfully developed an *operando* electrochemical platform to investigate the mechanical effects on lithium metal intrusion behavior. Along with electrochemical modeling, their study identified two lithium growth modes of pre-intrusion and post-intrusion on a Li-La-Zr-O solid electrolyte.

Task 2.1 – Characterization and Modeling of Lithium-Metal Batteries: Model-System Synthesis and Advanced Characterization (Guoying Chen, Lawrence Berkeley National Laboratory)

Project Objective. This project will use a rational, non-empirical approach to design and develop solid-state electrolyte (SSE) materials and interfaces for next-generation Li-metal batteries. Combining a suite of advanced diagnostic techniques with carefully prepared model-system samples, the project will perform systematic studies to achieve the following goals: (1) obtain understanding on the role of SSE grain and grain boundaries (GBs) on ion conduction and dendrite formation, (2) obtain fundamental knowledge on rate-limiting and stability-limiting properties and processes in SSEs when used in Li-metal batteries, (3) investigate the reactivities between SSE and electrodes, and gain insights on the dynamic evolution of the interfaces, and (4) design and synthesize improved SSE materials and interfaces for safer and more stable high-energy Li-metal batteries.

Impact. The project will focus on fundamental understanding of SSE and relevant interfaces to enable its use in Li-metal batteries. Knowledge gathered from model-system-based studies will guide the design and engineering of advanced materials and interfaces. The use of the non-empirical, rational-design approach will develop high-energy battery systems with improved commercial viability.

Approach. The project will combine model-system synthesis and advanced diagnostic studies to investigate ion conduction and interfacial chemistry of SSE in Li-metal batteries. Single crystalline (SC), polycrystalline (PC), and amorphous model SSE samples with various grain and GB properties will be synthesized. Model interfaces between the SSE and electrodes with controlled properties will also be developed. Both bulk-level and single-grain-level characterization will be performed. Global properties and performance of the samples will be established from the bulk analyses, while the single-grain-based studies will utilize time-resolved and spatially-resolved analytical techniques to probe the intrinsic redox transformation processes and failure mechanisms under battery operating conditions.

Out-Year Goals. In the out years, the project will deliver fundamental knowledge on the role of SSE microstructure in Li^+ conduction and lithium dendrite formation/propagation. Insights on performance-limiting physical properties and phase transition mechanisms as well as dynamic evolution of SSE/electrode interfaces will be obtained. Mitigating approaches, such as use of surface coating or a "buffer layer" in stabilizing SSE/electrode interfaces, will be evaluated. Further, advanced SSE materials and interfaces for improved high-energy Li-metal batteries will be designed and synthesized.

Collaborations. This project collaborates with the following principal investigators: G. Ceder, K. Persson, M. M. Doeff, B. McCloskey, R. Kostecki, and R. Prasher (Lawrence Berkeley National Laboratory); W. Yang (Advanced Light Source); D. Nordlund and Y. Liu (Stanford Synchrotron Radiation Lightsource); C. Wang (Pacific Northwest National Laboratory); and J. Nanda (Oak Ridge National Laboratory).

- 1. Develop SSE/cathode model systems for studying the cathode interfaces. (Q1, FY 2022; Completed)
- 2. Synthesize SSE model samples and model SSE/cathode interfaces. (Q2, FY 2022; Completed)
- 3. Advanced diagnostic studies of SSE/cathode interfaces. (Q3, FY 2022; Completed)
- 4. Obtain mechanistic understanding and deliver design strategies to improve SSE/cathode interfaces. (Q4, FY 2022; On schedule)

Last quarter, the team demonstrated excellent cycling stability of an all-solid-state battery (ASSB) cell employing a composite cathode of SC LiNi_{0.8}Mn_{0.1}Co_{0.1} (NMC-811), Li₃YCl₆ (LYC) solid electrolyte (SE) and carbon black (57:40.5:2.5 weight ratio), a LYC separator layer, and a Li-In anode. Cycled under an external pressure of ~ 8 Mpa, a high-capacity retention of nearly 90% was achieved after 1000 cycles at C/2. This is a significant performance improvement over the equivalent cell with a PC NMC-811 cathode material, which delivered a capacity retention of ~ 70% after 820 cycles. The team's SC-NMC cell performance also surpasses that of reported ASSB cells equipped with a coated Ni-rich Ni-Mn-C (NMC) cathode and a highly conducting sulfide SE with an ionic conductivity of ~ 3 mS·cm⁻¹, which is an order of magnitude higher than that of LYC (0.32 mS·cm⁻¹).

To understand the superior performance of the SC NMC-811 cell, post-mortem analysis was carried out to examine the morphological changes in the PC and SC composite cathodes before and after cycling. Figure 72 compares the scanning electron microscopy (SEM) images collected in top-view as well as cross-sectional view using focused ion beam (FIB) processing. While pristine PC NMC-811 consists of dense agglomerates of primary particles (~ 500 nm size) free of cracking (Figure 72a-b), internal cracks with various sizes, shapes, and lengths are clearly seen within the secondary particles after 820 cycles (Figure 72c-d). In contrast to the intimate contact observed between the pristine NMC and LYC SE particles, large gaps are visible after cycling, leading to contact loss, isolated and inaccessible PC NMC-811 primary and secondary particles, and discontinuation in Li-ion diffusion pathways. These changes are somewhat expected, considering the large anisotropic volume changes experienced by the cathode particles during cycling. A number of previous studies have demonstrated intergranular cracking in PC particles, both in solid and liquid electrolyte cells. On the other hand, no discernible changes were observed by comparing the pristine and cycled SC NMC-811 composites. Both SEM and FIB-SEM images show crack-free SC NMC-811 particles before (Figure 72e-f) and after (Figure 72g-h) long-term cycling of 1000 cycles. The contact between the SC NMC-811 and LYC SE particles remains nearly unchanged, enabling efficient Li-ion migration during cycling. The two scenarios provide marked contrast in terms of the effect of cycling on the composite cathodes, with the former suffering significant loss of active materials due to isolation and inaccessibility, while the latter maintains the high utilization of the NMC cathode. The results support the performance differences observed on the two ASSB cells. Further analysis on cycling-induced changes in the cell components and at the interfaces is being conducted using electrochemical impedance spectroscopy.



Figure 72. Scanning electron microscopy images (a/c/e/g) and cross-sectional focused ion beam (FIB) – scanning electron microscopy images (b/d/f/h) collected from as-prepared (a/b/e/f) and cycled (c/d/g/h) NMC-811 composite cathodes. (a-d) Collected from polycrystalline NMC-811 and (e-f) collected from single-crystalline NMC-811. The vertical lines in (b/d/f/h) are imaging artifacts from FIB processing.

Patents/Publications/Presentations

Patent

• U. S. Patent Application No. 17/838,457. "High-Energy and High Power Composite Cathodes for All Solid-State Batteries." G. Chen, S. Kim, and Y. Lu. June 2022.

Publication

 Ahn, J., Y. Ha, R. Satish, R. Giovine, L. Li, J. Liu, C. Wang, R. J. Clement, R. Kostecki, W. Yang, and G. Chen. "Exceptional Cycling Performance Enabled by Local Structural Rearrangements in Disordered Rocksalt Cathodes." *Advanced Energy Materials* (2022): 220042. doi: 10.1002/aenm.202200426.

Presentation

 International Meeting on Lithium Batteries, Sydney, Australia (June 26 – July 1, 2022): "Understanding the Unique Performance of Mn-Rich Disordered Rocksalt Cathodes"; G. Chen et. al.

Task 2.2 – Interfacial Processes – Diagnostics (Robert Kostecki, Lawrence Berkeley National Laboratory)

Project Objective. The project objective is to establish specific design rules toward the next generation of low-impedance Li-metal rechargeable batteries that are capable of performing 1000 deep discharge cycles at Coulombic efficiency (CE) > 99.9% and suppressing lithium dendrite formation at high current densities (> 2 mA/cm²). This project aims at the following: (1) establishing general rules between Li⁺ transport properties in novel liquid/solid electrolytes, and (2) determining the mechanism of the solid electrolyte interphase (SEI) layer (re)formation. The other goal is development and application of far- and near-field optical probes and synchrotron-based advanced X-ray techniques to obtain insight into the mechanism of Li⁺ transport and interfacial reactions in lithium/liquid model systems. Through an integrated synthesis, characterization, and electrochemistry effort, this project aims to develop a better understanding of lithium / liquid electrolyte (LE) interface so that rational decisions can be made as to their further development into commercially viable Li-metal cells.

Project Impact. Chemical instability and high impedance at the interface of Li-metal electrodes limit electrochemical performance of high-energy-density batteries. A better understanding of the underlying principles that govern these phenomena is inextricably linked with successful implementation of high-energy-density materials in Li-metal-based cells for plug-in hybrid electric vehicles (PHEVs) and electric vehicles (EVs). New state-of-the-art techniques to identify, characterize, and monitor changes in materials structure and composition that take place during battery operation and/or storage will be developed and made available to BMR participants. The work constitutes an integral part of the concerted effort within the BMR Program, and it supports development of new electrode materials for high-energy, Li-metal-based rechargeable cells.

Approach. Pristine and cycled composite electrode and model thin-film electrodes will be probed using various surface- and bulk-sensitive techniques, including Fourier transform infrared (FTIR), attenuated total reflectance (ATR) - FTIR, near-field infrared and Raman spectroscopy/microscopy, and scanning probe microscopy to identify and characterize changes in materials structure and composition. Novel *in situ / ex situ* far- and near-field optical multifunctional probes in combination with standard electrochemical and analytical techniques are developed to unveil the structure and reactivity at interfaces and interphases that determine electrochemical performance and failure modes of materials.

Out-Year Goals. In the out-years, the project aims to achieve the following: (1) understand factors that control performance and degradation processes, (2) unveil structure and reactivity at hidden or buried interfaces and interphases that determine electrochemical performance and failure modes, and (3) propose effective remedies to address inadequate Li-metal-based battery calendar/cycle lifetimes for PHEV and EV applications.

Collaborations. Diagnostic studies will be carried out in sync with other diagnosticians (that is, G. Chen, B. McCloskey, R. Prasher, and L-W. Wang) and theory/computational scientists (that is, G. Ceder and K. Persson).

- 1. Fundamental physicochemical and electrochemical characterization of the considered primary and secondary Li-metal cell chemistries. (Q1, FY 2022; Completed)
- 2. *In situ* Fourier transform infrared nano-spectroscopy (nano-FTIR) experimental setup for probing Li/LE interface designed, built, and tested. Preliminary tests and results delivered. (Q2, FY 2022; Completed)

- 3. Near- and far-field optical and X-ray photoelectron spectroscopy (XPS) characterization of the baseline Li-metal cell chemistries and relevant interfacial phenomena and processes completed. (Q3, FY 2022; In progress)
- 4. Correlation of electrolyte chemistry and Li/SEI compositional structure in Li-metal baseline LE and solid electrolyte systems determined. (Q4, FY 2022; In progress)

This quarter, the team focused efforts on ex situ characterization of Li-metal anodes exposed to GEN 2 electrolyte [ethylene carbonate (EC) / ethyl methyl carbonate (EMC) 1.2 M LiPF₆] by near- and far-field spectroscopies: ATR-FTIR and nano-FTIR, respectively. Due to the reactivity of lithium metal, it is important to ensure the cleanliness of the prepared Li-metal foil to avoid any potential contamination. In laboratory settings, it is common practice to prepare Li-metal anodes in a glovebox that contains LEs. This leads to the accumulation of volatile organic compounds (VOCs) that will react with, and form a contamination film on, the lithium surface, even before coming in contact with an electrolyte. To address this issue, the team has developed a transfer method ensuring the pristine condition of the lithium surface before coming in contact with the electrolyte. Freshly rolled Li-metal foil was prepared in a solvent-free glovebox and placed in a plastic bottle with a septum cap. It was then transferred into a glovebox containing LE. Microliters of GEN 2 were then deposited onto the clean lithium surface (free of a VOC-induced contamination layer) in a controlled way, through a septum, via a syringe.



Figure 73. Attenuated total reflectance (ATR) – Fourier transform infrared (FTIR) spectra of Li-metal foil exposed to GEN 2 after various post-processing steps: (black) lithium metal with dried electrolyte under vacuum, (red) lithium metal with electrolyte removed from the surface by a porous Celgard[®] separator, (blue) lithium metal washed in DMC after contact with GEN 2, and (purple) fresh Li-metal surface exposed to N₂ atmosphere of ATR-FTIR.

On contact, lithium metal reacts with the electrolyte, forming a

thin film of products of the reaction: (1) inorganic components, such as LiF, Li₂O, Li₂CO₃, etc., (2) organic lithium salts, such as LiEDC (lithium ethylene decarbonate), and (3) organic products of electrolyte decomposition. The literature suggests that the latter group plays little role in the passivation of Li-metal anodes and should be removed to analyze buried SEI components. This can be achieved by washing the lithium metal in dimethyl carbonate (DMC), which will clean the passivated Li-metal surface of any components that are soluble in DMC.

The team has analyzed the effect of sample post-processing (washing, drying) on SEI components. The hypothesis is that inorganic lithium salts such as LiF and Li₂CO₃ are less soluble compared to LiEDC; therefore, some of the residuals of inorganic SEI components are going to stay on the lithium surface, which will be revealed by ATR-FTIR. The far-field technique, while lacking surface sensitivity and special resolution, is a good estimate of bulk SEI components. It is worth noting that before analysis, samples were dried under vacuum for 24 hours; therefore, any loosely physisorbed species and gasses that can be components of SEI are removed from the film. Figure 73 shows that even after 24 hours under vacuum, some of the EMC molecules are still present on the lithium surface. The signal of lithium metal exposed to GEN 2 electrolyte is dominated by P-F and LiEDC vibrations at ~ 830 cm⁻¹ and 1083 cm⁻¹, 1156 cm⁻¹, 1267 cm⁻¹, and 1654 cm⁻¹ (Figure 73). Interestingly, the removal of the electrolyte by Celgard[®] seems to remove most of the LiEDC, indicating that LiEDC is mainly dissolved in the electrolyte. The region 1000-1400 cm⁻¹ is still populated with peaks, showing that other lithium organic salts, such as butylene dicarbonate (Li₂BDC), LiO- (CH₂)₂CO₂(CH₂)₂OCO₂Li, and

Li(CH₂)₂OCO₂Li remain on the lithium surface. Washing with DMC removes the majority of organic salts, leaving Li₂CO₃ on the surface as a dominant feature. The peak at 737 cm⁻¹ is assigned to coordinated EC.^[1] The shoulder at lower wavenumbers is assigned to free EC and is present only in a sample with electrolyte dried under vacuum. Vibration at 927 cm⁻¹ is assigned to free EMC molecules, and it shifts to 950 cm⁻¹ in the case of Li-coordinated EMC molecules.^[2] Once the excess electrolyte is removed, either by Celgard[®] or by washing, mostly bound electrolyte molecules are remaining.



Figure 74. Topography and nano-FTIR spectra of Li-metal surface after contact with GEN 2 electrolyte. The excess of electrolyte was removed by Celgard[®] porous separator. Most of the Li-metal surface is covered by thin iridescent film. (a) Topography of a patch of Li-metal surface without a thin film. (b) Topography of a thin film covering Li-metal surface. (c) Nano Fourier transform infrared spectra of different spots of the Li-metal surface.

Optical microscopy clearly indicates the presence of a thin film on the surface of lithium metal (as show in Figure 74a), due to the surface's iridescence. This thin film seems to cover a majority of the sample surface. Atomic force microscopy measurements indicate that the iridescent film's root mean square roughness is ~ 1.2 nm. Additionally, the nano-FTIR signal from that film is mainly dominated by P-F vibrations at 830 cm⁻¹. LiEDC vibrations, usually containing separated peaks with relatively narrow full width at half maximum (FWHM), are now forming one broad with multiple shoulders in the feature region 1000-1300 cm⁻¹. The spectrum is consistent throughout the film. However, there are patches of the exposed surface under the iridescent film, where the nano-FTIR signal is dominated by Li₂CO₃. LiEDC peaks are present as well, with no shoulders or broadening compared to the previous locations. The topography imaging (Figure 74b) revealed that those regions contain patches of absorbed species, which have a new peak at 930 cm⁻¹ and 764 cm⁻¹. These peaks could be attributed to free EC and EMC molecules. The rest of the area is uniformly covered with LiEDC, Lithium carbonate, and GEN 2 electrolyte components, indicating a strong bond between passivated lithium surface and electrolyte molecules. This effort completes this quarter's milestone.

It is important to note that washing away organic components leads to potential damage of SEI and disturbing the passivation layer, preventing lithium from reacting with the environment. As an example, the rise of Li_3N peak in a washed Li-metal surface can be explained by a reaction with N_2 gas, which is present in the nano-FTIR and ATR-FTIR systems. Notably, the undisturbed SEI stays inert to the N_2 environment even after a month of storage.

References

- [1] Hou, T., et al. "The Influence of FEC on the Solvation Structure and Reduction Reaction of LiPF₆/EC Electrolytes and its Implication for Solid Electrolyte Interphase Formation." *Nano Energy* 64 (2019): 103881.
- [2] Lee, H., et al. "Why Does Dimethyl Carbonate Dissociate Li Salt Better than Other Linear Carbonates? Critical Role of Polar Conformers." *Journal of Physical Chemistry Letters* 11, 24 (2020): 10382–10387.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 2.3 – Advanced *In Situ* Diagnostic Techniques for Battery Materials (Xiao-Qing Yang and Enyuan Hu, Brookhaven National Laboratory)

Project Objective. The primary objective of this project is to develop new advanced *in situ* material characterization techniques and to apply these techniques to support development of new cathode and anode materials with high energy and power density, low cost, good abuse tolerance, and long calendar and cycle life for beyond Li-ion battery systems to power plug-in hybrid electric vehicles (PHEVs) and battery electric vehicles (BEVs). The diagnostic studies will focus on issues relating to capacity retention, thermal stability, cycle life, and rate capability of beyond Li-ion battery systems.

Project Impact. The Vehicle Technologies Office Multi-Year Program Plan describes the goals for battery: "Specifically, lower-cost, abuse-tolerant batteries with higher energy density, higher power, better low-temperature operation, and longer lifetimes are needed for development of the next-generation of HEVs [hybrid electric vehicles], PHEVs, and EVs [electric vehicles]." The results of this project will be used for development of technologies that will significantly increase energy density and cycle life, and reduce cost. This will greatly accelerate deployment of EVs and reduce carbon emission associated with fossil fuel consumption.

Approach. This project will use a combination of synchrotron X-ray diffraction and pair distribution function and of neutron diffraction and pair distribution function; X-ray spectroscopies including hard/soft X-ray absorption spectroscopy (XAS), X-ray photon emission spectroscopy; and imaging techniques including X-ray fluorescence microscopy, transmission X-ray microscopy (TXM), and transmission electron microscopy.

Out-Year Goals. The out-year goals are to develop spectro-tomography, X-ray diffraction (XRD), XAS, and pair distribution function (PDF) techniques, and to apply these techniques on Li-ion battery cathode, Na-ion battery cathode, and solid-state electrolyte (SSE).

Collaborations. The Brookhaven National Laboratory (BNL) team will work closely with material synthesis groups at Argonne National Laboratory (Y. Shin and K. Amine) for the high-energy composite, at Pacific Northwest National Laboratory for the S-based cathode and Li-metal anode materials, and with Oak Ridge National Laboratory on neutron scatterings. This project will also collaborate with industrial partners, as well as with international collaborators.

- 1. Complete XRD and X-ray PDF studies on SSE Li₇P₂S₈I_{0.5}Br_{0.5} to understand its degradation mechanism at high voltage. (Q1, FY 2022; Completed)
- 2. Complete cryogenic electron microscopy study to understand the positive role of LiNO₃ additive in solid electrolyte interphase (SEI) formation on Li-metal anode. (Q2, FY 2022; Completed)
- 3. Complete many-particle TXM studies on LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC) cathode to understand its chemical and morphological heterogeneities at the electrode level. (Q3, FY 2022; Completed)
- 4. Complete *ex situ* XAS and TXM studies on polymeric sulfur cathode to understand its redox mechanism and morphological evolutions during cycling. (Q4, FY 2022; In progress)

This quarter, the third milestone was completed. The BNL team has been focusing on developing advanced diagnostic techniques to achieve a thorough understanding of high-energy-density and long-cycle-life electrode materials. LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC-811), as an important high-energy-density cathode material for lithium batteries, suffers from capacity fading on cycling. Several factors such as oxygen loss, surface reconstruction, and particle cracking have been identified to be responsible for the fading but whether these factors are



Figure 75. (a) Computed tomography scan of cycled NMC-811 electrode. (b) Particles labeled based on their morphological damage extent. (c-e) Details of representative particles having various degrees of damage. (f) X-ray absorption near-edge structure data of selected particles in (b). (g) Fourier transformed – extended X-ray absorption fine structure data of selected particles in (b).

independent or correlated is not clearly understood yet. To answer this question, the BNL team used multimodal characterization tools at multiscale lengths to study long-cycled NMC-811 cathode (2.8-4.4 V after 100 cycles). This work is done in collaboration with scientists at Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory. An electrode-level computed tomography scan was done at the European Synchrotron Radiation Facility, with results shown in Figure 75a, indicating that after long cycling, the NMC-811 particles experience various levels of morphological degradation. To study the chemical nature of these individual particles and therefore identify the possible correlation between chemical and morphological properties, the same electrode was characterized at National Synchrotron Light Source II using a focused beam with beam size of $\sim 10 \,\mu\text{m}$ for a particle-level characterization. Figure 75b shows the color-coded particles that have been labeled according to their morphological degradation extent (the bigger the number, the more serious the degradation) and these labeled particles are further studied using XAS. Figure 75c-e shows the details of representative particles that have different degrees of morphological degradation. Figure 75f shows the X-ray absorption near-edge spectroscopy results at nickel K-edge for selected particles p1, p2, p3, p4, and p5. The more damaged particles have lower-edge energy that suggests lower oxidation state of the nickel, clearly indicating the correlation between morphological degradation and chemical state. Such trending can be seen more clearly in Figure 75g, where the Fourier transformed extended X-ray absorption fine structure spectra show a clear trend of the increased Ni-O bond distance at ~ 1.5 Å (not phase corrected) from p1 to p5, resulting from the reduced oxidation state of nickel. The decreased peak intensity going from p1 to p5 is likely due to oxygen vacancy induced by oxygen loss. These results demonstrated that the oxygen loss at high-voltage charging plays an important role in the crack formation and capacity degradation of NMC-811 particles. This study suggests that tuning the oxygen activity and suppressing the oxygen loss can potentially help to address the crack issue in NMC-811 particles.

Patents/Publications/Presentations

Publications

- Tan, S., Z. Shadike, J. Li, X. Wang, Y. Yang, R. Lin, A. Cresce, J. Hu, A. Hunt, I. Waluyo, L. Ma, F. Monaco, P. Cloetens, J. Xiao, Y. Liu*, X-Q. Yang,* K. Xu,* and E. Hu.* "Additive Engineering for Robust Interphases to Stabilize High-Ni Layered Structures at Ultra-High Voltage of 4.8 V." *Nature Energy* 7 (2022): 484–494. doi: 0.1038/s41560-022-01020-x.
- Lin, R.,* Y. He, C. Wang, P. Zou, E. Hu, X-Q. Yang,* K. Xu, and H. Xin.* "Characterization of the Structure and Chemistry of the Solid-Electrolyte Interface by CryoEM Leads to High-Performance Solid-State Li-Metal Batteries." *Nature Energy*. doi: 10.1038/s41565-022-01148-7.

Task 2.4 – Probing Interfacial Processes Controlled Electrode Stability in Rechargeable Batteries (Chongmin Wang, Pacific Northwest National Laboratory)

Project Objective. The main objective is to explore interfacial phenomena in rechargeable Li-ion batteries of both solid-state electrolyte (SSE) and liquid electrolyte (LE) configuration, to identify the critical parameters that control the stability of interface and electrodes as well as solid electrolyte (SE). The outcome will be establishing correlations between structural-chemical evolution of active components of batteries and their properties. These correlations will provide insight and guidance to battery materials development groups for developing high-performance battery materials.

Project Impact. The proposed characterization work focuses on atomic-level structural and chemical analysis and direct correlation with battery fading properties. The work can be directly used to guide design of electrode materials with tailored microstructure and chemistry for enhanced properties of increasing the energy density of Li-ion batteries and to accelerate market acceptance of electric vehicles (EVs), especially for plug-in hybrid electric vehicles as required by the EV Everywhere Grand Challenge.

Approach. The project will use integrated advanced microscopic and spectroscopic techniques, including *in situ* and *ex situ* scanning transmission electron microscopy (STEM), environmental STEM, cryogenic electron microscopy, and *in situ* liquid secondary ion mass spectrometry, in collaboration with theoretical modeling, to directly probe the structural and chemical information of active materials in rechargeable batteries. Cryogenic STEM (cryo-STEM) with analytical tools, such as energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS), will be used to gain chemical and electronic structural information at the interface between lithium metal and electrolyte of both solid-state and liquid configuration, which will allow direct correlation between the morphology and chemistry. STEM – high-angle annular dark-field atomic-level imaging and EDS/EELS will be used to probe the interface and bulk lattice stability of cathode and SE in solid-state batteries (SSBs). The work will be in close collaboration with the battery development group within the BMR and U. S. – Germany Collaboration on Energy Storage.

Out-Year-Goals. This project has the following out-year goals:

- Atomic-level multiscale *ex situ / in situ* and *operando* STEM and cryo-STEM investigation on the fading mechanisms of energy-storage materials and devices in the system of both LE and SE; gain a fundamental understanding of electronic and ionic transport characteristics and kinetics in energy-storage system.
- Develop new *in situ* and *ex situ* STEM capability for probing challenging questions related to energy storage technology for both SSE and LE energy storage systems.

Collaborations. This project collaborates with G. Chen (Lawrence Berkeley National Laboratory, LBNL); J. Nanda (Oak Ridge National Laboratory); Y. Yao (University of Houston); K. Amine (Argonne National Laboratory); D. Wang (Pennsylvania State University); A. Manthiram (University of Texas, Austin); W. Tong (LBNL); Y. Cui (Stanford University); J. Zhang, J. Liu, P. M. L. Le, W. Xu, X. Jie, and D. Lu (Pacific Northwest National Laboratory); X. Xiao (General Motors); and M. S. Whittingham (State University of New York, Binghamton).

- 1. Measure electronic properties of solid electrolyte interphase (SEI) layer and electrical double layers, identifying their effects on electrochemical properties. (Q1, FY 2022; Completed)
- 2. Identify correlation between electrical properties of SEI layer and lithium structural features, such as how mossy lithium and crystalline lithium form. (Q2, FY 2022; Completed)

- 3. Reveal the nature of reaction product between cathode and S-based SE. (Q3, FY 2022; Completed)
- 4. Measure mechanical properties of SEI layer and its correlation with the lithium morphology. (Q4, FY 2022)

Stability of cathode SSE interfaces represents a key challenge for using sulfide-based SSEs (S-SSE). Chemical incompatibility, electrochemical reaction, and mechanical issues may all play a role in degrading battery performance. Although remarkable progress has been achieved in increasing interfacial conductivity and enabling high-rate cycling, an in-depth and comprehensive understanding of the underlying mechanism of interface reaction between high-Ni LiNiMnCoO₂ (NMC) cathode and sulfide SE remain unclear.

Here, the team uses $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC-811) secondary particle and $\text{Li}_7\text{P}_2\text{S}_8\text{Br}_{0.5}\text{I}_{0.5}$ (LPS) as model materials to investigate the initial trigger of interfacial reactions, revealing the interface structural change between NMC-811 and LPS at pristine and after charge by transmission electron microscopy (TEM). They compare the structure of NMC-811 secondary particles without embedding and embedded in LPS electrolyte at the state of pristine and after charging to 4.2 V using LE 1 M LiPF₆ ethylene carbonate / diethyl carbonate (V/V). Figure 76 shows the low-magnification scanning electron microscopy (SEM) image of NMC-811

secondary particle at pristine and after charging to 4.2 V, which is compared with NMC-811/LPS and NMC-811/LPS after charging to 4.2 V. To examine the mechanical damage accumulating in the cathode owing repetitive to lattice volume changes on cycling, the team investigated crosssections of NMC-811 and NMC-811/LPS charged to 4.2 V (Figure 76e-h). The team reveals that, during



Figure 76. Low magnification scanning electron microscopy (SEM) images of (a) pristine NMC-811 secondary particle, (b) NMC-811 secondary particle charged to 4.2 V, (c) pristine NMC-811 secondary particles mixed with LPS solid-state electrolyte, and (d) NMC-811 mixed with LPS after charging to 4.2 V. (e-f) SEM images of NMC-811 secondary particles viewed in cross section.

the initial charging, pure NMC-811 cathode particles show high density of intergranular cracking. In contrast, the NMC-811/LPS (Figure 76h) shows no significant intergranular cracking. Apparently, introducing LPS into NMC-811 cathode could effectively prevent formation of intergranular cracking in the secondary particles.

To assess the interfacial reaction between NMC-811 and LPS on cycling of the battery, the team uses high-resolution transmission electron microscopy (HRTEM) to analyze the surface structural and chemical evolution of NMC-811. Figure 77a-d shows the low-magnification TEM images of the morphology of NMC-811 and NMC-811/LPS at pristine and after charging to 4.2 V. As shown in Figure 77e-h, pristine NMC-811 surface has a layer structure, as confirmed by the HRTEM image and the corresponding fast Fourier transforms. After charging to 4.2 V, a rock-salt layer with a thickness of ~ 2 nm is formed on the surface of NMC-811 primary particle. A cathode electrolyte interphase (CEI) of ~ 3 nm on the surface of rock-salt layer, indicating the electrolyte permeation along the grain boundary of NMC-811 secondary particle. Apparently, formation of the CEI layer on the surface and along the crack of the cathode particles led to electrolyte consumption and salt depletion in the electrolyte.



Figure 77. Microstructure of NMC-811 and NMC-811/LPS before and after charge. (a) Pristine NMC-811. (b) NMC-811 charged to 4.2 V. (c) Pristine NMC-811/LPS. (d) NMC-811/LPS charged to 4.2 V. Insets are the selected area electron diffraction patterns acquired from primary particle. High-resolution transmission electron microscopy images of (e) pristine NMC-811, (f) NMC-811 charged to 4.2 V, (g) pristine NMC-811/LPS, and (h) NMC-811/LPS charged to 4.2 V. Insets are fast Fourier transform patterns acquired from primary particle surface (orange color) and bulk region (blue color).

The pristine state of NMC-811/LPS interface shows perfect layer structure, indicating that the chemical reaction between NMC-811 and LPS SSE does not affect cation mixing. After charging, the interface between NMC-811 and LPS still remains as a layer structure, as shown in Figure 77h. These results demonstrate that the chemical reaction and electrochemical reaction between NMC-811 and LPS SSE will not affect the NMC-811 surface structure. The absence of surface phase transformation on NMC-811/LPS interface after charge indicates that NMC-811/LPS interface is more stable than that of the NMC-811/LE. Moreover, this shows that the direct contact of LE with the layer cathode plays a key role in initiating the widely documented layer-to-rock-salt transformation at the cathode surface.

The team also acquired elemental mapping of NMC-811 and NMC-811/LPS before and after charging to 4.2 V, as shown in Figure 78. The element distribution of pristine NMC-811 is very uniform. However, after charge, there are very wide cracks formed inside of NMC-811 primary particle. As fluorine and carbon are components of the LEs, but not the part of cathode particles, the spatial distribution of fluorine and carbon can be used to trace the interaction of the LE and the cathode particles. As shown in Figure 78f, both fluorine and carbon showed enrichment along the surface of intergranular crack, further confirming the penetration of the LE along the intergranular crack. The element distribution of pristine NMC-811/LPS indicates a sharp interface between NMC-811 and LPS, as shown in Figure 78g, indicating a lack of element diffusion between the NMC-811 and LPS has electrochemically reacted with NMC-811 particles, leading to the diffusion of sulfur and phosphorus into NMC-811 particle. This observation accounts for the high interface impedance between NMC-811 and LPS.

In summary, the team reveals the interfacial chemical and electrochemical reactions between NMC-811 and LPS SSE by a comprehensive analysis of SEM, focused ion beam, TEM, and STEM. They found that mixing NMC-811 with LPS could form solid-solid interface, and this interface is more stable than cathode-liquid interface. Direct contact of LE and NMC-811 cathode plays a big role in initiating the widely documented layered-to-rock-salt phase transformation and intergranular crack formation inside of cathode particle. Detailed structural and chemical analysis reveals that the solid-solid interface provides a fast path for the Li-ion transport and simultaneously prevents penetration of the LE into the cathode particle. This eliminates several detrimental factors, including the solid-liquid interfacial reaction, intergranular crack, and layered-to-rock-salt phase transformation, which critically affects the battery cycle stability of both capacity and voltage. The interface between NMC-811 cathode and LPS SSE is unstable during electrochemical cycling, as indicated by the

diffusion of certain components of LPS into NMC-811 particle, which could account for the large interfacial resistance between cathode and LPS. The present work provides insights for the rational design of SSE-based all-solid-state batteries in the future.



Figure 78. Elemental composition of NMC-811 and NMC-811/LPS before and after charging to 4.2 V. (a-d) Overlapped energy dispersive X-ray spectroscopy elemental maps, showing the element distribution across the secondary particle interior and surface. (e-h) Elemental maps acquired from NMC-811 and NMC-811/LPS.

Patents/Publications/Presentations

Publications

- Shi, L. L., C. S. Anderson, H. Qiao, N. Canfield, Y. B. Xu, Z. X. Yu, S. Feng, P. M. L. Le, C. M. Wang, J. Liu, J. Xiao, and D. P. Lu. "Early Failure of Lithium-Sulfur Batteries at Practical Conditions: Crosstalk between Sulfur Cathode and Lithium Anode." *Advanced Science* 9, No. 21 (2022): 2201640.
- Jin, Y., P. M. L. Le, P. Y. Gao, Y. B. Xu, B. W. Xiao, M. H. Engelhard, T. D. Vo, X. Cao, J. T. Hu, L. R. Zhong, B. E. Matthews, R. Yi, C. M. Wang, X. L. Li, J. Liu, and J-G. Zhang. "Low-Solvation Electrolytes for High-Voltage Sodium-Ion Batteries." *Nature Energy* (2022). doi: 10.1038/s41560-022-01055-0.
- Jin, Y., Y. B. Xu, B. W. Xiao, M. H. Engelhard, R. Yi, T. D. Vo, B. E. Matthews, X. L. Li, C. M. Wang, P. M. L. Le, and J-G. Zhang. "Stabilizing Interfacial Reactions for Stable Cycling of High-Voltage Sodium Batteries." *Advanced Functional Materials* (2022). doi: 10.1002/adfm.202204995.

Task 2.5 – Integrated Atomic-, Meso-, and Micro-Scale Diagnostics of Solid-State Batteries (Yi Cui, William Chueh, and Michael Toney; Stanford University / SLAC National Accelerator Laboratory)

Project Objective. By developing a characterization toolkit that tackles length scales (Å to mm), cell pressure (1-100 bars), and dynamics (during synthesis, fabrication, and cycling), the project aims to generate insights to engineer solid-state batteries (SSBs) for deployment in electric vehicles. This interdisciplinary team aims to achieve this objective by merging a broad range of characterization approaches as well as modeling to track the evolution of nanoscale chemistry and structure, microstructure, and transport.

Project Impact. The project will have an impact in several areas: (1) accelerate rational design of coatings and artificial solid electrolyte interphases (SEIs) in SSBs; (2) inhibit the root causes leading to cell shorting, and enable high current cycling; (3) accelerate design of cathode coating and composite electrode architectures; and (4) reduce degradation and variability during SSB manufacturing via composition and surface engineering.

Approach. The project has a multifold approach that will encompass the following: (1) resolve nanoscale structure and chemistry of SEIs via cryogenic transmission electron spectroscopy (cryo-TEM); (2) track solid electrolyte (SE) and lithium microstructure evolution in three dimensions via X-ray micro and diffraction tomography; (3) visualize nanoscale ionic and electronic transport at grain boundaries via conducting atomic force microscopy; (4) map current distribution in cathodes via scanning transmission X-ray microscopy; and (5) monitor nanoscale SE evolution with gas impurity via *in situ* environmental TEM.

Out-Year Goals. The project will develop an integrated characterization toolkit to characterize SSBs within a single cycle and over hundreds of cycles, spanning a wide range of relevant length scales.

Collaborations. Project collaborations include work with Stanford Synchrotron Radiation Lightsource, Advanced Light Source, and Advanced Photon Source synchrotron light sources.

- 1. Quantify effect of microindentation pressure on fracture formation of Li₇La₃Zr₂O₁₂ (LLZO) SE using *in situ* electrochemical scanning emission microscopy (SEM). (Q1, FY 2022; Completed)
- 2. Quantify degree of H/Li exchange for acid-treatment LLZO before and after heat treatment. (Q2, FY 2022; Completed)
- 3. Characterize chemical nature of the Ag-LLZO interface via cryo-TEM. (Q3, FY 2022; Completed)
- 4. Characterize lithium plating on LLZO coated with five metallic electrodes using *in situ* electrochemical SEM. (Q4, FY 2022; In progress)

Throughout this year, the team developed an *operando* electrochemical platform to investigate the mechanical effects on the lithium intrusion behavior (Figure 79). Local stress of very high magnitude is applied by varying the probe contact force and is quantified via a spring table located inside the SEM (Figure 79a).

Figure 79c-f shows the progression of a force-controlled SEM microprobe experiment where a tungsten microprobe is brought into contact with the LLZO surface in a region without any obvious microstructural defects (large pores, cracks, etc.), and with minimal contact load between the tungsten probe and the surface. On performing linear sweep voltammetry, as shown in a representative current-voltage curve in Figure 79c, the team observes rapid growth of Li-metal whiskers on the surface of the LLZO (at ~ $V_{app} < |-0.1|$ V), as shown in Figure 79d. As the applied potential is swept to more anodic potentials, the current increases non-linearly. At a certain point in the experiment, metallic lithium is observed via SEM to induce cracks in the LLZO, resulting in lithium intrusion. This typically occurs after the lithium whisker has reached many microns in diameter. These two lithium growth modes, pre-intrusion and post-intrusion, are shown in a tilted SEM image in Figure 79f, with the Li-metal whisker highlighted in red and intrusions highlighted in orange. Once the onset of intrusions (indicating fracture) is visible in the SEM, the team observes rapid propagation of intrusions on the LLZO surface with an accompanying increase in current magnitude.

To interpret the electrochemical data, the team models two sources of overpotential: charge-transfer kinetics at the Li–LLZO (working electrode) interface, η^{WE} , and the ohmic, semi-infinite constriction (current focusing) resistance of the LLZO, η^{Ohm} . In this simple model, they assume that the Li-LLZO contact is circular in shape and that the charge-transfer kinetics are symmetric Butler-Volmer (BV) in nature. The applied potential, V_{app} , is given by:

$$V_{app} = \eta^{Ohm} + \eta^{WE} = \frac{i}{2\sigma_{ion}d} + \frac{2RT}{F} \operatorname{arcsinh}\left(\frac{j}{2j_0}\right)$$

where *i* is the current, *d* is the effective diameter of the Li-LLZO contact, σ_{ion} is the ionic conductivity of LLZO, *j* is the areal current density, and j_0 is the exchange current density. The team employs this model to calculate the lithium whisker diameter (*d*) from the electrochemical data at every point in the voltage sweep, as shown in Figure 80a-b. From *d*, they then determine the current density and working electrode overpotential, as shown in Figure 80c-d. The geometrically averaged current density at failure is extremely high, as shown in Figure 80c, several orders of magnitude greater than reported for macroscopic Li-metal cells, consistent with previous microprobe work. The team notes that *d* and the current density are not sensitive to either the choice of the charge-transfer mechanism (that is, BV) or the exchange current density, as η^{WE} is much smaller than η^{Ohm} in their experiments. Specifically, neglecting the charge-transfer overpotential (second term) in Equation 1 translates only to a difference in the estimated whisker diameter of < 10%.

The Li-metal whisker diameter increases monotonically with V_{app} for all plating experiments. As shown in Figure 80b, the whisker diameter (at the interface with LLZO) grows from ~ 1 micron to over 10 microns before intrusions are observed. The diameter estimated by this model is somewhat smaller than lithium whisker diameter observed in SEM. However, the electrochemical estimate of the whisker diameter more accurately reflects the Li-LLZO contact area than the area obtained by SEM imaging because there are a significant number of voids at the Li-LLZO interface.

The estimated value of the working electrode overpotential, in contrast to whisker diameter, does not change monotonically with applied potential (Figure 80d). Counterintuitively, for many experiments the estimated magnitude of η^{WE} actually decreases with applied potential. This occurs because the current density decreases as the whisker diameter grows. Therefore, the applied voltage primarily controls the diameter of the lithium whisker, rather than the charge-transfer overpotential. The magnitude of η^{WE} estimated by this method (typically tens of mV) is significantly smaller than the magnitude of V_{app} at fracture (typically 1 V), in agreement with
previous literature on LLZO interfacial kinetics, verifying that the results here are insensitive to the charge-transfer mechanism assumed in the model.

The team has also carried out this method on LLZO coated with silver, platinum, and carbon, and has shown that the current density at failure is significantly higher than without coating. TEM and secondary ion mass spectrometry showed chemical diffusion of the metal into the LLZO (Milestone 3).



Figure 79. Electroplating lithium metal onto LLZO via *operando* microprobe experiments inside scanning electron microscope. (a) Schematic of the local force-controlled scanning electron microprobe experiment. (b) Representative result of a linear sweep voltammetry experiment. (c-e) Colorized *operando* SEM images of lithium plating experiments outlined in (a) with each image corresponding to the position on plot (b).



Figure 80. Electrochemical analysis of three nominally identical scanning electron microprobe experiments as a function of applied potential (at a contact load of 0.1 mN) and histograms of lithium whisker diameter and current density at failure at different contact loads. (a) Measured current. (b) Estimated effective diameter at Li–LLZO interface calculated using Equation 1. (c) Estimated current density (area averaged). (d) Estimated charge-transfer overpotential. These parameters are computed for current between 50 nA and the spike when intrusion initiates. (e) Histogram of lithium whisker failure diameters (d_{fail}) for 0.1 mN and 5 mN probe contact. (f) Histogram of current density at failure (j_{fail}) for 0.1 mN and 5 mN probe contact.

Patents/Publications/Presentations

Publication

 McConohy, G., X. Xu, T. Cui, E. Barks, S. Wang, E. Kaeli, C. Melamed, X. W. Gu, and W. C. Chueh. "Mechanical Origins of Lithium-Metal Intrusions into Garnet Solid Electrolytes Revealed by Failure Statistics." ChemRxiv (2022). doi: 10.26434/chemrxiv-2022-33210.

Presentations

- Bessel Award Lecture, Max Planck Institute for Solid State Research, Stuttgart, Germany (May 13, 2022):
 "Collective Phenomena in Mixed Ionic & Electronic Conductors"; W. C. Chueh.
- Department of Energy Resource & Engineering, Stanford University, Stanford, California (May 9, 2022):
 "Designing a More Homogenous Battery: Emergent Electrochemical Phenomena at the Mesoscale";
 W. C. Chueh.
- Materials Research Society, Honolulu, Hawaii (May 9, 2022): "Learning Governing Relations in Battery Electrodes: Hybridizing Physics- and Data-Driven Approaches"; W. C. Chueh.
- California Research Alliance, University of California, Berkeley, California (May 4, 2022): "The Dynamic Local Chemistry of Cathodes: During Synthesis, Operations & Aging"; W. C. Chueh.

Task 2.6 – Fundamental Understanding of Interfacial Phenomena in Solid-State Batteries (Xingcheng Xiao, General Motors)

Project Objective. The project objective is to develop a comprehensive set of *in situ* diagnostic techniques combined with atomic/continuum modeling schemes to investigate and understand the coupled mechanical/ chemical degradation associated with dynamic interfacial phenomena in solid-state batteries (SSBs). Specifically, *in situ* observations and characterizations of lithium plating-stripping processes, lithium dendrite formation, interphase formation, and the induced interfacial stresses, as well as the mechanical and electrochemical properties of interfaces and interphases, are paramount. The study will provide useful guidelines for optimizing cell structure design and engineering interfaces and interphases to enable SSBs.

Project Impact. The project will provide fundamental understanding of the dynamic interfacial phenomena and the coupled mechanical and chemical degradation. In addition, it will establish a critical guideline to design safe and durable SSBs with energy density > 500 wh/kg for electric vehicle (EV) applications.

Approach. The multiscale *in situ* diagnostic tools, including atomic force microscopy, nanoindentation, dilatometer, stress sensors, and pressure cells, will be used to investigate mechanical behavior and microstructure evolution at interface/interphase during lithium plating and stripping. The information (along with Li-ion transport properties and microstructure evolution obtained using the advanced spectroscopic ellipsometry, and *in situ* transmission electron microscopy will be correlated with electrochemical performance toward high cycle efficiency and dendrite-free SSBs. The goal of this understanding is to develop strategies for surface and interface engineering, apply them to commercially available solid electrolytes (SEs) including powder, pellets, and foils, and assemble SSBs for further validation and optimization, eventually extending cycle life for EV application.

Out-Year Goals. The project seeks to develop SSB model systems to capture critical mechanical properties and probe the coupled mechanical-chemical degradation by further developing comprehensive *in situ* diagnostic tools. All results obtained from these *in situ* studies, combined with advanced postmortem analysis and modeling, will be correlated with the cycling stability of SSBs. The *in situ* tools developed will be applied to the following two periods to deeply understand the coupled mechanical and chemical degradation of interface/interphase.

Collaborations. The co-PIs involved in experiments and simulation will be as follows: B. W. Sheldon and Y. Qi (Brown University), and Y-T. Cheng and A. Seo (University of Kentucky).

- 1. Artificial interlayer can regulate mechanical/chemical properties of interfaces. (Q1, FY 2022; Completed)
- 2. Artificial interphase has good ionic conductivity and chemical stability. (Q2, FY 2022; Completed)
- 3. Model to predict the governing mechanical and material properties of interfaces responsible for failures. (Q3, FY 2022; Completed)
- 4. Pouch cells of SSBs with optimized interlayers with energy density > 350 Wh/kg and cycle life > 500 cycles. (Q4, FY 2022)

Investigation of Different Polymer Nanocomposite-Based Interlayers to Reduce Interfacial Resistance of SSBs

Recently, the team developed a polymer nanocomposite as the interlayer to maximize interfacial contact between lithium metal and SE, thus facilitating ion transport through the interface. They first deposited a thin film on Li-metal surface by soaking it in DTL solution, which stands for 1,2-dimethoxyethane (DME) solvent with trimethyl phosphate (TMP) and LiNO₃ additives. In addition, they also replaced DME with 1,3-dioxolane to form a more flexile coating. Electrochemical impedance spectroscopy (EIS) shows that the interlayer can significantly reduce impedance by almost two orders of magnitude, as shown in Figure 81.

This quarter, to correlate battery performance and the components and properties of the coating layer formed in the soaking process, the team performed density functional theory based *ab initia* melagular dynamics (AD(D) simulation



Figure 81. The comparison of interfacial impedance of lithium versus LLZO with different interlayers.

theory based *ab initio* molecular dynamics (AIMD) simulations together with experimental investigation to study the reaction mechanism of the DTL solution on Li-metal surface.

When constructing the structures for lithium metals covered by the DTL solution, to resemble the 0.8 M LiNO_3 in DME/TMP (volume ratio = 5:1) solution in the experiment, 6 DME molecules, 1 TMP molecule, and 1 LiNO₃ molecule were packed as the liquid solution, relaxed, and formed an interface with lithium (001) surface. The AIMD simulation using the NVT ensemble (that is, constant temperature, constant volume ensemble) was performed at 400 K with the Nose-Hoover thermostat. The higher temperature (below the lithium melting point, 454 K) was used to accelerate the calculations. The system was first run for 5 ps with a time step of 1 fs. If no bond breakage or decomposition was observed, another 15 ps was added.

Figure 82a-c shows the final structures of one molecule on the lithium metal after the AIMD simulations. No reactions occur between DME and the lithium metal after 20 ps (Figure 82a). In contrast, after 5 ps, one of the C-O bonds breaks in TMP (Figure 82b), forming a CH₃ radical, while the LiNO₃ completely decomposes to nitrides and oxides (Figure 82c). These observations are consistent with the scanning electron microscopy images for lithium surfaces soaked in DME or TMP for 1 hour.



Figure 82. Structures after *ab initio* molecular dynamics simulations. (a) DME molecule, (b) TMP molecule, (c) $LiNO_3$ molecule, and (d) DTL solution on the lithium metal. Purple: lithium; brown: carbon; white: hydrogen; red: oxygen; blue: nitrogen; and green: phosphorus. The colors for different elements are consistent across all the figures.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 2.7 – Multidimensional Diagnostics of the Interface Evolutions in Solid-State Lithium Batteries (Yan Yao, University of Houston)

Project Objective. The project objective is to develop a platform combining focused ion beam – scanning electron microscopy (FIB-SEM) tomography, Time-of-flight secondary ion mass spectrometry (TOF-SIMS), and *in situ* SEM nanoindentation-based stiffness mapping for structural, chemical, and mechanical characterizations in solid-state lithium batteries (SSLBs). Assessment of the influence of cell design and testing conditions (that is, external pressure, current density, and temperature) on the evolutions of interfaces will be performed.

Project Impact. The consolidated *in situ* structural–chemical–mechanical diagnostic platform established in this project will provide unprecedented insights into the failure mechanisms of SSLBs.

Approach. Space- and time-resolved structural, chemical, and mechanical characterizations of the cathode-electrolyte and anode-electrolyte interfaces will be performed on lithium all-solid-state batteries (ASSBs) using FIB-SEM, TOF-SIMS, and in-SEM nanoindentation. Tasks include the following: (1) development of solid-state cell thin stacks and test-cell configurations that are suitable for *in situ* characterizations; (2) quantitative characterization and *in situ* tracking of interfacial voids formation within composite cathode and electrolyte layer; (3) identification and *in situ* tracking of the chemical composition, spatial distribution, and mechanical properties of electrolyte decomposition products at the lithium- and cathode-electrolyte interfaces; and (4) visualization, chemo-mechanical properties detection, and *in situ* tracking of lithium dendrites grown within the solid electrolyte layer.

Out-Year Goals. In the out years, the project will develop thin-stack solid-state cells, micro-cells, in-SEM nanoindentation, and testing protocols. The correlation between structural evolution, electrolyte decomposition, and interfacial resistance increase will be investigated.

Collaborations. The University of Houston team (Y. Yao, Z. Fan, and Y. Liang) works closely with the Rice University team (J. Lou and H. Guo).

- 1. Multiscale structural investigations. (Q1, FY 2022; Completed)
- 2. Composition and spatial distribution study. (Q2, FY 2022; Completed)
- 3. Selected region mechanical property probing. (Q3, FY 2022; Completed)
- 4. Real-time monitoring of structural evolutions. (Q4, FY2022; In progress)

Understanding the chemo-mechanical behaviors of electrodes is critical to the rational engineering of a solid-state battery (SSB) system with robust solid-solid contact during operation. Here, pyrene-4,5,9,10-tetraone (PTO) / $\text{Li}_6\text{PS}_5\text{Cl}$ composite cathode was chosen as a model materials system to demonstrate capability on probing the chemo-mechanical behavior of SSBs. The chemical and mechanical characterizations of composite electrode were performed by combining TOF-SIMS with an in-SEM nanoindenter system. First, PTO/ $\text{Li}_6\text{PS}_5\text{Cl}$ composite cathode sample was prepared by argon ion polishing to achieve a clean and smooth cross section for characterization. The cross-section image of the composite cathode is presented in Figure 83a, where the domains with low contrast and high contrast correspond to the PTO and $\text{Li}_6\text{PS}_5\text{Cl}$ phases, respectively. TOF-SIMS analysis was performed to acquire the composition and spatial distribution of composite cathode. First, the mass spectra of the pristine PTO, pristine $\text{Li}_6\text{PS}_5\text{Cl}$, and composite cathode have

been compared to identify the chemical characteristic ions of PTO and Li₆PS₅Cl species, as shown in Figure 83b. The Li_xPTO fragments (LiC₂⁻ at m/z of 31.0166 and LiC_4^- at m/z of 55.0166) can be clearly localized in the composite cathode sample, which has confirmed lithiation of the PTO species. Smaller peaks at m/z of 31.0166 and 55.0166 in pristine Li₆PS₅Cl



Figure 83. (a) Cross-section scanning electron microscopy image of composite cathode pellet. (b) Zoomed-in mass spectra of pristine PTO, Li₆PS₅Cl electrolyte, and composite cathode. (c) Secondary ion images of Li₆PS₅Cl fragments, PO_x⁻ fragments, PTO fragments, and Li₂OH⁺ fragments in composite cathode, respectively.

and pristine PTO samples, respectively, may originate from contamination during sample preparation. Additionally, the peak intensity ratio between PO_2^- and PS^- was dramatically increased in the composite cathode as compared to the pristine Li_6PS_5Cl , which implies occurrence of oxidation of the Li_6PS_5Cl electrolyte in the composite cathode. Similar intensity changes in the peak ratio were also observed between PO₃ and PSO fragments. PO_x^{-} (PO_2^{-} , PO_3^{-}) fragments were also observed in pristine Li₆PS₅Cl sample, which can be explained by the high reactivity of Li_6PS_5Cl with a trace amount (ppm) of oxygen and water, leading to slight oxidation of the electrolyte during storage in the glovebox or transportation through the transfer vessel. TOF-SIMS secondary ion images were then used to confirm the chemical evolution in the composite cathode. To spatially identify the chemical changes in the composite cathode, ion mapping of the composite cathodes from the same region as shown in Figure 83a was also performed. Figure 83c shows the two-dimensional distribution of fragments corresponding to the Li_6PS_5Cl (red, Cl⁻), PTO (blue, C_2H^{-}), interphase component (green, PO_x^{-}) and Li_xPTO (gold, Li_2OH^+). The Li_2OH^+ species was used to represent the distribution of Li_xPTO due to its strong signal in the image mode. The oxidation fragments (PO_x^{-}) from Li₆PS₅Cl can be observed at the interface, which indicates occurrence of chemical reactions at the PTO and Li₆PS₅Cl electrolyte interface. Meanwhile, the Li_xPTO related fragments can also be found inside the PTO domains. The team believes these originated from spontaneous redox reactions between PTO and Li₆PS₅Cl. In summary, TOF-SIMS analysis has allowed highlighting the chemical evolution of PTO electrode and Li₆PS₅Cl electrolyte with a sufficient spatial resolution.

Effects of such important chemical evolution on mechanical properties of composite cathodes have seldom been reported, mainly due to the limited spatial resolution of nanoindentation tests under optical microscope. To overcome this limitation, in-SEM nanoindentation tests were performed on the composite cathodes and mechanical properties of different phases were measured with much higher spatial resolutions, as shown in Figure 84a. Mechanical properties of pristine PTO and pristine Li₆PS₅Cl were also tested as references. More details about in-SEM nanoindentation measurements on different phases are demonstrated in

supplemental movies. The load-displacement typical curves of PTO and Li₆PS₅Cl in the composite cathode are shown in Figure 84b and Figure 84c, respectively. The average Young's modulus (using the Oliver-Pharr method) of PTO and Li_6PS_5Cl in the composite cathode measured, was respectively. as 15.0 ± 2.5 GPa and



Figure 84. (a) Schematic illustration of *in situ* scanning electron microscopy nanoindentation test on the identical region of interest for time-of-flight secondary ion mass spectrometry characterizations. (b-c) Load-displacement curves of PTO and Li₆PS₅CI in composite cathode, respectively. (d) Comparison of mechanical properties of pristine PTO, pristine Li₆PS₅CI, PTO in composite cathode, and Li₆PS₅CI in composite cathode.

 30.3 ± 4.5 GPa. The average hardness of PTO and Li₆PS₅Cl in the composite cathode was measured as 0.92 ± 0.27 GPa and 1.56 ± 0.27 GPa, respectively. More deformation should have occurred in the softer PTO phase when preparing the composite cathode by mortar mixing and uniaxial compaction, resulting in Li₆PS₅Cl fragments surrounded by the PTO domains. Young's modulus and hardness of pristine PTO were measured as 5.6 ± 0.7 GPa and 0.28 ± 0.05 GPa, respectively, which is consistent with reported values. The Young's modulus and hardness of pristine Li₆PS₅Cl electrolyte were measured as 25.7 ± 4.0 GPa and 1.19 ± 0.29 GPa, respectively, which is on the same order as the theoretical value reported by Z. Deng (Deng, Z., et al. Journal of the Electrochemical Society 163 (2016): A67). The average Young's modulus and hardness of pristine PTO, pristine Li₆PS₅Cl, PTO in composite cathode, and Li₆PS₅Cl in composite cathode are shown in Figure 84d. The Young's modulus and hardness value of PTO in composite cathode dramatically increased compared to pristine PTO, while the Li₆PS₅Cl did not. The team believes that the dramatic modulus and hardness increase in the PTO in composite cathode should be originated from the partial lithiation of PTO in the composite cathode during the sample preparation process. As mentioned in the earlier TOF-SIMS analysis, chemical reactions did occur in the composite cathode. In this regard, the average Young's modulus and hardness data of different phases in the composite cathodes are not sufficient to reflect the actual composition variations in such cathodes.

Figure 85a-b shows the Young's modulus and hardness mapping of the PTO phase at a specific location of interest. Figure 85c shows the lithium distribution in the same area by TOF-SIMS analysis. The secondary ion image of Li⁺ fragment in PTO domains confirmed lithiation of PTO even before the electrochemical operation of the cathode. It is important to note that the normalized lithium intensity here does not directly reflect the quantitative lithium concentration in the material, but the intensity variation provides information about distribution of the Li⁺ concentration difference in the PTO domains. Figure 85d shows the Young's modulus and hardness of the pristine PTO and Li_xPTO with different lithium concentrations. All LixPTO phases are stronger than the pristine



Figure 85. (a) Young's modulus mapping results in the PTO domains of the composite cathode; scale bar 5 μ m. (b) Hardness mapping results in the same PTO domains of the composite cathode; scale bar 5 μ m. (c) Lithium distribution mapping in PTO domains overlapping with the indented area; the intensity is normalized by the total ion counts from time-of-flight secondary ion mass spectrometry analysis; scale bar 5 μ m. (d) Mechanical properties of PTO domains with different lithium concentration.

PTO, and the Li_xPTO with higher lithium concentration shows higher Young's modulus and hardness. The above trend effectively illustrates the chemical reaction affected mechanical properties in the PTO domains and potentially provides a new dimension for understanding chemo-mechanical behaviors in ASSBs.

Patents/Publications/Presentations

Presentations

- Pittcon Conference and Exhibition, Virtual (June 9, 2022): "Understanding Solid Electrolyte-Lithium Interfaces via Multiscale Characterizations"; Y. Yao. Invited.
- Electrochemical Society Meeting, Vancouver, British Columbia, Canada (May 29 June 2, 2022):
 "Advanced Characterizations of Interfaces in Solid-State Batteries"; Y. Yao. Invited.
- Materials Research Society Spring (MRS) Meeting, Honolulu, Hawaii (May 8–11, 2022): "Understanding Solid Electrolyte-Lithium Interfaces via *Operando* Multiscale Characterizations"; Y. Yao. Invited.
- MRS Spring Meeting, Honolulu, Hawaii (May 8–11, 2022): "Constructing Favorable Microstructures in Solid-State Organic Cathodes via Mechanical Property Manipulation"; Z. Chen, Y. Yao, et al. Contributed.
- MRS Spring Meeting, Honolulu, Hawaii (May 8–11, 2022): "Alloying-Induced Morphological Stability of Li Metal Anode for Sulfide-Based All-Solid-State Batteries"; L. Zhao, Y. Yao, et al. Contributed.
- Organic Battery Days Satellite Meeting, Virtual (May 9, 2022): "Constructing Favorable Microstructures in Solid-State Organic Cathodes via Mechanical Property Manipulation"; Z. Chen, Y. Yao, et al. Contributed.
- Materials Science and Engineering Department Seminar, University of California, Los Angeles, California (April 15, 2022): "Next-Generation Batteries for Electric Vehicles and Stationary Storage"; Y. Yao. Invited.
- Chemistry and Biochemistry Department, Biochemistry Divisional Seminar, Ohio State University, Virtual (April 6, 2022): "Next-Generation Batteries for Electric Vehicles and Stationary Storage"; Y. Yao. Invited.

TASK 3 – MODELING

Team Lead: Venkat Srinivasan, Argonne National Laboratory

Summary and Highlights

Achieving the performance, life, and cost targets outlined by the Vehicle Technologies Office will require moving to next-generation chemistries, such as higher capacity Li-ion intercalation cathodes, silicon and other alloy-based anodes, Li-metal anode, and sulfur cathodes. However, numerous problems plague development of these systems, from material-level challenges in ensuring reversibility to electrode-level issues in accommodating volume changes, to cell-level challenges in preventing cross talk between the electrodes. In this task, a mathematical perspective is applied to these challenges to provide an understanding of the underlying phenomenon and to suggest solutions that can be implemented by the material synthesis and electrode architecture groups.

The effort spans multiple length scales, from *ab initio* methods to continuum-scale techniques. Models are combined with experiments, and extensive collaborations are established with experimental groups to ensure that the predictions match reality. Efforts also focus on obtaining parameters needed for the models, either from lower-length scale methods or from experiments. Projects also emphasize pushing the boundaries of the modeling techniques used to ensure that the task stays at the cutting edge.

A major focus of the effort is around Li-metal-based solid-state batteries. While these chemistries hold promise, numerous challenges such as reactivity, conductivity, and mechanical stability prevent their commercialization. Mathematical models are ideal to provide the guidance and insights needed to solve these issues.

In the area of Li-metal anodes, the focus is on understanding how materials can be designed to prevent dendrite growth using continuum modeling approaches, combined with calculations on mobility in solid conductors. The results are used to guide materials development by providing the properties needed to prevent dendrites, while also achieving the energy and power goals. Models examine the role of the solid electrolyte interphase (SEI) on the morphology of the dendrite and describe the mechanical-electrochemical coupled effects that are critical for dendrite formation. Finally, efforts are focused on discovery of new solid ion conductors with properties that far exceed existing materials. The focus is on using these models as a guide before embarking on extensive experimentation.

Lithium metal with solid electrolytes (SEs) will be paired with cathode materials, often intercalative in nature. Models are being developed to examine the solid-cathode interface in Li-metal-based systems, where side reactions and interface debonding issues are known to limit cycling. These models are being used to understand how to prevent chemo-mechanical failure at the interface. Coatings, an effective strategy for high-voltage operation, are being explored with the aim of providing a rational design approach for new coating materials. In addition, focus is paid to porous electrodes with cathode particles to predict the impact of heterogeneities on electrode behavior.

Highlight. Controlling the reactivity of SEs with the electrode has remained a challenge for the commercialization of solid-state batteries. B. Narayanan's group has been using molecular dynamics to understand the reaction at the Li/Li₇PS₆ and S₈/Li₇PS₆ interfaces. Simulations suggest that Li₇PS₆ undergoes reductive decomposition through the progressive breakdown of the PS₄³⁻ motifs present in the electrolyte. These products bind with lithium atoms to form SEI. Growth of the SEI occurs by formation of bonds between lithium and the P/S atoms from the electrolyte. The insights gained here can help with designing approaches to control the SEI formation and limit side reactions.

Task 3.1 – Characterization and Modeling of Lithium-Metal Batteries: First-Principles Modeling and Machine Learning (Kristin Persson, Lawrence Berkeley National Laboratory)

Project Objective. This project supports Vehicle Technologies Office programmatic goals by developing next-generation, high-energy cathode materials and enabling stable cathode operation at high voltages through target particle morphology design, functional coatings, and rational design of electrolytes. The end-of-project goals include the following: (1) understanding of the factors that govern charge transport in nonaqueous, superconcentrated liquid electrolytes (LEs), (2) critical surface and coating design and optimization strategies that will improve cycling of Li-ion battery cathodes by reducing cathode degradation from oxygen loss, and (3) simulation and machine learning (ML) of the early formation of the solid electrolyte interphase (SEI) on Li-metal electrodes.

Project Impact. This project is aimed at providing fundamental insights into the atomistic mechanisms underlying surface reactivity and performance of Li-ion cathode materials and electrolytes, with the ultimate goal being to suggest improvement strategies, such as coatings, surface protection, novel electrolyte formulations, and particle morphology design. Transport modes as a function of solvent and salt concentrations will be clarified, and a data-driven reaction network framework will be designed and implemented to predict early SEI formation on lithium metal.

Approach. First-principles calculations, both static and dynamic approaches, are used to model solid-state electrolyte (SSE) material thermodynamics and kinetics. LEs are modeled through coupled classical molecular dynamics (CMD) and first-principles methods to accurately capture solvation structure as well as reactivity of the liquid system. The reaction network is built on large-scale first-principles data, using graph theory and ML models.

Out-Year Goals. Electrolyte work will be aimed toward understanding the atomistic interactions underlying performance of lithium electrolytes, specifically elucidating conductivity (as a function of salt concentration) and impact on the charge transport mechanisms at play. Amorphous coatings will be evaluated based on ionic transport metrics and thermodynamic stability. The reaction network will be tested against known interfacial species forming on lithium metal in LiPF₆/ ethylene carbonate (EC) electrolytes.

Collaborations. This project is highly collaborative among several BMR principal investigators: G. Chen (Lawrence Berkeley National Laboratory), G. Ceder (University of California, Berkeley), and R. Kostecki (Argonne National Laboratory). Improved coating formulations will be examined by Chen and Ceder, and interfacial reactivity insights will be corroborated by Kostecki.

- 1. Correlate electrolyte chemistry, and Li/SEI compositional structure determined for Li-EC-based electrolyte. (Q1, FY 2022; Completed)
- 2. Determine sensitivity of molecular dynamics (MD) parameters to diluent effect on transport in at least one superconcentrated electrolyte. (Q2, FY 2022; Completed)
- 3. Develop high-throughput (HT) infrastructure for MD simulations. (Q3, FY 2022, In progress)
- 4. Determine chemistry and structural motifs that control cathode amorphous coating performance, screening over 50,000 compositions. (Q4, FY 2022; Completed)

To evaluate the sensitivity of the force field (FF), the team scaled the charges of the diluent molecule by $0.5 \times$ the default charges, obtained from the optimized potentials for liquid simulation FF. They found that the relevant structural motifs dramatically changed: in the 0.5 × scaled charges, the coordination number (CN) in the primary lithium solvation shell is 0 (Figure 86c, green). However, with default charges, the CN is about 1, suggesting that the diluent is present in the primary solvation shell (Figure 86c, blue). This contradicts the design principle of high-concentration electrolytes (HCEs) with diluent where the diluent is chosen to allow the primary shell to consist only of the polar cosolvent (not the diluent). They also found that for the neat diluent surprisingly remained constant (ε =4). Although requiring further investigation, the team speculates that this is due to a tradeoff between magnitude of dipole moment and intermolecular interactions. The independence of the dielectric constant on charge scaling suggests that the dielectric constant alone may not be sufficient to use as a quantitative assessment of diluent MD FFs. It thus remains an open problem as to decisively distinguish between conventional co-solvent approaches and the HCEs for certain case studies via MD, and generally as partial solvation is challenging to quantify both experimentally and theoretically.



Figure 86. (a) Molecular dynamics (MD) "snapshot" of the solvation structure of a lithium cation in the high-concentration electrolyte (HCE) formulation, with the diluent in the second solvation shell. (b) MD "snapshot" of the solvation structure of a lithium cation in the HCE formulation with the diluent, in this case present in the first solvation shell. Atoms are shown in purple (lithium), red (oxygen), white (hydrogen), green (fluorine), and orange (phosphorus). (c) Radial distribution functions and coordination numbers for lithium coordinating with the diluent for different classical MD force field charge parameters of the diluent.

One of the main strategies to address the slow diffusivity of species in super concentrated electrolytes is to employ co-solvents. These co-solvents are often much less polar than their counterparts in solution. In certain cases, when such solvents are not expected to directly coordinate with the electroactive cation in the first solvation shell, they are referred to as diluents.^[1] Figure 86a shows the example of a diluent in an electrolyte. They investigated certain HCEs^[2] and HCEs with co-solvents previously using CMD (unpublished). However, they found that in the HCEs with diluent investigated, the diluent appeared in the first coordination shell of lithium (Figure 86b). One example formulation is 3 M of salt, ratio of Li:PC:diluent 1:2:0.3 where the Li⁺ counter anion is LiPF₆. As such it became a question as to whether such first shell coordination was an artifact of the CMD FF or in fact the previously reported effects of the diluent were wrong (that is, the diluent is effectively a conventional co-solvent).

References

- [1] Cao, X., P. Gao, X. Ren, L. Zou, M. H. Engelhard, B. E. Matthews, J. Hu, et al. "Effects of Fluorinated Solvents on Electrolyte Solvation Structures and Electrode/Electrolyte Interphases for Lithium Metal Batteries." *Proceedings of the National Academy of Sciences* 118, no. 9 (2021).
- [2] Self, J., K. D. Fong, and K. A. Persson. "Transport in Superconcentrated LiPF₆ and LiBF₄/Propylene Carbonate Electrolytes." *ACS Energy Letters* 4, no. 12 (2019): 2843–2849.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 3.2 – Electrode Materials Design and Failure Prediction (Venkat Srinivasan, Argonne National Laboratory)

Project Objective. The main project objective is to develop computational models for understanding the various degradation mechanisms for next-generation Li-ion batteries. This year's goal is to use the continuum-based mathematical model to estimate the conduction pathway through the solid electrolytes (SEs) and investigate interfacial stability between Li-metal electrodes and SEs during deposition and dissolution of lithium under externally applied currents. Electrolytes comprised of soft polymers, hard ceramics, and a combination of the two in the form of polymer-ceramic composites, will be investigated. SEs are expected to enable high-energy-density and liquid-free, safe, next-generation Li-ion batteries, while combined with thin Li-metal anodes. During charge, lithium dendrites are observed through the SEs, which are supposed to occur because of the non-uniform current distribution at the Li/electrolyte interface. Due to their lack of conformability, hard-ceramic-based SEs [such as Li₇La₃Zr₂O₁₂ (LLZO) and Li-Al-Ti-P (LATP)] are expected to experience loss of electrochemically active surface area during lithium plating and stripping, which can eventually lead to current focusing and subsequent dendrite growth. Sulfide-based soft ceramics Li-P-S (LPS) and Li-P-S-Cl (LPSCl), and/or polymer-ceramic composite electrolytes are expected to maintain better contact with the Li-metal electrode because of their higher deformability. The possibility of stabilizing the lithium deposition with composite electrolytes consisting of poly(ethylene oxide)-based soft-polymer matrix and LLZO-type hard ceramic fillers will be studied. Proper conduction pathways through the polymer and ceramic domains, and their influence on the effective conductivity of the SE, will be elucidated. Other soft SEs, such as polystyrene-b-poly(ethylene oxide) (SEO) polymer and sulfide-based soft ceramics, will be investigated for their capability to stabilize the lithium deposition on metallic anodes.

Project Impact. Findings from this research will give a better understanding of the ion transport mechanism within the polymer and ceramic domains of the composite SEs and will help elucidate the factors influencing the deposition of lithium at the electrode/electrolyte interface.

Project Approach. In the present project, mesoscale models are developed based on mass conservation, charge balance, and force balance relations at the continuum level to describe the physical processes occurring in the electrochemical systems during charge and discharge, which is then compared with the experimental observations for appropriate validation. The models are then used to provide insights and guidance for strategizing new design concepts and materials for the stabilization of Li-metal anodes.

Out-Year Goals. In this project, a computational framework will be presented that can capture the ionic transport through composite electrolytes and predict lithium deposition at the electrode/electrolyte interface.

Collaborations. This project collaborates with L. A. Curtiss, A. T. Ngo, S. Tepavcevic, and Y. Zhang at Argonne National Laboratory.

- 1. Investigating the current, focusing on the interface between Li-metal electrode and polymer/ceramic composite electrolyte. (Q1, FY 2022; Completed)
- 2. Elucidating ion transport mechanism through the polymer and ceramic phases in a composite electrolyte. (Q2, FY 2022; Completed)
- Deciphering the influence of stress state on the exchange current density experienced by Li-metal electrodes in contact with solid polymer electrolytes (SPEs) during lithium deposition and stripping processes. (Q3, FY 2022; Completed)
- 4. Understanding the impact of grain boundaries in soft inorganic SEs on the lithium deposition process and subsequent dendrite growth. (Q4, FY 2022; Not yet initiated)

Deciphering the Influence of Stress State on the Exchange Current Density Experienced by Li-Metal Electrodes in Contact with SPEs during Lithium Deposition and Stripping Processes

Non-uniform lithium deposition while operating with SEs leads to mechanical stress evolution within both the Li-metal electrode and the SE. Mechanical stress generation influences the electrochemical potential around the dendritic protrusion and overall reaction current density. During the nucleation process, the lithium deposit evolves on top of a flat electrode. For flat electrodes, both the electrode and electrolyte can be assumed to exist in stress-free configurations. Hence, during lithium nucleation, the total stress within the electrode and the electrolyte influences the stress-induced electrochemical potential term. However, during growth of the dendritic protrusion, both the electrode and electrolyte already exist in a stressed configuration. Further deposition of lithium helps to increase the stress. While estimating the change in stress-induced electrochemical potential associated with the growth of dendritic protrusions, change in stress state within the electrode and electrolyte needs to be taken into consideration, instead of the total stress values. This particular aspect is pointed out in Figure 87.



Figure 87. During dendrite growth, change in stress-induced electrochemical potential $(\Delta \mu_{e^-})$ depends on the Li-deposition-induced increase in pressure within the electrode and electrolyte. Note that the change, or increase, in pressure is important, not the total pressure within the electrode and electrolyte.

A Li-metal electrode located adjacent to the SE, containing a dendritic protrusion, is schematically demonstrated in Figure 88a. During dendrite growth, because only the *increase* in stress within the electrode and electrolyte impacts the change in stress-induced electrochemical potential, and not the *total* stress, the overall magnitude of stress-induced electrochemical potential decreases substantially, which is depicted in

Figure 88b. Even for very stiff electrolytes, the change in stressinduced electrochemical potential is only ~ 100 J/mol. which is equivalent to only 1-2 mV. Increase in the height of the dendritic protrusion is shown in Figure 88c during operation at 1 mA/cm^2 for 1000 seconds. It is evident that softer electrolytes cannot prevent growth of dendrites, whereas stiffer electrolytes block dendrite through plastic growth deformation. The development of a computational model with corrected stress potential coupling completes this quarter's milestone.



Figure 88. (a) Schematic diagram of the lithium electrolyte interface with a dendritic protrusion at the middle. Butler-Volmer reaction is assumed at the electrode/electrolyte interface. (b) During lithium deposition at 1 mA/cm², evolution of stress-induced electrochemical potential at the tip of the protrusion as a function of electrolyte modulus. (c) Increase in height of the dendritic protrusion as a function of electrolyte modulus. Softer electrolytes cannot suppress the dendrites. Stiffer electrolytes can successfully prevent dendrite growth due to plastic deformation of lithium metal.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 3.3 – Modeling of Amorphous Solid-State Conductors (Gerbrand Ceder, University of California, Berkeley)

Project Objective. Solid-state batteries are promising to achieve high energy density. The project objective is to determine the design principles needed to create solid-state electrolytes with high Li-ion conductivity, while also achieving stability against common Li-ion cathodes and Li-metal anodes.

Project Impact. The project will lead to understanding the factors that control Li-ion motion in crystalline and amorphous solids and will develop strategies to create stable interfaces against lithium metal and high-voltage cathode materials. The understanding of such processes is necessary to determine design principles to develop reliable all-solid-state batteries (ASSBs).

Approach. High-throughput computation is used to screen suitable solid electrolytes (SEs) with high electrochemical stability and high ionic conductivity, by incorporating nudged elastic band and an *ab initio* molecular dynamics (AIMD) method. Meanwhile, density functional theory is used to calculate bulk elastic constants of materials, surface energies, and interface decohesion energies of grain boundaries. Thermodynamic interface stability is assessed from *ab initio* computed grand potential phase diagrams in which the lithium voltage can be controlled. Kinetic limits for SE decomposition are assessed by topotactic lithium insertion and removal from the SE.

Out-Year Goals. Future goals include the following: (1) gain insight into what creates high Li-ion conduction in sulfide and oxide solids, and (2) develop stable, processable solid-state conductors that can be applied in ASSBs.

Collaborations. There are no collaborative activities this quarter.

- 1. Investigate lithium diffusion mechanism in activated network structures. (Q1, FY 2022; Completed)
- 2. Conduct diffusion network analysis in low-density structures. (Q2, FY 2022; Completed)
- 3. Perform detailed lithium transport modeling in one novel conductor. (Q3, FY 2022; Completed)
- 4. Conduct stability analysis of novel Li-ion conductor. (Q4, FY 2022; In progress)

Corner-Sharing Frameworks with Minimized Interaction between Lithium and Other Cations

The team investigated the tendency for corner-sharing (CS) framework structures to have high Li-ion conductivity. While distortion is one aspect of why CS frameworks tend to show high ionic conductivities among the oxides, they find another important advantage of CS frameworks. Due to the weak electrostatic screening and smaller radius of oxygen anions (and thus smaller interatomic distances) compared to sulfur anions, it is more difficult to achieve a flat energy landscape in oxides. They find that an important feature of CS frameworks is to provide reduced Li-cation interactions. In Figure 89a, they compare the polyhedral packing ratio between CS and non-CS frameworks. The polyhedral packing ratio is defined as the volume of the non-lithium polyhedrons divided by the volume of the unit cell. They find that the non-lithium cations in CS frameworks tend to occupy a significantly smaller portion of the unit cell and leave more space for lithium to occupy.

The team also compares the likelihood of a lithium site to be distant from any non-lithium cations. They define the site ratio β as the ratio of lithium sites that do not have any non-lithium cations within the cutoff distance of 1.95 Å over all possible lithium sites in the crystal structure. In Figure 89b, they show that due to the low non-lithium cation density in CS frameworks, a larger fraction of lithium sites are located far away from any non-lithium cations. As a result, lithium in CS frameworks experiences reduced electrostatic interaction from the non-lithium cations. Defining a reduced-repulsion (RR) channel as a percolating diffusion pathway of lithium sites that experience weak interaction between the non-lithium cations, they find that the CS frameworks tend to have significantly higher dimensionality of RR-channels, as shown in Figure 89c. The prevalence of the lithium sites to be located far away from any non-lithium cations leads to higher likelihood of such lithium sites to be connected, and leads to higher dimensionality of RR-channels in CS frameworks.



Figure 89. Structural features of corner-sharing (CS) frameworks and their reduced-repulsion (RR) channels. (a) Comparing the polyhedral packing ratio α . (b) Site-ratio β . (c) Dimensionality of RR channels of CS and non-CS frameworks. In (d-f), the lithium probability densities from *ab initio* molecular dynamics simulations are shown in red with isosurfaces P0/100, P0/1000, and P0/1000, respectively. The occupied and unoccupied lithium sites are shown in green and white spheres, respectively. The RR-channels are shown with black edges.

For several exemplary superionic conductors with CS frameworks, the team compares the RR-channel with the actual lithium diffusion pathways (Figure 89d-f), which were computed using AIMD simulations. They confirmed that lithium ions indeed follow the RR channel when diffusing through the CS frameworks, supporting their finding that the reduced interaction with non-lithium cations is a key feature in allowing high lithium ionic conductivity in oxide materials.

Patents/Publications/Presentations

Publication

 Jun, K., Y. Sun, Y. Xiao, Y. Zeng, R. Kim, H. Kim, L. J. Miara, D. Im, Y. Wang, and G. Ceder. "Lithium Superionic Conductors with Corner-Sharing Frameworks." *Nature Materials* (2022).

Presentations

- Materials Research Society (MRS) Spring Meeting, Honolulu, Hawaii (May 8–11, 2022): "Design Principles for Fast Oxide Lithium-Ion Conductors"; K. Jun.
- MRS Meeting, Honolulu, Hawaii (May 8–11, 2022): "The Mechanisms that Lead to High Li-Ion Conductivity in Solids"; G. Ceder.

Task 3.4 – *In Situ* and *Operando* Thermal Diagnostics of Buried Interfaces in Beyond Lithium-Ion Cells (Ravi Prasher, Lawrence Berkeley National Laboratory)

Project Objective. Transport at various interfaces in beyond Li-ion cells will play a major role in electrochemical performance and reliability. It has not yet been possible to thermally profile a Li-metal cell during operation to provide a spatially resolved map of thermal transport properties throughout the cell. The objective of this research is to create a metrology capable of spatially resolved *in operando* thermal property profiling, and then to relate thermal property to the quality of electrodes and interfaces, and to use the developed thermal metrology to understand electrochemical processes in Li-metal batteries, such as dendrite growth, interface kinetics, and ionic transport.

Project Impact. Characterizing electrochemical processes in Li-metal cells such as lithium deposition and dendrite growth at interfaces is of great significance for understanding and enhancing their electrochemical performance and reliability. *In situ* and *operando* micro electrothermal sensors can provide significant information regarding the impact of buried interfaces as a function of time, material, voltage, current, temperature, etc. Therefore, it is important to develop *operando* micro electrothermal sensors and develop models relating those signals to electrochemical performance for beyond Li-ion cells. The physics-based model relating thermal and electrochemical properties based on these measurements can facilitate future design of Li-metal batteries.

Approach. To accomplish project goals, the team will utilize an in-house adapted 3-omega (3ω) technique to probe thermal properties of a Li-metal cell while it is in operation, without affecting the operation of the cell. The 3ω sensors will be deposited and fabricated on Li-metal cells based on previous learning on 3ω sensor fabrication. The characteristic depth of the thermally probed region is defined by the wave's "thermal penetration depth," $\delta_n = \sqrt{D/2\omega}$, where D is the sample's thermal diffusivity, and 2ω is the heating frequency of the thermal wave. By depositing the project's 3ω sensors on the battery's outer surface and adjusting ω , the team controls δ_p to span the full range from the top to the bottom layer, thereby noninvasively probing the thermal transport in subsurface layers and interfaces within the bulk of the battery. Thermal transport can be related to quality of the interfaces. By doing concurrent thermal transport and electrochemical performance measurements, the team plans to relate thermal transport to electrochemical performance. As frequency-based thermal measurement techniques provide excellent spatial resolution within the cell, the team also plans to study heat generation at the electrolyte/Li-metal interface and to relate the thermal signals to the interface kinetics and ionic transport. The frequency dependence of heat generated due to transport resistance is different from that due to kinetic resistance. The team plans to utilize this difference to separate the contributions of kinetic and transport resistance at the interface, which will enable understanding of interface kinetics and transport at the Li-metal / solid-state electrolyte interface.

Out-Year Goals. The project will design, build, and implement the adapted 3ω metrology to examine thermal properties and a general frequency-dependent thermal metrology to examine heat generation. This will involve developing and testing the metrology itself along with accompanying theory, designing compatible battery samples, and applying the technique to live cells. The team will measure thermal transport properties of battery materials provided by collaborators. Combined with the electrochemical performance measurement, this will provide significant information relating the thermal signal to the electrochemical process.

Collaborations. This project collaborates with two Lawrence Berkeley National Laboratory groups: V. Battaglia's for cell assembly for 3ω studies, and R. Kostecki's for pristine battery active material growths for studies of thermal signals related to electrochemical process.

Milestones

- 1. Identification of theoretical model relating the interface morphology to thermal contact resistance (TCR). (Q1, FY 2022; Completed)
- 2. Measured change to TCR/morphology with cell cycling correlated with electrochemical impedance spectroscopy. (Q2, FY 2022; Completed)
- 3. *Ex situ* characterization of interface morphology to validate the theory relating the morphology to TCR. (Q3, FY 2022; Completed)
- Effect of temperature on TCR and self-heating study of thermally insulated Li₇La₃Zr₂O₁₂ (LLZO) cycling. (Q4, FY 2022; In progress)

Progress Report

This quarter, the team carried out *ex situ* characterization of the lithium-LLZO interface and compared the results against the interface information extracted from the thermal characterization.

With the effective contact hardness (H_{ep}) and the stack pressure (P) known, the thermal interface resistance (R_{int}) , measured from the 3 ω method, can be related to the mean contact spot size (a) and the density of contacts $(n_{contacts})$ by Reference [1]:

$$a = \frac{2}{\pi} k_{int} R_{int} \left(\frac{\left(\frac{P}{H_{ep}}\right)}{\left(1 - \sqrt{\frac{P}{H_{ep}}}\right)^{1.5}} \right)$$
(1)
$$n_{contacts} = \frac{\pi}{4} \frac{1}{R_{int}^2 k_{int}^2} \left(\frac{\left(1 - \sqrt{\frac{P}{H_{ep}}}\right)^3}{\frac{P}{H_{ep}}} \right)$$
(2)

For a lithium-LLZO cell, the team did optical profilometry to obtain the LLZO surface morphology before assembly and the morphology of lithium deposited on LLZO after 3 cycles. From the profilometry results, they calculated the mean contact spot size (*a*) and the density of contacts ($n_{contacts}$) and compared it against the results extracted from the 3 ω measurements. As shown in Figure 90a-b, the profilometry results (diamond) agree well with the thermal measurement results (triangle). Further, it is seen from the thermal measurements that as the number of cycles increases, the number density of contacts decreases while the average contact radius increases, indicating fewer larger contacts and an overall increase in the interface roughness with cycling. These results were verified qualitatively via *ex situ* scanning electron microscopy characterization of two different cells done pre-cycling (uncycled, Figure 90c) and after 3 cycles (Figure 90d).



Figure 90. Measured mean contact radius (a) and number density of contacts (b) from thermal interface resistance (triangle) and profilometry (diamond) measurement. The results from thermal-contact resistance measurement agree well with the results from profilometry and capture a general trend of interface degradation (decrease in contact density and increase in individual contact size), which is further verified by scanning electron microscopy images (c-d).

Reference

 Sridhar, M. R., and M. M. Yovanovich. "Elastoplastic Contact Conductance Model for Isotropic Conforming Rough Surfaces and Comparison with Experiments." *Journal of Heat Transfer* 118 (1996). doi: 10.1115/1.2824241.

Patents/Publications/Presentations

Presentations

- American Physical Society Meeting, Chicago, Illinois (March 14–18, 2022): "Multi-Harmonic ElectroThermal Spectroscopy (METS) for a Non-Invasive and Spatially Resolved Determination of Electrochemical Processes in an Electrochemical Cell."
- Materials Research Society Spring Meeting & Exhibit, Honolulu, Hawaii (May 2022): "Spatially Resolved Electrochemical-Thermal Signatures in Lithium-Ion and Lithium-Metal Batteries."

Task 3.5 – Multiscale Modeling of Solid-State Electrolytes for Next-Generation Lithium Batteries (Anh Ngo, Larry A. Curtiss, and Venkat Srinivasan, Argonne National Laboratory)

Project Objective. This project is part of a multiscale modeling effort to obtain an in-depth understanding of the interaction of the electrode and the solid electrolyte (SE) aimed at developing highly efficient solid-state electrolyte (SSE) batteries for vehicle applications. Input parameters needed for mesoscale (continuum) level calculations are being obtained from atomistic calculations including density functional theory (DFT) and classical molecular dynamics simulations. This atomistic input will enable a multiscale computational procedure for SSEs that is capable of successfully capturing the physicochemical aspects during charge and discharge process, including lithium transport mechanisms, interfacial phenomena during the insertion and extraction of lithium ions, and mechanical deformation of SSE.

Project Impact. A major safety concern experienced with commercially available Li-ion batteries under some scenarios is leakage of the liquid electrolyte (LE), which can potentially catch fire. Replacement of the LE is necessary to decrease the fire hazard and improve safety associated with present-day Li-ion batteries. In addition, use of SEs provides a path to prevent dendrites in Li-metal anodes, thereby leading to batteries with significantly higher energy density. The impact of this project will be to help in development of good SSEs as a replacement for the commercially used organic LEs to improve safety and energy density in Li-ion batteries.

Approach. Parameters needed for mesoscale modeling of grain interior, grain boundary (GB), and electrode-electrolyte interface will be calculated by DFT-based calculations along with Monte Carlo and molecular dynamics simulations. The calculations will be used to determine properties of the electrode with the SE as well as in GB regions of the SE. This will include calculations of structure, stability, ionic conductivity, Young's modulus, fracture toughness, exchange current density, and other properties.

Out-Year Goals. The out-year goals of this work are to calculate other properties such as fracture toughness and include other SSEs and coatings in the multiscale modeling.

Collaborations. This project collaborates with Y. Cui at Stanford University.

- 1. Determine the stable phase of Li₇P₃S₁₁ amorphous/disordered glass-ceramic SSE and S-C cathode / Li₇P₃S₁₁ interface. (Q1, FY 2022; Completed)
- 2. Conduct *ab initio* molecular dynamics (AIMD) study of an electrochemical interface between S-C cathode / amorphous Li₇P₃S₁₁ interface. (Q2, FY 2022; Completed)
- 3. Investigate Li-ion transport of the S-C cathode / amorphous Li₇P₃S₁₁ interface. (Q3, FY 2022; Completed)
- 4. Compute the exchange current density associated with charge transfer from amorphous Li₇P₃S₁₁ glass-ceramic SSE to the S-C cathode. (Q4, FY 2022; Initiated)

Li-S batteries have been under investigation for several decades due to the low-cost S-based cathode materials and demonstration of high specific capacity. In a LE system during the discharge process, the reduction reaction between lithium and sulfur occurs through a multistep process. The sulfur gets dissolved into the LE and forms polysulfide chains of various lengths before reacting with the lithium cations. These negatively charged polysulfide chains can easily migrate and diffuse through the LE toward the anode side and react with the lithium electrode surface to form a passivation layer that can effectively minimize capacity and enhance resistance of the cell. This detrimental shuttling of polysulfide chains can substantially limit the performance of Li-S batteries with LEs. To prevent this polysulfide shuttling mechanism, SEs have been invoked that can potentially prevent the dissolution of negatively charged polysulfides into the SE and their movement toward the anode during the discharge process.



Figure 91. Configuration of (a) graphene (GRA) and (b) carbon nanotube (CNT) based systems and temperature dependence of lithium diffusion coefficient obtained from *ab initio* molecular dynamics simulation for GRA and CNT systems at (c) 800 K, 1000 K, and 1100 K, and (d) 700 K, 800 K, and 1100 K.

Successful operation of an electrochemical Li-S cell depends not only on the reaction between lithium and sulfur, but also on various ion and charge transfer processes occurring within the bulk of the electrode and electrolyte materials and at their interfaces. To understand the impact of these transport mechanisms, and their impact on overall cell resistance, mesoscale simulations of Li-S cells conducted at larger length scales are necessary. Since the majority of the bulk and interfacial phenomena occurring within an electrochemical cell are usually taken into consideration in the continuum-level simulations, it is always easier to compare the model predictions from larger length scales with the experimental observations. However, the large-scale simulations require various parameters, such as ionic conductivity in the bulk, reaction rate constants at the interface, and equilibrium potentials where electrochemical reactions occur, as input to the model. All these material and interface specific thermodynamic and transport parameters can be estimated using calculations conducted at atomistic length scales. Hence, for successfully predicting the performance curve and understanding the various reaction pathways in Li-S batteries with SEs, development of a multiscale computational framework is necessary.

This quarter, the team focused on lithium transport across the S-C cathode and amorphous $Li_7P_3S_{11}$ interface. They have studied the dynamics of the S-C cathode and $Li_7P_3S_{11}$ amorphous glass-ceramic interface by carrying out AIMD simulations at different temperatures for two different interfacial models. From these simulations, they calculated the lithium mean square displacements and lithium diffusion coefficients. A summary of the diffusion coefficients versus temperature (T) results is shown in Figure 91. Figure 91c-d shows Arrhenius plots for Li-ion diffusivity across the S-C cathode and $Li_7P_3S_{11}$ amorphous interface for T = 700-1100 K. The graphene model system undergoes a higher lithium mobility at lower temperatures; however, the overall temperature dependence largely loses in comparison with the carbon nanotube (CNT) model. Therefore, one should expect a higher lithium mobility in CNT at T > 1000 K. The activation energies (E_a) for diffusion were extracted from the slope of these data. The calculated E_a of 0.42 eV and 0.48 eV is for graphene and CNT, respectively.

The team is performing a series of climbing image nudged elastic band calculations to determine the Li-ion migration barriers at the interfaces for two computational models and will combine those values with E_a obtained from AIMD. The calculated Li-ion migration barriers will be used for calculation of the exchange current density. The results of this approach will be used as input for continuum-level modeling of the interface.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 3.6 – First-Principles Modeling of Cluster-Based Solid Electrolytes (Puru Jena, Virginia Commonwealth University)

Project Objective. The objective of the project is to use cluster-ions, which are stable atomic clusters that mimic the chemistry of individual atoms, as the building blocks of new solid electrolytes (SEs) for Li-ion batteries and the corresponding battery system. The advantages of using cluster-ions to replace elemental ions is that the size, shape, and composition of the former can be tailored to achieve higher superionic conductivity, electrochemical stability, and charge transfer across the solid-state ions than the conventional materials. More specifically, the goal is to develop superior SEs based on cluster-ions and to model these SEs and their interfaces with electrodes, especially with the Li-metal anode, for successful integration into high-performance solid-state batteries (SSBs) for electric vehicles (EVs). The team will model and screen cluster-based solid electrolytes (CSEs) that, compared to conventional SEs, have low activation energies, practical room-temperature ionic conductivities, wide electrochemical stability windows, and desired mechanical properties that, for example, can inhibit the Li-metal anode dendrite growth. They will provide a fundamental understanding of the ionic conduction mechanism in the newly developed CSEs and will identify means to further improve property metrics via chemical and defect engineering. The team will model the interfacial properties, such as the structural, chemical, electrochemical, and ion/charge transfer properties, between the CSEs and electrodes at the atomic level, as well as find the interfacial coating materials with desired properties. Based on accumulated data from modeling, they will establish links between the basic parameters of the cluster-ions and the bulk/interface properties, which can directly guide experiments. Meanwhile, the team will work closely with experimentalists in the BMR Program to complement the project's theoretical efforts and to guide them in focused development of the predicted CSEs and the interfaces.

Project Impact. The proposed project will open a new avenue for guiding experiments in the synthesis of SSBs equipped with CSEs and capable of operating over a wide temperature range. Modeling and understanding of the ionic conduction of CSEs and their interfacial properties with electrodes, especially with Li-metal anode, will enrich current battery science and also train the future workforce in SSB development for next-generation EVs by supporting postdoctoral fellows.

Approach. This project will employ multiscale theoretical methods and computational techniques.

Out-Year Goals. The out-year goals involve modeling development of new CSE materials and database.

Collaborations. The team is working with J. Nanda of Oak Ridge National Laboratory, Y. Wu of Ohio State University, and D. Mitlin of University of Texas, Austin, on SEs.

- 1. Complete phase analysis for interfaces between the CSE and electrodes. (Q1, FY 2022; Completed)
- 2. Model structural properties of CSE interfaces. (Q2, FY 2022; Completed)
- 3. Model chemical/electrochemical and transport properties of CSE interfaces. (Q3, FY 2022; Completed)
- 4. Identify potential coating materials, and model electrolyte-coating-electrode interfaces. (Q4, FY 2022; In progress)

Last quarter, the team conducted explicit simulations for the electrolyte-electrode interface to study the chemical/electrochemical stability and the transport property. The studies are based on the models between the studied CSEs and the Li-metal anode as well as selected cathode materials. Each model is a coherent heterointerface, which allows both the SE and the anode/cathode supercell lattices to form periodicities along the interface. Then, *ab initio* molecular dynamics (AIMD) simulations are conducted at finite temperatures, and the obtained data are analyzed by charge analysis and ionic diffusion. A few systems are too large to be handled by the AIMD; the team has started 'training' force field models for these interface systems by machine learning.



Figure 92. Chemical/electrochemical stability and ion transport properties in the $Li_6PS_5(BH_4)$ -Li interface. (a) The charge transfer at the phosphorus and boron sites for different terminal (t) groups (H2, B, and LiS) at the interface. (b) Bond completeness for the clusters. (c) Calculated mean squared displacements of Li-ions as well as phosphorus and sulfur along different directions, with the c-axis the direction perpendicular to the interfacial plane.

Specifically, for the CSE-Li interface models, the team analyzed the charge transfer for the relevant species based on the models built in their previous studies. As a demonstration, Figure 92 shows results for the $Li_6PS_5(BH_4)$ -Li interface models with different terminal atomic groups (including H2, B, and LiS) at the interface. As shown in Figure 92a, at the interface, phosphorus from the PS_4^{3-} moieties will gain electrons (being reduced), which is accompanied with the continued breaking of the P-S bonds, as shown in Figure 92b. This is the dominant contributor for the CSE-Li interfacial reaction. The functional clusters BH_4^- , on the other hand, will not react, as indicated by the constant charge state of boron and the intactness of the B-H bonds, as seen in Figure 92a-b. Such a phenomenon is independent from the terminal group at the interface, as shown in Figure 92a. The ionic transport study in Figure 92c shows that the Li-ion diffusion becomes anisotropic in the interface, with the fastest ion-diffusion along the a-axis and the slowest diffusion across the interface. Some phosphorus and sulfur ions also start moving across the interface into the surface of Li-metal anode due the break-up of the PS_4^{3-} moieties around the interface.

For the CSE-cathode interfaces, the team constructed the interface models using the following procedure. First, slabs of the SEs and the selected cathode material are built according to the chosen Miller indices (hkl). Then, the slabs are matched according to the epitaxial constraint with the restriction of maximal surface area of 500 Å², maximal lattice length mismatch of 0.03 Å, and maximal lattice angle mismatch of 0.02 radians. For each model structure, there are a couple of different configurations with different terminal atomic groups at the interface. The initial distances between the electrolyte slab and the anode slab are set to about 60% of the sum of the van der Waals radii of the terminal elements in the closest contact. A vacuum padding of 13 Å above the interface is included to minimize the interactions between the cell images. The resulting interface model usually

contains about 300 or more atoms, testing the limit of the *ab initio* calculation. To make the computation affordable, only those interface models with the lowest matching surface areas are selected for investigation. Table 5 demonstrates the built interface models between the CSE and the Li_2S cathode.

Table 5. Coherent interfacial models built for the cluster-based solid electrolytes (SEs) and Li₂S cathode. In each case, surfaces (according to the Miller indices hkl) are chosen due to the minimum matching area (MA) between the solid electrolyte and Li₂S. The strain at the interface is measured by the von Mises strain. The number of formula units (FU) and the thickness (in atomic layers) of the SE and Li₂S are given.

Materials	hkl	MatchArea	von Mises	Thickness	FU	Terminal	Li_2S	
		$(Å^2)$	Strain	(layer)			hkl	Thickness
								(layer)
Li ₆ PS ₅ (BH ₄)	(111)	144.67	0.013	6	12	B/H2/LiS	(011)	4
Li ₆ POS ₄ (SH)	(111)	400.29	0.013	4	16	H2	(100)	3
Li ₆ PS ₅ (CN)	(011)	275.46	0.021	5	10	LiC/N2/PS2	(101)	4
Li ₆ PS ₅ (SCN)	(101)	323.76	0.018	5	10	C/Li2PN/LiS	(111)	4
Li ₆ PS ₅ (BF ₄)	(110)	270.50	0.012	4	8	LiBP/LiF	(100)	3

The team has also conducted the structural, stability, and ion transport studies on the CSE-cathode interfaces. Figure 93 shows the results for the $Li_6PS_5(CN)-Li_2S$ interface as a demonstration. Figure 93a shows the optimized interface model constructed according to Table 5. The AIMD (at 300 K) suggests that $Li_6PS_5(CN)$ is stable against the cathode Li_2S , as shown in Figure 93b, where the calculated radial distribution functions of N-P and Li-S keep the same patterns with the optimized structure and throughout the simulation time. This is further corroborated by the intactness of the PS₄ and CN clusters in the interface, as shown in Figure 93c. The absence of reaction between the CSE and the cathode in this case leads to less anisotropic ion transport property at the interface, as shown in Figure 93d. The modeling and simulation suggest the compatibility between the $Li_6PS_5(CN)$ and the Li_2S cathode.



Figure 93. Results for the Li₆PS₅(CN)-Li₂S interface. (a) Optimized structure of the interface. (b) Radial distribution function analysis of N-P and Li-S at the interface throughout the simulation at 300 K compared to those of the optimized structure at 0 K. (c) P-S and C-N bonds in the cluster-ions during the simulation. (d) Calculated mean squared displacements of Li-ion along different directions in the interface.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 3.7 – Predictive Engineering of Interfaces and Cathodes for High-Performance All-Solid-State Lithium-Sulfur Batteries (Badri Narayanan, University of Louisville)

Project Objective. The primary project goal is to leverage data-driven methods and machine-learning (ML) strategies to develop accurate multiphysics models for all-solid-state Li-S battery (ASSLSB) materials that can capture electrochemical and transport phenomena over atomic-to-mesoscopic length/timescales; these models will be rigorously validated by synthesis and advanced characterization experiments. The team will leverage the predictive power of these models, alongside synthesis/characterization experiments and battery fabrication, to address longstanding issues at the electrode/electrolyte interfaces in ASSLSBs. The project's proposed technology involves the following: (1) halide-doped solid sulfide electrolytes that can concurrently provide high Li^+ ion conductivity and suppress dendrite growth; (2) novel mesoporous cathode composed of interconnected carbon nano-cages co-infiltrated with sulfur and sulfide electrolyte, which hold potential to allow high sulfur loading and optimal ion/electron pathways; and (3) functionalization of sulfide electrolyte with ionic liquids (ILs) to improve physical contact and minimize impedance at the cathode electrolyte interphase (CEI).

Project Impact. ASSLSBs remain far from commercialization due to poor understanding of fundamental electrochemical/chemical and transport processes that occur at the interfaces, especially at atomic-to-mesoscopic scales. Successful development of proposed predictive models (at multiple scales) will bridge this knowledge gap and will advance fundamental understanding of reaction chemistry, kinetics, charge transfer, and dendrite growth at electrified solid-state ions. This will enable predictive design of effective strategies to mitigate interfacial problems in ASSLSBs, including poor interfacial contact, interfacial impedance to Li⁺ ion transport, and poor electron/ion conduction within cathodes. Ultimately, the fundamental knowledge gained will lead to development of high-performance ASSLSBs that meet U. S. Department of Energy targets of specific energy (350 Wh/kg @C/3), sulfur loading (> 6 mg/cm²), and high cycle life (1000).

Approach. The project brings together innovative solutions in multiscale materials modeling, electrolyte synthesis, fabrication of cathode architecture, and electrolyte functionalization to overcome the issues at electrode/electrolyte interfaces in ASSLSBs. The central idea is to employ a data-driven and ML-based approach to develop accurate multiphysics battery models at atomic-to-mesoscopic scales. This approach overcomes critical problems with existing model development methods by foregoing the need for pre-defined functional forms, introducing deep-learning technique to describe reactivity, and employing optimization methods that do not require human intuition. Multiscale simulations based on the newly developed models will provide insights into electrochemical phenomena at electrode/electrolyte interfaces.

Out-Year Goals. In Year 3, the goal is to optimize the composite cathode, functionalize CEI, and understand interfacial reactions to design ASSLSBs with high-sulfur loading (> 4 mg/cm²) and good capacity retention (~ 1000 mAh/g, 100 cycles @C/10).

Collaborations. The team collaborates with the groups under A. Ngo and L. A. Curtiss at Argonne National Laboratory for quantum simulations of battery systems; they plan to collaborate with J. Nanda at Oak Ridge National Laboratory for advanced spectroscopic *in situ* characterization of interfaces.

- 1. Optimize cathode architecture to achieve good sulfur utilization at high sulfur loading. (Q1, FY 2022; Completed)
- 2. Develop composite cathodes and optimize CEI to achieve good electrochemical performance at high sulfur loading using insights from simulations and experiment. (Q2, FY 2022; Completed)

- 3. Utilize reactive molecular dynamics (RMD) and advanced sampling to gain insights into defect chemistry, microstructural evolution, and interfacial processes. (Q3, FY 2022; Completed)
- 4. Fabricate batteries that meet performance metrics. (Q4, FY 2022; In progress)

This quarter, the team employed large-scale RMD simulations within the framework of their newly developed reactive force-field (ReaxFF) for Li-P-S system (developed as part of this project) to gain a fundamental understanding of the electrochemical processes at electrified interfaces in solid-state batteries. In addition, they also improved the formulation of cathodes to enhance the extent of sulfur utilization at high sulfur loading (4 mg/cm²).

RMD Simulations of Electrified Interfaces with Argyrodite Electrolytes. The team employed RMD simulations using their newly developed ReaxFF interatomic potential to study the dynamic evolution of two representative interfaces, namely (a) Li (001) || Li₇PS₆ (001) (that is, anode-electrolyte), and (b) S₈(001) || Li₇PS₆(001) (that is, cathode-electrolyte), both in the absence and under applied electric field. To study interface between argyrodite Li₇PS₆ (cubic) electrolyte with Li-metal (body-centered cubic) anode, they employed a symmetric Li-cell model Li (001) || Li₇PS₆ (001) || Li (001) with dimensions of 8.6 nm × 8.6 nm × 26.3 nm. Periodic boundary conditions are employed along all directions; note the supercell size for the individual components (lithium, Li₇PS₆) in the plane of the interface is chosen such that the epitaxial strain is



Figure 94. Build-up of solid electrolyte interphase (SEI) at Li (001) || Li₇PS₆ (001) studied using reactive molecular dynamics simulations. Temporal evolution of the number of (a) P(e) - S(e), (b) Li(a) – S(e), and (c) Li(a) – P(e) at the interface under no bias (blue) and applied electric field of E = 0.5 eV/nm normal to the interface (orange). (d) Time-evolution of the thickness of the as-formed SEI. Li(a) denotes lithium atoms belonging to anode, while S(e) and P(e) are sulfur atoms and phosphorus atoms belonging to the electrolyte, respectively.

less than 1%. The team studies formation of the solid electrolyte interphase (SEI) in the absence/presence of applied electric field using RMD simulations within canonical ensemble (NVT: constant temperature, constant volume ensemble) under ambient conditions for 1 ns. (sulfide) Most argyrodite electrolytes are known to be unstable against lithium metal. Indeed, the team's RMD simulations indicate that Li₇PS₆ undergoes reductive decomposition near the $Li \parallel Li_7 PS_6$ interface via progressive breakdown of the

 PS_4^{3-} motifs present in the electrolyte (Figure 94a). These species bind with lithium atoms of the anode to form a SEI; as the SEI builds up, new bonds between anodic lithium (Li(*a*)) and the P/S atoms from the electrolyte [that is, P(*e*), S(*e*)] continue to appear (Figure 94b-c). Clearly, applied electric field significantly promotes the decomposition of PS₄ motifs, as indicated by a higher fraction of broken P-S bonds at E = 0.5 eV/nm in Figure 94a. Interestingly, the thickness of the as-formed SEI layer reaches an equilibrium at ~ 0.6 ns. On the other hand, applying electric field (0.5 eV/nm) normal to the interface causes the SEI to grow progressively even until 1 ns (Figure 94d).

Next, the team analyzed the composition of the SEI by analyzing the charge state of the phosphorus and sulfur atoms in the as-formed SEI. In the pristine electrolyte, Li_7PS_6 , the phosphorus and sulfur atoms are present in their unreduced states with charges of -0.4*e* and -0.57*e*, respectively. During reductive decomposition of Li_7PS_6 ,

the atomic charges of phosphorus (q_P) and sulfur are expected to become more negative, up to -0.73*e* for phosphorus (corresponding to Li₃P) and -0.7*e* (corresponding to Li₂S) in their fully reduced states. Applied electric field enables vigorous decomposition of Li₇PS₆, which in turn, yields more reduced species, as indicated by the largely more negative charges on phosphorus and sulfur atoms in the SEI, as compared to that at E = 0(Figure 95). Direct visualization of the atomic snapshot at the end of the RMD runs clearly shows that the thickness of as-formed SEI is significantly higher under applied electric field (Figure 95a/d). Their analysis of the atomic charges showed that the phosphorus atoms do not get fully reduced (that is, do not form Li₃P), even under applied bias (Figure 95b/e). Importantly, ~ 33% and ~ 37% of phosphorus atoms reduce partially at E = 0 and E = 0.5 eV/nm, respectively, with atomic charges -0.6 < q_P < -0.45 (Figure 95b/e). In other words, PS₄³⁻ motifs decompose only down to PS₃, PS₂, and PS species, which bind with lithium to form LiPS_x phases, with the more reduced phases occurring at E = 0.5 eV/nm (that is, more negative q_P). On the other hand, ~ 10% of sulfur atoms get fully reduced to form Li₂S in the SEI, even in the absence of electric field; under applied field (E = 0.5 eV/nm), slightly higher fraction of sulfur (~ 12%) gets fully reduced (Figure 95c/f). In addition, a significant fraction of sulfur atoms (~ 18%, ~ 21% at E = 0, 0.5 eV/nm, respectively) reduce partially to form Li_xS phases (Figure 95c/f). Essentially, the SEI is composed of Li_xS, Li₂S, and LiPS_x phases.



Figure 95. Composition of the SEI formed at interface formed between Li-metal anode and Li₇PS₆ electrode obtained by reactive molecular dynamics simulations. Evolution of the interface is studied (a-c) in absence of electric field (E = 0), and (d-f) under applied electric field E = 0.5 eV/nm along the positive z-direction (that is, normal to the Li (001) || Li₇PS₆ (001) interface). Atomic snapshots of the Li (001) || Li₇PS₆ (001) interface after 1 ns are shown in panels (a) and (d) for E = 0 and E = 0.5 eV/nm, respectively. The phosphorus atoms (b/e) and sulfur (c/f) are colored by their charges.

To investigate the electrochemical reactions at the CEI, the team performed RMD simulations on symmetric model of S₈ (001) || Li₇PS₆ (001) || S₈ (001) composed of ~ 100,000 atoms (~ 8.8 nm × 5.9 nm × 30 nm) with minimal epitaxial strain at the interface (< 1%). Detailed analysis of their simulation trajectories reveals that the lithium atoms from the electrolyte move into the cathode, reduce the nearby sulfur, and cause opening of the S₈ rings (Figure 96). Similar reactions are observed regardless of the applied electric field (Figure 96). Interestingly, the applied electric field does not cause significant acceleration of CEI formation. The reduction of the sulfur atoms near the S₈ (001) || Li₇PS₆ (001) is clearly evidenced by their more negative charges ($q_s \sim -0.45 \ e$) as compared to that in S₈ ($q_s \sim 0$), Figure 96b/d. Notably, the sulfur atoms do not reduce fully down to Li₂S ($q_s \sim -0.7 \ e$), but form partially reduced Li_xS phase. The growth of the as-formed Li_xS layer is rapid initially, but it becomes stagnant at ~ 0.2 ns. The extent of reduction of sulfur decreases as they move away from the interface. Interestingly, the sulfur proximal to the Li_xS region amorphize, possibly due to the strain induced by the Li_xS layer (Figure 96a/c). RMD simulations to understand the effect of defect structures (for example, grain boundaries) on Li⁺ ion conduction, and electrochemical reactions are under way.



Figure 96. Structural evolution of the interface between S₈ cathode and Li₇PS₆ electrode obtained by reactive molecular dynamics (RMD) simulations. (a) Initial configuration of the symmetric S₈ (001) || Li₇PS₆ (001) || S₈ (001) slab, and (b) distribution of charges in the sulfur atoms in the initial configuration. Evolution of the interface is studied (c-d) in absence of electric field (E = 0), and (e-f) under applied electric field E = 0.5 eV/nm along the positive z-direction (that is, normal to the S₈ (001) || Li₇PS₆ (001) interface). Atomic snapshots of the S₈ (001) || Li₇PS₆ (001) interface after 0.4 ns are shown in panels (c) and (e) for E = 0 and E = 0.5 eV/nm, respectively. Panels (b/d/f) show only the sulfur atoms (colored by their charge) in the snapshots shown in (a), (c), and (e), respectively.

Improvement of Cathode Formulation at High Sulfur Loading to Enhance Sulfur Utilization. In previous quarters, the team identified that the low capacity of their solid-state Li-S battery at high sulfur loading can be attributed to poor sulfur utilization and lower ionic conductivity of the S-cathode. To increase the

Li-ion conductivity in the cathode, they incorporated solid-state electrolyte (SSE; Li₆PS₅F0.5Cl₂) into the optimized Super P-S cathode; they added 5 µL IL [LiTFSI in PYR:DOL (1:3) at 3M] to ensure sufficient wetting. This was possible after the team learned how to handle the entire battery assembly including the cathode formulation inside the glovebox. In all cases, cathode containing SSE powder (ball milled together) was pressed with the SSE powder in a stainless-steel pellet die inside the glovebox. They optimized their cathode formulation to enhance sulfur utilization and minimize capacity fading during cycling (Figure 97). The battery with 25% SSE in the cathode showed the best performance, with an initial discharge capacity of ~ 700 mAh/g, and retention of ~ 400 mAh/g after 60 cycles at 30° C; note, the same battery retains ~ 500 mAh/g after 25 cycles at 60°C (Figure 97). Interestingly, the capacity fade is appreciable only over the initial 5 cycles (where it drops from \sim 700 mAh/g to



Figure 97. Optimization of cathode formulation at high sulfur loading. Cycling performance of batteries consisting of lithium anode, SP-S cathode with 4.0 mg/cm² loading and (a) 30% solid-state electrolyte (SSE), (b) 20% SSE (c) 25% SSE, and (d) 25% SSE, Li₆PS₅F_{0.5}Cl₂ SSE, with 5 μL ionic liquid [LiTFSI in PYR:DOL (1:3) at 3M] at the cathode-SSE interface 30°C. All the batteries are cycled at C/20. The batteries in panels (a-c) are cycled at 30°C, while that in panel (d) is tested at 60°C.

~ 430 mAh/g); thereafter, the capacity remains nearly stable, with a slow drop down to ~ 400 mAh/g at 60 cycles. Currently, they are optimizing the pressure employed in the press to reduce the amount of dead sulfur in the cathode and, consequently, to increase the battery capacity at high sulfur loading.

Patents/Publications/Presentations

Presentation

 Solid-State Batteries – From Electro-Chemo Mechanics to Devices, Materials Research Society Spring Meeting, Honolulu, Hawaii (May 8–13, 2022): "Understanding Ion Transport and Interfacial Stability in Fluorine-Containing Argyrodite Electrolytes for Solid-State Lithium Batteries"; S. Gupta, V. Shreyas, and B. Narayanan.* Task 3.8 – Predicting the Nucleation and Evolution of Interphases in All-Solid-State Lithium Batteries (Sabrina (Liwen) Wan, Lawrence Livermore National Laboratory)

Project Objective. The goal of this project is to develop and apply a suite of new computational tools to predict early-stage formation of metastable interphases in solid-state batteries (SSBs). To achieve this goal, this project focuses on meeting three primary objectives corresponding to different regimes within the early-stage interphase formation: (1) identify chemical motifs for pre-nucleation; (2) predict possible interphase structures; and (3) model the kinetics of interphase formation.

Project Impact. Degradation of solid-state electrolyte and formation of undesired secondary interphases at the solid electrolyte/electrode interfaces are some of the key issues that limit SSB technology from practical applications. The computational tools developed in this project will allow modeling of nucleation and formation of interphases with quantum-level accuracy as well as significantly improved efficiency compared to currently available methods. Completion of this project will also provide valuable insights into the correlation between local chemistry and interphase formation, which can be used to inform design of interfacial structures to lower interfacial resistance, and to extend cycling life of SSBs.

Approach. The project approach centers on close integration of *ab initio* molecular dynamics (AIMD) simulations, machine learning (ML), and stochastic methods to probe chemistry and nucleation across broad ranges of time and length scales. First, the team will identify chemical motif, which acts as chemical precursor for pre-nucleation based on ML and large-scale AIMD simulations. Second, they will predict possible interphase structures based on stochastic minimizations of population-weighted chemical motifs identified from the molecular dynamics (MD) simulations. Third, they will model the kinetics of interphase formation and evolution using metadynamics and solid-state nudged elastic band (SS-NEB) methods. To test the general applicability of the proposed computational methods, the team considers various commercially viable solid electrolyte (SE) and cathode materials, including cubic Li₇La₃Zr₂O₁₂ (LLZO) and LiPON SEs, and Li-Co-O (LCO) and Li-Fe-P (LFP) cathodes. These materials also represent a range of degrees of stability arising from their intrinsic properties—in particular, LiPON|LCO, LLZO|LCO, and LLZO|LFP are expected to form stable, less stable, and reactive interfaces, respectively.

Out-Year Goals. The future goal is to predict practical strategies either (1) to facilitate formation of the desired interphase that allows for fast Li^+ diffusion and is stable on cycling, or (2) to suppress formation of undesired interphase to reduce interfacial impedance of all-solid-state batteries.

Collaborations. There are no collaborative activities this quarter.

- 1. Establish a library of meta-stable interphase structures. (Q1 FY 2022; Completed)
- 2. Identify initial phase transformation pathways. (Q2, FY 2022; Completed)
- 3. Obtain lowest energy phase transformation pathways. (Q3, FY 2022; Completed)
- 4. Extract phase transformation kinetics as a function of composition. (Q4, FY 2022; In progress)
Progress Report

This quarter, the team continued efforts to identify distinct pathways for phase evolution of previously identified LaCoO₃ and La₂CoO₄ phases as potential stable secondary phases formed at the LLZO/LCO interfaces. They surveyed more than 20 distinct pathways for the phase evolution of LaCoO₃ and La₂CoO₄ from Basin Hopping sampling and calculated the corresponding kinetic energy barriers using the SS-NEB method. Figure 98 shows example distribution of the calculated energy barriers for the LaCoO₃ and La₂CoO₄ phase evolution following more than 10 distinct pathways. As evidenced in Figure 98, these activation energies span from 0.5 eV to over 2 eV for both LaCoO₃ and La₂CoO₄, with LaCoO₃ showing slightly lower activation energies on average for the phase nucleation/transition. The pathways with kinetic energy barriers above 1.5 eV are less likely to occur, and thus are neglected for further investigation.



Figure 98. Example kinetic barrier distribution plots following more than 10 distinct phase evolution pathways in (a) $LaCoO_3$ and (b) La_2CoO_4 .

It is interesting to note that during the team's Basin Hopping survey of the potential energy surface of La₂CoO₄, they identified a few lower energy structures compared to the lowest energy structure reported in the literature (The Materials Project Database). Their identified lowest energy structure of La₂CoO₄ shows a distinct local coordination environment as compared to the one reported in the Materials Project. To determine relative stability of the newly identified phase, they further calculated its energy above the convex hull with respect to decomposed phases of La₂O₃ and CoO. As shown in Figure 99, the calculated E_{convex_hull} for this new La₂CoO₄ phase is 0.014 eV/atom as compared to 0.044 eV/atom for the reported La₂CoO₄ phase in the Materials Project. Such low energy phases may follow distinct phase evolution pathways and may be kinetically stabilized at the LLZO|LCO interfaces.





The team admits that the current SS-NEB calculations for the phase evolutions in LaCoO₃ and La₂CoO₄ are restricted to small simulation cells under periodic boundary conditions. To further enhance the sampling of potential phase evolution pathways and to incorporate more realistic chemical environment around the phase nucleation sites, they also developed and validated neural-network-based ML interatomic potentials for La-Co-O compounds. They are applying these ML potentials in large-scale MD simulations to directly model the phase evolution kinetics of La-Co-O composition as observed at the LLZO/LCO interface to the potential stable secondary phase compositions, such as LaCoO₃, La₂CoO₄, La₂Co₃O₇, La₂Co₃O₆, etc.

To enable large-scale simulations of the LLZO/LCO interface, the team developed machine learning force field (MLFF) to directly probe chemical reactions and phase evolutions of the LLZO/LCO interface. This quarter, they have significantly improved their MLFF by adding a variety of high-temperature AIMD data of small LLZO/LCO mixture models. Their current ML model shows low force error predictions and is able to reproduce the radial distribution function, vibrational spectra, and lithium diffusivities of both simple components LLZO, LCO, and the LLZO/LCO interfaces, as shown in Figure 100 and Figure 101. These validation results confirm that their MLFF is capable of simulating highly disordered LLZO/LCO interfaces with various local atomic environments. Currently, the team is further validating the MLFF by predicting properties of additional small LLZO/LCO mixture models that the MLFF did not learn during training to verify the generalizability for various local compositions at LLZO/LCO interfaces.



Figure 100. (a) Comparison of radial distribution functions of La-Co and Co-Co pairs between *ab initio* molecular dynamics (AIMD, blue) and molecular dynamics with machine learning force field (MLMD, orange). (b) Comparison of mean squared displacement between AIMD (black) and MLMD (the other five lines with colors) for a small LLZO|LCO mixture model at 2000 K.



Figure 101. Vibrational spectra of species in a small LLZO|LCO mixture model at 2000 K predicted by *ab initio* molecular dynamics (blue) and molecular dynamics with machine learning force field (MLMD, orange).

Patents/Publications/Presentations

Presentation

 Materials Research Society Spring Meeting & Exhibit, Honolulu, Hawaii (May 2022): "Predicting the Nucleation and Formation of Secondary Phases in All Solid-State Lithium Batteries"; A. M. Dive, K. Kim, W. Jeong, and L. Wan.

Task 3.9 – Design of Strain Free Cathode – Solid-State Electrolyte Interfaces Using Chemistry-Informed Deep Learning (Hakim Iddir, Argonne National Laboratory)

Project Objective. The main objective of this project is to use state-of-the-art machine learning (ML) techniques and high-performance computing (HPC) to model complex oxide materials that will allow the team to develop cathode / solid electrolyte interfaces that exhibit minimal or no strain as well as provide chemical stability at the interface between the cathode material and the solid-state electrolyte (SSE). A deep understanding and control of the cathode/SSE interface (including its chemical and mechanical stability) is needed to develop an effective solid-state battery (SSB). The active cathode material changes volume during cycling, particularly at high task state of charge (SOC). This volume change leads to strained interfaces triggering loss of contact and delamination, and hence reduction/elimination of electron and ion transport pathways. The increased strain could also generate cracks within the SSE, creating new paths for lithium dendrite growth channels. These structural changes degrade the electrochemical performance of the battery. Several strategies have had limited success in alleviating these drawbacks, including mixed SSE, buffer layers between the cathode and the SSE, and dopants to improve chemical stability of the interface. These approaches, although promising, could not resolve issues with both the chemical and mechanical stability of the interface. In this project, the team proposes a new approach that takes advantage of well-established ML techniques and HPC to screen for candidate dopants of high-Ni-content Ni-Mn-Co (NMC) cathodes that would both reduce the volume expansion and the chemical reactivity (mixing) at the interface, with minimum impact on electrochemical performance and energy density of the cathode.

Project Impact. Structure-property relationships are at the heart of most fundamental scientific approaches. However, the link between structure and property remains a challenge in the materials science of complex systems, such as the oxides that form battery components. In particular, the chemical and mechanical stability of the cathode-SSE interface presents a challenge to development of SSBs. High-performance density functional theory (DFT) calculations provide the necessary framework to understand such systems. Unfortunately, given the limited number of atoms and time scales accessible by the method, along with the myriad calculations required to achieve satisfactory results, the computational cost of simulating all the possible configurations of a multicomponent oxide is prohibitive. In this work, the team augments the DFT data with ML (especially deep learning) techniques that allow them to access the large system sizes and longer time scales necessary to build thermodynamic models. They focus on understanding the nature of benchmark $Li_{1-\alpha}Ni_{1-x-y-z}Mn_xCo_yM_zO_2$ structures (M dopant, α , x, y, z < 1), their volume change with lithium content, the nature and concentration of the dopants, and chemical stability of the SSE-cathode interface. The DFT and ML approach will provide new cathode compositions that will reduce the strain of the SSE-cathode interface and hence improve its mechanical and chemical stabilities.

In this project, the team aims at developing a methodology that will allow them to explore and expand the configurational space using HPC approaches in a systematic and efficient way. The methodology will encompass DFT, *ab initio* molecular dynamics (AIMD), molecular dynamics (MD), and ML. The methodology will also take advantage of various software already developed at Argonne National Laboratory (ANL) and at other U. S. Department of Energy laboratories (for example, Balsam) to automate, manage, and control the large number of calculations needed to achieve the project goal.

Approach. All calculations will be performed by spin-polarized DFT as implemented in the Vienna *ab initio* simulation package (VASP). After geometry optimization within the DFT+U framework, electronic relaxation will be performed using a single-point calculation with the hybrid functional HSE06. For production calculations, they will use the message-passing interface (MPI) parallelized version of VASP.

Exploration of the potential energy surface is needed to predict the structure of solid materials and interfaces. Such calculations are infeasible using MD or DFT calculations alone. Thankfully, the potential energy surface of a system can be represented by the sum of the energies of the local neighborhoods surrounding each atom.

This enables the use of ML surrogate models trained with DFT calculations to capture the energies in local neighborhoods. The input to the ML surrogate must be a unique representation of the system under study. Consequently, the local environment of each ion is described using a local environment descriptor that renders the atomic configuration invariant to rotations, translations, and permutations of the atoms. In recent years, several different descriptors have come to prominence with advantages and disadvantages. Once the ML surrogate is trained, the total energy and forces over all the ions of any structural configuration can be determined. Such information can be used for atomistic simulations, namely, MD and Monte Carlo.

In this project, the team proposes to use the open-source DeepMDkit python/C++ package to construct the ML potential energy surface and force field (FFs). The promise of DeepMDkit in this work is to provide near-DFT accuracy at orders-of-magnitude lower computational expense, comparable to traditional MD simulations. Efficiency in training is facilitated through integration with TensorFlow and MPI / graphics processing unit support.

One of the challenges of developing ML potential energy surface is achieving accurate predicted forces and energies across the entire configurational space, while minimizing the total number of calculations required for training. In recent years, active learning has been highlighted for its ability to target training examples most likely to improve the model quality or to achieve some other objective (that is, maximizing a predicted material property). DP-GEN, an open-source python package based on DeepMDkit, implements a similar active learning scheme with HPC support, and has been employed to construct ML potential energy surface with accuracy approaching DFT and sometimes exceeding embedded atom potential for experimentally measured properties of interest. In this work, the team proposes to leverage DeepMDkit and DP-GEN to efficiently generate ML potential energy surfaces for cathode-electrolyte systems including a variety of dopants.

Out-Year Goals. One out-year goal involves developing a DFT-trained ML model on NMC / $Li_7La_3Zr_2O_{12}$ (LLZO) interface, ready to use for large screening of new cathodes, SSE compositions, and cathodes/SSE interfaces. A second is to provide fundamental understanding on critical parameters limiting performance and stability of the cathode/SSE interface and hence of the SSB.

Collaborations. Project collaborators include J. Croy, C. Johnson, and E. Lee from ANL Chemical Sciences and Engineering Division for the synthesis phase of the project.

Milestones

- 1. Determine cationic distribution in LiNi_{0.8}Mn_{0.1}Co_{0.1-y}X_yO₂ (NMCX) for X (X = Ti, Zr, Al, Fe, Ca, Mg, Y, W, Nb, B, La). (Q1, FY 2022; Completed)
- 2. Determine elemental segregation, volume changes, and phase transformation during charging of doped (including fluorine anionic substitution) LiNi_{0.8}Mn_{0.1}Co_{0.1} (NMC-811) using the developed DFT-trained ML model. (Q2, FY 2022; Completed)
- 3. Determine doped NMC-811-LLZO interface reactivity and structural stability. (Q3, FY 2022; In progress)
- 4. Screen for compositions with low interfacial strain, and elemental mixing (NMCX-LLZO). (Q4, FY 2022)

Progress Report

The team has previously demonstrated (see Publication section) that the decrease in lithium slab space is the main cause of volume change during charging for Ni-rich materials. The lithium slab space is the distance between oxygen layers adjacent to a lithium layer. NMC-811 has a very similar behavior as LiNiO₂. On delithiation at very high SOC, the lithium slab space collapses. For NMC-811, the lithium slab space goes from 2.58 Å when fully discharged to 2.35 Å when fully charged (0% lithium), a 9.8% total decrease (see Figure 102a). The dopants titanium, zirconium, aluminum, iron, magnesium, niobium, boron, and tungsten do not have a major effect on the lithium slab space collapse. They all prefer to stay in the transition metal (TM) layer of NMC-811. For these dopants in the TM layer, the Coulombic repulsions between adjacent oxygen layers at high SOCs remain similar to those of undoped compositions. On the contrary, calcium, lanthanum, and yttrium dopants prefer to be in the lithium layer, mainly because of their size, which is comparable or larger than lithium ions. On delithiation, these dopants stay in their octahedral position in the lithium layer, acting as pillars. The team found that for calcium, the lithium slab space decreases from 2.66 Å to 2.45 Å (see Figure 102b), a 7.8% total decrease (compared to 9.8%). For lanthanum, the lithium slab space changes from 2.68 Å to 2.49 Å (Figure 102c), a 7.0% total decrease. They are reprocessing yttrium simulations, which present similar trends.



Figure 102. Schematic representation of atomic arrangements for (a) NMC-811, (b) Ca-doped NMC-811, and (c) La-doped NMC-811. Red, green, gray, purple, blue, light blue, and orange spheres represent oxygen, lithium, nickel, manganese, cobalt, calcium, and lanthanum, respectively. Lithium slab space is also indicated.

The distribution of the dopants plays a major role in the structural characteristics of layered materials. The team has tested hundreds of configurations with the dopants dispersed in NMC-811. To understand the effect of temperature, they have calculated the configurational density of states (DOS), which accounts for the configurational entropy of the system. Multiplying the configurational DOS by the Boltzmann factor and normalizing, they obtained the probability of occurrence of a given configuration. The probability of occurrence is equivalent to the mole fraction of a configuration in the material. Figure 103 shows two examples of the probabilities of occurrence of certain configurations for calcium (Figure 103a) and lanthanum (Figure 103b). Given the moderate range of possible energies for these materials, the temperature has no significant effect on their dispersion. For calcium (Figure 103a), the lowest energy configurations are characterized by calcium well dispersed and located in the lithium layer. However, given that the probability of finding other configurations is also high, a mix of calcium in the lithium layer. Given a narrower distribution near the ground state, lanthanum will not form clusters or be located in the cobalt layer. Hence, lanthanum is a more suitable candidate as a dopant.



Figure 103. Energy of configurations, configurational density of states, Boltzmann factor, and probability of occurrence of each tested configuration for (a) calcium and (b) lanthanum.

A major project deliverable will be the determination of dopant/concentration that will inhibit volume contraction with cathode delithiation. This requires first determining low energy structure for different dopant configurations and concentration levels. To this end, the team employs an ensemble of previously trained MLFFs to predict the total energies for a large number of configurations and employ a batch Bayesian

optimization strategy to identify a lowest energy structure via DFT. Figure 104 shows the ensemble mean and standard deviation of total energies for 100,000 structures, and the structure batch Bayesian optimization would select with access to different random subsets. The figure illustrates that there is little difference between the "best" 50 structures overall and the best 50 structures selected from ten random subsets of 10,000 structures. There are six classes of configurations that must be explored. There are three dopant concentrations (that is, where 1, 2, or 3 out of 3 cobalt atoms are replaced by the dopant atom) and two mechanisms (replacement in the TM layer or insertion into the lithium channels), corresponding to six total categories. The team is writing a manuscript that highlights this methodology and illustrates its use in identifying promising dopants for reducing volume changes in high-Ni battery cathode materials.

At a high SOC, NiO_2 undergoes a phase transition from the O3 to the O1 phase. The O1 appears to be more thermodynamically stable than the O3 phase. However, DFT often predicts higher stability for O3, depending on the DFT approximation. The energy difference between the O1 and O3 phases is on the order of 10 meV/atom. DFT correctly



Figure 104. The predicted ensemble mean and standard deviation total energies are plotted for each of 100,000 structures for the case where one cobalt atom is replaced by magnesium in the transition-metal layer. Structures with the best combination of low mean and high standard deviation total energy are plotted for all structures in red, and then in other colors corresponding to the most promising structures from selected subsets of structures.

ranks the relative energies of phases that differ by < 10 meV/atom about 80% of the time.^[1] However, DFT is reliable for larger energy differences. The team finds that proton defects are more stable in the O1 phase than

in the O3 phase by ~ 90 meV per proton. Defects in NiO₂ can drive the O3-O1 phase transition observed in a high SOC in Li_xNiO_2 . The protonated O1-NiO₂ is more stable because the proton can more easily hydrogen bond to oxygens in the neighboring layer. Nudged elastic band calculation shows that the barrier of 27 meV for a proton moving between layers is much lower than the barrier of 1278 meV for a proton moving between layers of the same layer (Figure 105). This is consistent with the observed motion of protons between layers in AIMD and not between oxygens in a layer. Proton defects in NiO₂ lower the energy of O1-NiO₂ relative to O3-NiO₂ and could be the source of the stability of O1-NiO₂ relative to O3-NiO₂.



Figure 105. Energy changes along the reaction coordinate of proton diffusion in LiNiO₂. The orange line represents the interlayer diffusion, and the blue line represents the intralayer diffusion.

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Patents/Publications/Presentations

Publication

Garcia, J. C., J. Gabriel, N. H. Paulson, J. Low, M. Stan, and H. Iddir. "Insights from Computational Studies on the Anisotropic Volume Change of Li_xNiO₂ at High States of Charge (x < 0.25)." *Journal of Physical Chemistry C* 125, no. 49 (2021): 27130–27139. doi: 10.1021/acs.jpcc.1c08022. Task 3.10 – Tackling Solid-State Electrochemical Interfaces from Structure to Function Utilizing High-Performance Computing and Machine-Learning Tools (Shinjae Yoo, Feng Wang, and Deyu Lu, Brookhaven National Laboratory; Nongnuch Artrith and Alexander Urban, Columbia University)

Project Objective. This project aims at elucidating the structural evolution and other dynamic properties of the interphases at the solid-state ions (SSIs) in solid-state batteries (SSBs) under processing and electrochemical cycling conditions that strongly impact cell performance. By leveraging synergies of first-principles theory, high-performance computing, machine learning (ML), and computational/experimental spectroscopy, this project involves a comprehensive investigation of solid electrolyte systems and SSIs that may enable the practical use of lithium anodes and high-Ni Ni-Mn-Co (NMC) cathodes in SSBs. Specific project objectives are as follows: (1) develop realistic atomic-scale structure models of the heterostructural SSIs, (2) determine the impact of structural evolution on stability and transport properties of SSIs, and (3) identify the coating/doping chemistry that may stabilize SSIs during formation and electrochemical cycling.

Project Impact. Interfacial properties and the dynamical evolution of interphase structures are crucial for the stability and performance of SSBs. This project will lead to fundamental understanding of current materials limits and will identify key materials parameters for optimizing the performance of SSBs. By corroborating atomic-scale theory with experiment, the project will identify structure–property relationships of the heterostructural SSIs in SSB systems that are relevant for electric vehicles (EVs). The outcomes of this project will therefore accelerate development of high-energy-density, safe SSBs for EVs.

Approach. Accurate ML potentials will be trained on an extensive database from density functional theory (DFT) calculations to simulate the structure evolution and electrochemical properties of the SSIs. Using a second ML model, key physical descriptors will be extracted from electron energy loss spectroscopy (EELS) and X-ray absorption spectroscopy (XAS) measurements. This spectral fingerprinting will enable the automated interpretation of spectroscopy measurements, thereby bridging between atomistic modeling and experiment. An experimental platform will be developed to integrate experimental/computational spectroscopy and modeling of SSIs. In combination, the two ML models and the spectroscopic data will facilitate the construction of a physics-based model to unravel the structure-property relationships of the SSIs.

Out-Year Goals. The project will progress toward establishing dynamic composition-structure-property relationships for interface stability and transport within and across the electrochemical SSIs in SSBs. The ML approach will be further developed to a general model for thermodynamic and transport properties of dynamic heterostructural electrochemical interfaces and will eventually be applied to the practical SSB systems.

Collaborations. The project is collaborating with Y. Du at Brookhaven National Laboratory.

Milestones

- 1. Determine electrochemical stability of Li-P-S (LPS)/lithium interfaces during cycling through spectroscopy characterization aided by ML, data-analysis, and modeling. (Q1, FY 2022; Completed)
- 2. Analyze impact of halide-substitution on chemical and electrochemical stabilities of LPS-X (X = Cl, Br, I) systems in contact with lithium metal. (Q2, FY 2022; Completed)
- 3. Identify key limitations to interfacial stability of LPS and LPS-X systems in contact with lithium metal through combined computational/experimental investigations. (Q3, FY 2022; Completed)
- 4. Establish doping/coating-based approaches for enabling long cycling stability of the LPS-X based half and full cells at high current density. (Q4, FY 2022; In progress)

Progress Report

This quarter, the team has combined electrochemical, spectroscopic, computational, and ML techniques to study the interfacial stability of the LPS, on contact with lithium metal or during cycling in SSBs. They found that the second cycle went through a different process than the first cycle, which is evidenced by different current peak positions in the cyclic voltammetry (CV) profiles and distinct spectral features in phosphorus and sulfur K-edge XAS at voltage close to 5 V. These spectral features are partially reversible. Computational and ML studies provide atomic-scale insight into the reaction mechanism. In particular, the new peak at the K-edge XAS is originated from the strongly distorted PS_4 local motifs and the formation of S-S bridge. Their study sheds light on the microscopic origin of the interfacial stability of the LPS on contact with lithium metal and during cycling in SSBs.

Experimental XAS Measurement

The team used the LPS-C | LPS | Li-In cells to study the stability of LPS in the LPS-C composite electrodes during cycling between 0-5 V in CV experiments (with details provided in the first quarter report for FY 2022). The samples were characterized at different charge states using phosphorus and sulfur K-edge X-ray absorption near-edge structure (XANES) spectroscopy, as shown in Figure 106. At each charge state, two identical samples with LPS particle size of 2-10 μ m were measured using two detection modes, electron yield (EY) and fluorescence yield (FY), at Beamlines TES and SST-2 at National Synchrotron Light Source II (NSLS-II), respectively. The detection depths of EY and FY are about 10 nm and 5 μ m. Thus, EY and FY can provide information on the surface and bulk of the sample, respectively.



Figure 106. Experimental X-ray absorption near-edge structure spectroscopy data collected on LPS-C composite electrodes. LPS-C electrodes are cycled to different states in 0-5 V cyclic voltammetry (CV) experiment and measured *ex situ* after cell disassembly. (a) Phosphorus K-edge and (b) sulfur K-edge spectra measured in partial electron yield (PEY) mode at SST-2 beamline. (c) Phosphorus K-edge and (d) sulfur K-edge spectra measured in fluorescence yield (FY) mode at TES beamline. (e) Current (red solid line) and voltage (green dashed line) profiles of the CV experiment with 0.1 mV/s scan rate for the 1st and 2nd cycles; the markers indicate the states that the samples were prepared for X-ray absorption spectroscopy measurement.

During the first delithiation from open circuit voltage to 5 V, corresponding to pristine LPS and A1 spectra in Figure 106, the phosphorus K-edge XANES white line peak at 2148.5 eV decreases and broadens. In the sulfur K-edge spectrum, a peak at 2473 eV appears, as indicated by arrows in Figure 106b/d, which can be attributed to the formation of bridging S bonds.^[1-2] During the second delithiation from 2.3 V to 5 V (A3 to A4), they observe a large change in the phosphorus spectra, where a new peak emerges at 2151 eV, as indicated by arrows in Figure 106a/c. This new spectral feature indicates that the second delithiation went through a different reaction mechanism from the first delithiation, which is also reflected in the different current peak positions in the CV profile (detailed in the first quarter FY 2022 report). Spectra A5 shows that the changes in phosphorus and sulfur are (partially) reversible, with both peaks (at 2151 eV in phosphorus K-edge, and at 2473 eV in sulfur K-edge) decreasing during the second lithiation.

The EY and FY experiments exhibit the same overall trend of spectral evolution, but with several subtle differences. The first difference is that the peaks in EY spectra are sharper, and the intensities of the white line peaks are higher. The sharper peaks in EY are due to the higher energy resolution, because EY spectra are measured at the insertion device beamline, while FY spectra are measured at the bending magnet beamline. The difference in peak intensities is due to self-absorption, because the peaks in FY spectra are dampened by self-absorption, while the EY spectra do not have self-absorption. The second difference comes from the different probe depths. Taking the A1 spectra of sulfur K-edge as an example, both EY and FY spectra show the emergence of 2473 eV peak, but the ratio between this peak and the original white line peak is much higher in EY than in FY, indicating that the reaction occurs mainly at the surface of LPS particles. The signal from unreacted bulk LPS is negligible in EY, while FY measures the mixed signal from both bulk and surface. A similar behavior can be found in the A4 spectra for both phosphorus and sulfur K-edge.

To unravel the atomic-scale structural details during the redox reactions of LPS, the team combines first-principles calculations and unsupervised ML to analyze the key spectra features, in particular the new peak at 2151 eV in the phosphorus K-edge XANES during the second delithiation.

Computational Delithiation of *β*-Li₃PS₄

In addition to the experimental characterization of the electrochemical degradation of β -Li₃PS₄ (β -LPS), the team performed a computational delithiation with DFT calculations. They employed the enumeration method by Hart and coworkers^[3-6] using the Python Materials Genomics (pymatgen) package^[7] to systematically



Figure 107. (a) Formation energies of $Li_{12-x}P_4S_{16}$ structures with enumerated Li/vacancy orderings. Those structures with formation energies on the lower convex hull (orange line) are predicted to be thermodynamically stable at 0 K; however, given the shallow depth of the hull, other compositions might be observable at room temperature. (b-c) PS_x structure motifs found in the stable delithiated structures (sulfur, yellow; phosphorus, violet).

enumerate symmetrically distinct Li/vacancy orderings in unit cells with the general composition $Li_{12-x}P_4S_{16}$ (that is, four LPS formula units). In total, the enumeration yielded ~ 800 atomic configurations with varying lithium contents that were fully optimized (atomic positions and lattice parameters).

Figure 107a shows the formation energies of the delithiated LPS structures. Three intermediate compositions are predicted to be thermodynamically stable at 0 K, (that is, LiPS₄, Li_{0.5}PS₄, and Li_{0.25}PS₄) though the convex hull is shallow and additional compositions might be accessible at room temperature. Based on the calculations, LPS is fully delithiated at potentials above ~ 3.4 V versus Li/Li⁺. In β -Li₃PS₄, sulfur and phosphorus atoms form isolated tetrahedral PS₄ motifs. On lithium extraction, they find that the PS₄ tetrahedra form chains via S-S bonding, indicating that sulfur atoms are oxidized (Figure 107b-c). The number of bonds per PS₄ unit increases with the degree of delithiation; in the fully delithiated P₄S₁₆ structure, most PS₄ groups form three bonds with neighboring PS₄ groups.

The S–S bonding indicates that sulfur oxidizes when lithium is extracted from LPS. This mechanism is corroborated by a Bader charge analysis, finding that only sulfur atoms participate in the redox reaction and gradually oxidize from initially S^{II-} in Li₃PS₄ to a 1:3 mixture of S^{II-} and S^{I-} in the fully delithiated P₄S₁₆. The calculations do not show any evidence of phosphorus oxidation, which remains in V+ valence state throughout.

Data-Driven Phosphorus K-Edge XANES Analysis

The team performs phosphorus K-edge XANES calculations on a database of ~ 800 delithiated β -LPS (Li_{12-x}P₄S₁₆) compounds described in the previous section using the Vienna *Ab Initio* Simulation Package (VASP). They identify local structural motifs that are correlated with the peak ~ 2.5 eV above the white line in the simulated spectra. Since the simulated LPS XANES spectra reproduce very well the features in the experimental standards (see last quarter's report), these structural motifs correspond to the experimental peak at 2151 eV during the second delithiation.

The simulated phosphorus XANES spectra are first aligned to the first major peak position and then are clustered into four groups using the K-Means algorithm. These clusters are shown in the four rows of Figure 108a-d. The clustered spectra are ordered such that they reflect the changes occurring in Figure 106a/c, specifically going from "LPS" to "A4." Spectra in Figure 108a correspond to a tetrahedral PS₄ motif in LPS, consistent with the strong single peak in Figure 106c. The trend in Figure 108b-d shows the single peak splitting into two, which, notwithstanding various broadening effects (for example, the finite-temperature broadening), are consistent with the features in Figure 106a/c (A4).



Figure 108. (a-d) Simulated phosphorus K-edge X-ray absorption near-edge structure spectra of delithiated β -LPS clustered into four groups using K-Means. (e-h) The corresponding patterns from the structural principal component analysis using the SOAP descriptor.

To further analyze the structural changes, the team performed two complementary analyses. First, in Figure 108e-h, they computed the SOAP (that is, smooth overlap of atomic positions) descriptors^[8] for each absorbing phosphorus site, and then used principal component analysis to decompose those descriptors into two dimensions. The clustering patterns in the "structural space" clearly mirror the changes in the spectral space, confirming the team's hypothesis that indeed it is the local structural changes that drive the changes in the XANES spectra. Note that there are two types of local structures in cluster 4 (red and yellow dots in Figure 108h), while their corresponding spectra are similar (red and yellow curves in Figure 108d).

Second, the team carried out data-driven analysis by plotting various structural descriptors averaged within each cluster, as shown in Figure 109. Multiple important trends are strongly correlated with the spectral trends going from cluster 1 to 4. First, while the maximum S-P-S bond angle stays relatively constant, the minimum bond angle decreases by almost a factor of 2, indicating that sulfur atoms bonded to the central phosphorus atom are moving into closer proximity. Second, the overall lithium count, both stoichiometrically and present in the second coordination shell of phosphorus (no lithium atoms are present in any first coordination shell of phosphorus), decreases monotonously with respect to the cluster index. This confirms that the order of the cluster tracks the degree of the delithiation from low to high. Finally, the largest S-P bond length of the original PS₄ motif increases from ~ 2.05 Å in cluster 1 to 2.4 Å in cluster 4 during the delithiation. In fact, the two types of structural motifs in cluster 4. as shown in Figure 108h, represent the aforementioned distorted tetrahedrons (yellow) and PS₃ motifs, often with S-S bridges (red), respectively.

Through combining the electrochemical measurement, XAS measurement, first-principles structure models, XANES simulation, and unsupervised ML, the team provided strong evidence on the structural distortion of the PS₄ tetrahedra that occurred during the repeating delithiation. During delithiation to high voltages (at ~ 5 V), two first shell sulfur atoms move close to each other, resulting in a small S-P-S angle of ~ 70 degrees; some PS₄ tetrahedra are ruptured, forming PS₃ motifs with S-S bridges. These strongly distorted phosphorus local motifs have a spectral fingerprint, as a



Figure 109. Averaged structural descriptors in each of the four clusters identified in Figure 108: (a) minimum and maximum S-P-S bond angles, (b) number of lithium atoms, and (c) S-P bond length.

second peak at 2151 eV in phosphorus K-edge XANES. Their study sheds light on the microscopic origin of the interfacial stability of the LPS on contact with Li-metal and during cycling in SSBs.

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Patents/Publications/Presentations

Publication

 Guo, H., Q. Wang, A. Urban, and N. Artrith. "Artificial Intelligence-Aided Mapping of the Structure– Composition–Conductivity Relationships of Glass–Ceramic Lithium Thiophosphate Electrolytes." *Chemistry of Materials* 34, no. 15 (2022): 6702–6712. doi: 10.1021/acs.chemmater.2c00267.

Presentations

- National Synchrotron Light Source II (NSLS-II) and Center for Functional Nanomaterials (CFN) Users' Meeting, Virtual (May 23–26, 2022): "Machine Learning Models for Simulating Complex Battery Materials with Non-Crystalline Structures"; N. Artrith.
- NSLS-II & CFN Joint Users' Meeting, Virtual (May 23–26, 2022): "Redox Process of Lithium Phosphorus Sulfide Solid Electrolytes: A Combined Study of Spectroscopy, Computation, and Machine Learning"; C. Cao. Poster.

Task 3.11 – Integrated Multiscale Model for Design of Robust, Three-Dimensional, Solid-State Lithium Batteries (Brandon Wood, Lawrence Livermore National Laboratory)

Project Objective. This project is developing and applying multiscale, multiphysics models that connect composition, microstructure, and architecture to mechanical integrity in three-dimensional (3D) solid-state batteries (SSBs). The models integrate multiple computational methods, informed and validated through collaborations with complementary experimental efforts. The project scope addresses three objectives: (1) develop multiphysics, multiscale chemomechanics models; (2) assess interface- and microstructure-induced mechanical failure thresholds; and (3) simulate chemomechanical evolution under battery operating conditions.

Impact. This project will deliver multiscale, multiphysics models that connect composition, microstructure, and architecture to mechanical integrity in 3D SSBs. The tools will be used to examine common interfaces in commercially viable electrolyte and cathode materials and to provide design principles for maintaining mechanically robust operation. The modeling framework will address the shortcomings of existing modeling strategies that either lack coupling of the multiphysics nature of various processes active in 3D batteries or fail to incorporate processes at different length scales to understand function. Connections will be made to understand the limits of operability and to co-optimize ionic conductivity and mechanical robustness in solid electrolyte-cathode matrix composites.

Approach. The project approach integrates atomistic, mesoscale, and continuum simulation methods to predict chemomechanical properties of interfaces in ceramic (Li-La-Zr-O, or LLZO) and halide-based solid electrolytes (SEs). Both internal grain boundaries (GBs) and interfaces with LiCoO₂ and Ni-Mn-Co (NMC) cathode materials are considered. The project is aligned along three tasks, each of which uses simulations to probe a different fundamental length scale relevant to the performance of 3D-SSB architectures. First, atomic-scale interfacial properties are computed using density functional theory and machine learning approaches. These include local bond strength and mechanical response, as well as stress distributions associated with formation of cracks. Second, using digital reproductions of 3D electrodes and electrolytes, the local stress distributions and stress hotspots in SEs and cathode-electrolyte composites are computed within a mesoscale model. Third, materials performance is coupled to cycling conditions within an operating device by incorporating phase-field models that can simulate rate-dependent fracture likelihood under cycling and extract microstructure-fracture-transport relationships.

Out-Year Goals. The team will focus on the following out-year goals: use *ab initio* methods to generate models for GBs and cathode electrolyte interphases (CEIs); compute local bond strength and mechanical response of model interfaces; reconstruct microstructures of electrodes and electrolytes using phase-field models; and develop a phase-field model for cathode-induced volume evolution on cycling.

Collaborations. This project collaborates with N. Adelstein from San Francisco State University on atomistic diffusion modeling, and J. Ye from Lawrence Livermore National Laboratory (LLNL) on 3D printing of SSB materials. They also partner with T. Danner and A. Latz from Deutsches Zentrum für Luft- und Raumfaurt (DLR) on impedance modeling and electro-chemo-mechanical interface models, with P. Zapol from Argonne National Laboratory (ANL) on modeling of interfaces in LLZO, and with D. Fattakhova-Rohlfing from Forschungszentrum Jülich (FZJ) and E. Wachsman from University of Maryland on properties of LLZO with varying densities and microstructures as part of the U. S.–Germany partnership on SSB research.

Milestones

- 1. Complete atomistic CEI models. (Q1, FY 2022; Completed)
- 2. Determine composition profiles of CEIs. (Q2, FY 2022; Completed)

- 3. Set up model for local stress mapping. (Q3, FY 2022; Completed)
- 4. Train machine learning force fields (MLFFs) for disordered interfaces. (Q4, FY 2022; Completed)

Progress Report

ML Interatomic Potentials for Accelerated Atomistic Simulations. This quarter, the team improved the MLFF for Al-, Ba-, and Ta-doped LLZO by adding structure data at a wide range of temperatures. To test their performance, the team compared the MLFF predicted radial distribution function (RDF) of dopant pairs and the vibrational spectra of aluminum in a crystalline Al-LLZO. Figure 110a shows that the predicted vibrational spectrum of aluminum by the MLFF is close to that calculated from *ab initio* molecular dynamics (AIMD) simulations. In addition, Figure 110b shows that the MLFF predicts the RDF of Ta-Ta pair in amorphous Ta-LLZO is similar to that computed from AIMD trajectories. The RDFs for Al-Al and Ba-Ba pairs predicted by the MLFFs of Al- and Ba-doped LLZO are also close to those obtained from AIMD results. They are finetuning the MLFFs by performing additional parameter tests to reduce the force and energy errors and are collaborating with P. Zapol's group at ANL to further test the performance of these MLFFs to model ordered and disordered GBs in doped LLZO systems.



Figure 110. (a) Vibrational spectra of aluminum in a crystalline AI-LLZO at 1200 K. (b) Radial distribution function of Ta-Ta pair in an amorphous Ta-LLZO at 3000 K predicted by *ab initio* molecular dynamics (blue) and molecular dynamics with machine learning force field (orange).

Mesoscale Modeling and Effective Property Calculation of Hybrid SE Microstructures. This quarter, the team's mesoscale modeling effort has been focused on experimentally relevant microstructures and their effects on transport and mechanical properties of polymer/LLZTO (Ta-doped LLZO) hybrid systems. Their colleague J. Ye at LLNL has been investigating the performance of 3D-printed polymer/LLZTO hybrid SE, through another Vehicle Technologies Office sponsored project. The team first analyzed the topological features of the experimentally characterized microstructure. These features are key inputs for generating digital representations of the microstructures using the workflow they developed based on the stochastic microstructure generation method last quarter. They then applied this approach to integrate the digital microstructures with LLNL's *MesoMicro* codes to compute the effective mechanical and transport properties. Figure 111 includes a few examples of preliminary two-dimensional (2D) modeling results on microstructural impacts on effective ionic conductivity and micromechanical responses of the layered polymer-porous LLZTO hybrid SE systems.

The scanning electron microscopy images of the selected polymer/LLZTO/polymer layered system reveal the interfacial structure between the LLZTO and polymer (Figure 111a), as well as the interior microstructure of polymer-infiltrated LLZTO layer (Figure 111b). The images clearly indicate structurally distinct interfaces with a roughness on the order of a few microns. To mimic the characterized sandwiched structure, the team uses a 2D layered model with two homogenous polymer layers on both ends and a polymer-infiltrated LLZTO electrolyte in between (see the schematic in Figure 111c). To generate the porous microstructure in the center layer, they embedded stochastically distributed spherical particles to represent the LLZTO particles as initial seeds for subsequent phase-field grain-growth simulation, leading to realistic representations of polygranular microstructures that incorporate connectivity between discreate particles as seen in the experiments

(Figure 111b). As shown in Figure 111c from (1) to (5), the polygranular microstructure evolves with time in the simulation, driven by the coalescence of the particles and the reduction of porosity. The resultant digital microstructure reproduced key features of the experimental observations, including (1) the porous nature of the LLZTO layer; (2) the connection between LLZTO particles; and (3) the rough interfaces between the LLZTO and polymer layers.

The team chose two snapshots (that is, (2) and (5)) as representative microstructures (Figure 111d) of different porosity and particle sizes for effective-property calculations. They obtained the current density distribution under an applied electric voltage (Figure 111e) and von Mises stress distribution under a compressive longitudinal strain (Figure 111f) for the selected microstructures. For the more porous structure, the electrical current tends to concentrate at a limited number of channels provided by the more conductive LLZTO ceramic, as seen in the current-density hotspot (see Figure 111e). In contrast, the current density is more uniformly distributed in the dense structure, as shown in Figure 111f. For mechanical responses, the porous structure exhibits local stress hotspots at some internal porous area between LLZTO particles, while the dense structure results in stress hotspots concentrated at the roughed interfacial regions where the polymer and the LLZTO layer meet. These results suggest that (1) connectivity of LLZTO particles is critical for enhanced Li-ion conduction; and (2) mechanical failure may occur at the porous area of the LLZTO layer for the porous structure, whereas it may occur at the LLZTO/polymer interfacial regions for the denser structures.



Figure 111. Experimental characterization and mesoscale modeling of the microstructure of a polymer/LLZTO/polymer hybrid solid electrolyte system. (a-b) Scanning electron microscopy images of polymer/LLZTO/polymer system (a) at the polymer/LLZTO interface and (b) inside the porous bulk LLZTO. The scale bars in both images represent 10 μ m. (c) A schematic of the polymer/LLZTO/polymer system and the numerically generated LLZTO polycrystalline microstructure from phase-field grain-growth simulation. The porosity of the polymer within the LLZTO layer (marked by the yellow dashed lines) can be visualized in each snapshot. (d-f) Mesoscale modeling of selected grain structures in (c), including (d) grain structures, (e) normalized electric current flux $(\overline{J_e})$ and density $(|\overline{J_e})$ mapping, and (f) normalized von Mises stress (σ_{vM}) mapping. (g) Calculated effective elastic modulus and effective conductivity as a function of porosity in the LLZTO layer for all cases in (c). (h) Histogram of the von Mises stress distribution for all cases in (c).

The team also evaluated the effective ionic conductivity and effective elastic modulus as a function of porosity of the LLZTO layer (see Figure 111g), and the statistical distribution of the von Mises stress for analyzing the mechanical hotspots (see Figure 111h). It is found that both the mechanical and transport properties drop rapidly with the increase of porosity due to the intrinsically lowered ionic conductivity and elastic modulus of the polymer phase as compared with the LLZTO phase. The statistical distribution of the von Mises stress suggests that more hotspots may develop more frequently in denser structures, perhaps due to more population of the polymer-LLZTO intralayer interfaces. They note that, in the simple 2D model reported here, they used the literature values of the ionic conductivity and mechanical modulus of the polymer phase, and the interfacial resistance between the LLZTO and polymer phases have not been explicitly considered. To further improve model fidelity, they are collaborating with J. Ye to better parameterize their mesoscale models by incorporating experimentally measured interfacial resistance and properties of the polymer phase.

Patents/Publications/Presentations

Publication

Kim, K., A. Dive, A. Grieder, N. Adelstein, S. Kang, L. Wan, and B. Wood. "Development of Machine-Learning Interatomic Potential for Crystalline/Amorphous Li₇La₃Zr₂O₁₂ Solid Electrolyte for Solid-State Batteries." *Journal of Chemical Physics* 156 (2022): 22110.

Presentation

 Materials Research Society Spring Meeting & Exhibit, Honolulu, Hawaii (May 2022): "First-Principles Evaluation of Dopant Impact on Structural Deformability of LLZO Solid-State Electrolyte: Towards Realization of Co-Sintering with High-Energy Cathodes"; A. M. Dive, K. Kim, R. Shi, S. Kang, M. Wood, L. Wan, and B. C. Wood.

TASK 4 – METALLIC LITHIUM

Team Lead: Jagjit Nanda, SLAC Stanford Battery Research Center

Summary and Highlights

The use of a metallic lithium anode is required for advanced battery chemistries like Li-ion, Li-air, and Li-S to realize dramatic improvements in energy density, vehicle range, cost requirements, and safety. However, use of metallic lithium with liquid and solid polymer or ceramic electrolytes has so far been limited due to parasitic solid electrolyte interphase (SEI) reactions and dendrite formation that eventually short circuit the battery. Adding excess lithium to compensate for such losses negates the high-energy-density advantage of a Li-metal anode and leads to further concern for battery safety. For a long lifetime and safe anode, it is essential that no lithium capacity is lost either (1) to physical isolation by roughening, dendrites, or delamination processes, or (2) to chemical isolation from side reactions. The key risk, and current limitation, for this technology is the gradual loss of lithium over the cycle life of the battery.

The BMR, Battery500 Consortium, and other U. S. Department of Energy programs are addressing this challenge with many innovative and diverse approaches. Key to all is the need for a much deeper analysis of the degradation processes and new strategies to maintain a dense, fully connected lithium and a dendrite-free electrolyte so that materials can be engineered to fulfill the target performance metrics for electric vehicle application, namely 1000 cycles and a 15-year lifetime, with adequate pulse power. Projecting the performance required in terms of just the lithium anode, this requires a high rate of lithium deposition and stripping reactions, specifically about 30 μ m of lithium per cycle, with pulse rates up to 10 and 20 nm/s (15 mA/cm²) charge and discharge, respectively, with little or no excess lithium inventory. This is daunting in the total mass and rate of material transport that must be achieved without failures.

The efficient and safe use of metallic lithium for rechargeable batteries is then a great challenge, and one that has eluded research and development efforts for years. This project takes a broad look at this challenge for both solid-state batteries and batteries continuing to use liquid electrolytes (LEs). The electrolytes reported here include conventional LEs including localized high-concentration electrolytes, gel-type polymer-in-a-salt, composites of ceramic polymer phases, common and novel polymer electrolytes, and both oxide and sulfide ceramic electrolytes. Researchers are typically working toward cycling of full cells with relevant and balanced capacities using both thin lithium metal and anode-free configuration, prelithiation methods, and post-cycling observation of the disassembled cell components to assess stability of the Li-metal/electrolyte interface.

Highlights

The highlights for this quarter are as follows:

- The Pacific Northwest National Laboratory team led by W. Xu and co-workers has developed a non-carbonaceous three-dimensional (3D) current collector as a host for Li-metal. The 3D porous membrane consists of a network of electrospun polyimide fibers coated with copper using electroless plating methods. SEI formation on the 3D current collector was characterized using *operando* reflective interference microscope.
- Y. Cui's group at SLAC National Accelerator Laboratory / Stanford University demonstrated chemical and morphological homogeneity of lithium distribution using their solvent-free *in situ* prelithiation method developed for silicon electrodes. Scanning electron microscopy and high-resolution X-ray photoelectron spectroscopy results showed uniform homogeneity and lithium distribution at various electrode regions utilizing Li-mesh prelithiation.

Task 4.1 – Lithium Dendrite Prevention for Lithium Batteries (Wu Xu, Pacific Northwest National Laboratory)

Project Objective. The objective of this project is to enable lithium metal to be used as an effective anode in Li-metal batteries with good thermal stability and safety. The investigation in FY 2022 will focus on the following aspects: (1) continuing evaluation of separators with high thermal stability in Li-metal batteries, (2) developing three-dimensional (3D)-structured, lightweight, flexible current collectors for Li-metal anode and Li-metal batteries, and (3) obtaining mechanistic insight on Li-metal deposition/stripping behavior.

Project Impact. Lithium metal is an ideal anode material for next-generation, high-energy-density, rechargeable batteries. However, the application of Li-metal anode has been hindered by concern for safety and short cycle life. The safety concern regarding Li-metal batteries mainly arises from lithium dendrite growth and electrolyte flammability; the short cycle life is largely associated with the high reactivity of lithium metal with electrolyte and the lithium loss due to formation of solid electrolyte interphase (SEI) and electrochemically inactive or "dead" lithium during cycling. Although much progress has been achieved in suppressing lithium dendrites and increasing lithium Coulombic efficiency in liquid electrolytes in recent years, the intrinsic problems of Li-metal anode still exist. This fiscal year, the Pacific Northwest National Laboratory (PNNL) team will continue to evaluate the effectiveness of separators with high thermal stability in improving the thermal stability of Li-metal batteries. Meanwhile, the team will develop 3D porous current collectors for Li-metal anode to suppress lithium dendrite growth, increasing the utilization of lithium metal and consequently extending the cycle life of Li-metal batteries. The success of this project will increase safety and cycle life of lithium batteries and accelerate market acceptance of electric vehicles (EVs), as required by the EV Everywhere Grand Challenge.

Approach. The approach will encompass the following areas: (1) continue comparative evaluation of separators with high thermal stability in lithium || $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}$ (NMC-622) cells during cycling and heating process, (2) develop current collectors with 3D structure for Li-metal anode to suppress lithium dendrite growth, increase lithium utilization, and extend cycle life of Li-metal batteries, and (3) conduct mechanistic studies on lithium deposition behavior to lay groundwork for future improvement of Li-metal batteries.

Out-Year Goals. The long-term goal of the proposed work is to enable Li-metal and Li-ion batteries with a specific energy of > 350 Wh/kg (in cell level), 1000 deep-discharge cycles, 15-year calendar life, and less than 20% capacity fade over a 10-year span to meet the goal of the EV Everywhere Grand Challenge.

Collaborations. This project collaborates with C. Wang of PNNL on characterization by transmission electron microscopy / scanning emission microscopy (SEM); K. Xu and M. Ding of U. S. Army Research Laboratory on differential scanning calorimetry (DSC) measurements; A. Bates, Y. Preger, and L. Torres-Castro of Sandia National Laboratory on DSC microcell tests; Y. Zhang and A. Simmons of ANL on electrospinning polyimide, polysulfone, and polycarbonate porous membranes; and X. Shan and G. Xia of University of Houston (UH) on studying SEI formation using reflection interference microscope.

Milestones

- 1. Evaluate thermal properties of polyimide and polyethylene separators in Li||NMC cells during heating. (Q1, FY 2022; Completed)
- 2. Evaluate cell performance and thermal properties of other separators in Li||NMC cells. (Q2, FY 2022; Completed)
- 3. Fabricate 3D-structured current collectors and characterize their physical properties; elucidate influencing factors on lithium deposition/stripping behavior by *in situ* characterization. (Q3, FY 2022; Completed)

4. Evaluate effect of new separator and 3D-structured current collector on cycling performance of Li||NMC cells. (Q4, FY 2022; In Progress)

Progress Report

Fabrication of 3D Current Collector

The 3D current collector has great potential to suppress lithium dendrite growth due to its increased surface area and pore volume that can improve lithium utilization and therefore increase the energy density of Li-metal batteries. However, the mainstream 3D current collectors are carbonaceous materials, which suffer from poor wettability with metallic lithium and relatively poor flexibility. To address these issues, a 3D current collector based on polymer fibers was designed and synthesized.

 (a) Pristine Electrospun PI
 (b) Cu/PI Current collector
 (c) EDX of Cu/PI Current collector

 V00
 O-K

 V00
 O-K

 V00
 C-K

 V00
 C-K
</t

Figure 112. (a-b) Scanning electron microscopy images showing morphologies of (a) pristine polyimide fiber and (b) polymeric 3D current collector (Cu/polyimide membrane). (c) Energy dispersive X-ray spectroscopy image showing copper distribution of Cu/polyimide membrane.

Electroless plating was selected to transform the insulating polymer fibers to electronically conductive matrix.

Electrospun polyimide was selected as the precursor because of its high thermal stability. The copper-coated polyimide (Cu/polyimide) current collector was fabricated via electroless plating of polyimide porous

membrane in an appropriate electroless plating solution containing copper ions. The electroless plating conditions were carefully studied. The obtained composite materials were characterized with SEM. As shown in Figure 112a, the pristine electrospun polyimide fibers exhibit a smooth Figure 112b exhibits the morphology surface. of Cu/polyimide 3D porous membrane after electroless plating. It can be observed that a smooth layer of elemental copper is covered on polyimide fiber surface. It is also worth noting that the Cu/polyimide sample was not sputtered with any electronically conductive material prior to SEM characterization. Furthermore, the energy dispersive X-ray spectroscopy images in Figure 112c demonstrate uniform coverage of copper film on the surface of polyimide fibers, indicating that a porous, lightweight, and conductive current collector was successfully prepared. However, certain strands of the fiber are not fully covered with copper, as the C signals can still be observed. The synthesis process will be further optimized.

Investigations on SEI Formation using Reflection Interference Microscope (RIM)

The quality of SEI dictates the performance of Li-metal batteries. The team collaborated with X. Shan and G. Feng at UH to study the SEI formation behavior with *operando* RIM (Figure 113a). Two electrolytes, $1 \text{ mol } L^{-1} \text{ LiPF}_6$ in PC with and without 50 ppm water, were employed to study

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Figure 113. (a) Schematic diagram of using reflection interference microscopy to image the solid electrolyte interphase formation dynamics. (b) Cyclic voltammetry (CV) curves of the 1st three cycles in 1 M LiPF₆/PC with 50 ppm H₂O as additive. (c) The optical reflection signal along with three CV cycles on copper electrode in 1 M LiPF₆/PC with 50 ppm H₂O. (d) The corresponding current density (black curve and left axis) and voltage (red curve and right axis) in the 1st three cycles of CV scans. (e) The derivative of optical signals (the curve in c).

the effect of water additive on the SEI formation process. RIM exhibits extremely high sensitivity toward the SEI formation process. The thicknesses of LiF-rich inner layer and organic-rich outer layer can be correlated to the intensities of the RIM signals (Figure 113c-e). It is revealed that the presence of a trace amount of water (50 ppm) in the electrolyte induces a thicker and higher quality LiF-rich layer at the inner SEI and a much thinner organic-rich layer in the outer SEI, which leads to less electrolyte consumption, and more uniform lithium nucleation on the electrode surface.

Patents/Publications/Presentations

Publication

Jia, H., and W. Xu.^{*} "Electrolytes for High-Voltage Lithium Batteries." *Trends in Chemistry*, 4, no. 7 (2022): 627–642. doi: 10.1016/j.trechm.2022.04.010.

Presentations

- International Meeting on Lithium Batteries, Virtual, Sydney, Australia (June 28, 2022): "Influences of Electrolyte Additives on Lithium Deposition Behavior Revealed by In-situ Atomic Force Microscopy"; H. Jia, J. Tao, P. Gao, M. H. Engelhard, J-G. Zhang, and W. Xu.
- Vehicle Technologies Office Annual Merit Review, Washington, D. C. (June 22, 2022): "Lithium Dendrite Prevention for Lithium Batteries"; W. Xu. Poster.
- Materials Research Society Spring Meeting & Exhibit, Honolulu, Hawaii (May 9, 2022): "Functional Composite Separator for High Energy Density Lithium Metal Batteries"; H. Jia, H. Lim, C. Zeng, M. H. Engelhard, M. Weber, J-G. Zhang, and W. Xu.

Task 4.2 – Prelithiation for High-Energy Lithium-Ion Batteries (Yi Cui, Stanford University)

Project Objective. Prelithiation of high-capacity electrode materials is an important means to enable those materials in high-energy batteries. This study pursues three main directions: (1) development of facile and practical methods to increase 1st-cycle Coulombic efficiency (CE) of anodes, (2) synthesis of fully lithiated anode to pair with high-capacity, Li-free cathode materials, and (3) prelithiation from the cathode side.

Project Impact. Prelithiation of high-capacity electrode materials will enable those materials in the next generation of high-energy-density Li-ion batteries. This project's success will make high-energy-density Li-ion batteries for electric vehicles.

Approach. Silicon electrode film will be prepared by coating the slurry of silicon nanoparticles, carbon black, and binder mixture on copper foil through a doctor-blading method. The silicon electrode film will be prelithiated by pressing a Li-metal foil on top of it and heating it in an argon glovebox for a certain time. Then, Li_xSi electrode film can be obtained by removing the redundant lithium foil through a peeling-off approach. The redundant lithium foil is reusable for the next prelithiation. The structure, morphology, and other properties can be analyzed by scanning electron microscopy (SEM), transmission electron microscopy, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, X-ray diffraction, etc. In the first year, the team aims to fabricate Li_xSi freestanding electrode film and improve its air stability. In the second year, the team aims to improve the electrochemical stability in full cells.

Out-Year Goals. Materials containing a large quantity of lithium will be synthesized for pre-storing lithium ions inside batteries. Materials and processes will be developed to be compatible with battery electrode and cell fabrication. First-cycle CE of anodes will be improved and optimized by prelithiation materials. Materials for prelithiation from the cathode side will be developed.

Collaborations. This project engages in collaboration with the following: BMR principal investigators; SLAC National Accelerator Laboratory: M. Toney (*in situ* X-ray); and Stanford University: W. Nix (mechanics).

Milestones

- 1. Demonstrate a new solvent-free dry prelithiation strategy through *in situ* prelithiation. (Q1, FY 2022; Completed)
- 2. Demonstrate that the *in situ* prelithiation strategy can delicately control the prelithiation amount. (Q2, FY 2022; Completed)
- 3. Demonstrate that the *in situ* prelithiation strategy can achieve uniform prelithiation. (Q3, FY 2022; Completed)
- 4. Investigate the prelithiation kinetics in the *in situ* prelithiation strategy. (Q4, FY 2022; In progress)

Progress Report

Substantial improvements on energy density of Li-ion batteries require development of high-capacity electrodes. Silicon anodes that have high theoretical capacities (3579 mAh/g)—ten times higher than the conventional graphite anodes (372 mAh/g)—hold great potential for application in high-energy Li-ion batteries. However, silicon anodes exhibit a low initial CE of 50-80%, which means 20-50% of battery capacity will be lost after 1st cycle due to side reactions. Therefore, a strategy to compensate the initial active lithium loss and improve initial CE is urgently needed to prevent battery capacity degradation.

In the team's previous reports, they present a new solvent-free *in situ* prelithiation method. Prelithiation reagents are added to the battery in the battery assembly step, and prelithiation *in situ* takes place in the cell resting period based on shorting mechanism. This *in situ* prelithiation process addresses the challenges of cell reassembly and solvent compatibility in traditional prelithiation methods. They developed lithium meshes of different porosity as new prelithiation reagents to achieve controllable prelithiation in *in situ* prelithiation. Here, they further investigate the uniformity of *in situ* prelithiation through lithium meshes.



Figure 114. Uniformity of Li-mesh prelithiation method. (a) Cross-sectional scanning electron microscopy images of Li-mesh prelithiated silicon anode of three locations, center (m-center), edge (m-edge), and beneath (m-beneath), shown in the inset schematics. (b) Silicon 2p X-ray photoelectron spectra of Li-mesh prelithiated silicon anode of three different zones, sputtering time = 0.5 minutes.

The team's *in situ* prelithiation method achieves reasonable uniformity through Li-mesh patterning. Uneven prelithiation is not ideal because the accompanied irregular volume expansion is likely to cause high local stress and thus produce suboptimal electrode performance. To investigate uniformity of their prelithiation method, patterned p-70 lithium mesh was used as an example prelithiation reagent whose grid structure divided the silicon anode into 9 zones, among which, one center (m-center) and one edge (m-edge) were chosen for SEM and XPS characterizations. As shown in Figure 114a, the cross-sectional SEM images of Li-mesh prelithiated silicon anode in three different zones show similar features, indicating morphological homogeneity. Moreover, XPS study is conducted to study the chemical uniformity. The high-resolution spectra of silicon 2p peak in three zones of Li-mesh prelithiation were acquired (Figure 114b). The silicon 2p peak was deconvoluted into three components: Li_xSi at 98.2 eV, silicon at 99.2 eV, and Li_xSiO_y at 102 eV. As shown in Figure 114b, Li-mesh prelithiated silicon anode displays similar chemical compositions in the studied three zones.

Particularly, the similar Si/Li_xSi ratio indicates silicon anodes are prelithiated to similar degree in these three zones, supporting their achievement of chemically uniform prelithiation through Li-mesh design. These studies demonstrate homogeneity at different locations in the prelithiated electrodes. The uniformity along the thickness of the electrodes will need further studying.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 4.3 – Anode-Free Lithium Batteries (Ji-Guang Zhang and Xia Cao, Pacific Northwest National Laboratory)

Project Objective. The main objective of this project is to explore the feasibility of anode-free lithium batteries (AFLBs) for high-energy-density energy storage systems. An AFLB is an extreme case of Li-metal battery and Li-ion battery, where all active lithium is stored in cathode in the as-assembled batteries. Because of the many similarities among AFLBs, Li-metal batteries, and Li-ion batteries, extensive experiences and approaches developed for Li-metal and Li-ion batteries can be applied to AFLBs. Likewise, new approaches and knowledge to extend the cycle life and calendar life of AFLBs can also be used for development of Li-metal and Li-ion batteries, thus accelerating the market penetration of Li-based rechargeable batteries.

Project Impact. The ever-increasing need for electric vehicles (EVs) continually pushes the boundary of high-density energy storage systems. To date, the state-of-the-art Li-ion batteries consisting of graphite anode and high-voltage lithium intercalation cathodes cannot satisfy the energy demand from these applications. By replacing graphite anode with Li-metal anode, the specific energy density of Li-metal batteries can increase by more than 50% because Li-metal anode has a much higher specific capacity (3820 mAh g⁻¹) than that of graphite (372 mAh g⁻¹). To further increase the energy density of lithium batteries, the concept of AFLBs has been explored. An as-assembled or fully discharged AFLB consists of a cathode and an anode current collector (such as copper). All lithium source is stored in cathode. This cell design not only increases energy density of the battery, but also improves battery safety because no lithium metal is present in the battery in its as-assembled or discharged state. However, the cycle life of AFLBs is still very limited due to loss of active lithium during the cycling process. Therefore, there is an urgent need to understand the correlation between lithium Coulombic efficiency (CE), cathode CE, and electrolyte (including its electrochemical properties and consumption), as well as lithium dendrite growth and the formation of "dead" lithium, so that AFLBs and Li-metal batteries can be designed to achieve desired energy density and cycle life. In the end, the combination of these two efforts will accelerate the understanding and application of high-energy-density rechargeable batteries for EV applications.

Approach. This task will investigate the main factors affecting the performance of AFLBs and identify the solutions to enable long-term cycling and safety of these batteries. The lithium loss due to solid electrolyte interphase (SEI) formation and "dead" lithium generation by dendrite growth in the lithium deposition and stripping processes will be analyzed. The lithium dendrite suppressing principles and strategies for both liquid and solid-state AFLBs, ranging from materials design (electrolytes, cathodes, and current collectors), cell fabrication, operation controls (pressure, temperature, and cycling protocol) will also be investigated.

Out-Year Goals. The long-term goal of the proposed work is to enable lithium batteries with a specific energy of > 350 Wh/kg (in cell level), 1000 deep-discharge cycles, 15-year calendar life, and less than 20% capacity fade over a 10-year span to meet the goal of the EV Everywhere Grand Challenge.

Collaborations. This project collaborates with the following: C. S. Wang of University of Maryland on approaches to improve the CE of lithium cycling; C. M. Wang of Pacific Northwest National Laboratory on characterization by transmission electron microscopy / scanning electron microscopy; and Battery500 principal investigators on understanding and approaches to improve the calendar life of lithium batteries.

Milestones

- 1. Optimize cycling parameters of AFLBs to improve cycle life using localized high-concentration electrolyte with high CE and safety. (Q1, FY 2022; Completed)
- 2. Develop approaches to treat copper substrate to minimize lithium loss during cycling. (Q2, FY 2022; Completed)

- 3. Improve CE efficiency of electrolyte by forming a lithiophobic SEI layer. (Q3, FY 2022; Completed)
- 4. Extend the cycle life of AFLBs to be more than 100 cycles. (Q4, FY 2022; In progress)

Progress Report

The test protocol for AFLB and the type of cathode materials have significant influence on the cycling stability of AFLB such as Cu || Ni-Mn-Co (NMC) cells. As reported last quarter, the team found that the optimized discharge cut-off voltage of Cu||NMC cells is ~ 3.5 V. To further optimize the operating range of Cu||NMC cells, the effect of charge cut-off voltage on cell performance was investigated using both LiNi_{0.6}Mn_{0.2}Co_{0.2} (NMC-622) and LiNi_{0.8}Mn_{0.1}Co_{0.1} (NMC-811) cathodes. Figure 115a shows the electrochemical performance of Cu||NMC-622 and Cu||NMC-811 cells. In the cut-off voltage of 3.5-4.5 V, the Cu||NMC-811 cell demonstrates better capacity and cycling stability than the Cu||NMC-622 cell. Therefore, the

team has further investigated the Cu||NMC-811 cell using a charge cut-off voltage of 4.4-4.7 V and the same discharge cut-off voltage of 3.5 V. The results in Figure 115b-c show that the cell cycled with a charge cut-off voltage of 4.4 V



Figure 115. (a) Cycling performances of Cu||NMC-622 and Cu||NMC-811 cells cycled between 3.5-4.5 V. (b) Cycling performances and (c) Coulombic efficiencies of Cu||NMC-811 cells cycled with different charge cut-off voltages.

exhibits the most stable cycling stability (63% at 100^{th} cycle) with the highest cycling CE (99.65% at 100^{th} cycle). Thus, 4.4 V is considered the optimized charge cut-off voltage when matched with an optimized discharge cut-off voltage of 3.5 V.

The surface stability of copper anode is another important factor in the cycle life of AFLBs. The side reactions between the interface of copper current collector and liquid electrolyte during operation of AFLB will consume both lithium and electrolyte, therefore leading to reduced CE. To address this problem, an artificial protection layer [containing poly(ethylene oxide) coordinated with lithium salt (named PL_RX)] has been coated on the surface of copper anode in a process illustrated in Figure 116a-b (note that PLCu and PLCu RX represent polymer layer coated copper before relaxation/cooling). and after Figure 116c shows the cycling profiles and calculated average



Figure 116. (a) The schematic of lithium deposition/stripping on copper with and without PL_RX layer. (b) Digital photographs of the bare copper, PLCu, and PLCu_RX. (c) Lithium deposition/stripping voltage profiles of the bare copper and PLCu_RX with an average CE value. (d) Scanning electron microscopy images of the copper surfaces after lithium stripping from bare copper substrate and (e) PL_Rx coated copper substrate .

CEs of Li||Cu cells with or without the PL_RX layer. The results show that cells with and without PL_RX protected copper substrate exhibit CE of 99.65% and 99.3%, respectively. This is consistent with smoother surface morphology shown in Figure 116e, as compared to those shown in Figure 116d.

Patents/Publications/Presentations

Presentation

 Electrochemical Society Meeting, Vancouver, British Columbia, Canada (May 29 – June 2, 2022): "Anode-Free Li Metal Batteries with Localized High Concentration Electrolytes"; X. Cao, P. M. L. Le, Y. Jin, W. Xu, and J-G. Zhang.^{*}

TASK 5 – LITHIUM-SULFUR BATTERIES

Team Lead: Prashant N. Kumta, University of Pittsburgh

Summary

The collected work of the projects in this Task encompasses the following areas:

- Conducting focused fundamental research on the mechanism of "shuttle effect" inhibition for rechargeable Li-S batteries.
- Developing electrode and electrolyte systems that can mitigate the "shuttle effect" so the low self-discharge and long cycle life can be achieved.
- Synthesizing sulfur composite materials with an emphasis on polymer sulfur composite materials.
- Developing creative electrode-making processes to improve processability and aerial capacity; for example, polymeric sulfur composites may not be suitable for the traditional slurry casting process.
- Developing a novel S_xSe_y cathode material for rechargeable lithium batteries with high energy density and long life, as well as low cost and high safety.
- Delivering an electrochemically responsive self-formed hybrid Li-ion conductor as a protective layer for Li-metal anodes, enabling them to cycle with high efficiency.
- Developing high-energy, low-cost Li-S batteries with long lifespan.

Highlights

The highlights for this quarter are as follows:

- Task 5.1 led by K. Amine's group at Argonne National Laboratory continued work in Li-S systems. Their time-of-flight secondary ion mass spectrometry studies of the interphase of the cycled sulfur cathode and Li-metal anode indicate that their double-end binding (DEB) system showed clearly lower peak intensities for sulfur migration compared to the control of pure carbon and sulfur validated by observation of no sulfur migration layer in cycled electrodes of the DEB system containing ZnS, Co-N-C/S. Similarly, these systems show very weak sulfur signal due to formation of S-containing solid electrolyte interphase (SEI) layer on cycled Li-metal anode surface compared to the control. They also developed a 1 Ah Li-S pouch cell with an energy density of 350 Wh/kg, with their system exhibiting a specific capacity of ~ 1000 mAh/kg and calculation projecting attainment of 352 Wh/kg at electrolyte-to-sulfur (E/S) ratios of 4 μL/mg S with the cells sustaining only few cycles and failing at E/S of 2.5 μL/mg S. Electrochemical impedance spectroscopy (EIS) of the system under lean electrolytes and loadings of 14.3 mg/cm² S show a high charge-transfer resistance, R_{ct} of1800 Ω with low E/S ratio of 2 μL/mg S. These results demonstrate the promise of their system for attaining high energy density of 500 Wh/kg.
- Task 5.2 led by J. Liu's group at Pacific Northwest National Laboratory studied the structural differences between use of large particle cathode (LPC; low porosity of ~45% and high discharge capacity > 1000 mAh/g), and small particle cathode (SPC; high porosity) under lean electrolyte conditions of E/S = 4 µL/mg S using high-resolution synchrotron X-ray diffraction. Their results have shown that at 2.2 V, the a-S₈ peaks are rapidly converted to polysulfides, with LiPS decreasing in the subsequent discharge. In the 2.1-1.9 V range, the LiPS decreases with formation of Li₂S. In the SPC system, the conversion of S₈ to LiPS is sluggish, with large amounts of sulfur still being retained after discharging to 2.2 V coexisting until 2.1 V. At the end of discharge also, only weak peaks for Li₂S are seen, with strong peaks for LiPS. In the next step, the LiPS-to-Li₂S conversion is also restricted because only portions of the

LiPS can re-access the active surface to form Li_2S or Li_2S_2 , resulting in low capacity. These interesting results lay the framework of controlling the microstructure for achieving high energy density in the Li-S system using large particle electrodes.

- Task 5.3 led by Y. Cui's group at Stanford University report on their continuing work on all-solid-state batteries (ASSLSBs). Thev report further on the efficacy of 1.5-bis(2-(2-(2-Li-S methoxyethoxy)ethoxy)ethoxy)anthra-9,10-quinon (AQT) beyond the 1st activation cycle in ASSLSBs by testing the cycling performance of lithium sulfide (Li₂S) cathodes without/with AQT in Li-metal batteries (type 2032) with solid polymer electrolytes (SPEs). Results show that adding AQT considerably enhances cycling stability of ASSLSBs. The bare Li₂S cathode displays significant capacity fade from 579 m Ah/g to 384 m Ah/g within 20 cycles at 0.1C with a Coulombic efficiency of \sim 85%. On the other hand, the Li₂S@AQT systems shows a stable capacity of 997 m Ah/g after 20 cycles. The team attributes this difference to elimination of cumulative growth of insulating S/Li₂S film and reduced amount of soluble sulfur species in the SPE compared to the bare Li₂S that is further confirmed by EIS. These results demonstrate the potential of using redox mediators for realizing high-energy-density ASSLSBs.
- Task 5.4 led by E. Hu's group at Brookhaven National Laboratory in partnership with D. Qu at the University of Wisconsin, Milwaukee, report on research related to development of a novel bio-inspired nitrogen-doped carbon with a unique porous structure as carbon host of sulfur cathodes with the hierarchical porous structure serving to trap the high order polysulfides, while nitrogen dopants can serve to favorably enhance interaction between the host carbon and the long-chain polysulfide ions. They observed that carbonization temperature of 800°C was the best for a S:C ratio of 6:4, giving an initial discharge capacity of 1410 mAh/g at 0.1C. When they increased the sulfur content to S:C = 8:2, the system exhibited a capacity of ~ 600 mAh/g with a low decay rate of 0.043%/cycle. These results show the promise of these new N-containing polymers as sulfur hosts for high-energy-density Li-S batteries.
- Task 5.5. led by G. Liu's group at the University of California, Berkeley, focused their work on addition of a small amount of 1,3-dioxolane (DOL) solvent to their F4EO2 (or F4, that is, 1,1,1,2,2,3,3,4,4-nonafluoro-6-(2-methoxyethoxy)hexane) / TTE (1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether) (1:5) 0.5 M LiTSI amphiphilic electrolyte to improve the ionic conductivity and polysulfide solubility and thereby result in higher sulfur utilization. They therefore studied the addition of 10% by weight of DOL to the electrolyte to form a new electrolyte system, F4/TTE (1:5) 0.5M LiTFSI 10% DOL which showed a sulfur utilization reaching 1000 mAh/g. To explore the effect of the salt on the SEI layer on lithium metal, they studied using all or partial Li-bis(fluorosulfonyl)imide (LiFSI) salt in place for Li-bis(trifluoromethanesulfonyl)imide (LiTFSI) salt in a Li-S battery. They observed that F4/TTE (1:5) 0.5 M LiTFSI 10% DOL electrolyte gives the best capacity retention, while the capacities of the remaining two with LiFSI salt fade very rapidly with LiFSI additions, worsening the electrochemical response. Moreover, the Li-metal electrode with LiTSI appears smooth and shiny in the scanning electron microscopy images, whereas the surface with the LiFSI salt is filled with surface deposition, giving a dull appearance. They therefore conclude that LiFSI salt degrades the Li-metal electrode in a Li-S cell, possibly due to interaction of polysulfides with the bis(fluorosulfonyl)imide (FSI) anion. The results of these new electrolyte systems seem to show an interesting response indicating their promise for high-energy-density Li-S batteries.
- Task 5.6 led by Y. S. Meng's group at the University of California, San Diego, continued their work using the hexaazatrinaphthylene polymer sulfur (HATN-S) composite electrode. In this report, they specifically address generating a small batch of the hexaazatrinaphthylene / carbon nanotube (HATN/CNT) polymer composite ~ 200 mg by adding CNTs into the melting and polymerization process. The composite polymer then interacts with sulfur to form the HATN/CNT-S cathode. The cathode has a low porosity of 31%, and the optimized cathode was evaluated using a lean baseline electrolyte of E/S ratio of ~ 6 µl mg_{sulfur}⁻¹ by pairing with 100 µm Li-metal foils [N/P ratio of 5.7; that is, the capacity ratio between anode (negative electrode) and cathode (positive electrode)] received from General Motors. The HATN/CNT-S system delivers a capacity of ~ 1050 mAh/g sulfur and an areal capacity of ~ 3.6 mAh/cm² at 0.05C due to the CNT additive. They have reported achieving long cycling stability of 680 cycles with an areal capacity of ~2 mAh cm⁻² at 0.2C. They also developed a new electrolyte devoid of LiNO₃ exhibiting a capacity of

~ 1000 mAh/g S using C-S cathode at 0.05C with E/S ratio of 10 μ L/mg S. This electrolyte also yields an areal capacity of ~ 2.5 mAh/cm² with capacity retention of ~ 75% after 320 cycles as opposed to cells cycling for only ~ 75 cycles with the baseline electrolytes. These results demonstrate the promise of the HATN/CNT system for high-energy-density Li-S batteries.

- Task 5.7 led by P. N. Kumta's group at the University of Pittsburgh, Pennsylvania, focused their work on generating new sulfur confinement cathodes using aqueous polymer binder containing sugar monomer repeating units that not only finetune dissolution of polysulfides, but also modify the cathode interface. They have used a functional polymer binder with repeating cyclic monomer of new sugar molecule serving as a promising stabilizer. This new polymer binder with carbon framework matrix serving as the sulfur host material yields an initial discharge capacity of ~ 1090 m Ah/g, stabilizing at ~ 725 m Ah/g for over 25 cycles at a sulfur loading of 4.3 mg/cm² and E/S ratio of 8 µL/mg of S. They have also identified new porous inorganic covalent framework materials (PICOFM) with a specific surface area of ~ 1000 m²/g, enabling compact electrode preparation with a sulfur loading of 3.2 mg/cm². This PICOFM system shows an initial discharge capacity of ~ 950 m Ah/g, stabilizing at ~ 500 m Ah/g for over 80 cycles. They have additionally conducted computational studies using density functional theory to identify multicomponent alloy (MCA) anodes functioning not only as functional dendrite-free anodes but also as dendrite-resistant anode current collectors. Accordingly, they identified new low-density MCA alloys that can accommodate > 60 at% of lithium, resulting in more than 15 mAh/cm² areal specific capacity of lithium. These results show the promise of new confinement sulfur cathode systems and novel dendrite-free anodes and current collectors for high-energy-density Li-S batteries.
- Task 5.8 led by D. Wang's group at Pennsylvania State University focused on exploring the dependence of synthetic parameters on electrochemical performances of the sulfurized polyacrylonitrile (SPAN) baseline system. They have developed polysulfide-free SPAN, demonstrating performance with an initial discharge capacity of > 600 mAh/g based on the cathode weight at an E/S ratio of < 10 µL/mg following a heat treatment of 2 and 4 hours in ether-based electrolytes. Their results show that long heat treatment times yield amorphous patterns, while short heat treatment times of 2 hours result in crystalline patterns of sulfur with higher sulfur content yielding high initial discharge capacities of > 700 mAh/g based on the weight of the entire cathode; however, the system also demonstrated rapid fade in capacity, suggesting the need for a balance of heat treatment time and cycling stability. Based on these optimized synthetic strategies for SPAN baseline system, they have also leveraged the strategy for preparing sulfur polymerized composite (SPC) derived active materials containing heteroatoms (SPC-G2) with a short heat treatment time of 4 hours that demonstrates a high initial discharge capacity of > 650 m Ah/g based on the cathode weight, which shows desirable stability for 70 cycles in carbonate electrolytes. These results demonstrate the potential of SPAN and sulfur-containing polymerized composite systems for high-energy-density Li-S batteries.

Task 5.1 – Novel Chemistry: Lithium Selenium and Selenium Sulfur Couple (Khalil Amine, Argonne National Laboratory)

Project Objective. The project objective is to develop novel S_xSe_y cathode materials and advanced liquid electrolytes for rechargeable lithium batteries with high energy density and long life, as well as low cost and high safety.

Project Impact. Development of a new battery chemistry is promising to support the goal of plug-in hybrid electric vehicle and electric vehicle applications.

Approach. The dissolution of lithium polysulfides in nonaqueous electrolytes has been the major contribution to the low energy efficiency and short life of Li-S batteries. In addition, insulating characteristics of both end members during charge/discharge (sulfur and Li₂S) limit their rate capacity. To overcome this problem, sulfur or Li₂S is generally impregnated in a carbon-conducting matrix for better electronic conductivity. However, this makes it difficult to increase the loading density of practical electrodes. It is proposed to solve these barriers using the following approaches: (1) partially replace sulfur with selenium, (2) nano-confine the S_xSe_y in a nanoporous conductive matrix, and (3) explore advanced electrolytes with suppressed shuttle effect.

Out-Year Goals. This new cathode will be optimized with the following goals:

- A cell with nominal voltage of 2 V and energy density of 600 Wh/kg.
- A battery capable of operating for 500 cycles with low capacity fade.

Collaborations. This project engages in collaboration with the following: C. Sun and X. Zuo of Advanced Photon Source at Argonne National Laboratory (ANL), Y. Liu of the Center for Nanoscale Materials at ANL, and L. Cheng of the Materials Science Division at ANL.

Milestones

- 1. Fabrication of single-layer Li-S pouch cell with stable cycle life and *in situ* diagnostics. (Q1, FY 2022; Completed)
- 2. Development of 1 Ah Li-S pouch cell with a cell energy density of > 300 Wh/kg and stable cycle life. (Q3, FY 2022; Completed)
- Time-of-flight secondary ion mass spectrometry (TOF-SIMS) studies on the cycled lithium metal and sulfur cathode and optimization of Li-S pouch cells: cell-level diagnostic, electrolytes, and interlayer optimization. (Q3, FY 2022; Completed)
- 4. Development of novel SeS cathode with high areal capacity of >4 mAh/cm² for 100 cycles. (Q4, FY 2022; In progress)

Progress Report

This quarter, the team reports three updates in developing high-energy Li-S batteries, as discussed below.

TOF-SIMS Studies of Interphase of the Cycled Sulfur Cathode and Li-Metal Anode using Different Host Materials

The macroporous host with double-end binding (DEB) sites developed by the team has demonstrated excellent binding and catalytic effect against polysulfides and will be used as their standard carbon host for Li-S battery development in the future. To clearly understand its advantages over the traditional carbon host, they have conducted TOF-SIMS characterization on the cycled sulfur cathode and cycled Li-metal anode using different hosts. As shown in the TOF-SIMS depth profiles of S^{-} secondary ions in various cycled sulfur cathodes at 1 C for 100 cycles (Figure 117a), the cycled Ketjenblack (KB)/S and macroporous C/S cathodes exhibited the highest intensities of the sulfur migration layer caused by the lithium polysulfides shuttle, while the intensities of the S⁻ peaks in the case of macroporous C/ZnS/S and of macroporous C/Co-N-C/S became weaker, but still existed. No sulfur migration layer for the cycled macroporous C/ZnS,Co-N-C/S can be observed, confirming the effectiveness of the DEB sites in immobilizing polysulfides. Figure 117b compares the three-dimensional sulfur element reconstructions of the cycled sulfur cathodes, which show that the thickness of the sulfur migration layer follows a trend of macroporous C/ZnS,Co-N-C/S (Figure 117b, V)<macroporous C/Co-N-C/S (Figure 117b, IV)<macroporous C/ZnS/S (Figure 117b, III)<macroporous C/pure C/S (Figure 117b, II) <KB/S (Figure 117b, I). TOF-SIMS on the cycled lithium metal was also conducted to directly probe Li-metal corrosion. As shown in Figure 117c, many sulfur agglomerates were identified on the surface of the cycled Li-metal anodes in the cells with KB/S (Figure 117c, I) and macroporous C/pure carbon/S (Figure 117c, II) cathodes, indicating a severe shuttle effect and Li-metal corrosion. The intensities of the sulfur element on the surface of the cycled Li-metal anodes became weaker in the case of the single-end binding (SEB) sites (Figure 117c, III/IV), but were still visible, illustrating that the SEB sites cannot eliminate the shuttle effect and Li-metal corrosion. In sharp contrast, only a very weak sulfur signal due to formation of a S-containing solid electrolyte interphase (SEI) layer can be found on the surface of the cycled Li-metal anode using the DEB host (Figure 117c, V).



Figure 117. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) (a) depth profiles and (b) 3D rendering of S⁻ secondary ions distribution of cycled (I) KB/S, (II) Argonne National Laboratory macroporous C/S, (III) macroporous C/ZnS/S, (IV) macroporous C/Co-N-C/S, and (V) macroporous C/ZnS, Co-N-C/S cathodes after 100 cycles at 1 C. (c) TOF-SIMS S-element mappings on the surface of cycled Li-metal anode of (I) Li-KB/S, (II) Li-macroporous carbon/S, (III) Li-macroporous carbon/ZnS/S, (IV) Li-macroporous C/Co-N-C/S, and (V) Li-macroporous C/ZnS, Co-N-C/S cells after 100 cycles at 1 C. The color bar in (b) and (c) represents the signal intensity, with yellow representing high intensity and black representing low intensity. The region outlined by a red dashed line in (c) indicates the location of migrated sulfur species.

Developing 1-Ah-Level Li-S Pouch Cells with High Cell Energy Density of 350 Wh/kg

To further increase cell energy density of Li-S pouch cells, the team has reduced the electrolyte-to-sulfur (E/S) ratio from 4 μ L/mg to 2.5 μ L/mg. As shown in Figure 118a, the cell exhibits a main discharge working plateau of 2.05 V versus lithium and a specific capacity of ~ 1000 mAh/g. By considering the weight of all cell components (that is, cathode, anode, electrolytes, current collector, separator, etc.), the cell energy density is calculated to be 352.43 Wh/kg. Furthermore, as shown in results of the simulation using BatPaC (see https://www.anl.gov/cse/batpac-model-software), when cell capacity of Li-S pouch cells is increased to ~ 50 Ah, the cell energy density could be further increased to ~ 450 Wh/kg (Figure 118b). Moreover, the cost of their Li-S pouch cells will be significantly lower than that of current Li-ion batteries (Li-ion batteries). In addition, the natural abundance of sulfur could mitigate the critical raw material supply chain challenge of Li-ion batteries that use expensive and scarce nickel and cobalt elements. However, under a low E/S ratio of 2.5 μ L/mg, the cell could only sustain a few cycles of charge/discharge and then would exhibit sudden failure.



Figure 118. (a) The charge/discharge curve of the Li-S pouch cell using Argonne National Laboratory double-end binding host with an electrolyte-to-sulfur (E/S) ratio of 2.5 μ L/mg. (b) BatPaC simulation of the cell specific energy of the team's Li-S pouch cell based on various cell capacities.

Electrochemical Impedance Spectroscopy (EIS) Study of Li-S Batteries under Lean Electrolytes

In Li-S battery, the Li-ion transfer changes depend on the amount of electrolytes. In general, the lower the electrolyte amount in the cell, the slower the lithium ion transfer. To understand the rapid cell failure of Li-S batteries under lean electrolytes, the team has used EIS to reveal the impedance evolution during discharge of high mass loading sulfur electrodes at different E/S ratios. Figure 119a-c shows the 1st discharge curve of sulfur cathode with an areal sulfur loading of 14.3 mg/cm² at E/S ratio of 10 μ L/mg, 4 μ L/mg, and 2 μ L/mg, respectively. Figure 119d-c shows the corresponding EIS spectra at the 1st discharged state, which exhibit two semi circles at high and low frequency region, corresponding to interfacial (R_{int}) and charge-transfer (R_{ct}) resistances. As shown, for the cell with E/S ratio of 10 μ L/mg (Figure 119a) and 4 μ L/mg (Figure 119b), the cell can still exhibit two distinct discharge plateaus with R_{int} and R_{ct} resistances below 20 Ω (Figure 119d) and 200 Ω (Figure 119e), respectively. In contrast, when the E/S ratio is further reduced to 2 μ L/mg (Figure 119c), it shows only a short discharge plateau and increased R_{int} of the 400 Ω and R_{ct} of 1800 Ω (Figure 119f), which is mainly likely due to the substantial Li-ion transfer constraint at the interface. Figure 119g-i further shows the impedance evolution of high-loading sulfur electrodes during discharge at different E/S ratios, which shows that low E/S ratio significantly increases the resistance.

Indeed, it has been well discussed in the Li-S community that Li-metal failure and electrolytes deterioration will play a dominant role in the performance of Li-S batteries under high-loading cathode and lean electrolytes condition. On the one hand, it has been well known that the conventional 1,2-dimethoxyethane / 1,3-dioxolane electrolytes cannot enable efficient reversible lithium stripping/plating. For example, under high sulfur loading of 14.3 mg/cm² and 167.5 mA/g, the absolute current density applied onto lithium metal is as high as

2.4 mA/cm², raising a critical challenge (for example, dendrite formation) for the stabilization of lithium metal. On the other hand, lithium metal is highly reactive in contact with non-aqueous ether-based electrolyte solutions, which will inevitably consume a considerable quantity of electrolytes to form the SEI. Under lean electrolyte condition, the continuous parasitic reactions between lithium metal and electrolytes could result in electrolyte depletion of the cell, leading to large increase of the internal cell resistance (as shown in Figure 119c) and hence sluggish reaction kinetics of sulfur cathodes. Hence, further Li-metal protection technologies and cell configuration optimization (for example, internal pressure and tortuosity/porosity) are required to extend the cycle life.



Figure 119. Electrochemical characterization of Li-S cells at various electrolyte-to-sulfur (E/S) ratios. The 1st discharge voltage curves and electrochemical impedance spectroscopy results of sulfur cathode, with sulfur loading of 14.3 mg/cm² at 167.5 mA/g and E/S ratios of (a/d) 10 μ L/mg, (b/e) 4 μ L/mg, and (c/f) 2 μ L/mg. Inset in (d) shows the equivalent circuit. Panels (g-i) show the impedance evolution during discharge process at (g) 10 μ L/mg, (h) 4 μ L/mg, and (i) 2 μ L/mg. The red dotted circles in panels (a/b/c) correspond to the *ex situ* point shown in panels (g/h/i).

Patents/Publications/Presentations

Publication

Zhao, C., A. Daali, I. Hwang, T. Li, X. Huang, D. Robertson, Z. Yang, S. Trask, W. Xu, C. J. Sun, G. L. Xu,* and K. Amine.* "Pushing Lithium-Sulfur Batteries Towards Practical Working Conditions Through Cathode-Electrolyte Synergy." *Angewandte Chemie International Edition* (2022): e202203466.

Presentation

International Meeting on Lithium Batteries, Sydney, Australia (June 26, 2022 – July 1, 2022): "Cathode Engineering for High Energy and Stable Lithium Sulfur Batteries under Practical Pouch Cell Condition"; C. Zhao, G-L. Xu, and K. Amine. Poster.
Task 5.2 – Development of High-Energy Lithium-Sulfur Batteries (Dongping Lu and Jun Liu, Pacific Northwest National Laboratory)

Project Objective. The project objective is to develop high-energy, low-cost Li-S batteries with long lifespan. All proposed work will employ thick sulfur cathode ($\geq 4 \text{ mg/cm}^2$ of sulfur) at a relevant scale for practical applications. The diffusion process of soluble polysulfide out of thick cathode will be revisited to investigate cell failure mechanism at different cycling. The fundamental reaction mechanism of polysulfide under the electrical field will be explored by applying advanced characterization techniques to accelerate development of Li-S battery technology.

Project Impact. The theoretical specific energy of Li-S batteries is ~ 2300 Wh/kg, which is almost three times higher than that of state-of-the-art Li-ion batteries. The proposed work will design novel approaches to enable Li-S battery technology and accelerate market acceptance of long-range electric vehicles (EVs) required by the EV Everywhere Grand Challenge.

Approach. The project proposes the following approach: (1) to identify and address key issues of applying high-energy sulfur cathodes including materials, binders, electrode architectures, and functional electrode additives, (2) to advance the mechanism study of sulfur cathode and electrolyte by using *in situ / ex situ* techniques and custom-designed hybrid cell setup, and (3) to verify effectiveness of the new approaches with coin/pouch cells by using high-loading electrodes (> 4 mg/cm²), limited lithium (< 200% lithium excess), and lean electrolyte (electrolyte-to-sulfur, or E/S, ratio < 4 μ L/mg).

Out-Year Goals. This project has the following out-year goals:

- Fabricate Li-S pouch cells with thick electrodes to understand sulfur chemistry/electrochemistry in environments similar to those witnessed in real application.
- Leverage the Li-metal protection project funded by the U. S. Department of Energy and Pacific Northwest National Laboratory (PNNL) advanced characterization facilities to accelerate development of Li-S battery technology.
- Develop Li-S batteries with a specific energy of 400 Wh/kg at cell level, 1000 deep-discharge cycles, improved abuse tolerance, and less than 20% capacity fade over a 10-year period to accelerate commercialization of EVs.

Collaborations. This project engages in collaboration with the following: X-Q. Yang (Brookhaven National Laboratory, BNL), M. Cai (General Motors), J. Bao (PNNL), P. Khalifah (BNL), and Z. Liu (Thermo Fisher Scientific).

- 1. Build three-dimensional electrode models to understand electrolyte transport and sulfur reactions in high-loading and low-porosity sulfur electrodes. (Q1, FY 2022; Completed)
- 2. Optimize S/C material and electrode architecture to realize sulfur utilization > 1100 mAh/g in high loading electrode (> 4 mg S/cm²) with sulfur content > 70% and porosity < 35%. (Q2, FY 2022; Completed)
- 3. Study impacts of electrode architecture and topography on sulfur utilization rate and cell cycling. (Q3, FY 2022; Completed)
- 4. Process high-loading (> 4 mg/cm²) and dense (< 35% porosity) sulfur electrodes at a relevant scale for pouch-cell fabrication. (Q4, FY 2022; In progress)

Last quarter, the team demonstrated a concept of single-particle-layer electrode to realize low tortuosity in low-porosity sulfur cathode (that is, large particle cathode, or LPC). With such an LPC electrode, a high discharge capacity (> 1000 mAh g⁻¹) was successfully achieved in a low porosity (~ 45%) and high-loading sulfur cathode (~ 4 mg_s cm⁻²) at very lean electrolyte conditions (E/S = 4 μ L mg_s⁻¹). To understand the sulfur reaction processes in LPC, a high-resolution synchrotron X-ray diffraction (XRD) study was performed and compared with small particle cathode (SPC) with a multi-particle-layer structure.

Both LPC and SPC cathodes were charged/discharged to the designed voltages, and the transmission *ex situ* XRD data were collected. Figure 120a/c show the 1st discharge/charge profiles of the LPC and SPC electrodes under lean-electrolyte conditions (E/S = 4), respectively, where significant difference was observed for both

reversible capacities and voltage plateaus. The corresponding phase evolutions of S_8 , lithium polysulfides (LiPS), and Li₂S were also clearly identified by XRD for the SPC and LPC (Figure 120b/d). For simplicity, the comparison is focused on the main phases of S_8 , LiPS, and Li₂S by tracking their respective characteristic diffraction peaks: 2.86° and 3.2° for S_8 ; 1.2-2.6°, 2.4-2.6°, and 2.95-3.15° for LiPS; and 3.38° and 3.89° for Li₂S.

Before discharge, both the pristine LPC and SPC cathodes have an α -S₈ phase, but in an amorphous or nanocrystalline state. For the LPC electrode (Figure 120b), once the discharge process starts (cutoff at 2.2 V), the α -S₈ peaks quickly become very weak, indicating fast reaction kinetics. Accompanying this, a new set of diffraction peaks was observed in the 2-theta ranges of 2.4–2.6° and 2.95-3.15° (labeled with orange dashed squares), suggesting conversions of S_8 to LiPS. The



Figure 120. *Ex situ* synchrotron X-ray diffraction (XRD) characterization of the large-particle cathode (LPC) and small-particle cathode (SPC) at different depths of discharge. Typical 1st cycle discharge/charge curves and the corresponding XRD patterns (I = 0.19316) for the LPC (a-b) and SPC (c-d). Successive diffraction patterns are vertically offset by 6,000 relative to that of the pristine cathode (point 0, no offset).

intensity of the new peaks decreases in the subsequent discharging (cutoff: 2.1 V), indicating continuous reactions of LiPS. In the voltage range of 2.1 V to 1.9 V, with the decrease in LiPS diffraction intensity, a new set of peaks grows at 3.38° and 3.89° (labeled with violet dashed lines), corresponding to cubic-phase Li₂S.

While in the SPC electrodes, distinct behaviors were identified for each voltage range; in contrast to the quick disappearance of S_8 in the SPC electrode, the S_8 phase is still maintained at a high content after discharging to 2.2 V and coexists with the LiPS phase until 2.1 V. This suggests sluggish kinetics of the S-to-LiPS conversion. At the end of discharge, only very weak diffractions of Li₂S were identified, while the LPS diffractions stayed strong (Figure 120d). Compared to the LPC electrode, the SPC electrode has much slower S-to-LiPS reaction kinetics and lower conversion degree, which may be caused by restricted electrolyte wetting of high tortuous electrode. In addition, the LiPS diffuses out more quickly in the SPC and accumulates outside the electrode. During the next step, the LiPS-to-Li₂S conversion, only part of the LiPS can re-access the active surface and

form Li_2S (or Li_2S_2) passivation layers, blocking the inflow of LiPS. As a result, blocked LiPS inflow would speed up sulfur irreversible loss (Figure 120c), which explains the low capacity and very weak Li_2S diffractions in the SPC at the end of discharge (Figure 120d). More details of this study will be published in *Energy & Environmental Science* journal soon.

Patents/Publications/Presentations

Publication

Shi, L., C. S. Anderson, L. Mishra, H. Qiao, N. Canfield, Y. Xu, C. Wang, T. Jang, Z. Yu, S. Feng, P. M. L. Le, V. R. Subramanian, C. Wang, J. Liu, J. Xiao, and D. Lu. "Early Failure of Lithium–Sulfur Batteries at Practical Conditions: Crosstalk between Sulfur Cathode and Lithium Anode." *Advanced Science* 9 (2022): 2201640.

Presentation

 Vehicle Technologies Office Annual Merit Review (June 21–23, 2022): "Development of High-Energy Lithium-Sulfur Batteries"; D. Lu and J. Liu.

Task 5.3 – Nanostructured Design of Sulfur Cathodes for High-Energy Lithium-Sulfur Batteries (Yi Cui, Stanford University)

Project Objective. The charge capacity limitations of conventional transition metal oxide cathodes are overcome by designing optimized nano-architectured sulfur cathodes. This study aims to enable sulfur cathodes with high capacity and long cycle life by developing sulfur cathodes from the perspective of nanostructured materials design, which will be used to combine with Li-metal anodes to generate high-energy Li-S batteries. Novel sulfur nanostructures as well as multifunctional coatings will be designed and fabricated to overcome issues related to volume expansion, polysulfide dissolution, and the insulating nature of sulfur.

Project Impact. The capacity and cycling stability of sulfur cathodes will be dramatically increased. This project's success will allow Li-S batteries to power electric vehicles and decrease the high cost of batteries.

Approach. The approach involves three main efforts:

- Advanced nanostructured sulfur cathodes design and synthesis, including (1) engineer empty space into sulfur cathode to solve the problem of electrode volume expansion, (2) develop novel sulfur nanostructures with multifunctional coatings for confinement of S/Li polysulfides to address issues of active materials loss and low conductivity, (3) develop/discover optimal nanostructured materials that can capture the polysulfide dissolved in the electrolyte, (4) develop space-efficiently-packed nanostructured sulfur cathode to increase volumetric energy density and rate capability, and (5) identify interaction mechanism between sulfur species and different types of oxides/sulfides, and find optimal materials to improve capacity and cycling of sulfur cathode.
- Structure and property characterization, including *ex situ* scanning electron microscopy, X-ray photoelectron spectroscopy analysis, and *in operando* X-ray diffraction and optical microscopy.
- Electrochemical testing including coin cells and pouch cells as well as a set of electrochemical techniques.

Out-Year Goals. The cycle life, capacity retention, and capacity loading of sulfur cathodes will be greatly improved (200 cycles with 80% capacity retention, $> 0.3 \text{ mAh/cm}^2$ capacity loading) by optimizing material design, synthesis, and electrode assembly.

Collaborations. This project collaborates with the following: BMR principal investigators; SLAC National Accelerator Laboratory: M. Toney (*in situ* X-ray); and Stanford University: W. Nix (mechanics) and Z. Bao (materials).

- 1. Designing redox mediators (RMs) to facilitate Li₂S activation for all-solid-state Li-S Batteries (ASSLSBs). (Q1, FY 2022; Completed)
- 2. Understanding redox chemistry in ASSLSBs using *operando* X-ray absorption measurements. (Q2, FY 2022; Completed)
- 3. Demonstrating cycling performance of ASSLSBs with designed RMs. (Q3, FY 2022; Completed)
- 4. Enabling ASSLSBs with high area capacity and high energy density. (Q4, FY 2022; In progress)

The team further proved the efficacy of 1,5-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)anthra-9,10-quinon (AQT) beyond the 1st activation cycle in ASSLSBs by testing the cycling performance of lithium sulfide (Li₂S) cathodes without/with AQT in Li-metal batteries (type 2032) with solid polymer electrolytes (SPEs). As-assembled cells are first charged to 3.8 V for Li₂S activation and then constructed for galvanostatic cycling tests from 1.6 V to 2.8 V. Figure 121a-b shows that adding AQT significantly enhances cycling stability of ASSLSBs. For the bare Li₂S cathode, significant fade in capacity (from 579 mAh g_s⁻¹ to 384 mAh g_s⁻¹) is observed within 20 cycles at 0.1 C with a lower average Coulombic efficiency of 85%. In contrast, the Li₂S@AQT cell shows a stabilized capacity, retained at 997 mA h g_s⁻¹ after 20 cycles.

The enhanced cycling performance of $Li_2S@AQT$ cathodes is attributed to eliminating the cumulative growth of a thick insulating S/Li₂S film and decreasing the amount of soluble sulfur species in the SPEs, which are further confirmed by *in situ* impedance study. Before cycling, the impedance spectrum of the as-assembled bare Li_2S cells showed a larger semicircle than $Li_2S@AQT$ cells in the low-frequency region, which indicates higher charge-transfer resistance in the former case (Figure 121c-d). After cycling, the impedance of the $Li_2S@AQT$ cell remains low and stable over 10 cycles, in contrast to the high and increased impedance in the bare Li_2S cell. It is noted that the decreased impedance after the 1st cycle for bare Li_2S cathodes results from enhanced contact between cathodes and SPEs.



Figure 121. Electrochemical performance of Li₂S cathodes without/with AQT redox mediator (RM) in all-solid-state Li-S batteries. (a) Cycling performance and Coulombic efficiency of Li₂S cathodes without/with AQT at 0.1 C for 30 cycles. (b) Typical charge-discharge voltage profiles of Li₂S cathodes without/with AQT at the 5th cycle and the 20th cycle at 0.1 C. Nyquist plots of (c) the Li₂S-Li cell and (d) the Li₂S@AQT-Li cell before and after different cycles. Inset in (d) shows the zoomed-in Nyquist plot for the Li₂S@AQT-Li cell.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 5.4 –Investigation of Sulfur Reaction Mechanisms (Enyuan Hu, Brookhaven National Laboratory; Deyang Qu, University of Wisconsin, Milwaukee)

Project Objective. The primary objectives are as follows:

- To optimize and down select polymeric sulfur electrode. The team will focus on the overall dissolution of polysulfide in an electrolyte and effectiveness of polymeric sulfur electrodes.
- To develop small organosulfur materials for all solid electrolyte Li-S batteries.
- To continue developing alternative anode materials having low reactivity with dissolved polysulfide ions.
- To continue investigating the interaction of polysulfides in the cathode solid phase.

Project Impact. The results of this project will be used for development of technologies that will significantly increase energy density and cycle life and will reduce the cost of beyond Li-ion battery systems. This will greatly accelerate deployment of electric vehicles and reduce carbon emission associated with fossil fuel consumption and help in the direction of building the U. S.-based energy storage manufacture chains.

Approach. The team will first down select the cross-linked polymerized sulfur compounds, in which sulfur is attached to the conductive backbone with covalent bonds; therefore, the polysulfides can be immobilized within the matrix. They will also explore the small organosulfur molecules in all-solid-state Li-S batteries (ASSLSBs). They will continue exploring alternative anode materials that can cycle well and do not react with dissolved polysulfide and sulfur in the electrolyte to mitigate the "shuttle effect." In addition, they will continue to engage in fundamental *in situ* electrochemical investigations of the sulfur redox mechanisms to guide material and engineering designs. They will also continue optimizing alternative electrode fabrication processes.

One-Year Goals. The interim goal is to develop a Li-S battery with S-containing cathode of 600-800 mAh/g capacity with mitigation of the "shuttle effect."

Collaborations. The principal investigator (PI) works closely with beamline scientists at synchrotron facilities to develop novel Li-S characterization tools. The PI and co-PI collaborate closely with top scientists at Argonne National Laboratory, Lawrence Berkeley National Laboratory, and Pacific Northwest National Laboratory, as well as U. S. industrial collaborators at General Motors, Duracell, Clarios, etc. The PI and co-PI also collaborate with scientists in China, Japan, and South Korea. These collaborations will be strengthened and expanded to give this project a vision on both today's state-of-the-art technology and tomorrow's technology in development, with feedback from the material designer and synthesizers upstream and from industrial end users downstream.

- 1. Selection of small organosulfur compounds and complete design of all-solid-state testing. (Q1, FY 2022; Completed)
- 2. Complete initial testing of prelithiated tin anode. Complete initial testing of small organo-sulfur molecules in an ASSLSB. (Q2, FY 2022; Completed)
- 3. Complete testing of full Li-S cell with alternative prelithiated anode. Complete synthesis of potential polymeric sulfur materials. (Q3, FY 2022; Completed)
- 4. Complete testing full cell with selected polymeric sulfur, small organosulfur cathodes, and alternative anode. (Q4, FY 2022; In progress)

5. Complete investigations on the sulfur redox reaction mechanism in the solid phase in cathode and the interplay between dissolved polysulfide ions in electrolyte and sulfide compounds in the solid. Complete and continue testing of polymeric sulfur cathode, small organosulfur cathode, and alternative anode in full cell format. (Annual milestone; In progress)

Progress Report

Last quarter, the team reported an organo-sulfur cathode based on small organic molecule (dipentamethylenethiuram hexasulfide). A full ASSLSB cell was made. The cell retained 80% of its capacity after 500 deep cycles.

This quarter, they report research on development of a novel bio-inspired N-doped carbon with a unique porous structure as carbon host of sulfur cathodes. The hierarchical porous structures generated by a carbonization process can physically trap high-order lithium polysulfides and sustain the volume change of sulfur while N-dopant can enhance interaction between the host carbon material and long-chain polysulfide ions.



Figure 122. (a) Rate capability of S/NC750, S/NC800, S/NC900, and S/NC950 cathodes (carbonized at different temperatures of 750° C - 950° C) at different C-rates. (b) Galvanostatic charge-discharge curves of S/NC800 at different C-rates. (c) Cycling performance of S/NC800 composite with 80 wt% sulfur at the C-rate of 0.2 C.

Cells with different cathodes were cycled at various current densities from 0.1 to 2 C. As shown in Figure 122a, the S/NC800 (carbonized at 800°C) displays the best rate performance among all the samples (S:C ratio = 6:4). The S/NC800 delivered an initial discharge capacity of 1410 mAh g⁻¹ at 0.1 C. When the current rates were increased to 0.2C, 0.5C, and 1C, the corresponding reversible discharge capacities reduced to 786 mAh g⁻¹, 672 mAh g⁻¹, and 563 mAh g⁻¹, respectively. Even at a high rate of 2C, the S/NC800 still remained the highest

specific capacity of 497 mAh g⁻¹ among all the samples. As the current density was reduced back to 0.1C, the specific capacity of the S/NC800 recovered to 740 mAh g⁻¹, indicating good stability of the cathode. Figure 122b shows the charge/discharge profiles of the S/NC800 cathode at various current rates. Figure 122c shows cycling performance of S/N800 with a high content of sulfur (S:C ratio = 8:2). The capacity decay occurring in the initial 70 cycles could be attributed to the loss of excess sulfur that crystalized on the outer surface of the NC800 during the cycling process. Then, over the next 400 cycles, a low capacity decay rate of 0.0428% per cycle was observed.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 5.5 – New Electrolytes for Lithium-Sulfur Battery (Gao Liu, Lawrence Berkeley National Laboratory)

Project Objective. The project objective is to develop new electrolytes, additives, and electrode compositions for Li-S battery with high ion-conductivity, stable toward polysulfide, and promoting the polysulfide affiliation with the electrode substrate to prevent polysulfide dissolution.

Project Impact. This work will address the high cost and low energy density of Li-ion rechargeable batteries. The emerging Li-S batteries could feature both high energy density and low cost. This project enables applications of the low-cost, abundant sulfur element as a major chemical component for electrical energy storage. This project will develop new approaches for electrolytes and electrode compositions of Li-S rechargeable batteries.

Approach. This project aims to develop new electrolytes and additives for Li-S battery. The properties of the ideal electrolyte for sulfur electrode would be high ion conductivity, stable toward polysulfide, and promoting the polysulfide affiliation with the electrode substrate to prevent polysulfide dissolution. The project is designed to first understand the electrode substrate interaction with the polysulfides in different electrolytes. This will lead to better understandings of the polysulfide nucleation and precipitation mechanisms in common electrolytes. The second stage of the project will focus on chemically modifying the structures of the solvent and salt electrolyte molecules to increase electrolyte stability and ionic conductivity, to prevent polysulfide dissolution, and to promote polysulfide precipitation.

Out-Year Goals. The team will also investigate the contribution of Li-metal electrodes to overall Li-S battery performance and will develop methods to stabilize Li-metal surface.

Collaborations. This project collaborates with J. Guo and C. Zhu (Advanced Light Source / Lawrence Berkeley National Laboratory, LBNL), A. Minor (National Center for Electron Microscopy at LBNL / University of California, Berkely), G. Nagy and W. Heller (Neutron National Science User Facility / Oak Ridge National Laboratory), and P. B. Balbuena (Texas A&M University).

- 1. Synthesize and formulate amphiphilic electrolytes using combination solvents, salts, and ionic liquids. (Q1, FY 2022; Completed)
- 2. Optimize sulfur positive electrode to balance ionic and electronic conductivity, as well as dissolution and precipitation properties. (Q2, FY 2022; Completed)
- 3. Implement at least one strategy to stabilize Li-metal anode electrode. (Q3, FY 2022; Completed)
- 4. Combine the electrolyte, sulfur electrode, and Li-metal stabilization strategies to achieve stable cell cycling. (Q4, FY 2022; In progress)

Research this quarter explored the solvent, lithium salt, and mixed lithium salts as additives to stabilized lithium metal in the Li-S battery with amphiphilic electrolytes. As reported previously, the F4EO2 (or F4, that is, 1,1,1,2,2,3,3,4,4-nonafluoro-6-(2-methoxyethoxy)hexane) / TTE (1,1,2,2-tetrafluoroethyl-2,2,3,3tetrafluoropropyl ether) (1:5) 0.5 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) has superb capability to prevent polysulfide dissolution reaction during Li-S battery charge and discharge process. However, because of the extremely low polysulfide solubility, the sulfur utilization in the cathode is low. Additionally, the ionic conductivity of the electrolyte is also low due to the limited solvation capability of the F4 amphiphilic additives. The team explored the addition of a small amount of 1,3-dioxolane (DOL) solvent to the F4/TTE (1:5) 0.5 M LiTFSI electrolyte both to adjust polysulfide solubility and enhance electrolyte conductivity. In this case, 10% by weight of DOL is added to the electrolyte to form a new electrolyte composition of F4/TTE (1:5) 0.5 M LiTFSI 10% DOL. With the new electrolyte, the sulfur utilization in the electrode reaches over 1000 mAh/g. Two different lithium salts are used to investigate the effect to the Li-metal electrode. It was reported that the lithium bis(fluorosulfonyl)imide (LiFSI) salts tend to form better solid electrolyte interphase layer on lithium metal and graphite surface when used as salt and salt additives. Last quarter, the team reported that the Li-metal electrochemical deposition on copper surface forms smoother lithium deposition layer and has a high Coulombic efficiency when the LiFSI salt is used with F4/TTE (1:5) co-solvents, while Li-metal counter electrode is used. This quarter, they explored using all or partial LiFSI salt in place for LiTFSI salt in a LiS battery. The electrolyte compositions are formulated including F4/TTE (1:5) 0.5 M LiTFSI 10% DOL, F4/TTE (1:5) 0.5 M LiFSI 10% DOL, and F4/TTE (1:5) 0.25 M/0.25 M LiTFSI/LiTFSI 10% DOL. The LiS battery cycling results demonstrate the F4/TTE (1:5) 0.5 M LiTFSI 10% DOL electrolyte gives the best capacity retention, while the capacities of the remaining two with LiFSI salt fade rapidly. The more LiFSI salt added, the worse is the performance. The LiS cells after 20 cycles were dissembled and their electrodes analyzed under scanning electron microscopy. In Figure 123, the electrodes from the cells made with F4/TTE (1:5) 0.5 M LiTFSI 10% DOL, and F4/TTE (1:5) 0.5 M LiFSI 10% DOL are shown. The Li-metal electrode with LiTFSI salt electrolyte is smooth and appears shiny with a metallic luster, whereas the lithium metal with LiFSI salt is full of surface deposition and appears dull. The sulfur electrodes are all covered with sulfide depositions. The team concludes that the LiFSI salt degrades the Li-metal electrode in a LiS cell. It is likely that the polysulfides interact with FSI anion to interrupt the Li-metal surface.



Figure 123. Scanning electron microscopy images and photo images (inset) of LiS cell electrodes after 20 cycles. (a-b) Lithium anode (a) and sulfur cathode (b) using F4/TTE (1:5) 0.5 M LiTFSI 10% DOL electrolyte. (c-d) Lithium anode (c) and sulfur cathode (d) using F4/TTE (1:5) 0.5 M LiFSI 10% DOL.

Patents/Publications/Presentations

Patent

 Liu, G. "Novel Electrolyte Additives for Lithium-Sulfur Rechargeable Battery." U. S. Patent Application; filed May 2022.

Presentation

 Vehicle Technologies Office Annual Merit Review, Washington, D. C. (June 21–23, 2022): "Development of New Electrolytes for Lithium-Sulfur Batteries"; G. Liu. Task 5.6 – Strategies to Enable Lean Electrolytes for High Loading and Stable Lithium-Sulfur Batteries (Y. Shirley Meng, University of California, San Diego)

Project Objective. The project aims to develop high energy density (> 500 Wh/kg) and low cost (< 65 \$/kWh) Li-S pouch cells.

Impact. The project focuses on addressing the fundamental bottleneck in enabling high-energy-density Li-S batteries. This has been identified as the need to reduce liquid electrolyte excess and enable high areal loading electrodes. The challenges are overcome via the use of a dense polymer – sulfur electrode composite, which significantly reduces electrode porosity in conventional C-S systems while improving capacity retention. These capabilities, combined with project collaborator Ampcera's material scaling and collaborator General Motor's (GM's) pouch prototyping capability using thin lithium metal, will result in breakthroughs in next-generation Li-S battery chemistries that meet the energy density (> 500 Wh/kg) and cost goals (< \$65/kWh) of this project.

Approach. Novel electrode architectures using hexaazatrinaphthylene polymer – sulfur composite (HATN-S) electrode will be explored to reduce the porosity and increase the active loading of the composite electrode. Additionally, advanced electrolyte systems and optimization of Li-metal anode will be applied to further increase energy density of the Li-S pouch cell. If successful, the proposed HATN-S electrode should have less than 20% porosity with high areal capacities of > 10 mAh cm⁻², which will enable lean electrolyte conditions < 2 g/Ah in the full Li-S pouch cell.

Out-Year Goals. The out-year goals involve demonstration of baseline cell chemistries with reduced cathode porosity and increased cathode areal loading pairing with limited electrolyte and lithium inventory. The conventional electrode drying process (solvent evaporation) limits sulfur loading in the electrode, as higher loading leads to cracking. Thus, the HATN-S electrode will be prepared by optimizing the electrode architecture to increase sulfur loading and reduce electrode porosity. The electrolyte system will be optimized to reduce lithium usage (low N/P ratio) and improve cell stability.

Collaborations. Project collaborators include GM and Ampcera. This quarter, the work has been accomplished by University of California, San Diego (UCSD). Ampcera has scaled up the synthesis of hexaazatrinaphthylene (HATN) monomer and polymer and imported the nuclear magnetic resonance (NMR) solvent of CF₃COOD for HATN validation. GM provides thin lithium metal (100 μ m) and conventional C/S cathode materials for this project.

- 1. Achieve a benchmark performance metric of 80% capacity retention of HATN-S electrodes after 200 cycles using baseline electrolyte system. (Q1, FY 2022; Completed)
- 2. Process synthesis to demonstrate HATN-S electrode with reduced porosity and increased areal loading. (Q2, FY 2022; Completed)
- 3. Demonstrate cyclability of optimized HATN-S electrode with limited electrolyte and lithium inventory. (Q3, FY 2022; Completed)
- 4. Demonstrate stable cycling of optimized HATN-S electrode, which should be able to cycle with limited electrolyte (< 2 g/Ah) and low N/P ratios (< 1.2). (Q4, FY 2022; In progress)

Introduction

The project objective is to develop high energy density (> 500 Wh/kg) and low cost (< 65 \$/kWh) Li-S pouch cells. To achieve that, novel electrode architectures using the HATN-S electrode will be explored to achieve the low cathode porosity and high sulfur active loading of the composite electrode. Additionally, advanced electrolyte systems and the optimization of Li-metal anode will be applied to further increase the energy density of the Li-S pouch cell. If successful, the proposed HATN-S electrode will achieve < 20% porosity, significantly decreasing electrolyte usage with high areal capacities of > 10 mAh cm⁻², enabling lean electrolyte conditions < 2 g/Ah in the full Li-S pouch cell. This quarter, major activities include the following: (1) optimizing synthesis of HATN/CNT polymer – sulfur composite (HATN/CNT-S) electrodes with the baseline electrolyte, (3) identifying the passivation layer of Li₂S that protects lithium metal from polysulfide corrosion under lean electrolyte conditions, (4) updating long cycling behavior using the new electrolyte system for Li-S batteries to address capacity fade, and (5) evaluating the electrochemical performance of the GM C-S cathode for future study under lean electrolyte conditions.

Specifically, a small-batch synthesis for the HATN/CNT polymer composite (~200 mg) has been established by putting CNT into the melting polymerization process of the HATN polymer. HATN/CNT further composites with sulfur to obtain HATN/CNT-S cathode. The cathode has a low porosity of 31%, which is close to that of the HATN-S cathode (~ 29.8%, reported last quarter). The optimized HATN/CNT-S cathode was evaluated using a lean baseline electrolyte (electrolyte-to-sulfur, or E/S, ratio of ~ 6 μ l mg_{sulfur}⁻¹) by pairing with 100 μ m Li-metal foils [N/P ratio of 5.7, that is, the capacity ratio between anode (negative electrode) and cathode (positive electrode)] received from the team's collaborators at GM. Long cycling stability of 680 cycles with an areal capacity of ~ 2 mAh cm⁻² was achieved. Details of the cell construction and performance results are described in this report.

In a conventional Li-S system, LiNO₃ is required to form a LiN_xO_y-containing passivation layer that protects lithium from polysulfide shuttle. The results last quarter also revealed the issue of LiNO₃ depletion on cycling. New findings this quarter unveil that, due to the depletion of LiNO₃, the lithium inventory loss is the same by using lean baseline electrolyte and baseline electrolyte without LiNO₃. It is identified that the passivation layer on the lithium surface consists of solid electrolyte interphase compounds and Li₂S, which inhibits polysulfide corrosion. Last quarter's report presented the new electrolyte (NewEle) system using a stable alternative additive to avoid reliance on decomposition-based LiNO₃. This report illustrates that this new additive is non-sacrificial and enables bulky lithium deposition with a smooth, uniform passivation layer on the surface. Under lean lithium and electrolyte conditions using the NewEle, the C-S cathode features stable cycling behavior with a capacity retention of ~ 75% after ~ 300 cycles, in sharp contrast to the baseline LiNO₃-containing electrolyte that shows severe degradation after 75 cycles. Lastly, this report covers evaluating the electrochemical performance of the GM C-S cathode, which will be used for future study under lean electrolyte conditions.

Optimized Synthesis of HATN/CNT Polymer Composite and HATN/CNT-S Cathode for Li-S Battery (UCSD and Ampcera)

In the HATN-S cathode, carbon additives (CNT / super phosphorus mass ratio, 1/1) were mixed with HATN-S active materials during electrode making (last quarter). To improve the sulfur utilization (higher S-specific capacity, mAh g_{sulfur}^{-1}), carbon additive, that is, CNT, was introduced during the melting polymerization process of the HATN polymer (Figure 124a). The HATN monomer was synthesized as described in last quarter's report with a synthesis scale of > 10 g batches. Then, the monomer was mixed with CNT for 20 minutes by manual grinding, and the mixtures were transferred to a vacuum system for HATN polymerization. HATN polymer presents in bulky size (Figure 124b) and the HATN/CNT retains the bulk architecture as sulfur host materials (Figure 124c). First, the UCSD team has prepared a small batch of HATN/CNT (200 mg) in the laboratory. In

efforts to meet the scale-up targets (50 g per batch in Year 1) by Ampcera, the methodology of HATN/CNT synthesis can be easily transferred to Ampcera's production site for scale up. This quarter, the team reports the scaling up of monomer synthesis using larger flasks, while the vacuum sealing polymerization has a lab-scale limit of 10 grams per batch. Moreover, Ampcera has large vacuum sealing setups to realize the goal of 50 g per batch.



Figure 124. (a) The schematic of the synthesis of the HATN polymer and HATN / carbon nanotube (CNT) composite. (b-c) Field emission scanning electron microscopy images of (b) HATN polymer and (c) HATN/CNT composite.

Ampcera has assembled a lab-scale synthesis as part of the scale-up process. Several trials have been conducted to optimize the monomer synthesis process to obtain the product vellow-green (Figure 125). Α preliminary batch of HATN monomer (synthesized at Ampcera) was received by UCSD for NMR conformation. Using a proprietary polymerization process, Ampcera has been able to form the HATN monomer, which will be validated by UCSD using Fourier transform infrared and Brunauer-Emmett-Teller analysis. Further, Ampcera has already established the setup of scaling-up of the synthesis of the HATN monomer (Figure 126). Once the baseline is established, monomer synthesis will be scaled to deliver 50 g per batch by the end of Year 1. However, validation has been delayed due to supply chain issues associated with the NMR solvent.



Figure 125. The lab-scale trial of the HATN monomer synthesis at Ampcera.



Figure 126. The scaling-up synthesis of HATN monomer at Ampcera.

Benchmarking Electrochemical Performance of the Optimized HATN/CNT-S Electrodes (UCSD)

After preparation of the HATN/CNT polymer composite, sulfur was incorporated into this host material by sulfur melting infusion to produce the HATN/CNT-S composite. Figure 127a shows the field emission scanning electron microscopy image of a single HATN/CNT-S particle as prepared, showing its bulky nature. The energy dispersive X-ray spectrum (Figure 127b) measured within the circled region of Figure 127a shows sulfur signals with comparative intensity to that of carbon signals, indicating effective sulfur infusion into the HATN/CNT host. Then, a slurry recipe containing HATN/CNT-S composite, a small amount of binder, and carbon additive (super phosphorus) was applied to prepare the cathode electrode sheet using C-coated aluminum foil as the current collector for better adhesion, which contains a sulfur content of 64% (in the entire cathode). A low cathode porosity of ~ 31% was calculated with a moderately high sulfur loading of ~ 3.5 m_{sulfur} cm⁻². Figure 127c shows that the electrochemical performance of the HATN/CNT-S cathode was evaluated by pairing against the 100-µm Li-metal foil obtained from the team's collaborator, GM, and a lean electrolyte (E/S ratio of ~ 6 μ l mg_{sulfur}⁻¹) using baseline electrolyte [1 M LiTFSI in a DOL/DME mixture (1:1, v/v) with 2 wt% LiNO₃]. HATN/CNT-S delivers a higher S-specific capacity of ~ 1050 mAh g_{sulfur}^{-1} than ~ 900 mAh g_{sulfur}^{-1} for HATN-S cathode (last quarter). Further, an areal capacity of ~ 3.6 mAh cm⁻² at a formation current density of 0.05 C was achieved. This shows the effectiveness of constructing a better conductive network by adding carbon additive [that is, CNT (flexible)], to HATN polymerization directly without sacrificing the bulky host structure. The HATN/CNT-S cathode delivers subsequent areal capacities of 3 mAh cm⁻², 2.5 mAh cm⁻², and 2 mAh cm⁻² at 0.05 C, 0.1 C, and 0.2 C, respectively. The initial discharge plateau is observed to be slightly lower than that of the following because sulfur redistribution in the cathode is deterred by a slower initial wetting process and slower polysulfide diffusion in lean electrolyte conditions. Figure 127d presents the long cycling behavior of capacity retention of 80% after ~ 680 cycles with an areal capacity of ~ 2 mAh cm⁻² at 0.2 C. This indicates meeting the quarterly target milestone of the project by demonstrating the cyclability of optimized HATN/CNT-S cathode. By contrast, the C/S cathode is unable to cycle consistently under such lean lithium and electrolyte conditions (last quarter). The C/S cathode cycles at 0.2 C for less than 100 cycles with a drastic capacity decay due to rapid depletion of $LiNO_3$ in the baseline electrolyte. In last quarter's review meeting, the team reported that the high-performance liquid chromatography (HPLC) methodology was developed, and the LiNO₃ depletion issue was verified by the remarkable decrease in the intensity of absorbance peak of LiNO₃ in the HPLC – ultraviolet chromatogram. It is suggested that $LiNO_3$ is well preserved due to the use of a bulky host of HATN/CNT rather than the nanostructured carbon host in the conventional C-S cathode.



Figure 127. (a) Scanning electron microscopy image of HATN/CNT-S composite. (b) Energy dispersive X-ray spectrum of the yellow circled area in (a). (c) Voltage profiles of HATN/CNT-S cathode at different C-rates using 100 μ m lithium and electrolyte-to-sulfur (E/S) ratio of 6 μ l mg_{sulfur}¹, and (d) the corresponding cycling stability.

Updating Long Cycling Behavior Using NewEle System for Li-S Batteries (UCSD)

Last quarter, the team reported that the LiNO₃ reservoir limits cycling behavior of the Li-S battery in the baseline electrolyte, and there is a tradeoff between energy density and cycling stability. To realize the long cycling behavior and high-energy-density performance of Li-S batteries, the team is working to develop alternative electrolytes. The electrolyte design is based on considerations for Li-metal compatibility and polysulfide solubility. The team studied localized high-concentration electrolyte (LHCE) of Li-bis(fluorosulfonyl)imide (LiFSI) : 1,2-dimethoxyethane (DME) : 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) with a 1:1.2:3 molar ratio during the first quarter. The Li-S battery using this LHCE generates large polarization and very low S-specific capacity, though LHCE enables large granular lithium deposition morphology and high Coulombic efficiencies. Last quarter, the team designed the NewEle, which does not contain LiNO₃. A new type of N-containing salt is synthesized in the lab, and the resulting electrolyte shows high chemical compatibility with lithium metal, verified from the shiny surface of lithium observed when kept in the team's electrolyte for 48 hours (last quarter). Using the NewEle system, the Li-S battery can undergo a successful charge-discharge process without any over-charge issues that happen without LiNO₃. The team also demonstrates that both NewEle additive salt and $LiNO_3$ are more active and pivotal in the cathode part to preclude the over-charge problem, which is deemed as the "polysulfide shuttle" effect. In last quarter's review meeting, the team reported that NewEle contains only 10 mM of the as-synthesized additive, which is much smaller than ~0.4 M of LiNO3 in the baseline electrolyte (2 wt% LiNO3). In the NewEle system, the C-S cathode delivers a similar initial specific capacity of ~ 1000 mAh g_{sulfur}^{-1} at a formation current density of 0.05 C with a low E/S ratio of 10 μ l mg_{sulfur}⁻¹, compared to that of baseline electrolyte (Figure 128a). The C-S cathode delivers a higher S-specific capacity of 800 mAh g_{sulfur}⁻¹ than 600 mAh g_{sulfur}⁻¹ in the baseline electrolyte when cycling at 0.2 C, indicating higher sulfur utilization (practical S-specific capacity / theoretical S-specific capacity) in NewEle. Finally, the C-S cathode boasts stable cycling with an areal capacity of ~ 2.5 mAh cm⁻² with capacity retention of ~ 75% after 320 cycles (ongoing) using lean NewEle. In contrast, in the baseline electrolyte, the cells can only cycle for ~ 75 cycles before a drastic capacity drop (Figure 128b).



Figure 128. The cycling behavior of C/S cathode in baseline electrolyte of 1 M LiTFSI in a DOL/DME mixture (1:1, v/v) with 2 wt% LiNO₃ and in New Electrolyte, using 100 μ m lithium and E/S ratio of 10 μ l mg_{sulfur}⁻¹. Cycling behavior by S-specific capacity (a) and areal capacity (b).

In last quarter's review meeting, the team verified the consumption of LiNO₃ using the HPLC methodology (Figure 129a-b) by obtaining the liquid samples from the disassembled cells. It is evidenced that the LiNO₃ peak intensity of the cell after C-S cycling in baseline electrolyte is fragile, suggesting the depletion of LiNO₃ (Figure 129b). In contrast to the decomposition-based LiNO₃, in the next quarter, apart from figuring out whether the NewEle additive can be decomposed, the quantification of lithium and sulfur loss in NewEle will be conducted using both the C/S and HATN/CNT-S cathodes to identify the capacity loss root cause.

Electrochemical Performance of GM C-S Cathode (GM)

In the benchmarking scope of work, all the C-S baseline composite electrodes were studied using a low electrode loading. Compared to the high loading HATN-S (> 10mAh cm⁻²) electrodes demonstrated, the loadings of the C-S reference electrodes need to be increased for meaningful comparisons. However, due to the limitations of the slurry-based casing of low-density C/S-based composites, it is difficult to achieve such high-loading cast layers at the laboratory scale. To this end, GM has produced C/S cathode electrodes with high loading > 5mg-S/cm² by developing a new slurry coating technology (for example, plasma treatment of aluminum substrate) and further optimizing slurry compositions.



Figure 129. (a) Schematic of the high-performance liquid chromatography (HPLC) methodology used to investigate the LiNO₃ amount. (b) HPLC spectra of the fresh electrolyte, DOL/DME solvent, and LiNO₃ and LiTFSI in DOL/DME solvent.

Figure 130a shows the potential versus specific capacity retention curves of the GM C-S cathode with 5.2 mg_{-Sulfur}/cm². The areal discharge capacity can reach up to ~ 6 mAh/cm² initially under the first C/20 formation cycle with an E/S ratio of 8 μ L/mg, which quickly stabilizes at 4 mAh/cm² after switching to the C/10 discharge current rate for the following cycles. The cell lasts for about 50 cycles till the discharge capacity decreases to below 60% retention (Figure 130b). GM C-S cathode also shows major capacity decay by using the lean electrolyte. This quarter, GM has a personnel change in this project, and the delivery of GM C-S cathode to UCSD has been delayed. Next quarter, UCSD will evaluate the electrochemical performance of the high-loading GM C-S cathode and use it for future comparison studies.



Figure 130. Electrochemical performance of 5.2 mg_{-sulfur} / cm² sulfur cathode electrode (a) charge-discharge profiles and (b) discharge-discharge capacities and Coulombic efficiency versus cycle number.

Patents/Publications/Presentations

The project has a non-disclosure invention in preparation regarding the new electrolyte additive and formula.

Task 5.7 – New Engineering Concepts to High-Energy-Density Lithium-Sulfur Batteries (Prashant N. Kumta, University of Pittsburgh)

Project Objective. The major objectives of this project are to develop a Li-S pouch cell with a cell capacity > 300 mAh with energy density \ge 500 Wh/kg, \ge 750 Wh/L with cycling over 1000 cycles @C/3 rate, cycle life of 1000 at C/3 and \le 20% fade in energy @ C/10-C/3, and \le \$80/kWh. To achieve the proposed objectives, the following major goals will be successfully attained over the first year of the project: (1) identification of effective electrocatalysts and Li-ion conductors (LICs) lowering the activation barrier; (2) *in situ* synthesis of electrocatalysts and LIC dispersed complex carbon-based framework material (CFM) and sulfur nanocomposite with sulfur content \ge 90 wt%; (3) ~ 15 mAh/cm⁻² areal capacity of sulfur electrode with sulfur loading \ge 10mg/cm⁻²; (4) Li-containing structurally isomorphous alloy (Li-SIA) of \ge 1000 cycles with 15 mAh/cm⁻² areal capacity @C/3 rate; and (5) identification of optimal electrolyte compositions giving Li⁺ conductivities ~ 10⁻² S/cm and polysulfide dissolution < 1 ppm.

Impact. The work from this project will have a strong impact on development of high-energy-density Li-S batteries. The results of this work will lead to new knowledge on identification and generation of high-capacity sulfur cathodes and dendrite-free Li-metal anodes using scalable synthesis and fabrication approaches. Both fundamental and applied knowledge will be gathered from the study. Systematic characterization will provide new scientific insights into the mechanisms contributing to the corresponding response in coin-cell and pouch-cell formats. Results of this work also will likely have an impact on other fields such as electrocatalysts for water splitting and fuel cells and other fields engaged in electrochemistry. Plans are also in place to engage under-represented minority undergraduate students to gain research experience in various aspects of the project. With new materials identified as the project is executed, opportunities will emerge for filing invention disclosures, and provisional/non-provisional patent applications. The training and opportunities presented by this project to undergraduate and graduate students as well as postdoctoral research associates will foster next-generation work force training, equipping workers with the necessary skillsets to transform the quality of life all over the globe by generating high-energy-density systems that can be deployed in electric vehicles as well as in laptops and cell phones including innumerable portable and wireless devices, opening the doors to a new green and sustainable energy environment improving overall quality of life.

Approach. Work involves executing a theory-driven study directed at identification of electrocatalysts for efficient conversion of polysulfides to Li₂S during the forward discharge process and backward charge process to elemental sulfur and lithium. Also, first-principles computational approaches will be applied to identify solid-state LICs with conductivity $> 10^{-4}$ S/cm. Employing expertise in the principal investigator's laboratory, suitable low-temperature ($< 240^{\circ}$ C) scalable synthesis techniques will be used to generate theoretically identified electrocatalysts and LICs. Low polysulfide solubility and stable solid electrolyte interphase forming electrolytes will then be prepared from commercially available solvents, additives, and salts. The effectiveness of the electrocatalysts and LICs to improve the polysulfide to Li₂S transformation kinetics and the ability to achieve the targeted specific capacity by trapping polysulfides, including desired structural transformation during charging/discharging, will be assessed; accordingly, suitable modification of electrocatalysts and LICs will be performed to generate the ideal microstructures. Suitable modification if required of lithium allow as anode will also be performed by alloying with other metals to improve the Li-ion diffusivity kinetics and the Gibbs-Thomson parameter. The scalable approaches developed will be further refined to optimize sulfur utilization in the cathode, engineer the surface and bulk structure of the novel Li-SIA and lithium multicomponent alloy (Li-MCA) anodes to yield the desired areal capacity with optimal Coulombic efficiency, and finally optimize the electrolyte structure to minimize and eliminate polysulfide dissolution with desired Li⁺ conductivities. Finally, the developed systems will be scaled up, fabricated, and tested in pouch-cell configurations.

Out-Year Goals. The following goals will be achieved in subsequent years: (1) determine optimal cell component design parameters such as electrode thickness and porosity exhibiting minimal polarization while maintaining cathode capacity \geq 1500 mAh/gS, (2) demonstrate excellent cycle life of > 1000 cycles with > 80% capacity retention, (3) electrochemically test cells with dendrite-free Li-alloy anodes comprising Li-SIA and Li-MCA of areal capacity of ~ 15 mAh/cm², (4) electrochemically test cells with modified electrolytes at charge-discharge rages of C/3 as well as other C-rates of C/10-C/3, (5) fabricate > 300-mAh pouch cell giving energy density of greater or equal to 500 Wh/kg at C/3 rate and demonstration of acceptable performance at other C-rates of C/10-C/3, and (6) demonstrate cyclability of a minimum of 1000 charge/discharge cycles with < 20% fade rate for operation in -40°C to +40°C temperature ranges with temperature measured external to the pouch cell.

Collaborations. The project involves collaboration with G. E. Blomgran of Blomgren Consulting Services, Ltd.

- 1. Computational identification of electrocatalysts and LICs will be completed: 80% lower activation barrier of polysulfide to Li₂S transformation and a 10-times improvement of reaction kinetics will be achieved. (Q4, FY 2022; In progress, October 2022)
- 2. Synthesis and characterization of ~ 20-nm-sized electrocatalysts and LICs homogeneously dispersed in the CFM/S will be completed. (Q1, FY 2023; In progress, January 2023)
- 3. Dendrite-free growth study will be completed, and ≥ 1000 cycles cyclability tests @C/3 rate will be completed for dendrite-free anode technology innovation. (Q2, FY 2023; In progress, April 2023)
- 4. Modified electrolyte with high Li-ion conductivity (~ 10⁻² S/cm) and minimum polysulfide solubility (< 1 ppm) will be achieved. (Q3, FY 2023; In progress, July 2023)

This quarter, preliminary work initiated in the fabrication of new sulfur confinement cathodes is reported. Considering the goal of generating advanced cathode architectures in mind, attempts were made to modify the

aqueous polymer binder with functional group additives. These functional polymer binders contain sugar monomer repeating units that not only can finetune the dissolution of polysulfides but also serve to modify the electrode interface on the cathode. Therefore, the studies conducted by the team report on an aqueous processable biopolymer for sulfur cathodes. The polymer binder can play a vital role in improving the cycle life of Li-S batteries. In this report, accordingly, the use of functional polymer binder with repeating cyclic monomer of the new sugar molecule serving as a promising stabilizer for use in Li-S batteries to improve the cycle life is described. It was observed that during electrochemical cycling, the polymer binder short-chain polysulfides complexes likely formed during charge-discharge processes not only modify the kinetics of formation of short-chain polysulfides, but also reduce

polysulfide dissolution. The results highlight the importance of use of appropriate amounts of the polymer binder and carbon framework matrix serving as the sulfur host material for the efficient functioning of the functional groups with repeating cyclic monomer units in Li-S batteries. Figure 131 shows the electrochemical cycling performance of sulfur-infiltrated high-surface-area carbon-based complex framework materials (HCFM-S) cathodes containing the aqueous polymer binder, tested in Li-S battery. The HCFM-S containing cathode was cycled at 0.05C with an average electrode loading of 4.3 mg cm⁻² electrode area. The HCFM-S shows an initial discharge capacity of ~ 1090 m Ah g⁻¹, which stabilizes at ~ 725 m Ah g⁻¹ after the 12th cycle. On prolonged cycling, the HCFM-S shows a very stable capacity of ~ 725 m Ah g⁻¹ for over 25 cycles. The electrolyte-to-sulfur ratio used here was 8 μ l mg⁻¹. Efforts to increase the sulfur loadings with use of *in situ* synthesized LICs and functional electrocatalysts identified by theoretical studies to enhance the specific capacity are in progress and will be reported in subsequent quarters.

Another system that was studied included the synthesis of redox-active porous inorganic covalent-organic framework materials (PICOFMs) serving as cathodes in Li-S battery. These systems serve as a Li₂S_x reactive-type hosts to regulate polysulfide electrochemistry, likely facilitating the transformation into nanostructured Li₂S and sulfur within the porous PICOFM matrix. This specific PICOFM was selected since it likely provides good specific surface area of ~ 1000 m² g⁻¹, which enables compact electrode preparation with high sulfur loading on C-coated aluminum foil. Thus, the PICOFM-S cathode was tested for Li-S battery performance, and the electrochemical cycling performance of PICOFM-S is shown in Figure 132. The PICOFM-S cells were cycled at 0.05C with an average electrode loading of 3.2 mg cm⁻² electrode area. The PICOFM-S shows an initial discharge capacity of ~ 950 m Ah g⁻¹, which stabilizes at



Figure 132. Electrochemical cycling performance and Coulombic efficiency of porous inorganic covalent-organic framework materials – sulfur electrode cycled between 1.8-2.8 V at C/20 and 1.7-2.8 V at C/10 current rates.

~ 550 m Ah g^{-1} after the 30th cycle. On prolonged cycling, the PICOFM-S shows a stable capacity of ~ 500 m Ah g^{-1} for over 80 cycles. Efforts to increase the sulfur loading with use of *in situ* synthesized LICs and appropriate functional electrocatalyst identified by theoretical studies to increase the specific capacity of these systems are in progress and will be reported in subsequent quarters.



Figure 131. Electrochemical cycling performance and Coulombic efficiency of complex framework material – sulfur electrode cycled between 1.8-2.8 V at C/20 and 1.7-2.8 V at C/10 current rates.

Also, during this period, computational study was conducted with the goal to identify multicomponent alloy (MCA) anodes that can not only function as functional dendrite-free anodes, but also serve as dendrite-resistant anode current collectors. These MCA anodes were identified using density functional theory methods to demonstrate formation of uniformly disordered, metastable, *bcc* solid solution alloys isostructural with metallic lithium. Based on theory, the ability of the MCA anodes to incorporate large amounts of lithium (above 50 at%) was studied in the previous and present quarters. The aim is that these systems will be able to electrochemically alloy theoretically demonstrated amounts of lithium (> 50 at%) experimentally in prototype coin cells during electrochemical cycling without the formation of pernicious lithium dendrites. Additionally, the goal of this project is to explore the



Figure 133. Lithiated phase stability of various multicomponent alloys.

ability of the system to cycle more than 100 cycles, attaining a targeted specific capacity larger than 15 mAh cm⁻². In the previous experimental study, the synthesis of a specific steel-based MCA, namely, MCA1, was demonstrated exhibiting an areal specific capacity of 4mAh cm⁻² without dendrite formation up to 300 cycles at C/2 rate. The low areal specific capacity is due to an insufficient amount of lithium that is accommodated or alloyed by the host alloy, MCA1, displaying the metastable *bcc* crystal structure preventing this material from widespread use as an anode in the Li-ion batteries. Thus, there is a need to identify better alloys containing lower atomic weight elements and displaying stronger ability of the base alloy structure to accept high lithium content without inducing phase separation and/or formation of any intermetallic phases that undergo structural as well as large volumetric phase changes, consequently leading to failure of the electrodes and the cells.

Calculation of phase stability, shown in Figure 133, indicates that the metastable MCA1 alloy exhibiting the *bcc* phase can accommodate only up to ~ 33 at% of lithium without causing phase separation (black line and arrow in Figure 133), which is insufficient to yield the desired target specific capacity of 15 mAh cm⁻². To achieve this target capacity, there is a need to incorporate at least 50 at% of lithium into the structure and use lighter constituent elements to reduce the total weight of the assembled anode and the ensuing fabricated full battery. Thus, in the present computational study, lighter elements were selected, and the corresponding phase stability of the several compositions studied was calculated. As shown in Figure 133, several MCAs can incorporate a significantly higher amount of lithium than the earlier identified and generated MCA1 alloy. For example, MCA2 can accommodate more than 60 at% of lithium, resulting



in more than 15 mAh cm⁻² areal specific capacity. Also, MCA2, MCA4, and MCA5 demonstrate much lower gravimetric density than that of MCA1, thus rendering it possible to increase the specific capacity of the current collector as a Li-anode even further.

Another computational task conducted this quarter was identifying alloying elements facilitating the likely enhancement of Li-ion mobility in the identified MCAs, thus improving the overall cyclability and performance of the MCA anode. Using first principles nudged elastic band approach, the activation barriers for Li-ion diffusivity were calculated and collected in Figure 134. The higher the barrier, the lower the Li-ion mobility in the alloy. One can see that the alloying elements El1, El2, and El3 exhibit a higher barrier and thereby decrease the Li-ion mobility compared to pure Li-*bcc* metal, while El4, El5, and El6 are more favorable and thus will noticeably likely enhance Li-ion mobility.

Experimental validations of these theoretical findings are in progress and will be reported next quarter.

Patents/Publications/Presentations

Publications

- Datta, M. K., R. Kuruba, T. P. Rao, O. I. Velikokhatnyi, and P. N. Kumta. "New Approaches to High-Energy Density Cathode and Anode Architectures for Lithium-Sulfur Batteries." In *Lithium-Sulfur Batteries: Advances in High-Energy Density Batteries*. Edited by P. N. Kumta, A. F. Hepp, M. K. Datta, and O. I. Velikokhatnyi. Elsevier (2022): 354–439. ISBN: 978-0-1-819676-2.
- Lithium-Sulfur Batteries: Advances in High-Energy Density Batteries. Edited by P. N. Kumta, A. F. Hepp, M. K. Datta, and O. I. Velikokhatnyi. Elsevier (2022). ISBN: 978-0-1-819676-2.

Presentation

• Lehigh University, Bethlehem, Pennsylvania (April 19, 2022): "Perspectives on Materials for Energy Applications"; P. N. Kumta. Invited.

Task 5.8 – Development of Lithium-Sulfur Battery Cells with High Energy Density and Long Cycling Life (Donghai Wang, Pennsylvania State University)

Project Objective. The objective of this project is to develop a new soluble-polysulfide-free sulfur cathode with a high sulfur content (> 50 wt%) and high discharge specific capacity (> 700 mAh g⁻¹, based on the weight of the whole cathode), and demonstrate performance of the sulfur electrode at high electrode capacity (> 7 mAh cm⁻²), low N/P ratio [< 2; that is, capacity ratio between anode (negative electrode) and cathode (positive electrode)], and low electrolyte-to-sulfur (E/S) ratio (< 2.5 μ L mg⁻¹). Prototype Li-S pouch cells with predicted energy density of 400 Wh kg⁻¹ and 80% capacity retention for over 300 cycles using conventional electrolyte and Li-metal anodes with a protective layer developed by the team will be demonstrated.

Impact. This project aims to develop new sulfur composite active materials and functional polymer binders that enable polysulfide-free, high-performance, low-cost sulfur cathode. The use of these high-performance and low-cost sulfur cathodes, in turn, enables Li-S batteries with high energy density and long cycle life. Such Li-S batteries, made using the developed cathodes paired with a Li-metal anode, can lead to 50% greater energy density than conventional Li-ion batteries. Meeting the technical targets will potentially develop high-energy-density lithium batteries, promote increased adoption of electric vehicles and plug-in hybrid electric vehicles, and reduce petroleum consumption in the transportation sector by helping battery-powered vehicles become accepted by consumers as a reliable source of transportation.

Approach. The overall approach will focus on synthesizing and optimizing a novel polysulfide-free sulfur composite active material and functional binders. Specifically, approaches to realize the project objectives include the following: (1) development of novel polysulfide-free sulfur composite active materials, (2) development of new functional polymer binders to facilitate Li⁺ transport and trap residual lithium polysulfide; and (3) diagnostics, characterization, theoretical simulation, and cell tests on the developed materials in Li-S batteries.

Out-Year Goals. The out-year goals are as follows: (1) develop new sulfur composite active materials, and (2) conduct characterization, simulation, and performance tests on material and electrode levels. The *Go/No-Go Decision* will be demonstration of Li-S batteries using the developed sulfur composite active materials with an initial discharge specific capacity > 600 mAh g⁻¹ (based on cathode weight) at an areal capacity of 4 mAh cm⁻² and E/S ratio < 8 μ L mg⁻¹.

Collaborations. Pennsylvania State University will collaborate with the University of Illinois at Chicago on theoretical simulation.

- 1. Demonstrate sulfur cathode using sulfur composite active material (generation 1) with an initial discharge capacity > 500 mAh g⁻¹ (based on cathode weight), at E/S ratio < 10 μ L mg⁻¹. (Q1, FY 2022; Completed)
- 2. Demonstrate sulfur cathode using sulfur composite active material (generation 2) with an initial discharge capacity > 500 mAh g⁻¹ (based on cathode weight), at E/S ratio < 10 μ L mg⁻¹. (Q2, FY 2022; Completed).
- 3. Demonstrate sulfur cathode using sulfur composite active material (generation 1) with an initial discharge capacity > 600 mAh g⁻¹ (based on cathode weight), at E/S ratio < 10 μ L mg⁻¹. (Q3, FY 2022; Completed)
- 4. Demonstrate sulfur cathode using sulfur composite active material (generation 2) with an initial discharge capacity > 600 mAh g⁻¹ (based on cathode weight), at E/S ratio < 10 μ L mg⁻¹. (Q4, FY 2022; In progress)

Summary

This quarter, the team further explored the dependence of synthetic parameters on electrochemical performances (especially for specific capacity) of the sulfurized polyacrylonitrile (SPAN) baseline. Based on the experimental results, they optimized and developed polysulfide-free, SPAN active material and demonstrated its cathode performance with a high initial discharge capacity of > 600 mAh g⁻¹ (based on cathode weight) at an E/S ratio < 10 μ L mg⁻¹. Moreover, based on their optimized synthetic strategies of SPAN baseline, they also leveraged the strategy for the preparation of sulfur polymerized composite derived active material (sulfur polymerized composite – generation 2, or SPC-2) and demonstrated its cathode performance with a high initial discharge capacity of > 600 mAh g⁻¹ (based on cathode weight) and desirable cycling stability at an E/S ratio < 10 μ L mg⁻¹. They first worked on the synthetic parameter optimization and evaluation of the electrochemical performance of the SPAN baseline.

Optimization of SPAN Baseline

Different types of SPAN active materials have been prepared and tested. The key synthesis conditions were tuned to yield expected enhancements in electrochemical performances. The team mainly explored the dependence of the heating procedure on the initial specific capacity of obtained SPAN samples since it largely affected the chemical composition (for example, sulfur content) and directly determined the theoretical capacity of SPAN cathode materials (Figure 135a). In detail, SPAN cathodes were prepared implementing different heating procedures with varying heating times of 2 hours, 4 hours, 6 hours, and 7.5 hours. SPAN cathodes prepared with reduced heating time were deemed to deliver higher sulfur content and thus enhanced initial capacities. As shown in Figure 135b, SPAN powders synthesized from procedures with a heating time of 4-7.5 hours exhibited amorphous structures according to their X-ray diffraction patterns, indicating the good confinement of polyacrylonitrile to sulfur and the accessibility for the construction of polysulfide-free cells. While on a reduced heating procedure of 2 hours, the obtained powder showed the crystal structure of sulfur, demonstrating the remaining, not-well confined sulfur (that is, ring-structured S₈). Therefore, although this batch of SPAN powders could provide very high initial capacities due to the intrinsically high sulfur content, the as-fabricated cells would suffer from low cycling stability resulting from the undesirable side-reactions between the polysulfide and carbonate electrolyte. For electrochemical performance evaluation, sulfur cathodes using the above SPAN powders were fabricated with 80 wt% of active material and an areal loading of $\sim 2 \text{ mg SPAN cm}^{-2}$. Their electrochemical performances were tested in conventional ether-based electrolytes, as shown in Figure 135c. After optimization, the initial discharge specific capacity of the SPAN cathode (2 hours and 4 hours) after activation could reach > 700 mAh g^{-1} (based on the weight of the whole cathode). Such initial discharge specific capacity fulfills the target for this reporting period. Two voltage plateaus at 2.36 V and 2.17 V were well defined on discharging. Despite its much-enhanced initial capacity, SPAN cathode (2 hours) demonstrated relatively fast capacity decay and limited cycling stability. Therefore, a balance should be further struck between reduced heating time (that is, sulfur content) and cycling stability to maximize the advantages of polysulfide-free Li-S cathodes in carbonate electrolyte, which the team will report on in upcoming quarters.



Figure 135. (a) Reduced heating procedure (that is, decreased heating time upon SPAN synthesis) was used to increase the sulfur content in obtained sulfurized polyacrylonitrile (SPAN) powders and improve the specific capacity. (b) X-ray diffraction spectra of SPAN cathodes synthesized with varying heating times from 2 hours to 7.5 hours. (c) Cycling performances of SPAN cathodes synthesized with varying heating times from 2 hours to 7.5 hours.

Optimization of Sulfur Composite Active Material (Generation 2)

In the team's SPC-2 cathode materials, heteroatoms are introduced to modify the backbones and side chains of previously reported sulfur polymerized composite – generation 1 (SPC-1) materials. The introduced heteroatoms could stabilize the sulfur chains in SPC-2 cathode materials on recurring conversion reactions for Li-S batteries in carbonate electrolyte, but would limit sulfur content as well as specific capacity. Therefore, according to the optimized synthetic strategy from the SPAN baseline system discussed above, they also leveraged an optimized fabrication method with reduced heating time (that is, 4 hours) for the synthesis of SPC-2 with both high initial capacity (sulfur content) and cycling stability. As a result, batteries based on optimized SPC-2 (4 hours) demonstrated enhanced initial specific capacity over 650 mAh g⁻¹ (Figure 136a). Such initial discharge specific capacity meets the target for this reporting period. In addition, due to the stabilization of introduced heteroatom in the sulfur chain, the obtained SPC-2 cathode also delivered high cycling stability. Benefiting from the combined advantages of introduced heteroatom and reduced heating procedure, the SPC-2-based Li-S cells demonstrated enhanced specific capacity and cycling performances compared with the SPAN baseline (Figure 136b).



Figure 136. (a) Cycling performances of optimized sulfur polymerized composite – generation 2 (SPC-2) cathodes with reduced heating procedure of 4 hours in carbonate electrolyte. (b) Optimized SPC-2 cathodes delivered enhanced specific capacities over 630 mAh/g compared with SPAN baseline in carbonate electrolyte.

Next quarter, the team will screen and optimize the electrolyte for the optimized SPC-2 materials and further improve the specific capacities of SPC-1 materials in both carbonate and ether electrolytes. The milestone for the next quarter would be demonstrating sulfur cathode using sulfur composite active material (generation 1) with an initial discharge capacity > 600 mAh g⁻¹ (based on cathode weight) at an E/S ratio < 10 μ L mg⁻¹. In addition, they will continue to optimize the synthetic parameters of SPAN baseline, SPC-1, and SPC-2 cathode materials.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

TASK 6 – LITHIUM-AIR BATTERIES

Team Lead: Ji-Guang Zhang, Pacific Northwest National Laboratory

Summary and Highlights

The Task objective is to develop rechargeable Li-O_2 batteries with long-term cycling stability through in-depth research on more stable electrolytes and highly efficient catalysts for air electrodes, protection of Li-metal anodes, and deeper understanding on the oxygen reduction reaction and oxygen evolution reaction mechanisms behind the electrochemical performance of Li-O₂ cells.

Highlights

The highlights for this quarter are as follows:

- The Argonne National Laboratory (ANL) team further investigated the formation of LiO₂ in an air electrode containing Ir₃Li. The discharge product morphology is made up of small primary particles (< 5 nm) that appear to be connected via amorphous regions to form much larger secondary particles of ~ 200 nm in size. These particles show no change under low electron beam accelerating voltage (80 kV); however, they eventually form Li₂O under a high-voltage electron beam (200 kV).
- The ANL / University of Illinois, Chicago (UIC) team investigated SnI₂ as a new bifunctional additive. The Sn²⁺ cation enables the formation of a Sn²⁺/Sn-Li artificial solid electrolyte interphase layer, and thus protects the anode from parasitic side reactions, oxygen/superoxide crossover, and shuttle effect of redox mediators. At a current density of 0.3 mA/cm², the discharge potential remained above 2.45 V over 100 cycles with 125 mM of SnI₂. This is much better than the cells with no additive or with LiI additive.
- The UIC team used density functional theory to investigate the Li₂CO₃/C formation on a (NbTa)_{0.5}BiS₃ catalyst as well as the stability of the catalyst. They found that the high-rate capability of the new (NbTa)_{0.5}BiS₃ catalyst is consistent with the extremely small surface energies found in these calculations. This is also consistent with experimental characterization by transmission electron microscopy that confirms the excellent stability of the catalyst.

Task 6.1 – Lithium-Air Batteries (Khalil Amine and Larry A. Curtiss; Argonne National Laboratory)

Project Objective. This project will develop new cathode materials and electrolytes for Li-air batteries for long cycle life, high capacity, and high efficiency. The goal is to obtain critical insight that will provide information on the charge and discharge processes in Li-air batteries to enable new advances to be made in their performance. This will be done using state-of-the-art characterization techniques combined with state-of-the-art computational methodologies to understand and design new materials and electrolytes for Li-air batteries.

Project Impact. The instability of current nonaqueous electrolytes and degradation of cathode materials limits performance of Li-air batteries. The project impact will be to develop new electrolytes and cathode materials that are stable and can increase energy density of electrical energy storage systems based on lithium.

Approach. The project is using a joint theoretical/experimental approach for design and discovery of new cathode and electrolyte materials that act synergistically to reduce charge overpotentials and increase cycle life. Synthesis methods, in combination with design principles developed from computations, are used to make new cathode architectures. Computational studies are used to help understand decomposition mechanisms of electrolytes and how to design electrolytes with improved stability. The new cathodes and electrolytes are tested in Li-O₂ cells. Characterization, along with theory, is used to understand the performance of materials used in the cell and to make improved materials.

Out-Year Goals. The out-year goals are to find catalysts that promote discharge product morphologies that reduce charge potentials and to find electrolytes for long cycle life through testing and design.

Collaborations. This project engages in collaboration with K. C. Lau (University of California, Norridge), Y. Wu (Ohio State University), and R. Shahbazian-Yassar (University of Illinois, Chicago).

- 1. Design functionalized cathodes to achieve high electrochemical performance of Li-O₂ batteries. (Q1, FY 2022; Completed)
- 2. Characterize cathode materials and investigate electrochemical behaviors. (Q2, FY 2022; Completed)
- 3. Gain understanding of the lithium superoxide discharge product resulting from use of new templating Ir₃Li alloy. (Q3, FY 2022; Completed)
- 4. Engineer new catalysts with improved catalytic performance to suppress side reactions. (Q4, FY 2022; In progress)

A major challenge for Li-O batteries is the high charge overpotential, which results in low energy efficiency. It was recently shown that lithium superoxide (LiO_2), which is a good electronic conductor and has a low charge overpotential, can be formed in a Li-O₂ battery using iridium as a catalyst. It was speculated that an Ir₃Li alloy

forms, acting as an effective template for growth of the LiO₂. In this previously reported work, Ir₃Li was thermally synthesized in bulk prior to implementation on the reduced graphene oxide cathode of a Li-O₂ cell. The discharge product was found to be nearly 100% LiO₂ and had a low charge potential, as was found previously when using iridium nanoparticles as the cathode. The team has further investigated formation of LiO₂ for the case of the Ir₃Li alloy and reports here on results.

A deep discharge of the Li-O₂ cell using the Ir₃Li-based cathode was used for investigation of the LiO₂ product by transmission electron microscopy (TEM). A low-resolution TEM image of a representative $\sim 80 \times 100$ nm large raspberry-shaped discharge product that was attached to the cathode surface is shown in Figure 137a. The raspberry-shaped secondary particle consisted of smaller primary particles of < ~ 5 nm. Additional secondary particles with similar morphology were also observed on the surface of the larger cathode particles, one of which is shown in Figure 137c. Selected area electron diffraction (SAED) was performed on the raspberry-shaped particle shown, and the diffraction pattern is provided in Figure 137b. The SAED pattern of the particle is consistent with that of LiO₂ surfaces. The TEM images taken at 80 kV were collected over a two-day time frame, indicating that the LiO₂ particles are quite stable.

The discharge product morphology is made up of small primary particles that appear to be connected via amorphous regions to form much



Figure 137. (a) Low-resolution transmission electron microscopy (TEM) image of discharge product particle. (b) Electron diffraction pattern of discharge product particle. (c) TEM image snapshots during electron beam irradiation of discharge product particle. (d) High-resolution image of particle formed during electron beam irradiation of discharge product. (e) Electron diffraction pattern of particle formed during electron beam irradiation of initial discharge product.

larger secondary particles, which suggests several possible formation mechanisms. Previously, experimental, and theoretical investigations of other types of materials grown in solution have demonstrated that similar morphologies result from the primary nucleation and growth of crystalline particles from solution, and subsequent diffusion-controlled agglomeration of these primary particles or 'secondary nucleation' of new particles on primary particles. In the case of the Ir₃Li cathode material in Li-O₂ battery, the discharge seems to result in formation of secondary particles of ~ 200 nm in size. The team refers to these secondary particles as ultra-nanocrystalline lithium superoxide (UNLS) because they are comprised of the very small (< 5 nm) primary particles and amorphous regions between them.

The UNLS particles show no change under low electron beam accelerating voltage (80 kV); however, they underwent reaction during a high-voltage electron beam (200 kV). Figure 137c is a combination of selected snapshots taken from the electron irradiation of a large hemispheric UNLS particle greater than 200 nm in diameter. It can be seen that the original hemispheric UNLS particle reduces in size and new platelet particles form on the surface of the original particle. Small platelet particles dissolved and redeposited onto larger particles. At the end of the series, one platelet particle grew to 90×70 nm in size. A high-resolution image of the newly formed platelet particle is shown in Figure 137d. The image shows that the platelet particle is highly crystalline. Electron diffraction was performed on the particle. The diffraction pattern, shown in Figure 137e, is consistent with diffraction peaks of Li₂O (that is, cubic, antifluoride structure).

This is the first time such large LiO_2 particles have been grown. In addition, they are remarkably stable compared to previously grown lithium superoxide that has a relatively short lifetime due to disproportionation. The growth of these large UNLS particles may be due to the use of large (up to 2 μ size) Ir₃Li particles for the cathode, which results in oxygen reduction reaction as well as nucleation/growth on the same substrate. Further study is required to determine more about the mechanism by which the UNLS discharge product is formed on the large Ir₃Li surfaces and why this morphology is particularly stable.

Patents/Publications/Presentations

Publication

Plunkett, S. T., C. Zhang, K. C. Lau, M. R. Kephart, J. G. Wen, D. Y. Chung, D. Phelan, Y. Ren, K. Amine, S. Al-Hallaj, B. P. Chaplin, H-H. Wang, and L. A. Curtiss. "Electronic Properties of Ir₃Li and Ultra-Nanocrystalline Lithium Superoxide Formation." *Nano Energy* 90 (2021): 106549. Note: This publication is associated with content this quarter and has not been reported previously.

Task 6.2 – Lithium Oxygen Battery Design and Predictions (Larry A. Curtiss / Anh Ngo, Argonne National Laboratory; Amin Salehi-Khojin, University of Illinois, Chicago)

Project Objective. The objective of this work is to develop new materials for Li-O_2 batteries that give longer cycle life and improved efficiencies in an air environment. New electrolyte blends and additives will be investigated that can reduce clogging and at the same time promote the cathode functionality needed to reduce charge overpotentials. New cathode and anode materials will be investigated that can work in conjunction with the electrolytes to improve cycle life in the presence of air components.

Project Impact. Li-air batteries are considered as a potential alternative to Li-ion batteries for transportation applications due to their high theoretical specific energy. The major issues with the existing Li-O_2 systems include degradation of the anode electrode, reactions with air components, clogging of the cathode, and electrolyte instability. Thus, this project is using a comprehensive approach to improve cycle life and efficiency through developing new materials for electrodes, and electrolytes that work in synergy.

Approach. The experimental strategy is to use cathode materials based on two-dimensional transition metal dichalcogenides (TMDs) that the team has found to be among the best oxygen reduction reaction / oxygen evolution reaction (ORR/OER) catalysts. These cathode materials will be combined with new electrolyte blends and additives that work in synergy to reduce charge potentials and increase stability of the Li-air system. Density functional theory and *ab initio* molecular dynamics simulations are used to gain insight at the electronic structure level of theory of the electrolyte structure, and function both in bulk and at interfaces with the cathode, anode, and discharge product. The team is using classical molecular dynamics to obtain understanding at longer length and time scales of processes occurring in the electrolyte and growth mechanisms of discharge products. They will also utilize a high-throughput (HT) screening strategy based on experiment and theory to develop a large database of properties and outcomes of electrolyte combinations that can be analyzed using machine learning to predict electrolytes and additives with the best performance.

Out-Year Goals. The out-year goals are to find electrolytes that give high capacities and long cycle life in an air atmosphere using HT screening.

Collaborations. This project engages in collaboration with R. Assary, J. G. Wen, and S. Tepavcevic of Argonne National Laboratory; B. Narayanan of University of Louisville; T. Li of Northern Illinois University; and F. Khalili-Araghi and R. Klie of University of Illinois, Chicago.

- 1. Investigation of a highly active tin sulfide (SnS)-based catalyst for high-rate Li-O₂ battery performance. (Q1, FY 2022; Completed)
- 2. Computational studies of the active sites and electronic structure of the SnS catalyst. (Q2, FY 2022; Completed)
- 3. Development of new electrolyte redox mediators (RMs) that work with the SnS catalyst to decrease charge potentials and computational studies. (Q3, FY 2022; Completed)
- 4. Investigation of new Li-anode coatings for longer life Li-O₂ batteries with high rates. (Q4, FY 2022; In progress)

Li-air batteries are considered as strong candidates for the next-generation energy storage systems designed for electrical transportation. However, low cyclability and low current rates are two major drawbacks that hinder these batteries from actual use as batteries. These issues necessitate discovery of novel electrocatalytic processes to significantly enhance the formation and decomposition of the products during battery cycling. The team is working on a system comprised of SnS nanoflakes (NF) / reduced graphene oxide (rGO) as a solid catalyst. The goal this work is to develop a system that enables operating the battery at high current rates of up to 1 mA/cm². It was reported previously that the catalytic activity of a SnS NFs / rGO catalyst for both ORR/OER occurring during the discharge and charge, respectively, far exceed those of state-of-the-art catalysts from carbon, noble metal, and TMD families. This quarter, the team investigated using a new bifunctional additivity for RM and lithium anode protection.

The bifunctional additive used in the electrolyte was SnI₂, which acted as the RM to enhance decomposition of the discharge product and as a reactant to protect the lithium anode. The Sn^{2+} cation enables formation of the Sn²⁺/Sn-Li electrolyte artificial solid interphase (SEI) layer, and thus protects the anode from parasitic side reactions. oxygen/superoxide crossover, and shuttle effect of RMs. On the other hand, the anion redox couple of I^{-}/I_{3}^{-} enables active mediation of Li₂O₂ during the process, which charging effectively reduces the charge potential. Thus, the SnI_2 is referred to as a bifunctional additive. At a current density of 0.3 mA/cm^2 , the discharge potential remained above 2.45 V over 100 cycles with



Figure 138. Characterization results of the anode in Li-air battery with redox mediator of Snl₂. The results include (a) X-ray photoelectron spectroscopy of tin three-dimensional region after 5 cycles. (b) Low-angle annular dark field and inserted bright field image of the tin protected anode. (c) Energy dispersive X-ray spectroscopy mapping of the anode surface. The area taken was from the rectangular box marked in (b). All scale bars represent a length of 100 nm. (d) Electron energy loss spectroscopy results from the same region of the tin protected anode surface. (e) Anode electrochemical impedance spectroscopy results. The dots represent the experimental data, and the lines represent the fitted data. Symmetrical study of electrolyte with the cell consists of two Li-metal electrodes for (f) attenuation test under different current densities and (g) long-time durability test of electrolyte at a constant current density of 0.5 Acm⁻².

125 mM of SnI₂. The charge potential for SnI₂ is as low as 3.5 V at the 1^{st} cycle and is gradually increased to 4.2 V after the 120^{th} cycle with capacity of 3000 mAh/g.

For comparison, the team performed the battery experiments with LiI as the most reported RM and SnS/rGO cathode. The battery with RM of LiI lasts for only 20 cycles before its discharge potential drops below 2.45 V. Since both LiI and SnI₂ involve the I'/I_3^- couple, it is concluded that the protective SEI layer formed from Sn²⁺ helps to achieve higher cycle life of the cell. In addition, the team noticed that LiI-mediated cells possess fewer life cycles than the cell without the additive. This early death of the cell may be attributed to the shuttling effect of LiI that poisons the anode with accumulated cycles. Furthermore, a battery with neither catalyst nor additive (rGO only) is only able to run for 12 cycles before reaching the discharge cut-off voltage. This is 10-times lower than the cyclability of SnI₂/SnS co-catalyst system.

X-ray photoelectron spectroscopy was carried out for studying the chemical composition of the protected lithium anode resulting from the reaction with SnI_2 . As shown in Figure 138a, two major tin peaks were

observed at 486.5 eV (Sn 3d5/2) and 495eV (Sn 3d3/2), which were indexed to Sn^{2+} . Moreover, two minor peaks located at 484.3eV (Sn 3d5/2) and 493eV (Sn 3d3/2) correspond to the formation of metallic Sn/Li-Sn components on the SEI layer. Transmission electron microscopy was also carried out to further study the SEI layer formed on the anode surface. Figure 138b shows the low-angle annular dark-field image, and the inset figure exhibits the bright-field image of the protected lithium anode. Energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) were performed on the selected region in Figure 138b to further identify the elemental composition of the protective surface (SEI layer) on the surface of the anode. As shown in Figure 138c, EDS mapping of a selected area reveals the existence of tin along with oxygen (dissolved in electrolyte). Figure 138d shows the EELS results of lithium K-edge and tin K-edge taken from the top of the same flake in Figure 138b. The sharp lithium K-edge and tin K-edge in the spectra confirm the presence of these elements in the surface layer after the 5th cycling of the batteries. At the same time, neither EDS nor EELS results show substantial existence of nitrogen or iodine. These results suggest the absence of shuttling effect resulting from RMs or parasitic side products (for example, Li₃N) during cycling, which further confirms the effectiveness and robustness of the Sn-based SEI layer under high current densities. In addition, electrochemical impedance spectroscopy was conducted on the anode, as shown in Figure 138e. The team's results indicate a rise in the charge transfer resistance from 15 Ω to 70 Ω after 20 cycles. Furthermore, the difference between the charge transfer resistance, Z_{Real} , from 15th to 20th cycles is < 5 Ω , implying that the SEI layer becomes stable.

Apart from the anode protection, it is also critical to confirm the long-term durability of the SnI₂ electrolyte. For this purpose, an attenuation test was performed on Li|Li symmetric coin cells with a fixed capacity of 0.2 mAcm⁻² and a current density sweeping between 0.1 mA cm⁻² and 2 mA cm⁻² (shown in Figure 138f). The team observed no loss in Columbic efficiency while the cell runs for up to 57 hours. The long-term performance of the lithium anode was also studied inside Li|Li symmetrical cells with the current density of 0.5 mA cm⁻² during stripping and plating (Figure 138g). Results indicate that the symmetrical cell was able to cycle for more than 1000 hours while the range of the operating voltage remains almost constant (-0.09 V to 0.09 V). These results confirm the robustness and high ionic conductivity of the SnI₂ electrolyte, which is suitable for fast charging.

Patents/Publications/Presentations

Publication

 Jaradat, A., C. Zhang, S. K. Singh, J. A. A. Ahmadiparidari, L. Majidi, S. Rastegar, Z. Hemmat, S. Wang, A. T. Ngo, L. A. Curtiss, M. Daly, A. Subramanian, and A-S. Salehi-Khojin. "High Performance Air Breathing Flexible Lithium–Air Battery." *Small* 17, no. 42 (2021): 2102072.

Task 6.3 – Development of a High-Rate Lithium-Air Battery Using a Gaseous CO₂ Reactant (Amin Salehi-Khojin, University of Illinois, Chicago)

Project Objective. The main objective of this project is to develop a novel strategy to enable operation of Li-CO₂ batteries at high-capacity high-rate with a long-cycle-life. The experiments will be performed in both Swagelok and pouch cells. In the former case, the team will use: (1) a novel co-catalyst system comprised of inexpensive and earth-abundant transition metal dichalcogenide (TMD) materials that work in synergy with ionic liquid (IL) – based electrolytes to enhance efficiency of reactions during discharge and charge processes, (2) a solution-based catalyst (redox mediator) to reduce charge overpotential and increase energy efficiency of the battery, (3) high-porosity cathode electrodes to increase electrode surface area, gas permeability, stability, electrical conductivity, and lifetime of battery operation, and (4) solid electrolyte interphase layer to protect the anode against oxidation without affecting the ionic transport of Li⁺ species in the system. At the pouch-cell level, the team will design and construct a stackable pouch cell to deliver a capacity of > 200 mAh.

Impact. Li-air batteries are considered as a potential alternative to Li-ion batteries for transportation applications due to their high theoretical specific energy. Most work in this area focuses on use of O_2 as the reactant. However, newer concepts for using gaseous reactants (such as CO_2 , which has a theoretical specific energy density of 1,876 Wh/kg) provide opportunities for further exploration. This project will produce a thorough understanding of key chemical and electronic parameters that govern the operation of Li-CO₂ batteries in realistic conditions. Achieving the project objectives will generate a library of fundamental properties of TMD- and IL-based electrolytes with the most promise for Li-CO₂ battery applications. The methodologies employed, and the insight generated, will also be valuable beyond advancing the field of Li-CO₂ batteries.

Approach. The above targets will be achieved through an integrated approach based on materials synthesis, testing, characterization, analysis, and computation. The team will synthesize catalysts and test them in cells along with developing new electrolytes and additives. These cathode materials with new electrolyte blends and additives will work in synergy to reduce charge potentials and increase battery stability. Density functional theory (DFT) and *ab initio* molecular dynamics simulations will be performed to understand battery operation and make predictions of new materials for the Li-CO₂ battery.

Out-Year Goals. The out-year goals are to find novel two-dimensional (2D) catalysts and IL-based electrolytes that give high capacities and long cycle life in a CO₂ atmosphere.

Collaborations. This project collaborates with L. A. Curtiss (Argonne National Laboratory), F. Khalili-Araghi (University of Illinois, Chicago, or UIC), A. Subramanian (UIC), and Z. Huang (Stockholm University).

- 1. Successful synthesis and characterization of bulk and 2D forms of six alloy TMDs for electrocatalysis and battery experiments. (Q1, FY 2022; Completed)
- 2. Successful exfoliation of TMD alloys with desired lateral sizes for battery experiments. (Q2, FY 2022; Completed)
- 3. Computation studies of surface stabilities of TMD alloy for batteries. (Q3, FY 2022; Completed)
- 4. Charge transfer properties of different TMD alloys. (Q4, FY 2022)
Progress Report

In the previous two quarters, the team reported on a novel combination of transition metal chalcogenide, $(NbTa)_{0.5}BiS_3$, as a cathode catalyst and a ZnI₂ additive that works in synergy with IL-based electrolyte to operate a Li-CO₂ battery at the high rate of up to 0.5 mA/cm². Their results indicate that at such a high current density, the battery can operate up to 125 cycles with the capacity of 0.25 mAh/cm². They now report on computational studies of the catalyst used in this battery and the reason it can operate at high rates.

DFT was used to investigate the Li_2CO_3/C formation on a (NbTa)_{0.5}BiS₃ catalyst as well as the stability of the catalyst. The team first investigated the energies of different (NbTa)_{0.5}BiS₃ surfaces including (001), (010), (011), (100), (101), (110), and (111). The surface energies were determined for different terminations of each facet, including niobium, tantalum, sulfur, and bismuth terminations. All 21 surfaces were optimized with and without spin polarization due to the possible magnetic properties. The equation given below was used to calculate the surface energies for each niobium, tantalum, sulfur, and bismuth termination of the different (NbTa)_{0.5}BiS₃ surfaces.

$$\sigma = \frac{1}{2A} (E_{slab} - n_{slab} E_{bulk})$$
(2)

where, A is the area of the surface, E_{slab} is the energy of the slab, E_{bulk} is the energy of one unit in the bulk, and n_{slab} is the number of bulk units in the surface slab. Figure 139a shows the surface energies calculated for all the surfaces for the spin polarized case, and Figure 139b shows results for the cases without spin. For spin polarized calculations, the Nb-terminated (110) surface has the lowest surface energy of 0.000044 eV/A², while the Nb-terminated (010) surface is the lowest surface energy of 0.0044 eV/A² for non-spin calculations. The energy difference between these two surfaces is very small, so the team can assume that they are similar. They note that the high-rate capability of the new (NbTa)_{0.5}BiS₃ catalyst is consistent with the extremely small surface energies found in these DFT calculations, which suggests that by use of a multielement alloy the catalyst can be very stable and withstand high current density without degradation. This is also consistent with experimental characterization by transmission electron microscopy that confirms the excellent stability of the catalyst.



Figure 139. (a) Surface energies for spin polarized surface. (b) Surface energies for without spin polarized surface. (c) Top and side views of (i) Ta-terminated, (ii) Nb-terminated, and (iii) Bi-terminated (NbTa)0.5BiS3 (110) surfaces. The niobium, tantalum, bismuth, and sulfur atoms are in green, blue, purple, and yellow, respectively. (d) The potentialdependent mechanistic analysis of Li₂CO₃ and carbon formation on a Nb-terminated, (NbTa)0.5BiS3 (110) surface. Adsorption configurations are present in the bottom panels. The niobium, tantalum, bismuth, sulfur, carbon, and oxygen atoms are in green, blue, purple, yellow, brown, and red, respectively.

Based on the above calculations showing many possible facets and terminations with very low surface energies, the team chose the (110) facet to investigate the reaction mechanism for C/Li_2CO_3 formation. The mechanism was evaluated on three (110) terminated (NbTa)_{0.5}BiS₃ surfaces, that is, niobium terminated, tantalum

terminated, and bismuth terminated. The structures of these surfaces are shown in Figure 139c. For the free energy calculations, they considered the entropy changes and zero-point energies for CO_2 adsorption step by assuming these two terms are small and negligible for surface reactions. The potential dependence for free energies was calculated based on the computational hydrogen electrode by referencing to the Li/Li⁺ electrode.

The potential dependent reaction mechanism for Li_2CO_3 and carbon formation on the Nb-terminated (110) $(NbTa)_{0.5}BiS_3$ surface, the most stable termination from the team's calculations, is displayed in Figure 139d. The applied potentials were intended to level up the potential dependent step, that is, CO and Li₂CO₃ formation step. The CO_2 adsorption with a Nb-O bond is slightly exergonic with a free energy of -0.01 eV. After CO_2 adsorption and dissociative adsorption of a second CO_2 , the formation of co-adsorbed CO^* and CO_3^* (CO^*/CO_3^*) is favorable, with negative free energy of -0.77 eV. The third step involves the $(Li^+ + e^-)$ pair transfer resulting in Li_2CO_3 formation with CO remaining on the surface (CO^{*}). This step is quite downhill (-4.18 eV) and is potential dependent due to addition of electrons. This electrochemical step is favorable below $\sim 2.09 \text{ V}$ versus Li/Li⁺, which is approximately consistent with the experimental discharge potential considering the approximation made in the model such as the lack of explicit electrolyte molecules. The most stable adsorption geometry for the remaining CO^{*} is the niobium site, indicating it is still the active site. The process by which the amorphous carbon forms to satisfy the bulk reaction stoichiometry can be explained by a reaction of another CO₂ with CO^{*}, which is only slightly endothermic on this surface with a reaction energy of 0.19 eV. In this adsorption configuration, CO₃ binds on the niobium site, while carbon binds on the 3-fold site of Nb-S-S. It is notable that Nb-terminated (110) surface is more favorable for C^*/CO_3^* formation compared with the Ta-terminated and Bi-terminated surfaces. These reaction pathways help explain the reaction mechanism on this new catalyst for a Li-CO₂ battery.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

TASK 7 – SODIUM-ION BATTERIES

Team Lead: Xiao-Qing Yang, Brookhaven National Laboratory

Summary

The Na-ion battery will require investigations to identify optimal electrode materials, electrolytes, separators, and binders to reach full potential. The BMR program will therefore have a limited effort directed toward identifying Na-ion battery materials that have potential value for vehicle applications. Progress on these projects this quarter is described in this report.

Highlights

The highlights for this quarter are as follows:

- The Argonne National Laboratory team has revealed the fundamental mechanism of synthesis-induced native lattice strain in triggering the structural earthquake in sodium layered oxide cathodes by advanced microscopy characterization, and further developed a single-crystalline high-entropy P2-type Mn-rich sodium layered oxide cathode that demonstrated significantly improved structural stability during high-voltage charge/discharge and enhanced thermal tolerance.
- The Brookhaven National Laboratory team completed *in situ* X-ray absorption spectroscopy studies for P3-structured Na_{0.66}[Cu_{0.33}Mn_{0.67}]O₂. The X-ray absorption near-edge structure (XANES) data of copper K-edge during the 1st cycle shifted to higher energies during charge and shifts back to lower energy during discharge. In contrast, the edge position of manganese XANES is mostly unchanged during the whole charge-discharge process. This clearly indicates that copper is the active element contributing to the capacity during charge-discharge, while manganese is inert. The Fourier transformed extended X-ray absorption fine structure results confirmed this conclusion.
- The Lawrence Berkeley National Laboratory team extended their investigation of the effect of the identity of the interlayer cation on the electrochemical performance of lepidocrocite titanate to include Li⁺, Na⁺, Mg²⁺, K⁺, and Rb⁺. The effect on the electrochemistry is profound. While the highest capacity is still found with Na⁺, the best cycling is obtained with Mg²⁺. Capacity was lower for all the larger cations, and, somewhat surprisingly, Li⁺.
- The Pacific Northwest National Laboratory (PNNL) team developed the ether-based electrolyte using monoglyme, diglyme, and tetraglyme. The glymes have been reported to stabilize the sodium metal in plating/stripping process. Specifically, diethylene glycol dimethyl ether (DEGDME) and tetraethylene glycol dimethyl ether (TEGDME) based electrolytes with 1 M NaPF₆ enable the highest Coulombic efficiency (> 99.5%) of sodium stripping/plating in NallCu half-cells. Ether-based electrolytes are also compatible with Na₃V₂(PO₄)₃ cathode for developing sodium anode-free cells.

Task 7.1 – Exploratory Studies of Novel Sodium-Ion Battery Systems (Xiao-Qing Yang and Enyuan Hu, Brookhaven National Laboratory)

Project Objective. To meet the challenges of powering plug-in hybrid electric vehicles and battery electric vehicles, new rechargeable battery systems with high energy and power density, low cost, good abuse tolerance, and long calendar and cycle life need to be developed. The primary objective of this project is to develop new advanced synchrotron-based material characterization techniques and apply these techniques to study the new rechargeable battery systems beyond the Li-ion batteries, namely the Na-ion battery systems for electric vehicles (EVs).

Project Impact. The results of this project will be used for developing technologies that will significantly increase the energy density and cycle life and reduce the cost of beyond Li-ion battery systems. This will greatly accelerate deployment of EVs and reduce carbon emission associated with fossil fuel consumption and will help in the direction of building U. S.-based energy storage manufacture chains.

Approach. This project will use synchrotron-based *in situ* X-ray diagnostics such as *in situ* X-ray diffraction (XRD) and *in situ* X-ray absorption (XAS) tools, combined with transmission electron microscopy (TEM), scanning transmission electron microscopy, and transmission X-ray microscopy imaging techniques developed at Brookhaven National Laboratory (BNL) to evaluate the new materials and redox couples to obtain in-depth understanding of the reaction mechanisms of these materials, aiming to improve existing materials and to provide guidance for new materials and new technology development for Na-ion battery systems.

Out-Year Goals. The out-year goal is to complete the synchrotron-based XRD, XAS, and X-ray absorption near-edge structure (XANES) studies of new cathode materials of NaMnFeCoNiO₂ (NMFCN) and P2-Na_{0.66}[Cu_{0.33} Mn_{0.67}]O₂ for Na-ion batteries.

Collaborations. The BNL team has been closely working with top scientists on new material synthesis at Argonne National Laboratory, Lawrence Berkeley National Laboratory, and Pacific Northwest National Laboratory, with U.S. industrial collaborators at General Motors and Johnson Controls, and with international collaborators.

Milestones

- Complete XRD and TEM studies on a high-capacity and high-C rate multicomponent sodium cathode materials NMFCN at pristine and after 1st charge state to study the structural changes of this material. (Q1, FY 2022; Completed)
- 2. Complete *in situ* XRD studies on a new P2-structured Na_{0.66}[Cu_{0.33} Mn_{0.67}]O₂ cathode material for Na-ion batteries during charge-discharge cycling. (Q2, FY 2022; Completed)
- 3. Complete *in situ* copper and manganese K-edge XAS studies on P2-structured Na_{0.66}[Cu_{0.33} Mn_{0.67}]O₂ materials during charge-discharge cycling to understand the redox contributions of copper and manganese of this material. (Q3, FY 2022; Completed)
- 4. Complete the soft XAS studies of Na_{0.66}[Cu_{0.33} Mn_{0.67}]O₂ materials at pristine, charged to 3.6 V, and charged to 4.1 V states to understand the redox contribution of oxygen. (Q4, FY 2022; In progress)

Progress Report

This quarter, in situ XAS studies have been completed for P3-structured Na_{0.66}[Cu_{0.33}Mn_{0.67}]O₂. Figure 140a shows the evolution of XANES of XAS for both copper and manganese K-edges during the 1st cycle. The edge position of copper XANES shifts to higher energies during charge and shifts back to lower energy during discharge. In contrast, the edge position of manganese XANES is mostly unchanged during the whole chargedischarge process. This clearly indicates that copper is the active element contributing to the capacity during charge-discharge, while manganese is inert. To study the local structural changes around copper and manganese, the extended X-ray absorption fine structure data are Fourier transformed, and the results are shown in Figure 140b. The first peak corresponds to the bond between transition metal (TM, copper or manganese) and oxygen, and the second one corresponds to the TM-TM correlation. Through fitting these spectra against the model structure, detailed local structural information can be obtained. Satisfactory fitting was obtained after considering the presence of copper manganese local ordering and Jahn-Teller distortion for copper atoms. The results are shown in Figure 140c. Jahn-Teller distortion splits the copper-oxygen bonds into short ones (changes during cycling plotted in the top panel of Figure 140c) and long ones (the middle panel of Figure 140c). At the beginning of charge, the short copper-oxygen bond shrinks and so does the long one with a larger value, meaning that the difference between them becomes smaller. This is likely due to the oxidation of copper cations that directly removes the three-dimensional (3D) electrons on copper and therefore weakens the Jahn-Teller distortion. Further charging leads to shrinkage of the short bond, but expansion of the long one. This could be associated with the oxygen redox process that no longer removes electrons directly from the copper 3D states, but more likely from the O-dominated states instead. The more complicated bond lengths' evolution at the end stage of charge may be associated with the phase transition in this material. The Mn-O bond length (bottom panel in Figure 140c) is mostly unchanged during the charge-discharge process, which is expected and consistent with the XANES results shown in Figure 140a.



Figure 140. (a) *In situ* X-ray absorption near-edge structure and (b) *in situ* Fourier transformed extended X-ray absorption fine structure for copper and manganese during the 1st charge-discharge process. (c) Evolution of bond lengths for fitted short Cu-O (top panel), long Cu-O (middle panel), and Mn-O (bottom panel) during charge-discharge. The error bar for Cu-O bond length is very small and cannot be seen in the figure.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 7.2 – Development of a High-Energy Sodium-Ion Battery with Long Life (Chris Johnson and Khalil Amine, Argonne National Laboratory)

Project Objective. The project objective is to develop a high-energy Na-ion battery with long life. Moreover, the battery chemistry should utilize low-cost materials. The energy density target is 200 Wh/kg and/or 500 Wh/L, wherein the anode and cathode capacity targets are 600 mAhg⁻¹ and 200 mAhg⁻¹, respectively.

Project Impact. A Na-ion battery on par with the energy density of a Li-ion battery can have a high impact in the transportation sector with the assumption that the cost is significantly below \$85/kWh and that the battery pack provides a 300-mile range. The consumer is not concerned about the battery chemistry employed if these metrics can be met. Development of these battery chemistries will situate the United States in a strong position as relates to new low-cost energy storage systems beyond lithium ion.

Approach. In a team approach, the Na-ion battery group will create a versatile Na-ion battery chemistry with beneficial advantages such as low cost, safety, recycling, and sustainability of materials used. The team will work synergistically so that the final design is the culmination of advances in phosphorus carbon composites mated with optimized lead or other highly dense metalloids, such as tin and/or antimony and derivatives thereof, for the recyclable anode. Synthesis and optimization of such blended composite anodes will be conducted in parallel to diagnostic characterization of structures, phase formation, and cycling stability. Cathode work will begin at the end of the first year and will involve gradient cathodes consisting of Fe-Mn compositions, as well as intergrowths of layer stacking sequenced oxides. If resources allow, the team also will attempt to stabilize cathode surfaces using atomic layer deposition methods, particularly for the benefit of staving off dissolution of manganese and iron / electrolyte reactivity. Electrolytes will be partly procured from H. Li at Pacific Northwest National Laboratory (PNNL).

Out-Year Goals. The state-of-the-art Na-ion battery in the literature has now been surpassed by this team, but performance is still too low for commercialization. Thus, the goal is to move forward and continually invent the most superior Na-ion battery chemistry that can compete worldwide through work output from this project.

Collaborations. Researchers from PNNL who are developing electrolytes for Na-ion batteries will provide this project with formulations to test with the various electrode combinations investigated at ANL.

Milestones

- 1. Synchrotron X-ray understanding on the capacity fade of O3 sodium layered cathodes. (Q1, FY 2022; Completed)
- 2. Transmission electron microscopy (TEM) characterization on the effect of native lattice strain. (Q2, FY 2022; Completed)
- 3. Develop engineered surface for better air-storage and high-voltage stability. (Q2, FY 2022; Completed)
- 4. Development of high-capacity single-crystal layered oxide cathodes with > 150 mAh/g and stable cycle life of > 100 cycles. (Q3, FY 2022; Completed)
- 5. Development of concentration gradient layered oxide cathode with 130 mAh/g and stable cycle life of > 200 cycles. (Q4, FY 2022; In progress)
- 6. Investigate novel local atomic structural features to stabilize the high oxidation state of iron active species. (Q4, FY 2022; In progress)

Progress Report

This quarter, the team has progressed in developing high-capacity and long-life sodium layered cathodes.

TEM Understanding of Native Lattice Strain Induced Structural Earthquake in Sodium Layered Cathodes

The team found that quenching could induce significant native lattice strain in the oxide layered cathode. for example, O3 NaNi_{0.4}Mn_{0.4}Co_{0.2}O₂ cathode. Figure 141a and Figure 141b show the low and high magnification TEM image of the pristine $NaNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ particle, respectively. The quenched cathode exhibited highly rough surface and fluctuated strain contours in a large area. These structural features have been mostly observed in the cycled cathodes materials, but barely in the pristine cathodes. The high-resolution transmission electron microscopy (HRTEM) image in Figure 141c illustrates that the *d*-spacing along the *c*-axis direction is about 0.549 nm, which is stretched by about 3.58% compared to that of standard O3 phase (0.530 nm). A closer examination (inset of Figure 141c) clearly shows the existence of severe lattice distortion along the c-axis direction, in which they can see the curved lattice fringe and overlap of transition metal



Figure 141. (a) Low and (b) high magnification. (c) High-resolution brightfield transmission electron microscopy image. (d) Select area electron diffusion pattern. (e) Geometric phase analysis. (f) Atomic structural model of the strained O3 NaNi_{0.4}Mn_{0.4}Co_{0.2}O₂. Inset in (c) is the zoomed-in view of the region marked by the white square. The color in (c) represents the intensity, with red indicating highest and blue showing lowest. θ is the angle between layered direction and strain direction. The yellow, red, blue, gray, and purple spheres in (f) represent sodium, oxygen, nickel, cobalt, and manganese atoms, respectively.

(TM) atoms and sodium atoms. Such lattice distortion might accelerate cation mixing or cation migration during cycling, leading to undesired structural evolution and hence capacity/voltage fade. The selected area electron diffraction pattern in Figure 141d is in good agreement with the [010] projection of layered O3 cathode, but exhibits obvious spot splitting. All these structural features are due to the native high lattice strain induced

during the quenching process, leading to the metastable nature of strained highly O3 cathode. The corresponding geometric phase analysis of Figure 141c provided the direct strain distribution of the NaNi_{0.4}Mn_{0.4}Co_{0.2}O₂ cathode, which showed an angle between layered direction and strain direction (Figure 141e). Such native lattice strain can be thus separated into tensile stress along the *c*-axis direction that tends to stretch the lattice, and shear stress along the *ab*-axis direction that will compress the lattice (Figure 141f). On extraction of Na⁺, such metastable structure tends to undergo spontaneous strain relaxation and cause significant structural degradation.

Figure 142a shows the bright-field TEM image of strained $NaNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ cathode after charge/discharge within BMR Quarterly Report



Figure 142. Transmission electron microscopy (TEM) characterization on cycled O3 NaNi $_{0.4}$ Mn $_{0.4}$ Co $_{0.2}$ O₂ cathode particle (2.0-4.4 V for 100 cycles). (a) Low and (b) high magnification TEM image. (c) Zoomed-in view of the dashed square area in (b). (d-e) Zoomed-in views of the dashed rectangle area in (a). (f) Zoomed-in view of dot-circle area in (a).

2.0-4.4 V at 0.08 C for 100 cycles. Compared to the pristine one (Figure 141b), a large portion of native lattice strain was relaxed since the strain contours disappeared. The HRTEM image (Figure 142b) and the zoomed-in view (Figure 142c) show that there are numerous stacking faults and dislocations as a catastrophic consequence of strain relaxation. In particular, the team can clearly see the bending of lattice (yellow dashed lines in Figure 142c) parallel to the layered direction due to the shear stress along the *ab*-axis. Moreover, the tensile stress along the *c*-axis direction led to evolution of lattice dislocations and stacking faults. As a result, it will be difficult to re-insert Na⁺ into the sodium layer because of the crossover of TM cations that might occupy the sodium sites and damage layered structure, implied by the disappearance of (00*l*) peaks in the *in situ* synchrotron-based X-ray diffraction patterns at the beginning of the discharge process. Hence, the material suffered from a dramatic capacity loss.

On the other hand, by examining the strain-relaxed region in Figure 142a (marked by white rectangle), the team found that the observed gaps between two layered planes are not empty; they are composed by low-crystalline fragmented domains. Figure 142d clearly shows that a layer of NiO-like rock-salt structure with (111) plane was formed at the tip of premature crack region. In general, the (111) plane of rock-salt structure is energetically and structurally favorable and has a high tolerance against compression strain. However, the native high lattice strain in the quenched cathode significantly exceeds both tensile and compression limit of rock-salt phase, thus leading to formation of rock-salt fragments with different orientations (Figure 142e). In contrast, in the strain-unrelaxed region (Figure 142a, red circle), the curved lattice fringes were preserved, and no formation of cracks or premature cracks can be observed even at the grain boundaries that have long been considered as the preferred crack-initiating sites (Figure 142f). The curved lattice fringes of strained layered oxide cathodes introduced by quenching during material synthesis are similar to the curved stratum of the earth during earthquake due to the stored elastic strain energy. The extraction/insertion of Na⁺ plays a similar role to plate motion, which leads to the release of stored energy (native strain) in a way of cracking, displacement, and dip/strike faulting that also occurred during the structural degradation of layered cathodes.

The team further investigated the influence of charge/discharge rates and temperature on the strain relaxation process. Figure 143 compares the structures of cycled strained NaNi_{0.4}Mn_{0.4}Co_{0.2}O₂ cathode after 100 cycles charge/discharge under different of conditions. Under a low charge/discharge rate of 0.08 C at room temperature, the strain relaxation was relatively smooth, leading to formation of straight incision (Figure 143a-b, white rectangles). This is because the extraction/insertion of Na⁺ is proceeding in a very slow manner, which can thus minimize the effect of stress heterogeneity. This is similar to common phenomena, such as smooth plate motion or tearing wrinkled paper in a slow manner. Again, they can see the tip of the gap was terminated at the end of the strain-unrelaxed region. With elevated temperature, they can see the propagation and



Figure 143. Strain relaxation under different conditions. Low and high magnification transmission electron microscopy images of O3 NaNi_{0.4}Mn_{0.4}Co_{0.2}O₂ cathode after 100 cycles within 2.0-4.4 V at different conditions: (a-b) 0.08 C under room temperature; (c-d) 0.2 C under 55°C, and (e-f) 1 C under room temperature.

widening of gaps (Figure 143c, yellow rectangles) as well as new formation of high-density nanogaps (Figure 143d, yellow rectangles). This might be because of the increased extraction/insertion kinetic of Na⁺ at high temperature. By switching to fast charging/discharging, the strain relaxation is aggressive and vigorous, thus leading to formation of both large (Figure 143e, red rectangle) and high-density nanocracks (Figure 143f, red rectangles) with curved incision.

In brief, through a combination of advanced diagnostics from material synthesis to cell failure, the team has discovered the essential role of synthesis-induced native lattice strain in triggering the structure earthquake of sodium layered oxide cathodes during cycling. The spontaneous relaxation of internal strain that exceeds the threshold limit is the fundamental origin of the abrupt degradation of sodium layered oxide cathodes. Furthermore, they showed that such a process is not regulated by the charge cut-off voltage, but is strongly coupling with working temperature and charging/discharging rates that can tailor the movement of Na⁺. Their work indicates an urgent need to revisit the crystallographic structure of sodium /lithium layered oxide cathodes such as strain, oxygen vacancies, nanopores, domain boundaries and other intrinsic defects, and to understand how they affect common battery phenomenon such as capacity fade and voltage decay/hysteresis. Their work also indicates that a rational strain management during cycling of sodium/lithium layered cathodes is required to maximize cycle life.

Developing High-Entropy P2 Single-Crystalline Layered Cathodes for Na-Ion Batteries

This quarter, the team further developed a series of P2 type single-crystal sodium layered $Na_{0.62}Mn_{0.67}Ni_{0.23}Cu_{0.05}Mg_{0.09-2y}Ti_yO_2$ cathode by simultaneously tuning their entropy and crystal facets, and investigated their electrochemical/thermal stability. The optimized composition is $Na_{0.62}Mn_{0.67}Ni_{0.23}Cu_{0.05}Mg_{0.07}Ti_{0.01}O_2$, denoted as CuMgTi-571. The CuMgTi-571 cathode could deliver an initial specific capacity of 148.2 mAh/g and a reversible capacity of ~ 133 mAh/g after 100 cycles at 12 mA/g during charge/discharge within 2.0-4.3 V, demonstrating good cycling stability.

To check the impact of entropy and crystal-facet tuning on the structural stability of the material, *in situ* synchrotron high-energy X-ray diffraction (HEXRD) was conducted on CuMgTi-571 during charge/discharge, and the results are displayed in Figure 144. Figure 144a and Figure 144b show the waterfall and contour plot of HEXRD patterns of the CuMgTi-571 electrode charged/discharged at 0.1 C (12 mA g⁻¹) between 2.0 V and 4.3 V, respectively. On Na⁺ extraction (charge), the (002) and (004) peaks shift toward lower $2\theta^{\circ}$ angle due to the increase in the repulsive electrostatic interaction between adjacent MO₂ sheets; while (010), (012), (108),



Figure 144. *In situ* high-energy X-ray diffraction (HEXRD) characterization in coin-cell configuration at 25°C. (a) Waterfall plot and (b) contour plot of *in situ* HEXRD patterns for CuMgTi-571 within 2.0-4.3 V. (c) Evolution of cell parameters and cell volume during the charge/discharge process.

and (112) peaks consecutively shift toward a higher $2\theta^{\circ}$ angle with the contraction of *a*-, *b*-axis. During the subsequent discharge, the XRD pattern of CuMgTi-571 exhibited an exactly opposite evolution. During the whole charge/discharge process, the well-defined peaks corresponding to the P2 phase are well maintained and returned to the initial states after one full cycle. No new peaks belonging to OP4, O2, or Z phase are detected when charged to 4.3 V, and no existing peaks vanish or split, indicating that new phase formation and phase



Figure 145. The two-dimensional contour X-ray diffraction plots of de-sodiated (a) CuMgTi-571 and (b) NaMNO₂ during the heating from 30°C to 450°C at 5°C min⁻¹; the tested samples during heating are de-sodiated cathode powder scraped from 4.2 V-charged cathodes.

transition do not occur in this material. The changes of lattice parameter on cycling based on the refinement results are displayed in Figure 144c. Clearly, the lattice parameter evolution is highly reversible during the charge and discharge process. The largest changes of the *a*, *c*, and *V* in the 1st cycle are only 0.74%, 0.91%, and 0.57%, respectively. The high reversibility of lattice parameter evolution and structural evolution on Na⁺ (de-)intercalation manifests the unusual structure stability of entropy and crystal facet tuned cathode.

In situ HEXRD during heating of de-sodiated cathode powder was also performed to investigate the phase stability of entropy and crystal-facet tuned cathodes at high temperature (heating from 30° C to 450° C) to investigate their thermal tolerance (Figure 145). The tested CuMgTi-571 and Na_{0.62}Mn_{0.67}Ni_{0.37}O₂ (NaMNO₂) materials were scraped from 4.2 V-charged cathodes. The (002) peak, which is most sensitive to the sodium content during charging/discharging, is usually used to monitor the phase transformation of P2-type layered cathodes during heating. The (002) reflection of charged CuMgTi-571 continuously moves to lower angle with increasing the temperature due to the lattice expansion caused by heating (Figure 145a). Distinct from CuMgTi-571, the (002) reflection of charged NaMNO₂ first shifts to lower angle on heating, and then moves to higher angle when the heating temperature reaches above 222°C (Figure 145b). Such phenomenon indicates that new phases such as spinel or rock-salt were formed in the charged NaMNO₂ during the heating. Moreover, the (002) peak fading starts at 350°C and 322°C for the CuMgTi-571 and NaMNO₂ cathodes, respectively, further confirming the inferior structural stability of the NaMNO₂. The formation of new phase and inferior structural stability would lead to irregular migration channel and hence sluggish Na⁺ diffusion.

In brief, configurational entropy could result in a thermodynamically stable structure through a local minimization of Gibbs free energy, and a high percentage of {010} facets in the layered cathodes could provide more channels for ion transport. Based on the advantages of high entropy and high active facets, a combinatorial strategy of entropy modulation and active-facet modulation was developed to stabilize the structure and optimize ion-migration pathways of P2-type layered cathodes.

Patents/Publications/Presentations

Patent

• Xu, G-L., X. Liu, and K. Amine. "Electroactive Materials for Secondary Batteries." U. S. Patent 11,394,022; granted.

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- Daali, A., C. Zhao, X. Zhou, Z. Yang, R. Amine, Y. Liu, O. Wilkistar, G. L. Xu,^{*} and K. Amine.^{*} "Tuning Working Potential of Silicon-Phosphorus Anode via Microstructure Control for High-Energy Lithium-Ion Batteries." *Journal of Solid State Electrochemistry* (2022). https://link.springer.com/article/10.1007/ s10008-022-05192-0.
- Holguin, K., K. Qin, E. P. Kamphaus, F. Chen, L. Cheng, G. L. Xu,^{*} K. Amine, and C. Luo. "Establishing Substitution Rules of Functional Groups for High-Capacity Organic Anode Materials in Na-Ion Batteries." *Journal of Power Sources* 533 (2022): 231383.

Presentation

 International Meeting on Lithium Batteries, Sydney, Australia (June 26 – July 1, 2022): "Beyond Phase Transition and Parasitic Reactions: Native Lattice Strain Induced Structural Earthquake in Sodium Layered Oxide Cathodes"; G-L. Xu and K. Amine. Invited poster.

Task 7.3 – Tailoring High-Capacity, Reversible Anodes for Sodium-Ion Batteries (Marca M. Doeff, Lawrence Berkeley National Laboratory)

Project Objective. The project objective is to understand the role that vacancies, surface defects, and bulk structure play in determining electrochemical properties of high capacity, stepped layered titanate anodes.

Project Impact. Although several suitable cathode materials for Na-ion batteries exist, there are few suitable anode materials due to low potential instabilities. Sodium titanate anodes are a promising class of materials for this application. The electrochemical properties can be manipulated through structural and surface modifications.

Approach. The structure and surface properties of candidate stepped layered titanates will be modified through manipulation of synthetic parameters. Materials will then be characterized electrochemically and physically to understand the role that surface defects, vacancies, and bulk structure play in determining electrochemical behavior.

Out-Year Goals. The out-year goal is to achieve development of an electrode that can deliver 225 mAh/g at C/3 rate with good capacity retention (80% or better) for 100 cycles.

Collaborations. The team collaborates with beam line scientists at Stanford Synchrotron Radiation Lightsource and the Advanced Light Source at Lawrence Berkeley National Laboratory.

Milestones

- 1. Conduct hot stage experiments on lepidocrocite titanates. (Q1, FY 2022; Completed)
- 2. Complete physical and electrochemical characterization of lepidocrocite titanates. (Q2, FY 2022; Completed)
- 3. Attempt surface modification of lepidocrocite titanates. (Q3, FY 2022; In progress)
- 4. *Go/No-Go Decision*: Surface modification methods; stop if performance is not improved. (Q4, FY 2022; In progress)

Progress Report

The team's previous findings have shown that the presence of Mg²⁺ instead of Na⁺ as the interlayer cation in lepidocrocite-type layered titanates results in distinctly different electrochemical performance. This quarter, they used lepidocrocite-type layered cesium titanate ($C_{s_{0.74}}T_{i_{1.815}}O_4$) as the precursor and further investigated the effect of different interlayer cations (Li⁺, Na⁺, K⁺, Rb⁺, Mg²⁺) on their electrochemical properties when used as Na-ion anodes. The Li⁺/Cs⁺, K⁺/Cs⁺, and Rb⁺/Cs⁺ ion-exchange was carried out by stirring one gram of Cs_{0.74}Ti_{1.815}O₄ powder in 100 mL aqueous 4 M LiCl, KCl, or RbCl solution at 80°C in a heated mineral oil bath for 7 days. The resulting powder was then vacuum filtered, washed, and dried at 100°C in an incubator. Scanning electron microscope – energy dispersive X-ray spectroscopy analyses confirmed the complete Cs⁺ exchange with Li⁺, K⁺, or Rb⁺. Figure 146a shows their synchrotron-based X-ray diffraction (SXRD) patterns. Although the hydration of interlayer cations complicates the detailed structure determination, the presence of (020) reflections in the SXRD patterns of all the prepared samples indicates that the layered structure was preserved after ion-exchange. Additionally, the different positions of (020) reflections suggested variations in the interlayer distance, which can be explained by the different hydration radius and dehydration behavior of these interlayer cations. Raman spectra of all the ion-exchanged materials show similar characteristic bands, implying that the ion-exchange process does not change the basic skeletons (TiO_6) octahedra) (Figure 146c). Red or blue shifting of Raman bands above 200 cm⁻¹ was observed due to changes in the bond length originating from different interactions between interlayer cations and the terminal oxygen of TiO_6 octahedra. Thermogravimetric analysis was also performed to reveal the water content of ion-exchanged materials (Figure 146b). The smallest cation Li⁺ with the largest hydration radius has the largest water content, whereas large Rb⁺ with smaller hydration radius has a lower water content. Titanium K-edge X-ray absorption near-edge structure spectra indicated that titanium atoms in all the studied materials remain Ti⁴⁺ (Figure 146d).



Figure 146. (a) Synchrotronbased X-ray diffraction (SXRD) patterns, (b) thermogravimetric analysis, (c) Raman spectra, and (d) titanium K-edge X-ray absorption near-edge structure spectra of cesium titanate Cs0.74Ti1.815O4 ion exchanged with Li⁺, Na⁺, K⁺, Rb⁺, and Mg²⁺ in aqueous solution.

The electrochemical performance of the ion-exchanged materials was then evaluated in sodium half cells (Figure 147). The achievable sodium capacity could be affected by multiple factors, including the available sites for Na⁺ accommodation, the interlayer spacing, and the Coulomb repulsion between interlayer cations that are relevant for the transport of Na⁺. As shown in Figure 147a, among all the studied interlayer cations, Na⁺ delivers the largest reversible capacities, whereas Rb⁺ shows the lowest capacities. Noteworthy, unlike the materials with interlayer Na⁺, K⁺, or Mg²⁺, the materials with interlayer Li⁺ or Rb⁺ do not show the plateau features around 1.25 V versus Na⁺/Na (Figure 147b) and exhibit more stable cycling than the former (Figure 147c).



Figure 147. (a) Fifth-cycle voltage profile, (b) the corresponding dQ/dV plots, and (c) the capacity retention of $C_{s_0.74}Ti_{1.815}O_4$ ion exchanged with Li⁺, Na⁺, K⁺, Rb⁺, and Mg²⁺. All the cells were cycled at a current rate of 8 mA g⁻¹ (0.008 mA cm⁻²) using a Na-metal anode and a solution of 0.5 M NaPhB₄ in DEGDME as the electrolyte.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.

Task 7.4 – Electrolytes and Interfaces for Stable High-Energy Sodium-Ion Batteries (Phung M. L. Le, Pacific Northwest National Laboratory)

Project Objective. The Na-ion battery is a potential alternative energy source for electric vehicles (EVs) and grid applications due to the low cost and the natural abundance of sodium. The performance of Na-ion batteries largely depends on development of electrode materials and electrolytes. In recent years, a series of potential electrode materials has been developed. However, a fundamental understanding of the electrochemistry of Na-ion batteries, especially the stability of the electrode-electrolyte interface in these batteries, is still not well established. This project will develop innovative electrolytes to enable fundamental understanding on the interface between electrode and electrolyte for stable operation of high-energy Na-ion batteries. A high-capacity anode will also be developed. The proposed research will enhance the achievable capacities of both anode and cathode for Na-ion battery and improve the stability of electrodes/electrolyte interface, establish correlation (electrolyte design rule) between electrochemical performances of Na-ion batteries and the electrolyte/interface properties, and enable long cycle life and safe operation of high-energy Na-ion batteries.

Project Impact. This project will develop new electrolytes to enable long cycle life and safe operation of Na-ion batteries. If successful, the resulting improvements in energy, life, and safety will provide a solid contribution to the understanding of fundamental scientific questions and the development for Na-ion battery technology and promote its practical application as a competitive alternative to the current Li-ion batteries and greatly reduce the cost of energy storage systems for EVs.

Approach. This project will continuously optimize the electrolyte components and concentrations to develop innovative electrolytes and additives with improved electrochemical and physical properties. Ether-based electrolytes with different salts and additives will be optimized toward both anode [sodium metal and hard carbon (HC)] and cathode. Phosphate-based localized high-concentration electrolyte (LHCE) will be optimized to improve cycling performance of Na-ion batteries. Solid electrolyte interphase (SEI) / cathode electrolyte interphase (CEI) components of Na-ion battery in ether and phosphate electrolytes will be studied using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy / transmission electron microscopy (TEM) techniques to reveal the fundamental mechanism behind the improved stable performance of Na-ion batteries. Electrolyte additives in carbonate electrolyte will also be investigated to improve the electrochemical cathode performance. These approaches will unravel the origin of the SEI at the dynamic interface, providing guidance for the electrolyte and interface design and enabling high capacity and long life of Na-ion batteries.

Out-Year Goals. This project will select electrolyte compounds and identify formation of interfacial SEI layer on HC and CEI layer-on-layer oxide cathode and its effect on electrode materials. It will also guide electrolyte optimization and improving Coulombic efficiency (CE) of sodium deposition/stripping to be more than 99%.

Collaborations. This project will collaborate with leading scientists at Argonne National Laboratory, Lawrence Berkeley National Laboratory, and other organizations in the field of cathode and anode materials for Na-ion batteries. It will also collaborate with C. Wang and M. Engelhard of Pacific Northwest National Laboratory (PNNL) for TEM and XPS characterization.

Milestones

- 1. Develop high-voltage electrolytes based on fluorinated solvent (≥4.2 V) to be compatible with high-voltage cathode material. (Q1, FY 2021; Completed)
- 2. Characterize CEI/SEI interphase properties in optimized electrolyte to probe the mechanism of high-voltage cycling stability of Na-ion batteries. (Q2, FY 2022; Completed)

- 3. Design new electrolytes to enable extremely high CE (> 99.5%) of sodium stripping/plating process on different current collectors. (Q3, FY 2022; Completed)
- 4. Investigate feasibility of anode-free sodium batteries using new electrolytes and $Na_3V_2(PO_4)_3$ cathode. (Q4, FY 2022; In progress)

Progress Report

The team's target this quarter was to design new electrolytes enabling an extremely high reversible sodium

stripping/plating process to develop anode-free sodium cell or Na-metal batteries. Herein, they report on developing the ether-based electrolyte using monoglyme, diglyme, and tetraglyme. The glymes have been reported to stabilize the sodium metal in the plating/stripping process.^[1] Specifically, tetraglyme-based electrolytes with 1 M salt (NaPF₆, NaOT_f, and NaBF₄) enable extremely high CE (> 99.5%) of the stripping/plating process using half-cell Na||Cu (Figure 148). The highest CE is obtained for 1 M NaOT_f in tetraethylene glycol dimethyl ether (TEGDME) solvent.

Based on the good results obtained for Na||Cu half-cell using tetraglyme-based electrolytes, different current collectors (aluminum, C-coated aluminum, and C-coated copper) were investigated for stripping/plating process (Table 6). It can be observed that using copper foil as current collector in half-cell exhibited the highest CE in



Figure 148. Voltage versus time, and Coulombic efficiency, calculated using the reported protocol of cycling^[2] in different electrolytes.

all three TEGDME- and diethylene glycol dimethyl ether (DEGDME)-based electrolytes (> 99.5 %). However, other current collectors displayed lower CE compared to the copper foil in half-cell.

Electrolyte	CE of stripping/plating process			
Electrolyte	Na Cu	Na C coated Cu	Na Al	Na C coated Al
1M NaBF ₄ /TEGDME	99.5	98.3	97.7	99.2
1M NaPF ₆ /TEGDME	99.7	-	-	97.3
1M NaOT _f /TEGDME	99.8	98.5	98.5	99.6
1M NaBF ₄ /DEGDME	95.6	-	-	-
1M NaPF ₆ /DEGDME	99.7	-	-	-
1M NaOT _f /DEGDME	99.5	99.0	98.2	99.6

Table 6. Coulombic efficiency of stripping/plating process in half-cell Na||different current collectors.

As the cycle life of sodium anode-free cell depends on the CE of sodium plating/stripping process, it would be better to select the electrolytes given the highest CE for further testing on the half-cell of $Na||Na_3V_2(PO_4)_3$ (NVP) cathode. Figure 149 presents the cycling performance of Na||NVP half-cell for 100 cycles in DEGDME-and TEGDME-based electrolytes. The highest capacity retention was obtained for 1M NaPF₆ in TEGDME.



Figure 149. Capacity retention of Na||NVP half-cell in DEGDME-based and TEGDME-based electrolytes for 100 cycles.

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Patents/Publications/Presentations

Publication

Jin, Y., P. M. L. Le, P. Gao, Y. Xu, B. Xiao, M. H. Engelhard, X. Cao, T. D. Vo, J. Hu, L. Zhong, B. E. Matthews, R. Yi, C. Wang, X. Li, J. Liu, and J-G. Zhang. "Low Solvation Electrolytes for High Voltage Sodium Ion Batteries." 7 *Nature Energy* (2022): 718–725.

Presentations

- Electrochemical Society Meeting, Vancouver, British Columbia, Canada (May 29 June 2, 2022): "Tetraglyme Based Electrolytes Enable Excellent Cycling Performance of Sodium Metal Batteries"; P. M. L. Le, et al.
- International Meeting on Lithium Batteries, Sydney, Australia (June 26 July 1, 2022): "Low Solvation Electrolytes for High Voltage Sodium Ion Batteries"; Y. Jin, et al. Poster.

Innovation Center for Battery500 (Jun Liu, Pacific Northwest National Laboratory; Yi Cui, Stanford University)

Project Objective. The overall goal of the consortium is to increase the energy density of advanced lithium batteries to beyond what can be achieved in today's state-of-the-art Li-ion batteries. The Battery500 Consortium aims to increase the specific energy (up to 500 Wh kg⁻¹) and achieve 1,000 charge/discharge cycles, with cost reduction of the cells to significantly less than \$100 per kWh⁻¹. This goal directly addresses the U. S. Department of Energy priority to achieve a carbon-free electricity sector by 2035 and to decarbonize the transportation sector by developing and manufacturing the next-generation, high-energy, low-cost batteries to enable a wide deployment of electric vehicles (EVs) in the marketplace.

Project Impact. Battery500 will develop next-generation lithium battery technologies that will significantly increase energy density, improve cycle life, and reduce cost. This will greatly accelerate deployment of EVs and reduce carbon emission associated with fossil fuel consumption. The consortium will utilize first-class expertise and capabilities in battery research in the United States and develop an integrated and multidisciplinary approach to accelerate development and deployment of advanced electrode and electrolyte materials in commercially viable high-energy batteries. The advances made in this consortium will also benefit improvement of current Li-ion battery technologies. This project will provide tremendous opportunities for students and scientists for battery-related training that will enhance the workforce for the United States to maintain global leadership in the battery research and development field.

Approach. This project focuses on the two most promising battery chemistries: Li-metal anode with high-voltage/high-capacity metal oxide cathodes like $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NMC), and lithium metal with sulfur cathodes. The project focus is to design novel electrode and cell architectures to meet the 500 Wh/kg goal. The consortium will work closely with battery/material manufacturers, suppliers, and end users / original equipment manufacturers in the United States to ensure the technologies being developed by this project are well aligned with industry needs, poised for transitioning to real production, and helpful in securing the supply chain in the United States.

Out-Year Goals. The out-year goals are to improve cycle life of the Li||NMC pouch cell with 400 Wh/kg energy density and cycle life of > 200, and to fabricate and test the pouch cells with 450 Wh/kg energy density and cycle life of > 100.

Collaborations. Collaboration among consortium team members will be well coordinated by the leadership team, which also includes four keystone project leads and co-leads along with principal investigators at all member institutions. Collaboration with the community outside of this consortium and with industry will be facilitated by the executive committee and the advisory board.

Milestones

- 1. Complete synchrotron-based transmission X-ray microscopy studies on cathode electrolyte interphase (CEI) protection for NMC cathode cycled at high-voltage limit. (Q1, FY 2022; Completed)
- 2. Complete electrochemical atomic force microscopy (AFM) imaging in glovebox to study the nucleation of Li-metal anode during lithium plating. (Q2, FY 2022; Completed)
- 3. Complete Li-metal anode morphology studies by cryogenic electron microscopy (cryo-EM) and modeling. (Q3, FY 2022; Completed)
- 4. Improve cycle life of Li||NMC pouch cell with 350 Wh/kg energy density with cycle life of > 800, and with 400 Wh/kg energy density with cycle life of > 200. Fabricate and test pouch cells with 450 Wh/kg energy density and cycle life > 100. (Q4, FY 2022; In progress)

Progress Report

Keystone Project 1: Materials and Interfaces

Li-Metal Anode

The Pacific Northwest National Laboratory (PNNL) team continued investigation of the solid electrolyte interphase (SEI) structure and lithium morphology at different states of charge (SOCs). A well-structured SEI frame is found after two formation cycles in the localized high concentration electrolyte (LHCE). These SEI frames have good mechanical strength and pore channels that enable a high reutilization efficiency of the formed SEI. Scanning electron microscopy (SEM) images in Figure 150a-c and Figure 150d-f show the top and cross-sectional views, respectively, of the three Li-metal anodes retrieved from the Li||LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC-811) cells initially charged at the target SOCs after two formation cycles. Figure 150g-i shows the schematic diagram of the pore channel structured SEI and its utilization in the subsequent lithium deposition. In the case of 0% SOC (after most of the deposited lithium is stripped from anode and intercalates back to the cathode after two formation cycles), SEI residuals form a frame with pore channel structures (10-15 µm) on the top of the Li-metal anode, as shown in Figure 150a. However, these residual SEI frames still partially retain their structures (see Figure 150a/d/g), which can facilitate subsequent lithium deposition. In the case of 50% SOC, the deposited lithium from the cathode can refill the SEI frames formed in the previous cycles to reutilize these SEI films and largely expand their shapes so that the total thickness of the accumulated lithium deposition can be almost fully recovered, as shown in Figure 150b/e/h. Some of the deposited lithium may also form new lithium particles covered by newly formed SEI. In the case of 100% SOC, previous SEI frames fully refilled with lithium and newly formed lithium particles will partially merge and form a bulky and dense layer of lithium deposition, as shown in Figure 150c/f/i. Comparison of Figure 150e/f shows that the deposited lithium at 50% SOC and 100% SOC of Li||NMC-811 has nearly the same thickness. These results indicate that the pore structure of SEI frame and reutilization can largely minimize the volume change of Li-metal anodes and then protect Li-metal anode against cycling and calendering aging.



Figure 150. Lithium structure and solid electrolyte interphase properties at initial states and after 18-month storage in LillNMC-811 cells at 30°C at different states of charge (SOCs). (a-c) Top views, (d-f) cross-sectional views, and (g-i) illustration of scanning electron microscopy images of Li-metal electrodes collected at initial state of different SOCs after two formation cycles at (a/d/g) 0% SOC, (b/e/h) 50% SOC, and (c/f/i) 100% SOC.

Electrolytes

For Ni-Rich Cathodes

The Pennsylvania State University (PSU) team continued optimization of the novel electrolyte achieving lithium Coulombic efficiency (CE) of 99.0% and fabricated the pouch cell to evaluate the electrolyte in practical conditions. The electrolyte was 1 M LiPF₆ in ethylene carbonate / diethyl carbonate (EC/DEC; v/v = 1:1) with 15 wt% fluoroethylene carbonate (FEC) and 1 wt% lithium difluoro(oxalate)borate (LiDFOB), which is denoted as EDFB. The Li-metal pouch cell has a high areal capacity (4.0 mAh cm⁻²) NMC-811 cathode, 50-µm-thin Li-metal anode, and lean electrolyte (3.0 g/Ah). The pouch cell demonstrated unprecedented cycling stability with 80% capacity retention after 335 cycles (Figure 151). Based on the weights of pouch-cell components (cathode materials, aluminum current collector, Li-metal anode, copper current collector, separator, and electrolyte), a high gravimetric energy density of 366 Wh/kg was calculated when discharging at 0.1C; even more impressively, 345 Wh/kg was achieved when discharging at 0.5C, outperforming state-ofthe-art LillNMC-811 pouch cells in terms of long cycle life (> 300 cycles) at such a high energy density. In addition, the electrolyte of EDFB was also studied by flammability testing to evaluate its safety characteristics. Unlike the high-performance ether-based electrolyte of 4 M lithium bis(fluorosulfonyl)imide (LiFSI) in 1,2-dimethoxyethane (DME) that immediately caught fire on the ignition, the carbonate electrolyte of EDFB was not ignited when exposed to a flame under the testing condition.





Figure 151. Electrochemical performance of Li(50 µm) || NMC-811 pouch cell in EDFB between 2.8-4.3 V. Lean electrolyte condition with an electrolyte/capacity (E/C) ratio of 3.0 g/Ah. Inset shows fully charged pouch cell after 300 cycles with PTFE clamps. 1C = 4 mA cm⁻². Note: The electrolyte of 1 M LiPF₆ in EC/DEC (v/v = 1:1) with 15 wt% FEC and 1 wt% LiDFOB is denoted as EDFB.

To reveal the roles of FEC and LiDFOB in enhancing cycling stability, ¹⁹F quantitative nuclear magnetic resonance (NMR) spectroscopic analysis of electrolyte evolution on cycling was conducted. Electrolytes with only additive LiDFOB or co-solvent FEC were first adopted to investigate electrolyte evolution in Li||NMC-811 full cells. The electrolyte of 1 M LiPF₆ in EC/DEC (v/v = 1:1) with 1 wt% LiDFOB is denoted as EDB. After only 10 cycles, as shown in Figure 152a, EDB shows a depletion of LiDFOB and considerable consumption of $LiPF_6$ (retention of 64.0%) in Li||NMC-811 full cell. These results confirm the immediate consumption of electrolyte (LiPF₆) and additive LiDFOB in the presence of Li-metal anodes. With only FEC as a co-solvent, electrolyte 1 M LiPF₆ in EC/DEC (v/v = 1:1) with 15 wt% FEC (denoted as EDF) delivers a reduced consumption of LiPF₆ (retention of 79.6%), although at the apparent cost of FEC (retention of 80.0%), as shown in Figure 152b. Both the electrolytes of EDB and EDF show fast consumption of electrolyte (LiPF₆) on cycling. In contrast, excellent LiPF₆ retention (99.4%) is achieved in the superior electrolyte of EDFB, along with high retention of LiDFOB and FEC at 81.0% and 97.8%, respectively (Figure 152c). These NMR experiments confirm that the combination of FEC and LiDFOB usage can effectively suppress the consumption of each other and reduce the consumption of carbonate electrolytes (LiPF₆) in Li||NMC-811 full cells. The impressive effects of this new superior electrolyte system enable decreased electrolyte consumption and improved cycling performances of Li-metal batteries. The major reasons are formation of a robust LiF-rich SEI layer on the Li-metal anode surface and stabilization of the microstructure of NMC-811 cathode materials by this carbonate electrolyte.



Figure 152. The 19F quantitative nuclear magnetic resonance (NMR) spectroscopic analysis on electrolyte evolution in Li||NMC-811 coin cells after 10 cycles. (a) 19F NMR spectra of EDB before and after cycling. (b) 19F NMR spectra of EDF before and after cycling. (c) 19F NMR spectra of EDFB before and after cycling. (d) Summary of F-containing components retention in EDB, EDF, and EDFB after 10 cycles. 15 μ L of electrolyte was employed for each case. *Note:* (1) The electrolyte of 1 M LiPF₆ in EC/DEC (v/v = 1:1) with 1 wt% LiDFOB is denoted as EDB, (2) the electrolyte of 1 M LiPF₆ in EC/DEC (v/v = 1:1) with 15 wt% FEC is denoted as EDF, and (3) the electrolyte of 1 M LiPF₆ in EC/DEC (v/v = 1:1) with 15 wt% LiDFOB is denoted as EDFB.

The University of Texas (UT), Austin, team developed a novel concept of electrolyte, namely localized saturated electrolyte (LSE), to stabilize high-Ni layered oxide cathodes. Different from the state-of-the-art LHCEs based on LiFSI with high solubilities, the developed LSE is based on lithium salts with low to medium solubility. Specifically, the lithium salts in an LSE include, but are not limited to, LiPF₆, LiBF₄, LiDFOB, lithium bis(oxalate)borate (LiBOB), LiClO₄, LiAsF₆, and the combination of these salts. The main solvents could be any organic solvents that have low to medium solubility (1 to 5 M) of these salts, and the diluents could be any organic solvents that improve the wettability to the separator without breaking the contact ion pairs (CIPs) and aggregates (AGGs) solvation structure in the electrolytes. Figure 153a shows the schematics of the conventional LP57 electrolyte and the developed LiPF₆-based LSE. The change in the solvation structure in the saturated electrolyte and the LSE is supported by Raman spectra (Figure 153b) and NMR spectroscopy (Figure 153c). The Li⁺ solvation structure is dominated by CIPs and AGGs in the saturated electrolyte and the LSE, while it is mainly composed of solvent-separated ion pairs in the LP57 electrolyte.

Cobalt-free LiNiO₂ was selected to examine the effectiveness of the developed LSE electrolyte. The LiNiO₂ sample has a secondary particle diameter of ~ 12 μ m, which is composed of primary particles with a size on the order of 100 nm, as shown in the SEM images in Figure 153d. Figure 153e shows that the LSE improves the self-discharge performance of the LiNiO₂ electrode. The cell voltage with the LP57 electrolyte decreased fast and reached 4.160 V after being stored at 45°C for 100 hours. By comparison, the cell voltage remained at 4.235 V with the LSE after the storage. A full discharge at the C/10 rate was conducted after the storage to evaluate capacity retention. The capacity remaining was increased from 85.0% (LP57) to 98.8% (LSE). Figure 153f further illustrates that the LSE largely improves the cycling stability of the LiNiO₂ electrode. The LiNiO₂ cell with the LSE shows an initial discharge capacity of 221 mA h g⁻¹ at 1C rate and retains 80% of its

initial capacity after 500 cycles. Moreover, when the EC / ethyl methyl carbonate (EMC) solvent was replaced with the FEC/EMC, cycle life was further extended to 600 cycles with 81.3% of capacity retention. These cycling performances of LiNiO₂ are better than that with LP57 electrolyte, which showed only 55% capacity retention after 200 cycles, and the state-of-the-art LHCE (M47), which maintained 84% after 200 cycles. Atomic resolution annular dark-field scanning transmission electron microscopy (ADF-STEM) images of cycled LiNiO₂ were collected to examine the phase transformation at the surface (Figure 153g-h). By selecting and masking the reflections from the layered, spinel, and rock-salt structures in the fast Fourier transformed (FFT) pattern, followed by an inverse FFT analysis, the areas containing each structure can be identified, which are labeled in the figures. LiNiO₂ with the LP57 electrolyte (Figure 153g) contains the rock-salt phase (red color) with a depth of 4-5 nm and a significantly transformed area of the spinel phase (yellow). In contrast, LiNiO₂ cycled in the LSE (Figure 153h) only contains a very thin rock-salt phase of 1-2 nm, and the spinel phase is sporadically distributed in small areas. Therefore, the LSE suppresses oxygen loss and a deep reduction of nickel ions on the surface of LiNiO₂ cathode and prevents formation of electrochemically inactive phases (spinel-like or rock-salt structure) during long-term cycling. Moreover, the lithium CE of the LSE was measured in a LillCu cell. Figure 153i shows that the lithium CE reaches 98.2% after stabilization, which is lower than that of the state-of-the-art value of 99.5% for LHCE. Future work will focus on increasing the lithium CE of the LSE by adding more appropriate additives.



Figure 153. (a) Schematic illustrations of the LP57 electrolyte and localized saturated electrolyte (LSE). (b) Raman spectra of the three electrolytes in the range of 600-1000 cm⁻¹. (c) 7Li nuclear magnetic resonance spectra of different electrolytes to study Li⁺ coordination. (d) Scanning electron microscopy images of LiNiO₂ microspheres with an average diameter of 12 µm (secondary particles). The insert zooms into the surface of a secondary particle to show the primary particles. (e) Self-discharge performance of LiNiO₂ cathodes tested at 45°C. (f) Cycling performances of LiNiO₂ with the LP57 electrolyte (300 cycles), LiFSI-based localized high-concentration electrolytes (M47, 300 cycles), LSE(EC/EMC) (500 cycles), and LSE(FEC/EMC) (600 cycles) at room temperature with 2 mA h cm⁻² loading. The charge rate was C/2, and the discharge rate was 1C in the voltage range of 2.8-4.4 V. Scanning transmission electron microscopy images at the surface of a cycled LiNiO₂ particle with (g) the LP57 electrolyte, and (h) the LSE. (i) Coulombic efficiency of the developed LSE measured with a Li||Cu coin cell. The test current and capacity were, respectively, 0.5 mA cm⁻² and 1 mAh cm⁻².

For Sulfurized Polyacrylonitrile (SPAN) Cathodes

The University of Maryland (UMD) team developed a new nitrate-reinforced carbonate-based electrolyte using the conventional salt concentration of ~ 1 M for Li-SPAN batteries. SPAN has recently emerged as a promising transition-metal-free and high-energy-cathode material for metal-based batteries. Compared to the conventional C-S composite, SPAN provides better dispersion and confinement of the S-based active species via means of covalent interaction. That being said, SPAN is typically preferred to contain a small amount of elemental sulfur to enhance the specific capacity. Therefore, the electrolyte needs to be designed accordingly to ensure cycling stability. It is well known that highly concentrated ether-based electrolytes can support decent SPAN cycling. However, their high cost and high viscosity as well as volatility/flammability of ethers might be of concern. The UMD team developed a new nitrate-reinforced carbonate-based electrolyte using the conventional salt concentration of around 1 M. This electrolyte allows desired amount of decomposition of NO₃⁻ and PF₆⁻ anions to form inorganic-rich interphases on both lithium and SPAN surfaces. The combination between low electronic conductivity of LiF and high ionic conductivity of N-contained species provides good protection against side reactions, enabling good performance for both SPAN cathode (> 200 cycles, Figure 154c) and Li-metal anode (CE 99.66%, Figure 155a). The Li||SPAN full cell also showed promising cyclability (Figure 155b). In contrast, the baseline electrolyte (4 M LiFSI in DME) shorted the SPAN half cell after 130 cycles (Figure 154a). In upcoming quarters, the team will continue to optimize other cell parameters toward practical conditions using the nitrate-reinforced electrolyte to achieve the goal of high-energy-density Li-S batteries.



Figure 154. Charge-discharge curves of Li||SPAN half cells in (a) 4 M LiFSI in DME, and (b) the nitratereinforced electrolyte. (c) Long-term cycling performance in both electrolytes.



Figure 155. (a) Lithium plating/stripping efficiency and (b) cycling performance of Li||SPAN full cell in nitrate-reinforced electrolyte.

J. Liu's team at University of California, San Diego (UCSD) studied four LHCEs with high areal loading (> 6 mAh cm⁻²) SPAN as the cathode, a material that is known to offer stable cycling with no polysulfide dissolution problem when the appropriate electrolyte is chosen. Based on the understanding of the role of transport, the UCSD team identified a DME-based LHCE as the optimal choice to fabricate a 2 Ah pouch cell. The study demonstrates the significance of electrolyte bulk in realizing stable cycling of high-energy-density Li-metal batteries with high areal capacity cathodes. Four LHCEs were prepared using LiFSI as salt and four different ethers as main solvents due to the superior stability of ether with Li-metal anode. The four ethers are dibutyl ether (DBE), diisopropyl ether (DiPE), diethyl ether (DEE), and DME; the four electrolytes are LDBE, LDiPE, LDEE, and LDME, respectively. These four electrolytes were saturated with LiFSI salt and then diluted by bis(2,2,2-trifluoroethyl) ether (BTFE) in 1:2 solvent-to-diluent mole ratio.

Several physical properties had been tested and calculated for these four electrolytes, including the concentration, conductivity, viscosity, and transference number. The concentration follows the trend of LDME > LDEE > LDBE > LDiPE. The ionic conductivity measured in Swagelok cells without separator shows the trend of LDME >> LDEE > LDiPE > LDBE, consistent with the dielectric constants of the four primary solvents. Furthermore, the electrolyte viscosity and transference number were also measured. LDME showed the highest viscosity and lowest transference number. LDiPE is the least viscous and of the highest transference number. The viscosity trend follows the same trend as the concentration. The team also calculated the Sand's capacity, and the LDME showed the highest Sand's capacity (LDME > LDEE > LDBE). This implies that cells with LDME are less prone to ion depletion, which is one of the main driving forces for uncontrollable dendrite growth.

The UCSD team's previous report has shown that to deliver > 300 Wh kg⁻¹ energy density at cell level, a SPAN cathode with > 6 mAh cm⁻² areal capacity is needed. Figure 156a shows the cycling performance of four electrolytes in full-cell configuration, when > 6 mAh cm⁻² SPAN cathodes were paired with lithium metal. The charge and discharge current density was 1.2 mA cm⁻² for all cells. Cells with LDBE, LDiPE, and LDEE electrolytes failed at the 23rd, 27th, and 46th cycle, respectively, while the cell with LDME electrolyte lasted 130 cycles without noticeable capacity fading. The symptoms of cell failure are classic soft shorting behavior. The charging capacity exceeded the theoretical value as lithium dendrites penetrated the separator and leaked electrons. The voltage fluctuated as the lithium dendrites propagated to the cathode and broke after reacting with the positive electrode (Figure 156b).

The UCSD team correlated the electrolyte transport properties with the cell shorting behavior. The onset of shorting started earlier for electrolytes with lower conductivities rather than with lower CE values. Figure 156c-d illustrates the correlation between cycle number and Sand's capacity, where a clear linear relationship of cycled number with increasing Sand's capacity is observed. When considering the effect of the separator, the cells are substantially cycled longer than those without a separator, as predicted by the Sand's capacity. This provides a theoretical explanation for the dendrite shorting behavior. In systems with low

Sand's capacities, ion depletion can be triggered when paired with high-capacity cathode, which will accelerate dendrite growth. The other electrolyte properties, including the viscosity and transference number, show no apparent correlation with the shorting behavior. LDME shows the highest viscosity and lowest transference number, but the longest cycle life among the four electrolytes. LDiPE is the least viscous and of the highest transference number, but only delivered 27 cycles before shorting. Therefore, this study challenges the assumption that both great efficiency and outstanding transport properties are needed for electrolytes to enable high-energy-density Li||SPAN cells.



Figure 156. Capacity retentions and voltage profiles of high areal capacity (> 6 mAh cm⁻²) Li||SPAN cells in different electrolytes. (a) Charge/discharge areal capacity retention of Li||SPAN cells with different electrolytes. (b) Voltage profiles of Li||SPAN cells with different electrolytes. Cycle numbers versus Sand's capacity of cells with different electrolytes based on data measured (c) without and (d) with separator. Cells were cycled under C/20 for 2 cycles, and then followed by C/5 cycling.

Separators

In previous reports, the University of Washington (UW) team successfully prepared the $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP)-coated polyethylene separator with a coating-layer thickness of ~ 1.25 µm, and the Li||NMC-811 batteries using ceramic-coated polyethylene separators showed higher capacity retention than those using bare polyethylene separators. This quarter, UW used radio-frequency magnetron sputtering to directly deposit a thin layer of LATP on polyethylene separators. The deposition was carried out for 2 hours at a power density of 2.63 W cm⁻² in pure 5 mTorr Ar environment at ~ 40°C. The thickness of the coated LATP layer is

~ 40 nm measured by a Bruker DektakXT Contact Profilometer. The mass of the polyethylene separator only increased by 4.5% after coating with LATP, which is beneficial to realizing high-energy-density batteries. Figure 157a shows the Nyquist plots of the SS/separator/SS cells, where SS stands for stainless steel. The ionic conductivities of the bare polyethylene and LATP-coated polyethylene separators infiltrated with carbonate electrolyte [1 M LiPF₆ in EC/EMC (3:7 by wt) with 2 wt% vinylene carbonate (VC) additive] at room temperature are calculated to be 0.53 mS cm⁻¹ and 0.71 mS cm⁻¹, respectively; this is based on

$\sigma = d/(RA)$

where d is the thickness of the separator, A is the area of the SS electrode, and R is the bulk resistance obtained from the high-frequency intercept of the Nyquist curve on the x-axis. The higher ionic conductivity of the LATP-coated polyethylene separator as compared to the bare polyethylene can be ascribed to better electrolyte wettability of the LATP-coated polyethylene and can help to improve the rate performance in battery cells. The electrochemical performance of separators was evaluated by cycling the Li||NMC-811 half cells [N/P ratio = 0.4; that is, the capacity ratio between anode (negative electrode) and cathode (positive electrode)] with the LHCE [LiFSI:DME:TTE (1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether) = 1:1.2:3 by mol.] at 25°C. The mass loading of the NMC-811 cathode is ~ 20 mg cm⁻². As shown in Figure 157b, the battery using LATP-coated polyethylene separator exhibits an initial reversible capacity of 196.4 mAh g⁻¹ with a CE of 86.7% at 0.1C between 2.8 V and 4.4 V, similar to that using bare polyethylene separator (193.5 mAh g⁻¹, 85.8%). After the formation cycles, both batteries deliver similar discharge capacities and CEs at 0.33C. These batteries are still being cycled, and the team will examine if the battery using ultrathin LATP-coated polyethylene separator presents better cycling performance in the LHCE electrolyte.



Figure 157. (a) Nyquist plots of the bare polyethylene and LATP-coated polyethylene separators. (b) Cycling performance of the Li||NMC-811 batteries with bare polyethylene or ultrathin LATP-coated polyethylene separator.

Characterization

Controlling Chemical Corrosions of Li-Metal Anodes

Y. S. Meng's team at UCSD explored the effect of porosity on the corrosion rate of lithium last quarter. It was found that the porosity of the plated lithium is the major factor in determining the lithium corrosion rate. The corrosion rate of lithium is directly related to the porosity of the lithium. This quarter, the team further explored the effect of surface chemistry on the corrosion rate of lithium. To elucidate the effects of surface chemistry on the corrosion rate of lithium metal, X-ray photoelectron spectroscopy (XPS) with depth profiling was performed on the freshly deposited and corroded lithium metal to verify the interphases chemical information (Figure 158). Two representative electrolyte systems [that is, (1) high-concentration ether-based electrolyte, bisalt [4.7 M LiFSI + 2.3 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in DME], and (2) carbonate-based electrolyte, Gen 2 (1.2 M LiPF₆ in EC:EMC), were chosen for this study. Meng's team identified that the fresh SEI components in the two electrolyte systems are almost identical. In the bisalt samples, the change of intensity of C-F peak with depth implies the presence of lithium salt (LiTFSI and LiFSI) on the surface of the lithium, which can be confirmed by the 533 eV peak in oxygen 1s and peaks in carbon 1s spectra as well (C-F at 293 eV and C-S = O at 289 eV). Other than the lithium salts, Li-F, Li₂O, and typical organic species such as 251 FY 2022 - Q3 (v. 30 September 2022) **BMR Quarterly Report**

C-O/C = O/ROLi can be recognized. Figure 158b demonstrates the results from Gen 2 sample, which is quite like the bisalt samples, considering the major components include Li-F, Li₂O, and typical organic species in the freshly deposited samples. After 3 weeks of resting, in the bisalt samples, there is an accumulation of lithium salt in the surface of the lithium, while other SEI components still preserve well in the surface layers. However, in the Gen 2 case, the Li₂O content mostly disappeared after 3 weeks of resting. The surface layers mainly consist of LiF after the corrosion. The results of Gen 2 samples show that the SEI layers have undergone a significant change during the resting period (highlighted by blue and violet shades), which correspond to the corrosion trend of the lithium deposited in Gen 2, where a fast corrosion rate is observed throughout 5 weeks of resting. Based on the results so far, it can be concluded that in the case of bisalt electrolyte, where ether-based solvents are used, the SEI components are much more stable than those of the Gen 2 electrolyte. Although XPS depth profiling can provide the team with valuable information about the evolution of the SEI components during the corrosion period, the exact SEI structure of the lithium deposited from each electrolyte remains unclear. More work should be done to carefully examine the nanostructure of the lithium SEI, which might be the key in determining stability of the SEI. The importance of a stable SEI layer was also reflected in the slow corrosion trend in the bisalt samples. Therefore, the team believes that the SEI layers need to be stable enough to survive the corrosion process for mitigating the continuous mass loss of lithium in liquid electrolyte (LE).



Figure 158. The X-ray photoelectron spectroscopy (XPS) depth profiling of deposited lithium metal. Chemical evolution of fluorine 1s, oxygen 1s, carbon 1s, and lithium 1s of (a) bisalt electrolyte and (b) Gen 2 electrolyte before and after 3 weeks of resting in the corresponding electrolyte.

XPS Primer for SEI Characterization in Li-Metal Anodes

XPS is commonly used to characterize SEI and help people understand the connections between the chemical speciation of SEIs and the performance of Li-metal batteries. However, the state of the SEI might be affected by artifacts introduced during XPS experiments, resulting in erroneous extraction of chemical information. The SLAC National Accelerator Laboratory / Stanford University team has identified specific procedures that may introduce errors during lithium SEI analysis and provided guidelines for accurate SEI characterization in future studies. Herein, four themes were identified that could contribute to erroneous extraction of chemical information from the XPS analysis of SEIs. An SEI formed on top of lithium anode (2 mAh cm⁻² of lithium deposited at 0.5 mA cm⁻² with L40 electrolyte) was investigated as an example. Four avenues for errors during XPS analysis of SEIs were discovered and are discussed below.

Effects of Sample Preparation Method. Up to 98% variation in the ratios of chemical species in the SEI was identified through variations in sample rinsing methods (Figure 159a). Residual solvents (EC) and salts were observed to coexist with the SEI and contribute to the variations; thus, the sample preparation methods should be clearly reported to ensure that SEI analysis results are consistent in the future.

Spatial Location of Sampling Region. Variations in spatial location of XPS analysis on a given SEI result in up to 66% variation in the F/C ratio in the SEI (Figure 159b). The results show that the XPS analysis was subject to the inhomogeneity of SEI samples. The team recommends that measurements be carried out on at least three distinct SEI spots to provide statistical confidence.

Time-Dependence of SEI Species. The duration of SEI exposure under ultrahigh vacuum in the XPS chamber changed the SEI chemical markers by as much as 84%, resulting in both changes in elemental ratios and specific chemical species in the SEI (Figure 159c). Therefore, it is important that XPS data collection, especially across different SEIs, is carried out within a short time window to ensure that SEI states are comparable.

Effect of Sputtering. A mixture of Li_2CO_3 and LiF particles was studied as a model SEI. Ar⁺ sputtering significantly altered the F/C and O/C ratios of the model SEI (Figure 159d). It also preferentially decomposed SEI components (for example, Li_2CO_3) and introduced artifacts in the form of new chemical species (for example, Li_2O) into SEI analysis. Therefore, caution is in order when carrying out Ar⁺ sputtering of SEI samples during XPS analysis because it could introduce artifacts into the data.



Figure 159. Chemical species changes during X-ray photoelectron measurement. (a) Atomic ratio as a function of three solid electrolyte interphase (SEI) preparation methods. (b) SEI atomic ratio as a function of sampling region. (c) SEI atomic ratio as a function of duration of SEI inactivity under ultrahigh vacuum. (d) Atomic concentration of model SEI ($Li_2CO_3 + LiF$ mixture) for different Ar⁺ sputtering times.

Highlights of Keystone Project 1

The highlights for this quarter are as follows:

- The PSU team's electrolyte EDFB of 1 M LiPF₆ in EC/DEC (v/v = 1:1) with 15 wt% FEC and 1 wt% LiDFOB enabled the high-energy-density Li||NMC-811 pouch cell using a high areal capacity (4.0 mAh cm⁻²) cathode, 50-µm-thin Li-metal anode, and lean electrolyte (3.0 g/Ah), with a high gravimetric energy density of 366 Wh/kg and an unprecedented cycling stability with 80% capacity retention after 335 cycles.
- The UT Austin team developed a new electrolyte (LSE) for LiNiO₂ cathode. The cell using LSE improved self-discharge performance at 45°C and cycle retention (~ 81.3%) after 600 cycles. The cycled cathode showed a thin rock-salt phase of 1-2 nm via STEM images, and the spinel phase is sporadically distributed in small areas resulting in suppression of undesired oxygen loss and deep reduction of nickel ions during cycling.
- The UCSD team developed four LHCEs using different ether solvating solvents. Among them, DME-based LHCE showed the highest Sand's capacity, implying that cells with LDME electrolytes are less prone to ion depletion, which is a main driving force for uncontrollable dendrite growth. Based on the LDME important discovery on the key role of Sand's capacity, Li||SPAN (> 6 mAh cm⁻²) cell delivered a stable cycle performance up to 130 cycles at a current density of C/5 (= 1.2 mA cm⁻²), even though LDME has the highest viscosity and lowest transference number.

Keystone Project 2: Electrode Architecture

The goal of the Keystone 2 is to design, model, fabricate, and characterize the effect of electrode architecture on the electrode and cell performance in support of reaching the project goal of 500 Wh kg⁻¹ cell specific energy. Studies conducted this quarter include: (a) exploring electrolyte additives for high-capacity cathode materials involving high nickel content, namely, NMC; (b) studying the sulfur inventory and understanding the reaction mechanisms, including reducing the irreversible loss in sulfurized polymer cathode of SPAN; (c) identifying new functional electrocatalysts promoting conversion of polysulfides to Li₂S, as well as (d) developing new solid-state-electrolyte (SSE)-containing separators to substitute for polypropylene (PP)-based separators for Li-S batteries. This report for Keystone 2 project thus includes highlights involving studying the reaction mechanisms in SPAN cathodes (PNNL); studying the electrolyte additive influence on the performance of high nickel content, NMC cathode, and the use of SSE-containing separators for Li-S batteries (UT Austin); and identification of new functional electrocatalysts for reducing the kinetic barriers for conversion of the polysulfide to Li₂S (University of Pittsburgh, or U-Pitt).

Unraveling Reaction Mechanisms in SPAN Cathodes

The PNNL team continued the study of root causes for the CEI formation and evolution on SPAN cathode surface in Li||SPAN cells with two electrolytes, LFSI-ether (that is, an LHCE of LiFSI-1.2DME-3TTE, by mol.) and LPF-carbonate [that is, a baseline electrolyte of 1 M LiPF₆ in EC-EMC (3:7 by vol) + 2 wt% VC], through experimental investigation and computational simulations.

The surfaces of SPAN cathodes were examined through *ex situ* XPS characterization at different discharge states (Points I, II, and III in Figure 160a, corresponding to discharge specific capacities of ~ 40 mAh g⁻¹, ~ 1060 mAh g⁻¹, and ~ 1770 mAh g⁻¹, respectively) and after the first cycle (Point IV in Figure 160a) in both LPF-carbonate and LFSI-ether, as well as after 5 cycles in LFSI-ether. Li₂S₂ is revealed to be the main active product of lithiation in SPAN, and the Li⁺ trapped by Li-S, Li-N, and Li-C bonds are the main contribution of irreversible capacity loss in the 1st cycle for Li||SPAN batteries, regardless of the electrolyte system. In addition, the reactions between Li₂S₂ and C-O/C = O in LPF-carbonate or C-F of TTE and N-S of LiFSI in LFSI-ether initiate the growth of a CEI layer. In LPF-carbonate, the solvent-dominated decomposition process in the initial cycle leads to formation of CEI on the inner and outer layers of the SPAN surface. In contrast, for LFSI-ether, the DME decomposition is suppressed, and the decomposition process is dominated by LiFSI salt, resulting in fewer organic species that have large molecule size. Thus, the CEI formed in LFSI-ether can fill into the SPAN bulk and strengthen SPAN like a pinning layer. Furthermore, the CEI layer formed in LFSI-ether is demonstrated to be more conductive, robust, and thin, leading to long-term cycling stability with high sulfur loading under both room and high temperatures, fast discharge capability, and superior low temperature performance.

One SPAN structure (Structure III) with the polyacrylonitrile (PAN) chains connected by S-S-S-S bond (Figure 160b) was selected to reveal the lithiation products of SPAN with density functional theory (DFT) calculation and *ab initio* molecular dynamics (AIMD) simulation. The S-S bond lengths in the cross-linked SPAN structure by DFT were first calculated. The bond lengths of SS1 and SS2 are 2.04 Å and 2.12 Å, respectively. It implies that the SS2 bond is easier to be cleaved in Structure III. When the two SS2 bonds at the edge are cleaved in SPAN, it will generate Li₂S₂ as the lithiation product as well as S_x^{2-} anion or radical for longer polysulfide chain connector. AIMD simulations reveal that the S-S breakage in SPAN is very fast and that the bonding between lithium and sulfur is also rapid during the lithiation [see the radial distribution functions (RDFs) of S-S and Li-S in Figure 161]. The cleavage of S-S bond will generate C-S-Li species when SPAN meets Li⁺. Moreover, as suggested by the observation in RDFs between carbon and sulfur atoms (Figure not shown here), some of the C-S bonds also can be cleaved and then generate a certain amount of Li₂S_x (x > 2), which is likely the reason for the lithiation process, AIMD simulations also reveal the rapid breakage of Li-S bonds and fast formation of S-S bonds between PAN chains (Figure 161); however, a certain Li-S

peak still exists until 20 ps, indicating that some lithium atoms still bond to sulfur atoms after the 1st cycle. That not all Li-S bonds go back to S-S implies certain loss of capacity during the 1st cycle. This explains the large capacity loss of SPAN cathode during the 1st lithiation and delithiation cycle.



Figure 160. (a) The initial discharge/charge profiles of Li||SPAN cells with different electrolytes at C/10 rate. Sampling points (I, II, III, and IV) for X-ray photoelectron spectroscopy (XPS) characterizations are marked with dots and numbers. (b) One SPAN structure used in *ab initio* molecular dynamics simulation. (c-d) Sulfur 2p and fluorine 1s XPS spectra collected on the surfaces of SPAN cathodes at different discharge states (points I, II, and III) and charge state (point IV) in (c) LPF-carbonate and (d) LFSI-ether electrolytes, respectively. (e-f) Nitrogen 1s XPS spectra at signal depth of 0 nm for SPAN (e) at point I in LPF-carbonate and (f) at point IV in LFSI-ether. (g-h) Sulfur 2p, fluorine 1s, and nitrogen 1s XPS spectra collected on the surfaces of (g) pristine SPAN and (h) SPAN after 5 cycles in LFSI-ether. (Signal depth = 10 nm)

This study indicates that the Li-S reaction rate will mainly depend on the diffusion rate of Li⁺ through the CEI layer and in the bulk SPAN. Consequently, the conductivity of the CEI layer could be a critical determinant for electrochemical performance of Li||SPAN cells.



Figure 161. Radial distribution functions of (a) S-S and (b) Li-S atoms at different periods of time during the initial discharge/charge processes.

Influence of Electrolyte Additive on Performance of High-Nickel-Content, NMC-811 Cathode

This quarter, UT Austin focused on introducing a simple additive $Mg(ClO_4)_2$ into the LHCE to reduce electrolyte-Li reaction, protect lithium surface, and stabilize the anode architecture for long-term cycling. As shown in Figure 162, Li/NMC-811 cells assembled using LHCE with the additive demonstrate a superior capacity retention of 96.3% at C/10 rate after 100 cycles compared with a capacity retention of 93.0% for cells using pristine LHCE without the additive. The additive also helps improve rate capability and CE (Figure 162bc). The discharge capacities with pristine LHCE are 219 mAh g⁻¹, 212 mAh g⁻¹, and 197 mAh g⁻¹ at, respectively, C/10, C/3, and 1C rates. When the rate is increased to 2C, a fast capacity decay is evident, and a capacity of 174 mAh g⁻¹ and 170 mAh g⁻¹ is seen at, respectively, 3C and 5C rates. The cell capacity returned to 210 mAh g⁻¹ when the rate was reduced back to C/3, which may have been caused by the damage to lithium anode at high current densities during fast charge. In contrast, the cell with LHCE with Mg(ClO₄)₂ additive performs significantly better at high charge rates, showing stable specific discharge capacities of ~ 186 mAh g⁻¹, 184 mAh g⁻¹ and 178 mAh g⁻¹ at, respectively, 2C, 3C, and 5C rates. The specific capacity then recovers to 214 mAh g⁻¹ after the charge rate is back to C/3. These results clearly show that the LHCE with additive reduces damage to the integrity of the SEI and enables high current density cycling. The additive also enhances the CE, as seen in Figure 162c.



Figure 162. Electrochemical characterizations of the Li/NMC-811 cells. (a) Charge and discharge curves of Li/NMC-811 cells with localized high-concentration electrolyte (LHCE) with and without $Mg(CIO_4)_2$ additive at C/10 rate for 100 cycles. (b) Charge and discharge profiles of LHCE with additive under various rates. (c) Rate performance, long-term cycling performance, and Coulombic efficiency of the Li/NMC-811 cells with LHCE with and without $Mg(CIO_4)_2$ additive.

Study of SSE-Containing Separator for Li-S Batteries

This quarter, UT Austin also synthesized a separator composed of Li_6PS_5Cl (LiPSCl) SSE as a substitute for the conventionally used PP-based separators in Li-S batteries. The commercially available PP-based separators have a porosity of ~ 50% through which the electrolyte percolates. Therefore, 50% of the volume of the separator does not contribute to ion-conduction. As both sulfur and Li_2S are poor ionic conductors, the redox chemistry of sulfur is dependent on facile access to Li^+ ions. Facilitating additional Li^+ ion transport by replacing the non-conducting PP with ion-conducting LiPSCl could potentially promote sulfur utilization. With this aim, LiPSCl SSE was synthesized, blended with 1 wt% polytetrafluoroethylene (PTFE), and rolled into thin, compact sheets, as shown in Figure 163a, which could be punched into separators, as shown in Figure 163b. SEM imaging shows that LiPSCl particles are held tightly by a web of PTFE fibrils (Figure 163c). This separator design also presents the added advantage of presenting a tortuous path for the electrolyte-soluble lithium polysulfides, which could mitigate the polysulfide "shuttle" effect. Initial studies (Figure 163d) found that the improved ionic conductivity does indeed lower the nucleation barrier for Li_2S_4 and improve capacity. However, the team soon found that the LiTFSI salt conventionally used in Li-S batteries degrades on contact with LiPSCl. To circumvent this issue, LiI was used as the supporting salt, which resulted in a significant increase in the discharge capacity to 1353 mA h g⁻¹. Long-term testing is under way to determine the stability of this system.



Figure 163. (a) Image showing the facile fabrication of large sheets of LiPSCI electrolyte. (b) Images of the separator. (c) Scanning electron microscopy image showing the microstructure of the separator. (d) Performance of the Celgard[®] and LiPSCI separators with 1 M LiTFSI + 0.2 M LiNO₃ in DME/DOL electrolyte and that of LiPSCI separator with 1 M LiI in DME/DOL electrolyte.

Computational Identification of Functional Electrocatalysts for Li₂S₂ to Li₂S Conversion, U-Pitt

U-Pitt conducted theoretical modeling to probe the kinetic barriers related to the conversion of Li_2S_2 , the intermediate polysulfide phase, to Li_2S , the final phase, with the main goal being to identify functional electrocatalysts. As already discussed in the previous report, achieving the complete conversion of Li_2S_2 to Li_2S is of prime importance for the discharge process since the very sluggish kinetics of this reaction prevents full utilization of sulfur in the sulfur cathode.

The overall transformation reaction for the *charge* process could be written as follows:

 $2 \text{ Li}_2 S \rightarrow \text{Li}_2 S_2 + 2\text{Li}$

which will involve three possible elementary steps:

$$Li_{2}S^{(1)} \rightarrow LiS + Li \quad (reaction 1)$$
$$LiS \rightarrow Li + S$$
$$Li_{2}S^{(2)} + S \rightarrow Li_{2}S_{2}$$

Similarly, the *discharge* reaction path can be represented by:

 $Li_2S_2 + 2Li \rightarrow 2Li_2S$,

and will comprise the following corresponding elementary steps:

$$\begin{array}{ll} Li_2S_2 \rightarrow Li_2S^{(1)} + S & (reaction \ 2) \\ Li^{(1)} + S \rightarrow & LiS \\ LiS + Li^{(2)} \rightarrow & Li_2S^{(2)} \end{array}$$

Out of these six elementary steps, reaction 1 and reaction 2 are the principal reactions, and should be considered for estimation of the electrocatalytic ability of the materials to promote conversion of Li_2S_2 to Li_2S in the forward reaction and the corresponding backward reaction.

In the previous report, the U-Pitt team reported demonstration that Reaction 1 ($\text{Li}_2S^{(1)} \rightarrow \text{Li}S + \text{Li}$) in the *discharge* direction (from right to left) is almost spontaneous without registering any appreciable activation barrier, which indicates that the formation of Li_2S by seizing Li-ion during the discharge process does not hinder the overall kinetics of $\text{Li}_2S_2 \rightarrow \text{Li}_2S$ conversion; Reaction 2 ($\text{Li}_2S_2 \rightarrow \text{Li}_2S + S$) has a barrier in both the *charge* and *discharge* directions (see Figure 164a), thus rendering this reaction as the rate determining step (RDS) in the overall conversion of Li_2S_2 to Li_2S . Hence, for future acceleration of the materials screening process, there is no need to consider Reaction 1 ($\text{Li}_2S^{(1)} \rightarrow \text{Li}S + \text{Li}$); thus, all future research study should focus on addressing the kinetic properties (activation barriers) of Reaction 2.

To obtain thermodynamic properties, the team has used the DFT approaches implemented in Vienna *ab initio* simulation package (VASP), while utilizing a climbing image nudged elastic band (CNEB) method for determination of the activation energies and other pertinent kinetic parameters of the elementary reactions on the different prospective electrocatalytic surfaces.

The model of the functional electrocatalyst consists of a surface slab with the most stable crystallographic orientation containing the attached Li_2S_2 or Li_2S molecules. The slab with a thickness of approximately 5-7 Å is separated from its image perpendicular to the surface direction by ~ 20 Å to avoid their mutual interaction. The bottom two-three layers of the slab are fixed with lattice parameters corresponding to the bulk state, while the remaining top layers, along with the attached polysulfide molecule, are allowed to completely relax. All the species are adsorbed on the electrocatalyst surface including the lithium and sulfur atoms.

Activation barriers for elementary reactions were estimated using the CNEB method, where five intermediate points were chosen for calculations of the potential energy profile between the initial and final position of the Li-ion for Reaction 1 and sulfur atom for Reaction 2 at the electrocatalytic surface (totally 7 points).

All the computations have been executed within the projector-augmented wave method and the generalized gradient approximation for the exchange-correlation energy functional in a form described by J. P. Perdew and Y. Wang implemented in the VASP software. To maintain high precision for all of the total energy and electronic structure calculations, the plane wave cutoff energy of 520 eV was chosen. The relaxation procedure has been used to optimize the internal positions as well as the lattice parameters of atoms within the supercell. Also, the Monkhorst-Pack scheme has been used to sample the Brillouin zone and create the k-point grid for all the electrocatalytic surface slabs used in the current study. The selection of the appropriate numbers of k-points in the irreducible parts of the Brillouin zone was made on the grounds of the convergence of the total energy to 0.1 meV/atom.

The potential energy profiles for Reaction 2 calculated for functional electrocatalysts (comprising (1) Functional Catalysts I, Type I, and (2) Functional Catalysts II, Type II) are shown in Figure 164a-b, respectively. Figure 164a is reproduced from the last report (Q2 FY2022) for clarity and comparative purposes only. It can be observed that for all the probed materials of both types, Reaction 2 in the discharge direction is exothermic, as expected, with the final product (Li₂S+S) being more energetically favorable compared to Li₂S₂. However, in contrast to the Reaction 1, this reaction is not spontaneous with substantial activation barriers needed for the different electrocatalytic materials considered and is averaged around ~ 1 eV for Type I and ~ 0.6 eV for Type II functional electrocatalysts. Type II functional electrocatalysts, therefore, demonstrate significantly lower average activation barriers than those observed and calculated for the Type I functional electrocatalyst catalyst Cat8 in Figure 164b demonstrates the lowest activation barrier among all of the prospective electrocatalytic materials considered so far (~ 0.3 eV). However, there is still a need to further decrease the activation barriers for Reaction 2, which will then likely yield much higher specific capacity values for sulfur in the sulfur cathode. Studies to further identify better functional electrocatalysts are planned, and the research work is ongoing and will be reported in future quarters. Results of the experimental work to validate the findings of the theoretical calculations will also be reported.



Figure 164. Potential energy profiles for Reaction 2 ($Li_2S_2 \rightarrow Li_2S + S^*$) for the two types of functional electrocatalysts considered.

Another computational task conducted this quarter is identification of effective Li-ion conductors (LIC) needed for encapsulation of sulfur nanoparticles to prevent dissolution of polysulfide species and the corresponding shuttling effect. For these purposes, several materials belonging to the stoichiometric formula (that is, $Li_7(TM)N_4$, TM = transition metals), identified in Table 7, have been chosen as potential LICs for the computational evaluations of the Li-ion conductivity/mobility as well as structural and electrochemical stability in the presence of an electric field during electrochemical cycling of the battery. The nudged elastic band method has been used as the main computational approach for calculating the potential energy profiles of the Li-ion paths through the different types of channels present in the considered LIC materials.

LIC	E _{coh} (eV/at)	E _{BG} (eV)
Li ₇ NbN ₄	-4.06	3.35
Li ₇ VN ₄	-3.95	3.01
Li ₇ NiN ₄	-3.14	0
Li ₇ MnN ₄	-3.56	0

Table 7. Cohesive energies and band gaps.

The crystal structures of many of the $Li_7(TM)N_4$ type compounds are very similar and demonstrate open Li-channels that do not contain TM atoms, as shown in Figure 165. Thus, the TMs do not noticeably affect Li-ion conductivity through these channels, and the computational estimation of the Li-ion mobility for these systems could be executed only for one typical compound in this materials family, such as Li_7NbN_4 belonging to the cubic space group #205 (Pa-3).

It can be observed that the structure in the [110] direction contains channels representing rows of quite large interstitial sites. These channels may serve as efficient pathways for Li-ion mobility during electrochemical cycling. In this case, the lithium pathway would have a zig-zag shape, as shown with the green arrows in Figure 165.

Furthermore, a computational study was conducted to compare the Li-mobility/diffusivity in these two directions. This involved estimation of the activation barriers of the Li-ion diffusion pathways and, in turn, identification of crystallographic directions in which the Li-ions can move the most effectively with minimal resistance from other atoms in the lattice.


Figure 165. Crystal structure of Li₇NbN₄ as the typical Li-ion conductor with Li-ion channels in [100] and [110] directions. Green arrows denote the hopping of Li-ions/vacancies for the different Li-hopping pathways.

Here again, the CNEB approach was used to calculate the activation barriers of the Li-ion diffusivity in the [100] and [110] directions. For estimation of the activation barriers across these two directions, seven intermediate points were chosen for performing calculations of the potential energy profile between the initial and final positions of the Li-ion for the selected pathways in these two directions (totally 9 points). Both energy profiles for these two directions are shown in Figure 166. It can be construed that the Li-ion mobility profile in the [100] direction demonstrates higher activation barrier than that in the [110] direction (0.284 eV versus 0.223 eV), which indicates that the [110] direction is noticeably preferable for facilitating and channeling the Li-ion mobility contrasted with the [100] direction. This result also proves the notion regarding efficiency of Li-ion mobility through the large interstitial channels presented in the crystal structure.

Finally, for assessing structural and electrochemical stability of the LICs in the presence of the electric field, a very approximate rudimentary evaluation can be presented by comparison of cohesive energies, E_{coh} , and the band gaps, E_{BG} , obtained from the electronic structure calculations. The higher the E_{coh} and the E_{BG} , the material system can be perceived to be likely more stable in harsh electrochemical conditions. Thus, from the values of E_{coh} and E_{BG} listed in Table 7, it can be deciphered that Li_7NbN_4 and Li_7VN_4 could be such prospective LIC candidates for promoting facile transport of lithium ions and thus serving as effective additives in the sulfur cathode configuration for use in Li-S batteries.

0.25 0.20 0.20 0.10 0.10 0.05 0.00 Li-vacancy hopping path

[100] direction

Li7NbN4

0.35

0.30

0.284 eV

Screening of other potential LIC materials and identification of the most optimal system in terms of Li-ion conductivity and electrochemical stability are planned and will be reported in the



corresponding quarters. Results of the experimental validation of these theoretical calculations of promising LIC materials will also be reported.

Highlights of Keystone Project 2

The highlights for this quarter are as follows:

- The PNNL team used AIMD calculations and XPS characterization to study the root causes for CEI formation and evolution on SPAN cathode surface using two electrolytes, LFSI-ether, and LPF-carbonate, respectively. Their results indicate that not all Li-S bonds revert to S-S in the aromatic chains contributing to 1st cycle irreversible loss. They also show that diffusion rate of Li⁺ through the CEI is critical for ensuring performance of Li||SPAN cells.
- The team at UT Austin identified Mg(ClO₄)₂ as an additive to LHCE electrolyte to protect the lithium surface and stabilize the anode structure in cycling of Li/NMC-811 cells, resulting in capacity of 178 m Ah g⁻¹ at 5C rate as opposed to 170 m Ah g⁻¹ when the cell is cycled in pristine LHCE without the additive. They also showed that use of Li₆PS₅Cl SSE as a substitute for conventionally used PP-based separators using LiI as the supporting salt resulted in increasing the discharge capacity to 1353 m Ah g⁻¹.
- The U-Pitt team has used computational approaches to identify functional electrocatalysts for use in the Li-S cathode that can lower the activation barrier for conversion of Li₂S₂ to Li₂S from an average value of ~ 1 eV to ~ 0.6 eV, with the best system demonstrating a value of ~ 0.3 eV. They also identified Li₇NbN₄ as a promising LIC with preferred Li-ion conduction in the [110] direction with reduced barrier of 0.223 eV for use in Li-S cathodes.

Keystone Project 3: Cell Fabrication, Testing, and Diagnosis

The General Motors (GM) team completed installation and system calibration of the ultrasonic scanning system. Initial trials using the commercial Li-ion batteries were conducted to check the system. Figure 167 shows the cell that was soaked in the silicon oil bath and hooked up with the cycler during the scan. Figure 168 shows the transmission image obtained by the ultrasonic scanning system with both fresh and end-of-life cells. The electrode wetted by electrolyte has higher ultrasonic transmissivity than the dry electrodes. In the mapping plot, transmission intensity is correlated to the electrolyte distribution in the cell. Further testing and system calibration is under way to achieve better resolution and intensity correlation.

For the cathode fabrication, the GM team started a larger batch mixing trial with a new mixer, targeting longer coating per batch. The initial coating test and validation was completed for double-sided coating with the previous selected loading. The loading variation between two sides can be controlled within 10% difference under continuous coating condition. In addition to the double-sided coating, the team continued single-sided coating with "standard" loading for baseline purposes. Last quarter, they sent single-sided coated baseline electrode to all other Li-S teams for evaluation. They also provided Brookhaven National Laboratory (BNL) with some single-layer pouch-format cells using the same batch of the electrode for studies using synchrotron beamlines.



Figure 167. Photo of testing cell within oil bath during testing.



Figure 168. Ultrasonic transmission image of the fresh cell and end-of-life (EOL) cell.

The Idaho National Laboratory (INL) team has completed scaling up of SPAN at 10 g per batch. As a promising cathode candidate, SPAN has attracted more attention due to fewer shuttling problems compared with traditional Li-S batteries using elemental sulfur cathode. For practical application, scaling up high-quality and reproducible SPAN materials is required. The INL team is responsible for providing high-quality SPAN powders and electrodes to the Batt500 Li-S teams. In this scale-up work, 5 g PAN with 20 g of sulfur was sealed and vulcanized at 450°C for 6 hours and then heated at 300°C to remove remaining elemental sulfur with flowing argon gas in a tube furnace. Pure SPAN powders > 10 g per batch were successfully synthesized (Figure 169a-b). The sulfur content in SPAN was found to be largely affected by the sealing state during the vulcanization process. The improved seal can enhance the sulfur content of SPAN from 42 wt% to 50 wt% based on the elemental analysis.

The SPAN electrodes with SPAN mass loading of ~ 6 g/cm² and ~ 9 g/cm² as well as porosity of ~ 60% were prepared and tested in Li||SPAN coin cells. High-concentration electrolyte (4 M LiFSI in DME) was used. The coin-cell assembly and testing follow the standard protocols made by the Battery500 team. The enhanced sulfur content in SPAN due to the improved seal during the vulcanization process resulted in specific capacity in terms of SPAN to be increased from 583 mAh/g to 727 mAh/g (Figure 169c) after two formation cycles at a charge/discharge rate of C/20 (1C = 600 mA/g). Additionally, as can be seen in Figure 169d, the two electrodes with different SPAN mass loadings show good cycling performance at a charge/discharge rate of C/10. The cells are still running, and the cell performance will be used as a baseline for development of new materials (for example, electrolytes) used in Li-SPAN batteries. More than five batches of SPAN powders (> 10 g per batch) have been synthesized with the same approach. The SPAN electrodes prepared with the obtained SPAN powders from different batches all showed high specific capacity of > 700 mAh/g. Therefore, the improved seal during synthesis process cannot only increase SPAN quality with improved sulfur content, but also improve reproducibility. However, the current synthesis process requires excess sulfur. To increase yield per batch, the removal of the large amount of elemental sulfur might cause a safety issue due to solid sulfur stuck at the outlet of the tube furnace. Thus, a new, improved synthesis approach needs to be developed.



Figure 169. (a) SPAN powders with > 10 g per batch. (b) X-ray diffraction pattern of SPAN powders after vulcanization and removal of elemental sulfur. (c) Discharge curves of SPAN prepared at different sealing states. (d) Cycling performances of Li-SPAN cells with different SPAN mass loadings.

The PNNL team successfully demonstrated a prototype 400 Wh/kg Li-metal pouch cell with 284 stable charge-discharge cycles and 80% capacity retention (Figure 170a), meeting/exceeding the goal in the Battery500 Consortium's FY 2022 Government Performance and Results Act (GPRA) milestone. The cell also maintained 80% of its energy (cell level) for 280 cycles. Through continuous integration of innovations developed under Battery500, the polarization of the Li-metal pouch cell on cycling has been significantly reduced (Figure 170b). Only at the 250th cycle of this 400 Wh/kg pouch cell is a slight increase of polarization observed. This reduction of polarization is an important achievement, establishing a good foundation for further stabilization of Li-metal batteries.



Figure 170. (a) Cycle performance and Coulombic efficiency of a 2.5 Ah prototype 400 Wh/kg Li-metal pouch cell. (b) Charge and discharge profiles of the Li-metal pouch cell at different cycles.

Highlights of Keystone Project 3

The highlights for this quarter are as follows:

- The GM team completed installation and system calibration of the ultrasonic scanning system and started larger-batch sulfur cathode coating.
- The INL team successfully synthesized SPAN powders at 10 g per batch with sulfur content 50 wt% and validated the quality of the materials in coin-cell test.

 The PNNL team successfully developed a prototype 400 Wh/kg Li-metal pouch cell and demonstrated 284 stable cycles with an 80% capacity retention, meeting/exceeding the Battery500 Consortium's FY 2022 GPRA milestone.

Keystone Project 4: Cross-Cutting Efforts

The goal of the Cross-cutting team is to develop and deploy advanced characterization tools in support of the three Keystone efforts, with a focus on probing specific materials and interfaces for Keystone 1, probing individual electrodes for Keystone 2, and probing the whole cell for Keystone 3. Included in this Keystone are *operando* diffraction studies of inhomogeneity in Li-S pouch cells (BNL, GM, and INL), polysulfide quantification (UCSD), Li-SPAN reaction mechanism (UCSD), novel electrolyte additive design for high-voltage cathode (BNL, PNNL), *operando* electrochemical – atomic force microscopy (EC-AFM) imaging of lithium plating and SEI growth (SLAC) and effects of electrolyte on SEI formation and sulfur reduction (Texas A&M University). Highlighted this quarter are recent advancements in the demonstration of *operando* synchrotron X-ray diffraction (SXRD) for probing the inhomogeneity in Li-S pouch cells, deciphering the 1st cycle irreversible capacity loss in SPAN cathodes, quantifying polysulfide species in the LE, elucidating the electrolyte additive effects on the performance of high-voltage NMC-76 cathode, quantifying the SEI growth rate on lithium metal plated in LHCE, and elucidating the effects of electrolyte on SEI formation and sulfur reduction and sulfur reduction by computational methods.

Baseline Operando Diffraction Studies of Inhomogeneity in Li-S Pouch Cells

The BNL team worked together with INL and GM to apply synchrotron diffraction methods to investigate the speciation and inhomogeneity in Li-S pouch-cell batteries. In the first set of beamline experiments, it was observed that the capacity and rate capabilities of Li-S cells used for *operando* cycling experiments had severely degraded relative to the performance measured at INL for equivalent cells that were not shipped to the beamline. Despite the poor cycling behavior of cells during the team's first *operando* diffraction experiments, the diffraction data suggested that *operando* diffraction studies would have sufficient sensitivity to track many important changes that occur during cycling. Through the partnership with the industrial labs at GM, a set of three very high-quality Li-S cells was obtained for the next synchrotron experiments (Figure 171a). Two of these had the same relatively high sulfur loading of 6 mg/cm², with one cell (GM-1) subjected to an additional 2 weeks of aging relative to the other cell (GM-2). The third cell (GM-3) was prepared with half the sulfur loading. By comparing the data from the cells, it is possible to test both the effects of calendar life and sulfur loading on the speciation and inhomogeneity of Li-S cells. From the electrochemical data collected during the



Figure 171. (left) Photograph of the three Li-S pouch cells used in *operando* synchrotron diffraction experiments with points being probed marked with red squares. (right) Voltage profile for the three cells. Blue: GM-1 (high loading, longest calendar aging). Red: GM-2 (high loading). Green: GM-3 (low loading). Cells were evaluated with a CC-CV-rest protocol.

operando diffraction studies (Figure 171b), it could be seen that the highest specific capacity during the first discharge was obtained for the low-loading sulfur cell (GM-3, 1200 mAh/g S), while the capacity of the high-loading cell was slightly lower (GM-2, 1100 mAh/g S) and that of the cell with both high-loading and a longer calendar life was substantially lower (GM-1, 900 mAh/g S). However, all three capacities remained comparable to typical literature values for high-quality Li-S cells (~ 1000 mAh/g S).

During *operando* diffraction testing, each of the three cells was monitored at 16 different points, with 4 points near the center of the cell and with 4 points near each of 3 different edges of the cell. Most points in all three cells showed a similar sequence of phases during cycling (Figure 172a), with the a-S₈ that was initially present disappearing over the first few hours of discharge, and Li₂S appearing and growing in intensity as the discharge continued. During the subsequent charge process, the Li₂S was gradually eliminated, followed by the subsequent appearance of S₈ in the form of b-S₈, which is behavior consistent with prior literature. Although this type of behavior was observed for many of the studied points, it was not universal. This can be seen for the points at the bottom of cell GM-2 (Figure 172b). They had substantially worse behavior, which can be seen both in the persistence of a-S₈ to much later times during the first discharge and in the lack of formation of Li₂S at all during the first discharge. This inhomogeneity was greatly mitigated in the low-loading cell, which highlights the extra challenges of meeting the Battery500 goal of realizing long lifetimes in high-energy-density cells that necessarily have high loadings. These initial results provide the groundwork for continuing studies that probe the effect of the environment (for example, applied pressure, temperature), cycling conditions (for example, C rate), and cell aging on the inhomogeneity in the cell, all of which may be playing an important role in controlling the accessible capacity of the sulfur cathodes.



Figure 172. (a) Points exhibiting a typical response during cycling. (b) Points with low activity.

Y. S. Meng's team at UCSD carried out studies on quantification of sulfur inventory loss in Li-S batteries. Li-S batteries consist of sulfur on the cathode side and lithium metal on the anode side. Polysulfides have been identified as the necessary evil in Li-S batteries that start to form during the 1st discharge cycle. However, very few efforts have been put into quantifying or understanding the effect of polysulfides on cell performance. Previously many qualitative ex situ high performance liquid chromatography (HPLC) studies have been done by derivatizing the polysulfides into stable methylated species to differentiate different polysulfides dissolved in the electrolyte. These studies proved its applicability in this system, and identifying the species based on their chain lengths became possible. However, due to the lack of absorptivity data for the derivatized polysulfides or lack of standards for longer chain polysulfides, quantitative interpretation has not been yet possible. Also, the analysis was limited to qualitatively identifying elemental S_8 and polysulfides. It did not include a consolidated picture of potential losses in the form of dead lithium from the Li-metal anode and other insoluble polysulfides on the cathode side. A comprehensive methodology needs to be developed to track both the lithium and sulfur inventory evolution in the cell at different stages of cycling. The UCSD team proposed to utilize a series of characterization tools to decipher the key bottleneck that limits the cycle life of Li-S systems (Figure 173). On the sulfur cathode side, insoluble species such as S_8 and Li_2S that remained in the cathode after cycling will be quantified by thermogravimetric analysis (TGA). Titration Gas Chromatography (TGC) has already been established in the team's previous work and will be used to track lithium inventory losses. The soluble polysulfide species in the electrolyte will be quantified by HPLC. In the end, a correlation between the lithium and sulfur inventory loss with the overall cell capacity evolution will be obtained.



Figure 173. Schematic of methodology to quantify and track inventory losses in Li-S battery.

Sulfur Quantification by HPLC – Ultraviolet (UV). Previously, Y. S. Meng's group at UCSD had shown the separation and identification of each polysulfide species in DME solution using HPLC-UV. This quarter, the group further established the calibration curve of S_8 in DME. To do that, 6.045 mg of S_8 was first dissolved in 5 mL of DME to get 4.722 mM S_8 , which was further diluted to 0.9445 mM, 0.7556 mM, 0.378 mM, 0.0756 mM, and 0.0151 mM of S_8 . S_8 quantification was achieved by obtaining the calibration curve for the elemental S_8 by calculating the area under the intensity versus retention time data and the concentration (Figure 174). A linear relation with $R^2 = 0.99999$ was achieved. For these measurements, five different concentrations of S_8 dissolved in DME were loaded in the autosampler, and UV measurements were done at 210 nm, 230 nm, 300 nm, and 800 nm. S_8 had maximum absorbance at 210 nm and was chosen for all sulfur quantification measurements. These results demonstrated that the calibration curve of S_8 in DME through HPLC-UV is successfully established. Next quarter, Meng's group will continue to develop calibration curves for each individual polysulfide species to quantify the concentration of each of them in a mixed solution.



Figure 174. (a) Chromatograms of different elemental sulfur concentrations. (b) Calibration curve for elemental sulfur.

Reducing the 1st Cycle Irreversible Capacity Loss in SPAN Cathode

Last quarter, J. Liu's and Y. S. Meng's groups at UCSD, in collaboration with B. Liaw from INL, characterized the working mechanism of SPAN as the cathode materials in Li-S batteries. Based on the mechanism, this quarter, the two groups unveiled directions on minimizing the 1st cycle irreversible capacity loss in SPAN cathode.

The groups propose a working mechanism for the 1st and subsequent cycling of SPAN (Figure 175). The role for each functional group is summarized in Figure 175a. During the 1st discharge as shown in Figure 175b, in SPAN, the aromatic functional groups contribute to the reversible capacity, while the irreversible capacity loss is due to transformation of the non-aromatic functional groups. After the 1st discharge, they will either form H_2S or be dissociated from the polymer chain (Li₂S) or be converted into the aromatic functional group. Furthermore, the conductive carbon is crucial to completing the irreversible transformation. Otherwise, the intermediates (N-Li and C-Li components) will remain in SPAN. The formation of more aromatic structure leads to an increased electrical conductivity and subsequently to highly reversible cycling in further cycles.



Figure 175. Working mechanism for SPAN in a battery. (a) Summary of the roles of components in SPAN. (b) Proposed SPAN working mechanism in battery. The UCSD team then hypothesized a post-thermal annealing method that can be effective to minimize the 1^{st} irreversible capacity loss for SPAN. SPAN has residual hydrogen as well as polysulfide chains. An intra-polymer elimination of H₂S is certainly possible. J. Liu and Y. S. Meng's groups first use TGA to determine the proper temperature for SPAN post-thermal treatment (Figure 176a). As a reference, a precursor mixture (4:1 weight ratio PAN:S) is also analyzed. The mixture loses 80% of its weight between 155-280°C, consistent with sulfur vaporization. In contrast, SPAN loses 20% of its weight between 210°C and 410°C. They thus select 350°C as the post-thermal treatment temperature, which is higher than the end of elemental sulfur evaporation (280°C), and below the temperature (410°C) of further decomposition of SPAN. TGA for the post-treated SPAN (Figure 176a, red curve) shows no weight loss before 410°C. Fourier transform infrared (FTIR) shown in Figure 176b indicates that the non-aromatic C-S component has decreased as compared to the pristine SPAN without thermal treatment. The decreased full width at half maximum (FWHM) also indicates the reduced sulfur components.

SPAN with or without post-treatment is then tested electrochemically (Figure 176c). Both samples show nearly identical reversible capacity of over 520 mAh g⁻¹. However, in the 1st cycle there is only a ~ 100 mAh g⁻¹ irreversible capacity loss for the post-treated SPAN. In comparison, this value is 225 mAh g⁻¹ for the SPAN without post-thermal treatment. Post-thermal treatment thus eliminates over 50% of irreversible capacity loss. Additional optimization is expected to reduce the irreversibility even further. Future research is expected to further reduce the amount of non-aromatic structure, leading to a highly reversible material for the 1st cycle.



Figure 176. Reducing the 1st discharge irreversible capacity loss in SPAN battery by post-thermal treatment method. (a) Thermal gravimetric analysis and (b) Fourier transform infrared C-S bond for the SPAN before and after post-thermal treatment. (c) Discharge/charge profile for the SPAN before and after post-thermal treatment.

Novel Electrolyte Additive Design for High-Voltage Cathode

The BNL team (E. Hu and Y. Yang), in collaboration with the PNNL team (J. Xiao) of Battery500, as well as with scientists at Army Research Laboratory (ARL) and SLAC, demonstrated that stable charge-discharge cycling with an ultrahigh cutoff voltage of 4.8 V can be realized by using appropriate amount

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of electrolyte additive lithium difluorophosphate (LiPO₂F₂, or LiDFP). The LiNi_{0.76}Mn_{0.14}Co_{0.10}O₂ (NMC-76)||Li cell retains 97% of the initial capacity (235 mAh/g) after 200 cycles. Systematic characterizations reveal the effect of LiDFP on both the interphase and the bulk: its self-decomposition product PO₂F is adsorbed strongly and uniformly on the surface of NMC-76 cathode, followed by further decomposition into Li₃PO₄ and LiF catalyzed by TMs. Li₃PO₄ and LiF are desirable components of CEI. The results of this study open a new low-cost approach to protect the high-nickel-content NMC cathode at high-voltage charging.

To investigate the effect of LiDFP in protecting Ni-rich NMC at high voltage, the cycling behaviors of NMC-76 cathode in baseline electrolyte (1 M LiPF₆ in EC/EMC 3:7 by volume) and electrolytes with 1 wt% or 2 wt% LiDFP were compared at different cutoff voltages (that is, 4.4 V, 4.6 V, and 4.8 V), where C/3 was adopted for all the tested cells following two formation cycles at C/10. At lower charging cutoff voltage (4.4 V), negligible difference was observed in electrochemical performances of these three electrolytes, with similar capacity retention (above 90%) after 200 cycles. Increasing cutoff voltage renders higher delivered capacity at the 1^{st} cycle, that is, ~ 222 mAh g⁻¹ at 4.6 V and ~ 230 mAh g⁻¹ at 4.8 V. However, significant differences arise in capacity retention as well as the overpotential between the charging and discharging plateaus, as shown in Figure 177a, with only 77.27% capacity left after 200 cycles for the baseline electrolyte. This deteriorated performance suggests incessant electrolyte decomposition in the highly oxidative environments at high voltage, the oxidation of the interphase, or degradation of cathode itself during high-voltage cycling. In strong contrast, cells using electrolyte with additive of LiDFP demonstrate much more stable capacity retention during long-term high-voltage cycling. Particularly, the cell using 1% LiDFP electrolyte maintained a high discharge capacity of 228.02 mAh g⁻¹ (97.64%) even after 200 cycles at 4.8 V, as shown in Figure 177a, which suggests that a new interphase is likely formed by adding LiDFP as additive that effectively prevents continuous electrolyte decomposition and cathode degradation.

The reasons for the capacity decay at high voltage could be the impedance hike due to incessant electrolyte decomposition, the unstable SEI, the formation of rock-salt species on cathode surface, and the combination of them. To evaluate the impedance resulting from different electrolytes at high voltage, electrochemical impedance spectroscopy was performed, which indeed reveals the impedance buildup from the initial cycle to the 10th cycle. The effect of electrolyte on impedance becomes more pronounced after 200 cycles, while the LiDFP additive effectively suppresses impedance growth (Figure 177b). Quantitative analysis by fitting the equivalent circuit model (Figure 177c) yields the contact resistance (R_b), surface film resistance (R_{sf}), and charge transfer resistance (R_{ct}), which are summarized in Figure 177d. For electrolyte using 1% LiDFP, the extremely small R_{ct} indicates the formation of highly conductive interphase, enabling facile charge transfer reactions on the interphase even after long-term cycling. When the additive amount is increased to 2%, both R_{sf} and R_{ct} are increased, but R_b is mostly the same, suggesting the worse performance in excessive additive at 2% is caused by interphasial resistance. The origin of this optimum LiDFP amount (1%) might stem from the fact that the decomposition of LiDFP produces both LiF and HF simultaneously. While LiF is generally regarded as a desired interphase component, excessive LiF makes interphase more resistive. On the other hand, HF is known to be detrimental as it can attack the cathode surface and damage the interphase.

To reveal the surface structure evolution in NMC-76 cathode during cycling, high-angle annular dark-field (HAADF) – STEM imaging was obtained for the cycled samples (Figure 178). In baseline electrolyte, a 2~3 nm thick disordered rock-salt phase can be seen on the cathode surface, suggesting that the interfacial section of NMC-76 undergoes a phase transition due to the interaction between NMC-76 and electrolyte. In contrast, for the sample cycled with the 1% of LiDFP additive, a layered structure with a clean surface is maintained without any detectable rock-salt phase under identical cycling conditions, indicating that the surface reconstruction has been effectively suppressed.



Figure 177. Electrochemical performance of Li||NMC-76 cells using different electrolytes. (a) Charge-discharge profiles from selected cycles within 2.8-4.8 V. The baseline electrolyte is 1 M LiPF₆ in EC||EMC (3:7) and the 'with additive' electrolyte is the baseline electrolyte with 1% LiDFP (by weight) or 2% LiDFP (by weight) added. (b) Electrochemical impedance spectroscopy (EIS) results of Li||NMC-76 after 200 cycles using different electrolytes. (c) Equivalent circuit for EIS modeling (R_b : contact resistance, R_{sf} : surface film resistance, R_{ct} : charge transfer resistance). (d) EIS fitting results for Li||NMC-76 cells after 200 cycles with different electrolytes.

Differing from transmission electron microscopy (TEM), which provides information about the shallow surface (~ 2 nm), soft X-ray absorption (XAS), when used in total electron yield (TEY) mode, probe deeper (~10 nm) structures and provide complementary information. The oxygen K-edge spectra collected in TEY mode for pristine NMC-76 and NMC-76 after 1st and 200th cycles are shown in Figure 179. The peak at ~ 534 eV for pristine electrochemical cycling, this peak disappeared due to chemical erosion by the acidic electrolyte. A new species at ~ 532 eV appeared after NMC-76 cycled in baseline electrolyte, which intensified after 200 cycles, indicating the emergence and growth of rock-salt phase.



Figure 178. High-angle annular dark-field – scanning transmission electron microscopy images of cycled NMC-76 particles between 2.8-4.8 V using different electrolyte. Left panel: using baseline electrolyte (1 M LiPF₆ in EC/EMC 3:7 by volume). Right panel: using electrolyte with 1% LiDFP additive.



Figure 179. Oxygen K-edge soft X-ray absorption spectroscopy results of NMC electrodes in total electron yield mode.

The team collected TM L-edge spectra for all three TM cations (that is, manganese, cobalt, and nickel) as shown in the three panels of Figure 180. A noticeable feature at low photon energy of manganese L₃-edge appeared after only one cycle in baseline electrolyte, whose intensity grew higher after 200 cycles. This feature, attributed to Mn^{2+} and Mn^{3+} , reflects the reduction of manganese on the NMC-76 electrode surface almost immediately in electrolyte, and the reduction sustained during cycling. Meanwhile, the shoulder at ~ 778 eV in cobalt L3-edge spectra that is associated with Co^{2+} was absent initially, but clearly intensified after 200 cycles, indicating that the reduction of cobalt proceeded in long term. In striking contrast, both manganese and cobalt spectra for the cathode recovered from the LiDFP-containing electrolyte show little changes, if any, due to the excellent stability of the NMC-76 surface well protected by LiDFP-derived interphase. For the nickel L₃-edge, spectra for both baseline and LiDFP-containing electrolytes display little changes during cycling, probably because once the surface is dominated by divalent nickel, it is difficult to be further reduced.

It is well accepted that NMC faces both bulk and interfacial instabilities at ultrahigh voltages; this study shows that these two issues can be solved simultaneously by a simple interphase engineering approach that uses an ionic additive LiDFP in the electrolyte without other costly processing (such as making single crystals and/or surface coating). The decomposition of LiDFP catalyzed by Ni-rich NMC surface promotes the formation of protective CEI that is composed of Li_3PO_4 and LiF. Therefore, LiDFP is revealed to have multiple functionalities including suppressing surface reconstruction, mitigating TM dissolution, and contributing chemical ingredient to form a conductive interphase.





Operando EC-AFM Imaging of Lithium Plating and SEI Growth

The SLAC/Stanford team (W. Chueh and Y. Cui), building on the momentum from last quarter on *operando* EC-AFM imaging of lithium plating and SEI growth, investigated Li-metal SEI growth dynamics in a LHCE LiFSI-1.2DME-3TTE (in collaboration with Z. Bao). Using this unique experimental capability, the team probed the passivation behavior of lithium metal and assessed the SEI growth kinetics, a contributor to CE. This method complements other Battery500 SEI characterization capabilities such as cryo-EM as it measures the growth dynamics *in situ*, thereby removing the possibility of SEI damage and un-swelling during sample preparation.

The team developed a method to quantify the SEI growth kinetics on lithium metal. To establish a reference height, they first grow a substantially thick SEI on plated lithium on copper (growth time > 25 hours) (Figure 181a). Then, using the EC-AFM tip, they selectively remove the SEI and reveal unpassivated Li-metal "pit" (Figure 181b). By assuming that well-passivated region exhibits negligible further growth, it serves as a reference height against which the SEI thickness is measured. The exposed Li-metal pit increases in thickness with time, which is plotted in Figure 181c. Over 5 hours, the SEI grows by 14 nm and follows a power law of 0.47 with respect to time, suggesting a diffusion-limited behavior. This result contrasts sharply with the team's previous observation on Battery500 Gen2 electrolyte (1 M LiPF₆ in EC:EMC), where they observed two regimes: rapid SEI growth (linear/super-linear with time) and diffusive SEI growth. It appears that LiFSI-1.2DME-3TTE LHCE immediately passivates with no rapid SEI growth regime, pointing toward the benefit of this electrolyte in passivating lithium metal.



Figure 181. *Operando* electrochemical atomic force microscopy images of lithium metal deposited in LiFSI-1.2DME-3TTE electrolyte: (a) before indentation and (b) after indentation to measure the soft SEI thickness (c) over 6 hours.

SEI Morphology and Composition

The Texas A&M team completed an atomistic-level analysis that allows predictions of the SEI formation mechanisms and corresponding morphologies and compositions based on input of electrolyte formulations and electrolyte-to-anode ratios. It was found that low-concentration electrolytes yield dispersed inorganic SEI phases surrounded by dissolved Li⁺ ions. The highly stable DME solvent dissolves Li⁺ ions, yielding multicomponent "wet-SEI" structures. Fast reduction of carbonate DMC solvent leads to intermediate species further reacting with FSI⁻ reduction products. Such complexation promotes growth of likely unstable "dry-SEI" complexes that are prone to further electrolyte decomposition. The composition and density of the dry

SEI structures depend on salt concentration and nature/concentration of diluents. Decomposition of HCE electrolytes leads to growth of Li₂O structures enclosed by LiF, LiN, and LiF clusters. LHCE electrolytes result in SEIs dominated by LiF phases. Diluent decomposition is a clear source of fluorine species, and the diluent chemistry is important to regulate the presence of such phases. Another important conclusion relates to the electrolyte-to-anode ratio effect on SEI morphology. For the investigated systems, as the electrolyte-to anode ratio increases, the FSI⁻ decomposition becomes incomplete. Thus, the chemical composition of the SEI, and therefore its morphology, and ionic and electronic conductance properties drastically change as the electrolyte-to-anode ratio is varied. Work is in progress to characterize the existence of a critical LiFSI concentration and electrolyte-to-anode ratio that optimizes the SEI structure by balancing the rate of electrolyte depletion and lithium consumption. A manuscript is under review.

Electrolyte Effects on Sulfur Reduction

The Texas A&M team has studied electrolyte effects on the discharge reactions using a SPAN model. Two different solvent mixtures were employed to evaluate the extent and mechanisms of sulfur reduction. It is found that at low lithium loading, Li-S coordination controls the sulfur reduction progress. At intermediate loadings, lithium diffusion in the interfacial region controls S_x reduction/cleavage rate, with better diffusion rates found in DME/DOL mixtures compared to EC/VC mixtures. For a 1:1 Li:S ratio, a large number of S_2 and S_3 chains remain intact, whereas the PAN backbone retains a large part of the electronic charge. At high lithium loadings, the solvent chemistry and properties determine whether desolvation effects at the interface are the RDS for the discharge process. Quantitative analyses and computed S_x cleavage pathways in different solvents are in progress. In addition, SEI reactions were studied at discharge and over-discharge conditions. Interestingly, it is found that over-discharge voltages are not needed to detect the first electrolyte reduction reactions. A complete report is in preparation.

Highlights of Keystone Project 4

The highlights for this quarter are as follows:

- The operando SXRD characterization tool for probing the inhomogeneity in Li-S pouch cells has been demonstrated. The first set of preliminary diffraction data suggest that operando diffraction studies would have sufficient sensitivity to track many important changes that occur during cycling. (BNL, GM, and INL)
- The quantification of polysulfide species in the LE was studied. A calibration curve for quantifying sulfur in polysulfide species in Li-S battery using HPLC-UV with high accuracy has been developed. It was demonstrated that post-thermal treatment of SPAN to 350°C results in reducing the 1st cycle irreversible loss to only ~ 100 m Ah g⁻¹ contrasted to a 1st cycle irreversible loss of ~ 225 m Ah g⁻¹ for SPAN cathodes without post-thermal treatment. (UCSD)
- Degradation of NMC cathode cycling at high voltage can be solved by a simple interphase engineering approach that uses an ionic additive LiDFP in the electrolyte. A high discharge capacity of 228.02 mAh g⁻¹ (97.64%) even after 200 cycles at 4.8 V was obtained, opening a new approach to improve high-voltage performance of NMC cathodes. (BNL and PNNL)
- A method for quantification of the SEI growth rate on lithium metal plated in LHCE has been developed using *operando* EC-AFM. It was found that LiFSI-1.2DME-3TTE LHCE immediately passivates with no rapid SEI growth regime, pointing toward the benefit of this electrolyte in passivating lithium metal. (SLAC)
- The elucidation of electrolyte effects on SEI formation and sulfur reduction by computational methods was achieved. (TAMU).

Patents/Publications/Presentations

Publications

- Angarita-Gomez, S., and P. B. Balbuena. "Ion Motion and Charge Transfer Through a Solid-Electrolyte Interphase: An Atomistic View." *Journal of Solid State Electrochemistry* 26 (2022): 1931–1939. doi: 10.1007/s10008-022-05227-6.
- Angarita-Gomez, S., and P. B. Balbuena. "Ion Mobility and Solvation Complexes at Liquid-Solid Interfaces in Dilute, High Concentrated, and Localized High Concentrated Electrolytes." *Material Advances* 3 (2022): 6352–6363. doi: 10.1039/d2ma00541g.
- Yu, Z., W. Yu, Y. Chen, L. Mondonico, X. Xiao, Y. Zheng, F. Liu, S. T. Hung, Y. Cui, and Z. Bao. "Tuning Fluorination of Linear Carbonate for Lithium-ion Batteries." *Journal of the Electrochemical Society* 169 (2022): 040555. doi: 10.1149/1945-7111/ac67f5.
- Shin, W., and A. Manthiram. "Fast and Simple Ag/Cu Ion Exchange on Cu Foil for Anode-Free Lithium-Metal Batteries." ACS Applied Materials & Interfaces 14, no. 15, (2022): 17454–17460. doi: 10.1021/ acsami.2c01980.
- Su, L., E. Jo, and A. Manthiram. "Protection of Cobalt-Free LiNiO₂ from Degradation with Localized Saturated Electrolytes in Lithium-Metal Batteries." ACS Energy Letters 7, no. 6 (2022): 2165–2172. doi: 10.1021/acsenergylett.2c01081.
- Shi, L., C. S. Anderson, L. Mishra, H. Qiao, N. L. Canfield, Y. Xu, C. Wang, T. Jang, Z. Yu, S. Feng, P. M. L. Le, V. R. Subramanian, C. Wang, J. Liu, J. Xiao, and D. Lu.^{*} "Early Failure of Lithium–Sulfur Batteries at Practical Conditions: Crosstalk between Sulfur Cathode and Lithium Anode." *Advanced Science* 9, no. 21 (2022): 2201640. doi: 10.1002/advs.202201640.
- Datta, M. K., R. Kuruba, T. Prasada Rao, O. I. Velikokhatnyi, and P. N. Kumta. "New Approaches to High-Energy Density Cathode and Anode Architectures for Lithium-Sulfur Batteries." In *Lithium-Sulfur Batteries: Advances in High-Energy Density Batteries*, edited by P. N. Kumta, et al., 354–439. Cambridge: Elsevier, 2022. doi: 10.1016/ B978-0-12-819676-2.00014-1.
- Lithium-Sulfur Batteries: Advances in High-Energy Density Batteries. Edited by P. N. Kumta, et al. Cambridge: Elsevier, 2022. doi: 10.1016/C2018-0-04066-9.
- Tan, S., Z. Shadike, J. Li, X. Wang, Y. Yang, R. Lin, A. Cresce, J. Hu, A. Hunt, I. Waluyo, L. Ma, F. Monaco, P. Cloetens, J. Xiao, Y. Liu,* X-Q. Yang,* Kang Xu,* and E. Hu.* "Additive Engineering for Robust Interphases to Stabilize High-Ni Layered Structures at Ultra-High Voltage of 4.8 V." *Nature Energy* 7 (June 2022): 484–494. doi: 0.1038/s41560-022-01020-x.

Presentations

- Université de Sherbrooke, Sherbrooke, Canada (April 7, 2022): "Interfacial Phenomena in Batteries: What Can We Learn From Theory?"; P. B. Balbuena. Seminar.
- Texas A&M Research Computing Symposium, Texas A&M University, College Station, Texas (May 23, 2022): "Theory/Computation Role in Tuning Surface/Electrolyte Interfaces for Enhancing Catalytic Performance"; P. B. Balbuena.
- Texas A&M Research Computing Symposium, Texas A&M University, College Station, Texas (May 23, 2022): "Beyond Graphite for Li-ion Batteries: Searching for Lithium Metal Alternatives using Quantum Mechanical Methods"; J. M. Seminario.
- Saft America, Cockeysville, Maryland (June 24, 2022): "Development of Electrolytes for Lithium Batteries"; W. Xu.
- 2022 University of Washington Battery Class, University of Washington, Seattle, Washington (April 11, 2022): "Electrolytes for Lithium-ion Batteries"; W. Xu. Lecture.

- University of Washington, Seattle, Washington (April 18, 2022): "Challenges for Li Metal and Si Anodes"; J-G. Zhang.
- My Introduction to Engineering (MITE) Summer Enrichment Camp, Equal Opportunity in Engineering Program, University of Texas, Austin, Texas (June 6, 2022): "Clean Energy Technologies"; A. Manthiram.
- 2022 Spring Biannual Meeting: Science and Technology Enablers of a Domestic Extreme Battery Supply Chain, University of Maryland, College Park, Maryland (June 10, 2022): "Battery Chemistries for Relieving Supply Chain Issues of Today, Tomorrow, and Day-After-Tomorrow"; A. Manthiram.
- Automotive Electrification Tech Forum Speaker Series, 3M, Minneapolis, Minnesota (June 15, 2022): "Sustainable Battery Technologies for Relieving Supply Chain Issues"; A. Manthiram.
- 21st International Meeting on Lithium Batteries (IMLB), Sydney, Australia (June 26 July 1, 2022):
 "Delineating the Intricacies of High-Nickel Cathodes for Lithium-Ion Batteries"; A. Manthiram.
- Lehigh University, Bethlehem, Pennsylvania (April 19, 2022): "Perspectives on Materials for Energy Applications"; P. N. Kumta.
- International Meeting on Lithium Batteries (IMLB), Sydney, Australia (June 29, 2022): "Advanced Characterization and Metrology Development for Lithium Metal Batteries"; Y. S. Meng. Keynote.
- E02 Symposium, Electrochemical Society, Vancouver, Canada (June 1, 2022): "Rechargeable Lithium Metal Batteries"; Y. S. Meng. Invited.
- Gordon Research Conference on Batteries, Ventura, California (June 6, 2022): "Cryo-EM for Battery Materials"; Y. S. Meng. Invited.
- Ta-You Wu Memorial Lecture, University of Buffalo, Buffalo, New York (April 29, 2022): "The Lithium Battery: From a Dream to Readiness to Take-On Climate Change"; M. S. Whittingham.
- Derby Lecture Series, Department of Chemistry, University of Louisville, Louisville, Kentucky (May 5, 2022): "The Lithium Ion Battery: From a Dream to Domination of Energy Storage Future Chemistry and Materials Challenges"; M. S. Whittingham. Technical lecture.
- Clariant, Louisville, Kentucky (May 6, 2022): "The Challenges Facing Lithium Batteries as they Address Climate Change"; M. S. Whittingham.
- Derby Lecture Series, Department of Chemistry, University of Louisville, Louisville, Kentucky (May 6, 2022): "The Electric Economy and Climate Change: The Critical Role of Energy Storage"; M. S. Whittingham. Public Lecture.
- Materials Research Society, Honolulu, Hawaii (May 9, 2022): "The Pros and Cons of Solid vs Liquid Electrolytes in Lithium Batteries"; M. S. Whittingham.
- Vestal High School, Vestal, New York (May 19, 2022): "The Electric Economy and Climate Change: The Critical Role of Energy Storage"; M. S. Whittingham.
- Van Vlack Public Lecture, University of Michigan, Ann Arbor, Michigan (May 23, 2022): "Overcoming Climate Change: The Critical Role and Challenges of Energy Storage"; M. S. Whittingham.
- 241st Electrochemical Society Meeting, Vancouver, British Columbia, Canada (May 31, 2022): "Pushing the Limits of NMC Cathodes"; M. S. Whittingham, B. Pei, I. Buyker, K. Lee, F. Xin, and H. Zhou.
- IMLB 2022, Sydney, Australia (June 27, 2022): "Pushing the Limits of Lithium Batteries"; M. S. Whittingham. Opening plenary.

APPENDIX – ACRONYM GUIDE

Acronym	Full Description
1,4-DX	1,4-dioxane
1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
3DOM	three-dimensional ordered microporous
3D-OMSH	three-dimensionally ordered microporous sulfur host
AB	acetylene black
ABL	active buffer layer
AC	alternating current
ACN	acetonitrile
ACS	American Chemical Society
ADF	annular dark-field
AFLB	anode-free lithium battery
AFM	atomic force microscopy
AGG	aggregate
AIMD	<i>ab initio</i> molecular dynamic
AIR	areal interfacial resistance
ALD	atomic layer deposition
ALS	Advanced Light Source
ANL	Argonne National Laboratory
ANN	artificial neural network
AOM	amphipathic organic molecules
APS	Advanced Photon Source
APUP	Alliance Partner University Program
AQC	anthraquinone-2-carboxylic acid
AQT	1,5-bis(2-(2-(2methoxyethoxy)ethoxy)ethoxy) anthra-9,10-quinone
ARC	accelerating rate calorimetry
ARL	U. S. Army Research Laboratory
ASR	area specific resistance
ASSB	all-solid-state battery
ASSLB	all-solid-state lithium battery
ASSLMB	all-solid-state Li-metal battery
ASSLSB	all-solid-state Li-S battery
ATR	attenuated total reflectance
β-LPS	β-phase Li ₃ PS ₄
BBP	benzyl butyl phthalate
BE	baseline electrolyte
BEV	battery electric vehicle
BL	bottom layer
BMIM	1-butyl-3-methylimidazolium
BMR	Advanced Battery Materials Research Program
BNL	Brookhaven National Laboratory
BTFE	bis(2,2,2trifluoroethyl) ether

Acronym	Full Description
BV	Butler-Volmer
c-AIMD	constrained – <i>ab initio</i> molecular dynamics
CA	chronoamperometry
CAM	cathode active material
CC	Constant current
CCCV	constant current / constant voltage
CCD	critical current density
CCD ^{plating}	plating critical current density
CCD ^{stripping}	stripping critical current density
CE	Coulombic efficiency
CEI	cathode electrolyte interface
CFM	carbon-based framework material
CIP	contact ion pair
CLP	cycle life projection
CMC	carboxymethyl cellulose
CMD	classical molecular dynamics
CN	coordination number
CNC	carbon nano-cage
cNEB	climbing image nudged elastic band
CNM	Center for Nanoscale Materials
CNT	carbon nanotube
COF	covalent organic frameworks
СОР	critical overpotential
СРЕ	composite polymer electrolyte
cryo	cryogenic
cryo-EM	cryogenic electron microscopy
cryo-FIB	cryogenic – focused ion beam
cryo-STEM	cryogenic – scanning transmission electron spectroscopy
cryo-TEM	cryogenic – transmission electron microscopy
CS	corner-sharing
CSE	cluster-based solid electrolyte
CSM	continuous symmetry measure
СТ	computed tomography
CV	cyclic voltammetry
DBE	dibutyl ether
DB-ML-FF	density-based machine-learning force field
DC	direct current
DCA	dicyanamide
DEB	double-end binding
DEC	diethyl carbonate
DEE	1,2-diethoxyethane
DEGDME	diethylene glycol dimethyl ether
DEMS	differential electrochemical mass spectrometry
DFE	defect formation energy
DFT	density functional theory
DiPE	diisopropyl ether

Acronym	Full Description
DIW	direct ink writing
DLR	Deutsches Zentrum für Luft- und Raumfaurt
DMC	dimethyl carbonate
DME	1,2-dimethoxyethane
DMF	dimethyl formamide
DMSO	dimethylsulfoxide
DOD	depth-of-discharge
DOE	U. S. Department of Energy
DOL	1,3-dioxolane
DOS	density of states
dP/dV	differential pressure
dPEO	dynamic bonds between polymer chains
dQ/dV	differential capacity
DRT	distribution of relaxation times
DSC	differential scanning calorimetry
DTL	1,2-dimethoxyethane solvent with trimethyl phosphate and LiNO ₃ additives
E/C	electrolyte/capacity
EC	ethylene carbonate
eCAD	electrochemical analytic diagnosis
EC-AFM	electrochemical atomic force microscopy
ECS	The Electrochemical Society
EDB	denotation for electrolyte of 1 M LiPF ₆ in ethylene carbonate / diethyl carbonate
	(v/v = 1:1) with 1 wt% % lithium difluoro(oxalate)borate
EDF	denotation for electrolyte of 1 M LiPF ₆ in ethylene carbonate / diethyl carbonate
	(v/v = 1:1) with 15 wt% fluoroethylene carbonate
EDFB	denotation for electrolyte of 1 M LiPF $_6$ in ethylene carbonate / diethyl carbonate
	(v/v = 1:1) with 15 wt% fluoroethylene carbonate and 1 wt% lithium
	difluoro(oxalate)borate
EDL	electrical double layer
EDLi	electrochemically deposited lithium
EDS	energy-dispersive X-ray spectroscopy (also known as EDX)
EELS	electron energy loss spectroscopy
eGF	exfoliated graphene fluoride
EIS	electrochemical impedance spectroscopy
eLi	engineered lithium
EM	electron microscopy
EMC	ethyl methyl carbonate
EMIM-BF ₄	1-ethyl-3-methylimidazolium tetrafluoroborate
eNMR	electrophoretic nuclear magnetic resonance
EO	ethylene oxide
EPR	electron paramagnetic resonance
EQ-SANS	extended Q-range small-angle neutron scattering diffractometer
E/S	electrolyte/sulfur
EtOH	ethylene
EV	electric vehicle
EXAFS	extended X-ray absorption fine structure

Acronym	Full Description
F4EO2	1,1,1,2,2,3,3,4,4-nonafluoro-6-(2-methoxyethoxy)hexane
F5DEE	fluorinated-1,2-diethoxyethanes electrolyte
FAM	functional monomer additive molecule
FDMB	fluorinated 1,4-dimethoxylbutane
FDMH	fluorinated 1,6-dimethoxyhexane
FDMO	fluorinated 1,8-dimethoxyoctane
FDMP	fluorinated 1,5-dimethoxypentane
FEC	fluoroethylene carbonate
FEM	finite element method
FESEM	field emission scanning electron microscopy
FF	force field
FFT	fast Fourier transform
FIB	focused ion beam
fs	femtosecond
FSI	bis(fluorosulfonyl)imide
FTIR	Fourier transform infrared
FWHM	full width at half maximum
FZJ	Forschungszentrum Jülich
GB	grain boundary
gc	glass/ceramic
GC-MS	gas chromatography – mass spectrometry
GCPL	galvanostatic cycling with potential limitation
GDL	gas diffusion layer
GE	gel electrolyte
GITT	galvanostatic intermittent titration technique
GM	General Motors
GOMD	Glass & Optical Materials Division
GP	Gaussian process
GPC	gel permeation chromatography
GPRA	Government Performance and Results Act
Gr	graphene
GSE	glassy solid electrolyte
GtO	graphite oxide
HAADF	high-angle annular dark-field
HATN	hexaazatrinaphthylene
HATN/CNT-S	HATN/CNT polymer – sulfur composite
HATN-S	hexaazatrinaphthylene polymer – sulfur composite
НС	hard carbon
HCE	high-concentrated electrolyte
HCFM-S	sulfur-infiltrated high-surface-area carbon-based complex framework materials
HEV	hybrid electric vehicle
HEXRD	high-energy X-ray diffraction
HFB	hexafluorobenzene
HFE	hydrofluoroether
HFP	hexafluoropropylene
HG	hand grinding

Acronym	Full Description
HOPG	highly oriented pyrolytic graphite
НРС	high-performance computing
HPLC	high-performance liquid chromatography
HRTEM	high-resolution transmission electron microscopy
HT	high throughput
IBA	International Battery Materials Association
IEEE	Institute of Electrical and Electronics Engineers
IL	ionic liquid
INL	Idaho National Laboratory
in-SEM	in situ scanning electron microscopy
IOFM	inorganic-organic framework material
IPA	isopropanol
IR	infrared
ISEL	Israel Electrochemical Society
ISU	Iowa State University
KAIST	Korea Advanced Institute of Science and Technology
КВ	Ketjenblack
КМС	kinetic Monte Carlo
KPFM	kelvin probe force microscopy
LATP	Li-Al-Ti-P, such as $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ or $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$
LBNL	Lawrence Berkeley National Laboratory
LBO	Li-B-O, such as Li ₃ BO ₃
LBS	Li-B-S
LCE	low-concentration electrolyte
LCO	LiCoO ₂
LCRC	Laboratory Computing Resource Center
LDBE	1.8 M LiFSI in dibutyl ether
LDEE	1.8 M LiFSI in diethyl ether / BTFE
LDiPE	1.8 M LiFSI in diisopropyl ether
LDME	1.8 M LiFSI in 1,2-dimethoxyethane
LE	liquid electrolyte
LFP	lithium iron phosphate
LGPS	Li-Ge-P-S, such as Li ₁₀ GeP ₂ S ₁₂
LHCE	localized high-concentration electrolyte
LHS	left-hand side
Libob	lithium bis(oxalate)borate
LIC	Li-ion conductor
Lidfob	lithium difluoro(oxalate) borate
Lidfp	lithium difluorophosphate
LIEDC	lithium ethylene decarbonate
LiFSI	Li-bis(fluorosulfonyl)imide
Li-MCA	lithium multicomponent alloy
Li-NMC	lithium – nickel manganese cobalt oxide
LiPS	lithium polysulfide
Li-SIA	Li-containing structurally isomorphous alloy
LiTFSI	lithium bis(trifluoromethanesulfonyl)imide

Acronym	Full Description
LLNL	Lawrence Livermore National Laboratory
LLTO	Li-La-Ti-O, such as Li _{3x} La _{2/3-x} TiO ₃
LLZ	Li-La-Z
LLZO	Li-La-Z-O, such as Li ₇ La ₃ Zr ₂ O ₁₂
LLZTO	Li-La-Zr-Ta-O, such as Li _{6.75} La ₃ Zr _{1.75} Ta _{0.25} O ₁₂
LMR-NMC	Li- and Mn-rich Ni-Mn-Co
LNO	LiNiO ₂
LOB	Li-O battery
LPC	large particle cathode
LPS	Li-P-S, such as Li ₃ PS ₄
LPSB	Li-P-S-Br, such as Li ₃ PS ₄ + ½LiBr
LPSBI	Li-P-S-Br-I, such as Li ₇ P ₂ S ₈ Br _{0.5} I _{0.5}
LPSBr	Li-P-S-Br, such as Li ₆ PS₅Br
LPSCI	Li-P-S-Cl, such as Li ₆ PS ₅ Cl
LPSI	Li-P-S-I, such as Li ₃ PS ₄ + ½LiI
LPSIB	Li-P-S-I-Br, such as Li ₇ P ₂ S ₈ I _{0.5} Br _{0.5}
LSE	localized saturated electrolyte
LSiPCI	Li-Si-P-Cl, such as Li _{9.54} Si _{1.74} P _{1.44} S _{11.7} Cl _{0.3}
LSnS	Li-Sn-S, such as Li _{3.85} Sn _{0.85} Sb _{0.15} S ₄
LSV	linear sweep voltammetry
LTO	Li ₄ Ti ₅ O ₁₂
LYC / LYCI	Li-Y-Cl, such as Li ₃ YCl ₆
MC	Monte Carlo
MCA	multicomponent alloy
MD	molecular dynamics
METS	multiharmonic electrothermal spectroscopy
MGF	mixed glass former
MIC	molecular ionic composite
ML	machine learning
MLFF	machine learning force field
MLMD	molecular dynamics simulation with machine-learning potential
MOF	metal-organic framework
MOS	mixed oxy-sulfide
MOSN	mixed oxy-sulfide nitride
MPI	message-passing interface
MRS	Materials Research Society
MS	mass spectrometry
MSD	mean square displacement
MSE	mean squared error
MTU	Michigan Technological University
MWCNT	multiwalled carbon nanotube
MYEGA	Mauro–Yue–Ellison–Gupta–Allan model
NA	LiNi _{0.95} Al _{0.05} O ₂
NaFSI	sodium bis(fluorosulfonyl)imide
NaNMC	Na-N-Mn-Co, such as $NaNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ and $NaNi_{0.68}Mn_{0.22}Co_{0.1}O_2$
nano-FTIR	Fourier transform infrared nano-spectroscopy

Acronym	Full Description
NASICON	sodium super ionic conductor
NATM	Ni-Al-Ti-Mg, such as LiNi _{0.93} Al _{0.05} Ti _{0.01} Mg _{0.01} O ₂
NBO	nonbridging oxygen
NBR	nitrile butadiene rubber
NBS	nonbridging sulfur
NC	Ni-Co, such as LiNi _{0.94} Co _{0.06} O ₂
NCEM	National Center for Electron Microscopy
NCM	Ni-Co-Mn
NCM-85105	LiNi _{0.85} Co _{0.10} Mn _{0.05} O ₂
NCSE	non-calendered sulfur electrode
ND	di-coordinated nitrogen
NEB	nudged elastic band
NewEle	New Element
NF	nanoflake
NLNMF	Na-Li-Ni-Mn-Fe, such as $Na_{0.85}Li_{0.1}Ni_{0.175}Mn_{0.525}Fe_{0.2}O_2$
NM	
NMC	Ni-Mn-Co
NMC-111	LiNi1/3Mn1/3C01/3
NMC-622	$LiNi_{0.6}Mn_{0.2}Co_{0.2}$
NMC-811	LiNi _{0.8} Mn _{0.1} Co _{0.1}
NMDC	Nanotechnology Materials and Devices Conference
NMF	nonnegative matrix factorization
NMFCN	Na-Mn-Fe-Co-Ni
NMP	N-methyl-pyrrolidone
NMR	nuclear magnetic resonance
NN	neural network
N/P ratio	capacity ratio between anode (negative electrode) and cathode (positive electrode)
NP	nanoparticle
NPCE	nonflammable polymer composite electrolyte
n-PDF	neutron diffraction and pair distribution function
NPT	constant number of atoms (N), pressure (P), and temperature (T)
NREL	National Renewable Energy Laboratory
ns	nanosecond
NSLS	National Synchrotron Light Source
NT	tri-coordinated nitrogen
NTO	sodium titanate
NVE	constant number (N), volume (V), and energy (E)
NVT	constant temperature, constant volume ensemble
OBD	Organic Battery Days Workshop
OCV	open circuit voltage
OER	oxygen evolution reaction
OMSH	ordered microporous sulfur host
ORNL	Oak Ridge National Laboratory
ORR	oxygen reduction reaction
OSU	Ohio State University

Acronym	Full Description
РАН	polycyclic aromatic hydrocarbon
PAN	polyacrylonitrile
PAQS	poly (anthraquinonyl sulfide)
PBDT	poly(2,2'-disulfonyl-4,4'-benzidine terephthalamide)
PC	propylene carbonate
РСА	principal component analysis
PCC	Pearson correlation coefficient
PC-LCHE	polymeric colloidal localized high-concentration electrolyte
PDF	pair distribution function
PDMS	polydimethylsiloxane
PE	polyelectrolyte, or polymer electrolyte
PEEK	polyether ether ketone
PEG	poly(ethylene glycol)
PEGDA	poly(ethylene glycol) diacrylate
PEGMA	poly(ethylene glycol) methacrylate
PEGMEA	poly(ethylene glycol) methyl ether acrylate
PEI	polyethylenimine
PEM	poly(ethylene malonate)
PEO	poly(ethylene oxide)
PES	photon emission spectroscopy
PETEA	pentaerythritol tetraacrylate
PFG	pulsed field gradient
PFIB	plasma focused ion beam
PFPE	perfluoropolyether
PGE	polymer gel electrolyte
PHEV	plug-in hybrid electric vehicle
PHM	poly(hexylene malonate)
PI	principal investigator
PICOFM	porous inorganic covalent-organic framework materials
PI-G	polyimide-graphene
PLIMTFSI	poly((trifluoromethanesulfon)imide lithium methacrylate)
PM	planetary mill
PMMA	polymethyl methacrylate
PMTH	dipentamethylenethiuram hexasulfide
PNNL	Pacific Northwest National Laboratory
POSS	polyhedral oligomeric silsesquioxane
PP	polypropylene
ppm	parts per million
PPM	poly(pentylene malonate)
РРО	poly(phenylene oxide)
PS-SEI	polymer-supported solid electrolyte interphase
PST	partially sintered tape
PSTFSI	poly(4-styrenesulfonyl(trifluoromethanesulfonyl)imide)
PSU	Pennsylvania State University
PTFE	polytetrafluoroethylene
PTFSI	triflimide-based polyion

Acronym	Full Description
PTM	poly(trimethylene malonate)
РТО	pyrene-4,5,9,10-tetraone
PVB	polyvinyl butyral
PVDF	polyvinylidene (di)fluoride
PVP	polyvinylpyrrolidone
Ру	pyrrolidinium
PyTFSI	pyrrolidinium (trifluoromethanesulfon)imide
RAFT	reversible addition-fragmentation chain-transfer
RDF	radial distribution function
RDS	rate determining step
RE	rare earth
ReaxFF	reactive force field
RF	random forest
rGO	reduced graphene oxide
RHS	right-hand side
RM	redox mediator
RMD	reactive molecular dynamics
RMSE	root mean square error
RP	red phosphorus
RPT	reference performance test
RR	reduced-repulsion
R _{wp}	weighted-profile R-factor
SAED	select area electron diffraction
SAEP	salt affinitive electrolyte phobic
SAM	scanning Auger microscopy
SANS	small angle neutron scattering
SASP	salt affinity solvent phobic
SAXS	small angle X-ray scattering
SBR	styrene-butadiene rubber
SC	single crystalline
SE	solid electrolyte
SEB	single-end binding
SEI	solid electrolyte interphase
SEM	scanning electron microscopy
SEO	polystyrene-b-poly(ethylene oxide) block copolymer
SERS	surface-enhanced Raman spectroscopy
SFSU	San Francisco State University
SHE	standard hydrogen electrode
SIA	structurally isomorphous alloy
SIC	single ion conductor
SIL	solvate ionic liquid
SIMS	secondary ion mass spectrometry
SLAC	Stanford Linear Accelerator Center
SLD	scattering length density
SNL	Sandia National Laboratory
SnS	tin sulfide

Acronym	Full Description
SOC	state of charge
SPAN	sulfurized polyacrylonitrile
SPC	small particle cathode
SPC-1	sulfur polymerized composite – generation 1
SPC-2	sulfur polymerized composite – generation 2
SPE	solid polymer electrolyte
SPM	scanning probe microscopy
SPZ	sulfur polymerized composite
SQUID	superconducting quantum interference device
SRO	short-range order
SS	stainless steel
SSB	solid-state battery
SSE	solid-state electrolyte
SSI	solid-state ion
SSLB	solid-state lithium battery
SSLMB	solid-state Li-metal battery
SS-NEB	solid-state nudged elastic band
SSPC	Solid-State Proton Conductors Conference
SSRL	Stanford Synchrotron Radiation Lightsource
S-SSE	sulfide-based solid-state electrolyte
STD	standard deviation
STEM	scanning transmission electron microscopy
SWCNT	single-walled carbon nanotube
SXRD	synchrotron-based X-ray diffraction
Тс	glass crystallization temperature
TCR	thermal contact resistance
TEGDME	tetraethylene glycol dimethyl ether
TEM	transmission electron microscopy
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
TEP	triethyl phosphate
TES	tender energy X-ray absorption spectroscopy
TEY	total electron yield
TFC	thin-film composite
TFP	tris(2,2,2-trifluoroethyl) phosphate
TFSI	(trifluoromethanesulfonyl)imide
Тg	glass transition temperature
TGA	thermal gravimetric analysis
TGC	titration gas chromatography
THF	tetrahydrofuran
TL	top layer
TM	transition metal
TMA	trimethylaluminum
TMD	transition metal dichalcogenide
TMP	trimethyl phosphate
TMS	tetramethylsilane
TOF-SIMS	time-of-flight secondary ion mass spectrometry

Acronym	Full Description
TRL	technology readiness level
TTE	1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether
TXM	transmission X-ray microscopy
UCB	University of California, Berkeley
UCSD	University of California, San Diego
UH	University of Houston
UHV	ultrahigh vacuum
UIC	University of Illinois, Chicago
UM	University of Michigan
UMD	University of Maryland
UNLS	ultra-nanocrystalline lithium superoxide
UT	University of Texas
UV	ultraviolet
UW	University of Washington
UWM	University of Wisconsin, Madison
VASP	Vienna <i>ab initio</i> simulation package
VBM	valence band maximum
VC	vinylene carbonate
VE	virtual electrode
VE-SAM	virtual electrode scanning Auger microscopy
VE-XPS	virtual-electrode X-ray photoelectron spectroscopy
VGCF	vapor-grown carbon fibers
VOC	volatile organic compound
VTO	Vehicle Technologies Office
XAFS	X-ray absorption fine structure
XANES	X-ray absorption near-edge structure
XAS	X-ray absorption spectroscopy
x-PDF	synchrotron X-ray diffraction and pair distribution function
xPEO	crosslinked poly(ethylene oxide)
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence
XRT	X-ray tomography
zPU	zwitterionic polyurethane