Fiscal Year 2019: Second Quarter

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

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Tien Q. Duong, Program Manager Advanced Battery Materials Research Program & Battery500 Consortium Vehicle Technologies and Electrification Program Energy Efficiency and Renewable Energy

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

This document summarizes the BMR Program investigators' activities performed during January 1, 2019, through March 31, 2019. This quarter, you will notice that we expanded our efforts in sodium-ion batteries, which are a promising new alternative to today's batteries. In contrast to lithium, sodium is naturally abundant and is expected to be more affordable than today's Li-ion batteries. This quarter, we introduce the following Na-ion efforts: "High-Capacity, Low-Voltage Titanate Anodes for Sodium-Ion Batteries" by Dr. Marca Doeff of Lawrence Berkeley National Laboratory; "Development a High-Energy Sodium-Ion Battery with Long Life" by Dr. Christopher Johnson of Argonne National Laboratory; and "Electrolytes and Interfaces for Stable High-Energy Sodium-Ion Batteries" by Dr. Huilin Pan of Pacific Northwest National Laboratory.

A few notable achievements from the BMR investigators this quarter are summarized below:

- Pacific Northwest National Laboratory (Wang's group) used cross-sectional scanning transmission electron microscopy (STEM) studies and 3D tomography reconstructions to understand bulk lattice degradation in Li-rich transition metal oxide cathodes. The results show nano-void formation and lattice structure transformation, both of which are related to electrochemically driven oxygen vacancy formation at particle surface and the subsequent injection into the bulk lattice.
- Lawrence Berkeley National Laboratory (Chen's group) obtained a degradation mechanism for cation-disordered rocksalt cathodes based on surface-densification. The results suggest bulk structural modification that can prevent the deep migration of surface reduced transition metal cations into the bulk as an alternative stabilizing strategy.
- West Virginia University (Wu's Group) synthesized several plasticized cross-linked PEGDA-LisTFSI polymers with different molar ratios of ethylene oxide monomer to lithium monomer ([EO]/[Li⁺] = 32, 28, 24, 20, 16). At room temperature, the PEGDA-LisTFSI CLP with a [EO]/[Li⁺] ratio of 24:1 gave the highest ionic conductivity of 1.4×10⁻⁴ S cm⁻¹. The Li⁺ transference number of PEGDA-LisTFSI CLP ([EO]/[Li⁺]=24:1) is as high as 0.82.
- Pacific Northwest National Laboratory (Lu/Liu's Group) developed a new solid electrolyte of low-temperature phase Li₇P₂S₈Br_{0.5}I_{0.5} (LT-LPSBI) demonstrating a high ionic conductivity of 4.7 mS/cm at room temperature.

Highlights from the Battery500 consortium team include the following:

- **Keystone Project 1** (Materials and Interfaces): A new Li-metal anode on which dendrite-free lithium can be plated/stripped rapidly at a relatively low impedance from either a liquid or a solid electrolyte was demonstrated. (University of Texas at Austin; Goodenough's Group)
- **Keystone Project 2** (Electrode Architectures): A new electrode architecture based on pyrolized eggplant with aligned porosities was shown to have high lithium loading and high efficiency when the host is protected with a LiF coating. (Stanford University; Cui's Group)

• Keystone Project 3 (Cell Fabrication, Testing, and Diagnosis): A study to determine polysulfide redistribution during the pouch cell cycling revealed that even on the same cathode layer the electrochemical reaction is highly inhomogeneous. (Pacific Northwest National Laboratory, Xiao's Group; and Brookhaven National Laboratory, Yang's Group).

We encourage you to follow our progress as we proceed. Our next report is expected to be available in September 2019.

Sincerely,

Tien Q. Duong

Tien Q. Duong Manager, Advanced Battery Materials Research Program & Battery500 Consortium Vehicle Technologies and Electrification Program Energy Efficiency and Renewable Energy U.S. Department of Energy

TASK 1 – Liquid/Polymer Solid-State Electrolytes

Summary and Highlights

The BMR Program goal is to develop long-life batteries superior to commercial Li-ion systems in terms of cost, vehicle range, and safety. The BMR Program addresses the fundamental problems of electrode chemical and mechanical instabilities that have slowed development of affordable, high-performance, automotive batteries. The aim is to identify electrode/electrolyte materials that yield enhanced battery performance and lead to greater acceptance of electric vehicles (EVs). Currently, the U. S. Department of Energy (DOE) Vehicle Technologies Office (VTO) supports ten projects in the BMR Program under this Electrolytes Task. These projects can be categorized into three general topics:

- Liquid. The projects for liquid electrolyte aim to develop electrolyte formulations, based on fluoro-chemistries, to achieve significantly improved operating voltage, increased durability, and increased energy density of Li-ion batteries at a reasonable cost. Nonaqueous polyelectrolyte solutions with high Li⁺ transference numbers will be developed to achieve high rate capabilities at room temperature. In addition, electrolytes with new polymer binders bearing a pentafluorophenyl group on the backbone will be designed, synthesized, and tested.
- **Polymer.** The targets of polymer electrolyte (PE) projects include inorganic/polymer and polymer/gel hybrid electrolytes that have flexibility, mechanical strength, thermal stability, high ionic conductivity, stable interfaces against lithium metal, and polysulfide-trapping capability enabling energy density Li-S batteries, with comparable cycle life.
- Self-Forming & Self-Healing. The self-forming, self-healing electrolyte projects are focused on developing and implementing Li-metal-based metal fluorite and metal iodide batteries, capable of energy densities > 400-500 Wh/kg and 1000 Wh/L.

Highlights

At the Daikin group, thickness measurements of pouch cells were obtained to determine the relative rate of thickness increase as a function of operating voltage, electrolyte composition, and time. They found that there are minimal changes to thicknesses in NMC-532 cells at 4.2 V when comparing hydrocarbon to fluorinated electrolyte (20% HFE). An additional method to measure cell thickness changes that are less than 1 μ m is necessary due to the resolution of the contact sensors. They also measured concentration of dissolved metals deposited on the anode under various conditions.

This quarter, the Berkeley group focused on synthesis and initial characterization of triflimide-based styrene (PS-LiTFSI) and acrylate (PA-LiTFSI) ionomers. These polymers were produced via a straightforward one-step synthesis using reversible addition-fragmentation polymerization. They demonstrated successful synthesis of both polymers with a molecular weight of 13,700 and 14,400 and polydispersity of 1.28 and 1.15 for the styrene and acrylate polymers, respectively. Furthermore, a coin cell was constructed with commercial LiFePO₄ and graphite electrodes with 0.4 molal PS-LiTFSI in ethylene carbonate/dimethyl carbonate (EC/DMC) used as the electrolyte. The cell was cycled galvanostatically at a rate of C/20. Initial results show good cyclability at this low charge and discharge rate. While further measurements are needed, these triflimide polymers seem to be promising for future studies in conventional Li-ion cells.

At Argonne National Laboratory (ANL), 11 anion receptors, some related to the tris(2,2,2-trifluoroethyl)borate (TFEB) studied experimentally, were investigated using density functional theory (DFT) to determine their binding energies to polysulfide species. Nitrotriolborate (NTB) and ortho-phenylenebridged diborane $(1,2-[B(C_6F_5)_2]_2C_6F_4)$ (DB) are predicted to bind Li₂S and Li₂S₂ the most strongly. Triolborate without the nitro (not shown) was also found to bind Li₂S strongly. Both have strong binding due to the cage structure where oxygen lone pairs cannot interact with the boron. The other species investigated, including TFEB, do not have very strong binding to the polysulfides, with the longer chain polysulfides having weaker binding. These results from the computational screening suggest that there are several anion receptors that could be effective at preventing loss of active material in Li-S batteries, assuming that the lithium anode was protected.

At University of Maryland (UMD), carbon nanotube (CNT) solution (1 mg/ml in NMP) was infiltrated into the pore structure of garnet ceramic fibers and overcoated the exposed surface of garnet phase, which led to the formation of a mixed electron/ion conductor. Lithium polysulfide solution (1 mol/L Li₂S₈ in dioxolane/dimethoxyethane, or DOL/DME) was synthesized for sulfur cathode fabrication. The solution was infiltrated into the pore structure of the mixed electron/ion framework to achieve desired sulfur loading. In addition, a 3D host material with aligned microchannels was used for loading sulfur with high mass loading. Sulfur was infiltrated into the pores of the c-wood/graphene host material with a mass loading of ~ 20 mg/cm². The electrochemical performance of the high-loading sulfur cathode (S@c-wood/graphene) was first demonstrated in liquid electrolyte, 1 M LiTFSI dissolved in DOL/DME, and shows a high discharge capacity at 0.01 C and extremely high areal capacity.

The University of Washington (UW) group has demonstrated the increased overpotential associated with ionic liquid electrolytes in Li-S cells can be successfully mitigated to acceptable levels. They have accomplished this in the design through use of a solvating diluent (anisole), a cathode fabrication process that circumvents electrolyte wetting problems, and a gel composite separator that successfully restricts polysulfide migration without incurring large overpotentials or significant extra weight/volume. In addition, they carefully optimized the ratio between PENDI-350 and tri-Py to achieve high-loading sulfur cathode with mechanical integration.

At West Virginia University (WVU), several plasticized cross-linked PEGDA-LisTFSI polymers were synthesized with different molar ratios of ethylene oxide monomer to lithium monomer ([EO]/[Li+] = 32, 28, 24, 20, 16). At room temperature, the PEGDA-LisTFSI CLP with a [EO]/[Li⁺] ratio of 24:1 gives the highest ionic conductivity of 1.4×10^{-4} S cm⁻¹. The Li⁺ transference number of PEGDA-LisTFSI CLP ([EO]/[Li+]=24:1) is as high as 0.82.

The Stanford group has synthesized a series of different supramolecular polymers comprising various content of non-covalent interactions and polymer entanglements using polymerization of polydimethylsiloxane (PDMS) with urea linkages. They demonstrated that the range of the polymers shows wide differences in the molecular properties, reflective in the macroscopic relaxation behavior as well as the modulus. They further analyzed the electrochemical characteristics of the PDMS self-healing polymer (SHP) using Coulombic efficiency (CE) measurements in a Li||PDMS-SHP@Cu cells. The results indicate that a higher degree of electrodeposition stabilization is achievable by incorporating polymer coating with high flowability and abundance of strong dynamic bonding units.

The Lawrence Berkeley National Laboratory (LBNL) group has investigated the lithium/electrolyte interface in hybrid block copolymer electrolytes using impedance spectroscopy. Lithium symmetric cells were fabricated using a triblock POSS-PEO-POSS, a PEO-POSS, and a PEO (where POSS is acryloisobutyl polyhedral oligomeric silsesquioxane, and PEO is polyethylene oxide). Cells were conditioned using a current density of 0.02 mA cm⁻² for 10 cycles, with each cycle consisting of 4 hours of charge, 45 minutes of rest, 4 hours of discharge, and 45 minutes of rest. In the case of POSS-PEO-POSS, the team found that the bulk resistance is unchanged, and the interfacial resistance increases by approximately 10% and stabilizes. Interfacial resistance was measured with impedance spectroscopy as a function of salt concentration. It appears that the interfacial resistance is interface between PEO-based electrolytes (both homopolymers and block copolymers) and lithium metal is the observation that good mechanical and electrical contact are maintained even when tens of micrometers of lithium are displaced during cycling.

At Stony Brook University (SBU), cell design B was constructed with four interface variations: B-Interface I (B-I), B-Interface II (B-II), B-Interface III (B-III), and B-Interface IV (B-IV). Longer-term cycling was conducted this quarter where the four different cell design B cell constructs (I, II, III, and IV) were compared with cell design A I. Three of the B-type cell designs (I, II, and III) show a significant increase in efficiency

over the first 10 cycles. This is similar to the behavior observed in cell design A I. Notably, cell design B I shows CE of between 90 and 100% throughout the testing regime. With full utilization of the LiI of the current electrolyte/cell chemical composition, the energy density is ~ 450 Wh/kg. A cell was cycled under a sufficiently high current density to induce the growth of dendrites and internal short. The same cell is cycled under a reduced current density. The cell demonstrates no evidence of internal shorts and continues to function effectively, thus demonstrating self-healing.

At Rutgers, the group showed that the cell design property of smaller electrode spacing was beneficial in improving the cell performance for both the single and 12-V cell configurations. Utilizing this modification in conjunction with the project's previously investigated changes of decreased electrode aspect ratio and increased electrolyte thickness or cell orientation allowed them to increase the positive electrode utilization and electrode pairs' energy density. To overcome the transport limitations that are still occurring, these findings will be combined with the nanolayered electrode architecture investigated and optimized in previous studies to reach closer to the cell performance goals.

Task 1.1 – Advanced Lithium-Ion Battery Technology: High-Voltage Electrolyte (Joe Sunstrom, Ron Hendershot, and Alec Falzone, Daikin)

Project Objective. The project objective is to identify electrolyte formulations, based on fluoro-chemistries, that will allow significantly improved operating voltage, increased durability, and increased energy density of Li-ion batteries at a reasonable cost. The project seeks to understand the conditions under which the electrolyte degrades, the effect on battery performance, and solutions that can overcome current limitations of the electrolyte. Gassing in Li-ion batteries is one of the most common failure mechanisms and poses the greatest safety risk in consumer devices. This project aims to investigate gas composition as a function of cathode material, electrolyte formulation, and operating voltage, and proposes optimal cell compositions at decomposition voltages.

Project Impact. Developing an understanding of the operating conditions in which gasses form in Li-ion batteries enables the project to propose optimized cell compositions, which operate at higher voltages for a longer period. Different fluorinated electrolyte components and additives may suppress and/or eliminate gas generation at or above hypothesized decomposition voltages. To investigate these topics, it is imperative that the project utilize multiple approaches, including, but not limited to: cathode material, electrolyte composition, operating voltage, and cycle number.

Approach. The evolving composition of the electrolyte in the battery will be examined by various analytical instruments to study volatiles [gas chromatography – mass spectrometry (GC-MS)/thermal conductivity detector (TCD)], liquid [liquid chromatography MS (LC-MS)], and solid [time-of-flight secondary ion mass spectrometry (TOF-SIMS), thermogravimetric analysis MS (TGA-MS), X-ray photoelectron spectroscopy (XPS), and auger electron spectroscopy (AES)] electrolyte decomposition products during battery operation. In the first year, the team addressed the gas composition and kinetics for both hydrocarbon and fluorocarbon as a function of several charge/discharge conditions. In the second year, the project will transition into analysis of the solid-state electrolyte (SSE) decomposition components of its tested batteries to obtain valuable information about solid electrolyte interface (SEI) layer formation and how it manifests change in both the anode (graphite) and cathode (LCO and NMC). The third year is focused on measuring changes in the solid-state structure of the cathode following high-voltage operation. The project aims to quantify any dissolved metal ions originating from the cathode, and deposited on the anode using inductively coupled plasma – mass spectrometry (ICP-MS). It will also study changes in the cathode structure using powder X-ray diffraction (XRD).

Out-Year Goals. Work will progress toward understanding how electrolyte formulation and cell operation affect the stability of transition metals (TMs) in the cathode structure. Specifically, the project aims to quantify metal ions, if any, dissolved into solution as a function of operating parameters (that is, voltage, time, etc.) and electrolyte formulation. In addition, measurements will be made using powder XRD to detect changes in the crystal structure of the cathode (LCO and NMC). Understanding effects on the solid-state structure in Li-ion batteries will provide valuable information on the required cathode chemistry for increased performance at high voltage.

Collaborations. The project has initiated a collaboration with Dr. Yi Cui (Stanford University) for cryogenic transmission electron microscopy (cryo-TEM) measurements on solid battery components.

- 1. Film composition (elemental) versus time/voltage complete Milestone 2.2. (Q1, FY 2019; Completed)
- 2. Battery thickness (non-gas) versus time/voltage complete Milestone 2.3. (Q3, FY 2019; In progress)
- 3. Metal dissolution versus time/voltage Milestone 3.1. (Q3, FY 2019; In Progress)

Progress Report

Thickness measurements of pouch cells were obtained to determine the relative rate of thickness increase as a function of operating voltage, electrolyte composition, and time. Figure 1 depicts the thickness increase of NMC-532 cell cycled at 4.2 V with a hydrocarbon electrolyte (left) versus a fluorinated electrolyte (right) throughout the duration of a cycle life experiment.



Figure 1. NMC-532 cell thickness change as a function of time/electrolyte. Low signal-to-noise ratio corresponds to minimal thickness increase, and at the limit of instrument capabilities (.1 mm).

There are minimal changes to thicknesses in NMC-532 cells at 4.2 V when comparing hydrocarbon to fluorinated electrolyte (20% HFE). An additional method to measure cell thickness changes that are less than 1 μ m is necessary due to the resolution of the contact sensors.

Efforts this quarter transitioned into investigating changes in the solid-state structure of materials in cells as a function of time/voltage/electrolyte. The initial approach utilizes ICP-MS to determine the concentration of dissolved metals that have deposited on the anode. Figure 2 depicts the concentration of nickel, manganese, and cobalt from tested NMC-532 cells at high voltage (4.5 V and 4.6 V) as a function of electrolyte composition.

There is an increase in concentration of all metals in cells cycled at 4.6 V versus 4.5 V, which is expected. In the anodes from 4.5-V cells, there is little to no change in cobalt or nickel concentrations as a function of electrolyte. The manganese levels are highest in the electrolyte, with 20% HFE at both 4.5 V (112 ppm) and 4.6 V (163 ppm), and decrease significantly with the addition of fluoroethylene carbonate (FEC) to 40 ppm at 4.5 V and 59 ppm at 4.6 V. Additional anodes are to be submitted for dissolved metals analysis to determine the concentration of cobalt, manganese, and nickel as a function of FEC.



Figure 2. Inductively coupled plasma mass spectroscopy of anode material following cycle life test in NMC-532 cells. Cells cycled at 4.5 V (left) and 4.6 V (right).

Patents/Publications/Presentations

Publication

 Sunstrom, J., A. J. Falzone, M. Gilmore, R. Hendershot, et al. "Pushing the Energy Limits of Lithium-Ion Batteries through Fluorinated Materials." SAE Technical Paper 2019-01-0595 (2019). Task 1.2 – Multi-Functional, Self-Healing Polyelectrolyte Gels for Long-Cycle-Life, High-Capacity Sulfur Cathodes in Lithium-Sulfur Batteries (Alex Jen and Jihui Yang, University of Washington)

Project Objective. The project objective is to develop self-healing and polysulfide-trapping polyelectrolyte gels containing room-temperature ionic liquid (RTIL) for the Li-S battery system. The battery design will be able to achieve gravimetric and volumetric energy densities of ≥ 800 Wh/kg and ≥ 1000 Wh/L, respectively.

Project Impact. The Li-S battery system is currently hampered by poor capacity retention, primarily caused by dissolution of polysulfide reaction intermediates in typical organic electrolytes, as well as poor electrical contact between insulating sulfur and the conductive carbon matrix. This project aims to produce a high-capacity, long-cycle-life Li-S battery system by using rational molecular design strategies to address each capacity loss mechanism directly. A long-cycle-life Li-S battery system with the capability of doubling Li-ion energy density would enable production of lighter, longer range EVs at a cost affordable to the average U. S. household.

Approach. The team will develop Li-S coin cells that utilize self-healing, interpenetrated ionomer gel electrolytes in both the cathode and separator. The team will synthesize necessary starting materials and fabricate components of these gels while testing their relevant electrochemical and mechanical properties. All components will be combined into interpenetrating structures, which will be tested both alone and in cell configurations. Device performance data will be collected and used to further optimize designs of both material and cell, culminating in an optimized Li-S battery design capable of doubling the energy density of traditional Li-ion batteries. During the first year, the team is focusing on (1) synthesis of a variety of precursors for gel electrolytes, (2) fabrication and testing of both baseline materials and novel materials made from these precursors, and (3) iterative validation and improvement of design principles through both materials and device testing.

Out-Year Goals. Work will progress toward developing structure-property relationships for the self-healing, interpenetrated gel ionomer electrolyte and its individual components, as well as successful incorporation of such an electrolyte into a working Li-S cell. The team plans to demonstrate significant improvements in both capacity and retention when using the project's novel materials, as compared to state-of-the-art baseline systems.

Collaborations. This project funds work at UW. Dr. Alex Jen, principal investigator (PI), focuses on design, synthesis, and testing of novel materials, as well as device-based verification of design principles. Dr. Jihui Yang (co-PI) focuses on optimization of device fabrication and testing, as well as investigation of failure mechanisms in devices using novel materials. Pacific Northwest National Laboratory (PNNL) facilities will be used for detailed study of device operation.

- 1. Provide detailed cell performance data for practical-loading cells containing currently best materials designs, along with conclusions regarding the origin of performance details. (Q2, FY 2019; Completed)
- 2. Provide detailed cell performance data for concept cells containing currently best materials designs, which should meet, or nearly meet, performance targets. (Q4, FY 2019)

Progress Report

Multifunctional Ionomer Gels / Gel Cathode. The team continued fabrication and characterization efforts for quasi-solid-state (QSS) Li-S cells, which contain rationally designed solvate ionogel (SIG) in both the cathode and separator. Previously, the team observed that the QSS cells benefit from increased specific capacity and retention compared to traditionally constructed Li-S cells with either organic electrolyte or Li(G4)TFSI solvate ionic liquid (SIL). They also noticed distinct changes to the discharge voltage traces in QSS cells (less-distinct and lengthened upper plateau, downward shift of the lower plateau), and ruled out the influence of anode or separator processes as being the primary source of these changes, leaving the cathode as the most likely source. However, it was still unclear whether the behavior observed was due to overpotentials in the cathode—whether ohmic and/or state-of-charge-dependent—or a reflection of changes to the chemical pathways for sulfur conversion, that is, thermodynamic changes brought on by the SIG electrolyte.

To clarify the influence of these disparate factors on QSS cell behavior, the team performed Galvanostatic Intermittent Titration Technique (GITT) tests on Li-S cells of varying design (Figure 3a-f). This experiment allowed them to calculate the overpotential for each cell as a function of state of charge (SOC), and thus determine the open-circuit or "true" thermodynamic shape of the charge/discharge curves in each case. Since open circuit voltage (OCV) depends solely on the chemical potentials of reactive species within the cell, this provides insight into the chemistry of the project's SIG cathodes, and also suggests areas of improvement within the design. For clear comparison, the team has marked the point of least overpotential during the lower discharge plateau of each cell. First, they may compare these discharge overpotentials among cell designs. Unsurprisingly, the control cell with organic electrolyte (Figure 3a) requires the least overpotential, and the cell with a traditional cathode [S/C/polyvinylidene difluoride (PVDF)] and limited volume of SIL (Figure 3c) requires the most overpotential. This is due to significantly increased charge transfer resistance at both the anode and cathode for the latter case, and highlights the limitations of "dropping in" a new electrolyte without considering its effects on the entire battery system. Adding a large excess of SIL electrolyte (Figure 3b) alleviates this effect slightly, most likely due to improved wetting of the cathode and total capacity of the electrolyte to dissolve lithium polysulfides. On the other hand, replacing half of the volume of SIL with a SIG composite separator (Figure 3d) gives a similar result without requiring an increase in total electrolyte volume. This is almost certainly related to decreased anode overpotential, as previously observed for SIG composite separators.

Cells containing SIG-based cathodes, on the other hand, outperform all cell designs based on S/C/PVDF cathodes and SIL electrolyte, with the lowest overpotential observed for the QSS cell (Figure 3f). The team can partially attribute this to the improved wetting of the cathode achieved by the fabrication technique, as well as the influence of polysulfide-solvating diluent anisole. Overall, this result indicates that the internal resistance of the QSS design can only partially explain its altered discharge characteristics. By process of elimination, this implies that some fundamental change to the chemical pathway of discharge has also occurred in SIG-based cathodes. Comparing OCV traces (red curves in Figure 3) further implicates this hypothesis. The team notes that merely switching from an organic electrolyte to SIL electrolyte in the cathode has very little effect on the open circuit behavior, mostly manifesting as a slight decrease in the upper plateau voltage and less-sharp transition to the lower plateau. The differences in current-applied voltage between these cells can therefore mostly be attributed to overpotential. On the other hand, the open-circuit behavior of cells with SIG-based cathodes closely resembles their current-applied behavior, starting with a broad, extended, downward-sloping region that begins at a *higher* voltage than the upper plateau of traditional designs but ends at a *lower* voltage. This is followed by a lower plateau that is downward shifted by ~ 50 mV from the other cells.

While the team cannot yet identify the exact changes in cathode chemistry that cause these features, it seems safe to say that the SIG-based electrolyte has a dramatic effect on the sulfur conversion chemistry. These results also suggest that the increased overpotential associated with ionic liquid electrolytes in Li-S cells can be successfully mitigated to acceptable levels. The team has accomplished this in their design through use of a solvating diluent (anisole), a cathode fabrication process that circumvents electrolyte wetting problems, and a

gel composite separator that successfully restricts polysulfide migration without incurring large overpotentials or significant extra weight/volume. The team is fabricating cells with higher cathode loadings ($\geq 4 \text{ mg}_{\text{s}}/\text{cm}^2$) based on these strategies and adjusting design accordingly to retain favorable cycling characteristics while minimizing overpotential.



Figure 3. Galvanostatic Intermittent Titration Technique (GITT) results for six different Li-S coin cell designs, with the cell structure indicated as Li | (electrolyte) | (cathode). All data were collected at 30°C and C/10 rate (assuming 1672 mAh/gS), with GITT being performed on the 3rd cycle. All cathodes have ~ 1 mgS/cm² areal loading. The blue and red curves connect the current-applied voltages and open-circuit voltages, respectively, measured directly before current interruption and after a 1-hour rest, respectively. Their difference represents the cell overpotential at that point of charge/discharge. The point of minimum overpotential during the lower discharge plateau of each cell is labeled on the corresponding graphs.

Self-Healing Materials. In the previous study, the project has demonstrated the multi-functional properties of its PENDI-350/tri-Py (PP) SHP system. First, NDI moiety can be reversibly reduced into NDI²⁻ ions, which can trap polysulfides via strong ion-dipole interaction. Second, NDI can also function as a redox-mediator to promote the charge transfer and increases the utilization of sulfur during discharge process. Third, the tunable self-healing property helps mitigate volume expansion and enable increased sulfur loading. This multi-functioning helps improve the capacity retention of sulfur cathode to almost 100% after 100 cycles at 1C. With the significant improvement of capacity retention at low sulfur loading (around 1 mg/cm²), the team has refocused efforts on fabricating cathode with higher sulfur loading (> 4 mg/cm²).

This quarter, the team fabricated high-loading sulfur cathode via systematic design of the sulfur cathode components, including current collector, ratio design between PENDI-350 and tri-Py, choice of carbon conductive additive, and even the loading amount of S/C composite. Carbon-coated aluminum foil was used as current collector, which improves adhesion between current collector with sulfur cathode. Multi-wall CNTs were used as conductive additive to replace black carbon. The 1D structure of CNT is known to assist forming interpenetrating conductive 3D network, which improves not only mechanical integration but also electrical conductivity of sulfur cathode. The sulfur ratio of S/C composite was improved to 70%. Based on the new composition, the team has fabricated cathodes with PP and PVDF as binder (shown in Figure 4a). After 40 cycles, the discharge capacity of cathode with PP binder retains as high as 1070 mAh/g (capacity retention of 92%). On the contrary, the capacity retention of cathode with PVDF binder after 40 cycles is about 76% (909 mAh/g). Meanwhile, the team has noticed decrease of CE, especially for cathode based on PVDF. This is attributed to the side reactions on the anode.

In addition, the team has carefully optimized the ratio between PENDI-350 and tri-Py to achieve high-loading sulfur cathode with mechanical integration. As mentioned, a more robust binder system is needed to mitigate the increasing mechanical stress for sulfur cathode with higher loading. As shown in Figure 4b, the sulfur cathode with PENDI-350:tri-Py ratio of 3:1 is prone to cracking as the sulfur loading amount increases to around 4 mg/cm². After increasing the amount of tri-Py by changing the ratio to 1:1, a continuous sulfur cathode was achieved, even with sulfur loading amount greater than 4.2 mg/cm². The cycling performances of cathode with PP binder (PENDI-350:tri-Py = 1:1) with varying sulfur loading are shown in Figure 4c. The initial capacity of cathode with loading of 4.2 mg/cm² is around 800 mAh/g and remains almost constant within the first several cycles. This implies successful operation of sulfur cathode with high sulfur loading and good capacity retention. However, a sudden drop happens following CE decrease. Therefore, this further demonstrated that the side reaction on the anode is the possible failure mechanism of sulfur cathode with high sulfur loading. The team is investigating the detailed mechanisms and developing methods to protect the anode further.



Figure 4. (a) Cycling performances of sulfur cathodes with PENDI-350/tri-Py (PP) and polyvinylidene difluoride (PVDF) as binder, respectively. (b) Sulfur cathodes fabricated using PP as binder with different ratio between PENDI-350 and tri-Py. (c) Cycling performances of sulfur cathodes with PP (PENDI-350:tri-Py = 1:1) as binder with different loading amount of sulfur.

Patents/Publications/Presentations

Publications

- Hubble, D., J. Qin, F. Lin, I. A. Murphy, S-H. Jang, J. Yang, and A. K-Y. Jen. "Designing Lithium Solvate Ionogels with Very High Conductivity and Lithium Transference Number." *Journal of Materials Chemistry A* 6 (2018): 24100–24106. doi: 10.1039/C8TA08808J.
- Qin, J., F. Lin, D. Hubble, Y. Wang, Y. Li, I. A. Murphy, S-H. Jang, J. Yang, and A. K-Y. Jen. "Tuning Self-Healing Properties of Stiff, Ion-Conductive Polymers." *Journal of Materials Chemistry A* 7 (2019): 6773–6783. doi: 10.1039/C8TA11353J.
- Li, Y.,* I. A. Murphy,* Y. Chen, F. Lin, X. Wang, S. Wang, D. Hubble, S-H. Jang, K. T. Mueller, C. Wang, A. K-Y. Jen, and J. Yang (*co-first author). "Surface Functionalization of Mesoporous Carbon for Polysulfide Trapping in Lithium Sulfur Batteries." In peer review at *Journal of Materials Chemistry A*.

Presentations

- 233rd Electrochemical Society (ECS) Meeting, Seattle, Washington (May 13–17, 2018): "Rationally-Designed Solvate Ionogel Electrolytes for Improved Lithium-Sulfur Battery Performance"; D. Hubble, J. Qin, F. Lin, I. A. Murphy, Y. Li, S-H. Jang, J. Yang, and A. K-Y. Jen. Poster.
- 233rd ECS Meeting, Seattle, Washington (May 13–17, 2018): "Tunable Surface Modification of Mesoporous Carbon Particles for Polysulfide Trapping in Lithium Sulfur Batteries"; I. A. Murphy, Y. Li, Y. Chen, F. Lin, X. Wang, S. Wang, D. Hubble, S-H. Jang, K. T. Mueller, C. Wang, J. Yang, and A. K-Y. Jen. Poster.
- 233rd ECS Meeting, Seattle, Washington (May 13–17, 2018): "Tuning Self-Healing Property of Stiff Supramolecular Polymer for Flexible Electronics"; J. Qin, F. Lin, Y. Wang, D. Hubble, Y. Li, J. Yang, and A. K-Y. Jen. Poster.
- BMR Electrolytes Meeting, Berkeley, California (October 11–12, 2018): "Multifunctional, Self-Healing Polyelectrolyte Gels for Long-Cycle-Life, High-Capacity Sulfur Cathodes in Li-S Batteries"; D. Hubble, J. Qin, F. Lin, I. A. Murphy, Y. Li, S-H. Jang, J. Yang, and A. K-Y. Jen.

Task 1.3 – Construct and Test Lithium-Metal/Composite Electrolyte/Lithium-Metal Symmetric Cells (Nianqiang (Nick) Wu, West Virginia University; Xiangwu Zhang, North Carolina State University)

Project Objective. The project objective is to develop SSEs based on the highly conductive inorganic nanofibrous network in the polymer matrix for lithium batteries.

Project Impact. The team will conduct research and development (R&D) on solid-state inorganic nanofiber-polymer composite electrolytes that will not only provide higher ionic conductivity, improved mechanical strength, and better stability than the polyethylene oxide (PEO) polymer electrolyte, but also exhibit better mechanical integrity, easier incorporation, and better compatibility with the Li-metal anode than the planar ceramic membrane counterparts. The proposed inorganic nanofiber-polymer composite electrolytes will enable practical use of high-energy-density, high-power-density Li-metal batteries, and Li-S batteries.

Approach. Integration of the highly Li⁺-conductive inorganic nanofiber network into the polymer matrix not only provides the continuous Li⁺ transport channels, but also kinetically inhibits crystallization from the amorphous state of polymer electrolyte. The inorganic nanofibers will be fabricated with an electrospinning technique; the ionic conductivity of inorganic nanofibers will be improved by chemical substitution or doping. Highly ionic-conductive polymers will be developed by cross-linking and/or creation of a block-copolymer structure. The composition and microstructure of the composite electrolyte will be designed to suppress the lithium dendrite formation.

Out-Year Goals. Work will progress toward synthesis of the inorganic nanofibers and polymer matrix. The goal is to find the optimal synthetic route to achieve the desirable conductivity.

Collaborations. This project funds work at WVU and North Carolina State University (NCSU). Dr. N. Wu at WVU serves as PI, and Dr. X. Zhang at NCSU acts as co-PI. P. Zheng and X. Gao (Ph.D. student at WVU), H. Yang (Postdoctoral Fellow at WVU), B. Liu (Ph.D. student at WVU), C. Yan (Ph.D. student at NCSU), and M. Dirican (Postdoctoral Fellow at NCSU) contributed to the project.

- 1. Construct the Li-metal/composite electrolyte/Li-metal symmetric cells Subtask 3.1.1. (Q4, FY 2019; Completed)
- 2. Test electrochemical performance of the Li-metal/composite electrolyte/Li-metal symmetric cells, such as interfacial resistance as a function of time derived from impedance spectroscopy and the electrochemical stability window derived from anodic/cathodic scans Subtask 3.1.2. (Q4, FY 2019; 80% Completed)
- 3. Investigate interfacial stability under both open-circuit and Li-metal plating-stripping conditions; measure the end of half-cycle voltage during lithium plating-stripping cycling for the symmetric cells Subtask 3.1.3. (Q4, FY 2019; 50% Completed)
- 4. Examine effectiveness of composite electrolytes in suppressing formation and growth of lithium dendrites Subtask 3.1.4. (Q4, FY 2019; 30% Completed)
- 5. Construct the Li-metal/composite electrolyte/cathode cells Subtask 3.2.1. (Q4, FY 2019; 80% Completed)
- 6. Test the electrochemical performance of the Li-metal/composite electrolyte/cathode full cells; plot the charge and discharge profiles of the full cells made of composite electrolytes; plot the voltage versus the time profile for galvanostatic cycles; and plot the capacity and the CE versus cycles Subtask 3.2.2. (Q4, FY 2019; 30% Completed)

Progress Report

This quarter, the project investigated the structures and electrochemical performance of single-ion conducting cross-linked polymer (CLP) electrolytes.

Construct and Test the Li-Metal/Composite Electrolyte/Li-Metal Symmetric Cells

Propylene carbonate (PC) was introduced as a plasticizer to enhance chain mobility and ionic conductivities of poly(ethylene glycol)diacrylate (PEGDA) CLPs coupled with lithium (4-styrenesulfonyl) (trifluoromethane-sulfonyl)imide (LisTFSI). Figure 5a shows the synthesis procedure of cross-linked poly(ethylene glycol) dimethyl acrylate-co-lithium (4-styrenesulfonyl) (trifluoromethanesulfonyl)imide polymer electrolyte (PEGDA-LisTFSI CLP). Lithium (4-styrenesulfonyl) (trifluoromethanesulfonyl)imide (LisTFSI) monomer was first synthesized based on the procedure shown in Figure 5b. The solid polymer electrolytes were then obtained by homogeneously mixing the prepolymer solution [PEGDA and LisTFSI monomers, PC plasticizer, and azobisisobutyronitrile (AIBN) initiator] and cross-linking at 80°C for 2 h. The content of PC plasticizer was controlled at 50 wt% based on the total weight of PEGDA and LisTFSI monomers. Several plasticized cross-linked PEGDA-LisTFSI polymers were synthesized with different molar ratios of ethylene oxide monomer to lithium monomer ([EO]/[Li⁺] = 32, 28, 24, 20, 16).



Figure 5. Synthesis procedure of (a) plasticized cross-linked PEGDA-LisTFSI polymer electrolyte and (b) KsTFSI monomer. (Potassium salt was typically synthesized first, which was then converted to lithium salt by reacting with excess LiCIO₄).

Figure 6a-b demonstrates the corresponding ionic conductivities of PEGDA-LisTFSI P-CLPs with different [EO]/[Li+] ratios. At room temperature, the PEGDA-LisTFSI CLP with a $[EO]/[Li^+]$ ratio of 24:1 gives the highest ionic conductivity of 1.4×10^{-4} S cm⁻¹. As shown Figure 6b, ionic conductivity increases first with increase in LisTFSI content, reaching its maximum at 24:1 ($[EO]/[Li^+]$) ratio due to the increased concentration of charge carriers in the polymer electrolyte. However, subsequent growth of LisTFSI content results in decreased ionic conductivities, which might be caused by the aggregation in ion clusters or reduced flexibility

of polymer chains owing to the higher content of hard anionic block. As shown in Figure 6c, The Li^+ transference number of PEGDA-LisTFSI CLP ([EO]/[Li⁺]=24:1) is as high as 0.82. Possible reasons for having such a high transference number value less than unity are as follows: (1) anions are attached to the main polymer chain by a flexible spacer that likely allows for short-range motion of negative charges, and (2) impurities and additional negative charges may arise from lithium monomer synthesis and/or cell fabrication. As shown in Figure 6d, the stability window of PEGDA-LisTFSI P-CLP polymer electrolyte is between 1.1 V to 4.7 V versus Li/Li⁺.





Patents/Publications/Presentations

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

Task 1.4 – High Conductivity and Flexible Hybrid Solid-State Electrolyte (Eric Wachsman, Liangbing Hu, and Yifei Mo, University of Maryland)

Project Objective. The project objective is to develop flexible hybrid electrolyte with garnet nanofibers to achieve the following: (1) flexible, with greater mechanical strength (~ 10 MPa) and thermal stability than polymer electrolytes; (2) high room-temperature ionic conductivity, ~ 0.5 mS/cm; (3) stable interface with lithium metal and effective blocking of lithium dendrites at current densities up to 3 mA/cm²; and (4) battery performance with Li-S chemistry with an energy density of \geq 450 Wh/kg (and \geq 1000 Wh/L) and maintaining \geq 80% of capacity up to 500 cycles.

Project Impact. Instability and/or high resistance at the interface of lithium metal with various solid electrolytes limit(s) the use of the metallic anode for batteries with high energy density, such as Li-air and Li-S batteries. The critical impact of this endeavor will be focused on developing a new type of SSE that is highly conductive, highly flexible, and electrochemically stable. The new SSE will enable Li-metal anodes with excellent interfacial impedance and blocking of lithium dendrite formation.

Approach. The project will synthesize garnet nanofibers, fill the porous region with polymer electrolyte, and characterize the flexible hybrid membrane properties. The flexible hybrid SSE microstructure will be determined using focused ion beam / scanning electron microscopy (FIB/SEM) and integrated with electrochemical methods to investigate the properties and stability with Li-metal anode.

Out-Year Goals. The project will develop a fundamental understanding of the mechanism of Li-ionic diffusion in garnet nanofibers and their mechanical properties, as well as these properties for hybrid garnet-fiber/polymer hybrids. Work will progress toward study of the electrode assembly during electrochemical cycling of the anode.

Collaborations. This project funds work at UMD, College Park. Dr. E. D. Wachsman (PI) will focus on optimizing the garnet network to achieve high ionic conductivity and flexibility using FIB/SEM and electrochemical impedance spectroscopy (EIS) characterization. Dr. L. Hu (co-PI) focuses on synthesis of the hybrid electrolyte and on test for Li-metal anode with the hybrid electrolyte. Dr. Y. Mo (co-PI) will lead efforts on computational modeling of the garnet nanofiber hybrid electrolytes for fundamental mechanistic understanding.

- 1. Modeling of lithium dendrite protection: Understand lithium dendrite growth and protection effect of polymer and interphase layers on garnet nanofiber. (Q1, FY 2019; Completed December 2018)
- 2. Fabricate porous mixed electron/ion conductor: Fabricate and evaluate porous framework of mixed electron and ion conductor (to fill sulfur cathode). (Q2, FY 2019; Completed)
- 3. Li-S full cell with hybrid SSE: Fabricate and evaluate Li-SSE-S full cell with a size of 1 cm by 1 cm. (Q3, FY 2019; In progress)
- 4. Full cell performance: Achieve full cell of 10 mAh and energy density of 450 Wh/kg. (Q4, FY 2019; In progress)

Progress Report

Porous ion-conducting framework composed of garnet ceramic fibers was fabricated by a sacrificial template method as reported previously. CNT solution (1 mg/ml in NMP) was infiltrated into the pore structure and overcoated the exposed surface of garnet phase. Therefore, mixed electron/ion conductor was achieved in Figure 7a. The gray composite conductor could provide both ion and electron conduction by sintered garnet electrolyte and CNT layer, respectively. The ionic conductivity was measured by Solartron 1260 impedance analyzer. The AC impedance plot shows a typical compressed semi-circle in high frequency range in Figure 7b, representing the ion conduction process that occurred along the interconnected fibrous garnet phase. The electronic conductivity was measured by Keithley 2400 source meter, as shown in Figure 7c. The linear relationship between the applied voltage and the resulting electric current obeys the Ohm's law, indicating that the conformal CNT coating layer has created electron conduction network.



Figure 7. Porous mixed electron/ion conductor and electrochemical performance. (a) Photo image. (b) AC impedance plot. (c) DC resistance plot.

Lithium polysulfide solution (1 mol/L Li_2S_8 in DOL/DME) was synthesized for sulfur cathode fabrication. The solution was infiltrated into the pore structure of the mixed electron/ion framework to achieve desired sulfur loading. The microstructure of sulfur infiltrated mixed conductor was studied by SEM in Figure 8. Deposition of CNTs and lithium poly-sulfide reconstructed the surface of garnet fiber to generate well-bonded garnet/carbon/sulfur three-phase microstructure. Elemental mapping confirmed the existence of garnet phase, carbon phase, and polysulfide phase, indicating successful infiltration of CNTs and polysulfide into the porous garnet fiber framework. The fibrous garnet structure, together with the CNT coating layer, formed a continuous network of pathways for both ion and electron transport, which successfully built the backbone for a 3D solid-state high-loading sulfur cathode.

To fabricate the sulfur cathode with higher areal capacity, a 3D host material with aligned microchannels was used for loading sulfur with high mass loading. As schematically shown in Figure 9a, a piece of carbon with perpendicular channels was carbonized (c-wood) and filled with graphene. Sulfur was then melted and

infiltrated into the pores of the c-wood/graphene host material with a mass loading of ~ 20 mg/cm². The electrochemical performance of the high-loading sulfur cathode (S@c-wood/graphene) was first demonstrated in liquid electrolyte, 1 M LiTFSI dissolved in DOL/DME; the discharge/charge voltage Figure 9b. profile is shown in The S@c-wood/graphene shows a high discharge capacity at 0.01 C and extremely high areal capacity. In the first discharge, the areal capacity is ~ 14 mAh/cm², which can be used with the flexible hybrid solid electrolyte for high-capacity Li-SSE-S full cells.



Figure 8. Sulfur cathode infiltrated porous mixed electron/ion conductor.



Figure 9. (a) Schematic of preparation and structure of the high-loading sulfur cathode in c-wood with graphene. (b) First discharge/charge voltage profile of the S@c-wood/graphene cathode.

Patents/Publications/Presentations

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

Task 1.5 – Self-Forming Thin Interphases and Electrodes Enabling 3D Structured High-Energy-Density Batteries (Glenn Amatucci, Rutgers University)

Project Objective. The project objective is to develop and implement a novel *in situ* formed Li-metal-based metal fluoride battery that will enable packaged 10-mAh batteries of energy densities > 1000 Wh/L and > 400 Wh/kg at 12 V.

Impact. Successful realization of 3D batteries formed *in situ* with a practical approach to large-scale fabrication would address some of the DOE EV performance goals, including: (1) areal capacity increase, (2) improved rates, and (3) designs to enable high-voltage unit cells.

Approach. The project is divided into two main tasks that focus on advance of the self-forming chemistry concurrent to cell design and fabrication. The self-forming chemistry task is comprised of three subtasks encompassing the negative and positive reactive current collectors, and the bi-ion glass conductor. The cell design and fabrication are targeting development and integration of the bipolar configuration to achieve the 12-V single-cell goal.

Out-Year Goals. Work will continue toward improving reactive current collectors and cell design to optimize electrochemical performance of the cell stack in terms of energy density both gravimetric and volumetric, as well as capacity retention on cycling. A secondary focus will be implementation of bipolar design within the cell structure.

Collaborations. All project tasks will be performed at Rutgers University.

- 1. Design and fabricate 10-mAh cell stack that achieves 12 V and delivers energy densities of 1400 Wh/L and 600 Wh/kg per cell stack. (Q1, FY 2019; In progress)
- 2. Establish negative current collector compositions that enable high efficiency of lithium plating and stripping in excess of 95% during the *in situ* formation step and > 99% during subsequent cycles. (Q2, FY 2019; In progress)
- 3. Achieve < 30% increase in electrolyte impedance after 50 cycles as characterized by EIS. (Q3, FY 2019)
- 4. Establish positive current collector compositions that achieve 90% of the theoretical energy density based on complete utilization of the initial amount of the positive reactive current collector. (Q4, FY 2019)
- 5. *Deliverables:* Deliver 12 baseline and 12 improved packaged cells with 10-mAh capacity. Improved cells will offer > 1000 Wh/L and > 400 Wh/kg, and output voltage of 12 V.
During the first quarter of FY 2019, a collection of optimizations was transferred from the single-cell design to the 12-V architecture to advance performance. Electrode design, electrolyte of enhanced conductivity, optimized cycling protocols, and more detailed cell characterization revealed that diffusion limitations were the ultimate barrier in further progress, thereby prompting additional examination.

From an aggregate of the project's previous studies, it has been found that ion diffusion of both F- and

Li⁺ directly and significantly affects functionality of the formation electrolyte's interaction with the reactive current collectors to generate reversible reactions with desirable capacities and utilization. As such, this quarter the main focus for further development and improvement of cell performance featured decreased electrode spacing in both the single and 12-V cell configurations. In addition, electrode spacing was reduced by a third from 90 microns in the standard design to 60 microns in the advanced design.

In the single-cell configuration, spacing adjustments were applied with modified aspect ratio alterations, which also maintained mechanical integrity of the electrodes. Additionally, the orientation of the single, parallel cell design was reengineered in similar fashion to the 12-V design discussed in the third quarter of FY 2018. Figure 10 shows results for the single-cell design, comparing the positive electrode utilization and energy densities of the electrode pairs for three cell designs. The three variations include the original orientation with the



Figure 10. Comparison of the positive electrode utilization and electrode pairs' energy densities for the single cell configuration with variations in cell design. Variations include orientation, electrode aspect ratio, and electrode spacing.

larger electrode spacing of 90 microns and larger aspect ratio electrodes, the design consisting of the new orientation with the electrode aspect ratio 4 times smaller and the 90-micron electrode spacing, and finally the last design concept included the new orientation with 4 times smaller electrode aspect ratio and smaller spacing of 60 microns. Compared to the original design, the smaller aspect ratio, 60-micron electrode spacing, and new orientation design yielded some of the project's best results, with 54% positive electrode utilization and 1318 Wh/L energy density based on electrode pairs. These results demonstrate an improvement of approximately 116% in utilization and about 60% in energy density from the standard original design. This cell design optimization shows that the aspect ratio and/or the cell orientation have the largest effect on cell performance; however, lower electrode spacing is also a critical design parameter to achieve good cell performance. As such, further reduction of electrode spacing may promote additional advances in cell performance, although adjustments to the current fabrication equipment would be required to go beyond 60-micron electrode spacing.

For the 12-V cell design, modification to electrode spacing was combined with a decrease in electrode aspect ratio along with an increase in electrolyte reserve capacity. The reserve capacity of the electrolyte is important, as it represents the source of F^- ions to form electrodes during electrolytic formation. While Figure 11 presents a voltage profile showing the *in situ* formation of a 12-V cell described last quarter, Figure 12 compares the positive electrode utilization and the energy densities of the electrode pairs for the advanced 12-V cell design of this quarter with last quarter's design as well as with the original and early designs of last year. Figure 12 demonstrates cell design modifications on the 12-V architecture to produce increased cell performance, with the best results being 44% positive electrode utilization and 1059 Wh/L for the energy densities of the electrode

pairs. Comparing results from this quarter to last quarter, utilization increased by 19% and energy density increased by about 21%. The adjustments of increased electrolyte thickness and decreased electrode spacing had a positive outcome on cell performance. As mentioned with the single-cell design, further decreasing electrode spacing may improve cell performance.

Despite the advantages associated with the cell design modifications with smaller electrode spacing as described above, there was also evidence of a different mechanism affecting cycling stability. It was found that carbon particles from the glove box filter medium play a key role in the cycling ability of cells with the smaller electrode spacing. Post mortem analysis of the cells with smaller electrode spacing shows that the particle size of contaminants from the glove box atmosphere was typically similar to that of the 60-micron spacing. This caused undesirable effects leading to shorting of the cell. Preventive avenues to limit these contamination features are being investigated.





Addressable challenges that remain due to the nature of the cell design chemistry are transport limitations: (1) ionic (Li^+ and F^-) and (2) electronic. Both limitations induce loss in discharge capacity despite an increase in charge capacity after modification of the cell designs as described above, thereby limiting overall discharge utilization. Ionic transport limitations occur because of a deficiency of fluorine ions at the interface of the electrolyte with the electrode inhibiting further reactions to occur. The electronic transport limitations occur because the thickness of the metal fluoride affects conductivity and ability of electrons to reach the electrolyte from the current collector through the electrode to promote further reactions. Each of these mechanisms create inactive material, making the improvements on charge capacity nonequivalent in discharge capacity. Next quarter, the team will focus on combining the improvements found with decreased electrode spacing and other cell design modifications with the nanolayered multicomponent electrode composition described in the second quarter of FY 2018. The nanolayered electrode architecture utilizing mixed conductor additives provides both ionic and electronic conducting promoters that can overcome the described transport limitations.

In summary, the cell design property of smaller electrode spacing was beneficial in improving cell performance for both the single and 12-V cell configurations. Utilizing this modification in conjunction with previously investigated changes of decreased electrode aspect ratio and increased electrolyte thickness or cell orientation allowed the team to increase positive electrode utilization and energy density of electrode pairs. To overcome remaining transport limitations, these findings will be combined with the nanolayered electrode architecture investigated and optimized in previous studies to reach closer to cell performance goals.



Figure 12. Comparison of positive electrode utilization and energy density of electrode pairs for the 12-V configuration with variations on the cell design. The tested variations include electrode aspect ratio, electrolyte thickness, and electrode spacing.

Patents/Publications/Presentations

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

Task 1.6 – Dual Function Solid-State Battery with Self-Forming, Self-Healing Electrolyte and Separator (Esther Takeuchi, Stony Brook University)

Project Objective. The project objective is to demonstrate a solid-state rechargeable battery based on a Li-metal anode and iodine cathode with a self-forming, self-healing electrolyte and separator with high gravimetric and volumetric energy density.

Project Impact. This program will enable demonstration of the proposed rechargeable battery with improved power capability, high energy density, and a self-forming, self-healing SSE/separator. Technical insight will be gained regarding improved conductivity of the solid lithium iodide (LiI) based electrolyte, power capability of the proposed system, the self-healing nature of the LiI layer, the nature of the electrode-electrolyte interfaces, and feasibility of the system to reach the DOE targets.

Approach. The proposed concept is a dual function rechargeable solid-state battery utilizing LiI combined with silver iodide (AgI) as the electrolyte, with lithium metal (and small quantities of silver metal) as the anode and iodine as the cathode with a self-forming, self-healing separator/electrolyte. The battery will be assembled in the discharged state where the anode and cathode will be created during the first formation (charge) step. Initially, silver ion (Ag⁺) will diffuse toward the negative electrode and be reduced to silver metal (Ag⁰), and iodine ion (Γ) will be oxidized to elemental iodine (I₂) at the cathode side. As the formation of the battery continues, lithium ion (Li⁺) will form a Li-metal layer at the anode, with generation of iodine at the cathode. LiI will remain and serve as both the separator and electrolyte.

Out-Year Goals. This is a multiyear program where the effort is divided into three major tasks.

- Year 1 involves electrolyte preparation and characterization including preparation of SSEs and conductivity measurements.
- Year 2 will focus on cell construction and testing including both *in situ* and *ex situ* analysis.
- Year 3 will focus on cell characterization. Under the program, cycle life, efficiency, energy density, and the functional capacity of cells will be determined.

Collaborations. This project collaborates with A. Marschilok and K. Takeuchi of SBU.

- 1. Determine functional capacity and energy density of construction A cells. (Q1, FY 2019; Completed December 30, 2018)
- 1. Determine functional capacity and energy density of construction B cells. (Q2, FY 2019; Completed, March 31, 2019)
- 2. Destructive analysis of construction A cells. (Q3, FY 2019; Initiated)

Determine Functional Capacity and Energy Density of Construction B Cells

This quarter's milestone was to determine functional capacity and energy density of construction B cells. Cell design B included the composite LiI solid electrolyte with LiI(3-hydroxypropionitrile)₂ additive, as reported previously. Cell design B was constructed with four interface variations: B-Interface I (B-I), B-Interface II

(B-II), B-Interface III (B-III), and B-Interface IV (B-IV). Variation of the interface was studied to evaluate the effects on CE during charge-discharge cycling. Last quarter, it was observed that CE could be significantly impacted by interfacial modification, with improvement retained over 10 cycles. Longer term cycling was conducted this quarter where four cell design B cell constructs (I, II, III, and IV) were compared with cell design A I. The CE of the cells over 60 cycles is reported in Figure 13. Interestingly, three of the B-type cell designs (I, II, and III) show a significant increase in efficiency over the first 10 cycles. This is similar to the behavior observed in



Figure 13. Coulombic efficiency under extended cycling of solid-state cells of cell designs B I, B II, B III, and B IV compared with cell design A I.

cell design A I. Notably, cell design B I shows CE between 90% and 100% throughout the testing regime.

The energy density of the solid-state concept was determined for the various cell designs and relates to the composition of the electrolyte and the ability to effectively utilize the LiI material in the cell. With full utilization of the LiI of the current electrolyte/cell chemical composition, the energy density is ~ 450 Wh/kg.

Destructive Analysis of Cells

Solid-state cells in configuration A charged to $\sim 50\%$ were of theoretical capacity. The cells were then disassembled and examined using XRD. The diffraction pattern of the composite electrolyte prior to assembly is shown cell in Figure 14a, indicating the presence of LiI, LiI·H₂O, and LiI(3hydroxypropionitrile)₂. After charge, as shown in Figure 14b, the same three components can be



Figure 14. X-ray diffraction of the composite solid electrolyte. (a) Prior to cell assembly. (b) Removed from cell after charge, cathode side.

identified along with the presence of I_2 ·LiI(3-hydroxypropionitrile)₂, affirming the generation of iodine at the cathode interface of the solid electrolyte after charge.

Demonstration of Self-Healing

The hypothesis put forward in the initial concept for the cell was that cell chemistry would be self-healing. If a lithium dendrite formed during charge of the cell and reached the iodine cathode, the reaction of the lithium dendrite with the iodine would consume the tip of the dendrite to form lithium iodide, more of the solid electrolyte. The formation of the solid electrolyte would allow the cell to recover and continue to function.

Exploration of this concept was conducted as shown in Figure 15a, where a cell was cycled under a sufficiently high current density to induce the growth of dendrites and internal shorts. The same cell is shown in Figure 15b cycled under a reduced current density. The cell demonstrates no evidence of internal shorts and continues to function effectively.



Figure 15. Demonstration of self-healing of the cell. (a) Cycling of a solid-state cell under high current density, sufficient to cause internal short. (b) Same cell cycled under lower current density showing no evidence of shorting.

Patents/Publications/Presentations

Publications

- Abraham, A., M. R. Dunkin, J. Huang, B. Zhang, K. J. Takeuchi, E. S. Takeuchi, and A. C. Marschilok. "Interface Effects on Self-Forming Rechargeable Li/I₂ Based Solid State Batteries." *MRS Communications*. Invited and accepted.
- Stackhouse, C. A., A. Abraham, K. J. Takeuchi, Esther S. Takeuchi, and A. C. Marschilok. "Progress and Outlook on Few Component Composite Solid State Electrolytes." *MRS Advances*. Accepted.

Presentation

 American Chemical Society (ACS) Spring Meeting, Division of Energy and Fuels, Session on Innovative Chemistry & Materials for Electrochemical Energy Storage, Orlando, Florida (March 31 – April 4, 2019): "High-Energy Density Solid-State Rechargeable Battery Based on Li/I₂"; Invited. Task 1.7 – High-Conductivity, Low-Temperature Polymer Electrolytes for Lithium-Ion Batteries (Bryan D. McCloskey, University of California at Berkeley)

Project Objective. Design of electrolytes with enhanced transport properties compared to conventional liquid organic electrolytes is key to improving the rate at which a Li-ion battery can be discharged or charged. Ideally, electrolytes would allow high mobility for lithium ions and disallow mobility of inactive ions (for example, the counteranion of the Li⁺). However, current liquid electrolyte compositions usually provide higher mobility for the counteranion than Li⁺, which results in high concentration polarization that disallows fast charging, particularly in batteries that employ thick porous electrodes, as is necessary for EVs to provide high energy densities. The project objective is to develop a high Li⁺ transference number (t_{Li} , the fraction of ionic current carried by Li⁺ in an electrolyte of uniform composition) polymer-based electrolyte that, when used in a Li-ion battery, can support current rate capabilities sufficient for EV propulsion at room temperature.

Impact. Development of practical high t_{Li} polymer-based electrolytes for Li-ion batteries would enable safer Li-metal and graphitic anode cycling and thicker porous electrode designs, leading to improved specific and volumetric battery energy densities consistent with the EV Everywhere Grand Challenge. High-energy anode and cathode materials, such as lithium metal, silicon, and high-voltage layered or spinel structures, could be enabled by electrolytes with high t_{Li} and large operating voltage windows, such as those based on sulfones, as proposed here.

Approach. Lowering the operating temperature of polymer electrolytes has been cited as an important challenge to their viability as Li-ion battery electrolytes. The project will address this challenge by using Li⁺ neutralized anionically charged polymers as salts in conventional liquid solvents. Using these so-called polyelectrolyte solutions, initial results indicate that the project can access t_{Li} values typical of single-ion conducting polymer electrolytes ($t_{Li} > 0.9$) and conductivity values (> 1 mS/cm at room temperature) that approach those of traditional battery electrolytes.

Out-Year Goals. The optimization of transport and stability properties of these polyelectrolyte systems, through understanding of appropriate polymer and solvent design, is the objective. The goal is to develop new polyelectrolyte compositions that provide superior transport properties (specifically, higher t_{Li} and conductivity) than conventional liquid electrolytes and enable use of high-energy electrode materials, such as lithium metal.

Collaborations. Collaborations on this project include V. Battaglia (porous electrode preparation) and K. Persson (atomistic modeling) at LBNL.

- 1. Complete synthesis and characterization of a new Li⁺-neutralized charged polymer (pFTO) with a triflate-like ion (-CF₂-SO₃-) appended to the polymer backbone to improve ion dissociation. (Q1, FY 2019; Completed October 2018)
- 2. Complete nuclear magnetic resonance (NMR) transport and viscosity measurements of pFTO dissolved in carbonate-based solvents. Progress measure: Publish an article describing transport properties of polyelectrolyte solutions comprised of sulfonated polysulfone-co-poly(ethylene oxide) in carbonate-based solvents. (Q2, FY 2019; Progress measure completed November 2018.)
- 3. Complete electrochemical transport measurements of pFTO in symmetric cells with Li-metal electrodes and SSEs. (Q3, FY 2019)
- 4. Complete characterization of rate capabilities of cells comprised of lithium metal, a porous NMC cathode, and pFTO-containing carbonate solutions during electrochemical cycling. (Q4, FY 2019)

Last quarter, the team reported on characterization of sulfonated polysulfone-co-poly(ethylene glycol) polymers, particularly the differences in transport properties of these polymers in dimethylsulfoxide (DMSO) and carbonates. The publication of this study satisfied the progress measure for this quarter. The team also reported on the difficulty in synthesizing regular homogeneous triflate-based ionomers based on PEO and polysulfone (pFTO). To overcome the synthetic challenges observed for pFTO polymers, this quarter, the team focused on synthesis and initial characterization of triflimide-based styrene (PS-LiTFSI) and acrylate

(PA-LiTFSI) ionomers. These polymers were produced via a straightforward one-step synthesis using reversible addition-fragmentation polymerization (RAFT, Figure 16). Characterization of the raw polymers via gel-permeation chromatography and NMR showed the successful synthesis of both polymers with a molecular weight of 13,700 and 14,400 and polydispersity of 1.28 and 1.15 for the styrene and acrylate polymers respectively (based on polystyrene standards). No side reactions were observed, and expected lithium content was confirmed via ⁷Li NMR spectroscopy.



synthesis scheme for triflimide-based styrene polymer

Polyelectrolyte solutions were produced, with both TFSI-based polymers showing good solubility up to at least

3M in a 2:1 EC/DMC mixture. Conductivity and viscosity measurements were performed on these solutions, showing both promising conductivity, over 1 mS/cm, and low viscosity (Figure 17). Initial Pulsed-Field Gradient NMR (PFG-NMR) diffusion measurements on the PS-LiTFSI in carbonate polyelectrolyte solution show significantly higher diffusion coefficients for lithium species than for the polymer backbone with values on the order of 2 x 10^{-6} cm²/s and 5 x 10^{-7} cm²/s, respectively.

(PS-LiTFSI).



To test battery-condition stability of the polymer, a coin cell was constructed with commercial LiFePO₄ and graphite electrodes with 0.4 molal PS-LiTFSI in EC/DMC used as the electrolyte (Figure 18). The cell was cycled galvanostatically at a rate of C/20. Initial results show good cyclability at this low charge and discharge rate. While further measurements are needed, these triflimide polymers seem to be promising for future studies in conventional Li-ion cells. The team will continue to probe transport properties next quarter with complete transference number measurements based on concentrated solution theory, and more electrochemical testing.

Patents/Publications/Presentations

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

Task 1.8 – 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 CE of Li-metal electrodes will be increased by implementation of a polymer-based protective layer that functions as an artificial 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 project 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, the team chose a few representative polymers to systematically understand structure property relationships. Here, the team investigates the correction 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. There are no active collaborations this quarter.

Milestones

1. Identify at least two different types of SHPs with promise to suppress dendrites. (Q1, FY 2019; Completed)

2. Characterization of the SHPs. (Q2, FY 2019; Completed)

Rational design of the electrode-electrolyte interphase is essential to stabilize electrodeposition of metallic lithium. Thus, it is important to design an artificial interfacial layer that can accommodate the stress generation due to the volume changes during battery operation and at the same time maintain ionic continuity. In this report, the team designs artificial SEI with two distinct concepts that can enable stable deposition of metallic lithium. The two concepts are based on self-healable dynamic polymers and single-ion conducting elastomers.

Self-Healable Polymeric Architectures

The team hypothesizes that stimuli-responsive polymeric architectures can be effective in preventing morphological instabilities during electrodeposition compared to covalently bonded rigid polymers and crosslinked elastomers, when used as artificial interfaces between the electrode and electrolyte. The fundamental working mechanism of the dynamic polymeric coatings can arise from the spontaneous structural response of the polymer in response to the roughening electrode during electrodeposition. As the polymer coating is free to flow, if there is a 'hotspot' (uneven deposit) on the surface of the lithium metal, the dynamic polymer coating can rearrange and cover these regions, resulting in increased overpotential. Thus, successive Li⁺ ions deposit on the flatter regions, resulting in uniformity of deposition. Furthermore, the tortuous pathway in the polymeric interface can enable uniform distribution of lithium ions during charging process, thus leading to uniform deposition.

In this work, a series of different supramolecular polymers will be designed comprising various content of non-covalent interactions and polymer entanglements using polymerization of PDMS with urea linkages. Figure 19a shows the chemical structure of the SHP comprising a PDMS soft block where *n* (number of siloxane monomers) was changed from 10 to 350, while the urea linkages were formed using diisocyanate units. Two different hard block units were utilized in this work, specifically, isophrone (IDPI) and bis methylene diphenyl units (MDI). These units enable different strength of hydrogen bonding in the supramolecular polymer network. The MDI block can form pi-pi stacking and also quadrupolar H-bonding at each site, while the IDPI unit forms weaker H-bonding due to steric hindrance and low symmetry of the molecule. Thus, the synthesized polymers will help the team understand the effect of the entanglements and dynamic bond formation in the coatings for stabilizing electrodeposition.



Figure 19. (a) Chemical structure of polydimethylsiloxane (PDMS) self-healing polymer (SHP). Top structure with isophrone units; middle structure with bis methylene diphenyl units. (b) Oscillatory shear measurements at strain of 1% for the different PDMS-based SHPs.

The team performed the frequency dependent oscillatory shear measurements to analyze the mechanical and molecular properties of the supramolecular polymers. Specifically, they utilized a strain of 1% and temperature of 25°C. The high frequency regime corresponds to the elastic behavior of the material, while the low frequency corresponds to the viscous effects. It can be seen that changing the hard unit from IDPI to MDI increases the

cross-over frequency storage and loss modulus, reflecting a higher relaxation time. Also, variation of the number of monomers in the soft unit (PDMS from 10 to 700) leads to decrease in the elastic modulus of the polymer by about three orders of magnitude. Thus, the range of the polymers shows wide differences in the molecular properties, reflective in the macroscopic relaxation behavior as well as the modulus.

The team analyzed the electrochemical characteristics of the PDMS SHP using CE measurements in Li||PDMS-SHP@Cu cells. In this measurement, a fixed amount of lithium was deposited onto the copper electrode, followed by repeated stripping and plating for shorter timeframes. Thereafter, the amount of lithium remaining from the copper electrode was quantified for obtaining the CE of electrodeposition. The electrolyte utilized in this experiment was 1 M DOL/DME LiTFSI with 1% LiNO₃. Figure 20a shows the typical voltage profile in the measurement. Figure 20b compares the CE of the different PDMS-SHP coatings with varying sizes of PDMS blocks and different molecular weights. It is observed that the CE values for all the coatings are nearly identical at values between 90-95%, except for the stiffest polymer (n=10). However, there appears to be a trend in the relative lifetimes of the cells. It is seen that the PDMS-SHP with the higher flowability outperforms the polymers with higher stiffness. Furthermore, the higher H-bonding units have higher CE, as seen from the differences between the MDI versus IDPI hard block based PDMS SHP. Thus, the results indicate that a higher degree of electrodeposition stabilization is achievable by incorporating polymer coating with high flowability and abundance of strong dynamic bonding units.



Figure 20. (a) Typical voltage profile of Li||PDMS-SHP@Cu cells. (b) Coulombic efficiency comparisons of the polydimethylsiloxane (PDMS) self-healing polymer (SHP) with varying sizes of PDMS soft blocks as well as H-bonding strengths in the co-polymer.

Patents/Publications/Presentations

Publications

- Tsao, Y., M. Lee, E. C. Miller, G. Gao, J. Park, S. Chen, T. Katsumata, H. Tran, L-W. Wang, M. F. Toney, Y. Cui, and Z. Bao. "Designing a Quinone-Based Redox Mediator to Facilitate Li₂S oxidation in Li-S Batteries." *Joule* 3, no. 3 (2019): 872–884.
- Lopez, J., D. Mackanic, Y. Cui, and Z. Bao. "Design Polymers for Advanced Battery Chemistries." *Nature Review Materials* (2019). In press.

Presentations

- Battery500 Q1 Meeting (2019): "Dynamic Polymer Coatings for Lithium Electrodes"; S. Choudhury, C. V. Amanchukwu, Y. Cui, and Z. Bao. Poster.
- Battery500 Q1 Meeting (2019): "Organic Li-Metal Interfaces"; Z. Bao.

Task 1.9 – Improving the Stability of Lithium-Metal Anodes and Inorganic-Organic Solid Electrolytes (Nitash Balsara, Lawrence Berkeley National Laboratory)

Project Objective. The project objective is to establish a new hybrid electrolyte that will be stable against cells with a Li-metal anode.

Project Impact. Polymer electrolytes offer increased stability in lithium batteries in comparison to more widely used liquid electrolytes. Nanostructured electrolytes containing both soft, ion-conducting domains and rigid nonconducting domains offer the opportunity to tune both mechanical and electrical properties separately. Such electrolytes are conveniently made by block copolymer self-assembly. Most of the block copolymer electrolytes studied thus far comprise organic polymer chains for both the conducting and rigid domains. The team hopes to synthesize new electrolytes that simulataneously have high transport properties and have greater stability against lithium in comparison to organic diblock copolymers.

Approach. First, the team synthesizes hybrid diblock copolymers by incorporating monomers that contain an inorganic component. Then, electrolytes are prepared by mixing these diblock copolymers with salt. Electrochemical and mechanical characterization of these materials is performed before carrying out cycling X-ray tomography (XRT) experiments. The combination of these approaches enables rational design of materials that exhibit improved stability against lithium metal.

Out-Year Goals. The project will synthesize a new hybrid electrolyte that is designed to be stable against lithium metal. The material is a block copolymer wherein acryloisobutyl polyhedral oligomeric silsesquioxane (POSS) is covalently bonded to the chain. The second block is a conventional polymer electrolyte, PEO. Electrochemical characterization of this polymer will include measurement of all transport properties including conductivity, diffusion coefficient, and the transference number. The stability against lithium metal will be evaluated by cyclic voltammetry (CV), while its applications as an electrolyte will be evaluated and visualized using cycling XRT experiments on symmetric Li-hybrid-Li cells.

Collaborations. There are no active collaborations this quarter.

- 1. Determine limiting current in solid electrolytes. (Q1, FY 2019; Completed)
- 2. Determine the nature of lithium/electrolyte interface. (Q2, FY 2019; Completed)
- 3. Study the effect of lithium metal purity and failure mechanisms. (Q3, FY 2019)
- 4. Determine parametric range over which stable lithium electrodeposition is obtained. (Q4, FY 2019)

Electrolyte Interface of POSS-PEO Block Copolymers

The nature of the lithium/electrolyte interface in hybrid block copolymer electrolytes was probed using impedance spectroscopy. Lithium symmetric cells were fabricated using a triblock POSS-PEO-POSS (5k-35k-5k) electrolyte with $r = \frac{[Li]}{[EO]} = 0.04$. Cells were conditioned using a current density of 0.02 mA cm⁻² for 10 cycles, with each cycle consisting of 4 hours of charge, 45 minutes of rest, 4 hours of discharge, and 45 minutes of rest. Figure 21 shows that the effective resistance of the electrolyte during conditioning cycles was stable for 10 cycles. Figure 22 is a Nyquist plot showing bulk and



Figure 21. Voltage as a function of time during preconditioning cycles for a lithium symmetric cell and a POSS-PEO-POSS/LiTFSI r=0.04 electrolyte. This cell was cycled at a current density of 0.02 mA cm⁻² without significant increase in resistance over 10 cycles.

interfacial resistance components before and after the 10 conditioning cycles shown in Figure 21. The bulk resistance is unchanged, and the interfacial resistance increases by approximately 10% and stabilizes.



Figure 22. Nyquist plot of a lithium symmetric cell before and after the conditioning cycles shown in Figure 21. Bulk resistance was unchanged, and interfacial resistance increased by approximately 10%. Frequencies sampled were 1 Hz to 1 MHz with 30 mV perturbations.



Figure 23. Interfacial resistance of PEO-POSS 5k-1k with ethyl, isobutyl, and isooctyl end groups as a function of salt concentration.

The lithium/electrolyte interface was also probed in PEO-POSS electrolytes with approximate molecular weight while changing end (5k-1k) groups -isobutyl, -isooctyl) on the (-ethvl. POSS component to see if the end groups on the POSS component have significant interactions with lithium at the electrode/ electrolyte interface. Interfacial resistance measured was with impedance spectroscopy as a function of salt concentration. It appears that the interfacial resistance is not a strong function of POSS end group or salt concentration.

Electrolyte Interface of PEO and Lithium

As the conducting phase of PEO-POSS and POSS-PEO-POSS electrolytes is PEO, a study was completed to better understand the nature of the electrode-electrolyte interface with homopolymer PEO. A remarkable property of the electrolytes interface between PEO-based (both homopolymers and block copolymers) and lithium metal is the observation that good mechanical and electrical contact are maintained even when tens of micrometers of lithium are displaced during cycling. This is especially surprising in block copolymers with high elastic moduli which contradicts that adhesion strength declines with increasing modulus.^[1] The underpinnings of this observation may be explained by a surprising result: lithium metal is sparingly soluble in PEO. While the solubility of alkali metals in polar solvents is well known,^[2] a solution of a metal and a polymer has not been previously reported.

To demonstrate this, the team annealed PEO samples with various molecular weights at 130°C against lithium metal and preformed 7Li NMR on the PEO after removing the excess lithium foil. A reference solution of bis(trifluoromethylsulfonyl)amine lithium salt (LiTFSI) in tetraglyme was used to quantify the dissolved lithium concentration in molality, *m*. The results are shown in Figure 24. Figure 24a-c shows the ⁷Li NMR spectra for the dissolved lithium/PEO sample in a coaxial configuration with the reference solution in the outer compartment. The sharp peak at roughly -0.2 ppm is due to the LiTFSI in tetraglyme (this peak is not present

in samples without the reference). By fitting the data (red lines), the team obtains the integrated intensity of the two peaks and calculates the molar concentration of lithium in the PEO sample. They plot m as a function of PEO molecular weight in Figure 24d.

The dissolved lithium species also affects the conductivity of the PEO. The team assembled Li/PEO/Li cells and measured the conductivity over time while annealing the cell at 120°C; they compared the result to cells with stainless-steel electrodes. The PEO initially contained no lithium salts. The results are shown in Figure 25. There is a sharp increase in the conductivity of the cells with lithium electrodes, which is attributed to the dissolved lithium species. The result suggests that the lithium species exists in solution as a lithium cation and solvated electron. This conclusion is consistent with reports of lithium solubility in liquid ammonia^[3] and other alkali metals in ether solvents.^[4]

The team has also seen evidence of lithium dissolution in PEO-containing block copolymers. The observation of lithium dissolution in PEO provides new insight to the Li/electrolyte interface. When a solid is immersed in a solvent in which it is soluble, the interface is not well defined. Because the kinetics of dissolution are slow



Figure 25. Conductivity of 35 kg mol⁻¹ PEO, containing no lithium salts, annealed at 120°C in a lithium symmetric cell (closed symbols) and a stainless-steel symmetric cell (open symbols) as a function of time.

and/or

the

5 kg/mol 35 kg/mol (a) (b) 9 n 0 Li shift (ppm) Li shift (ppm) 275 kg/mol (c) 0.105 (d) 0.08 2 0.06 D L 0.04 Ē 0.02 0.00 10 1 100 M, (kg mol) Li shift (ppm)

Figure 24. ⁷Li nuclear magnetic resonance (NMR) spectra (open circles) of (a) 5 kg mol⁻¹, (b) 35 kg mol⁻¹, and (c) 275 kg mol⁻¹ PEO annealed against lithium metal for 12 days at 130°C in a coaxial NMR tube with a reference solution in the outer compartment. Red lines are fits to experimental data. (d) Lithium molality as a function of PEO molecular weight.

solubility is low (resulting in the low concentrations reported in Figure 24d), the team still observes a well-defined interface macroscopically. While, at first glance, the solubility of lithium metal in PEO may seem problematic, it may be the underlying phenomenon that allows dendrite-preventing block copolymers with high moduli to be implemented in Li-metal battery applications.

[1] Stone, G. M., S. A. Mullin, A. A. Teran, D. T. Hallinan, A. M. Minor, A. Hexemer, and N. P. Balsara. *Journal of the Electrochemical Society* 159, no. 3 (2012): A222–A227.

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[3] Seely, C. The Chemical News 23, no. 594 (1871): 169-170.

[4] Cafasso, F., and B. R. Sundheim. *Journal of Chemical Physics* 31 (1959): 809–813.

Patents/Publications/Presentations

Publication

 Galluzzo, M. D., D. M. Halat, W. S. Loo, S. A. Mullin, J. A. Reimer, and N. P. Balsara. "Dissolution of Lithium Metal in Poly(Ethylene Oxide)." ACS Energy Letters 4 (2019): 903–907.

Presentations

- American Physical Society (APS) March Meeting, Boston, Massachusetts (March 4–8, 2019): "Dissolution of Lithium Metal in Poly(Ethylene Oxide)"; M. D. Galluzzo and N. P. Balsara.
- APS March Meeting, Boston, Massachusetts (March 4–8, 2019): "The Effect of Chemical Structure on the Morphology, Ion Transport, and Modulus of Hybrid Inorganic-Organic Diblock Copolymer Electrolytes"; K. Gao and N. P. Balsara.
- APS March Meeting Boston, Massachusetts (March 4–8, 2019): "Phase Behavior of Hybrid Inorganic-Organic Diblock Copolymer Electrolytes"; G. Sethi, I. Villaluenga, and N. Balsara.

Task 1.10 – Electrolyte/Binder for High Efficiency Lithium-Sulfur Battery: New Materials Design and Computation (Zhengcheng Zhang, Larry A. Curtiss, and Ahn Ngo, Argonne National Laboratory)

Project Objective. Li-S batteries have received great attention because sulfur exhibits an order of magnitude higher theoretical capacity than that achievable with intercalation-type cathode materials in Li-ion batteries and is considered as a promising battery chemistry to power long-range, low-cost EVs. Sulfur is abundant in nature and nontoxic, which leads to low cost of the cell and environmental benefits. However, low active material utilization and poor cycle life hinder the practical application of Li-S batteries. The objective of this project is to develop new electrolyte materials to help overcome these challenges and enable high-efficiency Li-S batteries for vehicle application.

Project Impact. Development of novel functional electrolytes tailored for Li-S electrochemistry will enable improved materials utilization and longer cycle life as needed to take advantage of the high potential capacity of Li-S batteries to power long-range, low-cost EVs.

Approach. This project takes a new approach, combining organic synthesis and quantum chemistry computations to obtain an in-depth understanding of the interaction of the discharged lithium polysulfides with the electrolyte solvents and the lithium salt, aiming to develop new electrolyte materials for Li-S batteries. Based on the team's previous study, the fluorinated-ether-based electrolytes have shown very limited Li_2S_x solubility, and at the same time could effectively passivate the lithium anode surface, affording a reversible electrochemistry with high CE. However, the low active material utilization compromises its advantages of high theoretical capacity and energy density. To overcome this, the team will investigate boron-containing fluorinated polyethers as a new class of electrolytes for Li-S batteries. To further improve the cycle life, the project also proposes to design and synthesize new polymer binders bearing a pentafluorophenyl group on the backbone. First principles DFT and wave-function based quantum chemistry methods will be employed to provide accurate atomic/molecular level insight into the experimental studies. The team will also employ *ab initio* molecular dynamics (AIMD) simulations of the solvents for different finite temperatures and concentrations. The AIMD simulations will provide information on the structures of the electrolytes based on the fluorinated ethers synthesized in the experimental part of this project.

Out-Year Goals. The out-year goals are to find electrolytes that promote longer cycle life through electrolytes to reduce material loss.

Collaborations. This project engages in collaboration with Prof. A. Salehi at University of Illinois at Chicago (UIC).

- 1. Design and synthesis of new fluorinated borate electrolytes and baseline studies of sulfur utilization, CE, and cycle life. (Q1, FY 2019; Completed December 30, 2018)
- 2. Quantum chemical calculations of the chemical stability and reactivity properties of new borate and fluorinated ethers solvents and with electrode surfaces. (Q2, FY 2019; Completed, March 30, 2019)
- 3. Electrochemical characterization of performance of various fluorinated ether electrolytes in Li-S cells. (Q3, FY 2019; Initiated)
- 4. Correlation of experimental and theoretical results on Li-S cells with ether decomposition during cell operation. (Q4, FY 2019; Initiated).

One of the issues for successful development of Li-S battery is loss of active materials in the form of insoluble Li_2S_2 species. Such species are generated both on a full discharge and during parasitic shuttling reactions occurring in Li-S electrochemistry in Li-S cells. This project has been investigating several avenues of mitigating such reactions using an integrated experimental/computational approach. Previously, the team reported on experimental studies of additives to resolve lost materials that were deposited away from the cathode in the forms of Li_2S or Li_2S_2 using TFEB. Upon addition of the TFEB additive to lithium polysulfide (Li_2S_8) solution in DME, the characteristic brown/dark color of polysulfide anions was reduced to light color. Failure of cells using this additive is probably caused by the chemical reactivity of the additive with Li-metal anode leading to the fast capacity fade. Thus, TFEB is apparently a strong anion-receptor suffering from a

lithium compatibility issue. As part of this study, the team has investigated the reaction of TFEB as well as other borates for their reactions with polysulfides.

Eleven anion receptors, some related the TFEB borate studied to experimentally, were investigated using DFT to determine their binding polysulfide energies to species, including Li₂S₈, Li₂S₆, Li₂S₄, Li₂S₂, and Li₂S. The wB97xd DFT method was used with the 6-31G* basis set for geometry optimization. The geometries of the complexes between polysulfides and the anion the receptors were thoroughly explored through optimization of all parameters along with stability investigations. Solution phase effects on the binding energies were included by a continuum



Figure 26. Binding energies in eV for interactions of various anion receptors to lithium polysulfides (see right).



model with a dielectric used to represent commonly used Li-S electrolytes. The results are shown in Figure 26 for all eleven anion receptor candidates.

NTB and ortho-phenylene-bridged diborane $(1,2-[B(C_6F_5)_2]_2C_6F_4)$ (DB) are predicted to bind Li₂S and Li₂S₂ the most strongly. Triolborate without the nitro (not shown) was also found to bind Li₂S strongly. Both have strong binding due to the cage structure where oxygen lone pairs cannot interact with the boron. The other species investigated, including TFEB, do not have very strong binding to the polysulfides, with the longer chain polysulfides having weaker binding. These results from the computational screening suggest that there are several anion receptors that could be effective at preventing loss of active material in Li-S batteries assuming that the lithium anode was protected.

Patents/Publications/Presentations

Publication

• "Li-S Battery with Partially Fluorinated Ether Electrolytes: Interplay between Capacity, Coulombic Efficiency and Li Anode SEI Formation." In preparation.

TASK 2 – DIAGNOSTICS

Summary and Highlights

To meet the goals of the VTO Multi-Year Program Plan and develop lower-cost, abuse-tolerant batteries with higher energy density, higher power, better low-temperature operation, and longer lifetimes suitable for the next-generation of EVs, hybrid EVs (HEVs), and plug-in hybrid EVs (PHEVs), there is a strong need to identify and understand structure-property-electrochemical performance relationships in materials, life-limiting and performance-limiting processes, and various failure modes to guide battery development activities and scale-up efforts. In pursuit of batteries with high energy density, both high cell operating voltages and demanding cycling requirements lead to unprecedented chemical and mechanical instabilities in cell components. Successful implementation of newer materials such as silicon anode and high-voltage cathodes also requires better understanding of fundamental processes, especially those at the solid/electrolyte interface of both anode and cathode.

This Task takes on these challenges by combining model system ex situ, in situ, and operando approaches with an array of start-of-the-art analytical and computational tools. Three subtasks are tackling the chemical processes and reactions at the electrode/electrolyte interface. Researchers at LBNL use in situ and ex situ vibrational spectroscopy and far- and near-field scanning probe spectroscopy to understand the structure of active materials and the physio-chemical phenomena at electrode/electrolyte interfaces, particularly those of the high-voltage cathodes. GM is developing a number of *in situ* diagnostic techniques, including atomic force microscopy (AFM), nanoindentor, dilatometer, and stress-sensor, to be combined with atomic/continuum modeling schemes to investigate and understand the coupled mechanical/chemical degradation of the SEI layer on Li-metal anode. ANL aims to first understand the pathways/mechanisms of the parasitic reactions of the electrode/electrolyte interfaces and then stabilize them by developing functional surface coating and electrolyte additives. Subtasks at Brookhaven National Laboratory (BNL) and PNNL focus on the understanding of fading mechanisms in electrode materials, with the help of synchrotron-based X-ray techniques (diffraction and hard/soft X-ray absorption) at BNL and high-resolution transmission electron microscopy (HRTEM) and spectroscopy techniques at PNNL. UC San Diego (UCSD) is developing advanced diagnostic tools, including scanning transmission electron microscopy / electron energy loss spectroscopy (STEM/EELS), operando Bragg coherent diffraction imaging (BCDI) and *ab initio* computation, to probe anion redox and oxygen evolution in Li-excess NMC materials. At LBNL, model systems of electrode materials with well-defined physical attributes are being developed and used for advanced diagnostic and mechanistic studies at both bulk and single-crystal 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. The final subtask at Stanford University / Stanford Linear Accelerator Center (SLAC) develops and utilizes a correlative X-ray microscopy platform to investigate the lithiation dynamics and understand factors that determine the rate capability and degradation mechanisms in cathode materials. The diagnostics team not only produces a wealth of knowledge that is key to development of next-generation batteries, it also advances analytical techniques and instrumentation that have a far-reaching effect on material and device development in a variety of fields.

Task 2.1 – Model System Diagnostics for High-Energy Cathode Development (Guoying Chen, Lawrence Berkeley National Laboratory)

Project Objective. This project will use a rational, nonempirical approach to design and synthesize next-generation high-energy, high-voltage cathode materials. Combining a suite of advanced diagnostic techniques with model cathode materials and model electrode/electrolyte interfaces, the project will perform systematic studies to achieve the following goals: (1) obtain new insights into solid-state chemistry, particularly cationic and/or anionic redox activities during charge and discharge of high-capacity lithium TM oxides, (2) gain fundamental understanding on cathode/electrolyte interfacial chemistry and charge transfer process as a function of operating voltage, (3) reveal performance- and stability-limiting properties and processes in high-energy, high-voltage cathodes, and (4) develop strategies to mitigate the structural and interfacial instabilities.

Impact. The project will improve the commercial viability of next-generation high-energy cathode materials. The findings will enable more stable high-voltage cycling of existing Li-TM oxides as well as development of novel high-capacity cathode materials for advanced Li-ion batteries.

Approach. The project will prepare crystal samples of Li-stoichiometric and Li-excess TM oxides with well-defined physical attributes. It will perform advanced diagnostic and mechanistic studies at both bulk and single-crystal levels. Global properties and performance of the samples will be established from the bulk analyses, while the single-crystal-based studies will utilize time and spatially resolved analytical techniques to probe the material redox transformation process and failure mechanisms under battery operating conditions.

Out-Year Goals. In the out-years, the project will obtain fundamental knowledge on performance-limiting physical properties, phase transition mechanisms, parasitic reactions, and transport processes that prevent cathode materials from delivering higher capacities and achieving more stable cycling at high voltages. It will develop approaches to mitigate cathode structural and interfacial instabilities during high-voltage operation. Further, it will design and synthesize optimized Li-TM oxide cathodes as well as novel high-energy electrode materials.

Collaborations. This project collaborates with the following: G. Ceder, K. Persson, M. Doeff, B. McCloskey, and P. Ross (LBNL); V. Srinivasan (ANL); D. Nordlund and Y. Liu (Stanford Synchrotron Radiation Lightsource, SSRL); C. Wang (PNNL); C. Grey (Cambridge); and A. Huq and J. Nanda (Oak Ridge National Laboratory, ORNL).

- 1. Understand the interplay between cationic and anionic redox processes in model TM oxides. (Q1, FY 2019; Completed)
- 2. Characterize interfacial processes and surface changes on anion-active model oxides. (Q2, FY 2019; Completed)
- 3. Evaluate the effect of particle size/morphology on oxygen redox chemistry and kinetics. (Q3, FY 2019; On schedule)
- 4. Develop design strategies to improve performance of anion-active oxide cathodes. (Q4, September 2019; On schedule)

The team's previous studies showed significant capacity fade and voltage decay in cation-disordered $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$ (LNMO) half-cells cycled to 4.8 V. The involvement of oxygen redox leads to a high initial discharge capacity of ~ 275 mAh/g, but only ~ 75 mAh/g remained after 50 cycles at a current density of

10 mA/g, as shown in Figure 27a. To understand the degradation mechanism, kinetic studies were performed on LNMO cathodes recovered after 50 cycles. Figure 27b compares the 1st-cycle voltage profiles collected using a constant current density of 10 and 1 mA/g, respectively. Voltage plateau was not observed under the higher current density, suggesting limited contribution from oxygen redox. About 80 mAh/g total charge capacity was obtained, corresponding to a change of manganese oxidation state from +2.5 to - +3.15 (or removal of ~ 0.26 Li^+). Manganese valence was estimated from manganese K-edge X-ray absorption edge energy collected at



Figure 27. (a) Voltage profiles of LNMO half-cell cycled 50 times at 10 mA/g between 1.5-4.8 V. (b) 1^{st} -cycle voltage profiles of half-cells under different current densities, using the LNMO cathode recovered from (a).

SSRL BL2-2. When a lower current density of 1 mA/g was used, ~ 110 mAh/g was obtained in the slope region before 4.5 V, corresponding to a much improved manganese oxidation process from + 2.5 to ~ + 3.5 (or removal of ~ 0.4 Li⁺). A plateau contributing to a further charge capacity of ~ 40 mAh/g was also observed at the high-voltage region, suggesting more extensive involvement of oxygen oxidation. The total capacity obtained



Figure 28. Schematics for the degradation process occurring during cycling of a LNMO cathode: (a) after 1st charge, (b) after 1st discharge, (c) charged after extensive cycling, and (d) discharged after extensive cycling. White, blue, green, pink, and red circles represent lithium vacancies (Li, Nb, Mn, and O, respectively). The rock salt lattice was projected along the [110] direction.

was ~ 175 mAh/g, nearly twice that obtained under the current density of 10 mA/g. The massive capacity recovery under slower rate suggests much of the cathode performance decay is related to kinetic limitations. This is also supported by the significant differences observed in the polarization, with a charge and discharge voltage gap (at the average voltage) of 2 and 1.2 V for 10 and 1 mA/g current densities, respectively.

Based on these results previous experimental and observations, surfacea densification-based degradation mechanism was proposed for cation-disordered LNMO. As shown in the schematic in Figure 28a, after the 1st charge, oxygen vacancies are created on

the surface due to the loss of lattice oxygen, possibly through O_2 gas evolution and/or side reactions with the electrolyte. Previous experiments showed that about 2% of oxygen vacancies can exist after extraction of 1.1 Li⁺. This creates a destabilized rock-salt lattice on the surface where the uncoordinated Mn⁴⁺ (γ =0.67 Å) may

be reduced to Mn^{3+} (γ =0.785 Å). The reduced cations may migrate into the neighboring octahedral vacancy sites left by Li⁺ (γ =0.9 Å). The net effect is a densified surface layer with fewer lithium vacancies and lower manganese oxidation state compared to that in the bulk. During the subsequent discharge process (Figure 28b), lithium cations are reinserted into the oxide, but the surface has lower lithium content due to the densification and loss of lithium sites. This process continues in the following cycles and further degrades the original percolating network for Li⁺ transport, accompanied by the progression of reduced manganese oxidation state and increased lithium resistivity from the surface to the bulk (Figure 28c-d). After extensive cycling, the changes can be seen well into the bulk of the material. The team notes that different from layered LMR with a 2D cation-ordered structure, the presence of 3D percolation network in cation-disordered rock-salts serves as pathways for lithium cation transport; however, it may also facilitate the deep migration of reduced TM cations.

Patents/Publications/Presentations

Publications

- Kan, W. H., C. Wei, D. Chen, T. Bo, B-T. Wang, Y. Zhang, Y. Tian, J-S. Lee, Y. Liu, and G. Chen. "Evolution of Local Structural Ordering and Chemical Distribution upon Delithiation of Rock-Salt Structured Li_{1.3}Ta_{0.3}Mn_{0.4}O₂ Cathode." *Advanced Functional Materials* 1808294 (2019). doi: 10.1002/adfm.201808294.
- Zhu, J., and G. Chen. "Single-Crystal Based Studies for Correlating Properties and High-Voltage Performance of Li[Ni_xMn_yCo_{1-x-y}]O₂ Cathodes." *Journal of Materials Chemistry A* 7 (2019): 5463. doi: 10.1039/C8TA10329A.

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

Project Objective. This collaborative project will develop and apply advanced experimental methodologies to study and understand the mechanism of operation and degradation of high-capacity materials for rechargeable cells for PHEV and EV applications. The objective is to develop and apply *in situ* and *ex situ* far- and near-field optical multi-functional probes and synchrotron-based advanced X-ray techniques to obtain detailed insight into the active material structure and physio-chemical phenomena at electrode/electrolyte interfaces at a spatial resolution corresponding to the size of basic chemical or structural building blocks. Through an integrated synthesis, characterization, and electrochemistry effort, the project aims to develop a better understanding of electrode and electrolyte materials so that rational decisions can be made as to their further development into commercially viable cathode materials.

Project Impact. Instability and/or high resistance at the interface of battery electrodes limits 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-based cells for PHEVs and EVs. Pristine and cycled composite and thin-film model electrodes are investigated using 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. The proposed 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. The 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 (IR) and Raman spectroscopy and 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 materials electrochemical performance and failure modes.

Out-Year Goals. In the out-years, the project aims to (1) understand the factors that control charge/discharge rate, cyclability, and degradation processes, (2) design and apply new diagnostic techniques and experimental methodologies capable of unveiling the structure and reactivity at hidden or buried interfaces and interphases that determine material, composite electrode, and full-cell 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. Electrode materials and composite solid electrolytes tested under different cycling regimes by V. Battaglia and M. Doeff (LBNL) will be studied. The diagnostic studies will be carried out in sync with other diagnosticians in this research program.

- Manufacture model thin-film and composite LLZO and lithium thiophosphate (LPS) SSEs by pulsed laser deposition (PLD) as model systems for fundamental electrochemical studies of Li-metal battery systems. (Q1, FY 2019; Completed)
- 2. Characterize the bulk and surface structure of lithium anode, NMC cathode electrodes, and SSEs and the relationship to electrochemical and interfacial properties. (Q2, FY 2019; On schedule)

- 3. Characterize the chemistry of SSE/Li and electrolyte/cathode interfaces with *ex situ* near-field IR, X-ray absorption spectroscopy (XAS) and XPS. (Q3, FY 2019; On schedule)
- Design and develop new XAS/XPS experimental setup to characterize *in situ* solid/solid (for example, NMC/SSE Li/SSE) interfaces. *Go/No-Go Decision*: Demonstrate feasibility of *in situ* measurements of solid-solid electrochemical interfaces. (Q4, FY 2019; On schedule)

The high solubility of intermediate products in Li/S batteries, that is, lithium polysulfide, and the resultant shuttle effect lead to a rapid capacity fading along with a low CE. This quarter, the team investigated the effect of a co-block polymer binder to mitigate some of these issues. The PEO unit in the co-block polymer can strongly bond with the lithium polysulfide and suppress the active materials dissolution, whereas the insoluble polysulfide polymer chain can maintain the mechanical strength of the binder in the DOL/DME electrolyte.



Figure 29. Optical images (a) and ultraviolet-visible absorbance spectra (b) of polyvinylidene difluoride and co-block polymer (65% PEO, 82% PEO) binder in 0.05 mmol/L polysulfide solution in DOL/DME.

The galvanostatic cycling of Li/S coin cells show (Figure 30a) that co-block polymer-based (65% PEO, 82% EPO) cathodes exhibit higher cell capacity and CE than PVDF-based cathodes. The Li⁺-conductive PEO enhances sulfur utilization and better capacity retention during the electrochemical charge-discharge process. The K-edge XAS in operando sulfur spectra (Figure 30c-e) show peaks at 2472.2 and 2480.0 eV, attributed to polysulfides and sulfonyl groups in LiTFSI, respectively. The increase of the polysulfide peak intensity is suppressed in the presence of the co-block polymer binder. This observation suggests the 65% PEO co-block polymer binder inhibits dissolution of polysulfides into the electrolyte during electrochemical charge-discharge process. This report summarizes efforts toward Milestone 2.

In situ ultraviolet-visible (UV–vis) spectroscopy of 0.02 g PVDF and co-block polymer in 5 mL 0.5 mmol/L polysulfide in DOL/DME solution (1:1 v/v) over 24 h is shown in Figure 29. In the presence of co-block polymer binder, the polysulfide absorption bands at 287, 316, and 430 nm continuously decrease during the test. These results indicate that the ethylene oxide group in PEO can bind polysulfides and remove them from the solution.



Figure 30. Discharge capacity and Coulombic efficiency at 0.2 C (a), and discharge/charge voltage profiles at 0.05 C of sulfur composite cathodes with polyvinylidene difluoride (PVDF) and co-block polymer binder. *In operando* sulfur K-edge X-ray absorption spectrum of PVDF (c) and co-block polymer-based (d-e) composite cathodes after 1st discharge. 2472 eV polysulfides peak normalized intensity (f).

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 Seong-Min Bak, 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 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 VTO 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, PHEVs, and EVs." The knowledge gained from diagnostic studies through this project will help U. S. industries develop new materials and processes for next-generation Li-ion batteries in the effort to reach these VTO goals.

Approach. This project will use the combined synchrotron-based *in situ* X-ray techniques (XRD; and hard and soft XAS) with other imaging and spectroscopic tools such as HRTEM and MS to study the mechanisms governing performance of electrode materials.

Out-Year Goals. In the out years, the project will complete development of diagnostic techniques using X-ray pair distribution function (x-PDF), XRD, and XAS combined with neutron diffraction and neutron PDF (n-PDF), as well as STEM imaging and transmission X-ray microscopy (TXM) for cathode materials studies. It will then apply these techniques to study the structural changes of various new cathode materials.

Collaborations. The BNL team will work closely with material synthesis groups at ANL (Drs. Shin and Amine) for the high-energy composite and at PNNL for the S-based cathode and Li-metal anode materials, and with ORNL on neutron scatterings. This project will also collaborate with industrial partners at GM and Johnson Controls, as well as with international collaborators.

- 1. Complete the *ex situ* soft x-ray absorption (sXAS) studies at oxygen K-edge of novel organic disulfide cathode material (1,2,4,5,6,7,9,10-octathia bis cyclopenta antraquinone-3,8-dithone, or TPQD) for Li-S batteries at different charged and discharged states. (Q1, FY 2019; Completed)
- 2. Complete the *ex situ* sXAS studies at sulfur K-edge of novel organic disulfide cathode material (TPQD) for Li-S batteries at different charged and discharged states. (Q2, FY 2019; Completed)
- 3. Complete XAS studies of sulfur electrode harvested from failed high-energy Li/S pouch cells after multiple cyclings. (Q3, FY 2019; In progress)
- 4. Complete the spatially resolved XAS at sulfur K-edge and imaging of sulfur-based chemical species using XRF on the Li-metal anode in a cycled high-energy Li/S pouch cell. (Q4, FY 2019; In progress)

Last quarter, the second milestone for FY 2019 was completed. BNL has been focused on ex situ sXAS studies at sulfur K-edge of novel organic disulfide cathode material for Li-S batteries at different charged and discharged states. At BNL, the team has designed and synthesized novel organodisulfide electrode material 2,3,4,6,8,9,10,12- Octathia biscyclopenta [b,c]-5,11-antraquinone-1,7-dithone (TPQD) for li-ion batteries. The electrochemical results indicate that the TPQD electrode exhibits a high initial capacity of 251.7 mAh g⁻¹, which is corresponding to the 4.7 electron redox per formula unit. To study the redox behavior of the disulfide bond (-S-S-) in the dithiolane, sulfur K-edge XAS spectra of TPQD electrodes were collected at pristine, after the first discharge, and after first charge states, as shown in Figure 31a. For all three spectra, there are three main peaks located at 2469.5 eV, 2472.0 eV, and 2473.6 eV, which are assigned to the transition from sulfur 1s to S=C π^* (marked as 3), S-S σ^* (marked as 4), and S-C σ^* (marked as 5) states, respectively. No changes of peak 3 before and after discharge and charge were observed, indicating S=C groups in the TPQD are not involved in the charge storage process at all. By comparing the spectra of the discharged samples with that of the pristine one, two significant changes can be found: (1) the intensity of peaks 4 and 5 decreased; (2) a new broad peak appeared at 2479.8 eV. A slight decrease in the intensity of peaks 4 and 5 is related to the breakage of disulfide bonds (that is, -C-S-S-C) and its lithiation (that is, formation of -C-S-Li). The newly formed feature at 2479.8 eV can be assigned to the transition from sulfur 1s to the S-O σ^* in SO₃²⁻ or COSO₂⁻, which are possibly formed by a side reaction between the -C-S-C bond and DOL.



Figure 31. (a) Sulfur-K-edge X-ray absorption spectra of TPQD electrodes at different states of charge. (b) Structural evolution of TPQD electrodes during lithiation process.

Patents/Publications/Presentations

Publication

Mao, Y., X. Wang, S. Xia, K. Zhang, C. Wei, S-M. Bak, Z. Shadike, X. Liu, Y. Yang, R. Xu, P. Pianetta, S. Ermon, E. Stavitski, K. Zhao, Z. Xu, F. Lin, X-Q. Yang, E. Hu, and Y. Liu. "High-Voltage Charging-Induced Strain, Heterogeneity, and Micro-Cracks in Secondary Particles of a Nickel-Rich Layered Cathode Material." *Advanced Functional Materials*. doi: 10.1002/adfm.201900247, Publication Date: March 7, 2019.

Task 2.4 – Advanced Microscopy and Spectroscopy for Probing and Optimizing Electrode-Electrolyte Interphases in High-Energy Lithium Batteries (Shirley Meng, University of California at San Diego)

Project Objective. The proposed research aims to develop advanced microscopy and spectroscopy tools to probe, understand, and optimize the anion activities that govern the performance limitations such as capacity and voltage stabilities in high-energy Li-excess TM (such as nickel, cobalt, manganese) oxides cathode materials. The approach uniquely combines atomic resolution STEM, EELS, *operando* BCDI, and first-principles computation to probe anion redox and oxygen evolutions in Li-excess NMC materials. Furthermore, the project will track the lithium and oxygen dynamics under electrochemical testing via *operando* neutron diffraction, which will enhance understanding of the overall structural changes due to anion activities. Ultimately, this will home in on the synthesis efforts to produce the modified materials with optimum bulk compositions and surface characteristics at large scale for consistently good performance. The above-mentioned characterization tools will be extended to diagnose various anode types, such as Li-metal anode.

Project Impact. If successful, this research will enable *operando* imaging at the single-particle level by advanced microscopy imaging and high-energy-resolution oxygen K-edge EELS. This work will provide an in-depth understanding of anion activities in high-voltage electrode materials, which can lead to significant improvement in stabilizing operation voltage and electrode-electrolyte interface for future generation high-energy-density electrodes.

Approach. This unique approach combines STEM/EELS, *operando* BCDI, and *ab initio* computation as diagnostic tools for probing anion redox and oxygen evolutions in Li-excess NMC materials. This allows for pinning down the atomistic/molecular mechanism of anion oxidation and determining the speciation compositions and surface characteristics for enabling high rate and long life in the proposed materials. Neutron enables the characterization of bulk material properties to enhance and further optimize high-energy electrode materials.

Out-Year Goals. The goal is to improve the cycle life and efficiency of Li-excess NMC materials through the modification of both the cathode and the electrolyte. Single particle behavior of the modified Li-excess NMC with new electrolytes will be characterized.

Collaborations. This work funds collaborations on EELS (M. Chi, ORNL); neutron diffraction (K. An, ORNL); and sXAS (M. Doeff, LBNL). It supports collaborative work with Z. Liu and Y. Xia at Ningbo Institute of Materials Technology and Engineering in China. It also supports collaboration with the Battery500 Consortium.

- 1. Benchmarking electrochemical performance with the optimized Li-excess materials. (Q1, FY 2019; Completed)
- 2. Conducting XPS characterization of anion evolution on modified Li-excess NMC. (Q2, FY 2019; Completed)
- 3. Carrying out STEM/EELS characterization on modified Li-excess NMC single particle using optimized electrolyte. (Q3, FY 2019; In progress)
- 4. Performing EELS and XPS characterization of SEI on electrochemically deposited lithium metal with new electrolyte systems. (Q4, FY 2019; In progress)

Electrolyte Additive LiBOB for the Cycling Performance Improvement of Li-Rich Layered Oxide (LRLO) Cathodes

As described in last quarter's report, GSIR modified Li[Li_{0.144}Ni_{0.136}Co_{0.136}Mn_{0.544}]O₂ (denoted as LR-NCM) was chosen as the project's benchmark cathode material for its high specific capacity and CE. To further optimize this material, a novel electrolyte with LiBOB additive (lithium bis(oxalato) borate) is introduced to the system. The baseline electrolyte used in this study is 1 M LiPF₆ in EC: DMC=3:7 by volume (denoted as Standard); the novel electrolyte is $0.98 \text{ M LiPF}_6 + 0.02 \text{ M LiBOB}$ in EC:DMC=3:7 by volume (denoted as 2% LiBOB). The voltage profiles and cycling performances of LR-NCM with different electrolyte are shown in Figure 32a-d. All the cells were charge/discharged at C/20 (1C=250 mAh/g) for two cycles and C/10 for the rest of the cycles. For the first cycle, LR-NCM delivers a discharge capacity of 321 mAh/g and an energy density of 1133 Wh/kg in Standard electrolyte. The LR-NCM cycled in 2% LiBOB exhibits slightly lower capacity of 317 mAh/g and energy density of 1123 Wh/kg. After 50 cycles in the Standard electrolyte, LR-NCM remains at a specific capacity of 264 mAh/g (82.2% retention) and an energy density of 870 mWh/g. In comparison, the LR-NCM cycled in 2% LiBOB exhibits much better cycling stability with capacity of 279 mAh/g (88.0% retention) and energy density of 933 Wh/kg after 50 cycles. XPS was conducted on the pristine LR-NCM electrode and LR-NCM after 50 cycles in different electrolyte. Figure 32e shows the XPS carbon 1s spectra where 4 different carbon types are detected, including C-C peak at 284.8 eV, C-O peak at 286.5 eV, O-C=O peak at 289.1 eV, and C-F (from PVDF) at 291.1 eV. A noticeable feature for the cathode cycled in 2% LiBOB is the appearance of the 289.1 eV peak. This can be attributed to the semi-carbonate species produced by the LiBOB decomposition. A more intense peak corresponding to C=O at around 533.2 eV in oxygen 1s spectra is thus observed for LR-NCM cycled in 2% LiBOB, indicating the formation of a stable cathode electrolyte interfacial (CEI) layer (*Electrochimica Acta* 104 (2013): 170-177). Due to this stable CEI layer, the cycling performance of LR-NCM is largely improved with the LiBOB additive. Future work will focus on investigating other novel electrolyte systems for LR-NCM and further characterizations of the CEI layer through STEM-EELS.



Figure 32. Characterization of the lithium-rich NCM (LR-NCM) in different electrolyte. (a) Voltage profiles and (b) cycling performance of the LR-NCM cycled in standard electrolyte. (c) Voltage profiles and (d) cycling performance of the LR-NCM cycled in 2% LiBOB electrolyte. (e). X-ray photoelectron spectroscopy (XPS) carbon 1s and (f) XPS oxygen 1s comparison of pristine LR-NCM electrode and LR-NCM cycled in different electrolyte after 50 cycles.

Comparison of Cycled Li-Rich Layered Oxides and Classical Layered Oxides under Heat Treatment

In the previous report, the team explored the voltage and structural recovery of LRLO under heat treatment, which provides an insight in optimizing the performance of LR-NCM. After annealing under 300°C for 1 hour, the cycled LR-NCM exhibits the characteristic "oxygen plateau" around 4.5 V (Figure 33a). To further study the recovery behavior in LRLO, a classical layered oxide material LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (denoted as NMC-811) is introduced for comparison. NMC-811 samples after first cycle were also annealed under 300°C for 1 hour. It is clearly shown in Figure 33c that the cycled NMC-811 sample after heat treatment has a lower capacity and larger polarization. *In operando* neutron diffraction reveals that heat treatment assists lithium migration into the TM layer for both the cycled LR-NCM and NMC-811 (Figure 33b/d). The increase of lithium occupancy in TM layer for cycled LR-NCM recovers the ordered structure and the local Li-excess environment, while the



Figure 33. Electrochemical performance of the (a) initially cycled lithium-rich-NCM (LR-NCM) and (c) initially cycled NMC-811 with or without heat treatment. The changes in the occupancy of lithium in transition-metal layer during heat treatment in the (b) initially cycled LR-NCM and (d) initially cycled NMC-811 obtained from *operando* neutron diffraction. High-resolution transmission electron microscopy images and corresponding fast Fourier transform pattern of the (e) 10-cycled NMC-811 and (f) 10-cycled NMC-811 after annealing at 300°C for 1 hour.

increase of lithium in the TM layer for cycled NMC-811 results in the structure disordering. Figure 33e-f compares the single particle structure difference of the cycled NMC-811 before and after heat treatment. Lavered phase of NMC-811 is well maintained after cycling, but transformed to rock salt structure after heat treatment. This comparison once more manifests that voltage and structural recovery is a unique feature for anionic redox related cathode materials. Future work will focus on the characterization of the local structure evolution of cycled LRLO under heat treatment utilizing neutron PDF and resonant inelastic X-ray scattering (RIXS).

Patents/Publications/Presentations

Publications

- Fang, C., X. Wang, and Y. S. Meng. "Key Issues Hindering a Practical Lithium-Metal Anode." *Trends in Chemistry*. Accepted, 2019.
- Qiu, B., M. Zhang, Y. S. Meng, et al. "Structural and Voltage Recovery for Practicability of Anionic Redox in Li-Rich Layered Oxide Cathode Material." *Energy & Environmental Science*. Submitted, 2019.

Presentation

 International Battery Association (IBA) Meeting, San Diego, California (March 2019): "Advanced Characterization Tools for Probing Anionic Redox in Layered Cathode Materials"; M. Zhang, M. Olguin, Y. S. Meng, et al. Poster. Task 2.5 – *In Situ* Diagnostics of Coupled Electrochemical-Mechanical Properties of Solid Electrolyte Interphases on Lithium-Metal Rechargeable Batteries (Xingcheng Xiao, General Motors; Brian W. Sheldon, Brown University; Yue Qi, Michigan State University; and Y. T. Cheng, University of Kentucky)

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 of the SEI layer/lithium system during lithium cycling. The goal of this understanding is to develop a new coating design strategy to achieve dendrite-free high cycle efficiency and extend the cycle life of high-energy-density batteries with lithium as the anode for EV application.

Project Impact. The fundamental understanding of the coupled mechanical/chemical degradation of the SEI layer during lithium cycling will enable the project to identify the desirable mechanical properties on SEI/lithium as a system and the specific transport properties that enable the homogenous lithium stripping/plating while avoiding the mossy structure. Furthermore, it will allow the project to develop a highly impactful strategy to protect lithium metal and achieve dendrite-free high cycle efficiency, which can dramatically increase the energy density of lithium batteries for EV applications.

Approach. Different *in situ* techniques, including AFM, nano-indentor, dilatometer, and stress-sensor, will be developed to investigate the mechanical compatibility between SEI and soft lithium and the relationship between surface morphology and current density distribution that results in an inhomogeneous lithium plating/stripping process. Multiple strategies will be developed to tailor the mechanical and transport properties of SEI and to properly engineer the protective coating/lithium interface.

Out-Year Goals. The out-year goals involve using *in situ* electrochemical tools to reveal failure mechanisms of SEI/lithium as a whole electrode system, including correlating mechanical failure mechanisms of SEI/lithium, morphology evolution, cycle efficiency, and transport properties of SEI. Then, the project will develop continuum framework to establish the failure modes of SEI layer on lithium metal and provide the governing mechanical/material properties of SEI responsible for the critical failure mode based on the experimental results and atomic-scale simulation.

Collaborations. Prof. H. Gao (Brown University) and Dr. Q. Zhang (GM) will be the key researchers involved in continuum simulation and postmortem analysis. Dr. C. Wang (PNNL), Dr. W. Yang (LBNL), and Dr. J. Xiao (PNNL) will be collaborators on advanced *in situ* analysis and electrolyte additives.

- 1. Determine coating design window required to achieve mechanically stable coating on lithium metal. (Q1, FY 2019; Completed)
- 2. Determine impact of stress on morphological evolution of coated Li-metal surface, and identify failure modes of protective coatings on lithium. (Q2, FY 2019)
- 3. Vary coating modulus and investigate its impact on interfacial strength and cycle efficiency, and develop coating with desirable mechanical and transport properties. (Q3, FY 2019)
- 4. Establish a design strategy of protective coatings as artificial SEI on Li-metal electrode to achieve high cycle efficiency (> 99.8%). (Q4, FY 2019)

Investigated EIS Measurements at the Various Stages of Plating and Stripping of Li | Li Symmetric Cells. The typical U-shaped voltage profile of a Li | Li symmetric cell is shown in Figure 34a. Point A corresponds to the initial plating/stripping of the lithium electrodes, which continues through point B and finishes at point C. At all three points along the curve, EIS measurements were conducted following an 8-hour rest period at open circuit potential. Once EIS measurements were completed, cycling continued. As shown in Figure 34a, the voltage profile merges to a typical voltage versus time curve, suggesting that the 8-hour rest period and EIS measurements have little or no effect on the voltage versus time curve. This implies that the structural and compositional changes in the Li | Li symmetric cell during the rest period are minimal. Figure 34b shows the results of the EIS evolution along the U-shaped voltage curve. The EIS curve associated with the final plating at point C has the largest overall impedance of the three points. The lowest overall impedance is found in the valley of the U-shaped curve at point B. This trend is unsurprising since impedance is directly related to the overpotential. In addition, the size ratio of the two semicircles at point B is significantly different from that at points A and C. Typically, the semi-circle at higher frequencies is assigned to the resistance due to SEI, while the second semi-circle at lower frequencies is assigned to the charge transfer resistance. Thus, at point B, the relatively small semi-circle at higher frequencies could indicate that the SEI layer may have fractured. If found true, this could have other implications. The next step is to develop an equivalent circuit that represents the physical model of the Li | Li cell. This will further the study by allowing the EIS results to be quantified, and possibly provide new insights into lithium plating and stripping.



Figure 34. (a) The U-shaped voltage-time profile of the first cycle of a Li | Li symmetric cell under an external pressure of 0.05 MPa. (b) The electrochemical impedance spectroscopy measurements were taken at the three points along the U-shaped voltage profile over a frequency range from 1 MHz to 1 mHz.

Proposed a Strategy to Quantify the Work of Separation/Delamination of the Li/Polymer Interface, $W_{sep}(polymer)$ **Based on DFT Calculations of Simpler Li/Oligomers Interfaces.** For each polyacrylic acid (PAA) oligomer (tetramer, hexamer, and nanomer), five fully relaxed adsorption configurations were studied. It was found that the major chemical bonds formed at the Li/PAA-oligomers interface include the following: (1) the oxygen atoms in the PAA bond with multiple surface lithium atoms, and (2) deprotonation reactions lead to enhanced Li-O ionic bonding and hydrogen incorporation into the lithium substrate. For interface delamination, three possible delamination routes were considered for each interface: breaking all Li-O bonds,

breaking all Li-Li bonds (Li decohesion), and breaking all Li-O bonds and Li-Li bonds, as shown in Figure 34a-c. The DFT calculated $W_{sep}(oligomer)$ (Figure 35d) reveals that the likely route when PAA is delaminated tends to involve breaking partial Li-O bonds and partial Li-Li bonds, especially the surface lithium atoms that are ionized; those are bonded with two oxygen atoms in the PAA oligomers and tend to delaminate along with the PAA oligomer. Since it is impossible to sample all the configurations at an Li/PAA polymer interface, the team first calculated the average adhesion energy contribution from each bonded oxygen at the interface, $\langle E_{BO} \rangle$, by fitting the lowest $W_{sep}(oligomer)$ as a linear function of the number of oxygen bonded with lithium, N_{BO} . As shown in Figure 34d, $\langle E_{BO} \rangle$ is ~ 1.40 eV/per bonded oxygen. Then, the $W_{sep}(polymer)$ is estimated based on $\langle E_{BO} \rangle \propto A_{BO}(polymer)$, where A_{BO} is the areal density of oxygen that is bonding with lithium surface. Based on the density of PAA polymer (1.41g/mL), the oxygen number density is 0.024 O/Å³. Assuming an interface thickness region that is similar to Li-O bond length, the areal density of oxygen is 0.057 O/Å². Based on the DFT relaxed oligomers/lithium interface structures, ~ 76% ± 13% oxygen atoms in this region form Li-O interfacial bond. Therefore, A_{BO} is estimated to be 0.043 O/Å², leading to a $W_{sep}(polymer)$ of 0.97 J/m².

Table 1 compares the work of separation of Li/PAA(polymer) to the interfaces comprised of lithium and other SEI inorganic components. The strongest Li/SEI interface adhesion is Li/Li₂O, which is comparable to the Li/PAA(polymer) interface adhesion. The team attributes the high interface adhesion of Li/Li₂O to the high oxygen density (0.0406 O/Å³) and that of Li/PAA(polymer) to exposed oxygen atoms (ρ_0 = 0.024 O/Å³) allowing more Li-O bonds. From the project's results, it is expected that other polymer coatings, such as PEO, would exhibit low PEO/Li interface adhesion due to fewer –O atoms available for binding (ρ_0 = 0.017 O/Å³).



Figure 35. Delamination of polyacrylic acid oligomers by (a) breaking all Li-O bonds, (b) breaking all Li-Li bonds, and (c) breaking mixed Li-O and Li-Li bonds. (d) The work of separation in terms of energy, $W_{sep}(oligomer)$, as a function of the number of bonded oxygen of oligomers, N_{BO} .

Table 1. Work of separation (adhesion or delamination) of	
Li/PAA(polymer) and Li/SEI components interfaces.	

Interface	Work of Separation (J/m ²)
PAA(polymer)/Li(001)	1.00
LiF(001)/Li(001)	0.23
Li ₂ CO ₃ (001)/Li(001)	0.17^{4}
Li ₂ O(110)/Li(001)	1.10
Li ₂ O(111)/Li(001)	0.72

Patents/Publications/Presentations

Patents

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- Xiao, X. "Methods for Manufacturing Electrode including Fluoropolymer Based Solid Electrolyte Interface Layers." P049559-US-NP (2019).
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Publications

- Dong, X., Y. X. Lin,* P. Li, Y. Ma, J. Huang, Z. Guo, D. Bin, Z. Wang, Y. G. Wang, Y. Qi, and Y. Y. Xia. "High Energy Rechargeable Metallic Lithium Battery at -70°C Enabled by a Co-Solvent Electrolyte." *Angewandte Chemie* International Edition (2019). doi: https://doi.org/10.1002/ange.201900266.
- Guo, K., W. Zhang, B. W. Sheldon, and H. Gao. "Concentration Dependent Properties Lead to Plastic Ratcheting in Thin Island Electrodes on Substrate under Cyclic Charging and Discharging." *Acta Materialia* 164 (2019): 261–271.
- Liu, Y., K. Guo, C. Wang, and H. Gao. "Wrinkling and Ratcheting of a Thin Film on Cyclically Deforming Plastic Substrate: Mechanical Instability of the Solid-Electrolyte Interphase in Li–ion Batteries." *Journal* of the Mechanics and Physics of Solids 123 (2019): 103–118.
- Wang, Y., D. Dang, D. Li, J. Hu, and Y. T. Cheng. "Influence of Polymeric Binders on Mechanical Properties and Microstructure Evolution of Silicon Composite Electrodes during Electrochemical Cycling." *Journal of Power Sources* 425 (2019): 170–178.
Task 2.6 – Microscopy Investigation on the Fading Mechanism of Electrode Materials (Chongmin Wang, Pacific Northwest National Laboratory)

Project Objective. This work will use a combination of *ex situ, in situ, operando* and cryo HRTEM and spectroscopy to probe the fading mechanism of both lithium and silicon as high-capacity anode as well as Ni-rich NMC as high-capacity cathode. For high-capacity anode, the research task will focus on revealing how lithium and silicon interact with liquid electrolyte to critically affect their fading process. For the Ni-rich NMC cathode, the project will focus on delineating the structural and chemical evolution of the Ni-rich NMC regarding their dependence on the operating voltage, charge rate, and chemistry of electrolyte.

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 the designing 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 EVs, especially for PHEV as required by the EV Everywhere Grand Challenge.

Approach. Aberration-corrected STEM high-angle annular dark-field (STEM-HAADF) and cryo-TEM imaging combined with EELS / energy-dispersive X-ray spectroscopy (EDX) chemical analysis will be used to probe the microstructural and chemical evolution of both cathode and anode. TOF-SIMS, nano-SIMS, and XPS will be used to explore the chemistry and the thickness of SEI layer on cathode and anode material. These characterization results will be used to guide the materials optimization process and establish a solid knowledge base on the correlation between materials selections and structure evolution in the Ni-rich NMC layered cathode materials.

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

- Multi-scale *ex situ/in situ* and *operando* TEM and cryo-TEM investigation of failure mechanisms for energy-storage materials and devices. Atomic-level *in situ* TEM and STEM imaging to help develop fundamental understanding of electrochemical energy-storage processes and kinetics of electrodes.
- Extension of *in situ* TEM capability for energy storage technology beyond lithium ions, such as Li-S, Li-air, Li-metal, sodium ions, and multi-valence ions.

Collaborations. This project collaborates with G. Chen (LBNL); J. Nanda (ORNL); K. Amine (ANL); D. Wang (Pennsylvania State University); A. Manthiram (University of Texas at Austin, UT Austin); W. Tong (LBNL); G. Liu (LBNL); Y. Cui (Stanford University); J. Zhang (PNNL); J. Liu (PNNL); X. Xiao (GM); S. Meng (UCSD); and S. Whittingham (State University of New York, SUNY, at Binghamton).

- 1. Resolve the true structural nature of the intragranular cracks in Ni-rich NMC and answer questions on the origin of such cracking behavior. (Q1, FY 2019; Completed)
- 2. Reveal the true structural and chemical information of Si-anode/liquid-SEI layer by integration of cryo-TEM and EELS. (Q2, FY 2019; Completed)
- 3. Determine the critical factor that controls the correlation between charging rate and fading behavior of Ni-rich NMC. (Q3, FY 2019; On schedule)
- 4. Reveal the true structural and chemical information of Li-metal anode/liquid-SEI layer by cryo-TEM and EELS. (Q4, FY 2019; On schedule)

Oxygen loss is a very well perceived degradation mechanism for layer structured cathode, contributing to the capacity loss and structural instability of the lattice. However, it is far from clear how the oxygen loss happens. Here, the team reveals the oxygen loss process of the Li-rich transition metal oxide (LTMO) layer cathode, giving direct information on the evolution of cathode lattice during battery cycling at a high charging cutoff voltage as the anionic redox process is triggered.

The team used FIB lift-out techniques to prepare crosssectional transmission electron microscopy (TEM) specimens to capture the surfaces and interiors of LTMO cathode particles as battery cycling proceeded. The images show that nano-void formation and lattice transformation start from the particle surface and gradually propagate toward the center as the battery is cycled. Computational simulations show that triggering anionic redox processes leads to lowering of both the formation energy of oxygen vacancy and the diffusion barrier of oxidized oxide ions, therefore facilitating inward migration of oxygen vacancies. This work highlights that although oxygen anions offer the opportunity to access extra capacity during high-voltage cycling in LTMO cathodes, they also trigger a



Figure 36. The needle-shaped specimen for tomography to reveal void formation in Li-rich layer structured cathode. Scanning transmission electron microscopy – high-angle annular dark-field (STEM-HAADF) images show the needle-shaped specimen for STEM tomography is made from Li_{1.2}Mn_{0.6}Ni_{0.2}O₂ cathode after 300 cycles. (a) Low-magnification image shows that this needle has three grains, marked as G1, G2, and G3. The boundaries between the grains are marked with dashed lines. (b) High-magnification image of the yellow rectangular marked region in (a) and the red rectangular marked region in (b) highlights the 3D reconstruction region.

degradation mechanism that is believed to play a significant role during prolonged battery cycling.

The team prepared a needle-shaped TEM specimen of a $Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$ electrode that had been cycled 300 times at a high charging cutoff voltage of 4.8 V. By collecting a tilting series of STEM-HAADF images ranging from -76° to $+78^{\circ}$, the team built a 3D tomography of this grain. Fragmentation analysis of the tomography data allowed direct visualization of the spatial distribution of the nano-voids in 3D, as shown in Figure 36. The team estimated the nano-void volume ratio to be 24% for this needle, indicating substantial mass loss and lattice reconstruction during cycling.

These cross-sectional STEM observations and 3D tomography reconstructions offer a unique opportunity for understanding bulk lattice degradation of LTMO cathodes. This bulk degradation involves nano-void formation and lattice structure transformation, which are consequences of electrochemically driven oxygen vacancy formation at particle surfaces and subsequent injection into the bulk lattice and a condensation process, which is sharply contrasted with the case of a thermally driven process. Although an anionic redox reaction coupled with a cationic redox reaction has been demonstrated to be a new route for developing a high-capacity cathode, excitation of anionic redox-induced lattice instability as revealed in this work indicates the conflicting roles of oxygen redox activity during high-voltage cycling. The progressive surface-to-bulk degradation indicates that the suppression of oxygen vacancy generation at the particle surface is the key factor for curtailing subsequent injection of vacancies.

Patents/Publications/Presentations

Patent

• "High Capacity and Stable Cathode Materials." U. S. Patent No. 10,243,206 (March 26, 2019).

Publication

 Yan, P., J. Zheng, Z-K. Tang, A. Devaraj, G. Chen, K. Amine, J-G. Zhang, L-M. Liu, and C. Wang. "Oxygen Vacancies Injection in the Bulk Lattice of Layered Cathodes." *Nature Nanotechnology* (2019). Accepted for publication.

Presentation

 Materials Research Society (MRS) Spring Meeting, Phoenix, Arizona (April 2019): "Advanced *In Situ* and *Ex Situ* S/TEM Probing of Interfacial Process in Rechargeable Batteries." Task 2.7 – Correlative Microscopy Characterization of Electrochemical Hotspots in Oxide Electrodes (Yi Cui, William Chueh, and Michael Toney; Stanford/SLAC)

Project Objective. This project aims to develop and utilize a correlative microscopy platform to investigate the lithiation dynamics of lithium- and manganese-rich (LMR) NMC and NCA, with the specific goal of understanding factors that determine the rate capability and degradation mechanisms at the single primary particle length scale. By developing a nanoscale and single-particle understanding of lithiation, the project addresses specific engineering problems including electrochemical hotspot, electrode utilization, safety, and capacity/voltage fade.

Project Impact. Fundamental insights from this new diagnostic capability are expected to increase the power density and cycle life of oxide electrodes by improving electrode utilization, reducing electrochemical hotspots, decreasing capacity and voltage fade, and enhancing safety, which all improve the viability of Li-ion batteries for vehicle transportation. By understanding lithiation at the single-particle level, this project's success will contribute to improving on-vehicle battery management, such as charging/discharging protocol, and state-of-charge and state-of-health monitoring.

Approach. As stated, the project aims to develop a correlative microscopy platform to investigate the lithiation dynamics of LMR-NMC and NCA, with the goal of understanding factors that determine the rate capability and degradation mechanisms at the single primary particle length scale. On recharging time, the specific phenomena to be addressed include nonuniform current distribution and the correlation between surface property and the local lithiation rate. On degradation, phenomena to be addressed include correlating local chemistry and phases to capacity and voltage fading.

Out-Year Goals. Develop X-ray microscopy to investigate NMC and LMR-NMC cathodes at the single primary particle and single secondary particle level.

Collaborations. Commercial battery electrode particles are being supplied by Samsung.

- 1. Quantify the local structure of Li-rich layered oxides using local X-ray probe. (Q1, FY 2019; Completed)
- 2. Assess the effect of synthesis condition of anion redox. (Q4, FY 2019)
- 3. Assess the effect of oxygen vacancies on anion redox. (Q4, FY 2019)

This quarter, the team characterized NMC-111 cathode platelet particles synthesized via molten salt route. Such a microstructure is ideal for studying lithium transport during charging and discharging because transport occurs along the in-plane direction during microscopy measurements. Similarly, this geometry allows phase boundary movement along the fast transport axis of layered oxides to be directly visualized. OCV is essentially the same as those synthesized from standard routes. The team notes that these particles exhibit modest rate capability (approximately ten times worse than those from coprecipitation synthesis), likely due to the low edge and basal facets in the platelet geometry.

As proof-of-concept, the team performed high-resolution scanning transmission X-ray microscopy measurements on these particles at various SOCs (Figure 37). Nickel oxidation state was used to infer the SOC. The team has shown that nickel is an effective indicator of SOC because it is the main redox partner in NMC-111. Imaging was carried out in standard transmission mode as well as in ptychography mode (scanning coherent diffractive imaging). As can be seen, high spatial resolution in ptychography mode was achieved. Two types of experiments were carried out. The first type was *ex situ* imaging, whereby particles were cycled to a predefined SOC, stopped, battery cell dissembled, and electrodes rapidly dried. This procedure takes about one minute and prevents the redistribution of lithium between particles, though it does not preclude lithium rearrangement within a given particle. Second, *operando* imaging was carried out, whereby the particles were cycled electrochemically while imaged. In both experiments, beam-induced damage (in terms of redox state change) was negligible.

The initial success paves the path toward full characterization of mesoscale charging and discharging dynamics of layered oxide cathodes. This fiscal year, the team is focused on understanding the importance of interfacial reaction and diffusion kinetics, chemo-mechanics, and equilibrium and rate-induced phase transitions, all of which will be studied by *operando* X-ray microscopy.



Figure 37. Scanning transmission X-ray microscopy (STXM) images of platelet $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ in (left) standard mode and (right) ptychography mode.

Patents/Publications/Presentations

Presentations

- Massachusetts Institute of Technology (MIT) Energy Initiative Seminar Series, Cambridge, Massachusetts (March 20, 2019); W. C. Chueh.
- Gordon Research Conference on Nanomaterials for Applications in Energy Technology, Ventura, California (February 26, 2019); W. C. Chueh.

Task 2.8 – Investigate the Impact of Doping on the Structural Stability and Conductivity of Solid Electrolytes (Zonghai Chen, Argonne National Laboratory)

Project Objective. The project objective is to develop high conductivity ceramic electrolyte through cation doping and to stabilize the structure and cathode/electrolyte interface through cation doping and co-sintering between electrolyte and cathode.

Project Impact. Development of structurally, chemically, and electrochemically stable high conductivity solid electrolytes can significantly improve (1) volumetric energy density and (2) safety characteristics of lithium batteries, and will accelerate the penetration of EVs.

Approach. The project approach is multi-fold: (1) understanding the physics behind the transformation between the low conductivity phase and the high conductivity phase; (2) investigating the bonding strength of the cathode/electrolyte interface using model systems; and (3) developing electrolytes with high ionic conductivity and good bonding to cathodes through cation doping.

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

- Using Li₇La₃Zr₂O₁₂ (LLZO) as a model material to investigate the pathway of path transformation during the synthesis of the solid-state electrolyte.
- Investigating the impact of cation doping on the kinetics of phase transformation.
- Initiating the research activity on the co-sintering of cathode/electrolyte model system for a chemically/mechanically strong interface.

Collaborations. The project collaborates with Dr. A. Ngo (ANL), Dr. L. Curtiss (ANL), Dr. V. Srinivasan (ANL), Dr. Y. Ren (ANL), Dr. J. Libera (ANL), Dr. T. Li (Northern Illinois University), and Dr. D. Chen (University of Houston).

- 1. Developing *in situ* high-energy XRD capability to investigate the phase transformation of ceramic electrolytes. (Q1, FY 2019; Completed)
- 2. Investigating the tetragonal/cubic phase transformation of LLZO. (Q2, FY 2019; Completed)
- 3. Investigating the impact of bonding between LLZO and cathode materials. (Q3, FY 2019; Partially completed)
- 4. Synthesizing W-doped LLZO for investigation on structural stability and mechanical stability. (Q4, FY 2019; Ongoing)

The ionic conductivity of a solid-state electrolyte is strongly dependent on the structure of the electrolyte. For instance, the Li⁺ conductivity of cubic LLZO is two magnitudes higher than that of tetragonal LLZO. Therefore, synthesis and maintaining cubic structure of LLZO during the sintering and co-sintering process are crucial to enable LLZO for high-performance, solid-state lithium batteries. In this project, LLZO was selected as the model material to investigate the thermodynamics and kinetics of formation of the high ionic conductivity phase, like c-LLZO. To serve this purpose, an *in situ* high-energy X-ray diffraction (HEXRD) technique was set up at sector 11-ID-C of APS at ANL. Figure 38 shows the phase evolution of electrolyte material during the solid-state synthesis of LLZO. The starting material used is a mixture of Li_2CO_3 , $La(OH)_3$, and ZrO_2 . Figure 38a shows that the starting material was converted to a cubic-like intermediate phase when it was heated to 950°C. When sintered at 950°C for up to 5 hours, the intermediate phase slowly converted to the desired c-LLZO; however, the material was still dominated by the intermediate phase. When the materials obtained after sintering at 950°C were cooled slowly, the intermediate phase was then converted to a tetragonal phase (t-LLZO) during the cooling process (see Figure 38b). Positively, the c-LLZO stayed as a cubic phase during the whole course of the cooling process. To further validate this finding, a new sample was heavily sintered at 1050°C for 5 hours before being slowly cooled to room temperature. Figure 38c clearly shows that the pure c-LLZO phase formed after the sintering retains its cubic structure during the whole course of the cooling process. Unlike the proposals in open literature, this project's results show no direction conversion between t-LLZO and c-LLZO, both of which are a direct conversion product of the intermediate phase. The team's results also imply that the *c*-LLZO is thermodynamically stable within the temperature window between room temperature and 1050°C, and that the kinetics for the formation of c-LLZO are very slow, so that a higher sintering temperature is needed for a full conversion from the intermediate phase to *c*-LLZO.



Figure 38. Phase evolution during the solid-state synthesis of Li₇La₃Zr₂O₁₂ when (a) the material is sintered at 950°C; (b) the material sintered at 950°C is cooled; and (c) the material sintered at 1050°C is cooled.

Patents/Publications/Presentations

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

TASK 3 – MODELING

Summary and Highlights

Achieving the performance, life, and cost targets outlined by VTO 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.

In the area of intercalation cathodes, effort is focused on understanding working principles of high nickel layered materials with an aim of understanding structural changes and associated changes in transport properties. 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 parallel, design of liquid electrolytes and gaining understanding of their behavior are used to determine their usability at high voltages. In addition, focus is paid to the assembling of porous electrodes with particles to predict the conduction behavior and impact of heterogeneities on electrode behavior. Efforts this quarter were aimed at examining the electrolyte formulations for silicon anodes to ensure lower SEI resistance and developing a framework to model amorphous coatings.

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 are also starting to examine the role of the SEI on the morphology of the dendrite and to describe the mechanical-electrochemical coupled effects that are critical for dendrite formation. Finally, models are being developed to examine the solid-cathode interface in Li-metal based systems, where interface debonding issues are known to limit cycling. This quarter, models examined the focusing of current in solid electrolytes due to defects and on examining the nucleation and growth of dendrites in solid electrolytes.

Highlights. To examine the use of coatings to protect the interface, the Persson group has developed a new framework that combines large-scale AIMD and DFT simulations to predict lithium and oxygen diffusion in amorphous coating materials. Amorphous coating layers tend to be conformal, with reduced grain boundaries, or other defective regions that exist in polycrystalline coating layers. This newly developed framework, which is integrated into the Materials Project database, presents a path to discover new coatings that can serve to improve the performance of batteries.

Task 3.1 – Design of High-Energy, High-Voltage Lithium Batteries through First-Principles Modeling (Kristin Persson, Lawrence Berkeley National Laboratory)

Project Objective. This project supports VTO 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: (1) understanding of the factors that govern charge transport in nonaqueous, superconcentrated liquid electrolytes (2) new fundamental understanding of the Li-ion dynamics in Si-Sn electrode alloys (and their native oxides), with a design focus on improving stability of the silicon electrode through tin alloying, and finally (3) critical surface and coating design and optimization strategies that will improve cycling of Li-ion battery cathodes by reducing cathode degradation from oxygen loss.

Project Impact. To enhance performance of Li-ion systems, improvements on the cathode and the electrolyte side are needed. This project is aimed to result in an improved understanding of the atomistic mechanisms underlying surface behavior and performance of the Li-ion cathode materials, with the ultimate goal being to suggest strategies, such as coatings, surface protection, and particle morphology design. Furthermore, fundamental studies of electrolyte conductivity and transport mechanisms, as a function of solvent and salt concentrations, and components will be conducted.

Approach. First-principles calculations, both static and dynamic approaches, are used to model solid-state electrode material thermodynamics and kinetics. Liquid electrolytes are modeled through coupled classical molecular dynamics (MD) and first-principles methods to accurately capture solvation structure as well as reactivity of the liquid system.

Out-Year Goals. For the electrolyte development, work will be aimed toward understanding the atomistic interactions underlying the performance of lithium electrolytes specifically elucidating conductivity (as a function of salt concentration) and impact on the charge transport mechanisms at play. Stable interfaces will be determined by focusing initially on degradation mechanisms related to release of surface oxygen at high charge. Tuning particle morphology and coating materials—both of crystalline as well as amorphous structure—will be explored using the Materials Project. Li-ion conduction mechanisms and electrode stability of Si-Sn alloys will be determined, in addition to the reactivity and ionic conduction of the native oxide surface phases.

Collaborations. This project is highly collaborative between BMR PIs G. Chen (LBNL), G. Ceder (LBNL), and V. Srinivasan (ANL). Cathode design and synthesis will be performed by Chen and Ceder, surface design by Persson, and electrolyte design and testing by Persson and Srinivasan.

- 1. Finish benchmarking of algorithms for obtaining reliable solvation structures and ionic conductivity in highly concentrated liquid electrolytes. (Q1, FY 2019; Completed)
- 2. Identify Li-ion conduction mechanisms in Si-Sn alloy anode, using first-principles modeling. (Q2, January 2019; In progress)
- 3. Evaluate SiO₂ and SnO₂ as surface phases from the perspective of ionic conduction and reactivity with lithium. (Q3, April–July 2019)
- 4. Conduct first evaluation of amorphous oxygen-retention and lithium diffusion enhancing coatings using the Materials Project infrastructure. (Q4, July–November 2019)

This project is aimed toward amorphous coating design that will improve performance of Li-ion battery cathodes. Amorphous coating layers tend to be conformal, with reduced grain boundaries, or other defective regions that exist in polycrystalline coating layers. Therefore, amorphous coating would reduce the kinetics of TM and/or oxygen ion transport (for example, effectively suppressing corrosion while promoting lithium transport).^[1] This report presents a framework, based on Materials Project infrastructure, that combines large-scale AIMD and DFT simulations to predict lithium and oxygen diffusion in amorphous coating materials.



Figure 39. A framework to generate optimized amorphous structure.

The amorphous structure is generated by implementing a "liquid-quench" process, in which heating, equilibration, and quenching are done through a series of AIMD simulations. To generate a liquid phase of the amorphous structure, the structure is heated at a temperature that is higher than the material's melting point. A sequence of AIMD simulations in the *NVT* ensemble are employed to equilibrate the amorphous structure until both energy and pressure are converged. The equilibrium structure is then quenched to 0K to obtain the optimized atomic positions in the amorphous structure. The entire framework can be seen in Figure 39.

To investigate lithium and oxygen diffusion at different temperatures, the amorphous structure is heated to several specific temperatures, and several structure snap shots are obtained by repeating the AIMD equilibration routine described above. Then, the trajectories of amorphous structure under different temperatures are collected for diffusion analysis. Figure 40 illustrates the trajectory of one lithium atom during the AIMD simulations. The self-diffusion coefficients D of lithium and oxygen in amorphous structure at T = 300K are calculated from the Einstein relation $D = \langle r^2 \rangle / 6t$, where $\langle r^2 \rangle$ is the mean square displacement. The team determines $\langle r^2 \rangle$ values of lithium and oxygen from the collected trajectories and calculates D at each T. Finally, the D value at T = 300K is extrapolated from the values at higher T using Arrhenius plot. The procedure described above is broadly applicable to evaluate lithium and oxygen diffusion in various amorphous materials.



Figure 40. Trajectory of a lithium atom in an amorphous structure. Yellow and green dots represent vibrational and translational motions, respectively.

[1] Aykol, M., and K. A. Persson. "Oxidation Protection with Amorphous Surface Oxides: Thermodynamic Insights from *Ab Initio* Simulations on Aluminum." *ACS Applied Materials & Interfaces* 10, no. 3 (2018): 3039–3045.

Patents/Publications/Presentations

Presentations

- International Coalition for Energy Storage and Innovation and Pacific Power Source Symposium (ICESI-PPSS), Kona, Hawaii (January 2019): "The Impact of Minority as well as Majority Species on the Performance of Liquid Organic Electrolyte"; Invited.
- IBA, San Diego, California (March 2019): "The Solvation Structure and Rational Design of Liquid Organic Electrolytes."

Task 3.2 – Understanding and Strategies for Controlled Interfacial Phenomena in Lithium-Ion Batteries and Beyond (Perla Balbuena and Jorge Seminario, Texas A&M University; Partha Mukherjee, Purdue University)

Project Objective. The project objective is to evaluate and characterize interfacial phenomena in lithiated silicon and Li-metal anodes and to develop guidelines for potential solutions leading to controlled reactivity at electrode/electrolyte interfaces of rechargeable batteries using advanced modeling techniques based on first principles.

Project Impact. Understanding SEI growth on constantly evolving silicon surfaces and on highly reactive Li-metal surfaces is expected to allow definition of the electrolyte properties required in high-performance cells. Strategies to control the silicon anode instability and pulverization issues and the well-known safety and short effective lifetimes of Li-metal anodes will be developed by tuning the electrolyte composition, structure, dynamic, and stability, as well as that of the electrode morphology and interactions with the electrolyte, based on multiple characterizations of interfacial phenomena.

Approach. A comprehensive multiscale modeling approach, including first-principles *ab initio* static and dynamics, classical MD, and coarse-grained mesoscopic models, will focus on the roles of the electrolyte's chemical, structural, and dynamical properties and of the electrode micro- and nano- structure on the formation and evolution of the SEI layer and the associated electrochemical performance on silicon and on Li-metal anodes.

Out-Year Goals. Work will progress toward characterizing lithiation and SEI formation at silicon surfaces as well as the subsequent cracking and reforming events under the most realistic modeling conditions. Similarly, the project will investigate electrolyte effects on reactivity and dendrite formation in Li-metal surfaces. The project aims to capture how the chemistry of the various electrolyte components (mainly liquids, but also solid polymers and gels) affects the main issues that influence the electrode performance.

Collaborations. This project funds work at Texas A&M University (TAMU) and Purdue University. The team has collaborated with Prof. G. Somorjai (UC Berkeley), Prof. S. Yassar (UIC), and Dr. V. Murugesan (PNNL).

- 1. Complete analysis of anode macroscopic effects during cycling. (Q1, FY 2019; Completed)
- 2. Complete study of improved electrolytes for silicon anodes. (Q2, FY 2019; Completed)
- 3. Complete study of improved electrolytes for lithium anodes. (Q3, FY 2019; In progress)
- 4. Complete evaluation of alternative charging strategies for lithium anodes. (Q4, FY 2019)

Electrolyte Formulation Strategies for Silicon Anodes: Additives and Coatings. High theoretical capacity of silicon does not translate to high practical capacity due to uncontrolled SEI growth and large volumetric strains (up to 300% for silicon) on repeated lithiation and delithiation. This alloying induced-strain leads to cracking and fracture of both particle and SEI resulting in fresh contact between the electrolyte and active material surface increasing the likelihood for harmful reduction events. The team has examined the effects of stress and fractures in the silicon particles and SEI using a multiscale modeling approach. Mitigation strategies such as the presence of graphene coatings and self-healing polymers on the silicon particle surface were also investigated. The results were published in the *Journal of Power Sources* (2019).



Figure 41. Effects of solvent activation energy (E_a , KJ/mol) for transport in the SEI on the total charging time (t_M , sec) and SEI thickness (h, nm) during a full charging process on Li-ion battery anodes. (b) SEI thickness contour (nm) under various activation energies of Li-ion (horizontal axis) and solvent (vertical axis).

Figure 41a shows that as the solvent transport resistance increases, the SEI thickness shrinks. In addition, the total charging time is slightly reduced with increasing solvent activation energy in the SEI, which is attributed to the following events. At the electrode-SEI interface, lithium intercalation into the electrode competes with the SEI formation. Because solvent available at the interface decreases with increasing activation energy for solvent transport, Li-loss for the reaction with solvent is reduced. Thus, more lithium atoms intercalate into the electrode instead of forming new SEI, which eventually shortens the total charging time. Figure 41b depicts the SEI thickness contour after the first charge. Thus, sluggish solvent transport through the SEI layer (which depends on the SEI structure and porosity) can help mitigate capacity fading due to SEI formation. In practice, the SEI film should be thin enough to reduce the resistance and thick enough to protect the active materials.

Charge and Dendrite Formation in a Full Li-Ion Battery Using Different Molarities in a Liquid Electrolyte. Classical MD simulations of a full nanobattery (NMC/electrolyte/lithium anode) yielded the following insights for a solution of LiPF₆ in EC, EMC, and VC at three different salt concentrations:

- PF₆ anions concentrate at both interfaces (anode/electrolyte and cathode/electrolyte), but only dissociate at the anode surface forming LiF.
- Reactions at the anode/electrolyte interface are different in the base and top of a nucleating structure. At the base, the reactions have sufficient time to form new molecules (the team detected CH₃F, C₂H₅F, and C₂H₄ anions). In contrast, since lithium deposition predominates at the top of the nucleating structure, the SEI reactions are slower.
- Increasing salt molarity decreases the ionic current even if all other conditions are the same because the Coulombic repulsion between Li⁺ ions slows down their transport.
- Regardless of the molarity, a lithium dendrite always grows; at higher molarities, dendrite formation becomes faster at longer times. Moreover, after lithium dendrite growth starts and dissociation of electrolyte molecules, lithium nucleation becomes unstable, making lithium dendrite formation accelerate sharply.

Analysis of Lithium Electrodeposition. New methodologies (Longo, et al. *Journal of Materials Chemistry*, 2019) were implemented to assess the effect of applied potential on lithium electrodeposition at various electrolyte conditions. The study was done on copper surfaces, and current work focuses on lithium surfaces. The team has also examined the effect of the nature of the electrolyte on lithium electron distribution. Work is in progress to examine effects of ion concentration, and nature and morphology of the substrate for lithium electrodeposition. This method will allow the team to determine the best electrolytes for stable lithium deposition. In collaboration with PNNL, the team also examined the role of various natural SEI layers (Li₂O, LiOH, and Li₂CO₃) on lithium reactivity.

Patents/Publications/Presentations

Publications

- Galvez-Aranda, D. E., A. Varma, K. Hankins, J. M. Seminario, P. P. Mukherjee, and P. B. Balbuena.
 "Chemical and Mechanical Degradation and Mitigation Strategies for Si Anodes." *Journal of Power Sources* 419 (2019): 208–218.
- Tewari, D., and P. P. Mukherjee. "Mechanistic Understanding of Electrochemical Plating and Stripping of Metal Electrodes." *Journal of Materials Chemistry A* 7, no. 9 (2019): 4668–4688.
- Hao, F., W. Wang, and P. P. Mukherjee. "Electrochemical-Reaction-Driven Interfacial Stress in a Solid-Solid Layered Architecture." *Physical Review Applied* 11, no. 3 (2019): 034038.
- Longo, R. C., L. E. Camacho-Forero, and P. B. Balbuena. "Charge-Mediated Cation Deposition on Metallic Surfaces." *Journal of Materials Chemistry A* 7 (2019): 8527–8539.
- Sharifi-Asl, S., F. A. Soto, Y. Yuan, T. Foroozan, P. Abbasi, R. Deivanayagam, R. Rojaee, B. Song, A. Salehi-Khojin, K. Amine, J. Lu, P. B. Balbuena, and R. Shahbazian-Yassar. "Anti-Oxygen Leaking LiCoO₂." *Advanced Functional Materials*. In press.

Presentation

• ACS Spring National Meeting, Orlando, Florida (April 4, 2019): "Interfacial Reactions at the Surface of Li Metal Anodes of Li-S Batteries: Effects of High Salt Concentration"; P. B. Balbuena. Invited.

Task 3.3 – 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 (1) investigate interfacial stability between electrodes and ceramic-based SSEs, and (2) experimentally measure and understand the impedance observed at the cathode/SSE interface. Ceramic-based SSEs are expected to enable high energy density and liquid-free, safe, next-generation Li-ion batteries. Li-metal anodes should be incorporated due to their substantially larger specific capacity, as compared to present day graphite-based anodes. During deposition, lithium dendrite growth through the SSEs and subsequent short circuit has been a major issue, limiting successful implementation of SSEs. Similarly, on the cathode side, diffusion of TMs into the SSEs along with delamination between cathode and SSE lead to increased interfacial resistance. The developed computational model will be used to investigate the impact of microstructural (grain size), physical (mechanical stiffness), and transport (conductivity) properties of the SSE on the overall interfacial degradation observed at both the cathode and anode sides. Due to the SOC-dependent electrochemical and mechanical properties of the cathode, an attempt will be made to experimentally measure the SOC-dependent impedance at the cathode/SSE interface. The main focus will be to elucidate interfacial issues, observed at both anode and cathode sides, and devise strategies to enable successful implementation of SSE in next-generation Li-ion batteries.

Project Impact. Findings from this research will give a better understanding of the factors, at the cathode/SSE interface, limiting the cycle life of solid-electrolyte-based Li-ion batteries. These results will help to enable incorporation of cathode particles within SSEs.

Project Approach. The approach used here is to develop mesoscale models, based on continuum modeling, to describe the critical processes in the materials, and combining them with electrochemical, microscopic, and spectroscopic data to ensure parameter estimation and model validation. The model is then used to provide insights on the impact of material properties on performance and life, and guidance for design of new materials.

Out-Year Goals. At the end of this project, a computational framework will be presented that is capable of estimating delamination and impedance at cathode/SSE interface.

Collaborations. The project has no collaborations this period.

- 1. Investigate impact of grain-interior (GI) / grain-boundary (GB) microstructure on overall dendrite growth observed at SSE/lithium interface. (Q1, FY 2019; Completed)
- 2. Analyze effect of delamination at the cathode/SSE interface as a mode of degradation. (Q2, FY 2019; Completed)
- 3. Investigate the impact of grain size of the electrolyte on the mechanical degradation occurring at the cathode/SSE interface. (Q3, FY2019; In progress)
- 4. *Go/No-Go Decision*: Estimate SOC-dependent impedance at cathode/SSE interface. If not possible, proceed with impedance measured at fixed SOC. (Q4, FY 2019)

Analyze the Effect of Delamination at the Cathode/SSE Interface as a Mode of Degradation. To improve the energy density and safety of next-generation Li-ion batteries, it is necessary to use Li-metal anodes and SSEs. However, to build a successful electrochemical cell, good cathode materials must also be incorporated as the positive electrode of the battery. Conventional cathode materials, for example, LCO, NMC, etc., store lithium atoms through an intercalation mechanism. During the charge process, lithium ions go out of these cathode particles, which results in their shrinkage. Similarly, during discharge, lithiation of these cathode materials results in their expansion. Usually, during the synthesis process, Li-ion cells are fabricated in a discharged state, which means that the cathodes are assembled in a lithiated condition. During the formation cycles, the cells are charged for the first time, which leads to the delithiation of the cathode particles. The initial delithiation gives rise to tensile stresses at the cathode/SSE interface, which may lead to interfacial delamination based on the amount of volume contraction of cathode, compliance of the SSE, and binding energy between the cathode and the SSE. Also, oxide-based SSEs (such as LLZO) demonstrate GI and GB microstructure. Since the GBs demonstrate lower mechanical stiffness than the GIs, stresses of different magnitude evolve at the GI and GB regions. The reaction current at the cathode/SSE interface is given by the Butler-Volmer equation (i_{RV}) , which takes into account the mechanical-stress-induced changes in the electrochemical potential $(\Delta \mu_{e^{-}})$. The overpotential is defined as, $\eta_s = \phi_s - \phi_e + (\Delta \mu_e - F)$, and the Butler-Volmer equation is written as, $i_{BV} = i_0 \exp(\Delta \mu_e - /2RT) \left[\exp(F\eta_s/2RT) - \exp(-F\eta_s/2RT)\right]$. Here, i_0 is the exchange current density, which depends on the concentration of lithium at the cathode/SSE interface and also the activation energy barrier for lithium transportation between cathode and SSE. In the present analysis, a constant magnitude of i_0 has been assumed. Figure 42 shows the LLZO/NMC interface modeled in the present study and current focusing at the GBs during both charge and discharge processes.



Figure 42. (a) Computational domain of the cathode/solid-state electrolyte interface with the presence of grain boundaries (GB). (b) Distribution of current density at the interface during the charge process (magnitude of current is positive because anodic current is active). (c) Distribution of current density at the interface during the discharge process (magnitude of current is negative because cathodic current is active).

Figure 43a shows a schematic representation of the NMC/SSE interface, which clearly indicates that delamination may occur at the time of delithiation due to the shrinkage of cathode. Such detachment may lead to a decrease in the electrochemically active surface area and an increase in cell resistance. The charge-discharge curves obtained at 10A/m², shown in Figure 43b, demonstrate the fade in first discharge capacity due to delamination during the first charge step. Successfully capturing the degradation at cathode/SSE interface and predicting its impact on cell performance complete the milestone this quarter.



Figure 43. (a) Schematic diagram of the cathode/solid-state electrolyte interface where delamination can occur during the first charge or delithiation process. (b) Charge and discharge curves obtained during the first delithiation and lithiation of the cathode particles. Delamination during the charge process manifests as a capacity fade during discharge.

Patents/Publications/Presentations

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

Task 3.4 – First-Principles Calculations of Existing and Novel Electrode Materials (Gerbrand Ceder, Lawrence Berkeley National Laboratory)

Project Objective. Solid-state batteries are promising to achieve high energy density. The project objective is to determine the design principles needed to create SSEs 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 of the factors that control Li-ion motion in crystalline and amorphous solids and 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.

Approach. High-throughput computation method is used to screen suitable solid electrolyte with high electrochemical stability and high ionic conductivity, by incorporating Nudged Elastic Band (NEB) and an AIMD method. Meanwhile, DFT 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 solid electrolyte decomposition are assessed by topotactic lithium insertion and removal from the solid electrolyte.

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 all solid-state batteries.

Collaborations. There are no current collaborations.

- 1. Modeling of the Li₂S-P₂S₅ phase diagram for SSEs: solid phases correctly modeled. (Q1, FY 2019; Completed)
- 2. Modeling of the Li₂S-P₂S₅ phase diagram for SSEs: include correct modeling of amorphous phase. (Q2, FY 2019; Completed)
- 3. Model Li-ion conductivity in amorphous LPS (Li-P-S) systems and glass ceramics. (Q3, FY 2019)
- 4. Develop understanding on which structural and compositional features make LPS an excellent ionic conductor. (Q4, FY 2019)

Due to high ionic conductivity $(0.2-3.0 \text{ mS/cm})^{[1, 2]}$ and ease of processing, LPS glasses and glass-ceramics, $xLi_2S \cdot (1 - x)P_2S_5$ (x = 0.7-0.8), represent promising electrolyte candidates to enable use of all-solid-state batteries. To understand their mechanisms of operation, the team has first undertaken modeling of the amorphous phase. Amorphous models for the composition $0.75Li_2S \cdot 0.25P_2S_5 -$ corresponding to the ortho-thiophosphate stoichiometry Li_3PS_4 – have been generated via AIMD with the PBE density functional^[3] by applying different melt-and-quench and simulated annealing protocols to a unit cell with 128 atoms in total. An example of the simulated amorphous structure is shown in Figure 44. All computed structures display PS₄ tetrahedra, both isolated and connected through S bridges (P₂S₇) or P-P bonds (P₂S₆), as well as "atypical" structural motives such



Figure 44. Amorphous Li₃PS₄ model from *ab initio* molecular dynamics. Lithium (green), phosphorus (violet), and sulfur (yellow).

as sulfur chains and tri-coordinated phosphorus. These structural motives signal the occurrence of electronic transfer reactions that have been also detected with the SCAN functional.^[4] Indeed, the team predicted SCAN to favor the redox reaction $2Li_3PS_4 \rightarrow Li_2S_2 + Li_4P_2S_6$ by about 60 meV with respect to PBE. The team has calculated PDFs for their amorphous LPS models and compared with experimental X-Ray scattering data (see



Figure 45. Comparison between calculated and experimental pair distribution functions for amorphous Li-P-S.



superposition in the measured total PDF does not allow an unambiguous interpretation for settling the question of the actual presence of the above-mentioned "anomalous" structural motives. То answer this question and characterize the amorphous LPS structure, it is necessary to resort to the additional support of spectroscopic data (for example, Raman spectra). Because groups of atoms have a specific vibrational fingerprint, Raman spectra help to identify such groups in the amorphous structure. To begin with, the team has calculated the Raman spectra of some crystalline reference structures, as shown in Figure 46. These allowed them to identify and factorize vibrational contributions from atomic groups involving phosphorus and sulfur atoms that are specific to different crystalline frameworks, namely $[PS_4]^{3-}$ for Li₃PS₄, $[P_2S_7]^{4-}$ for Li₇P₃S₁₁, and $[P_2S_6]^{4-}$ for Li₄P₂S₆.

Figure 45). Computed and experimental PDFs show fairly good agreement. However, the peaks

Figure 46. Raman spectra calculated for different Li-P-S crystalline phases.

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- [3] Perdew, J. P., K. Burke, and M. Ernzerhof. "Generalized Gradient Approximation Made Simple." *Physical Review Letters* 77 (1996): 3865–3868.
- [4] Sun, J., A. Ruzsinszky, and J. P. Perdew. "Strongly Constrained and Appropriately Normed Semilocal Density Functional." *Physical Review Letters* 115 (2015): 036402.

Patents/Publications/Presentations

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

Task 3.5 – Dendrite Growth Morphology Modeling in Liquid and Solid Electrolytes (Yue Qi, Michigan State University)

Project Objective. The project goal is to develop a validated model to predict lithium dendrite morphology evolution in both liquid and solid electrolytes during electrodeposition and stripping to accelerate the adoption of Li-metal electrodes in current and emerging battery technologies. To achieve this goal, the project has four objectives: (1) formulate a general framework that captures the electrochemical-mechanical driving forces for lithium morphology evolution; (2) consider the role of the nm-thin SEI in liquid electrolytes as well as the microstructures of μ m-thick solid electrolytes for lithium morphology evolution; (3) connect micron-scale phase-field models and atomic-scale DFT-based simulations via parameter- and relationship-passing to predict lithium dendrite nucleation and growth kinetics and morphology; and (4) validate the key input parameters and main conclusions of the multi-scale model as new capabilities are being developed step-by-step.

Project Impact. This atomically informed, fully coupled, electrochemical-mechanical dendrite morphology evolution model will allow the project to design the desired properties of artificial SEI coatings, the microstructure of solid electrolyte materials, and the corresponding battery operating conditions, so as to avoid dendrite growth during cycling. It will accelerate design of durable and safe lithium anodes for Li-S, Li-air, and all-solid Li-ion batteries. Thus, it directly impacts emerging technologies, such as Li-S, Li-air, and all-solid Li-ion batteries, which aim to meet the DOE target of the high-energy-density battery cells (> 350 Wh/kg) for EV applications and to push the cost below \$100/kWh_{use}.

Approach. A multiscale model approach is taken to connect micron-scale phase-field models and atomic-scale DFT-based simulations via parameter- and relationship-passing.

Out-Year Goals. The second-year goal is to establish the model to simulate metallic lithium precipitation in solid electrolytes while further developing the understanding of lithium dendrite growth in liquid electrolytes. To reach this goal, mechanical and electrochemical driving forces for lithium dendrite growth in solid electrolytes will be coupled in phase-field model, while DFT is used to address the lithium plating tendency in various solid electrolyte and coating materials. Validation of the model will come from experiments to correlate the distinctive transport properties of artificial SEI layers with their impact on lithium dendrite morphology.

Collaborations. This project collaborates with UMD, Sandia National Laboratories (SNL), PNNL, University of Arkansas, and University of Houston.

- 1. Identify an ideal microstructure of LLZO to avoid lithium dendrite growth. (Q1, FY 2019; It was predicted a coating layer, such as LiPON, between the Li/LLZO, will be more efficient in resisting lithium dendrite. A *Go* decision was made to experimentally vary this prediction.)
- 2. Develop a fully coupled Li/SEI/liquid electrolyte dendrite morphology model. (Q2, FY 2019; Completed)
- 3. Illustrate the relationship between Li/SEI interface roughness, adhesion, and dendrite morphology in a liquid electrolyte. (Q3, FY 2019; In progress)
- 4. Determine the effect of multicomponent SEI layer on dendrite morphology in a liquid electrolyte. (Q4, FY 2019; In progress)

Solid Electrolyte

Previously, the team has proposed that the excess electrons located on the internal defects of the solid electrolytes, such as pore and crack surfaces, will likely reduce Li-ions to metallic lithium. To compare with experiments, the team further developed a general phase field model of lithium plating in a polycrystalline solid electrolyte by incorporating Butler-Volmer kinetics, solid mechanics, and explicit lithium nucleation. The newly developed Li-metal phase evolution equation becomes,

$$\frac{\partial\xi}{\partial t} = -L_{\sigma}^{\xi} \left[\frac{\partial f_{ch}}{\partial\xi} - \kappa_{\xi} \nabla^{2} \xi + \frac{\partial f_{mech}}{\partial\xi} \right] - L_{\eta}^{\xi} h'(\xi) \left[-c_{Li+} c_{e} exp \frac{-\alpha n F \eta_{a}}{RT} + exp \frac{(1-\alpha)n F \eta_{a}}{RT} \right] + \omega \cdot \delta_{n}(c_{e}),$$

where the first term is the chemical-mechanical driving force, the second and third terms are the electrochemical driving force, and the third term describes the dendrite nucleation process. More specifically, the team obtained the local excess electron concentration, $c_e(x, t)$, based on the density of states (DOS) calculated from DFT. Since the GB electronic structures in the solid electrolytes are beyond the calculation limit of DFT, the GBs have taken the same electronic properties of the surfaces in the phase field model. This was indicated as "e@GB".

The team also compared with the case without any excess electrons on GB, labeled as "ideal."

The lithium plating processes in the solid electrolytes of grain sizes ranging from 75 to 500 µm were simulated in identical 500×500um 2D half-cells with a constant electric overpotential of 0.1 V. Figure 47a shows typical phase evolution over the simulation time of 800 s. Figure 47b shows the influence of grain size and excess electron at GBs on the lithium dendrite penetration depth. The excess electrons on the GBs have dramatically accelerated the rate of lithium dendrite growth. The sudden jumps of lithium dendrite penetration depth were associated



Figure 47. (a) Lithium dendrite growth morphology in polycrystalline LLZO with 75- μ m grain size and excess electrons on the grain boundaries. (b) The lithium dendrite penetration depth inside the solid electrolyte under different conditions. (c) Lithium dendrite intergranular morphology in LLAZO.

with isolated Li-metal nucleation process. An example of the isolated lithium (red) can be found in Figure 47a at 200 s. The isolated Li-metal nucleation did not occur when there were no excess electrons on the surface/GBs.

Experimentally, $Li_{6.25}La_3Zr_2Al_{0.25}O_{12}$ (LLZAO) pellets were prepared by solid-state reactions, and the cubic phase was confirmed by XRD. The critical current density (CCD), above which lithium dendrite will short circuit the pellet, was found to be around 0.025 mA cm⁻² in the Li|LLZAO|Li symmetrical cells. Several black lines showing up on the pellet after short circuit indicated the locations of lithium dendrite penetration. After fracture at the dendrite occurring places, the SEM images of the fractured surface from different view angles showed visible GBs, where accumulated lithium reacts with air, as shown in Figure 47c. Therefore, lithium dendrites propagate through intergranular paths inside the LLZAO sample.

Liquid Electrolyte

The above model for lithium dendrite growth inside a microstructure of a solid electrolyte can be used as the "explicit SEI" model for lithium dendrite growth in a liquid electrolyte, as the thickness of the solid electrolyte layer shrinks and a liquid phase is added.

Patents/Publications/Presentations

Publications

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- Liu, Z., Y. Li, Y. Ji, Q. Zhang, X. Xiao, Y. Yao, L-Q. Chen, and Y. Qi. "Atomically-Informed Phase-Field Modeling of Li and Mg Electrodeposition Morphologies." In preparation.
- Tian, H-K., Z. Liu, Y. Ji, L-Q. Chen, and Y. Qi. "Trapped electrons on the Internal Surfaces in Solid Electrolytes Accelerate the Li Dendrite Growth." In preparation.

Task 3.6 – First-Principles Modeling and Design of Solid-State Interfaces for the Protection and Use of Lithium-Metal Anodes (Gerbrand Ceder, University of California at Berkeley)

Project Objective. The project objective is to determine the design principles that control the solid electrolyte/lithium electrode interfaces by determining the reaction products stemming from pairing solid electrolytes and lithium metal. The project will conduct rigorous analysis based on computing electrolyte phase-diagrams closed and open to lithium. Li-ion transport properties in bulk electrolytes and interfacial products will be assessed through AIMD and NEB calculations. Simultaneously, a robust framework will be developed to identify factors controlling lithium dendrite propagation within solid electrolytes and interfacial products by accounting for irregularities, defects, and GBs, through a model that includes elements of fracture mechanics, thermodynamics, and electrochemistry.

Project Impact. The project will lead to understanding of the complex evolution of lithium metal/SEI during electrochemical cycling. The understanding of this process is necessary to determine design principles to develop reliable all solid-state batteries.

Approach. By incorporating NEB and AIMD methods, high-throughput computation is used to screen candidate solid electrolyte with high electrochemical stability and high ionic conductivity. DFT is used to calculate bulk elastic constants of materials, surface energies, and interface decohesion energies of GBs; continuum theory (elastic-plastic-fracture mechanics) is used to assess the resilience of solid electrolytes and grain/particle boundaries toward lithium dendrite growth and propagation. The finite element method is used to couple several physical processes, including electrochemical deposition, ionic diffusion, thermal expansion, and mechanical contacting.

Out-Year Goals. The out-year goals include the following: (1) obtain design criteria for solid electrolytes that can resist unstable lithium propagation by computing elastic properties, surface energies, and decohesion energies, and (2) adapt fracture mechanics models describing crack propagation to lithium dendrite propagation in different scenarios.

Collaborations. There are no collaborative activities this quarter.

- 1. Development of high-throughput framework to screen SSE materials based on phase stabilities. (Q1, FY 2019; Completed)
- 2. Adapt fracture models that describe crack propagation in materials to lithium dendrite propagation in perfect crystal with cracks. (Q2, FY 2019; Completed)
- 3. Adapt fracture models that describe crack propagation in materials to lithium dendrite propagation in perfect crystal with GBs. (Q3, FY 2019; On target)
- 4. Adapt fracture models that describe crack propagation in materials to lithium dendrite propagation in pressed/porous electrolyte. (Q4, FY 2019; On target)

Effect of Initial Defect Geometry on Current Density Distribution



Figure 48. Current density distribution near the crack on the surface of solid electrolyte.

The geometry of the initial defect on lithium metal / solid electrolyte interface is usually characterized by roughness measurements, which are commonly defined by several key parameters: (1) arithmetical mean length (the average length of defects on a rough surface), (2) density of peaks (represents the number of peaks per unit area, determining the width of the defect), and (3) Kurtosis (represents shape of the defect; the bigger this value, the sharper the defect is).

For perfect single crystal solid electrolytes, the existence of initial surface defects (including initial crack or void) is one of the main factors thought to enable lithium dendrite propagation. As shown in Figure 48, a small size surface defect would cause current density concentration, which would further lead to lithium accumulation near the defect and solid electrolyte fracture underneath the defect tip. The

shape of the initial defect can also affect the current density distribution, as shown in Figure 49. With the same

defect size, different shapes show the same maximal value of current density but different distributions: the smoothest distribution for a semi-circle shape defect, with the sharpest distribution for a cosine shape defect.

Initial defects (such as initial crack/void) on the surface of solid electrolytes are usually inevitable, with lengths ranging from 10 nm to 1 μ m. To prevent the penetration of lithium dendrite into solid electrolytes, surface engineering methods can be employed to make defects "shallow and wide." For example, mechanical polishing can reduce the defect length; surface corrosion and etching may increase defect width or change defect shape. Especially for initially narrow and long defects, a small increase of defect width or decrease of defect length can notably homogenize the distribution of current density, and therefore decrease the amount of lithium accumulation near defects.



Figure 49. Normal current density distributions along interface of three different defects.

Patents/Publications/Presentations

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

Task 3.7 – Large-Scale *Ab Initio* Molecular Dynamics Simulations of Liquid and Solid Electrolytes (Lin-Wang Wang, Lawrence Berkeley National Laboratory)

Project Objective. The project objective is to use AIMD simulations and other computational approaches to study the discharging mechanism in Li-S battery, especially for polysulfide interaction with liquid electrolyte solvent molecules, and cathode materials, as well as lithium diffusion mechanisms in various systems. The long-term goal is to use such theoretical understanding to provide guidance to develop better electrolyte and cathode systems to overcome the bottlenecks that prevent commercialization of the Li-S battery.

Project Impact. Making the Li-S battery a commercial reality will have a major impact on society and also help to realize the VTO goal of 500 km per charge for EV. However, the nature of chemical reaction makes it different from the traditional intercalation-based Li-ion battery. The molecular nature of Li_2S_n also allows solvation in the electrolyte. To address these problems, it is essential to have fundamental studies and understandings of the underlying mechanisms. The theoretical simulation can also play an important role in discovering and designing new cathode materials.

Approach. One major issue is solvation of Li_2S_n molecules in the electrolyte. The project seeks to solve this problem by both understanding the Li_2S_n -electrolyte interaction and discovering better cathode materials for optimal Li_2S_n -cathode binding. More specifically, it aims to develop reliable methods that combine classical force field (CFF) simulations with *ab initio* calculations to study the thermal dynamic properties of Li_2S_n in different electrolytes, as well as the interactions with different species within the electrolytes. It will also study Li_2S_n interaction with different cathode materials, especially for 2D cathode materials comprised with light elements in the right-upper corner of the periodic table. The goal is to have sufficient binding energy between the Li_2S_n molecules and the cathode material, so that, thermodynamically, the Li_2S_n will not be dissolved in the electrolyte. To study the Li_2S_n -electrolyte interaction, the project must accurately calculate the molecule entropy inside the solvent, which is a rather challenging task. It plans to use the bicanonical method to carry out the calculation. To design new cathodes, the project plans to focus on lightweight 2D materials. Genetic algorithm combined with DFT will be used to explore the structure and morphology of the Li_2S_n cluster on top of the 2D material. The stability of the solid electrolyte will be investigated by studying the surface reaction of such electrolytes.

Out-Year Goals. In outgoing years, the project will further develop the computational methods for more accurate entropy and interaction energy calculations for the electrolyte. This is a critical capability for studying the battery system. The project will also explore different cathode materials and morphologies. In particular, there is a vast space to explore using 2D materials as Li-S battery cathodes. Stability of the solid electrolyte is another topic to be investigated.

Collaborations. The project will collaborate with G. Liu and Y. Cui for cathode design. It has also collaborated with Prof. F. Pan of Beijing University for lithium battery research in general.

- 1. Develop reliable ways to calculate the diffusion barrier of lithium in either crystal or amorphous structure. (Q1, FY 2019; Completed)
- 2. Continue calculation of Li₂Sn/cathode binding energies, and phase diagrams, discovering new adequate cathode materials and morphologies. (Q2, FY 2019; Initiated)
- 3. Investigate the solid electrolyte, its pathways and surface stabilities, and electrolyte/anode interface. (Q3, FY 2019)
- 4. Develop method to calculate Li-ion chemical energy in liquid electrolyte with *ab initio* calculations. (Q4, FY 2019)

The team has finished their investigation of using sandwiched structure between layers of 2D material (like Mn-hexaaminobenzene, Mn-HAB) and layers of LiS as Li-S battery cathodes. The purpose is to design a cathode with high volumetric capacity. Although structurally such materials can be stable, one of the biggest challenges of the lithium diffusion is such material. Since the structure is amorphous for the Li-S layer, it is difficult to use traditional theoretical methods (like the NEB method) to calculate the diffusion barrier height. To overcome this problem, the team invented a new computational technology. In this method, a lithium atom is pulled by an external force, which makes it move along one direction and hence sample the energy landscape. A local thermostat is provided to the lithium atom, which allows it to explore the local environment and thus find the minimum energy patch. The team found that such an approach can reproduce the barrier height in a crystal structure as provided by the NEB method. More importantly, in an amorphous structure, where the



Figure 50. The effect of local thermostat. Two types of simulations are shown. The black line represents the normal Langevin thermostat where the whole system has a temperature of 300K, while the red curve represents a local thermostat where only the region surrounding the lithium atom that is pulled through the space has a higher temperature, while the other atoms have zero temperature.

NEB cannot be applied, this new method also provides information for barrier height (Figure 50). As shown in Figure 50, with a local thermostat surrounding the lithium atom, which is pulled through the space, the potential energy is much smoother and provides the necessary information to judge barrier height in the system.

Using this new method to calculate barrier height in an amorphous system, the team has calculated the diffusion constant in a Mn-HAB/LiS alternating layer sandwich system. The estimated barrier range and diffusion constants are shown in Figure 51. As the team can see, when the lithium content increases in the Li-S layer, the mobility decreases dramatically. For high lithium content, the low mobility might render the system impractical



Figure 51, Li-migration barriers distribution (a) and mobility as a function of temperature (b) of Mn-HAB-Li₁SS₈, Mn-HAB-Li₁SS₈, and Mn-HAB-Li₁SS₈ in X and Z directions. The mobility curve of lithium on graphene is also presented as a reference. The X direction is the in-plane direction, while Z is the out of plane direction.

to be used as lithium cathode material.

What the team has learned from this study is that, in order to design a Li-S cathode, in order to have sufficient reaction rate, the solvent has to be in direct contact with the Li-S species. Thus, instead of having a pure solid and closely packed Li-S 3D material, the team might need some porous structure, where the liquid lithium electrolyte can intrude inside the 3D lithium cathode material. In such cases, the study of liquid lithium electrolyte inside small confined space will become important. The team plans to investigate Li-ion diffusion within lithium solvent electrolyte inside such porous structure in the next phase of the study.

Patents/Publications/Presentations

Publications

- Chen, D., J. Jie, M. Weng, S. Li, D. Chen, F. Pan, and L. W. Wang. "High Throughput Identification of Li Ion Diffusion Pathways in Typical Solid State Electrolytes and Electrode Materials by BV-Ewald Method." *Journal of Materials Chemistry A* 7 (2019): 1300.
- Tsao, Y., M. Lee, E. C. Miller, G. Gao, J. Park, S. Chen, T. Katsumata, H. Tran, L. W. Wang, M. F. Toney, Y. Cui, and Z. Bao. "Designing a Quinone-Based Redox Mediator to Facilitate Li₂S Oxidation in Li-S Batteries." *Joule*. doi: https://doi.org/10.1016/j.joule.2018.12.018.

Task 3.8 – *In Operando* Thermal Diagnostics of Electrochemical Cells (Ravi Prasher, Lawrence Berkeley National Laboratory)

Project Objective. Effective heat dissipation in batteries is important for multiple reasons including performance, reliability, and safety. Currently, the thermal management of battery cells is provided at the system level by either forced air or liquid cooling, leading to reduced system-level energy densities and more failure-prone complex system designs. Furthermore, even given theoretically infinite system-level cooling applied to the external battery surface, peak temperature rise within a cell would still easily exceed acceptable threshold values due to poor thermal transport properties within the cell itself. It has not yet been possible to thermally profile a real cell during operation to provide a spatially resolved map of heat transfer 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 use this tool to reveal the largest thermal bottlenecks within a functioning Li-ion cell and create a complete materials-level cell thermal model.

Project Impact. The intrinsic thermal resistance of Li-ion cells is currently far higher than the theoretical value predicted by simply combining the known thermal properties of each macro component into an appropriate thermal model. The spatially resolved thermal transport property measurements from this project will reveal what key piece of information is missing. Preliminary data suggest that more than 75% of the total battery thermal resistance may be due to a single interface between the cathode and separator, previously unknown. An accurate understanding of the cell internal thermal transport is necessary to successfully optimize cell thermal performance to meet the challenges of extremely fast charging, mitigating thermal runaway, and improving battery performance, reliability, and safety.

Approach. To accomplish the project goals, the team will utilize two state-of-the-art thermal metrology techniques. They will build an in-house adapted 3ω technique to measure thermal transport properties throughout the bulk of a Li-ion cell while it is in operation, without affecting the operation of the cell. The 3ω system will work by using mm-scale sensors on the electrode current collectors to send variable-frequency thermal waves into the operational battery to quantitatively measure heat transport through different layers and interfaces. The team will also use the ultrafast optical time domain thermoreflectance (TDTR) technique to measure nanoscale thermal transport properties of constituent components of the cell that—unlike existing models—agrees with the empirical measurements of cell thermal performance.

Out-Year Goals. In outgoing years, the project will design, build, and implement the adapted 3ω metrology. This will involve developing and testing the metrology itself along with accompanying theory, designing compatible battery samples, and finally applying the technique to live cells. The team will use the already built TDTR system at LBNL to measure epitaxially grown cathode materials provided by collaborators. Combined, this will provide enough data to construct and validate a realistic all-scale thermal model of the battery.

Collaborations. This project collaborates with two LBNL groups: V. Battaglia's for cell assembly for 3-omega studies, and R. Kostecki's for pristine battery active material growths for TDTR studies.

Milestones

- 1. *Ex situ* high-accuracy measurements of thermal conductivity of individual battery components. (Q1, FY 2019; Completed)
- 2. Robust thermal model development. (Q2, FY 2019; Completed)
- 3. In situ battery 3-omega thermal measurements from anode and cathode side. (Q3, FY 2019; On schedule)
- 4. Detailed *in operando* thermal measurements performed. (Q4, FY 2019; On schedule)

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The team has successfully developed a robust thermal model for the 3-omega measurements. Furthermore, they have been able to fit their model to raw 3-omega data using the carefully measured *ex situ* properties from last quarter as input parameters (see Figure 52a). This measurement reveals that the separator-electrode thermal contact resistance (*TCR_{s-e}*) is the largest thermal resistance within the battery. For the just-assembled battery (before cycling), the team measures this contact resistance to be *TCR_{s-e}* = 1.74 cm²-C/W, which accounts for 45% of the battery unit cell's total thermal resistance of 3.87 cm²-C/W (see Figure 52b). In the case of the dry battery (before electrolyte is added), this contact resistance is much higher: *TCR_{s-e} Dry* = 5.35 cm²-C/W, which accounts for 56% of the battery unit cell's total thermal resistance of 9.58 cm²-C/W.



Figure 52. Fitted data and results. (a) Raw 3-omega data fitted with the project's robust thermal model. Input parameters from high accuracy *ex situ* measurements last quarter. (b) Schematic showing the breakdown of the contribution of each battery layer to the total thermal resistance. Interface resistance measured *in operando* using the project technique.

The project's thermal model accounts for the finite line width of its sensor, the multilayer geometry of the battery, the possible anisotropic thermal conductivity of each layer, and the surrounding environment of the battery (for example, pouch, external Styrofoam padding). It is based on continuum heat conduction equations and is solved in the frequency domain as the team drives the sensors with sinusoidally periodic heat fluxes.

Patents/Publications/Presentations

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

Task 3.9 – Multi-Scale 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 multi-scale modeling effort to obtain an in-depth understanding of the interaction of the electrode and the solid electrolyte aimed at developing highly efficient SSE batteries for vehicle applications. Input parameters needed for mesoscale (continuum) level calculations are being obtained from atomistic calculations including DFT and classical MD simulations. This atomistic input will enable a multi-scale 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, which can potentially catch fire. Replacement of the liquid electrolyte is necessary to decrease the fire hazard and improve safety associated with present-day Li-ion batteries. In addition, use of solid electrolytes 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 liquid electrolytes to improve safety and energy density in Li-ion batteries.

Approach. Parameters needed for mesoscale modeling of grain-interior, grain-boundary, and electrode-electrolyte interface will be calculated by DFT-based calculations along with Monte Carlo (MC) and MD simulations. The calculations will be used to determine properties of the electrode with the solid electrolyte as well as in GB regions of the solid electrolyte. 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 multi-scale modeling.

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

- 1. Computation of elastic. Conductivity properties of interfaces between LLZO with lithium as function of applied electric field for input into multiscale modeling. (Q1, FY 2019; Completed)
- 2. AIMD and interfacial binding energies calculations of the interface structure of the LLZO solid electrolyte and NMC-622 cathode material; Milestone 2. (Q2, FY 2019; Completed)

The use of ceramic solid electrolytes to create all solid-state batteries can enable use of lithium metal by preventing propagation of lithium dendrites, therefore enhancing safety and decreasing capacity fade. The interfaces between the cathode and solid electrolyte must be stable to enable use of these materials in batteries. Multi-scale modeling can provide insight into the mechanism for dendrite growth and other instabilities for guidance into how to prevent them. Mesoscale (continuum) modeling requires atomistic level input from theory or experiment to accurately capture physicochemical aspects during charge and discharge processes.

To understand the metal transport mechanism at the interface of NMC electrode and SSEs, it is critical to determine the various physical and chemical properties and reaction kinetics at the interface. The team is carrying out ab initio DFT calculations on LLZO interfaces with NMC cathode. They investigated two possible surfaces of NMC-622, (10-10) and (10-14), which are known to be the most stable surfaces and in previous literature reported to provide apparent Li-ion conduction paths. The interfacial supercell between NMC-622 cathode and LLZO(100) surface with lithium termination was then built. The lattice mismatch between LLZO(001) and NMC(10-14) is $\sim 11.19\%$, while LLZO(001) and NMC-622, (10-10), has 5.7% mean absolute strain. The calculations were carried out with the PBE functional with a plane wave basis and both generalized gradient approximation (GGA) and GGA+U calculations were performed.



Figure 53. Atomic relax structure of LLZO (001) and NMC (10–14) interface.

The stability of the interface between the NMC-622 electrode and the lowest energy LLZO surface [(100) lithium terminated] was investigated first with AIMD simulations. All production runs of the AIMD trajectories were obtained after 2 ps of thermal equilibration. The team then carried out calculations for the interfacial formation binding energy of the interfaces. The interfacial formation energy can be calculated as $E_f = E_{AB} - N_A E_A - N_B E_B$, where E_{AB} is the total energy of the fully relaxed interfacial supercell, containing N_A units of A and N_B units of B. E_A and E_B are the energy per unit of the stress-free pure A and B bulk structure, respectively. A summary of the results is given in Table 2 where binding energies are shown. Even with higher lattice mismatch, the interface of LLZO (001)/NMC (10-14) still shows higher interfacial formation energy.

A major issue encountered by SSEs is large resistance at the cathode/SEI. This large interfacial impedance is attributed partially to high charge transfer resistance, and partially to loss of contact between the cathode and solid electrolyte due to local delamination. Li-ion cells with solid electrolytes are fabricated with cathodes in a lithiated state. During the first charge process, the cathodes experience delithiation and shrink in size, which induces delamination at the cathode/SEI. Detachment between the electrode and electrolyte decreases the

	(10-10)	(10-14)
	NMC/LLZO	NMC/LLZO
GGA (SP)	1.27 J/m ²	1.81 J/m ²
GGA+U (SP)	1.23 J/m ²	1.75 J/m ²

Table 2. Interfacial formation energies obtained from *ab initio* calculations.

electrochemically active surface area, effectively increasing interfacial resistance. To correctly estimate the extent of the interfacial-delamination-induced increase in resistance, it is important to have an accurate estimate of the interfacial binding energy between the cathode and solid electrolyte. which will used future be in continuum modeling.

Patents/Publications/Presentations

Publication

 Barai, P., A-T. Ngo, K. Higa, L. A. Curtiss, and V. Srinivasan. "Mechanical Stress Induced Current Focusing and Fracture in Grain Boundaries." Submitted.

TASK 4 – METALLIC LITHIUM

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 polymer electrolytes has so far been limited due to parasitic SEI reactions and dendrite formation. Adding excess lithium to compensate for such losses effectively negates the high energy density for lithium in the first place. For a long lifetime and safe anode, it is essential that no lithium capacity is lost either (1) to physical isolation from 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.

BMR, Battery500, and other DOE 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 EV 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 µm of lithium per cycle, with pulse rates up to 10 and 20 nm/s (15mA/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 R&D efforts for years. This project takes a broad look at this challenge for both solid-state batteries and batteries continuing to use liquid electrolytes. For the liquid electrolyte batteries, MIT with Carnegie Mellon is investigating fluoridated components and other additives to form self-healing SEI coatings at the lithium surface. At University of Pittsburgh, alternatives to a standard Li-metal anode are being explored, including metal alloys and templated structures. Researchers at PNNL are pivoting from liquid electrolytes to hybrid electrolytes, with addition of a polymer component to a concentrated solvent-in-salt electrolyte. For solid-state batteries, programs are addressing both the electrolytes and the lithium interface. The stability of the garnet ceramic electrolyte with lithium is being investigated at ANL with materials from University of Michigan; this is now expanding to other solid electrolytes. The different mechanical and electrochemical mechanisms leading to the formation of shorting lithium features through the solid electrolytes is under study at ORNL, University of Michigan, and Michigan Technological University. And new ceramic-polymer composite electrolytes formed with scalable processing are investigated to reveal the properties of both the ceramic electrolyte interface and contacts of the solid electrolyte with the solid composite cathode and thin lithium anode.

Highlights. Promising Li-metal cycling was reported using electrolytes of organic solvent salt solutions with additive and different salts, highly concentrated solutions, and pure dense ceramic and glass electrolytes. The team observes how using thin (6- and 20- μ m) lithium as one of the contacts can provide a rapid assessment of the lithium stability.

For the solid electrolyte systems:

Full cells with a composite electrolyte composed of a polymer electrolyte heavily loaded with ceramic electrolyte particles were cycled with thin films of lithium and even as a Li-free battery where all the lithium comes from a LiFePO₄ cathode. Due to the thin lithium, degradation processes are quickly observed and are being analyzed. A new composite provides 0.1 mS/cm by reducing the interparticle resistance of the ceramic phase. (Task 4.5)

- Surface/bulk analysis was used to examine the reaction of LLTO with lithium metal as a function of the crystallographic orientation with respect to the interface. Further, amorphous films of LLTO were compared to the crystalline films, confirming earlier reports that the titanium in the amorphous films showed no indication of reduction. Here, XPS was used to evaluate the titanium oxidation state after three days of contact with lithium. (Task 4.7)
- Sol-gel processing was used to prepare carbon-coated nanopowders of Na₃MnSr(PO₄)₃, a sodium cathode material with a NASICON crystal structure. The Mn⁺⁴ is reduced to Mn⁺² with two voltage plateaus at 4.0 and 3.5 V versus sodium metal. The structure was stable for cycling and inhibited Jahn-Teller distortion of Mn⁺³. (Task 4.6)

For the liquid electrolyte system:

- Investigations of highly concentrated electrolytes continue, here with the mole ratio DME to LiFSI varying from 0.7 to 1.2. Raman reveals the fraction of lithium cations associated with FSI⁻ anion and with DME solvent molecules. With the more concentrate solutions, all of the Li⁺ ions are associated. The conductivity increased and T_g decreased with higher DME content. Hybrid electrolytes were also formed when PEO was added. With this electrolyte, lithium plated onto copper is denser, but the conductivity is slightly lower than for the PEO-free compositions. (Task 4.1)
- The identity of a promising electrolyte additive, 1,3,2-dioxanthiolan-2,2-oxide (DTD), was revealed. When added to the LiPF₆ FEC-DMC electrolyte, this additive reacts to form SEI containing LiF, Li₂SO₃, and Li₃PO₄ in agreement with DFT models. The DTD improves stability for cycling full cells of lithium versus LiCoO₂, assembled with only 20-µm-thick lithium anode, for 130 cycles with 80% capacity retention. (Task 4.2)

For the lithium anode:

- Lithium plating/de-plating on a nanostructured carbon-based electrode was examined. A small fraction of the capacity is associated with intercalation processes, while achieving a total capacity of ~ 3Ah/g carbon, and 4 mAh/cm². The overpotential is separated to reveal nucleation and steady-state growth processes. (Task 4.3)
- Studies of the buried interface of lithium with a solid electrolyte are leading to a description of how the creep and diffusion processes in metallic lithium provide mechanisms to accommodate inhomogeneities and stress generated by lithium plating and stripping processes. A comparison of the current-induced strain rate and the creep-induced strain rate suggests a critical stack pressure. In a separate study, the current-induced stress is mapped for different volumes of lithium metal features protruding into a solid electrolyte. The map identifies conditions with relaxation from diffusion and dislocation glide. (Task 4.8)

Task 4.1 – Lithium Dendrite Prevention for Lithium Batteries (Wu Xu and Ji-Guang Zhang, Pacific Northwest National Laboratory)

Project Objective. Enable lithium metal to be used as an effective anode in rechargeable Li-metal batteries for long cycle life. The investigation in FY 2019 will focus on effects of various organic solvents, inorganic solid electrolytes, and polymers on ionic conductivity, lithium CE, lithium anode morphology, and battery performances in terms of long-term cycling stability and rate capability at room temperature and elevated temperatures. The compatibility of such electrolytes with 4-V, high-Ni, NMC cathode will also be investigated.

Project Impact. Lithium metal is an ideal anode material for rechargeable batteries. Unfortunately, uncontrollable dendritic lithium growth and limited CE during repeated lithium stripping/deposition processes have prevented practical application. This work will explore the new hybrid composite electrolytes that can lead to dendrite-free lithium deposition with high CE. The success of this work will increase energy density of Li-metal and Li-ion batteries and accelerate market acceptance of EVs, especially of PHEVs as required by the EV Everywhere Grand Challenge.

Approach. The approach will encompass several areas. (1) Develop appropriate high-concentration electrolytes (HCEs) that have high lithium CE over 99% and are stable with high-Ni NMC (for example, NMC-532) cathodes. (2) Add a small amount of inorganic solid electrolytes and proper polymers into the HCEs to form uniform mixtures, which will be cast into thin films. (3) Solid-state polymer-in-salt electrolyte will be prepared through the hot-pressing method. The effects of the type and content of inorganic fillers and polymers on the ionic conductivity, the electrochemical window, the lithium CE and the morphology will also be tested.

Out-Year Goals. The long-term goal of the proposed work is to enable lithium and Li-ion batteries with > 120 Wh/kg (for PHEVs), 1000 deep-discharge cycles, 10-year calendar life, improved abuse tolerance, and less than 20% capacity fade over a 10-year period.

Collaborations. This project collaborates with C. Wang of PNNL on characterization by TEM/SEM; Drs. K. Xu and M. Ding of ARL on solvent purification and differential scanning calorimetry (DSC) measurements; and Dr. B. Polzin at ANL on coated electrode sampling.

- 1. Achieve over 300 cycles for 4-V Li||NMC batteries with ~ 2 mAh/cm² cathode loading. (Q4, September 30, 2018; Completed)
- 2. Investigate effects of high-concentration electrolytes on lithium CE and deposited lithium morphology. (Q1, January 15, 2019; Completed)
- 3. Investigate effects of polymers in hybrid electrolytes on lithium CE and deposited lithium morphology. (Q2, March 31, 2019; In progress)
- 4. Develop an HCE with lithium CE > 98% and oxidation potential up to 4.4 V. (Q3, June 30, 2019; In progress)
- 5. Achieve over 100 cycles for Li||NMC-532 batteries with medium cathode loading. (Q4, September 30, 2019; In progress)
This quarter, the team investigated the mechanism behind the improved oxidation-stability of hybrid electrolytes, the relationship between ionic conductivity and glass transition temperature (T_g), and the effects of polymer in hybrid electrolytes on lithium CE and deposited lithium morphology.

To better understand why the oxidation voltages of high-concentration liquid electrolytes and hybrid electrolytes are increased, the Raman spectra were investigated. Two bands at 826 cm⁻¹ and 851 cm⁻¹ are from free 1,2-dimethoxyethane (DME) solvent molecules, and the band at 879 cm⁻¹ is from Li⁺-solvated DME solvents (Figure 54a). The band at 720 cm⁻¹ is from the free FSI⁻¹ anion. In 1 M solution (where x=8.9 in Li(DME)_xFSI), there are both free and Li⁺-coordinated DME bands, and the majority of FSI⁻ exists as free anion. In Li(DME)_{0.7}FSI, there is no band for free DME molecules, indicating that all DME molecules coordinate to Li⁺. And there are no free FSI⁻ anions, either; all of them exist as Li⁺ associated FSI⁻. The series of Raman analysis suggests that in Li(DME)_{0.7}FSI, all FSI⁻ anions and DME solvents interact with Li⁺ and no free DME exists. The oxygen atoms on DME donate lone pairs to the Li⁺ cation, and the extraction of electrons from the lone pairs of [Li(DME)_{0.7}]⁺ cation becomes more difficult than that of free DME. Therefore, the oxidation stability is increased. Similarly, in the hybrid electrolyte, no free DME and EO exist, and it has improved the oxidation stability.

In the high-concentration liquid electrolytes, T_g decreases from -63.6°C for Li(DME)_{0.7}FSI to -79.1°C for Li(DME)_{1.2}FSI with increasing DME ratio. At the same time, the ionic conductivity of the electrolytes is increased several times with increasing DME ratio. The reverse trend implies a reciprocal relationship between ionic conductivity and T_g . The similar reverse trend is observed between ionic conductivity and T_g with the change of DME ratio in the hybrid electrolytes. This is consistent with the VTF equation: $\sigma = \sigma_0 T^{-1/2} \exp(-\frac{B}{T-T_0})$, where T_0 is normally called the equilibrium glass-transition temperature (around T_g -50 K); therefore, with the decrease of T_g , the conductivity σ increases.

Lithium CE of Li||Cu cells was tested. Li(DME)_{0.7}FSI has a lithium CE of 97.5% at 60°C. After adding PEO, the hybrid electrolyte Li(DME)_{0.7}FSI-PEO_{0.6} shows a lithium CE of 95.9%, only a little lower than the liquid electrolyte. Large granular-like particles can be observed in Li||Cu cell with Li(DME)_{0.7}FSI, and the thickness of deposited lithium metal is around 12 μ m. When Li(DME)_{0.7}FSI-PEO_{0.6} is used as electrolyte, there are fewer gaps between deposited lithium particles and the surface is smoother. The deposited lithium metal is around 13 μ m. PEO in the hybrid electrolyte leads to smoother deposition of lithium metal.



Figure 54. Raman spectra of (a) Li(DME)_xFSI and (b) Li(DME)_xFSI-PEO_{0.6}. Differential scanning calorimetry and conductivity of (c) Li(DME)_xFSI and (d) Li(DME)_xFSI-PEO_{0.6}. (e) Coulombic efficiency of Li||Cu cell at 0.5 mA cm⁻². Scanning electron microscopy images of deposited lithium particles at 0.2 mA cm⁻² with capacity of 1.5 mAh cm⁻² with (f) Li(DME)_{0.7}FSI and (g) Li(DME)_{0.7}FSI-PEO_{0.6}.

Publication

 Peng, Z., F. Ren, S. Yang, M. Wang, J. Sun, D. Wang,* W. Xu, and J. Zhang.* "A Highly Stable Host for Lithium Metal Anode Enabled by Li₉Al₄-Li₃N-AlN Structure." *Nano Energy* 59 (2019): 110–119.

Presentations

- 2019 International Battery Seminar & Exhibit, Fort Lauderdale, Florida (March 26–27, 2019): "Advancing Lithium Metal Batteries"; W. Xu. Featured presentation.
- International Battery Association 2019, La Jolla, California (March 3–8, 2019): "Effects of Separators on Lithium Metal Batteries"; X. Li, J. Tao, D. Hu, M. H. Engelhard, W. Zhao, J. Zhang, and W. Xu.

Task 4.2 – Self-Assembling and Self-Healing Rechargeable Lithium Batteries (Yet-Ming Chiang, Massachusetts Institute of Technology; Venkat Viswanathan, Carnegie Mellon University)

Project Objective. The project objectives are as follows: (1) investigate formation of lithium halide containing SEI, (2) characterize the structure and composition of the SEI surface film and morphology of the electrochemically deposited lithium, and (3) develop combinations of electrolytes (solvents + salts) and electrolyte additives that produce a highly Li-ion conducting, mechanically robust, and self-healing SEI to suppress lithium dendrite formation and improve CE.

Project Impact. Efforts to achieve practical use of the Li-metal anode in rechargeable lithium batteries have long been plagued by lithium dendrite formation and low CE. Lithium dendrites cause battery short-circuits, leading to serious safety hazards. The low CE of Li-metal anodes demands use of excess lithium to offset the lithium loss during cycling, which lowers the overall energy density of the battery. If successful, this project will enable self-forming and self-healing SEI containing alkali and/or alkaline earth halides that can suppress dendrite formation and improve CE. This will eventually enable high-energy-density (> 400 Wh/kg) and long-cycle-life (> 500 cycles, 80% capacity retention) Li-metal batteries.

Approach. The project approach involves the following: (1) identifying suitable combinations of solvents, Li-electrolyte salts, and halide and other additives that can produce highly Li-ion conducting, mechanically robust, and self-healing SEI, (2) using integrated theory and experiment, and (3) assembling and testing symmetric and asymmetric cells and Li-metal batteries comprising a high areal-capacity cathode (> 3 mAh/cm²) and a capacity-limited Li-metal anode (< 130% lithium excess).

Out-Year Goals. The project will down-select electrolyte compositions, develop designs for prototype full cells of > 10 mAh capacity, and fabricate/deliver cells to DOE-specified laboratories for testing and evaluation.

Collaborations. This project collaborates with 24M Technologies Inc. on $18 \text{ cm}^2/80 \text{ cm}^2$ pouch cell fabrication and tests.

- 1. *Go/No-Go Decision*: Demonstrate Li-Li symmetric cells that meet established criteria cycling at \geq 3 mAh/cm² at C/5 rate over 30 cycles. (Q1, FY 2019; Completed ahead of schedule)
- 2. Demonstrate at least one Li-Li symmetric cell that cycles ≥ 3 mAh/cm² at C/5 rate over 50 cycles without short-circuit. (Q2, FY 2019; Completed)
- 3. Deliver 12 baseline cells of > 10 mAh capacity for DOE testing. (Q3, FY 2019; June 30, 2019)
- 4. Establish quantitative criteria for solid-electrolyte/liquid electrolyte combinations that exhibit self-healing functionality. (Q4, FY 2019; September 30, 2019)

This quarter, cycling results are reported for asymmetric Li-Li cells and Li-LiCoO₂ full cells utilizing the electrolytes developed in this project. As shown in previous reports, an asymmetric Li-Li cell test was developed that is able to quantify both the CE and area-specific impedance (ASR) of Li-metal electrodes. In this quarter, efforts were focused on testing of both asymmetric Li-Li cells and Li-LiCoO₂ full cells, under conditions where the area capacity is \geq 3 mAh/cm², at C/5 rate. The team also reports the comparison of DFT results with XPS data obtained on the Li-anode surface.

The asymmetric Li-Li cells were assembled using Li-metal electrodes with different thicknesses and area-capacities. The working electrode is a 20-µm-thick lithium film coated on a copper foil (area capacity ~ 4.12 mAh cm⁻²); the counter electrode is a 750-µm-thick lithium foil. The two electrodes were assembled in a CR2032-type coin-cell with a Tonen polyethylene separator and 40-µL electrolyte. The cells were cycled at a current density of 0.6 m/cm⁻² to an area capacity of 3.0 mAh cm⁻² per deposition/stripping cycle. Li-metal full cells were assembled using a "high-voltage" LiCoO₂ cathode (area-capacity ~ 4.2 mAh/cm² when charged to 4.5 V versus Li+/Li), a 20-µm-thick lithium anode coated on a copper foil (areal capacity ~ 4.12 mAh/cm²), and a single-layer polyethylene separator. The full cells were first cycled at 0.1 C rate for 3 cycles, and then cycled at 0.2 C charge – 0.5 C discharge (1 C = 170 mA/g = 3.91 mA/cm² in the project's tests).

As shown in Figure 55, the $LiCoO_2$ full cell containing the 1 M LiPF₆ FEC-DMC showed 80 cycles to 80% of initial capacity, and the 1 M LiPF₆ FEC-DMC + DTD electrolyte showed 130 cycles, where DTD is 1,3,2-dioxathiolan-2,2-oxide. The team also made full cells with a 50-µm-thick lithium anode, and it showed 250 cycles for the same FEC-DMC+DTD electrolyte.

DFT simulations of the decomposition of EC, DMC, FEC, DFEC, CF₃EC and DTD on lithium surfaces were formed. FEC and DFEC spontaneously decompose to form LiF and other organic compounds, while EC, DMC, and CF₃EC undergo partial decomposition and form no LiF. DTD is a special compound that reacts with lithium and LiPF₆ to form LiF, Li₂SO₃, Li₃PO₄ and other organic species. These results are shown in Figure 56. XPS measurements on the lithium anodes using these different electrolytes are shown in Figure 56. They show significant LiF content in FEC, DFEC, and DTD cases, validating the DFT calculations. Also regarding the FEC+DMC+DTD electrolyte, the team observes an increase in the LiF content compared to the FEC+DMC case along with increase in sulfur content in the form of ROSO₂Li, Li₂SO₄, and Li₂SO₃ as the battery is cycled, which again validates the reaction pathway proposed for DTD using DFT.



Figure 55. Cycling results for Li-LiCoO₂ full-cell tests using three electrolytes from the standardized Li-metal full-cell tests. Comparison of 20- μ m and 50- μ m lithium anodes.



Figure 56. Density functional theory calculated decomposition products for five solvents. Narrow-scan X-ray photoelectron spectroscopy measurements of the lithium anode surface using the different electrolytes.

Patents

- Chiang, Y-M., V. Viswanathan, L. Li, V. Pande, D. Krishnamurthy, Z. Ahmad, and W. H. Woodford.
 "Lithium Metal Electrodes and Batteries Thereof." U. S. Patent Application No. 20170288281A1.
- Chiang, Y-M., V. Viswanathan, L. Li, V. Pande, and D. Wang. "Electrolytes for Alkali Metal Electrodes and Batteries Using Same." U. S. Patent Application No. 62/716150.

Publication

 Zhu, Y., V. Pande, L. Li, S. Pan, B. Wen, D. Wang, V. Viswanathan, and Y-M. Chiang. "Design Principles for Self-Forming Interfaces Enabling Stable Lithium Metal Anodes." arXiv preprint, arXiv:1903.09593.

Task 4.3 – Engineering Approaches to Dendrite-Free Lithium Anodes (Prashant Kumta, University of Pittsburgh)

Project Objective. This project will yield Li-metal anodes with specific capacity $\ge 2000 \text{ mAh/g}$ ($\ge 4 \text{ mAh/cm}^2$), ~ 1000 cycles, and CE $\ge 99.99\%$ with superior rate capability. The goal is to (1) systematically characterize different approaches for generation of dendrite-free Li-metal anodes while also providing understanding of the scientific underpinnings, and (2) evaluate the microstructure and electrochemical performance of dendrite-free Li-metal anodes. Generation of high-performance, dendrite-free Li-metal anodes will successfully demonstrate generation of novel sulfur cathodes, affording fabrication of Li-S batteries meeting the targeted gravimetric energy densities $\ge 350 \text{ Wh/kg}$ and $\ge 750 \text{Wh/l}$ with a cost target \$125/kWh and cycle life of at least 1000 cycles for meeting the EV Everywhere Grand Challenge blueprint.

Project Impact. Dendrite formation in electrochemical systems occurs due to inhomogeneous current densities coupled with local diffusion gradients, surface roughness, and kinetic roughening. Lithium dendrite formation and growth are, however, not well understood; adding to the complexity is SEI formation. Control and elimination of Li-metal dendrite formation are challenging. If overcome, this would render universal adoption of Li-anode batteries for stationary and mobile applications. This project is a scientific study of novel approaches to address dendrite formation in Li-anode batteries, electrolyte decomposition, and associated cell failure. Development of dendrite-free, high-performance lithium anodes will enable use of Li-free cathodes, opening a myriad of possibilities to push the envelope in terms of cathode capacity and battery energy density.

Approach. This project will explore several approaches focused on engineering new structurally isomorphous metallic alloys combined with engineering the surface of metallic lithium as well as the current collectors, including developing novel high Li-conducting conjugated polymers and composite structures. The unifying theme is to initiate a uniform nucleation with homogenous growth, eliminating preferential reversible plating and de-plating, and thus resulting in dendrite-free, high-energy-density Li-metal anodes. This project comprises three major phases to be successfully completed in three years. In the first year, the team developed foams as templates for lithium deposition. This year, the team will focus on developing Li-rich structurally isomorphous alloy (SIA) anodes and generating composite multilayer anodes (CMAs).

Out-Year Goals. The out-year goal is to utilize the novel anode architectures discovered in this project to design full batteries, likely Li-S, that achieve advanced high-energy-density, high-rate, extremely cyclable cell development.

Collaborations. The project works with Dr. M. K. Datta and Dr. O. I. Velikokhatnyi (University of Pittsburgh) as co-PIs. It also collaborates with Dr. A. Manivannan (Global Pragmatic Materials), XPS analysis; Dr. D. Krishnan Achary (University of Pittsburgh), solid-state magic angle spinning NMR (MAS-NMR) characterization; and Dr. J. R. Gaines (Kurt Lesker), thin-film system fabrication / characterization.

- 1. Integrated electrode (IE) generation to encompass the three different paths of development, that is, coating development/PF, development of CMAs and SIAs exploration including optimizing the maximize lithium content in SIA with no dendrite formation over extended cycling, especially at high rates to demonstrate high capacity. (Q1-Q3, June 2019; Ongoing)
- 2. Fabrication/characterization of for 10 mAh cell configurations. (October 2019; Ongoing)

The major fundamental issues related to lithium plating are the high plating over potential (both nucleation and growth) followed by inefficient electron transfer due to progressive growth formation and of electronically non-conducting SEI layers causing irreversible losses. Hence, a nanostructured carbon-based electrode was designed and fabricated to control the electronic conductivity as well as Li⁺ transfer from the solvent at the growing lithium site. The surface of nanostructured these electrodes



Figure 57. Nucleation and growth behavior of carbon nano -architectures at different current rates indicating the stability up to 7 mAh/cm².

provides uniform deposition sites causing homogenous growth yielding coalescence of the growth sites with a reduction in electron transfer resistance within the electrode from the surface of the lithium growth site.



Figure 58. Variation of lithium plating potentials on carbon nano-architectures at different current densities showing low nucleation over-potentials.



Figure 59. Columbic Efficiency for lithium de-plating at current density of 1 mA/cm² for plating areal charge capacity of 4 mAh/cm² in Li/Li⁺ cell.

Lithium intercalation and de-intercalation reaction in these carbon-based electrodes shows a capacity contribution of ~ 100-150 mAh/g and ~ 40-50 mAh/g at low (25 mA/g) and high (4 A/g) current rates, respectively, with a capacity loss of ~ 250-300 mAh/g during the initial cycles. Subsequently, sands time experiment for single plating experiment was conducted in a two-electrode pressure-less system to study the lithium plating stability (Figure 57). The electrodes show a stable plating capacity of ~ 3000 mAh/g with an areal capacity of ~ 6-7 mAh/cm² before arriving at the undesired mossy/fractal lithium plating for an active material loading of ~ 2-3 mg/cm². The steady-state growth region shows minimal fluctuations (data point recorded @0.5 mV voltage fluctuation) reflecting a uniform growth front. Even at high current density of 5 mA/cm², the system shows a low nucleation over-potential ~ 0.33V (Figure 58). This carbon-based nano-architecture shows CE of ~ 95-97% during initial cycles, stabilizing at ~ 99.71-99.87% for 150 cycles for a plating charge density of 4 mAh/cm² at current densities of 1 mA/cm² (Figure 59). Similar response is seen at 4 mA/cm². Continuing efforts will target mechanisms to further improve the CE.

Patents/Publications/Presentations

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

Task 4.4 – Composite Electrolytes to Stabilize Metallic Lithium Anodes (Nancy Dudney and X. Chelsea Chen, Oak Ridge National Laboratory)

Project Objective. The project has several objectives: (1) prepare composites of representative polymer and ceramic electrolyte materials to achieve thin membranes that have the unique combination of electrochemical and mechanical properties required to stabilize the metallic-lithium anode while providing for good power performance and long cycle life, (2) understand the Li-ion transport at the interface between polymer and ceramic solid electrolytes, which is critical to effective conductivity of the composite membrane, (3) identify key features of composite composition, architecture, and fabrication that optimize performance, and (4) using practical and scalable processing, fabricate thin electrolyte membranes to use with a thin metallic lithium anode to provide good power performance and long cycle life.

Project Impact. A stable lithium anode is critical to achieve high energy density with excellent safety, lifetime, and cycling efficiency. This study will identify key design strategies that should be used to prepare composite electrolytes to meet the challenging combination of physical, chemical, and manufacturing requirements to protect and stabilize the Li-metal anode for advanced batteries. By utilizing well characterized and controlled component phases, design rules developed for composite structures will be generally applicable toward substitution of alternative and improved solid electrolyte component phases as they become available. Success will enable DOE technical targets: 500-700 Wh/kg, 3000-5000 deep discharge cycles, and robust operation.

Approach. This project seeks to develop practical solid electrolytes to provide stable, long-lived protection for the Li-metal anode. Current electrolytes have serious challenges when used alone; oxide ceramics are brittle, sulfide ceramics are air sensitive, polymers are too resistive and soft, and many electrolytes react with lithium. Composites provide a clear route to address these issues. While work continues to emphasize study of ceramic electrolyte/polymer electrolyte interfaces, this effort has expanded to address (1) practical processing routes to fabricate full batteries using better composite electrolytes with a composite cathode and thin Li-metal anode, and (2) introduction of alternative polymer and ceramic phases to replace well-known model materials and develop improved composite electrolytes. In addition to solid-state devices, hybrid batteries are investigated using a fluid or gel catholyte within the porous cathode. Coatings have also been employed to stabilize electrode interfaces. These directions increase complexity of the studies, but are needed to improve cycling stability and rate performance and to advance practical implementation of the solid electrolyte and Li-anode technology.

Out-Year Goal. The goal is to use advanced manufacturing processes where the architecture of the composite membrane can be developed and tailored to maximize performance and cost-effective manufacturing.

Collaborations. Work is conducted by Dr. Y. Zhang and Dr. X. Chen. Ceramic electrolyte powders are obtained from Ohara Corporation and Prof. J. Sakamoto (University of Michigan). Polymer electrolytes are provided by Prof. Z. Bao (Stanford University) and T. Saito (ORNL). The team will work with new partners from U. S.–German Cooperation on Energy Storage.

- 1. Fabricate full cell using thin evaporated lithium anodes. Compare full-cell performance using thick and thin evaporated lithium anodes. (Q1, FY 2019; Completed)
- 2. Fabricate gel composite electrolytes with a target room-temperature conductivity of 1×10^{-4} S/cm. Evaluate ion transport, and thermal and structural properties. (Q2, FY 2019; Completed, achieved target)
- 3. Expand composite materials portfolio to include non-PEO type of polymer electrolytes. Identify promising polymer ceramic systems with interfacial ASR less than 10 ohm. (Q3, FY 2019)
- 4. Work with partners from U. S.–German Cooperation on Energy Storage on WP3, Interface of Lithium with Polymer Electrolyte. Complete milestones as detailed in the proposal. (Q4, FY 2019)

This quarter, the team constructed three cells with the same electrolyte and cathode design. The electrolyte consists of a layer of composite electrolyte (CPE) sandwiched by two layers of polymer electrolyte (PE), fabricated using the same protocol as last quarter. The cathode was also the same LiFePO₄ (LFP) composite cathode. The team compared three anode designs: cell 1, 6-µm lithium, vapor evaporated onto the PE layer; cell 2, 6-µm lithium, vapor evaporated onto the current collector copper; and cell 3, no lithium, just the current collector copper. Cycle 1 performance of the cells is shown in Figure 60. The CE of cell 2 (lithium on copper) is the highest. The cell 1 discharge capacity is lower than charge capacity. As shown by the inset of Figure 60, the evaporated lithium is discolored by reaction of the exposed surface and appears to be more uniform on copper than for the PE. Cell 3 without any pre-existing lithium has the lowest discharge capacity. This study suggests that a thin layer of lithium is adequate to make the cell cycle, but further effort is required to ensure that interfaces are protected from reaction.



Figure 60. Cycle 1 discharge and charge curves of three cells with the same *polymer electrolyte / composite electrolyte / polymer electrolyte* and LiFePO₄ cathode. The designs of anode layer differ.



Figure 61. Properties and performance of gel composite electrolytes with different loadings of ceramic. (left) Conductivity Arrhenius plot. (center) Storage modulus as a function of temperature. (right) Lithium symmetrical cell cycling.

Continuing effort from the last quarter of FY 2018, the team characterized the conductivity, mechanical modulus, and lithium symmetrical cell performance of gel composite electrolytes (GCE) with three ceramic loadings: 30 wt%, 50 wt%, and 70 wt% (GCE-30, GCE-50, and GCE-70), shown in Figure 61. The conductivity of GCE-30 and GCE-50 was the same as the gel polymer electrolyte (GPE) without any ceramic. GCE-70

showed 1 order of magnitude lower ionic conductivity. The storage modulus of GCE-30 and GCE-50 was merely slightly higher than GPE. However, the lithium symmetrical cell of GCE-50 showed the best performance, featuring smaller overvoltage and higher rate capability (rate data not shown). The team believes the local high modulus of the ceramic particles (inset, center panel) is more important than the overall mechanical modulus of the membrane.

This quarter, the team introduced a new approach to fabricate composite electrolytes that overcomes the barrier of large interparticle resistance. This method to fabricate the composite solid electrolyte film breaks away from the



Figure 62. A thin membrane of ceramic prior to filling pores with PEO.

traditional mixing-then-casting method. First, the ceramic powder is formed as a thin porous structure, $20-\mu m$ thick (Figure 62). This is filled with cross-linkable PEO. The composite has an ionic conductivity 1.0×10^{-4} at 30° C, with an activation energy of 0.44 eV. The high ionic conductivity was achieved by greatly reducing the interparticle resistance.

Patents/Publications/Presentations

Publications

- Chen, X. C.,* X. Liu, A. S. Pandian, K. Liu, F. M. Delnick, and N. J. Dudney.* "Determining and Minimizing Resistance for Ion Transport at the Polymer/Ceramic Electrolyte Interface." ACS *Energy Letters* 4 (2019): 1080–1085.
- Palmer, M. J., S. Kalnaus, A. S. Westover, N. J. Dudney, and X. C. Chen. "A Three-Dimensional Interconnected Structure of LATP/PEO as a Thin Film Composite Solid Electrolyte." In preparation.
- Zhang, Y., et al. "Thin Evaporated Li in the Cycling of Composite Solid-State Batteries." In preparation.

Presentations

- APS March Meeting, Boston, Massachusetts (March 2019): "Study of Segmental Dynamics in Polymer-Ceramic Composite Electrolytes using Quasi-Elastic Neutron Scattering"; X. C. Chen, R. L. Sacci, N. C. Osti, M. Tyagi, and N. J. Dudney.
- 14th China-U. S. Electric Vehicle and Battery Technology Information Exchange, Shaoxing, China (March 2019): "Challenge Facing Solid Electrolytes for Batteries"; X. C. Chen, A. S. Pandian, R. L. Sacci, Y. Zhang, and N. J. Dudney.

Task 4.5 – Lithium Batteries with Higher Capacity and Voltage (John B. Goodenough, University of Texas at Austin)

Project Objective. The project objective is to develop an electrochemically stable alkali-metal anode that can avoid SEI layer formation and alkali-metal dendrites during charge/discharge. To achieve the goal, a thin and elastic solid electrolyte membrane with a Fermi energy above that of metallic lithium and an ionic conductivity $\sigma > 10^{-4}$ S cm⁻¹ will be tested in contact with alkali-metal surface. The interface between the alkali-metal and the electrolyte membrane should be free from liquid electrolyte, have a low impedance for alkali-metal transport and plating, and keep good mechanical contact during electrochemical reactions.

Project Impact. A safe alkali-metal anode that can be plated/stripped reversibly at low resistance and high rates over many thousands of charge/discharge cycles would maximize the volumetric energy density for a given cathode of a rechargeable battery for powering an all-electric road vehicle. Such a battery could also be used for stationary back-up storage of electric power from energy sources other than fossil fuels.

Approach. The project will design, make, and test cells. The approach is to introduce a solid-electrolyte interfacing the anode and a coating on the anode current collector that is wet by a lithium anode. The solid electrolyte should also be wet by the anode to create a bond that is strong enough to constrain the anode volume changes to be perpendicular to the anode/electrolyte interface.

Out-Year Goals. The out-year goal is to develop coin cells that are safe and low-cost with a long cycle life at a voltage V > 3.0 V that can compete with the internal combustion engine for powering a road vehicle.

Collaborations. This project collaborates with A. Manthiram at UT Austin and K. Zaghib at HQ.

- 1. Test a new, low-cost ceramic separator concept with a liquid electrolyte and an alkali metal anode. (Q1, FY 2019; Completed)
- 2. Test redox energies and cyclabilities of novel NASICON-structured cathode materials in a Na-ion battery. (Q2, FY 2019)
- 3. Synthesize and evaluate solid sulfide electrolytes. (Q3, FY 2019)
- 4. Investigate oxygen redox chemistry for reversible high-voltage Na⁺ intercalation. (Q4, FY 2019)

The team has synthesized and tested a cathode material $Na_3MnZr(PO_4)_3$ with NASICON structure that could increase the energy density of current rechargeable sodium batteries while also reducing the cost through the use of earth-abundant TMs of manganese and zirconium. The voltage and energy density of a sodium battery is largely determined by the cathode material; the majority of research interest in sodium cathodes falls into three main categories: layered TM oxides, Prussian-blue analogues, and polyanionic compounds. However, an inferior cycling stability and a low working voltage are the major issues for the current cathode candidates. To reduce the cost and increase the energy density of current sodium battery technology, new cathode alternatives that have a high working voltage and excellent cycling stability must be explored.

The team started with a survey of current literature on the redox energies of TMs in polyanionic compounds that deliver a charge/discharge voltage within the electrochemical stability window of traditional liquid electrolytes with organic-carbonate as the solvents. This requirement coupled with a need for low-cost material candidates having a useful and high working voltage led the team to explore the redox energies of manganese in NASICON structures, Na₃MnZr(PO₄)₃. Rather than preparing the cathode material from a solid-state reaction that yields large cathode particles without a carbon coating, they developed the idea of synthesizing cathode Na₃MnZr(PO₄)₃ nanoparticles with an *in situ* generated carbon coating through a sol-gel method (Figure 63). This method gives a much better electrical conductivity than that of micrometer-sized cathode particles prepared from solid-state reactions to give a much higher rate capability of the cathode materials. These carbon-coated Na₃MnZr(PO₄)₃ cathode materials were first tested against a sodium-metal anode with 1M NaClO₄ in PC/FEC (90:10) as the electrolyte for proof of concept.

Both the Mn^{3+}/Mn^{2+} and Mn^{4+}/Mn^{3+} redox couples are accessed in the cathode, with the average discharge voltage at 4.0 V and 3.5 V versus Na⁺/Na (Figure 64). Half cells with a Na₃MnZr(PO₄)₃ cathode cycled very well at a current density of 0.5 C when compared to control cells using a standard polypropylene sheet as a separator. The experimental results coupled with theoretical calculations indicate that the excellent cycling stability exhibited by the Na₃MnZr(PO₄)₃ cathode is due to the structural stability of the NASICON structure and the inhibited Jahn-Teller distortion of Mn³⁺ in the intermediate phase of Na₂MnZr(PO₄)₃.



Publications

- Gao, H. C., I. D. Seymour, S. Xin, L. G. Xue, G. Henkelman, and J. B. Goodenough. "Na₃MnZr(PO₄)₃: A High-Voltage Cathode for Sodium Batteries." *Journal of the American Chemical Society* 140 (2018): 18192–18199.
- Gao, H. C., Y. T. Li, K. Park, and J. B. Goodenough. "Sodium Extraction from NASICON-Structured Na₃MnTi(PO₄)₃ through Mn(III)/Mn(II) and Mn(IV)/Mn(III) Redox Couples." *Chemistry of Materials* 28 (2016): 6553–6559.
- Zhou, W. D., L. G. Xue, X. J. Lu, H. C. Gao, Y. T. Li, S. Xin, G. T. Fu, Z. M. Cui, Y. Zhu, and J. B. Goodenough. "Na_xMV(PO₄)₃ (M = Mn, Fe, Ni) Structure and Properties for Sodium Extraction." *Nano Letters* 16 (2016): 7836–7841.

Task 4.6 – Advancing Solid-State Interfaces in Lithium-Ion Batteries (Nenad M. Markovic and Larry A. Curtiss, Argonne National Laboratory)

Project Objective. The project objectives are multifaceted, including development of a new mechanically and chemically stable and Li-ion conductive ($\geq 2 \times 10^{-4}$ S/cm at 298 K) solid electrolyte for a solid-state battery encompassing a Li-metal anode, Li-oxide-based cathode, and nonflammable crystalline and amorphous solid electrolytes that can operate at cathode potentials > 5 V (denoted as a S_{Li}-S_{EL}-S_C system).

Project Impact. Protective organic and inorganic compounds can enhance stability of the interface, improve Li-ion interfacial transport, minimize dendrite formation, and increase safety in Li-ion batteries.

Approach. The project proposes to develop and use interdisciplinary, atomic-/molecular-level insight obtained from integrating both experimental- and computational-based methodologies to define the landscape of parameters that control interfacial properties for a new generation of the Li-ion solid-solid battery systems. The strategy will involve transferring knowledge gained from well-characterized thin-film materials to real-world materials. This strategy forms a closed loop wherein the knowledge gained from model systems is used to design more complex, real-world materials, and vice versa. The work will focus on utilizing existing in-house synthesis and characterization methods to enable rapid transition from fundamental science to realistic cells.

Out-Year Goals. The out-year goals are to use and develop the physical and chemical synthesis methods for design of solid-solid interfaces with unique chemical/mechanical/conductivity properties. The proposed work will develop and exploit a variety of *ex situ* and *in situ* experimental optical and surface sensitive techniques and electrochemical methods to explore and explain bulk and interfacial properties of the selected materials. The results will serve to unravel many puzzling bulk and interfacial properties of S_{Li} - S_{EL} - S_{C} systems, including various types of ceramic and glass materials.

Collaborations. This project funds work at ANL and collaboration with J. Sakamoto at University of Michigan.

- 1. Understand the impact of different dopants in LLZO (niobium versus tantalum versus aluminum) on reactivity by surface and bulk sensitive techniques and spectroscopic methods. (Q1, FY 2019; Completed)
- 2. Determine the impact of solid electrolyte crystallinity (single crystal versus polycrystalline versus amorphous) on electrolyte reactivity by surface- and bulk-sensitive techniques and spectroscopic methods. (Q2, FY 2019; Completed)
- 3. Distinguish chemical versus electrochemical reactivity at the interface and bulk of model solid-state electrochemical systems with Li-metal anodes and LiCoO₂ cathodes by electrochemical testing and characterization. (Q3, FY 2019)
- 4. Determine dopant-dependent impact on chemical reactivity of different interfaces of solid-state electrolytes with lithium metal by computational characterization. (Q4, FY 2019).

Effect of LLTO(hkl) Orientation. Li_{0.33}La_{0.55}TiO₃ (LLTO) is a perovskite solid electrolyte that crystalizes in a pseudo-perovskite structure with ordered lanthanum (A-site) vacancies along the c-axis in a tetragonal structure, as shown in Figure 65a. Previous characterization showed after depositing ~ 20 nm of lithium on epitaxial LLTO(hkl) thin films, LLTO(001) exhibits ~ 33% titanium reduction in the bulk, whereas LLTO(100) films only exhibit ~13% titanium reduction. The differences in the extent of bulk titanium reduction are likely due to the ordered A-site vacancies along c-axis, which provides a faster lithium diffusion path into LLTO along the (001) direction. To confirm this, XRD scans were performed along the film's surface normal and in-plane directions, and show that the ordered A-site vacancy structure was preserved in epitaxial LLTO thin films after reaction with lithium. XRD scans indicate that, as proposed



Figure 65. (a) Atomic structure of LLTO showed ordered lanthanum vacancy along c-axis. Out-of-plane (b) and in-plane (c) X-ray diffraction scan of (100) and (001) oriented LLTO film shows the film maintains the ordered vacancy structure.

above, it is easier for lithium to diffuse into (001) oriented film due to the presence of more c-domain structure, with ordered vacancies along the surface normal. However, (100) films also have a minority c-domain component, allowing some amount of lithium diffusion into the structure and explaining the small amount of bulk reduction observed in these films.

Effect of LLTO Crystallinity. Although LLTO exhibits orientation-dependent differences in bulk reactivity after short-term exposure to thin lithium films, as shown above, long-term reaction (~ 3 days) with excess lithium eventually results in identical bulk reduction behavior regardless of orientation (Figure 66a). XAS spectra collected for four different orientations of LLTO(hkl) films reveal a similar amount of titanium reduction (Ti³⁺/Ti⁴⁺) and lattice expansion for all four orientations, indicating that the orientation-dependent differences observed above are kinetic, rather than thermodynamic in origin. This stands in contrast to amorphous LLTO thin films, which surprisingly exhibit no evidence of surface reactivity after deposition of (XPS, Figure 66b). Even more thin lithium films surprisingly, no reactivity is observed in the bulk (XAS, Figure 66c) even after 3 days of contact with excess lithium. As the same LLTO PLD target was used to deposit amorphous and LLTO(hkl) films, the team expects no significant differences in stoichiometry resulting in the observed differences in reactivity. This suggests that amorphous materials may represent a promising path forward toward realizing conductive solid electrolytes with reduced interfacial reactivity.



Figure 66. (a) X-ray absorption spectroscopy (XAS) of crystalline LLTO films after reaction with lithium. (b) X-ray photoelectron spectroscopy and (c) XAS spectra of amorphous LLTO film after contacting with lithium metal.

Publications

- Zhu, Y., J. G. Connell, S. Tepavcevic, P. Zapol, R. Garcia-Mendez, N. J. Taylor, J. Sakamoto, B. J. Ingram, L. A. Curtiss, J. W Freeland, D. D. Fong, and N. M. Markovic. "Dopant-Dependent Stability of Garnet Solid Electrolyte Interfaces with Lithium Metal." *Advanced Energy Materials* 9 (2019): 1803440.
- Zhu, Y., J. G. Connell, S. Tepavcevic, P. Zapol, J. W. Freeland, D. D. Fong, L. A. Curtiss, and N. M. Markovic. "Comparison of Chemical Reactivity of Amorphous LLTO to Epitaxial Films of Different Orientation towards Metallic Li Anode." In preparation (2019).

Task 4.7 – Mechanical and Defect Properties at the Protected Lithium Interface (Nancy Dudney, Oak Ridge National Laboratory; Erik Herbert, Michigan Technological University; Jeff Sakamoto, University of Michigan)

Project Objective. The project objective will be to understand the evolution of lithium metal on cycling in contact with a generic solid electrolyte under various intrinsic and extrinsic conditions. The team plans to construct a set of stability maps that will describe the predominate mass transport process and defect structure evolution in lithium metal. Simple maps may address current density, areal capacity, and layer thickness. Then, maps extending to many other cell designs, interfacial factors, and duty cycle parameters are envisioned. A key activity in FY 2018 will be to develop experimental tools with which to probe lithium morphology in real time. While initial work will focus on experimental characterization, modeling will be introduced to interpret kinetic processes and extrapolate for alternative properties and designs and extended cycling.

Project Impact. Stability maps can guide realistic design choices for solid electrolytes and cell design. Ideally, lithium is deposited and removed uniformly to maintain a fully dense anode in good contact with the solid electrolyte. However, in practice, this may not be realized depending on cycling conditions, nature of the electrolyte, nature of the lithium, and cell architecture. Mapping the lithium defect evolution will offer insight for when, how, and why the lithium structure is altered, along with a much deeper analysis of the degradation. With this insight, the team can realistically project the performance of optimized Li-metal anodes. Materials and cells can be engineered to fulfill the target level of performance for EV batteries, namely 1000 cycles, 15-year lifetime, with adequate pulse power.

Approach. The project will work to develop experimental tools to probe the lithium structure and its interfaces with mechanical, imaging, and electrochemical methods during mass transport and relaxation. Different constructions for the stability maps will be explored to identify the most useful graphical representation of what is expected to be a rich and detailed analysis of the formation and annealing of lattice and extended defects in the lithium metal.

Out-Year Goals. In the out-years, modeling efforts will be integrated to interpret and extrapolate the results to wide cycling conditions and detailed analysis of the solid electrolytes being used to stabilize the lithium metal.

Collaborations. This project funds work at ORNL, Michigan Technological University, and University of Michigan. This report marks the end of this program.

- 1. Analysis of creep tests for glassy LiPON electrolyte, assessing dependence on the temperature and displacement of the indenter. (Q1, FY 2019; Completed)
- 2. Analysis of neutron imaging for lithium transport in LLZO using isotope exchange. (Q2, FY 2019; Experiment complete, analysis in progress)
- 3. Evaluation of defect and microstructure formed in the cycled lithium metal and at the interfaces with the solid electrolyte. (Q3, FY 2019; Completed, March 2019)
- 4. With German partners, assess whether dynamic impedance will detect early onset of voids in the lithium. (Q4, FY 2019)

Taking advantage of abnormal grain growth, large single crystals and bi-crystals were harvested from LLZO hot pressed pellets. These were used for lithium isotope studies tracer diffusion studies to examine the lithium transport within the crystal and along the grain boundaries by neutron imaging. The data set, which is rather

noisy, is undergoing further analysis to assess whether statistically significant differences can be extracted to compare the different pathways.

The correlation between stack pressure and stripping current density has been established for lithium contacts on LLZO pellets. The plating and stripping contacts were separated with the addition of a reference electrode plated on the side of the LLZO pellet. An example of the results is shown in Figure 67. A complete discussion is presented in a manuscript that is under review. This is the basis for generating a stability map (the overall objective) mapping the different defects generated in the lithium as function of discharge current and stack pressure.



Figure 68. Deformation mechanism map and the corresponding shear stress within Li-filled defects at the Li/SEI.



Figure 67. Comparison of the pressure-induced strain rate and the current-induced strain rate for cycling at 0.1 mA/cm². The point where the current-induced strain rate becomes dominant is when unstable void growth occurs at the lithium interface.

The detailed nanoindentation study of lithium thin films was further analyzed in the context of other recently published investigations. From nanoindentation, the volume of lithium is critical to its response to applied stress, from the indenter or from the charging current. This analysis was used to generate the first map of the creep mechanism as a function of the volume of the Li-filled defect protruding into a solid electrolyte. This is illustrated in Figure 68, which was determined for an average current density of 1 mA/cm² and an aspect ratio of the lithium perturbation of 2π . Derivation of this map is discussed in a manuscript to be submitted shortly.

Publications

- Wang, M. J., R. Choudhury, and J. Sakamoto. "Characterizing the Li-metal/Solid-Electrolyte Interface Dynamics as a Function of Stack Pressure and Stripping Current Density." Submitted for review, March 2019.
- Wang, M., and J. Sakamoto. "Temperature Dependent Flux Balance of the Li/Li₇La₃Zr₂O₁₂ Interface." *Electrochemica Acta*. In press.
- Herbert, E., N. J. Dudney, V. Thole, and S. A. Hackney. "On the Mechanisms of Stress Relaxation and Intensification at the Lithium/Solid-State Electrolyte Interface." In final preparation.

Presentations

- MRS, Phoenix, Arizona (April 2019): "Growth and Properties of Lithium Thin Films for Solid State Batteries"; N. J. Dudney,* A. Westover, E. Herbert, and J. Sakamoto. Invited.
- MRS, Phoenix, Arizona (April 2019): "Evaluating Changes at the Li-Metal/Solid-Electrolyte Interface Under Dynamic Stack Pressure Conditions"; M. Wang* and J. Sakamoto.
- MRS, Phoenix, Arizona (April 2019): "Enhanced Grain Growth Kinetics in Polycrystalline Li_{6.25}Al_{0.25}La₃Zr₂O₁₂ Solid Electrolyte"; R. Garcia-Mendez* and J. Sakamoto.

TASK 5 – SULFUR ELECTRODES

Summary and Highlights

The collected work reported for this quarter involves six projects that have focused on the following:

- Conducting focused fundamental research on the mechanism of "shuttle effect" inhibition for rechargeable Li-S batteries.
- Developing electrode and electrolyte systems which 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 LIC as a protective layer for Li-metal anodes, enabling Li-metal anodes to cycle with a high efficiency.
- Developing high-energy, low-cost Li-S batteries with long lifespan.

Highlights. This quarter involved considerable work in both Li-S and Li-metal battery technology, as highlighted below:

- D. Wang's lab synthesized polymers containing P_xS_y components (polymer-P_xS_y) through the reaction of sulfur anion (S_n⁻) containing trifunctional crosslinker lithium polysulfidophosphate with a chlorine-rich polymer. During lithium plating/stripping, these polymers react with lithium metal and *in situ* release lithium sulfides and Li_xP_yS_z at the interface of the polymer and lithium metal to form an organo-Li_xS_y/organo-Li_xP_yS_z composite protection layer, likely providing good mechanical strength and integrity.
- Dr. K. Amine and researchers from ANL have used Raman spectroscopy and small-angle X-ray scattering (SAXS) combined with AIMD simulation to understand the solvation chemistry of dilute and concentrated siloxane-based electrolytes. Results show that at higher concentrations, there is no free solvent to interact with selenium and sulfur.
- D. Qu (University of Wisconsin at Madison) and X-Q. Yang (BNL) worked on the chemical synthesis of different new sulfur-containing copolymer materials along with investigating alternative lithium-containing anode materials to mitigate the chemical reactions between the lithium anode and the polysulfide ions. Fully prelithiated phosphorus anode paired with a S-C cathode (75% sulfur) (P/S) exhibited good rate capability and cycling stability even with a more limited lithium source than that in a metallic lithium anode. At 1 A/g discharge rate, it delivered an initial capacity of 460 mAh g⁻¹, based on sulfur and carbon weight (S/C). The P/S cell retained a reversible capacity of 312 mAh g⁻¹(S/C) after 300 cycles, with a capacity decrease of 0.10% per cycle and an average CE over 99%.
- D. Lu and J. Liu (PNNL) have constructed robust and high Li⁺ conductive networks for sulfur cathodes and developed a new solid electrolyte of low-temperature phase Li₇P₂S₈Br_{0.5}I_{0.5} (LT-LPSBI) demonstrating high ionic conductivity of 4.7 mS/cm at room temperature electrode. They evaluated the electrochemical voltage stability window of the electrolyte as well as the influence of atmospheric moisture on the ionic conductivity. They also developed a new dry processing approach to use the solid electrolyte for fabrication of sulfur cathodes.

Task 5.1 – Novel Chemistry: Lithium Selenium and Selenium Sulfur Couple (Khalil Amine, Argonne National Laboratory)

Project Objective. The project objective is to develop a novel $S_x Se_y$ cathode material 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 PHEV and EV 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, the 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: Professor C. Wang of UMD, Dr. Y. Ren, and Dr. C. Sun of Advanced Photon Source at ANL, and Dr. L. A. Curtiss at ANL.

- 1. Parasitic reactions study of Li/Se and Se-S systems in different electrolytes. (Q1, FY 2019; Completed)
- 2. Characterization on the solvation chemistry of concentrated siloxane based electrolytes. (Q2, FY 2019; In progress)
- 3. Modify the electrode/electrolytes interface using atomic layer deposition (ALD) and molecular layer deposition (MLD). (Q3, FY 2019; ongoing)
- 4. Interfacial understanding on the Li/Se-S batteries in different electrolytes. (Q4, FY 2019)

This quarter, the team further used Raman spectroscopy and SAXS combined with AIMD simulation to understand the solvation chemistry of dilute and concentrated siloxane-based electrolytes.

Figure 69a shows the Raman spectra of siloxane, dilute siloxane-based, and concentrated siloxanebased electrolytes. The Raman band between 580 and 650 cm⁻¹ is ascribed to the Si-O-C stretching in the siloxane solvent, while the Raman band between 730 and 760 cm⁻¹ is due to the coupled CF3 bending and S-N stretching in TFSI. As shown, with an increased LiTFSI concentration, the free siloxane and TFSI⁻ diminished to form contact ion pairs (CIPs) and aggregates (AGGs) with strong Coulombic interactions with multiple Li⁺ cations. The SAXS data of siloxane-based electrolytes showed a continuous intensity increase in the q range from 0.3 to 1 Å⁻¹, indicating formation of aggregate when increasing the concentration. The intensity change is due to the solvation structure changes of siloxane.



Figure 69. Raman spectra of siloxane, dilute siloxane-based, and concentrated siloxane-based electrolytes in the Raman shift range of 580-650 cm⁻¹ and (b) 730-760 cm⁻¹. (c) Small angle X-ray scattering data of siloxane-based electrolytes with increased concentration.

The team further applied AIMD simulation to have an atomic-scale understanding of the solvation structure around the Li^+ and TFSI⁻. Figure 70a-b shows the snapshot from the AIMD trajectories for the dilute and concentrated siloxane-based electrolytes. Li+ cations prefer a tetrahedral coordination with the oxygen atoms

in TFSI⁻ and siloxane. The result showed that with increased concentration, the ratio of coordinated oxygen atoms has been increased two-fold. Moreover, the lithium coordination number is simultaneously decreased from 4.0 to 3.6. The results indicate that there are no free solvents that can interact with Se-S. Therefore, Li⁺ can only react with Se-S in a solid diffusion way, leading to the observed solid-solid (de) lithiation chemistry (as confirmed by the *in situ* X-ray previously absorption fine structure, or XAFS). More importantly, the concentrated siloxane-based electrolytes with new solvation structure may also enable formation of unique SEI resulting from the derivation of LiTFSI, which would be different from that obtained in the dilute electrolyte. Hence, the team will further explore the interfacial property of SEI layers resulting from different electrolytes and use ALD and MLD to modify the interface to further improve the electrochemical performance next quarter.



Figure 70. Typical snapshot of the *ab initio* molecular dynamics (AIMD) optimized structures of (a) dilute and (b) concentrated siloxane-based electrolytes using AIMD simulation. (c) Ratio of coordinated oxygen atoms and (d) lithium coordination number with increasing concentration.

Presentation

 Spring 2019 ACS National Meeting, Orlando, Florida (March 31 – April 4, 2019): "Novel Chemistry for Automotive Application: Lithium-Selenium and Selenium-Sulfur Couple"; G-L. Xu, Z. Chen, and K. Amine. Invited.

Task 5.2 – Development of High-Energy Lithium-Sulfur Batteries (Jun Liu and Dongping Lu, 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 ($\geq 2 \text{ mAh/cm}^2$ 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 EVs required by the EV Everywhere Grand Challenge.

Approach. The project proposes to (1) identify and address key issues of applying high-energy sulfur cathodes including materials, binders, electrode architectures, and functional electrode additives, (2) advance mechanism study of sulfur cathode and electrolyte by using *in situ/ex situ* techniques and custom-designed hybrid cell setup, and (3) 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 (E/S < 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 real application.
- Leverage the Li-metal protection project funded by the DOE and 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: Dr. X-Q. Yang (BNL), Dr. D. Qu (University of Wisconsin at Madison), Dr. G. Zhang (University of Alabama), and Dr. J. Tao (PNNL).

- 1. Synthesize high Li^+ conductivity sulfide-based Li^+ conductors with room-temperature conductivity > 1 mS/cm for sulfur cathodes. (Q1, FY 2019; Completed)
- 2. Develop electrode preparation method for sulfur/Li⁺-conductor cathodes with sulfur mass loading $> 4 \text{ mg/cm}^2$ and sulfur > 75 wt% in whole electrode. (Q2, FY 2019; Completed)
- 3. Complete electrode composition and architecture optimization for low porosity sulfur electrodes (electrode density >1 g/cm³). (Q3, FY 2019; In progress)
- 4. Complete electrochemical evaluation of high-loading sulfur electrodes (> 4 mg/cm²) at E/S < 3 μ L/mg, and identify compatible liquid electrolytes with the cathodes. (Q4, FY 2019; In progress)

To construct robust and high Li^+ conductive networks for sulfur cathodes, a new solid electrolyte of low-temperature phase $Li_7P_2S_8Br_{0.5}I_{0.5}$ (LT-LPSBI) was developed that demonstrated a high ionic conductivity

of 4.7 mS/cm at room temperature. To verify availability of the solid Li⁺ conductor for preparation of composite sulfur cathodes, key material properties such as electrochemical window. air stability, and interfacial stability with the lithium anode were systematically studied this quarter. The electrochemical window of LT-LPSBI was characterized by CV. Rather than adopting the conventional configuration of M/SE/Li (M standards for an electrochemically inert planar metal electrode such as platinum), conductive carbon (5 wt%) was mixed with solid electrolyte for the working electrode to mimic the real scenario in an electrode. The CV scan started toward the negative direction. The onset of substantial increase in cathodic current was around 1.4 V, and the current increased continuously as the cathode potential was driven to



Figure 71. (a) Cyclic voltammogram for a C-SE/SE/Li cell at a scan rate of 5 mV/s (SE = LT-LPSBI). (b) The effect of exposure to dry room atmosphere on the ionic conductivity of LT-LPSBI. σ_x is the ionic conductivity at x h. (c) Nyquist plots of a Li/SE/Li cell at room temperature as a function of time (voltage modulation was 5 mV). (d) Cross-section scanning electron microscopy of the high-loading sulfur electrode with loading 5.2 mg/cm².

0 V versus Li/Li⁺. On the reverse scan, two broad peaks spanning from 0.2 V to 1.7 V and a relatively narrow peak at 2.7 V were observed. All peaks corresponded to oxidation of the reduction products during the forward scan, since the scan starting toward the positive direction showed no anodic current at 2.7 V. During the first scan, an efficiency of 85.0% was observed; it increased to 93.3% and 95.4% during the second and third scans, suggesting the redox reaction was partially reversible. These results indicate 1.4-2.7 V is a reasonably stable electrochemical window for the LT-LPBSI. The moisture stability of the LT-LPSBI was tested in the dry room atmosphere, and the conductivity decreased by only 5% within 2 h and by 15% in 24 h (Figure 71b). Therefore, LT-LPSBI can be handled in the dry room for a reasonable amount of time without substantial degradation. The interfacial transport behavior of LT-LPBSI with lithium anode was evaluated using potentiostatic EIS in two-electrode Li/SE/Li cells by monitoring the impedance change with time (Figure 71c). The left intercept of the impedance and the span increased with time, and the change was greatest between 0 h and 1 h. The change slowed down with time, and the impedance eventually became relatively stable. It can be concluded from these observations that the observed spectra are associated with interfacial processes. The dependence of the impedance with time is typical of growth of SEI layers that are kinetically stable, which can be attributed to the lack of metal or semiconductor elements in LT-LPSBI. It should be noted that the magnitude of the change may include contribution from temperature variation, as the assembly process may raise the system temperature above the environmental temperature temporarily. To use the solid electrolyte for sulfur cathode fabrication, a new dry-processing approach was developed. Uniform and relatively dense sulfur cathodes with high sulfur mass loading (> 4 mg/cm²) and high sulfur contents (64-75 wt% of whole electrode) were successfully prepared (Figure 71d).

Publication

 Wang, Y., D. Lu, J. Xiao, Y. He, C. Wang, J. Zhang, and J. Liu. "Superionic Conduction and Interfacial Properties of the Low Temperature Phase Li₇P₂S₈Br_{0.5}I_{0.5}." *Energy Storage Materials*. doi: doi.org/10.1016/j.ensm.2019.02.029.

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 TM 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 multi-functional 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 the cycling stability of sulfur cathode will be dramatically increased. This project's success will make Li-S batteries to power EVs and decrease the high cost of batteries.

Approach. The approach comprises the three main parts shown below, with primary activities listed.

- Advanced Nanostructured Sulfur Cathodes Design and Synthesis. (1) Engineer empty space into sulfur cathode to solve the problem of electrode volume expansion. (2) Develop novel sulfur nanostructures with multi-functional coatings for the confinement of S/Li polysulfides to address the 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 the volumetric energy density and rate capability. (5) Identify the interaction mechanism between sulfur species and different types of oxides/sulfides, and find the optimal material to improve the capacity and cycling of sulfur cathode.
- *Structure and Property Characterization*. (1) *Ex situ* SEM. (2) XPS analysis. (3) *In operando* XRD and optical microscopy.
- *Electrochemical Testing.* (1) Coin cells and pouch cells. (2) 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 engages in collaboration with the following: BMR PIs; SLAC National Accelerator Laboratory: Dr. M. Toney (*In situ* X-ray); and Stanford: Prof. Nix (mechanics) and Prof. Bao (materials).

- 1. Build *in situ* characterization platform to monitor nucleation/dissolution of sulfur/Li₂S_n. (Q1, FY 2019; October 2018, Completed)
- 2. Develop a noninvasive imaging method with sub-micron, sub-second resolution for Li-S battery in label-free, native organic liquid electrolyte. (Q2, FY 2019; January 2019, Completed)
- 3. Demonstrate the substrate-dependent electrochemical formation of super-cooled liquid sulfur and crystals, as well as rapid solidification of a super-cooled sulfur droplet. (Q3, FY 2019; April 2019, Completed)
- 4. Provide direct evidence about a long-debated reaction pathway of surface mechanism versus solution mechanism for sulfur and the current collector effect on sulfur evolution. (Q4, FY 2019; July 2019, In progress)

Last quarter, the team used the optical cell platform to directly observe multiple new phenomena in Li-S batteries for the first time, including electrochemical generation of metastable liquid sulfur at room temperature on different substrates, and the growth of sulfur crystals on the commonly used carbon materials. This quarter, the team has demonstrated rapid solidification of a super-cooled sulfur droplet and suggests the reaction pathway of sulfur nucleation and growth in Li-S batteries.



Figure 72. (a) Dark field light microscopy (DFLM) image of exfoliated graphite nano-platelets dispersed on Ni-metal grid for growing solid and liquid sulfur in the same cell. (b) High-magnification bright field light microscopy image of a single nano-platelet sitting on nickel grid, as shown in the red box in (a). (c) *In operando* DFLM image of the cell after charging, showing co-existing needle-shaped sulfur microcrystals and metastable sulfur droplets. (d-h) Time-lapse DFLM images showing the approach of a needle-shaped sulfur microcrystal toward a sulfur microdroplet and its rapid solidification upon touching.

Super-cooled liquids usually solidify quickly after the onset of nucleation. The electrochemically generated super-cooled sulfur droplets do not solidify by themselves over an observation window of 1 hour. The team induced nucleation at the microscale, to verify meta-stability. They spread exfoliated graphite nano-platelets on Ni-metal grids (Figure 72a-b) to electrochemically generate both sulfur droplets and crystals in one cell (Figure 72c), and recorded events when a sulfur crystal grown from graphite touches a sulfur droplet grown on nickel. As shown in the time-lapse images in Figure 72d-h, the sulfur microdroplets turned from transparent to frosted within one second upon the touch of a growing sulfur microcrystal, indicating solidification of the sulfur droplet. The rapid solidification preserved the spherical shape of the sulfur droplet (Figure 72g). On further growth (Figure 72h), the surface of the sulfur particle becomes rougher, indicating its solid and polycrystalline nature. A chain of such solidification events was also observed, confirming the meta-stability of electrochemically generated super-cooled sulfur droplets. Note that trace amounts of guest species may dope inside the liquid sulfur droplets and could originate from catalytic reactions of sulfur at metal-containing surfaces. However, the melting temperature of these solidified electrochemically generated sulfur microdroplets is high.

While most sulfur microdroplets form on the conductive nickel line (Figure 73a), the team observed a few instances when they formed on the insulating glass next to the nickel line (Figure 73b). This suggests that sulfur could electrochemically form via a solution mechanism, in addition to the traditionally hypothesized surface mechanism. As shown in Figure 73c, in surface mechanism, polysulfide anion transfers electrons to electrode and deposit locally, whereas in solution mechanism, electron transfer first generates soluble intermediate

species that diffuse off the conducting substrate before depositing. The team hypothesizes the diffusive intermediate specie to be S_8 molecule, because it is slightly soluble in the DOL/DME electrolyte. The surface mechanism will have the issue of electrode surface being fully covered by the insulating charge/discharge product (S/Li₂S) and limiting the areal capacity. The solution mechanism, however, allows the product to form off the electrode surface, therefore maintaining accessibility of electrode surface to electrolyte and enabling high areal capacity and rate capability. The solution mechanism also applies to the reverse process of solid sulfur dissolution on discharging. Large sulfur crystals dissolved isotropically, regardless of the accessibility of electron. After breaking into segments, the electrically disconnected sulfur still reacted. This finding contradicts the common belief regarding Li-S battery that for insulating sulfur to be electrochemically active, it needs to have small size and be electrically connected to current collector.



Figure 73. (a-b) Time-lapse light microscopy images of the initial formation of sulfur droplets, one on the nickel grid (a) and another off the nickel grid on glass (b). (c) Two general mechanisms for the nucleation and growth of sulfur on electrodes. The solution mechanism is consistent with the results in both (a) and (b).

Patents/Publications/Presentations

Publication

 Liu, N., G. Zhou, A. Yang, X. Yu, F. Shi, J. Sun, J. Zhang, B. Liu, C-L. Wu, X. Tao, Y. Sun, Y. Cui,* and S. Chu.* "Direct Electrochemical Generation of Supercooled Sulfur Microdroplets Well Below Their Melting Temperature." *Proceedings of the National Academy of Sciences of the United States of America* 116 (2019): 765.

Task 5.4 –Investigation of Sulfur Reaction Mechanisms (Deyang Qu, University of Wisconsin at Milwaukee; Xiao-Qing Yang, Brookhaven National Laboratory)

Project Objective. The primary objectives are:

- To continue conducting focused fundamental research on the mechanism of "shuttle effect" inhibition for rechargeable Li-S batteries;
- To continue developing the electrode and electrolyte systems that can mitigate the "shuttle effect" so low self-discharge and long cycle life can be achieved.
- To synthesize sulfur composite material with an emphasis on polymer sulfur composite materials.
- To develop creative electrode making processes to improve processability and aerial capacity; for example, polymeric sulfur composite may be unsuitable for the traditional slurry casting process.

The ultimate goal is to develop a practical rechargeable Li-S battery that meets the challenges of powering the next generation of EVs beyond Li-ion technologies.

Project Impact. With development of unique *in situ* electrochemical high-performance liquid chromatography (HPLC)/MS and *in situ* electrochemical microscopic techniques, the mechanisms of all reactions in a Li-S cell can be further understood. Better understanding the sulfur redox reaction will lead to mitigation of the "shuttle effect." The project results will thus guide development of polymer sulfur cathode and Li-S designs for EVs.

Approach. This project will use *in situ* electrochemical HPLC/MS, XPS, SEM, and XRD to study electrochemical reactions associated with sulfur electrodes. Electrochemical techniques such as AC impedance, rotation ring disk electrode, and galvanostat will be used to study the electrode process kinetics. The project will use an *in situ* electrochemical optical method to investigate the surface of lithium anode during cycling of a Li-S cell. It will develop thicker sulfur electrode with high areal capacity using dry process.

One-Year Goals. The one-year goals include the following areas: (1) complete investigations of new electrolytes for mitigating the "shuttle effect" and improving Li-anode performance, and (2) complete preliminary design of new electrode processes and tests of polymeric sulfur composite electrodes.

Collaborations. The PI, D. Qu, is the Johnson Controls Endowed Chair Professor; thus, the team from University of Wisconsin at Madison and BNL has close collaboration with Johnson Controls' scientists and engineers. This collaboration enables the team to validate outcomes of fundamental research in pilot-scale cells. This team has been closely working with top scientists on new material synthesis at ANL, LBNL, and PNNL, with U. S. industrial collaborators at GM, Duracell, and Johnson Controls as well as international collaborators 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. Literature review and molecular design of polymeric sulfur compounds. (Q1, FY 2019; Completed)
- 2. Complete screening electrolyte and additives for the Li-S batteries. Start synthesis of polymeric sulfur compounds. (Q2, FY 2019; Completed)
- 3. Complete preliminary designs of electrode manufacture process and start to explore feasibility for the synthesized polymeric sulfur composite. (Q3, FY 2019)
- 4. Complete initial design of electrode manufacture processes and tests of synthesized polymeric sulfur materials. (Q4, FY 2019)

This quarter, the team continued chemical synthesis of new sulfur-containing copolymer materials. For example, procedures for synthesis of conductive crosslinked polysulfur-*random*-PPV copolymer cathode material were further refined. The synthesis route and mechanism to copolymerize sulfur with *p*-Phenylene vinylene derivative is shown in Figure 74. Sulfur content can be adjusted during synthesis according to conditions. Physical properties of the resulting material vary with percentage of sulfur in the copolymer. Although cycle life was significantly improved, volumetric density is still lower than traditional S-C cathode due to the intrinsic elastic nature of the polymer; the copolymer did not dissolve well in organic solvents to form a slurry. New electrode fabrication methods are being developed to replace the slurry coating method.

To mitigate chemical reactions between the lithium anode and polysulfide ions, alternative Li-containing anode materials are also being investigated. Figure 75 shows performance of a coin cell made with fully prelithiated phosphorus anode paired with a S-C cathode (75% sulfur). The resulting P/S coin cell exhibited a good rate capability and cycling stability even with a more limited lithium source than that in a metallic lithium anode. At 1 A/g discharge rate, it delivered an initial capacity





Figure 74. Copolymerize sulfur with p-Phenylene vinylene to form crosslinked sulfur-rich S/Xant-copolymer.

of 460 mAh g⁻¹, based on sulfur and carbon weight (S/C). The P/S cell retained a reversible capacity of 312 mAh g⁻¹(S/C) after 300 cycles, with a capacity decrease of 0.10% per cycle and an average CE over 99%.



Figure 75. Rate performance of a coin cell made of fully prelithiated phosphorus anode and 75% sulfur/carbon cathode (upper); the cyclability of the cell (lower).

It demonstrated discharge capacities of 686, 589, 485, 421, 363, and 327 mAh g⁻¹(S/C) at 0.1, 0.2, 0.5, 1, 1.5, and 2 A g⁻¹, respectively. When the current density was back to 0.1 A g⁻¹, it delivered a reversible capacity of 681 mAh g⁻¹(S/C). The new configured S/P cell can provide a theoretical maximum energy density of 967 Whkg⁻¹ based on the therotical capacity of sulfur, fully prelithated phosphouous, and slightly lower discharge voltage of the cell. An energy density of 358 Wh kg⁻¹ has been realized based on total weight of cathode and anode at discharge capacity at 0.1 A g⁻¹.

Patents/Publications/Presentations

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

Task 5.5 – Electrochemically Responsive, Self-Formed, Lithium-Ion Conductors for High-Performance Lithium-Metal Anodes (Donghai Wang, Pennsylvania State University)

Project Objective. The project objective is to develop and deliver an electrochemically responsive self-formed hybrid LIC as a protective layer for Li-metal anodes, enabling Li-metal anodes to cycle with a high efficiency of ~ 99.7% at high electrode capacity (> 6 mAh/cm²) and high current density (> 2 mA/cm²) for over 500 cycles. The project will also demonstrate prototype ~ 300 mAh Li-S battery cells with energy densities of ~ 200 Wh/kg and ~ 80% capacity retention for ~ 300 cycles at ~ 80% depth of discharge using Li-metal anodes with this protective layer.

Project Impact. This project aims to develop a new hybrid LIC that enables safe and high-performance Li-metal anodes. Use of these anodes in turn enables Li-S batteries with high energy density and long cycling life. Such anodes can also lead to a 50% increase in the energy density of conventional Li-ion batteries with Li-metal oxide cathodes. Meeting the technical targets will potentially develop a new high-energy-density lithium battery, promote increased adoption of EVs and PHEVs, 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 novel multiphase organo- $\text{Li}_x S_y$ or organo- $\text{Li}_x P_y S_z$ hybrid ion conductors with tunable multi-functional organic components and controlled $\text{Li}_x S_y$ and $\text{Li}_x P_y S_z$ inorganic components will be designed and prepared, and thus enable safe use of lithium metal with high CE. In the third year, the team will develop the organo- $\text{Li}_x S_y$ /organo- $\text{Li}_x P_y S_z$ composite lithium protection layers with tuned functionality: (1) finding appropriate composition, (2) developing appropriate synthesis and fabrication methods, and (3) optimizing organo- $\text{Li}_x S_y$ /organo- $\text{Li}_x P_y S_z$ components in a protection layer to improve CE and Li-S battery performance.

Out-Year Goals. The project is working toward developing the organo- $\text{Li}_x S_y$ /organo- $\text{Li}_x P_y S_z$ composite lithium protection layers with tuned functionality. Characterization, performance, and compatibility tests on materials and systems will be conducted. Uniform, dendrite-free lithium deposition under protection of organo- $\text{Li}_x S_y$ /organo- $\text{Li}_x P_y S_z$ composite lithium protection layers will be demonstrated; CE will be improved.

Collaborations. There are no active collaborations.

- 1. Develop the organo-Li_xS_y/organo-Li_xP_yS_z composite lithium protection layers with tuned functionality. Conduct characterization and performance tests on the materials. (Q1, FY 2019; Completed)
- 2. Demonstrate uniform and dendrite-free lithium deposition under protection of the organo-Li_xS_y/ organo-Li_xP_yS_z composite lithium protection layers. (Q2, FY 2019; In progress)
- 3. Optimize the organo- Li_xS_y /organo- $\text{Li}_x\text{P}_y\text{S}_z$ composite lithium protection layers and demonstrate lithium anodes cycling with ~ 99.4% CE for ~ 200 cycles. (Q3, FY 2019)
- 4. Demonstrate lithium anodes with optimized organo-Li_xS_y/organo-Li_xP_yS_z composite lithium protection layers and ~ 99.7% CE for ~ 300 cycles. (Q4, FY 2019)

The team synthesized polymers containing $P_x S_y$ components (polymer- P_xS_v) through the reaction of sulfur anion (S_n) containing trifunctional crosslinker lithium polysulfidophosphate with a chlorine-rich polymer. During lithium plating/stripping, the polymers react with lithium metal and *in situ* release lithium sulfides and $Li_x P_y S_z$ at the interface of polymer and lithium metal to form an organo-Li_xS_v/ organo-Li_xP_yS_z composite protection layer. Figure 76a shows the image of a just mixed solution of chlorine-rich polymer and S_n⁻ containing trifunctional crosslinker lithium polysulfidophosphate in a molar ratio of 1.1/1 between Cl-C bond on chlorine-rich polymer and S_n , which appeared as a dark red solution. After standing at room temperature for 10 h, the color of the system turned into pale yellow and a gel-like solid formed (Figure 76b), indicated crosslinking reaction between these two starting materials. For fabrication of composite film, 50 µL of mixed solution of chlorine-rich polymer and S_n⁻ containing trifunctional crosslinker lithium polysulfido-



Figure 76. Optical images of (a) just mixed solution of starting materials and (b) after 10 h. Optical images of (c) just mixed solution on stainless-steel foil and (d) after drying overnight under vacuum.

phosphate was dropped onto stainless steel and dried under vacuum overnight. After drying, it can be seen that the coated dark red solution (Figure 76c) changed into a solid and uniform off-white film (Figure 76d).

XPS was performed to further demonstrate the successful crosslinking reaction between the starting materials, with results shown in Figure 77. From the Cl 2p spectra of chlorine-rich polymer and polymer- P_xS_y (Figure 77a/d), one can clearly see that peaks corresponding to C-Cl bond decreased and new peaks corresponding to LiCl formed, which is a reaction product between the starting materials. Accordingly, from the C 1s spectra of chlorine-rich polymer and polymer- P_xS_y (Figure 77b/e), one can see that the peak corresponding to C-Cl bond of chlorine-rich polymer decreased after reacting with S_n^- containing trifunctional crosslinker lithium polysulfidophosphate and a new peak corresponding to C-S bond formed for the polymer- P_xS_y . Moreover, from the comparison of S 2p spectra of S_n^- containing trifunctional crosslinker lithium



Figure 77. High-resolution X-ray photoelectron spectra of Cl 2p, C 1s, and S2p for: (a-b) pure chlorine-rich polymer, (c) Sn⁻ containing trifunctional crosslinker lithium polysulfidophosphate, and (d-f) polymer-P_xS_y film.

polysulfidophosphate and polymer-P_xS_v (Figure 77c/f), one can see that the peak at 161.4 corresponding to P-S and S-Li bonds in S_n⁻ containing trifunctional crosslinker lithium polysulfidophosphate decreased significantly, while the peak at 163.3 corresponding to S-S and C-S bonds apparently increased. The obvious changes of C1s, Cl2p, and S2p spectra between precursors and the as-prepared polymer- P_xS_y film strongly demonstrate successful reaction between the starting materials. The crosslinking structure of polymer-P_xS_y would ensure its good mechanical strength and integrity so as to provide effective protection for the in situ formed robust SEI layer.

Patent

 Wang, D. H., et al. "Porous Metal Ion Affinity Material." U.S. Application No. 62/656443 and PCT Application, 2019. Task 5.6 – 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 the Li-ion rechargeable batteries. The emerging Li-S batteries could be both high energy density and low cost. This project enables the 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 towards 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 and to prevent polysulfide dissolution and promote polysulfides precipitation.

Out-Year Goals. The team will also investigate the contribution of Li-metal electrodes to the overall Li-S battery performance and develop methods to stabilize Li-metal surface.

Collaborations. This project collaborates with Dr. J. Guo and Dr. W. Yang (ALS/LBNL), Prof. A. Minor (National Center for Electron Microscopy at LBNL/UC Berkeley), Dr. L-W. Wang (LBNL), and Prof. P. Balbuena, TAMU.

- 1. Identify the baseline electrolyte compositions and electrode composition and configuration for Li-S study. (Q1, FY 2019; Completed)
- 2. Develop polymer binders with different affiliation functional groups with polysulfides, and use baseline electrolytes to investigate dissolution and precipitation of polysulfides. (Q2, FY 2019; Completed)
- 3. Develop in situ cells for synchrotron analysis with improved spatial resolution. (Q3, FY 2019; In progress)
- 4. Formulate one composition of the new electrolyte for Li-S battery and test its performance. (Q4, FY 2019)

This quarter research is focused on understanding the effect of electrode composition on sulfur electrode performance. In particular, the polymer electrode binder interaction with the sulfur and dissolved polysulfides was investigated. A new approach was proposed and developed by the team to use nucleophilic substitution reaction between the dissolved polysulfides and of leaving groups on the polymer binder to immobilize polysulfides onto the electrode [*Nano Energy* 38 (2017): 82]. Polymer binders that form strong electronic static interaction or covalent binding with the polysulfide have been investigated this quarter. Polyisoprene (PIP) is a promising new binder material for sulfur electrode. PIP can play a dual role as a composite with sulfur materials and as a binder for the composite electrode.

A polyisoprene-sulfur (PIPS) copolymer and nano-sulfur composite materials (90 wt% sulfur) are synthesized through inverse vulcanization of PIP polymer with sulfur micron-size particles for high areal capacity Li-S batteries. The polycrystalline structure and nanodomain nature of the copolymer are revealed through HRTEM. PIP polymer is also used as a binder for the electrode to further capture the dissolved polysulfides. A high areal capacity of ca. 7.0 mAh/cm² and stable cycling are achieved based on the PIPS nano-sulfur composite with a PIP binder, crucial to commercialization of Li-S batteries. The chemical confinement at both the material and electrode level alleviates the diffusion of polysulfides and the shuttle effect. The sulfur electrodes, both fresh and cycled, are analyzed through SEM. This approach enables scalable materials production and high sulfur utilization in the cell level.



Figure 78. (left) Long-chain polysulfides confinement mechanism is illustrated at the top. The chemical bonds generated after vulcanization provide a reservoir for long-chain polysulfides instead of direct diffusion into electrolyte in micro-size sulfur electrode. The molecular process of polyisoprene (PIP) polymer and sulfur reactions to immobilize polysulfide in the polymer network is shown in the middle. The bottom panel presents the different phase evolution from micro-sulfur to polyisoprene-sulfur (PIPS) and sulfur nanocomposite materials. (right) Fourier transform infrared spectra of starting material sulfur and PIP, and product PIPS.

Patents/Publications/Presentations

The project has no patents, publications, or presentations to report this quarter.
TASK 6 – AIR ELECTRODES / ELECTROLYTES

Summary and Highlights

High-density energy storage systems are critical for EVs required by the EV Everywhere Grand Challenge. Conventional Li-ion batteries still cannot fully satisfy the ever-increasing needs because of their limited energy density, high cost, and safety concerns. As an alternative, the rechargeable lithium-oxygen (Li-O₂) battery has the potential to be used for long-range EVs. The practical energy density of a Li-O₂ battery is expected to be ~ 800 Wh kg⁻¹. The advantages of Li-O₂ batteries come from their open structure; that is, they can absorb the active cathode material (oxygen) from the surrounding environment instead of carrying it within the batteries. However, the open structure of Li-O₂ batteries also leads to several disadvantages. The energy density of Li-O₂ batteries will be much lower if oxygen must be provided by an onboard container. Although significant progress has been made in recent years on fundamental properties of Li-O₂ batteries, research in this field is still in an early stage, with many barriers to be overcome before practical applications. These barriers include:

- Instability of electrolytes—The superoxide species generated during discharge or O₂ reduction process is highly reactive with electrolyte and other components in the battery. Electrolyte decomposition during charge or O₂ evolution process is also significant due to high over-potentials.
- Instability of air electrode (dominated by carbonaceous materials) and other battery components (such as separators and binders) during charge/discharge processes in an O-rich environment.
- Corrosion of Li-metal anode in an electrolyte saturated with oxygen.
- Low energy efficiency associated with large over-potential and poor cyclability of Li-O₂ batteries.
- Low power rate capability due to electrode blocking by the reaction products.
- Absence of a low-cost, high-efficiency oxygen supply system (such as oxygen selective membrane).

The main goal of this Task is to provide a better understanding on the fundamental reaction mechanisms of Li-O₂ batteries and identify the required components (especially electrolytes and electrodes) for stable operation of Li-O₂ batteries. This task will investigate several new approaches to improve stability of Li-metal anode in Li-O₂ batteries:

- Li-metal anodes will be protected using two approaches: (1) *in situ* formation of a stable SEI layer before Li-O₂ cell operation through various electrolyte formulations and treatment protocols, and (2) *ex situ* formation of stable inorganic/polymeric hybrid electrolyte layers through dip-coating or tape-casting method to coat the inorganic/polymeric hybrid electrolyte layer on Li-metal surface.
- A joint theoretical/experimental approach for design and discovery of new cathode and electrolyte materials will act synergistically to reduce charge overpotentials and increase cycle life. Synthesis methods, in combination with design principles developed from computations, will be used to make new cathode architectures. Computational studies will be used to help understand decomposition mechanisms of electrolytes and how to design electrolytes with improved stability.
- A new cathode will be developed based on high-efficiency catalyst such as two-dimensional TM dichalcogenides. 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.

State-of-the-art characterization techniques and computational methodologies will be used to understand charge and discharge chemistries. Success of this Task will establish a solid foundation for further development of Li-O₂ batteries toward practical applications for long-range EVs. The fundamental understanding and breakthrough in Li-O₂ batteries may also provide insight on improving performance of Li-S batteries and other energy storage systems based on chemical conversion process.

Task 6.1 – Rechargeable Lithium-Air Batteries (Ji-Guang Zhang and Wu Xu, Pacific Northwest National Laboratory)

Project Objective. The objective of this project is to develop rechargeable lithium-oxygen (Li- O_2) batteries with long-term cycling stability. In FY 2019, the team will pay more attention to lithium anode stabilization and building a more stable Li- O_2 battery based on the protected lithium anode and optimized air-electrodes to develop practical Li- O_2 batteries with stable, long-term cycling capability.

Project Impact. Li-air batteries have a theoretical specific energy more than five times that of state-of-the-art Li-ion batteries and are potential candidates for use in next-generation, long-range EVs. Unfortunately, the poor cycling stability and low CE of Li-air batteries have prevented their practical application. This work will explore well-protected Li-metal anodes, new electrolytes, and high-loading air-electrodes that could lead to long cyclability and high CE in high-energy Li-air batteries that can be used in the next-generation EVs required by the EV Everywhere Grand Challenge.

Approach. Li-metal anodes will be protected using highly elastic and stable protective composite layers and gel-polymer crosslinked electrolytes. These membranes will be prepared through dip-coating or tape-casting method to coat the inorganic/polymeric hybrid electrolyte layers. Stable host structures for lithium metal will also be investigated to stabilize Li-metal anode in oxygen atmosphere. The electrochemical performances of Li-O₂ batteries using the protected Li-metal anodes and the previously developed carbon/catalyst composite air electrodes based on CNTs and TM oxides such as RuO₂ will be evaluated. The lithium anodes, air-electrodes, and Li-O₂ cells at different stages of cycling (including as-prepared, after discharge, after recharge, and after cycling) will be analyzed by microscopy and spectroscopy techniques such as SEM, EDX, TEM, XRD, and XPS.

Out-Year-Goals. The long-term goal is to enable rechargeable Li-air batteries with a specific energy of 800 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 long-range EVs.

Collaborations. This project collaborates with C. Wang of PNNL on characterization of cycled air electrodes by TEM/SEM.

- 1. Develop highly elastic and stable protective composite layers for lithium anode in Li-O₂ batteries. (Q1, FY 2019; Completed)
- 2. Protect Li-metal anode by using gel-polymer crosslinked electrolytes Li-O₂ batteries. (Q2, FY 2019; Completed)
- 3. Develop stable host structure to protect lithium anode in oxygen rich environment. (Q3, FY 2019)
- 4. Complete evaluation of cycling performance of Li-O₂ batteries with protected Li-metal anodes and optimized air-electrodes. (Q4, FY 2019)

This quarter, the milestone protecting Li-metal anode in Li-O_2 batteries through the gel-polymer crosslinked electrolytes has been accomplished. Lithium triflate (LiTf) and tetraethylene glycol dimethyl ether (TEGDME) have been demonstrated as stable salt and solvent, respectively, for rechargeable Li-O₂ batteries. The team has developed a kind of crosslinked electrolyte composed of LiTf, TEGDME, and PEO. Li-O₂ cells composed of Li-metal anodes and CNT air-cathodes with 1 M LiTf-TEGDME electrolyte with 5% PEO (Figure 79a), 3 M LiTf-TEGDME electrolyte with 5% PEO (Figure 79b), and 3 M LiTf-TEGDME electrolyte (Figure 79c) have been cycled at 25°C at a current density of 0.1 mA cm⁻² under a capacity control protocol of 1,000 mAh g⁻¹. Although PEO polymer was added into 1 M LiTf-TEGDME electrolyte, cycle life of corresponding cells based on 5% PEO-containing 1 M LiTf-TEGDME electrolyte is still very limited, as shown in Figure 79a. Interestingly, it is found that the cycle life of the cells increases when the salt concentration in the electrolyte is increased to 3 M, as shown in Figure 79b. In contrast, Li-O₂ cells with 3 M LiTf-TEGDME electrolyte but without PEO exhibit the worst cycling stability (Figure 79c) compared to Li-O₂ cells with two other polymer-based electrolytes. Therefore, addition of 5 wt% of PEO polymer in the electrolytes causes shortened cycle life of cells. After 30 cycles, the morphological changes of cycled Li-metal anodes with different electrolytes have been further investigated. As shown in Figure 79d, some black side-reaction products were found on Li-metal surface cycled in 1 M LiTf-TEGDME electrolyte containing 5% PEO (Figure 79d). In contrast, much less corrosion product was found on Li-metal anode recovered from Li-O₂ cells cycled in concentrated electrolyte (3 M LiTf-TEGDME) containing 5% PEO, as shown in Figure 79e. However, without addition of 5% PEO polymer, a much thicker corrosion layer was observed on cycled Li-metal anode recovered from Li-O₂ cells cycled in concentrated electrolyte (3 M LiTf-TEGDME), as shown in Figure 79f. These results indicate that a small amount of PEO can form a stable SEI layer on Li-metal anode and effectively suppress the corrosion of Li-metal anode in an O-rich environment and greatly enhance the cycling stability of $Li-O_2$ cells. It is worth noting that no efficient catalysts (such as nano-cluster of RuO_2 , as reported on previously) were used to decorate CNT-based air-cathodes used in the cells studied this quarter. Extensions of this work to include catalyst in cathode can further improve cycling stability of high-capacity Li-O₂ cells.



Figure 79. Cyclic stability tests based on Li-O₂ cells composed of Li-metal anodes and carbon nanotube air-cathodes at 25°C at a current density of 0.1 mA cm⁻² under a capacity protocol of 1,000 mAh g⁻¹ with different electrolytes: 1 M LiTf-TEGDME electrolyte with 5% PEO (a), 3 M LiTf-TEGDME electrolyte with 5% PEO (b), and 3 M LiTf-TEGDME electrolyte (c). Optical images of Li-metal anodes after 30 cycles in 1 M LiTf-TEGDME electrolyte with 5% PEO (d), 3 M LiTf-TEGDME electrolyte-5% PEO (e), and 3 M LiTf-TEGDME electrolyte (f).

Patents/Publications/Presentations

Publication

 Liu, B., W. Xu, L. Luo, J. Zheng, X. Ren, H. Wang, M. H. Engelhard, C. Wang, and J-G. Zhang. "Highly Stable Oxygen Electrodes Enabled by Catalysts Redistribution through an *In-Situ* Electrochemical Method." *Advanced Energy Materials* (2019). doi:10.1002/aenm.201803598.

Task 6.2 – 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 make improved materials.

Out-Year Goals. The out-year goals are to find catalysts that promote discharge product morphologies that reduce charge potentials and find electrolytes for long cycle life through testing and design.

Collaborations. This project engages in collaboration with Prof. K. C. Lau (UC at Norridge), Prof. Y. Wu (Ohio State University), Dr. D. Zhai (China), and R. Shahbazian-Yassar (UIC).

- 1. Synthesis and testing of low-cost TM catalysts that give low charge potentials in Li-O₂ batteries. (Q1, FY 2019; Completed)
- 2. Investigations of the role of mass and charge transport in discharge and charge reactions in Li-O₂ batteries. (Q2, FY 2019; Completed)
- 3. Characterization of electronic conductivity in discharge products via electrochemical impedance measurements. (Q3, FY 2019)
- 4. Investigation of dependence of discharge product properties on electrolytes with mixtures of sodium and lithium salts. (Q4, FY 2019)

The mechanism and underlying reasons for the evolution of Li_2O_2 morphology are still not well understood in $Li-O_2$ batteries, but this understanding is important for their development. In particular, the effect, if any, of the surface structure of the oxygen cathode on the morphology of the grown Li_2O_2 is still not clear, nor is the effect of Li_2O_2 formation on the mass and charge transport in the O_2 cathode. To clarify this, the team has carried out a systematic experimental and theoretical modeling study on the evolution of Li_2O_2 morphology at different stages of the discharge–charge cycle in a $Li-O_2$ cell.

To suitably monitor evolution of Li₂O₂, that is, the discharge product morphology during discharge, the team fabricated Li-O₂ cells to minimize variations in cell construction because variations in cathode weight, temperature, moisture, and electrolyte wetting can lead to significant changes in cell performance. Swagelok-type cells consisting of a Li-foil anode and a graphitized carbon cathode with PVDF binder were tested in an O₂ atmosphere with a MACCOR cycler. TEGDME with 1 M LiCF₃SO₃ was selected as the electrolyte because it has been demonstrated to be relatively stable toward the discharge product Li₂O₂, during the discharge reaction. The cells were discharged to different specific capacities with a constant current density, and subsequently subjected to SEM observation, impedance measurements, and XRD investigation. SEM images of the discharge dathodes after the 1st, 2nd, and 10th discharge cycles indicate that the discharge products on the carbon cathode are toroid particles; it seems that particle size and quantity increase with the cycle number. Figure 80 shows the voltage profile and XRD patterns as a function of amount of discharge and charge. From

the XRD pattern, it is evident that Li_2O_2 is the main discharge product. No by-products, such as Li_2CO_3 and LiOH, were obtained, indicating that the electrolyte did not decompose during cycling. The team also carried out DFT calculations of the evolution of Li_2O_2 clusters and O_2 mobility.

From this study, it was clear that the morphology and particle size of the discharge product changes significantly as a function of the depth of discharge as well as the cycle number. The impedance spectroscopy showed a gradual increase in resistance with an



Figure 80. (a) The voltage profile of a 1,200 mAh/g capacity-controlled cycle. (b) X-ray diffraction spectra of graphitized carbon cathodes at different discharge or charge capacities.

increase in depth of discharge, which might indicate the build-up of an insulation layer of Li_2O_2 . This phenomenon was confirmed by fitting of the impedance, which showed a lower O_2 diffusion, possibly due to clogging caused by the insulating layer of Li_2O_2 . The limitation in the mobility of O_2 was confirmed by AIMD calculations, which suggest that prior to formation of Li_2O_2 , the trajectories of both the active species (O_2 and Li^+) are found to be nearly linear and time dependent. However, the mobility of O_2 and Li^+ starts to diminish as Li_2O_2 starts forming. Furthermore, a sustainable mass transport of the diffusive active species (for example, O_2 and Li^+) and evolution of the underlying interfaces are critical to dictate desirable oxygen reduction (discharge) and evolution (charge) reactions in the porous carbon electrode of a Li-O₂ cell.

Patents/Publications/Presentations

Publications

- Dai, A., Q. Li, T. Liu, K. Amine, and J. Lu. "Fundamental Understanding of Water-Induced Mechanisms in Li-O₂ Batteries: Recent Developments and Perspectives." *Advanced Materials* (2018): 1805602.
- Wang, X., Y. Li, X. Bi, L. Ma, T. Wu, M. Sina, S. Wang, M. Zhang, J. Alvarado, B. Lu, A. Banerjee, K. Amine, J. Lu, and Y. S. Meng. "Hybrid Li-Ion and Li-O₂ Battery Enabled by Oxyhalogen-Sulfur Electrochemistry." *Joule* 2, no. 11 (2018): 2381–2392.

Task 6.3 – Lithium Oxygen Battery Design and Predictions (Larry A. Curtiss/Anh Ngo, Argonne National Laboratory; Amin Salehi-Khojin, University of Illinois at 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 the 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 development of new materials for electrodes, anodes, and electrolytes that work in synergy.

Approach. The experimental strategy is to use cathode materials based on 2D TM dichalcogenides (TMDCs) that the team has found to be among the best oxygen reduction and evolution 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. DFT and AIMD simulations are used to gain insight at the electronic structure level of theory of the electrolyte structure and function both in the bulk and at interfaces with the cathode, anode, and discharge product. Classical MD is used to obtain understanding at longer length and time scales of processes occurring in the electrolyte and growth mechanisms of discharge products. The team will also utilize a high-throughput 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 that will have the best performance.

Out-Year Goals. The out-year goal is to find electrolytes for Li-O₂ batteries that give high capacities and long cycle life in an air atmosphere using high-throughput screening.

Collaborations. This project engages in collaboration with Z. Zhang (ANL), R. Assary (ANL), B. Narayanan (University of Louisville), J. G. Wen (UIC), and R. Klie (University of Illinois at Chicago).

- 1. Investigate possible lithium anode protection additives and redox mediators for electrolyte blends that can work with MoS₂ cathode to extend cycle life and reduce charge overpotentials of Li-O₂ cells. (Q1, FY 2019; Completed)
- 2. Assess electrolytes blends and additives that will work in concert with MoS₂ cathode in Li-O₂ cells. (Q2, FY 2019; Completed)
- 3. Evaluate, using experiment and theory, properties of redox mediators for electrolyte blends to lower charge potentials for increased efficiency of Li-O₂ cells. (Q3, FY 2019; In progress)
- 4. Develop first-generation electrolytes that work in concert with MoS₂ cathode for increased efficiency of Li-O₂ cells running in a realistic air environment. (Q4, FY 2019; In progress)

Li-O₂ batteries are regarded as an advanced energy storage system that could provide a much higher specific energy than Li-ion batteries for transportation applications due to use of chemical transformations. Thus far, the research on the Li-O₂ battery has been largely limited to the short life cycle in a pure oxygen environment (Li-O₂ batteries). In the presence of actual components of air such as nitrogen, carbon dioxide, and moisture, the issues of side reactions become more complex because the small concentrations of these species can react with discharge products at the cathode or with the lithium anode. Another major challenge for Li-O₂ systems is that their volumetric energy density, due to the necessity of the storing of oxygen or purification of air, may not be large enough for practical applications. In this project, the team is exploring new avenues to improve on a Li-O₂ battery that can operate in a realistic air environment [*Nature* 555 (2018): 502], but requires a high charge potential (~ 4 V). To do this, the team is first investigating electrolyte blends and additives that can lower the charge potential for the MoS₂ cathode used in the Li-air battery with an O₂ environment. Last quarter,

the team found that LiI could lower the charge potential, while $LiNO_3$ could increase cycle life. This was done in separate studies in a $Li-O_2$ battery running in pure O_2 .

This quarter, the team has explored ways to get both longer cycle life and lower charge potentials at the same time in the same Li-O₂ cell in an O₂ atmosphere. They found that a cell configuration based on the molybdenum disulfide cathode with 25% ionic liquid in an electrolyte blend



Figure 81. (left) Voltage profiles for Li-O₂ battery with 1 M LiNO₃ and 1 M Lil in 75% TEGDME / 25% ionic liquid. (right) Raman spectra showing the presence of Li_2O_2 in the discharge product.

with 75% tetraglyme (TEGDME) containing both LiNO₃ and LiI was able to achieve a low charge potential (~ 3.4 V) and long cycle life (100 cycles). A unique aspect of this electrolyte is the large concentrations of both LiNO₃ and LiI used in it. These large concentrations along with the use of both salts at the same time seem to be an effective way to simultaneously reduce the charge potential and increase cycle life, which is not possible

when used separately. The voltage profile is shown in Figure 81. In addition, various techniques have been used to characterize the discharge product including Raman spectra, XPS, and HRTEM. All techniques show the presence of Li_2O_2 as the discharge product. The Raman spectra is shown in Figure 81. The lithium anode has been found to have an amorphous coating from HRTEM studies that results from the LiNO₃ and protects the anode from degradation.

The team is carrying out DFT computational simulations to help investigate the role of LiI as a redox mediator in the Li-O₂ cell. This has included simulations of LiI₃, the oxidized product of LiI at the interface between the electrolyte and a Li_2O_2 interface. Figure 82 shows that LiI₃ becomes three LiI moieties at the interface and probably helps to decompose the Li_2O_2 . Reaction pathways for this decomposition are being explored. The team is carrying out further characterizations and computations of this cell configuration to fully understand the role of LiNO₃ and LiI and how to modify the electrolyte to accommodate use of air in place of O₂.



Figure 82. Density functional theory simulation of Lil₃ molecule added to electrolyte showing it forming three Lil units on a Li₂O₂ surface.

Patents/Publications/Presentations

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

TASK 7 – SODIUM-ION BATTERIES

Summary

During FY 2019, the BMR will add five new projects, including several in the area of Na-ion batteries. The Na-ion battery will require investigations to identify optimal electrode materials, electrolytes, separators, and binders to reach its 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. These projects will be included in this new section as they get underway. More detailed information on this BMR Task will be provided in upcoming reports.

Task 7.1 – Exploratory Studies of Novel Sodium-Ion Battery Systems (Xiao-Qing Yang and Enyuan Hu, Brookhaven National Laboratory)

Project Objective. The objective of this project is to develop new advanced *in situ* material characterization techniques and apply these techniques to explore the potentials, challenges, and feasibility of new rechargeable battery systems beyond the Li-ion batteries, namely the sodium-ion battery systems for EVs, such as PHEV and BEV. To meet the challenges of powering PHEVs and BEVs, 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. This project will use the synchrotron based *in situ* x-ray diagnostic tools, combined with TEM and STEM imaging techniques developed at BNL, to evaluate the new materials and redox couples to obtain fundamental understanding of the reaction mechanisms of these materials aiming for improvement of and guidance for new material and new technology development regarding Na-ion battery systems.

Project Impact. In the VTO MYPP, the goals for battery were described as: "Specifically, lower-cost, abuse-tolerant batteries with higher energy density, higher power, better low-temperature operation, and longer lifetimes are needed for the development of the next-generation of HEVs, PHEVs, and EVs." The knowledge learned from diagnostic studies and collaborations with U. S. industries through this project will help U. S. research institutions and industries to develop new materials and processes for a new generation of rechargeable battery systems, namely Na-ion battery system, in their efforts to reach these VTO goals.

Approach. This project will use the synchrotron-based *in situ* X-ray diagnostic tools developed at BNL to evaluate the new materials and redox couples to enable a fundamental understanding of the mechanisms governing performance of these materials and provide guidance for new material and new technology development regarding Na-ion battery systems.

Out-Year Goals. Complete the synchrotron based *in situ* XRD and *ex situ* absorption (XAS) studies of low-cost P2-type iron-based cathode materials ($Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_2$) as new cathode materials for Na-ion batteries during charge-discharge cycling.

Collaborations. The BNL team has been closely working with top scientists on new material synthesis at ANL, LBNL, and PNNL and with U. S. industrial collaborators at General Motors and Johnson Controls, as well as international collaborators.

- 1. Complete *in situ* XRD studies of new low-cost P2-type iron based cathode materials (Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O₂) for Na-ion batteries during charge-discharge cycling. (Q1, December 2018; Completed)
- Complete the synchrotron-based XAS studies and XAS analysis of Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O₂ and Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O₂ electrodes at different SOCs at iron K-edge, copper K-edge, and manganese K-edge. (Q2, March 2019; Completed)
- 3. Complete the sXAS studies of Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O₂ and Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O₂ electrodes at different SOCs at iron L-edge, copper L-edge, and oxygen K-edge. (Q3, June 2019; In progress)
- 4. Complete *in situ* XRD studies of new stabilized global P2 phase cathode material (Na_{0.72}[Li_{0.24}Mn_{0.76}]O₂) for Na-ion batteries during charge-discharge cycling. (Q4, September 2019; In progress)

This quarter, the second milestone was completed. BNL has been focused on the synchrotron-based XAS studies and XAS analysis of $Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O_2$ and $Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O_2$ electrodes at different SOCs at iron K-edge, copper K-edge, and manganese K-edge. The XAS results for Na_{0.7}[Cu_{0.15}Fe_{0.3}Mn_{0.55}]O₂ at the 1st and the 11th cycles are shown in Figure 83. To have deep insight into the voltage fade, the K-edge XAS tests of electrodes cycled after 10 cycles were also performed, and results are shown in Figure 83a. No obvious difference is found around the absorption edge. However, the pre-edge intensity of both 11th charged and 11th discharged is higher than that of the first cycle. It can be concluded that more iron ions transport to the interlayer after the 11th charge and that more iron ions remained at the interlayer tetrahedral sites after the 11th discharge. The gradual accumulation of iron in interlayer leads to relative larger polarization, but such accumulation tends to stabilize within subsequent cycles, and the voltage fading phenomenon will weaken correspondingly. However, the pre-edge peak of the 1st charged or the 11th charged Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O₂ electrode at iron K-edge shows almost no changes compared with the pristine one (Figure 83d). This means that very few iron ions in the charged Na_{0.7}[Cu_{0.2}Fe_{0.2}Mn_{0.6}]O₂ electrode migrate from the TM layer to the interlayer tetrahedral site; thus, the structure maintained P2 stacking mode all around the circulations. The XANES spectra at copper K-edge of $Na_{0.7}[Cu_{0.15}Fe_{0.30}Mn_{0.55}]O_2$ and $Na_{0.7}[Cu_{0.20}Fe_{0.20}Mn_{0.60}]O_2$ electrodes were also measured during the first cycle, and are displayed in Figure 83b and 83e, respectively. Both absorption edges of these two electrodes show negligible shift below 4.0 V and an apparent shift between 4.0-4.2 V, indicating the oxidation of Cu²⁺ proceeds above 4.0 V. Moreover, the weak single pre-edge peak of copper K-edge doesn't change obviously, which indicates that the octahedral coordination of copper is maintained well, even charged to a high voltage. Figure 83c/f displays the normalized XANES spectra in $Na_{0.7}[Cu_{0.15}Fe_{0.30}Mn_{0.55}]O_2$ and $Na_{0.7}[Cu_{0.20}Fe_{0.20}Mn_{0.60}]O_2$ electrodes at different SOCs during the 1st and 11th cycles respectively.



Figure 83. X-ray absorption spectroscopy analysis of (a-c) Na0.7[Cu0.15Fe0.3Mn0.55]O2 and (d-f) Na0.7[Cu0.2Fe0.2Mn0.6]O2 electrodes at different states of charge during the 1st and 11th cycle: X-ray absorption near-edge structure spectra at (a/d) iron K-edge, (b/e) copper K-edge, and (c/f) manganese K-edge.

Patents/Publications/Presentations

Publications

- Rong, X., E. Hu, Y. Lu, F. Meng, C. Zhao, X. Wang, Q. Zhang, et al. "Anionic Redox Reaction-Induced High-Capacity and Low-Strain Cathode with Suppressed Phase Transition." *Joule* 3 (2019): 503. Publication Date: February 20, 2019; doi: 10.1016/j.joule.2018.10.022.
- Li, Y., X. Wang, Y. Gao, Q. Zhang, G. Tan, Q. Kong, S-M. Bak, G. Lu, X-Q. Yang, L. Gu, J. Lu, K. Amine, Z. Wang, and L. Chen. "Native Vacancy Enhanced Oxygen Redox Reversibility and Structural Robustness." *Advanced Energy Materials* 9 (2019): 1803087. Publication Date: January 24, 2019; doi: 10.1002/aenm.201803087.

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 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 U.S. in a strong position as relates to new low-cost energy storage systems beyond Li-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 in a synergistic way 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 (1) gradient cathodes consisting of Fe-Mn compositions, and (2) intergrowths of layer stacking sequenced oxides. If resources allow, the team also will attempt to stabilize cathode surfaces using ALD methods, particularly for the benefit of staving off dissolution of manganese and iron / electrolyte reactivity. Electrolytes will be partly procured from Dr. H. Pan at 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. Dr. H. Pan from PNNL, who is developing electrolytes for Na-ion batteries, will provide this project with formulations to test with its various electrode combinations instigated at Argonne. The project will also exchange commercial samples with Dr. J. Barker of Faradion Ltd. in the United Kingdom.

- 1. Report on the BatPaC cell cost and energy density for the proposed Na-ion battery cell couple. (Q1, FY 2019; Completed).
- 2. Report on the synthesis, characterization, and initial cycling performance data on relevant Na-ion anode battery materials. (Q2, FY 2019; In progress)
- 3. Optimize anode composites produced in Q2. Continue characterization of materials for understanding. (Q3, FY 2019)
- 4. Demonstrate cycle life of optimized anode. (Q4, FY 2019)

Argonne has been a leader in producing spreadsheet calculations that cost out a particular battery chemistry, by utilizing known metrics of raw material cost, cell voltages, capacities of electrodes and their densities. This program, called BatPaC, is used worldwide to project an EV-sized battery with the appropriate hardware in place.^[1] With regard to Na-ion battery chemistry, the BatPaC model outputs a cost of \$63.5/kWh, and a volumetric energy density of 549 Wh/L.



Figure 84. Example Microsoft Excel spreadsheet calculations used in the BatPaC model to project cost and energy density of Na-ion batteries.

Lead (Pb), Pb-Oxides/C Composite Anode

The development of recyclable lead and Pb-oxide/C composites as volumetrically energy dense anodes to be paired with phosphorus is the team's first approach. The Pb-based work was initiated by synthesizing a series of Pb-Pb oxide carbon composites using a high-energy SPEX ball mill. The samples synthesized and their weight ratios are given in Table 3. The XRD powder diffraction results (Figure 85a) show that both PbO and Pb_3O_4 are mostly converted to Pb-metal with a remaining oxide present. The SEM micrograph (Figure 85b) indicates a homogeneous mix is present. The carbon helps to disperse the lead particles such that the soft lead does not stick to the jar walls.

These composites were then cycle tested in a Na-battery cell with Na-metal as CE and with the Pb-Pb-oxide/C material as the WE. The voltage profile is in Figure 86a, and the dQ/dV results are shown in Figure 86b. In general, the Na_xPb_y phase formation is ideal and matches that of the literature results.^[2] Four independent binary phases are formed: $NaPb_3 \rightarrow NaPb \rightarrow Na_9Pb_4 \rightarrow Na_{15}Pb_4$. This first-cycle sodiation process occurs in four steps, and desodiation is reversible. However, the electrochemical mechanism on the second sodiation appears to be occurring through a different pathway. The team plans to study the reaction more in detail next quarter and to optimize performance.

The cycle performance and the voltage profile are shown in Figure 87. The stability through 100 cycles is quite respectable as compared to the baseline pure oxides of PbO and Pb_3O_4 electrodes. Because of the high mass per volume density of the Pb-Pb oxide/C composite, the volumetric capacity equates to about 1600 mAh/cc, which is greater than graphite (LIB) of 600 mAh/cc and approaches silicon (LIB) at 2200 mAh/cc. Certainly, the team also needs to improve on the first-cycle irreversible capacity loss (ICL) of about 43%. They have some strategy on pre-sodiation of the Pb-Pb oxide-C composite for the next quarter to improve first ICL.

Table 3. Experimental conditions associated with the processing of lead oxide materials with carbon powders.

- Lead oxide : carbon = 7 : 3 weight ratio
- Lead oxide sources: PbO and Pb3O4
- Carbon sources: super P and C45 (Timcal) carbon black
- Added, Stainless jar and sealed in glove box.



The sealed jar was shaken in SPEX 8000M MILL GRINDER for 6h

Method	Compound	Electrode laminate
Spexmill	Pb-O-C composite #1 (from PbO)	Active : Carbon : PVDF = 8 : 1 : 1
Spexmill	Pb-O-C composite #2 (from Pb ₃ O ₄)	Active : Carbon : PVDF = 8 : 1 : 1
	Commercial PbO (SIGMA)	Active : Carbon : PVDF = 7 : 2 : 1
	Commercial Pb ₃ O ₄ (SIGMA)	Active : Carbon : PVDF = 7 : 2 : 1
	Super-P	Carbon : PVDF = 9 : 1





Figure 85. (a) X-ray diffraction pattern of the sample coming out of the SPEX mixer mill after 6 h. (b) Scanning electron microscopy of this composite.



Figure 86. (a) Voltage profile of lead Pb-oxide/C composite electrode in sodium half-cell; note the electrolyte is EC:EMC with 1 M NaPF₆ and 10% FEC. (b) dQ/dV trace of the voltage profile. Numeric marks indicate Na-Pb alloy formations, and the asterisk is for decomposition of 10% FEC at the lead-metal surface. (c) The literature Coulometric titration curve of a pure lead electrode in sodium nonaqueous organic solvent electrolyte cell.^[2]



Figure 87. Cycle performance as specific capacity (math/g versus cycle number for the lead Pb-oxide/carbon composite anode in a sodium half-cell. The black markers/curves are for the baseline PbO and Pb₃O₄ anodes with carbon conductive additive.

[1] http://www.cse.anl/batpac/index.html

[2] Ellis, L. D., et al. Journal of Electrochemical Society 161 (2014): A416–A421.

Patents/Publications/Presentations

The project was initiated in January 2019 and has no patents, publications, or presentations to report this quarter.

Task 7.3 – High-Capacity, Low-Voltage Titanate Anodes for Sodium-Ion Batteries (Marca Doeff, Lawrence Berkeley National Laboratory)

Project Objective. Objectives are to understand the differences in sodium intercalation mechanism of various sodium titanate anodes through an array of synthetic, electrochemical, and structural characterization techniques, and overcoming practical impediments to their use, such as the high first-cycle Coulombic inefficiencies that are currently observed. The ultimate goal of the project is to produce a 200-250 mAh/g anode that cycles reversibly.

Project Impact. Although there are several suitable cathode materials for Na-ion batteries, there are few suitable anode materials due to their low potential instabilities. Therefore, sodium titanate variations will be synthesized through different routes to develop materials with various morphologies and dopants. Decreasing the first-cycle inefficiencies and improving cycling performance has the ability to enable technology for a practical high-energy Na-ion battery.

Out-Year Goals. A series of synchrotron characterization techniques will be used to further develop sodium titanate anode materials with stable cycling while delivering high capacities.

Collaborations. TXM is done in collaboration with Dr. Y. Liu (SSRL). Synchrotron hard, sXAS, and X-ray Raman efforts are in collaboration with Dr. D. Nordlund and Dr. D. Sokaras (SSRL). Electrolyte design is done in collaboration with Dr. K. Xu (U. S. Army Research Laboratory).

- 1. Hydrothermal synthesis of sodium nonatitanate. (Q1, FY 2019; Completed)
- 2. Ion exchange sodium nonatitanate with magnesium. (Q2, FY 2019; Completed No Go)
- 3. Complete synchrotron XRD and XAS analysis on sodium nonatitanate. (Q3, FY 2019; Completed)
- 4. *Go/No-Go Decision*: Magnesium exchange; stop if electrochemical properties are not improved. (Q4, FY 2019)

The hydrothermal synthesized sodium nonatitanate (NNT) with various morphologies and levels of crystallinity was subject to electrochemical analysis. Two types of electrodes were studied: conventional electrode with conductive additive and binder, and a carbon-free electrode, shown in Figure 88a. The carbon-free electrode was used to investigate the reduction mechanism of titanium in the various NNT materials-an intercalation mechanism or supercapacitor mechanism. Last quarter, the team demonstrated the first two cycles. After long-term cycling, the spherical particles outperform nanowire morphology. The rate limitations are evident in the nanowire morphology as well as fast capacity fading. Electrode optimization is ongoing because the PVDF binder is known to hinder performance of low-voltage anodes for both Na-ion and Li-ion batteries. Some of the binders



Figure 88. (a) Pristine carbon-free nonatitanate (NNT) electrode (90% active material: 10% PVDF binder). (b) Sodiated NNT electrode to 0.1 V at 4 mA/g current. (c) Desodiated NNT electrode after the first cycle. Diffraction patterns of sodium NNT synthesized by hydrothermal method. The material was dehydrated to different degrees. Scanning electron microscopy images of corresponding materials after dehydration at 600°C.

being tested are PAA and carboxymethyl cellulose. The carbon-free electrode was discharged to 0.1 V at 4 mA/g (slow rate) to allow the redox reaction to occur (Figure 88b), and the electrode subsequently turned blue due to partial reduction of titanium from 4+ to 3+, which provides initial evidence of charge transfer. After sodiation, the NNT maintains its blue color, suggesting that the increased electronic conductivity is maintained during cycling (Figure 88c).

The titanium reduction mechanism was further explored by XANES. Nanowire and spherical NNT were examined in the pristine state (OCV) and after the first discharge (Figure 89). All pristine samples overlap one



Figure 89. X-ray absorption spectroscopy comparing the titanium K-edge of the various nonatitanate (NNT) morphologies in the pristine state and first desodiation.

another to demonstrate that titanium is at 4+ oxidation state before electrochemical cycling. Once the electrodes are desodiated to 0.1 V, the titanium K-edge shifts to a lower energy, which results in reduction of titanium to 3+, consistent with the results in Figure 88. Three prepeaks, designated A1-A3, are also present in the pristine state; these correspond to the transitions of titanium 1s core electrons to unoccupied 3d-4s/4p states. However, after electrochemical cycling, the A1 peak decreases, which suggests partial filling of the Ti-3d t_{2g} band due to the charge compensation that occurs during the discharge state. The shift in titanium K-edge to lower energy and a decrease in the A1 prepeak further validate that reductive intercalation occurs during the electrochemical cycling of NNT. The team will utilize sXAS to further elucidate the redox behavior of NNT as well as the effect of binders and electrolytes on the SEI.

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 (Huilin Pan and Ji-Guang Zhang, Pacific Northwest National Laboratory)

Project Objective. This project will develop innovative electrolytes and enable fundamental understanding on the interface between electrode and electrolyte for stable operation of high-energy Na-ion batteries for potential application in EVs. 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, build 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 enable a fundamental understanding on the electrolyte/electrode interface in Na-ion battery systems. Successful project execution will improve their energy density, cycle and calendar life, and safety. The project will provide a solid contribution to development of Na-ion battery technology and promote its practical application as a competitive alternative to the current Li-ion batteries, as well as greatly reduce the cost of energy storage systems for EVs.

Approach. This project will optimize the electrolyte components and concentrations to develop innovative electrolyte and additives with improved physical and (electro) chemical properties. *In situ* and *ex situ* spectroscopy methods will be used to unravel the origin of the SEI at the dynamic interface, providing guidance for the electrolyte and interface design and enabling high achievable capacity and long life of Na-ion batteries.

Out-Year Goals. This project will select the electrolyte compounds and use *in situ* and *ex situ* techniques to identify the formation of interfacial SEI layer and its effect on the electrode materials. It will also provide guidance to electrolyte optimization to improve the hard carbon anode capacity to >300 mAh g⁻¹, and enable its long-term stable operations.

Collaborations. This project will collaborate with ANL and LBNL and other leading scientists in the field of cathode and anode materials for Na-ion batteries. It will collaborate with Dr. C. Wang and Dr. M. Engelhard for TEM and XPS characterization.

- 1. Determine the physical-chemical properties of carbonate-based electrolytes, and identify the key factor affecting the stability of these electrolytes in sodium batteries. (Q1, FY 2019; Completed)
- 2. Design new phosphate-based electrolyte with improved electrochemical and thermal stability in sodium batteries. (Q2, FY 2019; Completed)
- 3. Characterize chemical coordination structure of selected carbonate- and phosphate-based electrolytes for sodium batteries. (Q3, FY 2019; In progress)
- 4. Demonstrate improved capacity, CE, and cyclic stability of electrode materials using the electrolytes developed in this work; achieve hard carbon capacity of >250 mAh g⁻¹, initial cycle Coulombic efficiency (ICE) > 85%, and cycle life > 200 times. (Q4, FY 2019; In progress)

The milestones for the first and second quarters have been accomplished. The carbonate-based electrolyte composition (salt, solvent) was optimized for hard carbon anode in Na-ion batteries. New functional phosphate-based electrolytes were developed for TM oxide cathode with high compatibility. *In situ* three-electrode EIS measurement was designed to identify the electrode process at cathode/anode interface individually. For carbonate-based electrolytes, the solvent effect on the ionic conductivity was investigated, revealing an ionic conductivity sequence: EC+DMC (1:1 in mass) > PC+DMC (1:1 in mass) > EC+PC (1:1 in mass) > PC > DMC. This is independent of the electrolyte salt used. The salt effect was further studied in the optimal co-solvent of EC+DMC (1:1 in mass), showing a sequence in ionic conductivity of NaFSI ~ NaPF₆ > NaTFSI > NaTf. Na || Hard carbon (HC) cells were used for primary evaluation of electrolytes. (HC electrode: HC: PVDF: CB=90:5:5, mass loading: 2-3 mg/cm²). Solvent shows significant effect on capacity and rate performance of HC anode, in which EC in co-solvent is needed for good SEI formation resulting in higher CE and fast ion transport. Electrolyte of 1 M NaPF₆ in the co-solvent of EC+DMC (1:1 in mass) exhibits the best overall performance, with the highest reversible capacity of 313 mAh g⁻¹ in the 1st cycle at 0.1C, highest ICE of 85.2%, and the best rate performance of 243 mAh g⁻¹ at 1C (Figure 90a-b). Three-electrode EIS measurement indicates that the HC has the smallest electrochemical impedance in EC+DMC (1:1 in mass) co-solvent among

different solvents in the first cycle (Figure 90c). The rate performance of HC presents a sequence of NaPF₆ > NaTf > NaFSI> NaTFSI in electrolytes (at 1 M).

For phosphate-based electrolytes, triethyl phosphate (TEP) and trimethyl phosphate (TMP) with different solvent/salt (NaFSI) molar ration (8:1, 4:1, 2:1, 1.8:1) were prepared. The electrolyte of TEP:NaFSI (2:1) exhibits higher slightly ionic conductivity (~ 4 mS cm⁻¹ at 25°C) than that of TMP:NaFSI (2:1).The diluent of TTE in TEP:





NaFSI (2:1) shows no significant influence on the ionic conductivity, while the diluent of BTFE exhibits ~ 30% increase in the ionic conductivity (Figure 90d). Layered NalO3-NaCu_{1/9}Ni _{2/9}Fe_{1/3}Mn_{1/3}O₂ (Na-CNFM) cells were used to evaluate the TEP-based phosphate electrolytes (Na-CNFM weight ratio in cathode: 93.5%, mass loading: 10-16 mg cm⁻²). TEP-based electrolyte is more compatible with cathode than conventional carbonate electrolyte, with greatly improved CE and active material utilization. Compared with conventional carbonate-based electrolyte, the TEP:NaFSI (2:1) greatly improved ICE from 77% to 98% at the C/10 (Figure 90e). The CE for Na || Na-CNFM cell is stable over 50 cycles at 99.8-99.9% in TEP:NaFSI (2:1) electrolyte, while carbon-based electrolyte (1 M NaPF₆ / EC+DMC) exhibits a much lower cycling CE of ~ 90% and rapid fading to CE of ~ 70% after 45 cycles (Figure 90f).

Patents/Publications/Presentations

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

Innovation Center for Battery500 (Jun Liu, PNNL; Yi Cui, Stanford University)

Project Objective. The project aims to develop commercially viable lithium battery technologies with a cell-level specific energy of 500 Wh/kg through innovative electrode and cell designs that enable the extraction of the maximum capacity from advanced electrode materials. In addition to achieving high specific energy, the project aims to be able to achieve 1,000 cycles for the developed technologies.

Project Impact. The Battery500 Consortium will develop the 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 materials in commercially viable high-energy batteries. The advances made in this consortium will also benefit the improvement of current Li-ion battery technologies.

Approach. This project will utilize an assortment of national resources located at the national laboratory level and university level. The lithium anode combined with a compatible electrolyte system and two cathodes—one high-Ni LiNi_xMn_yCo_zO₂ and another sulfur—will be studied and developed to reach high-energy density. The project focus is to design novel electrode and cell architectures to meet the 500 Wh/kg goal. The consortium will work closely with R&D companies, battery/materials manufacturers, and end users/OEMs to ensure that the developed technologies are aligned with industry needs and can be transitioned to production.

Out-Year Goals. This project aims for the following out-year goals. (1) Integrate materials and components developed in FY 2018 into 1-Ah pouch cell and demonstrate 400-Wh/kg cell with more than 30 charge discharge cycles, and provide analytical results for materials selection, cell design and fabrication, and further refinement for FY 2019. (2) Evaluate the seedling projects for key findings.

Collaborations. The collaboration among consortium team members will be well coordinated by the leadership team, which includes the keystone project leads and co-leads along with PIs at all member institutions. Collaboration with the community outside of this consortium and with industry will be facilitated by the executive committee, the advisory board, and the industry committee.

- 1. Synthesize high-nickel layered oxide cathodes (nickel content > 90%) with a capacity of > 210 mAh/g and test. (Q1, FY 2019; Completed)
- 2. Implement lithium protection approaches to demonstrate 20% cycle life improvement. (Q2, FY 2019; Completed)
- 3. Fabricate and test a pouch cell capable of 350 Wh/kg and 250 cycles. (Q3, FY 2019; In progress)
- 4. Fabricate and test a pouch cell capable of 400 Wh/kg and 30 cycles. (Q4, FY 2019; In progress)

This quarter, the second milestone was completed, and progress toward other milestones was made. Lithium protection approaches to demonstrate 20% cycle life improvement were implemented and achieved.

The PIs delivered 29 invited talks and published 18 papers in peer-reviewed journals during this quarter.

The technical portion of this report is organized under three Keystone projects, as presented below.

Keystone Project 1: Materials and Interfaces

This quarter, the Keystone 1 project investigated a Li-metal anode on which dendrite-free lithium can be plated/stripped rapidly at a relatively low impedance from either a liquid or a solid electrolyte. The design of electrochemical cell used *in operando* XRD approches and simulation approaches was further improved. The

origin of the first-cycle capacity loss of high-Ni NMC and approaches to mitigate it are also proposed.

A Li-metal anode on which dendrite-free Li can be plated/stripped rapidly at a relatively low impedance from either a liquid or a solid electrolyte has been demonstrated in coin cells by J. Goodenough's group at UT Austin. The anode is fabricated in a glove box by incorporating graphite fluoride (GF) in molten lithium at 250 °C. The lithium bonds strongly with the GF to form a LiF layer, and the hydrophobic GF-LiF SEI protects the lithium metal from reaction with moist air. The formed GF–LiF–Li composite then can be removed from the glove box and assembled in a cell



Figure 91. *In situ* optical microscopy used to visualize the electrodeposition of lithium and long-term cycling on symmetric cells. (a) The optical images of the bare lithium (left column) and GF–LiF–Li (right column) interfaced with electrolyte after 0-, 10-, 15-, and 20-minute lithium plating at a current rate of 3 mA cm⁻². The scale bars are 200 μ m. (b-d) Cycling curves in symmetric cells for bare lithium foil (black) and GF–LiF–Li (red) at various current densities: (b) 1 mA cm⁻², (c) 5 mA cm⁻², and (d) 10 mA cm⁻². The specific capacity of the cell is 1 mAh cm⁻². (e) Cycling performance of symmetric GF–LiF–Li cells cycled at 2 mA cm⁻² rates for 2, 4, and 6 mAh cm⁻² capacity cells.

in ambient air. The GF–LiF composite is stable on contact with an organic liquid-carbonate electrolyte and bonds with metallic lithium to form a dendrite-free GF–LiF–Li composite anode. The GF–LiF–Li composite anode can reduce fabrication costs, enable a fast charge, increase cycle life, and increase the energy density in safe rechargeable Li-metal batteries.

To understand and quantify sources causing reduced CE during cycling, *in operando* XRD studies were carried out and the design of electrochemical cell was modified by M. Toney's group (SLAC) to provide better control over electrochemical surface area. The sources identified include "dead" lithium, reduction of electrolyte to form the SEI, and corrosion of the lithium metal. A pouch cell holder with well-controlled pressure applied to the cell was designed to be compatible for X-ray measurements. Therefore, the methodology of X-ray measurements of lithium metal can be extended to a realistic cell. The initial results in this controlled pressure cell indicate that the compression has a large influence on over potential and some of the "dead" lithium can be reactivated. The baseline 1 M LiPF₆ in EC/DMC electrolyte (LP30) with controlled amounts of HF additive is being studied in Li-copper cells as a model system to investigate the mechanistic link between

electrolyte composition, SEI properties, and Li-metal morphology. Results have determined that there is an optimum concentration range (~ 100 ppm) of HF additive that induces columnar growth, while lower and higher concentrations yield less-ordered morphologies. Initial AFM studies have shown the promise of this technique in producing valuable *operando* data even for very low capacity cell to visualize the link between the initial SEI formation on copper and initial Li-metal nucleation.

The voltage profiles of a Li||Cu symmetric cell were simulated by V. Subramanian's group (UW) and compared with experimental data obtained by *operando* XRD (Figure 92a). The variation of overpotentials as a function of time is shown in Figure 92b. The fitted polynomials predict a sharp drop in overpotential at the copper electrode, in addition to a smaller increase at the lithium electrode. The anodic signature is likely due to the transition between 'fast' and 'slow' pathways. At the lithium electrode, this may be the exhaustion of electrochemically deposited lithium and their



Figure 92. (a) Comparison between model prediction and experimental voltage response for lithium symmetric cells. (b) Simulated electrode overpotentials as a function of time.

associated faster kinetics, and gradual transition to stripping from the bulk. The sharp drop at the copper electrode is more pronounced than at the lithium electrode, suggesting a transition in lithium deposition from growing of the existing deposits to formation of new nuclei, possibly due to passivation by SEI formation. This likely explains the sudden drop followed by a gradual rise in overpotential. The trends in electrode polarization track the variations in fitted exchange current density. The increase in polarization of both electrodes is due to the reduction in effective exchange current densities, establishing the consistency of the model.

The origin of first-cycle capacity loss of high-Ni NMC was investigated by S. Whittingham's group (Binghamton). It was found that the slow in-diffusion of lithium ions was the main contributor to the first-cycle capacity loss for NMC-811. As shown in Figure 93a-b, increasing the temperature to 45°C significantly decreased this loss. This is indicative of a diffusion-limited reaction. This study also indicated that there are additional side-reactions for the highest charging voltaged cells, such as increased cycling hysteresis and discharge capacity loss. Elemental substitution in lattice and surface coatings might be mitigations to be used. In addition, it was found that calendering decreases first-cycle loss and that conductive carbon types and amount used have no impact (electrode conductivity is not an issue). Cathode active material loading also has no impact.

In a separate effort, the effect of separator coating on the performance of Li||NMC-811 cells was investigated by J. Yang's group (UW). As shown in Figure 93c, excellent cycling stability of cells using Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP)-coated PP separator has been demonstrated in a pouch cell prepared at PNNL. The cell using the LATP-coated PP separator has a reversible capacity of ~ 200 mAh g⁻¹ and a CE of 99.5% at 0.33 C rate cycling, higher than those of the cells using the bare PP separator (~ 195 mAh g⁻¹ and 98.5%).





Highlights of Keystone Project 1

- A new Li-metal anode on which dendrite-free lithium can be plated/stripped rapidly at a relatively low impedance from either a liquid or a solid electrolyte has been demonstrated.
- The design of electrochemical cell used in *operando* XRD has been further improved, and the results combining with modeling studies can provide better understanding and quantified causes of reduced CE of a Li-metal anode during cycling.
- The origin of the first-cycle capacity loss of high-Ni content NMC cathode has been identified, and approaches to mitigate it have been proposed.

Keystone Project 2: Electrode Architecture

The goal of the Keystone 2 is to design, model, fabricate, and characterize the effects of electrode architecture on electrode and cell performance in support of reaching the project goal of 500 Wh/kg cell specific energy. Included in this Keystone are architecture design of thick cathodes (UCSD), Li-metal electrode architectures (PNNL and Stanford), inorganic (UT-Austin) and polymer (Stanford) electrolytes, and electrode performance modeling (UW). Highlighted this quarter are recent advancement at UW on electrochemical modeling of lithium deposition and the development of transport measurement of thick cathodes at UCSD.

Work at Stanford on the lithium electrode architecture is the use of pyrolyzed eggplant (EP) to serve as a Li-metal host to take advantage of its aligned channels. Further, the host is coated with LiF (EP-LiF) to improve the interfacial stability in an ether electrolyte. Figure 94 illustrates the fabrication process of EP–LiF. A fresh EP was first frozen and dried to get rid of all the water in the structure without shrinkage. Then, the dry EP was cut into thin pieces and punched into round shape. Then the freeze-dried EP was carbonized under 1000°C and argon atmosphere for 4 h to form carbonized EP. The channel-like structure could be maintained after carbonization. This structure is also schematically illustrated in Figure 94b. EDX and XPS results confirm that the carbonized EP is composed essentially of carbon framework.



Figure 94. (a) Photo of an eggplant and its cross-section morphology. (b) Schematic illustration for a carbonized eggplant with interconnected channel-like structure. (c) Carbonized eggplant after Li-metal melt infusion. (d) Carbonized eggplant – Li-metal composite anode further coated with a layer of LiF thin film.



Figure 95. Top view of scanning electron microscopy (SEM) image of EP–LiF anode after (a) 1 cycle and (b) 10 cycles under 1 mA cm⁻² and 1 mAh cm⁻² in a symmetric cell. Top view of SEM image of Li-foil anode after (c) 1 cycle and (d) 10 cycles under 1 mA cm⁻² and 1 mAh cm⁻² in a symmetric cell. Cross section of (e) a pristine EP–LiF electrode, (f) an EP–LiF electrode after stripping \approx 10 mAh cm⁻² of capacity, and (g) an EP–LiF electrode after stripping \approx 10 mAh cm⁻² of capacity and plating it back. Li-metal morphology after cycling in a symmetric cell setup was observed under SEM. Figure 95a shows the top view image of an EP–LiF electrode after one symmetric cell cycle with current density of 1 mA cm⁻² and areal capacity of 1 mAh cm⁻², while Figure 95c shows that of a lithium foil. Dendritic growth could be clearly observed for bare lithium foil. Li-metal filaments with diameter from 200 nm to 2 µm tangled together, increasing Li-metal exposure area to the electrolyte and aggravating Li-metal capacity decay. On the contrary, EP-LiF was able to achieve a rather homogeneous Li-metal deposition morphology. The GB on the EP-LiF anode surface confirmed that the observed lithium metal was indeed freshly plated with high homogeneity instead of the initial infused lithium metal. Li-metal plating morphology after longer cycling was also characterized. Figure 95b shows the top view image of an EP-LiF anode after 10 symmetric cell cycles under 1 mA cm⁻² and 1 mAh cm⁻² areal capacity, while Figure 95d shows that of a lithium foil. Li-metal dendrites on bare lithium foil became thinner. This is because the continuous cycling created much dead lithium and also SEI shells from previous cycling. The thinner Li-metal dendrites not only exacerbated fresh Li-metal consumption, but also would increase possibility of short circuit and severe battery thermal runaway. As for EP-LiF, although the surface was roughened slightly, the plated lithium metal still maintained an intact piece without much increased surface area. After 100 cycles under 1 mA cm⁻² and 1 mAh cm⁻², EP-LiF was still able to maintain a rather uniform morphology.

Work at UCSD this quarter on thick cathode focused on developing and understanding the performance limits of thick oxide cathodes. To statistically study the thick electrode evolution during cycling and its influence on electrochemical performance, xenon plasma focused ion beam (PFIB) was applied to NMC-811 thick electrode for large volume serial section tomography. Emerging Xe+ PFIB-SEM technology led by Thermo Fisher Scientific offers materials removal rates at least 60 times greater than conventional Ga+ FIB, which has limited imaging volumes. As shown in Figure 96a, the pristine NMC-811 thick electrode with 30 mg/cm² loading and 20% porosity was PFIB cut at voltage of 30 kV and current density of 60 nA. The cutting width was 130 microns with rocking mill at +/-3 degree. Slices were cut every 25 nm, and imaging was recorded every 4th slice; thus, the slice thickness in the image stack is 100 nm. Secondary particles cracking is observed even from the pristine state (see Figure 96b). Segmentation of some phases is straightforward due to the difference in brightness ranges; other phases appearing in identical intensities in the PFIB-SEM images are differentiated based on their relative location. As shown in Figure 96c, the PFIB-SEM images are segmented into four separate phases: vacuum, bulks of particles, cracks, and additives. By volume fraction, these four phases occupy 10.64%, 60.32%, 5.35%, and 23.69% of the total reconstructed volume, respectively. In addition, EDX mapping of the NMC-811 thick electrode on one serial section shows uniform distribution of active materials, PVDF binder, and conductive carbon (see Figure 96d). This method of large volume tomography based on PFIB-SEM enables the monitoring of crack formation before and after cycling, which is being investigated.



Figure 96. (a) Scanning electron microscopy (SEM) cross-section image of pristine NMC-811 thick electrode. (b) Xenon plasma focused ion beam (PFIB) large volume serial section of the thick electrode. (c) 3D reconstructed volume and phase segmentation calculated using the PFIB-SEM data. (d) Energy-dispersive X-ray spectroscopy mapping of NMC-811 thick electrode on one serial section obtained from PFIB.

Highlights of Keystone Project 2

- The consortium continues to make advancements in both cathode and lithium anode architectures.
- The project has developed imaging methods to better understand performance limitations of thick cathodes.
- On the lithium anode, new electrode architecture based on a lithium host with aligned porosities has enabled high lithium loading and high efficiency when the host is protected with LiF coating.

Keystone Project 3: Cell Fabrication, Testing, and Diagnosis

Research of Keystone Project 3 focused on two key areas this quarter. The first was understanding the performance and limitations for high-energy Li-S batteries. Through collaborations between J. Xiao's group (PNNL) and X. Yang's group (BNL), polysulfide redistribution during the pouch cell cycling was visually studied; it was discovered that even on the same cathode layer, the electrochemical reaction is highly inhomogeneous. The work highlighted that not only were various polysulfide species generated, the relative concentration of these polysulfide species was different across the surface of the positive electrode (Figure 97). It seems that the center of sulfur cathode inherits the original microstructures more than the marginal parts, suggesting the reaction is not complete in the center. This spatial variation in reaction front is likely related to the wetting of the thick sulfur cathodes used in this cell to achieve high specific energy. Achieving uniform wetting is a key challenge which will need to be addressed at the pouch-cell level for future work. To more uniformly enhance electrode wetting, future work will reduce the sulfur loading and cell parasitic weight simultaneously so the cell-level energy will not be sacrificed. Further improvement of sulfur utilization will benefit the balance between high-energy and extended cycling of Li-S batteries.



Figure 97. Uneven reaction was identified by X-ray fluorescence (XRF) spectrscopy (b-g) and X-ray absorption spectroscopy (XAS) spectra (h-j) at different locations of sulfur cathodes harvested from the cycled Li-S pouch cell. (a) Photo image of the cycled cathode with labled locations for XRF and XAS analysis: R1 (b/e/h), R2 (c/f/i) and R3 (d/g/j). (b-d) XRF collected at 2469 eV. (e-g) XRF collected at 2480 eV. (h-j) XAS collected in (b), (c), and (d), respectively, within an energy range of 2468-2488 eV. Yellow and blue lines in the XAS spectra were collected at the yellow and blue dots of corresponding XRF image at 2469 eV.

The second research focus area was on the role of pressuring during cycling for Li||NMC-811 cells. It was found that in a quasi-fixed gap setting the pressure during cycling changed significantly across each cycle and that the cycle life for cells significantly increased as elevated pressure was applied to the cell exterior. When comparing the difference between 1 psi and 21 psi of external pressure, it was found that cycle life increased by slightly more than 3-fold. In addition to increasing cycle life of cells, application of higher pressure resulted in a more linear increase and decrease in pressure and in less cycle-to-cycle variation in pressure, as shown in Figure 98. The uniformity in pressure and the linearity of the increase is likely due to greater utilization of lithium metal deposited during charging of the cell. Activities are in progress to understand evolution over longer cycling and to further increase external pressure to understand limitations on increasing cycle life.



Figure 98. Pressure evolution over the first 28 cycles for a cell with 21 psi of external pressure applied. Similar, but more pronounced, variation was observed at lower pressures, which also exhibited decreased cycle life.

Highlights of Keystone Project 3

- Even for uniformly coated electrodes, polysulfide distribution varies after cycling.
- Wetting is a key issue on the interior of the cell for Li-S batteries.
- Increased pressure extends cycle life and leads to more uniform pressure evolution during cycling.

Patents/Publications/Presentations

Publications

- Liu, J.,* Z. Bao, Y. Cui, E. J. Dufek, J. B. Goodenough, P. Khalifah, Q. Li, B. Y. Liaw, P. Liu, A. Manthiram, Y. S. Meng, V. R. Subramanian, M. F. Toney, V. V. Viswanathan, M. S. Whittingham, J. Xiao, W. Xu, J. Yang, X-Q. Yang, and J-G. Zhang. "Pathways for Practical High-Energy Long Cycling Lithium Metal Batteries." *Nature Energy* 4, no. 3 (2019): 180–186. Publication date (web): February 25, 2019.
- Xin, F., H. Zhou, Q. Yin, Y. Shi, F. Omenya, G. Zhou, and M. S. Whittingham. "Nanocrystal Conversion-Assisted Design of Sn-Fe Alloy with a Core-Shell Structure as High-Performance Anodes for Lithium-Ion Batteries." ACS Omega 4 (2018): 4888–4895. Publication date (web): March 5, 2019.
- Xie, Q., W. Li, and A. Manthiram. "A Mg-doped High-Nickel Layered Oxide Cathode Enabling Safer, High-Energy-Density Li-ion Batteries." *Chemistry of Materials* 31, no. 3 (2019): 938–946. Publication Date (Web): January 22, 2019.
- Li, W., H. Y. Asl, Q. Xie, and A. Manthiram. "Collapse of LiNi_{1-x-y}Co_xMn_yO₂ Lattice at Deep Charge Irrespective of Nickel Content in Lithium-Ion Batteries." *Journal of American Chemical Society* 141, no. 13 (2019): 5097–5101. Publication Date (Web): March 19, 2019.
- Dawson-Elli, N., S. Kolluri, K. Mitra, and V. R. Subramanian. "On the Creation of a Chess-AI-Inspired Problem-Specific Optimizer for the Pseudo Two-Dimensional Battery Model Using Neural Networks." *Journal of Electrochemical Society* 166, no. 6 (2019): A886–A896. Publication Date (web): March 15, 2019.
- Alvarado, J., † M. A. Schroeder, † T. P. Pollard, † X. Wang, J. Z. Lee, M. Zhang, T. Wynn, M. Ding, O. Borodin, * Y. S. Meng, * and K. Xu. * "Bisalts Ether Electrolyte: A Pathway Towards Lithium Metal with Nickel-Rich Cathodes." *Energy & Environmental Science* 12, no. 2 (2019): 780–794. Publication date (web): January 25, 2019.

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- Liu, N., G. Zhou, A. Yang, X. Yu, F. Shi, J. Sun, J. Zhang, B. Liu, C-L. Wu, X. Tao, Y. Sun, Y. Cui,* and S. Chu. "Direct Electrochemical Generation of Supercooled Sulfur Microdroplets Well Below Their Melting Temperature." *Proceedings of the National Academy of Sciences of the United States of America* 116, no. 3 (2019): 765–770. Publication Date (Web): January 15, 2019.
- Lin, D., Y. Liu, Y. Li, Y. Li, A. Pei, J. Xie, W. Huang, and Y. Cui.* "Fast Galvanic Lithium Corrosion Involving a Kirkendall-Type Mechanism." *Nature Chemistry* 3 (2019): 382–389. Publication Date (Web): January 21, 2019.
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- Niu, C., H. Pan, W. Xu, J. Xiao, J-G. Zhang, L. Luo, C. Wang, D. Mei, J. Meng, X. Wang, Z. Liu, L. Mai, and J. Liu.* "Self-Smoothing Anode for Achieving High-Energy Lithium Metal Batteries under Realistic Conditions." *Nature Nanotechnology* (2019). doi:10.1038/s41565-019-0427-9, Publication Date: March 13, 2019.
- Ren, X., L. Zou, S. Jiao, D. Mei, M. Engelhard, Q. Li, H. Lee, C. Niu, B. Adams, C. Wang, J. Liu, J. Zhang,* and W. Xu.* "High-Concentration Ether Electrolytes for Stable High-Voltage Lithium Metal Batteries." *ACS Energy Letters* 4, no. 4 (2019): 896–902. Publication Date (Web): March 20, 2019.
- Chen, S., C. Niu, H. Lee, Q. Li, L. Yu, W. Xu, J-G. Zhang, E. J. Dufek, M. S. Whittingham, S. Meng, J. Xiao,* and J. Liu.* "Critical Parameters for Evaluating Coin Cells and Pouch Cells of Rechargeable Li-Metal Batteries." *Joule* 3, no. 4 (2019): 1094–1105. Publication Date (Web): February 28, 2019.
- Abboud, A. W., E. J. Dufek, and B. Liaw. "Implications of Local Current Density Variations on Lithium Plating Affected by Cathode Particle Size." *Journal of the Electrochemical Society* 166, no. 4 (2019): A667–A669. Publication Date (Web) March 2, 2019.

Presentations

- ICESI-PPSS Meeting, Kona, Hawaii (January 9, 2019): "Can Multi-Electron Intercalation Systems Supplant NMC Cathodes?"; M. S. Whittingham. Invited.
- ECS San Francisco Section, Oakland, California (January 23, 2019): "What are the Materials Limitations to Advancing Li-Batteries to the Next Level?" M. S. Whittingham. Invited.
- IBA Meeting, San Diego, California (March 8, 2019): "Materials for High Energy Density Li and Li-Ion Batteries"; M. S. Whittingham. Invited.
- 14th China–U.S. EV and Battery Technology Exchange, Shaoxing, China (March 30, 2019): "Pros and Cons of High Ni NMCAs vs 2 Li Systems"; M. S. Whittingham. Invited.
- Battery India 2019, Goa, India (January 5–7, 2019): "Near-Term and Long-Term Perspectives of Battery Technologies"; A. Manthiram. Invited plenary.
- 12th International Symposium on Advances in Electrochemical Science and Technology (iSAEST-12), Chennai, India (January 8–10, 2019): "Battery Technologies: Near-term and Long-term Perspectives"; A. Manthiram. Invited plenary.
- SRM Institute of Science and Technology, Chennai, India (January 9, 2019): "A Perspective on Electrical Energy Storage"; A. Manthiram. Invited.
- Seoul National University, Seoul, South Korea (January 28, 2019): "A Perspective on Next-Generation Battery Chemistries"; A. Manthiram. Invited Distinguished Lecture.
- Seoul National University, Seoul, South Korea (January 29, 2019): "A Deep-Dive on High-Nickel Lithium-Ion Batteries and Lithium-Sulfur Batteries"; A. Manthiram. Invited Distinguished Lecture.
- IBA Meeting, San Diego, California (March 3–8, 2019): "A Path Forward to Low-Cobalt or Cobalt-free Cathodes for Lithium-Ion Batteries"; A. Manthiram. Invited keynote.
- India Smart Grid Forum, New Delhi, India (March 12–15, 2019): "Battery Technologies for Grid Storage and E-Mobility"; A. Manthiram. Invited plenary.
- IBA Meeting, San Diego, California (March 3–8, 2019): "Lithium Sulfur Batteries: From Fundamental Understanding to Pouch Cell Integration"; J. Xiao and J. Liu. Invited.
- DOE/Office of Electricity Workshop on Non-Aqueous Redox Flow Cells, Santa Fe, New Mexico (2019): "Standardizations of Rechargeable Lithium Metal Battery Research"; J. Xiao and J. Liu. Invited.
- ECS Detroit Section, Detroit, Michigan (2019): "Battery500 Consortium: Fundamental Research to Enable Next-Generation Battery Technologies"; J. Xiao and J. Liu. Invited.
- Seminar at General Motors Global R&D Center, Warren, Michigan (2019): "Challenges and Opportunities of Lithium Metal Anode"; J. Xiao and J. Liu. Invited.
- International Battery Seminar & Exhibit, Fort Lauderdale, Florida (March 26, 2019): "Advancing Lithium Metal Batteries"; W. Xu. Invited featured presentation.
- ICESI-PPSS Meeting, Kona, Hawaii (January 9, 2019): "Ether-Based Electrolytes for High-Voltage Lithium Metal Batteries"; W. Xu,* X. Ren, S. Jiao, and J-G. Zhang. Invited.
- IBA Meeting, San Diego, California (March 3–8, 2019): "Lithium Plating: Understanding of a Very Complicated Phenomena"; G. Pawar, X. Wang, E. Dufek, S. Meng, and B. Liaw. Invited.
- General Motors Global R&D Center, Warren, Michigan (March 26, 2019): B. Liaw, "Can Failure Mode and Effect Analysis Redefine Battery Safety?" Invited.
- ICESI-PPSS Meeting, Kona, Hawaii (January 9, 2019): "Cell Variability: Implications for High Power and Energy Cell Design"; E. Dufek. Invited.
- ICESI-PPSS Meeting, Kona, Hawaii (January 5–10, 2019): "Exploring New Chemistries for Stationary Storage: H₂ Gas Batteries and Molten Lithium Metal Batteries." Invited keynote.

- Wilson College of Textiles, North Carolina State University (February 2, 2019): "Nanomaterials Design for Energy, Environment and Textile"; Y. Cui. Invited.
- Gordon Research Conference on Nanomaterials for Applications in Energy Technology, Ventura Beach, California (February 24–March 1, 2019): "Nanomaterials and Interface Design for Electrochemical Energy Technology." Y. Cui. Invited keynote.
- IBA Meeting, San Diego, California (March 3–8, 2019): "Designing Lithium Metal Anodes: Host Materials and Solid Electrolyte Interphase"; Y. Cui. Invited keynote.
- California Institute of Technology, Inorganic-Electrochemistry Seminar Series (March 11, 2019): "Materials and Interface Design for Electrochemical Energy Storage"; Y. Cui. Invited.
- Cornell Energy Systems Institute: Distinguished Lecturer, Cornell University (March 14, 2019): "Nanomaterials Design for Energy and Textile"; Y. Cui. Invited.
- International Battery Seminar, Fort Lauderdale (March 25–28, 2019): "Emerging Materials Selection and Design for Batteries with High Energy Density, Ultralong Cycle Life and Excellent Safety"; Y. Cui. Invited.
- 14th China–U.S. EV and Battery Technology Exchange, Shaoxing, China (March 30, 2019): "Lithium Metal Anode Host and Interface Material Design"; Y. Cui. Invited.
- ICESI-PPSS Meeting, Kona, Hawaii (January 5–10, 2019): "Stabilization of Metal Anodes by Localized High Concentration Electrolytes,"; J-G. Zhang. Invited.