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A MESSAGE FROM THE ADVANCED BATTERY MATERIALS RESEARCH PROGRAM MANAGER

You may have noticed a change in the title of this report. Starting this quarter, we will include the technical progress made under the Battery500 Consortium Program in addition to the Advanced Battery Materials Research Program efforts. The Consortium, led by Pacific Northwest National Laboratory, includes the following partners: Brookhaven National Laboratory, Idaho National Laboratory, SLAC National Accelerator Laboratory, Binghamton University (State University of New York), Stanford University, University of California at San Diego, University of Texas at Austin, and University of Washington. The program aims to triple the specific energy (500 watt-hours per kilogram, compared to the 170-200 watt-hours) of today's electric vehicle batteries. This document summarizes both the BMR and Battery500 investigators' activities performed during January 1, 2018, through March 31, 2018.

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

- Stanford University (Cui's Team). Nano-diamond coatings were found to be effective barriers to lithium dendrite growth. These ultra-strong interface layers were fabricated as a double layer to circumvent the effect of local defects. Improved performance was demonstrated with cycling of a Li-S cell.
- Pacific Northwest National Laboratory (Xu's and Zhang's Team). Various polyethylene and polypropylene separators with ceramic or polymer surface coatings were evaluated with two different electrolyte solutions. A maximum Coulombic efficiency (86%) was realized with the LiTFSI-LiBOB/ EC-EMC electrolyte with little variation due to the different coatings. Results suggest that the separators are not stable with lithium metal, particularly in the presence of a LiPF₆ salt or ceramic coating.
- Lawrence Berkeley National Laboratory (Chen's Team). The kinetics of disordered oxide cathodes with mixed cationic and anionic redox reactions were investigated. The study revealed that the reduction processes of the transition metal and oxygen are coupled. Repeated cycling involving oxygen redox leads to kinetic deterioration in the entire voltage window.
- University of California at Berkeley (McCloskey's Team). The synthesis and physical characterization
 of various molecular weight polysulfone and poly(ethylene oxide)-based ionomers were completed. A
 comprehensive article on understanding of design criteria of high transference number/high conductivity
 electrolytes was published.
- **Stanford University (Bao's Team).** The mechanical "solid-liquid" properties of Silly Putty were characterized. The team showed that Silly Putty coating on lithium functions to keep the lithium grains packed tightly through its solid-like mechanical properties, while suppressing any aberrant growths. Silly Putty-coated electrodes were shown to have improved cycle life and Coulombic efficiency.
- University of Washington (Jen's and Yang's Team). Li|Li symmetric cells containing solvate ionogel films as separators were cycled at 0.1 mA/cm². The team found that gels with a 5:1 mixture of Li(G4)TFSI with 1,4-dioxane (formula 5) enabled reversible stripping and plating of lithium metal with moderately low over-potential for more than 600 hours (100 cycles). This self-healing material exhibited excellent resistance to crack formation, even under large cyclic strains. In addition, surface modified mesoporous carbon showed improved capacity retention for high-loading Li-S cells.

Highlights from the Battery500 consortium team are shown below:

- Keystone Project 1 (Materials and Interfaces). The addition of low concentrations of aluminum to high-Ni NMC cathodes was found to reduce moisture degradation and improve cell capacity retention. 1 Ah Li||NMC-811 pouch cells delivered 350 Wh/kg for more than 50 cycles.
- Keystone Project 3 (Cell Fabrication, Testing, and Diagnosis). A continuum mathematical model that captures the dynamics of lithium deposition and stripping during cycling was developed. The model adds a moving boundary representation to the standard Butler-Volmer method. An increase in cell performance (50 cycles to 225 cycles) was observed when the pressure of pouch cells was controlled.

On a final note, the Vehicle Technologies Office held its Annual Merit and Peer Evaluation meeting on June 18–21, 2018. There were over 800 in attendance. The proceedings are available online (https://www.energy.gov/eere/vehicles/annual-merit-review-presentations).

Sincerely,

Tien Q. Duong

Tien Q. Duong Manager, Advanced Battery Materials Research Program & Battery500 Consortium Program 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 nine 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. In addition, nonaqueous polyelectrolyte solutions with high Li⁺ transference numbers will be developed to achieve high rate capabilities at room temperature.
- **Polymer.** The targets of polymer electrolyte 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

The Daikin group has completed cycle and calendar life tests for NCA cathodes; the group was able to retain > 85% capacity at high voltage (4.5 V and 4.6 V) after 200 cycles, but these cells do exhibit significant gassing. In addition, as a first step to investigate the solid electrolyte interphase (SEI) layer thickness and composition, the group was able to use scanning electron microscopy (SEM) to measure the thickness of various carbonaceous films.

The University of California at Berkeley (UC Berkeley) group completed synthesis and physical characterization of polysulfone and poly(ethylene oxide)-based ionomers of various molecular weights; the group also published a comprehensive article on the understanding of design criteria of high transference number/high conductivity electrolytes.

The University of Maryland (UMD) group has successfully completed fabrication of thin hybrid electrolyte with thickness of 20 μ m, using electrospinning polyacrylonitrile (PAN) fiber mat as a template to make garnet framework. The tortuosity of the ceramic and pore phases were assessed computationally and along different axes. These results will help understand the ion transport through the electrolyte.

The University of Washington (UW) group completed Li|Li symmetric cell cycling the solvate ionogel films as separators at 0.1 mA/cm². The group found that gels with a 5:1 mixture of Li(G4)TFSI with 1,4-dioxane (formula 5), enabled reversible stripping and plating of lithium metal with moderately low overpotential for over 600 hours (100 cycles). It also found that the self-healing material has excellent resistance to crack formation, even under large cyclic strains. In addition, the surface modified mesoporous carbon showed improved capacity retention for high-loading Li-S cells.

The West Virginia University (WVU) group progressed on characterizing the microstructure of composite electrolytes and studying the nanofiber-polymer interface. The group also measured the temperature-dependent ionic conductivity of composite electrolytes, the transference number and the electrochemical stability window, as well as various mechanical properties.

The Stanford University group has characterized mechanical "Solid-Liquid" properties of Silly Putty (SP). The group showed that SP coating on lithium functions to keep the lithium grains packed tightly through its solid-like mechanical properties, while suppressing any aberrant growths, and the SP-coated electrode has improved cycle life and Coulombic efficiency (CE).

The Lawrence Berkeley National Laboratory (LBNL) group has synthesized polyhedral oligomeric silsesquioxane – polyethylene oxide (POSS-PEO) block copolymer hybrid electrolytes and measured the ionic conductivity of these materials for a range of molecular weights of the POSS chain and for a range of Li-salt concentrations. It is found that for samples with lower molecular weights of POSS, at temperatures > 120°C, the ionic conductivity can be close or slightly exceeding 1 mS/cm.

At Stony Brook University (SBU), State University of New York (SUNY), cell construction A for Li/I₂ batteries is completed. Galvanostatic cycling test for a cell using 80% LiI + 20% LiI(HPN)₂ solid electrolyte showed that the impedance of the cell was the highest when first assembled. After initial charge, the impedance decreased significantly. Even when the cell was discharged to 0.0 V, the cell impedance remained lower than the as-prepared cell.

At Rutgers, the nanolayering process gave the ability through change of chemistry to tailor the type ionic $(Li^+ \text{ and } F^-)$ versus electronic and amount of transport pathways within the bulk of the solid-state electrode structure. Three nanolayered additives were explored to manipulate the ionic and electronic conductivity within the positive electrode. Layer additive "A" modified the composition of the positive electrode to try to enhance the ionic transport, which resulted in a slight increase in capacity retention. Layer additive "B" enhanced the electronic conductivity but was found to have a detrimental effect on capacity. And finally, layer additive "C" was a hybrid composition enabling enhanced electronic and ionic transport resulting in higher capacity by 40% and improved capacity retention.

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 atomic emission 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 SEI layer formation and how it manifests change in both the anode (graphite) and cathode (LCO and NMC).

Out-Year Goals. Work will progress toward understanding how electrolyte formulation and cell operation affect SEI layer formation/properties. Specifically, measurements of thickness and elemental composition as a function of fluorinated electrolyte composition and voltage will be performed. Understanding the SEI layer and other solid-state components of Li-ion batteries will provide valuable information on the required surface properties for increased performance at high voltage.

Collaborations. There are no active collaborations this quarter.

- 1. Film thickness versus time/voltage complete. (Milestone 2.1; In Progress)
- 2. Film composition (elemental) versus time/voltage complete. (Milestone 2.2; In Progress)

After investigating LCO, NMC-111, NMC-532, and NMC-622 cathode materials as previously reported, the project completed cycle and calendar life tests for NCA cathodes. Figure 1 shows cycle life tests as a function of fluoroethylene carbonate (FEC) content at three upper voltage cutoffs (4.2, 4.5, and 4.6 V).



Figure 1. 200-mAh NCA cells cycled at .7C at r.t. as a function of FEC concentration (0-20% v/v) and voltage (4.2 V, left; 4.5 V, center; and 4.6 V, right).

As seen with the project's reported work (NMC-111, -532, and -622 cells cathodes) cycling above 4.2 V requires an electrolyte with a minimum of 10% FEC, with an optimal concentration between 10 and 15%. The team was able to retain > 85% capacity at high voltage (4.5 V and 4.6 V) after 200 cycles; however, these cells do exhibit significant gassing. Figure 2 shows open circuit voltage (OCV) drop and gas volume change results in a 55°C calendar life test at 4.2 and 4.6 V.



Figure 2. Calendar life test [Δopen circuit voltage (OCV) and Δgas volume] at 55°C with 20% FEC at an OCV of 4.2 V (left) and 4.6 V (right).

Last quarter, the project completed AES installing new and XPS instrumentation at Daikin, which will be used to investigate SEI layer thicknesses and elemental composition (year 2 milestones). It was necessary to develop standards and a methodology to calibrate the equipment for accurate carbonaceous film measurements. The team had multiple silicon wafer standards fabricated externally, which have varying thicknesses of amorphous carbon (500,



Figure 3. Scanning electron microscopy images of the 500 Å (left) and 5000 Å (right) carbonaceous samples.

1000, and 5000 Å) deposited onto a 500 Å layer of aluminum. The first step in this process was to confirm the film thicknesses using SEM. Sputtering gold serves as a contrast aid. The carbon film is evident as the black void between the gold (bottom) and aluminum (top) layers seen in Figure 3.

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 that is 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 the 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. Select a particular self-healing gel formulation (set of organic starting materials) for continued study based on electrochemical and mechanical properties. (Q2, FY 2018)
- 2. Provide detailed cell performance data for concept cells containing currently-best materials designs. (Q4, FY 2018)

Multifunctional Ionomer Gels. Additional Li|Li symmetric cell cycling was performed using the project's solvate ionogel films as separators at 0.1 mA/cm². The team found that gels based on 20 vol% poly(ethylene glycol) dimethacrylate (PEGDMA) (3500 Da), with the balance being Li(G4)TFSI (formula 2) or a 5:1 mixture Li(G4)TFSI of with 1,4-dioxane (formula 5), enabled reversible stripping and plating of lithium metal with moderately low overpotential for over 600 hours (100 cycles). These data are summarized in Figure 4. The team is conducting tests to demonstrate the high



Figure 4. Voltage traces for Li|Li symmetric cells containing ionogels (0.2-0.25 mm) as separators, as opposed to liquid Li(G4)TFSI with a glass fiber separator (0.125 mm). All cells cycled for 600 hours with no short circuiting, but the cells with ionogels required lower overpotentials to do so.

resistance of these materials to lithium dendrite formation.

Self-Healing Materials. To better visualize the toughness of the self-healing materials, stretching tests were conducted by drop-casting a layer of PP-1 (PENDI-c6 and triPy, 1:1 NDI:Py molar ratio) onto a flexible poly(dimethyl siloxane) (PDMS) substrate. This substrate was then stretched to 100% strain and relaxed, a

process performed ten total times. The PP-1 surface was imaged before and after repeated stretching (Figure 5), showing that the film maintained adhesion to the PDMS and did not break or crack during this process. Wrinkles did develop in the film perpendicular to the direction of strain, indicating plastic deformation had occurred; this was unsurprising, given the reported stress-strain curves for PP-1. Overall, this result demonstrates the material's excellent resistance to crack



Figure 5. PP-1 film imaged before and after cyclic stretching to 100% strain on a poly(dimethyl siloxane) surface. The self-healing polymer film dissipates strain energy through plastic deformation (observable as wrinkles) rather than crack formation.

formation, even under large cyclic strains such as those likely to develop in a mechanically active sulfur cathode.

The team also characterized the ionic conductivity of PP-1 doped with LiTFSI (20:1 [EO]:[Li⁺]) over a broad range of temperatures (Figure 6a-b). This was done by annealing a PP-1 film between stainless steel discs, which served as the electrodes for electrochemical impedance spectroscopy (EIS) tests. To quantify the self-healing ability of PP-1 in terms of electrochemical properties, the team measured the recovery of ionic conductivity following self-healing (Figure 6c). Impedance spectroscopy was performed on a sandwich structure of PP-1 films, annealed on one side to stainless steel and mechanically contacted together under light pressure. The apparent ionic conductivity, adjusted for the films' combined thickness, decreased by nearly an order of magnitude due to interfacial resistance between the separate films. However, after heat treatment at 50°C for 12 hours, the interface between films disappeared due to self-healing in an electrochemical system. PP-1 was further found to be compatible with Li(G4)TFSI as an ion source, forming freestanding gels with large amounts of the solvate ionic liquid. A conducting film containing 33 wt% Li(G4)TFSI demonstrated a bulk ionic conductivity of ~10⁻⁵ S/cm at 25°C, about two orders of magnitude higher than the solid polymer

electrolyte variant of PP-1. The team is continuing to optimize the PP materials system for compatibility with the project's solvate ionogel components to produce high-conductivity, interpenetrated gels.



Figure 6. (a) Electrochemical impedance spectroscopy data for PP-1 solid polymer electrolyte ("X"s), collected from 1MHz - 10mHz at 10-55°C, along with curve fits (lines) showing good agreement with data. The equivalent circuit used for fitting is in the inset, where R_{bulk} is ohmic resistance due to ionic transport. (b) Plot of conductivity (log scale) versus inverse temperature. (c) Schematic and results of conductivity recovery test, depicting devices used to measure baseline conductivity (PP-1), conductivity pre-healing (diPP-1), and conductivity post-healing (healed diPP-1). The material recovers 100% of conductivity upon heat-induced closure of gap between films.

Mesoporous Carbon Functionalization. The team utilized XPS to investigate proposed tethering of lithium

polysulfides (LiPSs) to thiol-functionalized carbon host surfaces. Cathodes containing both modified and non-modified carbon were harvested in a discharged state from coin cells after 100 cycles, then washed in dioxolane : dimethoxyethane (DOL:DME) to remove any soluble or physisorbed sulfide species, followed by the XPS analysis. LiPS chains display signals at 164 and 162 eV for thiol (S⁰) cores and thiolate (S⁻¹) tails, respectively. These peaks are very weak in the non-modified sample (Figure 7a), but prominent in the modified sample (Figure 7b); this implies that LiPSs are strongly bound to the surface in this sample.

To probe overall effect of thiol carbon modification on Li-S cell performance in a realistic setting, a series of carbons containing various concentrations of thiol modifier was prepared (Figure 7c-d). These carbons were used as sulfur hosts for cathodes with 4 mg/cm^2 sulfur loading, which were cycled at C/10 rate. The team finds that cell overpotential is concentration dependent with respect to modifier (Figure 7e) and only pronounced once thiol concentration exceeds 10 wt%. This suggests overpotential is associated with an interaction between LiPSs and the surface modifier. The team sees similar concentration dependence in cycling data (Figure 7f), where discharge capacity and retention increase monotonically with thiol concentration. The team attributes this increase to a combination of LiPSs interaction with modifier groups and better utilization of active materials,



Figure 7. High-resolution S_{2p} X-ray photoelectron spectroscopy (XPS) scan of non-modified (a) and modified (b) cathodes after cycling and washing. Modified cathodes show evidence of covalent tethering of LiPS to their surfaces. (c) Sulfur peaks in XPS for modified carbons of varying thiol concentration. (d) Thermogravimetric analysis data for modified carbons of varying thiol concentration. (e) 2^{nd} cycle overpotentials for high-loading Li-S cells. (f) Cycling data for high-loading Li-S cells, demonstrating vastly improved, concentration dependent capacity retention in modified samples.

made possible by better wetting of electrolyte into the pores of modified carbon. Improved wetting was demonstrated by a decrease in contact angle of electrolyte on cathode from 24° to 8° on modification.

Patents/Publications/Presentations

Publications

- 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." Imminent submission to *Journal of the American Chemical Society*.
- 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." Imminent submission to *Energy & Environmental Science*.
- Hubble, D., J. Qin, F. Lin, I. A. Murphy, S.-H. Jang, J. Yang, and A. K.-Y. Jen. "Rational Design of High-Conductivity Lithium Solvate Ionogels Using a Poly(Ethylene Glycol) Dimethacrylate Matrix." In preparation.

Task 1.3 – Development of Ion-Conducting Inorganic Nanofibers and Polymers (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 research 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 the 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 Li-dendrite formation.

Out-Year Goals. Work will progress toward synthesis of the inorganic nanofibers and the 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. Nianqiang (Nick) Wu at WVU serves as PI, and Dr. Xiangwu Zhang at NCSU acts as Co-PI. Sujan Kasani (Ph.D. student at WVU), Hui Yang (Postdoctoral Fellow at WVU), Botong Liu (Ph.D. student at WVU), Chaoyi Yan (Ph.D. student at NCSU), and Mahmut Dirican (Postdoctoral Fellow at NCSU) contributed to the project.

- 1. Synthesize the inorganic nanofiber-polymer composite electrolytes by *in situ* polymerization of polymer on the surface of inorganic nanofibers Subtask 2.1. (Q2, FY 2018; 60%)
- Characterize microstructure of composite electrolytes; study nanofiber-polymer interface Subtask 2.2. (Q2, FY 2018; Completed, 50%)
- 3. Measure temperature-dependent ionic conductivity of composite electrolytes, transference number, and electrochemical stability window Subtask 2.3. (Q2, FY 2018; Completed, 50%)
- 4. Measure the mechanical properties such as the Young's modulus, the shear modulus, and the tensile and shear strengths Subtask 2.4. (Q2, FY 2018; Completed, 50%)

This quarter, the team investigated the effect of the nitrogen dopant content on the ionic conductivity of the perovskite-type lithium lanthanum titanate $Li_{0.33}La_{0.56}TiO_3$ (LLTO) nanofibers. A silane monolayer was coated on the $Li_{6.4}La_3Zr_2Al_{0.24}O_{12}$ (LLAZO) nanofibers to improve the ceramic/polymer interface in composite electrolyte, which resulted in an ionic conductivity of 5.3×10^{-4} S cm⁻¹ at room temperature for the LLAZO-polymer composite electrolyte. Liner sweep voltammetry (LSV) tests have exhibited electrochemical stability from 0 to 6 V (versus Li/Li⁺) for this composite electrolyte.

Task 1.1.2 - Synthesis of Inorganic Nanofibers

Calculation of N-doped LLTO. Nitrogen was doped into the LLTO nanofiber by annealing in the ammoniacontaining atmosphere at $525 \sim 600^{\circ}$ C. XPS analysis was performed to determine the atomic concentration of the nitrogen dopant in the LLTO. The nitrogen content in the sample after treatment at 525° C was below the limit of detection of XPS. When the annealing temperature increased, the nitrogen content increased, which resulted in 0.8 at%, 0.9 at%, and 1.1 at% nitrogen after treatment at 550° C, 575° C, and 600° C, respectively.

The theoretical calculation shows that doping the nitrogen atoms to $Li_{0.33}La_{0.56}TiO_3$ can modulate the transport energy barrier for lithium ions. When a single nitrogen atom was introduced into the $Li_{0.33}La_{0.56}TiO_3$ unit cell, the transport energy barrier was the lowest (0.262 eV) as compared to 0.365 eV for the pure LLTO. Two, three, and four nitrogen atoms in the unit cell modulate the transport energy barrier to 0.324 eV, 0.286 eV, and 0.444 eV, respectively (Figure 8a).



Figure 8. (a) Relative energy for pure and N-doped $Li_{0.33}La_{0.56}TiO_3$. The arrow shows the transport direction of lithium ions. Blue balls indicate nitrogen atoms. (b) Most stable single-N-doped $Li_{0.33}La_{0.56}TiO_3$ structure.

Task 2.1 - Development of Inorganic Nanofibers-Polymer Composites

Silane-Coated LLAZO-Incorporated Cross-Linked Polymer (CLP) Composite Electrolytes. Silane was introduced at the ceramic/polymer interface to promote interaction between the ceramic nanofibers and the polymer matrix in the composite electrolyte. Acrylate functional groups (C=C) were covalently bound to the surface of LLAZO nanofibers via a silane coupling agent (3-(trimethoxysilyl)propyl methacrylate), which enabled the chemical grafting of functional monomers directly from the nanofiber surface. The silane-coated nanofibers were incorporated into the CLP matric via *in situ* polymerization of the CLP monomers (8:2) to form the solid-state composite electrolytes. The new composite electrolytes were denoted as S-LLZAO-CLP-1, 2, 3,

and 4, respectively, based on the different silane coating thicknesses. Table 1 shows ionic conductivity of four composite electrolytes. Among all composite electrolytes studied, the S-LLAZO-CLP-2 showed the highest ionic conductivity of 5.3×10^{-4} S·cm⁻¹ at room temperature.

Samples	Silane Coating Time (h)	lonic Conductivity (S/cm) (at 25 °C)
S-LLZAO-CLP-1	3	3.3 × 10 ⁻⁵
S-LLZAO-CLP-2	6	5.3 × 10 ⁻⁴
S-LLZAO-CLP-3	12	5.1 × 10 ⁻⁴
S-LLZAO-CLP-4	24	4.9 × 10 ⁻⁴

Table 1. Room-temperature ionic conductivities of S-LLZAO-CLP composite solid electrolytes.

LSV was carried out to test the stability of the S-LLZAO-CLP composite electrolytes, as shown in Figure 9. Compared with CLP alone and the CLP-P4-LLTO-3 composite electrolytes, the S-LLZAO-CLP composite electrolyte exhibits much better electrochemical stability from 0 V to 6 V (versus Li/Li⁺) because a very low amount of CLP was used in S-LLZAO-CLP composite electrolytes (about 20%); the LLZAO structure was stable at both high and low voltages.



Figure 9. Linear sweep voltammetry of (a) S-LLZAO-CLP-4 composite electrolyte, and (b) cross-linked polymer (CLP), CLP-P4, and CLP-P4-LLTO-3 solid electrolytes.

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 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 (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. Eric D. Wachsman (PI) will focus on optimizing the garnet network to achieve high ionic conductivity and flexibility using FIB/SEM and EIS characterization. Dr. Liangbing Hu (Co-PI) focuses on synthesis of the hybrid electrolyte and test for Li-metal anode with the hybrid electrolyte. Dr. Yifei Mo (Co-PI) will lead efforts on computational modeling of the garnet nanofiber hybrid electrolytes for fundamental mechanistic understanding.

- 1. Fully characterize electrochemical, mechanical, and thermal properties of hybrid SSE. (Q3, FY 2018; Completed December 2017)
- 2. Fabricate hybrid SSE with 20-μm thickness and understand the Li-hybrid SSE interface through Li-SSE-Li symmetric cells. (Q2, FY 2018; Completed March 2018)
- 3. Understand lithium stripping and plating in thin SSE at a current density of 3 mA/cm². (Q3, FY 2018; Initiated)
- 4. *Go/No-Go Decision*: No lithium dendrites at 3 mA/cm² for 500 cycles. (Q4, FY 2018)

Thermal performance of the hybrid electrolyte was analyzed by thermogravimetry measurement, shown in Figure 10. The weight loss is caused by evaporation of the trapped solvent from room temperature to 300°C. The hybrid electrolyte shows thermal stablity up to 450°C. After final decomposition at 600°C, the garnet phase was the only component left. The electrochemical and mechanical performance were investigated and confirmed in line with the results shown in previous reports.

This quarter, the project focused on development of the thin hybrid electrolyte with thickness of 20 μ m. The team used electrospinning PAN fiber mat as a template to make garnet framework. Figure 11 shows the photo images of the PAN fiber template. The as-prepared PAN fiber mat by electrospinning was 81- μ m thick on the left. To reduce the thickness and retain fiber structure, hot press was applied, and the final thickness of 15 μ m was achieved after pressing at 82°C for 30 min. The pressed template stabilized in air at 260°C for 10 h was used for garnet precursor infiltration.

Figure 12 shows the SEM images of the sintered garnet fiber framework prepared from the pressed PAN fiber template. The thickness of the garnet framework is less than 30 μ m with a typical layer structure of the ceramic fiber phase. The thin garnet fiber framework will be used for conductive polymer infiltration to make hybrid electrolyte.

The structure of garnet nanofibers was analyzed by FIB-SEM. The 3D-reconstruction of the garnet nanofibers is shown in Figure 13. The dimensions of the reconstructed volume are $220 \times 207 \times 67 \mu m$. The tortuosity of the ceramic and pore phases was assessed computationally and along different axes (Table 2). These results will help understand the ion transport through the electrolyte.



Figure 10. Thermal properties of the garnet/polymer hybrid electrolyte.



Figure 11. Fabrication of 20-µm electrospinning fiber mat as template for garnet precursor infiltration. (left): as-prepared fiber mat by electrospinning; (right): mat hot pressed at 82°C for 30 min.



Figure 12. Sintered garnet precursor infiltrated fiber mat template. Sample was impregnated with epoxy for scanning electron microscopy analysis.



Figure 13. First scanning electron microscopy (SEM) image in the focused ion beam SEM image set of the ceramic fiber mat sample (left). A 3D model was generated from all images in the image set, with the front side (center) and right side (right) of the model shown above. For reference, the top of the overall fiber mat faces to the right of the image.

Table 2.	Average	tortuosity	values	along	different	directions	for the	ceramic	phase	in the	same	3D \	volume	imaged b	by fo	ocused i	on bea	m
scanning	g electror	n microsco	ру.															

	Average Tortuosity (across entire 3D volume)							
	Front-to-back	Top-to-bottom	Right-to-left					
Ceramic	1.366	1.617	3.028					
Pore	1.020	1.028	1.027					

Patents/Publications/Presentations

Publication

 Gong, Y., K. Fu, S. Xu, J. Dai, T. R. Hamann, L. Zhang, G. T. Hitz, Z. Fu, Z. Ma, D. W. McOwen, X. Han, L. Hu, and E. D. Wachsman. "Lithium-Ion Conductive Ceramic Textile: A New Architecture for Flexible Solid-State Lithium Metal Batteries." *Materials Today* (2018). Online February 2, 2018.

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 the advance of the self-forming chemistry concurrent to the 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 target the 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 upon cycling. A secondary focus will be implementation of bipolar design within the cell structure.

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

- Establish negative reactive current collector compositions that enable high efficiency of lithium plating and stripping in excess of 90% during the *in situ* formation step and >95% during subsequent cycles. (Q2, FY 2018; In progress)
- 2. Establish optimal type and composition of bi-ion conductors that achieve ionic conductivities in excess of 1 x 10⁻⁴ S/cm after *in situ* formation. (Q3, FY 2018; Concluded in Q1, FY 2017)
- 3. Establish cell-stack design with 75% utilization of the positive reactive current collector and 12 V. (Q1, FY 2018; In progress)
- 4. *Go/No-Go Decision*: Achieve self-formed cell-stack of at least 1000 Wh/L and 300 Wh/kg at a rate of C/10, output voltage of 12 V, and > 80% capacity retention after 100 cycles.

Last quarter, the project developed a unique vapor deposition technique that allowed for fabrication of multicomponent nanolayered structured architectures. Such development provided various benefits including: (1) a cost-effective fabrication technique, and (2) improved positive electrode utilization from 30% to 63% during the initial transformation into an active metal fluoride cell, leading to higher capacity. This quarter, the project focused on developing the cycle life for these structures.

The nanolayering process described above gave the team the ability through change of chemistry to tailor the type ionic (Li⁺ and F⁻) versus electronic and amount of transport pathways within the bulk of the solid-state electrode structure. This approach has been successful with the goal to achieve advancement in both capacity utilization and subsequent cycle life. Indeed, three nanolayered additives were explored to manipulate the ionic and electronic conductivity within the positive electrode. Layer additive "A" modified the composition of the positive electrode to try to enhance ionic transport, which resulted in a slight increase in capacity retention. Layer additive "B" enhanced electronic conductivity, but was found to have a detrimental effect on capacity. And finally, layer additive "C" was a hybrid composition enabling enhanced electronic and ionic transport resulting in higher capacity by 40% and improved capacity retention. Figure 14 shows the resulting discharge capacities for each of the compositions. It was concluded that to improve capacity retention and areal capacity of the self-formed cell, limitations to both the ionic and electronic transport needed to be overcome. Additive "C" will be utilized to further improve the long-term cycling stability of the positive electrode.



Figure 14. Comparison of discharge capacities in the 1st, 2nd, and 5th cycle for multicomponent structured architecture cells of compositions with various nanolayered solid-state transport additives.

Moving forward, the team will continue to build on these compositions to strive toward the FY 2018 goals for the cycling ability of the positive electrode. Focus on stabilization of the negative electrode will also begin.

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 Amy Marschilok and Kenneth Takeuchi of SBU.

- 1. Develop cell construction A (current collectors, tab configuration, etc.) for Li/I₂ batteries with or without poly-2-vinylpyridine additive (P2VP). (Q2, FY 2018; Completed)
- 2. Prepare construction A cells with the 3 most conductive electrolytes from Subtask 2.1.0. (Q3, FY 2018; Initiated)
- 3. *Go/No-Go Decision*: Formation of Li⁰, Ag⁰ at anode and iodine at cathode with charging. (Q4, FY 2018; Initiated)
- 4. Determine functional capacity and energy density of construction A cells. (Initiated)

Cell Construction A for Li/I2 Batteries with or without P2VP

This quarter's milestone was development of cell construction A for Li/I_2 batteries with or without use of P2VP. The electrolyte used for the cell testing included the use of $\text{Li}(\text{HPN})_2$ along with lithium iodide salts. The cell was charged under 10 μ A/cm², and EIS data were collected at several states of charge

ranging from < 1% to $\sim 10\%$ of total capacity (Figure 15). Notably, after each charge interval a stable OCV of ~2.7 V was seen and is an indicator of a successfully formed Li/I₂ battery. Analysis of the EIS data reveals decrease of cell resistance with charging. A large impedance of ~316 kilo ohm was initially observed for the as-prepared cell. Significant impedance decrease (factor of ~ 5 times) was observed after only 0.5% charge. The impedance then stabilized and remained at ~ 30-40 kilo ohm through the continuing charge steps. The data indicate that the impedance is not directly correlated to the



Figure 15. (a) Intermittent charging and (b) AC impedance results for Lil(HPN)₂ containing cell with stainless-steel current collectors.

quantity of electrolyte consumed in the charge step, as initially the amount was < 1% and progressed to $\sim 10\%$ electrolyte consumption. Thus, the $\sim 90\%$ decrease in impedance on initial charge can be attributed to a decrease of interfacial resistance upon formation of the lithium anode and iodine cathode. Interfacial resistance is being explored at both the negative and positive sides of the cells.

Modification of the cathode interface of the LiI(HPN)₂ containing cells was studied by inclusion of P2VP, which is known to create conductive charge transfer complexes with iodine. For one cell design, a thin layer of P2VP was used at cathode interface. Interestingly, EIS results indicated that the LiI(HPN)₂ containing cells with P2VP showed slightly higher impedance results before and after charging than the cells with no P2VP (Figure 16). Thus, cell construction A for measurements of different electrolytes (milestone) and demonstration of self-forming Li/I₂ battery (milestone) will explore the influence of the P2VP/iodine ratio.

Electrochemical Cycling Using Cell Construction A

Galvanostatic cycling was performed for cell construction A. A solid electrolyte based on 80% LiI + 20% LiI(HPN)₂ was used for the electrochemical cycling. Five full charge and discharge



Figure 16. AC impedance of $Lil(HPN)_2$ cells with and without poly-2-vinylpyridine (P2VP) additive.

cycles were performed on the cell where full discharge to 0 V was used for the test. The cell performance was evaluated by the discharge capacities and EIS after charge/discharge (Figure 17). Notably, the impedance of the cell was the highest when first assembled. After initial charge, the impedance decreased significantly.
Even when the cell was discharged to 0.0 V, cell impedance remained lower than the as-prepared cell. A difference in cell impedance was observed between each charge and discharge cycle.



Figure 17. (a) Discharge curves, (b) AC impedance, and (c) impedance results for Lil(HPN)₂ containing cell.

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 Vince Battaglia (porous electrode preparation) and Kristin Persson (atomistic modeling) at LBNL.

- 1. Complete COMSOL modeling to identify target transference number and conductivities for electrolytes that enable efficient fast charging (~ 3C). (Q1, FY 2018; Completed October 2017)
- 2. Complete synthesis and physical characterization of polysulfone and poly(ethylene oxide)-based ionomers of various molecular weights. Progress measure: Publish a comprehensive article on understanding of design criteria of high transference number/high conductivity electrolytes. (Q2, FY 2018; Completed February 2018)
- 3. Complete transport measurements for polyelectrolyte solutions comprised of various molecular weight polymers. *Go/No-go Decision*: Switch polymer chemistries if optimized polyelectrolyte solution transference number is less than 0.9 and conductivity at room temperature is less than 0.1 mS/cm. (Q3, FY 2018; On schedule)
- 4. Complete polyelectrolyte solution cycling measurements using Li-metal electrodes to confirm high transference number electrolytes suppress dendrite formation. (Q4, FY 2018)

Nonaqueous polyelectrolyte solutions have been shown as promising candidates for high transference number, high conductivity electrolytes.^[1] Previously, the project investigated poly(allyl glycidyl ether)-based polyelectrolyte solutions, finding conductivity on the order 0.1-1 mS/cm and transference number above 0.8.^[2] While polyelectrolytes have been studied for many years, the effect of polymer molecular weight on the transport properties of the solution is not well known.

The project has targeted synthesis of several different molecular weight sulfonated polysulfone polymers to investigate the effect of molecular weight on conductivity and transference number. Sulfonated polysulfone is synthesized by a condensation reaction between two difunctional monomers with no post-functionalization, allowing relatively simple and safe synthesis of many samples. The team previously employed this reaction to form copolymers of sulfonated polysulfone and PEO, and others have investigated sulfonated polysulfones for various membrane applications.^[3,4] Condensation polymerizations are not known for facile control of molecular weight, but groups have reported the use of either a monofunctional monomer or a stoichiometric excess of one monomer to produce sulfonated polysulfone of expected molecular weights.^[5,6] In these cases, the degree of sulfonation of the final polymer was always below 40% (the fraction of sulfone monomers with a sulfonate group). For a polyelectrolyte solution, it likely would be important to maximize the charge on the polymer chain, as high polymer content increases viscosity and thereby decreases conductivity.

The team first investigated synthesis of a controlled polysulfone with a tert-butyl phenol monofunctional endcap. In these cases, the polymer should not display any remaining terminal hydroxyl groups, but nuclear magnetic resonance (NMR) analysis consistently revealed remaining OH groups. It is likely that the reduced reactivity and solubility of the sulfonated sulfone monomer at high concentrations, relative to the lower concentrations other groups have reported, prohibit the reaction from completing. An alternative route to produce different molecular weight polysulfones has, however, been successful. By using a stoichiometric

excess of the sulfonated sulfone monomer, the team has successfully synthesized four polymers of varying molecular weights and polydispersity. Table 3 displays the polymer molecular weight immediately following the reaction without isolation from the reaction solution (raw) by gel permeation chromatography (GPC) referenced to PEO standards. The reaction is carried out in nmethyl-2-pyrrolidone (NMP), and these molecular weights are determined via GPC where the solvent is also NMP, allowing the raw reaction mixture to be injected directly. Following precipitation in isopropanol, each polymer was ion exchanged via dialysis in water to produce a lithium form polymer. The molecular weights by GPC of these polymers are also displayed in Table 3. Polymer 1 appears to have undergone some hydrolysis during dialysis, resulting in a slightly lower molecular weight, while the other polymers have been fractionated to some extent during precipitation, slightly increasing their molecular weight.



Figure 18. Proton nuclear magnetic resonance spectra, and proton assignment, of polymer 1 in Table 3. Polymers 2-4 in Table 3 have similar spectra, confirming successful synthesis of all polymers.

The structure of each polymer was verified by proton NMR, as shown in Figure 18, including the presence of peaks indicative of terminal monomer groups. Unfortunately, it is not possible to determine the molecular weight of these polymers, as the ratio of the type of endgroup is not clear. The lithium content of each polymer

was also verified within 4% of the expected value by quantification of 7-Li NMR. These polymers should therefore allow the study of the molecular weight dependence of conductivity and transference number, including the effect of polydispersity, as polymers 1 and 2 have a relatively similar number average molecular weight, but different PDIs. The successful synthesis of polysulfone polymers with various average molecular weights is the completed milestone this quarter.

Polymer	M _n Raw	M _n Li Form	PDI Li Form
1	42,000	32,000	1.9
2	29,000	31,000	1.6
3	14,000	15,000	1.7
4	9,000	10,000	1.9

Table 3. Synthesized sulfonated polysulfone polymers to be used to form polyelectrolyte solutions.

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Task 1.8 – Advanced Polymer 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 developed a coating using Silly Putty, a siloxane-based polymer with dynamic boronmediated cross-links. This polymer is viscoelastic and displays 'solid-liquid'-type behavior. At low shear rates, the polymer acts as a liquid and can flow to coat non-uniform regions of the Li-metal anode, accommodating the electrode volume change. However, when a protrusion extends out of the electrode surface, such as a lithium dendrite, the polymer stiffens to constrain the localized lithium growth through mechanical suppression. The SP thus serves as a smart, dynamic protection layer for the stable operation and uniform deposition/stripping of Li-metal electrodes.

Out-Year Goals. The project will also probe the effects of polymer properties such as chemical functionality/identity and dielectric constant on electrochemistry of Li-metal deposition, such as CE and electrochemical kinetics. 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.

- 1. Explore the effects of various commercial polymers on lithium nucleation and interfacial kinetics. (Q1, FY 2018; Initiated Q4, FY 2017)
- 2. Develop polymer coating to mechanically suppress lithium dendrites and improve cycle life. (Q2–Q3, FY 2018)
- 3. Understand effects of polymer coating properties such as dielectric constant and surface energy, among others, on lithium electrochemistry and electrode performance. (Q3–Q4, FY 2018; In progress)

Characterization of Mechanical "Solid-Liquid" Properties of SP

The viscoelastic behavior of the dynamic-crosslinked SP was studied by rheometer and compared to the mechanical properties of standard covalent crosslinked PDMS (Figure 19a-b). Here, the loss modulus (G') and the storage modulus (G') represent the viscous and elastic properties of SP. At low strain rates ($<10^{-2}$ s⁻¹) corresponding to standard, non-dendritic lithium deposition, G'' is much larger than G', indicating that the SP behaves as a viscous, flowable liquid that can uniformly coat the non-uniform lithium metal. At higher strain rates past the crossover point, G' exceeds G'' by an order of magnitude, indicating that SP exhibits more elastic solid-like behavior. This solid-liquid property arises from the temporal nature of the boron-mediated crosslinks within the material. At low deformation rates, the crosslinks can break and reform at different locations. However, when the deformation rate is high, the dynamic crosslinks cannot transiently reconnect, and the SP temporarily acts as an elastic solid with drastically increased stiffness.

Effect of the SP Coating on Lithium Dendrite Suppression

The team took advantage of the dynamic mechanical properties of SP and used it as a polymer coating to achieve

dendrite-free Li-metal deposition. Figure 20a illustrates the ability of SP to coat rough lithium electrodeposits uniformly due to its viscous flowability. The intrinsic roughness of electrodeposited lithium can lead to accelerated lithium local growth and possible dendrite-based cell shorting. By having a uniform layer of a lower conductivity electrolyte-swollen gel-type polymer coating, the Li-ion flux can be regulated to circumvent any hotspots and fill in any cracks or gaps resulting from SEI breakage upon lithium volume change.





After 75 cycles, lithium electrodes with and without the SP coating were disassembled. Figure 20b-c shows lithium deposited on a bare copper electrode in the deposited state after 75 cycles. Lithium filaments can clearly be seen to be growing out from between the grains of the deposited lithium metal, possibly arising from SEI breakage or enhanced local lithium flux. These high-surface area structures result in low CE and consume

liquid electrolyte. causing premature cell failure. In contrast, Figure 20d shows the Li-metal electrode with the SP coating that exhibits a remarkably flat and smooth surface. Upon removing the SP coating by washing, the underlying lithium metal is exposed, showing a tightly packed, smooth, dendrite-free morphology (Figure 20e). The SP functions to keep the lithium grains packed tightly through its solid-like mechanical properties, all while suppressing any aberrant growths.



Figure 20. Scanning electron microscopy images for the bare copper and Silly-Putty-modified electrode.

Electrochemical Performance of SP-Coated Electrodes

The project cycled the SP-coated electrodes and bare copper electrodes until failure. The SP-coated electrodes were able to cycle significantly longer for over 120 cycles at a high average CE of 97.6%, as compared to the bare copper electrodes that failed more quickly, with CE dropping to 90% after only 75 cycles (Figure 21). This cycle life enhancement can be attributed to the lack of lithium filaments that consume the ether electrolyte solvent, causing premature cell dry-out and failure.



Figure 21. Coulombic efficiency of lithium deposition and stripping for the Silly-Putty-coated electrode and bare copper electrode.

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 non-conducting 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 are performed before carrying out cycling X-ray tomography 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 X-ray tomography experiments on symmetric Li-hybrid-Li cells.

Collaborations.

There are no active collaborations this quarter.

- 1. Synthesis of POSS-PEO block copolymer hybrid electrolyte. (Q1, FY 2018; Completed)
- 2. Measurement of conductivity of the hybrid copolymer. (Q2, FY 2018; Completed)
- 3. Measurement of diffusion coefficient and transference number of electrolytes. (Q3, FY 2018; In progress)
- 4. Conduct the first Li-electrolyte-Li tomography experiments. (Q4, FY 2018; In progress)

Milestone 1 – **Completed.** The team successfully synthesized hybrid organic-inorganic diblock copolymer electrolytes. Poly(ethylene oxide) -*b*- poly(acryloisobutyl polyhedral oligomeric silsesquioxane) (PEO-POSS) diblock copolymer was synthesized by nitroxide-mediated radical polymerization. An acryloisobutyl POSS monomer was polymerized using PEO-based macroalkoxyamine as initiator. Molecular weight of the POSS block ranged between 1 kg mol⁻¹ to 18 kg mol⁻¹, determined using H-NMR, shown in Figure 22a along with the resulting molecule structure. GPC traces of PEO-POSS using tetrahydrofuran (THF) solvent in relation to PEO-acrylate confirm the polymerization of the POSS block, shown in Figure 22b.



Figure 22. Nuclear magnetic resonance (NMR) and gel-permeation chromatography (GPC) results of PEO-POSS. (a) Structure of hybrid organic-inorganic diblock copolymers and H-NMR that reveal the PEO characteristic peak at 3.7 ppm and POSS proton peaks at 0.63-0.65 ppm. (b) GPC data in tetrahydrofuran of PEO-POSS and PEO-acrylate confirm the successful polymerization reaction.

Milestone 2 – **Completed.** The team has measured the ionic conductivity of the hybrid diblock copolymer for a range of molecular weights of the POSS chain between 1 kg mol⁻¹ to 18 kg mol⁻¹. Electrolytes were prepared by mixing each polymer with lithium bis(trifluoromethane)sulfonimide (LiTFSI) salt at a concentration of [Li]/[EO] = 0.10, as shown in Figure 23a. Data at 90°C for salt concentrations ranging between [Li]/[EO] = 0.02 to 0.30 is shown in Figure 23b.



Figure 23. Ionic conductivity of PEO-POSS. Conductivity is plotted for organic-inorganic diblock copolymer electrolytes with PEO molecular weight 5 kg mol⁻¹ and POSS 1, 1.9, 2.7, and 18 kg mol⁻¹ (a) between 30° C and 130° C with [Li]/[EO] = 0.10 and (b) at 90° C with salt concentration ranging between [Li]/[EO] = 0.02 to 0.30. Conductivity decreases with POSS molecular weight and increases with temperature.

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 the start-of-the-art analytical and computational tools. Four 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. At Cambridge, NMR is being used to identify major SEI components, their spatial proximity, and how they change with cycling. 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. Argonne National Laboratory (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. The University of California at 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 material's physical properties and reaction mechanisms to its performance and stability, which is critical for further optimization. The final subtask at Stanford / 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.

The highlights for this quarter are as follows:

 LBNL (Chen's group) investigated the kinetics of disordered oxide cathodes with mixed cationic and anionic redox reactions and revealed that the reduction processes of transition metal (TM) and oxygen are coupled, and repeated cycling involving oxygen redox leads to kinetic deterioration in the entire voltage window.

- Cambridge (Grey's Group) used ²⁹Si dynamic nuclear polarization (DNP) NMR to probe the interfacial region between the SEI and silicon for the first time. The team found that the hydroxyl terminated SiO_x was gradually reduced to form organosiloxane species containing Si-C bonds, indicating formation of a covalent bond between the SEI and the silicon surface.
- PNNL (Wang's Group) investigated the correlation between charge-discharge rate and phase transformation of the layered cathodes. The team found that while high-rate cycling leads to layered to spinel transition, low-rate cycling leads to layered to rock-salt transition.

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, non-empirical 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 spatial-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. Characterize oxygen activities during charge/discharge and extended cycling of Li-TM oxides and understand effect on cathode structural and electrochemical reversibility. (Q1, December 2017; Completed)
- 2. Investigate analytical techniques to determine the kinetics of anion redox process, and evaluate factors influencing rate capability of Li-TM oxide cathodes. (Q2, March 2018; Completed)
- 3. Apply advanced diagnostic techniques to investigate the reactivities of model oxide surfaces and understand their impact on oxide performance and safety. (Q3, June 2018; On schedule)
- 4. *Go/No-Go Decision*: Reveal the impact of oxide chemistry and particle morphology on the extent of reversible oxygen redox versus lattice oxygen loss; understand how to fine tune oxygen activities at high voltages. *No-Go* if the processes of reversible oxygen redox and lattice oxygen loss cannot be decoupled with diagnostic studies. (Q4, September 2018; On schedule)

This quarter, the kinetics of oxide cathodes with mixed cationic and anionic redox reactions contributing to charge storage were evaluated. Previous reporting showed that for rock-salt structured $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$

cathode, the extent of oxygen redox involvement may be adjusted by controlling the upper cutoff voltage (UCV), with a UCV of 4.2 V and 4.8 V corresponding to negligible and significant oxidation of lattice oxygen, respectively. Thus, potentiostatic intermittent titration technique (PITT) measurements were carried out on Li_{1.3}Nb_{0.3}Mn_{0.4}O₂ half cells in the voltage window of 1.5-4.2 V and 1.5-4.8 V. A step size of 50 mV was used. At each step, the potential was held until the current reached a corresponding rate of C/150. Figure 24 shows the calculated chemical diffusion coefficients as well as the derived dQ/dV profiles from the measurements. In first charging to 4.2 V (Figure 24a), a broad anodic peak centered at ~ 3.2 V was observed on the dQ/dV profile, corresponding to oxidation of the TM cation (Mn³⁺). The diffusion coefficient during the oxidation process was ~ 1×10^{-10} cm²/s. When the charging voltage was extended to 4.8 V, a new strong peak centered at ~ 4.5 V along with a low-voltage peak centered at ~ 3.6 V were observed on the dQ/dV profile, corresponding to oxidation of oxygen and TM, respectively. While the diffusion coefficient for TM oxidation remains unchanged at $1 \times 10^{-10} \text{ cm}^2/\text{s}$, the oxygen oxidation process had a value of ~ 1×10^{-12} cm²/s, nearly two orders of magnitude lower. This suggests that lithium diffusion is significantly slower during oxygen redox.



Figure 25. The relationship between calculated diffusion coefficient and cell voltage during the first four cycles of $L_{11.3}Nb_{0.3}Mn_{0.4}O_2$ half cells: (a) charge and (b) discharge.

For the subsequent discharging process (Figure 24b), the dQ/dV profiles in both voltage



Figure 24. Calculated diffusion coefficients and dQ/dV profiles as a function of voltage during: (a) first charge and (b) first discharge of $Li_{1.3}Nb_{0.3}Mn_{0.4}O_2$ half cells.

windows show a single broad cathodic peak centered at $\sim 3.0-3.2$ V, consistent with previous results from CV studies. The primary difference lies in the current density, with significant current boost observed when oxygen oxidation was activated at the UCV of 4.8 V. For the diffusion coefficient in the voltage window of 1.5-4.2 V, it remained fairly stable at ~ 1×10^{-10} cm²/s during reduction of TM. With activation of oxygen, the value was significantly reduced to ~ 1×10^{-12} cm²/s. Furthermore, the diffusion coefficient in the entire voltage window decreased by nearly an order of magnitude. These results suggest that the reduction processes of TM and oxygen are likely coupled rather than being separate. Involving oxygen redox leads to broad kinetic reduction in the entire voltage window.

Changes in lithium diffusion kinetics as a function of cycling between 1.5 V and 4.8 V were also evaluated. Figure 25a-b shows the relationships during the first four cycles of charge and discharge. The profiles during the subsequent charging are considerably different from that during the first charge. Particularly, diffusion during oxygen oxidation appears to be much faster in the following cycles. This is

likely due to decreased contribution from slow oxygen gas evolution occurring in the first charge. Lithium diffusion during TM oxidation, however, becomes slower with cycling. A gradual reduction in kinetics was also observed during discharge. These results suggest that repeated cycling involving oxygen redox leads to kinetic deterioration in the entire voltage window.

Patents/Publications/Presentations

Publications

- Kan, W. H., D. Chen, J. K. Papp, A. K. Shukla, A. Huq, C. M. Brown, B. McCloskey, and G. Chen. "Unravelling Solid-State Redox Chemistry in Li_{1.3}Nb_{0.3}Mn_{0.4}O₂ Single-Crystal Cathode Material." *Chemistry of Materials* 30 (2018): 1655. doi: 10.1021/acs.chemmater.7b05036.
- Kan, W. H., B. Deng, Y. Xu, A. K. Shukla, T. Bo, S. Zhang, J. Liu, P. Pianetta, B.-T. Wang, Y. Liu, and G. Chen. "Visualizing the Effect of Local Short-Range Ordering on Lithium-Ion Diffusion in Li_{1.3}Nb_{0.3}Mn_{0.4}O₂ Single-Crystal Cathode." Under review (2018).

Presentation

35th Annual International Battery Seminar & Exhibit, Fort Lauderdale, Florida (March 26–29, 2018):
 "Achieving Higher Energy in Lithium-Ion Battery Cathodes"; G. Chen. Invited talk.

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 to obtain detailed insight into the active material structure and physicochemical phenomena at electrode/electrolyte interfaces at a spatial resolution corresponding to the size of basic chemical or structural building blocks. The goal is to design 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.

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-ion and Li-based cells for PHEVs and EVs. The proposed work constitutes an integral part of the concerted effort within the BMR and supports development of new electrode materials for high-energy 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) determine the degradation mechanism(s) of high-voltage cathodes; and (2) propose and test effective remedies to intrinsic interfacial instability of these materials and composite electrodes.

Collaborations. Electrode materials and composite electrodes tested under different cycling regimes by M. Doeff (LBNL) and C. Ban (National Renewable Energy Laboratory, NREL) will be studied. The diagnostic studies will be carried out in sync with differential electrochemical mass spectrometry (DEMS) analysis by B. McCloskey (LBNL) and other diagnosticians in the BMR program. He will also work closely with V. Battaglia (LBNL) to obtain samples from full-cell cycling experiments.

- 1. Controlled growth of model thin-film electrodes by pulsed laser deposition (PLD) as model system for fundamental electrochemical studies. *Go/No-Go Decision*: Stoichiometric thin films produced with sub-nanometer roughness. (December 2017; Completed)
- 2. Characterize bulk and surface structure of model PLD thin films and the relation to electrochemical properties. *Go/No-Go Decision*: Electrochemical performance of model system in line with that of bulk materials. (Q2, FY 2018; Completed March 2018)
- 3. Characterize chemistry of electrolyte decomposition at model PLD thin-film electrodes with near-field technique. (Q3, FY 2018; On schedule)
- 4. Determine electrochemical impedance contribution from interface between organic electrolyte and electrode active material. *Go/No-Go Decision*: Development of model electrodes with high electrochemical stability and low impedance. (Q4, FY 2018; On schedule)

This quarter, the team correlated the electrochemical behavior of the model NMC thin-film electrodes obtained by PLD with their structural properties (Q2 milestone completed). The electrochemical response of NMC thin-film electrodes was investigated in a Swagelok cell, employing Li-foil as counter and reference electrodes and 1 M LiPF₆ in an ethylene carbonate and diethyl carbonate (EC:DEC, 1:2 wt) electrolyte. The CV profile (Figure 26a) shows the main redox peaks, which are also observed for the NMC composite electrode (see inset Figure 26a^[1]). *Ex situ* Raman analysis (Figure 26b) shows a red shift of the E_g and A_{1g} peaks going from the pristine to charged state, and a blue shift back from charged to discharged state, corresponding to the lithiation-delithiation process of the R3m layer structure, in accordance with the reported *in situ* Raman study of NMC composite electrode.^[2]



Figure 26. (a) Cyclic voltammetry (CV) profile of NMC thin-film electrode. Scan rate: 0.2 mV s⁻¹. Inserted plot presents typical CV of NMC composite electrodes as reported.^[11] (b) *Ex situ* Raman of NMC thin-film electrodes at different states of charge: pristine, 1st delithiation, and 3rd lithiation.

The surface of the cycled NMC thin-film electrodes was then studied by FTIR. Figure 27a presents FTIR spectra of a thin-film electrode cycled 3 times, obtained after 5 s and 5 min washing in DEC. The FTIR spectrum of the sample washed for 5 s presents spectral characteristics of glycol species (indexed in the last report), while spectra from the sample washed for 5 min show an additional set of adsorption C=O, C-O, and C-O-C vibration modes. This simple washing procedure reveals a double-layer film structure that forms on the NMC surface. The characterized peaks that can differentiate these two layers are associated to the vibrations of C-O-C bonds (1080 cm⁻¹ for outer layer and 1150 cm⁻¹ for inner layer). Further, the double-layer film was observed not only for the initial charge process, but also during subsequent cycles (Figure 27b). As reported earlier, the organic film formed on the NMC surface might be associated with electrolyte reactions at the lithium anode side and the "chemical shuttle" effect.^[3] To investigate this, the NMC thin-film electrodes were cycled with a graphite anode instead of lithium. However, the FTIR surface analysis (Figure 27c) does not reveal any obvious difference of the organic layer structure and composition when compared to the one obtained using lithium anode. Thus, the team concludes that the observed film formation is intrinsic to reactions between NMC and electrolyte during the delithiation process.



Figure 27. Fourier transform infrared spectra of cycled thin-film electrodes with different washing time. (a) 3 cycled electrode (discharge end) using lithium anode. (b) 1, 2 and 3 cycled electrode (charge end) using lithium anode. (c) 3 cycled electrode using lithium or mesocarbon microbead anode.

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- [2] Otoyama, M., Y. Ito, A. Hayashi, and M. Tatsumisago. *Electrochemistry* 84 (2016): 812.
- [3] Bjorklund, E., D. Brandell, M. Hahlin, K. Edstrom, and R. Younesi. *Journal of The Electrochemical Society* 164 (2017): A3054.

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

Project Objective. The primary project objective is to develop new advanced *in situ* material characterization techniques and to apply these techniques to support development of new cathode and anode materials for the next generation of Li-ion batteries for PHEVs. To meet the challenges of powering the PHEV, Li-ion batteries with high energy and power density, low cost, good abuse tolerance, and long calendar and cycle life must be developed.

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 new 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 (X-ray diffraction, or XRD; hard and soft X-ray absorption spectroscopy, or 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 Si-based anode materials. The project will also collaborate with industrial partners at GM and Johnson Controls, as well as with international collaborators.

- 1. Complete the *in situ* TXM studies of LiCoO₂ cathode materials during charge-discharge cycling to evaluate the inhomogeneity of the charged (discharged) states among a large number of material particles and using a data mining technique to detect the under (over) reacted minority regions (particles). (Q1, December 2017; Completed)
- 2. Complete the neutron diffraction studies of LiCoO₂ as high-energy-density cathode material at high-voltage charge in comparison with the pristine state. (Q2, March 2018; Completed)
- 3. Complete the PDF studies of LiCoO₂ using both x-PDF and n-PDF probes to study the mechanism of anionic redox reaction in such widely used commercial cathode materials for Li-ion batteries and explore the potential of using this material for high-energy-density cell applications. (Q3, June 2018; In progress)
- Complete the experimental design, data collection and analysis of 3D STEM tomography studies of high-energy-density Li_{1.2}Ni_{0.15}Co_{0.1}Mn_{0.55}O₂ cathode materials at pristine state and after multiple cycling. (Q4, September 2018; In progress)

This period, the BNL team completed the second milestone and progressed on the other milestones. The team focused on studies of structure change associated with the oxygen-related redox reaction. The LiCoO₂ cathode was charged to 4.6 V to reach a deeply delithiated state. As shown in Figure 28a, when LiCoO₂ was charged to 4.6 V, a capacity of 225 mAh/g was obtained, corresponding to 0.83 lithium extraction. Upon discharge, a capacity of 205 mAh/g was reached, corresponding to 0.76 lithium re-inserted. This indicates that the electrochemical reaction is mostly reversible. To understand the phase transition route during lithium extraction, neutron power diffraction (NPD) was carried out on both the pristine sample and the *ex situ* sample charged to 4.6 V high voltage. The resultant diffraction patterns were fitted against model structures using Rietveld refinement, as shown in Figure 28b. For the pristine sample, the structure has the space group of R-3m, with lithium located at 3a site, cobalt at 3b site, and oxygen at 6c site. In terms of oxygen layer stacking sequence, it can be described as ABCABC, as illustrated in the lower-left corner of Figure 28a. Upon charging to 4.6 V, the oxygen layer stacking sequence changes into ABABCACABCBC, as illustrated in the right panel of Figure 28a.



Figure 28. (a) Electrochemical profile of LiCoO₂ charged to 4.6 V followed by a discharge to 3 V. The lower-left and the right insert show the structures of the pristine sample and the charged sample, respectively. (b) Rietveld refinement of the neutron power diffraction (NPD) pattern of pristine sample. (c) Rietveld refinement of the NPD pattern of charged sample.

Patents/Publications/Presentations

Publications

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Task 2.4 – Nuclear Magnetic Resonance and Magnetic Resonance Imaging Studies of Solid Electrolyte Interphase, Dendrites, and Electrode Structure (Clare Grey, University of Cambridge)

Project Objective. The growth of a stable SEI on most electrode materials is key to long-term capacity retention of a working Li-ion battery. On anodes such as silicon, this is particularly critical because the continual expansion and contraction of this intermetallic upon alloying with lithium exposes fresh, reactive surfaces that result in further electrolyte decomposition and SEI growth. This project will perform a detailed multinuclear NMR study of the SEI that forms on silicon, where thick SEIs typically grow and where SEI stability is a key aspect hindering commercialization. The focus will be to determine how additives (for example, FEC) and charging parameters (for example, voltage) influence SEI composition and stability. Fundamental studies of SEI structure *in operando* will be complemented by a synthetic program aimed at preparing new silicon coatings based on phosphazene (P-N) elastomeric polymers to increase CE. Further, the nature of SEI is one factor that appears to control the type of lithium microstructures that form on lithium metal during cycling. To test this hypothesis, the project will use magnetic resonance imaging (MRI) to investigate lithium dendrite versus moss formation in different electrolytes as a function of salt concentration and with different additives. Finally, it will compare lithium and sodium metal anode chemistries to determine composition, morphology, and stability of local structures that form on sodiating anodes such as tin and hard carbons.

Project Impact. The first impact of this project will be a molecular-level understanding of how factors such as applied voltage and electrolyte additives modify the SEI that forms on silicon anodes. The insight gained from these studies will guide the design of new P-N coatings for silicon. A rationally designed surface coating has the potential to improve SEI stability, and thus increase CE for silicon and beyond. A description of how SEI composition influences lithium microstructures will provide the foundation to mitigate dendrite formation during cycling that currently limits the safety of many promising electrode materials. These approaches will be extended to study Na-ion battery electrodes to provide an understanding of how to chemically manipulate both electrodes as well as the electrolyte to avoid adverse failure mechanisms in next-generation batteries.

Out-Year Goals. The project goals are as follows: (a) determine the effect of voltage and additives (for example, FEC) on the composition of the silicon SEI; (b) synthesize and test new inorganic coatings to increase the CE seen on cycling silicon; (c) identify correlations between SEI structure and thickness and Li-metal dendrite formation; and (d) determine the local and long-range structures formed on cycling sodium anode materials and compare with lithium. To facilitate these goals, the project will prepare ¹³C-enriched FEC for ¹³C NMR multinuclear studies to investigate the SEI that forms on silicon during cycling. It will synthesize new P-N polymers for coating silicon nanoparticles and probe changes in performance in the presence of these coatings. In addition, the project will use MRI to correlate lithium dendrite formation with the nature of the SEI. Finally, it will apply the methods developed to study lithium chemistries to investigate sodium electrodes.

Collaborations. This project collaborates with B. Lucht (University of Rhode Island); J. Cabana (University of Illinois at Chicago, UIC); Y. Shirley Meng (UCSD), S. Whittingham (SUNY – Binghamton); P. Bruce (St. Andrews); S. Hoffman and A. Morris (Cambridge); and P. Shearing (University College London).

- 1. Synthesize ¹³C FEC. (Q1, FY 2018; Completed)
- 2. Prepare P-N coatings on silicon; complete. Develop *in situ* ¹⁹F NMR studies of FEC; Ongoing. (Q2, FY 2018; Completed)
- 3. Prepare multinuclear NMR studies of SEI coatings on silicon with FEC. (Q3, FY 2018; Completed, with first manuscript published and second manuscript in preparation)
- 4. Test P-N coatings. (Q4, FY 2018; Ongoing MRI/dendrite studies of 2 ionic liquids; focus on additives)

FEC and vinylene carbonate (VC) are widely used as electrolyte additives in Li-ion batteries. In this work, the team analyzes the SEI formed on binder-free silicon nanowires (SiNWs) electrodes in pure FEC or VC electrolytes containing 1 M LiPF₆ by solid-state NMR with and without DNP enhancement. Pure FEC and VC show improved electrochemical performance compared to those cycled in standard LP30 based electrolytes (Figure 29). ¹³C NMR experiments of both ¹³C enriched and natural abundance electrolytes reveal that the organic electrochemical decomposition products of FEC and VC mainly consist of cross-linked PEO and alkyl chains with carbonate and carboxylate units forming 15% of the carbon content of the FEC-derived polymer, whereas VC contains more cross-linked poly(VC) than the FEC-derived polymer.



Figure 30. (a) Dynamic nuclear polarization enhanced 2D DQ-SQ $^{13}C^{-13}C$ dipolar correlation of silicon nanowires cycled in FEC + 5% $^{13}C_3$ FEC for 100 cycles. (b) Possible molecular fragments observed during FEC/VC decomposition.

of its adhesion (specifically, the formation of Si-C bonds) to the redox-active materials impart stability in the reducing environment. However, it is important to note that the presence of Si-C bonds alone do not necessarily correlate to improved electrochemical performance; it is likely the combination of the chemical structures of the organic SEI and the uniformity of the SEI coverage on the active material surface that influence the cycle life of silicon.



Figure 29. Electrochemistry of silicon nanowires cycled in LP30 (black), FEC (red), and VC (blue) showing the voltage profile after 50 cycles.

The formation of branched fragments is further confirmed by ¹³C-¹³C correlation NMR experiments (Figure 30). The presence of cross-linked PEO-type polymers in FEC and VC correlates with good capacity retention and high CE of the SiNWs. The highly cross-linked PEO has three potentially positive implications for the stability of silicon anodes; it may (1) reduce solvent penetration and swelling of the SEI, mitigating further solvent reduction, (2) accommodate the expansion and contraction of the silicon, and (3) improve Li-ion conductivities more than linear PE decomposition products found in EC-based electrolytes.

Using ²⁹Si DNP NMR, the team is able to probe the interfacial region between the SEI and silicon for the first time. The hydroxyl terminated SiO_x is gradually reduced to form organosiloxane species containing Si-C bonds,

indicating that a covalent bond forms between the SEI and the silicon surface (Figure 31, top red). The team suggests that both the polymeric structure of the SEI and the nature



Figure 31. ¹H-²⁹Si dynamic nuclear polarization nuclear magnetic resonance of silicon nanowires, pristine (bottom, gray) and after 100 cycles in FEC (top, red).

Patents/Publications/Presentations

Publications

• Pigliapochi, R., I. D. Seymour, C. Merlet, A. J. Pell, D. T. Murphy, S. Schmid, and C. P. Grey. "Structural Characterization of the Li-Ion Battery Cathode Materials $\text{LiTi}_x \text{Mn}_{2-x}O_4$ (0.2 $\leq x \leq 1.5$): A Combined Experimental ⁷Li NMR and First-Principles Study." *Chemistry of Materials* 30 (2018): 817.

Presentations

- Royal Society Conference on Energy Storage, London (January 2018)
- Stony Brook University, Stony Brook, New York (January 2018)
- University of Warwick, Coventry, United Kingdom (February 2018)
- Munich Battery Discussions, Technical University of Munich (February 2018)
- International Battery Association, Jeju Island, South Korea (March 2018)

Task 2.5 – 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 hone 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 probe and control defects generation due to oxygen activity in the high-energy composite cathodes and to characterize electrode/electrolyte interface in lithium anodes so that their cycle life and efficiency can be significantly enhanced.

Collaborations. This work funds collaborations on EELS (Miaofang Chi, ORNL); neutron diffraction (Ken An, ORNL); and soft XAS (Marca Doeff, LBNL). It supports collaborative work with Zhaoping Liu and Yonggao Xia at Ningbo Institute of Materials Technology and Engineering in China. It also supports collaboration with the Battery500 Consortium.

- 1. Benchmark electrode performance of bulk and surface modified Li-excess NMC. (Q2, March 2018; Completed)
- 2. BCDI and STEM/EELS characterization of modified Li-excess NMC single particle. (Q3, June 2018; On track)
- 3. Propose strategies to optimize the anion activities in Li-excess NMC cathode materials. (Q4, September 2018; On track)

BCDI Characterization on Kinetics in Single Particle of Li-Rich Layered Oxide (LRLO) during Electrochemical Cycling

The last report demonstrated the sluggish charging process of LRLO cathode during the plateau region that is dominated by the oxygen activity. As a result, no obvious average strain is built in the bulk of the particles during the higher rate charging process. *Operando* BCDI allows the team to directly compare the interior changes of a nanoparticle during battery cycling at different rates. Note that up to 4.4 V, almost the same amount of lithium (one third of total lithium in Li_{1.2}Ni_{0.133}Mn_{0.533}Co_{0.133}O₂) is extracted from the structure at both C/10 and C/5 rate. In other words, the influence of lithium concentration difference on structure changes until



Figure 32. *Operando* evolution of a Li-rich layered oxide nanoparticle during electrochemical charge at different rates, including the changes in the displacement field along q003 and the strain along the [001] direction (perpendicular to the layers) inside of the nanoparticle calculated from the 3D displacement fields.

4.4 V can be fairly excluded when comparing different charging rates. As shown in Figure 32, from the beginning of the charge to 4.1 V, a continuous displacement field is observed in the nanoparticle, and the displacement field changes slightly at both C-rates. When charged to 4.3 V, before the voltage plateau that signifies oxygen redox activity, the displacement field is qualitatively different and only lower rate shows charging singularities characteristic of dislocations, as pointed out by white arrows. The discontinuity in the displacement field around a singularity is the projection of the Burgers vector along the scattering vector q₀₀₃. Meanwhile, no obvious changes in the displacement field are found in the LRLO nanoparticle charged at a higher rate, even until 4.4 V. The strain field distribution yields further insights into the physical and processes electrochemical that

underpin the formation of dislocations (see Figure 32). For the nanoparticle charged at C/10 rate, the strain inhomogeneity in the slice shown increases between 4.0 V and 4.1 V, and the strain is larger towards the bottom left edge of the particle. At 4.3 V, the strain is compressive (reduced lattice spacing d) on the right and tensile on the left around dislocations, revealing extra half-planes on the right in agreement with the displacement field analysis. Not surprisingly, no obvious strain characteristics are found in the bulk of the nanoparticle charged at the higher rate. At higher rate charging, less oxygen redox is activated due to sluggish kinetics so that less dislocation and strain network is formed in the bulk of LRLO particles.

Influence of Metal-Ion Electrolyte Additive on Electrochemically Deposited Lithium Metal

The project's STEM/EELS characterization tool set can be extended to observe Li-metal anode if cryogenic holder can be enabled. The team recently succeeded in cryo analytical electron microscopy with new capability to quantify the chemistry and atomic structure of electrochemically deposited lithium metal. The lithium metal has poor reversibility of plating and stripping in the *conventional* carbonate electrolyte [1 mol L⁻¹ lithium hexafluorophosphate (LiPF₆) in EC/ethyl methyl carbonate (EC/EMC), 50/50 wt%]. The

CE is only 60% at the first cycle (see Figure 33), which is too low for practical use and eventually causes cell failure. To increase the CE, some functional additives have been added to the electrolytes, and positive effects are confirmed on improving the reversibility of the Li-metal plating and stripping. One group of the additives is the metal ions, which can be further categorized into alloyed species (for example, Mg^{2+} , Zn^{2+} , and Al^{3+}) and non-alloyed species (for example, Cs^+ and Rb^+) according to their reactivity with lithium. Taking Cs^+ and Zn^{2+} additives as examples, their influences on the nanostructures of the EDLi were explored to deepen the understanding of their underneath mechanisms on CE improvement. As expected, CE of the cells improved when 50 m mol L⁻¹ Cs⁺ and Zn²⁺ were added to the above carbonate electrolyte, which is 86% and 89%, respectively, at the 1st cycle. To investigate influence of these additives on morphology of the deposited lithium metal, SEM was employed; the images are shown in Figure 33. These electrolytes (pristine, Cs⁺-containing, and Zn^{2+} -containing electrolytes) show a similar ribbon morphology with different complexity. Clearly, dense interweaved lithium films tend to form in the electrolytes with additives. In particular, Cs⁺ facilitates the lithium metal to grow vertically and form aligned arrays. The smooth lithium deposition in the Cs⁺-containing electrolyte is proposed to be the result of a synergistic effect of the Cs^+ additive and LiF-rich thick SEI, which results from the decomposition of CsPF₆ at 2.05 V. Cryo-TEM will be applied to further disclose the effect of these additives on the nanostructure of the deposited lithium metal.



Figure 33. Compared cycling Coulombic efficiency of the Li-Cu cells with pristine, Cs⁺-containing, and Zn²⁺-containing electrolytes, and scanning electron microscopy images of the lithium metal deposited on the copper in pristine (a/d), Cs⁺-containing (b/e), and Zn²⁺-containing (c/f) electrolytes.

Patents/Publications/Presentations

Publications

- Zhang, M., H. D. Liu, Y. S. Meng, et al. "Modified Co-Precipitation Synthesis of Meso-Structure Controlled Li-Rich Layered Oxides for Minimizing Voltage Degradation." ACS *Applied Energy Materials*; under review.
- Singer, A., M. Zhang, Y. S. Meng, et al. "Nucleation of Dislocations and Their Dynamics in Layered Oxides Cathode Materials during Battery Charging." *Nature Energy*; under review.

Presentation

 American Physical Society Meeting, Los Angeles, California (2018): "Quantifying the Unusual Anion Redox Activity in Lithium Intercalation Compounds"; Y. S. Meng and M. Zhang. Invited talk. Task 2.6 – *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 high cycle efficiency/dendrite free 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 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. Huajian Gao (Brown University) and Dr. Qinglin Zhang (GM) will be the key researchers involved in continuum simulation and postmortem analysis. Dr. Chongmin Wang (PNNL), Dr. Wangli Yang (LBNL), and Dr. Jie Xiao will be collaborators on advanced *in situ* analysis and electrolyte additives.

- 1. A continuum model of SEI growth, which can predict potential SEI failure modes and incorporate them into the continuum model. (Q1, December 2017; Completed)
- 2. The impact of lithium deposition induced stress on lithium morphology and cycle efficiency. (Q2, March 2018; Completed)
- 3. The mechanical properties of SEIs measured by nanoindentation and the SEI composition measured by XPS. (Q3, June 2018; On schedule)
- 4. Interface adhesion energy calculations; and predication of where interface delamination will occur. Lithium plating kinetics at a lithium/single-component SEI/electrolyte interface predicted by molecular dynamics (MD) simulation. (Q4, September 2018; On schedule)

In Situ Measurement of Stress-Thickness of Li-Metal Anode. Previous reproducible studies involving MOSS measurements indicated that compressive stress is heavily accompanied by lithium plating on gold current collector (shown in Figure 34a.). This behavior was then hypothesized to the messy SEI layer, composed of electrolyte decomposition products, dead lithium, and porosity, which dominates the stress response during the cycling process.



Figure 34. Stress-thickness response during plating sequence and open circuit voltage hold of 5 consecutive symmetric cycles. (a) $-265uA/cm^2$ for 5 h. (b) $-265uA/cm^2$ for 10 h.

To validate this claim, experiments with asymmetric cycles were performed; by doubling the current density during plating sequence compared to the stripping sequence for the same number of hours, gold current collector continuously increased thickness of plated lithium as the cycles continued. This study would confirm which factor dominates the stress-thickness response. If the mechanical behavior of the system was largely dominated by plated lithium metal, the stress-thickness change would be proportional to the increasing lithium thickness. Conversely, stress-thickness change would not show much variance if the multi-phase SEI was the main contribution to the mechanics of the system.



Figure 35. (a) The distribution of von Mises stress in bulk lithium after nanoindentation. (b) Microstructure of an indent in a lithium foil after it is stored inside an Ar-filled glovebox for 30 days at room temperature. The insert shows the stress distribution on lithium surface along the red line direction.

Effects of Stress on Formation of Lithium Dendrites during Long-Term Storage at Room Temperature have been Investigated Using Nanoindentation. Indents were made on the surface of lithium foils to induce stress as well as damage to the naturally formed SEI. Finite element modeling was used to obtain maximum stress and stress distribution beneath the indent, as shown in Figure 35a. Lithium atoms may concentrate and

form dendrites in areas with high compressive stress since the stress gradient will drive the diffusion of lithium atoms to release the stress. Unlike tin alloys, no lithium dendrite was formed around or inside indents after storing the lithium foil at room temperature (25°C) for 30 days, as shown in Figure 35b. A possible explanation is that the stress gradient is not high enough to drive the diffusion of enough lithium atoms to form dendrites since lithium has very low yield strength and high creep tendency. Therefore, internal stress and interfacial stress (at Li/SEI) is unlikely to be a reason for the growth of lithium dendrites.

The Influence of Pressure on the Morphology of Lithium Dendrites has been Studied by Using Swagelok Cells. As shown in Figure 36a, the pressure applied on Li-metal electrodes is controlled by the compression deformation of the spring. Mossy lithium plated under high pressure (~ 19.39 MPa) has lower porosity than that under low pressure (~ 4.85 MPa). Lithium dendrites plated under low pressure have needle-like shape. In contrast, round lithium chunks form under high pressure, as shown in Figure 36b-c. Two reasons may explain these phenomena: (1) thermodynamics, that is, the external pressure may influence the thermodynamics in Li-ion diffusion, nucleation rate, growth rate, and competition of lithium dendrites; and (2) current density distribution. Li-metal electrodes can be easily deformed. Under high pressure, they become more smooth and flat, and the current density distribution would be more homogeneous than those under high pressure. Nanoindentation measurements with a flat punch indicate that the penetration depth of mossy lithium at the maximum depth is about the same with bulk lithium, but the creep displacement of mossy lithium during the holding period is much smaller than that of bulk lithium. In addition, the creep displacement of mossy lithium plated under high pressure is about half of that plated under low pressure, which partially results from their difference in porosity. Further studies will be focused on understanding the role of pressure in the morphology of mossy lithium and investigating the influence of pressure on the cycling life of Li-metal electrodes in half-cell and full-cell configurations.



Figure 36. (a) The schematic diagram of a Swagelok cell. Microstructure of mossy lithium plated under (b) 4.85 MPa and (c) 19.39 MPa.

Patents/Publications/Presentations

Patent

 Xiao, X. Method of Applying Self-Forming Artificial Solid Electrolyte Interface (SEI) Layer to Stabilize Cycle Stability of Electrode in Lithium Batteries. U. S. Patent Application P044686 (8540R-539), April 5, 2017.

Publications

- Guo, K., P. A. Tamirisa, B. W. Sheldon, X. Xiao, and H. Gao. "Pop-Up Delamination of Electrodes in Solid-State Batteries." *Journal of The Electrochemical Society* 165 (2018): A618–A625.
- Wang, A. P., S. Kadam, H. Li, S. Q. Shi, and Y. Qi. "Review on Modeling of the Solid Electrolyte Interphase (SEI) for Lithium-Ion Batteries." *npj Computational Materials* 4, no. 15 (2018). Invited review.
- Vinado, C., S. Wang, Y. Hec, X. Xiao, Y. Li, C. Wang, and J. Yang. "Electrochemical and Interfacial Behavior of All Solid-State Batteries Using Li₁₀SnP₂S₁₂ Solid Electrolyte." *Journal of Power Sources* (2018; accepted).
- Wang, Y., Q. Zhang, D. Li, J. Hu, J. Xu, D. Dang, X. Xiao, and Y. T. Cheng. "Mechanical Property Evolution of Silicon Composite Electrodes Studied by Environmental Nanoindentation." *Advanced Energy Materials* (2018): 1702578.
- Li, D., Y. Wang, J. Hu, B. Lu, D. Dang, J. Zhang, and Y. Cheng. "Role of Polymeric Binders on Mechanical Behavior and Cracking Resistance of Silicon Composite Electrodes during Electrochemical Cycling." *Journal of Power Sources* 387 (2018): 9–15.

Presentations

- 35th Annual International Battery Seminar & Exhibition, Fort Lauderdale, Florida (March 26–29, 2018):
 "Advanced Electrode Materials for Next Generation Lithium Ion Batteries"; X. Xiao. Invited.
- 35th Annual International Battery Seminar & Exhibition, Fort Lauderdale, Florida (March 26–29, 2018):
 "Working towards Making Better and Cheaper Lithium-Ion Batteries"; Yang-Tse Cheng.

Task 2.7 – Microscopy Investigation on the Fading Mechanism of Electrode Materials (Chongmin Wang, Pacific Northwest National Laboratory)

Project Objective. The objective will be using a combination of *ex situ, in situ*, and *operando* HRTEM and spectroscopy to probe the fading mechanism of layer structured cathode under high-voltage operating condition. To complement the HRTEM study, *in situ* liquid cell SIMS and atom probe tomography (APT) will also be used to gain structural and chemical evolution of electrodes and correlate the structural and chemical evolution with battery performance.

Project Impact. The proposed characterization work focused 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 EV, especially for PHEV required by the EV Everywhere Grand Challenge.

Approach. This project will use the unique *ex situ* and *in situ* TEM methods to probe the structure of Li-ion batteries, especially a biasing liquid electrochemical cell that uses a real electrolyte in a nano-battery configuration. It will also use various microscopic techniques, including *ex situ*, *in situ*, and especially the *operando* TEM system, to study the fading mechanism of electrode materials in batteries. This project will be closely integrated with other R&D efforts on high-capacity cathode and anode projects in the BMR Program to: (1) discover the origins of voltage and capacity fading in high-capacity layered cathodes, and (2) provide guidance for overcoming barriers to long cycle stability of electrode materials.

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

- Multi-scale (ranging from atomic-scale to mesoscale) ex situ/in situ and operando 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.
- Extend the *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 Michael M. Thackeray and Jason Croy (ANL); Guoying Chen (LBNL); Jagjit Nanda (ORNL); Chunmei Ban (NREL); Khalil Amine (ANL); Donghai Wang (Pennsylvania State University); Arumugam Manthiram (University of Texas at Austin, UT Austin); Wei Tong (LBNL); Gao Liu (LBNL); Yi Cui (Stanford University); Jason Zhang (PNNL); Jun Liu (PNNL); Xingcheng Xiao (GM); Shirley Meng (UCSD); and Stan Whittingham (SUNY – Binghamton).

- 1. Resolve the vacancy injection mechanism into the LM-NMC during the battery cycling and its correlation with battery fading mechanism. (Q2, March 31, 2018; Completed)
- 2. The functioning mechanism of electrolyte additive on the solid-liquid interphase in NMC cathode. (Q3, June 30, 2018; In progress)
- 3. Atomic level understanding of the mechanism of intergranular and intragranular cracking in NMC. (Q4, September 30, 2018; In progress)

The key new information of this work is to report the correlation between charge-discharge rate and structural phase transition of the layer structured cathode. The team discovered that high-rate cycling leads to the layer-to-spinel transition, while low-rate cycling leads to the layer to rock salt transition.

It is very well established that the battery performance critically depends on the charge and discharge rate. Fast cycling leads to performance deteriorations. The intrinsic roles of the cycling rate in the battery performance are poorly understood, and the correlation between cycling rate and cathode degradation, in terms of structure evolution, has not been established.

Two well-recognized phase transitions usually take place in the layer structured cathode during the battery operation: layered-to-spinel and the layered-to-rock-



Figure 37. High-angle annular dark field scanning transmission electron microscopy images of cycled $LiNi_{0.76}Co_{0.10}Mn_{0.14}O_2$, showing dependence of layer to disordered structure on the cycling rate. (a) Cycling at 0.33C is accompanied by the layer to rock salt phase transient. (b) Cycling at 2C is featured by the layer to spinel phase transition. This observation clearly demonstrates that the phase transition depends on the cycling rate of the battery.

salt phase transitions. Numerous studies have revealed the thermodynamic nature of such phase transitions to be a thermal decomposition process, where the reaction occurs as the temperature reaches the phase transition point. Most cathodes readily develop into the spinel-like or disordered rock salt phase on both surfaces and bulk upon cycling. However, the parameters associated with battery operation that control the phase transition products are far from clear. The two-phase transition products developed upon cycling are of distinct crystal structure and may affect the battery rate behavior differently; nevertheless, the battery community usually categorizes the two configurations into one group—Li⁺ insulating layers. However, the differentiation of deterioration effects of the two reconstruction layers on the battery performance remains vague.

This period, the team demonstrated the cycling rate/crystal structure/battery performance correlation in the Ni-rich cathode. The project finds that the electrochemical reaction products of the layered materials are effectively controlled by the cycling rate (in which the rock salt forms at the low cycling rate), whereas the spinel phase develops at the high cycling rate. The two kinds of reconstruction layers deteriorate the cycling performance distinctly, and a critical cycling rate at between 1C and 2C distinguishes the layered-to-spinel-like and layered-to-rock-salt phase transition. The project's simulations reveal that cycling rate controls battery performance via forming different phase transition products, which are kinetically governed by the amount of vacancies generated during the battery operation.

Using STEM, the team has systematically studied the structural features of $LiNi_{0.76}Mn_{0.14}Co_{0.10}O_2$ cycled at rates ranging from 0.33C to 2C. The work reveals that the phase transition products vary with the cycling rate and contribute distinctly differently to the battery decay in Ni-rich cathode materials. The project demonstrated the diverse phase transition paths in a range of battery operation rates, in which the layered-to-disordered rock-salt transition occurs at below 1C, while layered-to-spinel takes place at the rate above 2C. By combining the electrochemical tests with atomistic simulations, the team revealed that the abundant vacancies in the highly delithiated state, under the low charge/discharge rate, favor the thorough cation mixing between the lithium and TM layers and result in formation of disordered rock salt structure. In contrast, the limited vacancies resulting from Li-ion retention, at the high cycling rate, impede the fully cation mixing and give rise to the growth of spinel-like phase. The subtle characterizations at the atomic scale bridge the gap between the structure evolution and cycling rate and may provide mechanistic insight into tailoring the battery rate capability.

Patents/Publications/Presentations

Publications

- Kwak, Won-Jin, Langli Luo, Hun-Gi Jung, Chongmin Wang, and Yang-Kook Sun. "Revealing the Reaction Mechanism of Na–O₂ Batteries using Environmental Transmission Electron Microscopy." ACS *Energy Letters* 2 (2017): 2607-2615.
- Zhang, Yanyan, Mao Su, Xiaofei Yu, Yufan Zhou, Jungang Wang, Ruiguo Cao, Wu Xu, Chongmin Wang, Donald R. Baer, Oleg Borodin, Kang Xu, Yanting Wang, Xue-Lin Wang, Zhijie Xu, Fuyi Wang, and Zihua Zhu. "Investigation of Ion–Solvent Interactions in Nonaqueous Electrolytes Using *In Situ* Liquid SIMS." *Analytical Chemistry* 90 (2018): 3341–3348.

Presentation

 University of California at Irvine (March 16, 2018): "Scanning/Transmission Electron Microscopy and Spectroscopy beyond Aberration Correction: *In Situ* Microscopy for Watching while It Happens"; C. M. Wang. Invited departmental seminar. Task 2.8 – Understanding and Mitigating Interfacial Reactivity between Electrode and Electrolyte (Khalil Amine and Zhonghai Chen, Argonne National Laboratory)

Project Objective. To understand the pathway/mechanism of parasitic reaction between electrode materials and electrolyte for beyond lithium-ion chemistries, and to stabilize the electrode/electrolyte interface for long life and safe battery chemistries.

Project Impact. The project is designed to have several areas of impact:

- To maximize the practical energy of battery chemistries beyond lithium ion,
- To improve the life and roundtrip energy efficiency of battery chemistries using S-based cathodes, and O₂-based cathodes, and
- To stabilize the lithium/electrolyte interface for high-energy-density lithium battery chemistries.

Approach. The project approach is multi-fold: (1) fundamental investigation of the pathway/mechanism of parasitic reactions between electrolytes and electrode materials, (2) rational mitigation of parasitic reactions based on the identified reaction pathway, (3) developing functional surface coating and electrolyte additives to suppress the chemical reactions between electrolytes and electrode materials, and (4) formulating new electrolyte to control the direct electrochemical reaction of electrolyte components.

Out-Year-Goals. When the electrolyte interface is stabilized, the following results can be achieved:

- A cell with energy density of 600 Wh/kg, and
- A battery capable of operating for 500 cycles with low capacity fade.

Collaborations. The project collaborates with Dr. Gui-Liang Xu and Dr. Ang T. Ngo of ANL and with Prof. Chunsheng Wang of UMD.

- 1. Synthesis of S/C composite cathode materials for Li/S batteries. (Q1, FY 2018; Completed)
- 2. Electrochemical characterization of S/C cathode. (Q2, FY 2018; Partially completed)
- 3. Investigating the kinetics of parasitic reactions at the interface of S/C cathode. (Q3, FY 2018; Ongoing)
- 4. Investigating the impact of sulfur load on both the electrochemical performance and kinetics of parasitic reactions. (Q4, FY 2018; To be initiated)

This quarter, the project synthesized a series of S/C composite cathode materials with different loading of sulfur using ball milling process. The electrochemical performance of these materials was evaluated in button cells using lithium as the counter electrode. The electrolyte used was 1.0 M LiFSI, and 0.1 M LiNO₃ in

mixture solvent of DOL/DME. Figure 38 shows the basic electrochemical performance of the materials. Figure 38a shows the dependence of the reversible capacity on the content of sulfur in the composite cathode. A monotonic increase of the reversible capacity with the percentage of sulfur in the composite cathodes can be seen. However, even when the sulfur loading is as high as 90 wt%, a medium reversibility with about 790 mAh/g was obtained. Considering the theoretical capacity of sulfur is 1680 mAh/g, there is still about 45% of sulfur not fully activated yet. It is one of the project's short-term goals to optimize the structure of the S/C composite to achieve a higher utilization of sulfur in the composite cathode.

Interestingly, the team found that the irreversible capacity loss of the S/C composite cathode decreases with the percentage of sulfur in the composite cathode. This is a good indication of interfacial reaction between the S/C composite cathode and the electrolyte since a low sulfur content can be translated into a higher percentage of sulfur at the interface that has the direct exposure to the electrolyte. The long-term cycling of these cells is still ongoing. The kinetic study of the interface reaction is ongoing and will be reported soon.



Figure 38. Electrochemical performance of S/C composite cathodes for Li-S batteries. The dependence of (a) reversible capacity, (b) irreversible capacity loss, and (c) relative irreversible capacity loss on the loading of sulfur in the composite.

Task 2.9 – Correlative Microscopy Characterization of Electrochemical Hotspots in Oxide Electrodes (Yi Cui, William Chueh, Michael Toney; Stanford/SLAC)

Project Objective. This project aims to develop and utilize a correlative microscopy platform to investigate the lithiation dynamics of 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. This project aims to develop a correlative microscopy platform to investigate the lithiation dynamics of 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. On recharging time, the specific phenomena to be addressed include non-uniform 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.

Milestones

FY 2016

1. Development of correlative microscopy platform for imaging LMR-NMC cathodes. (Achieved)

FY 2017-2018

- 1. Synthesis and characterization of well-faceted NMC and NMC particles. Demonstrate *in situ* single particle imaging with spectro-ptychography of NMC. (Ongoing)
- 2. Use of correlative microscopy platform for imaging LMR-NMC and NMC cathode hotspots. (Ongoing)
- 3. Spectro-imaging of single NMC particles. (Ongoing)
- 4. *Ex situ* variable temperature (-20°C to +80°C) spectro-imaging of LMR-NMC particles. (Ongoing)
While many oxygen-redox-active materials have been developed, they almost universally exhibit a host of irreversible electrochemical behaviors such as voltage hysteresis and voltage fade. This is most notable in the anion-redox-active Li-rich layered oxides, $Li_{1+x}M_{1-x}O_2$, which exhibit capacities approaching 300 mAh g⁻¹ but have yet to achieve commercial success due to such electrochemical behavior. It was recently proposed that these properties arise from a coupling between the oxidation of oxygen and the migration of M into Li sites—a widely observed phenomenon—creating structural disorder in the form of M_{Li}/V_M antisite/cation vacancy defect pairs and an associated loss of in-plane honeycomb-like TM ordering. However, the two main mechanistic models for oxygen redox, describing the nature of the oxidized oxygen species as either a ~ 2.4 Å peroxo-like O_2^{n-} dimer or an isolated O^- anion, do not directly explain this coupling. As such, a robust understanding of the materials design criteria for achieving reversible anion redox remains elusive. In approaching this issue, the project turned to layered Li₂IrO₃ (equivalently, Li[Li_{0.33}Ir_{0.67}]O₂ or LIO) as a model system that is reported to exhibit anion redox, yet, unlike other Li-rich layered oxides, exhibits highly reversible structural and electrochemical behavior during cycling.

LIO exhibits two well-defined voltage plateaus with average potentials of 3.45 V and 4.15 V versus Li/Li⁺ and a capacity of $1.5e^-$ per iridium for several cycles without noticeable capacity or voltage fade (Figure 39a). High-resolution synchrotron XRD shows two consecutive, completely reversible two-phase reactions. Rietveld refinement shows that pristine LIO exhibits a typical layered structure with monoclinic *C2/m* symmetry, with the lithium and TMs in the TM layers ordered into a honeycomb-like arrangement, and accommodates delithiation through changes in the stacking of the TM layers. The project finds that LIO changes from O3 to T3 to O1 stacking at the Li₂IrO₃, Li₁IrO₃, and Li_{0.5}IrO₃ compositions, respectively.

To quantify the cation vacancy/antisite formation during electrochemical cycling, the team employs an iterative approach to simultaneously refine the in-plane and out-of-plane site disorder. This approach eliminates the difficulty in site occupancy determination resulting from the presence of stacking faults. The team confirms the absence of V_{Ir}/Ir_{Li} defects ($\leq 0.1 \pm 0.2\%$ of all lithium sites occupied by iridium) in the discharged state both before and after the first electrochemical cycle. Out-of-plane refinement shows negligible iridium occupancy in the lithium layer in the fully charged state. These results show why LIO exhibits reversible electrochemistry: minimal cation disordering occurs during cycling. This is unlike all other Li-rich materials in which anion redox is reported to occur.

To gain further insight into the bulk redox mechanism of LIO, the team performs *operando* transmission X-ray absorption near edge structure (XANES) measurements at the iridium L_3 edge (Figure 39b). Throughout the first galvanostatic charge/discharge, the white line (WL) energy increases and decreases linearly (Figure 39c), nearly returning to its original value at the end of discharge. This is in striking contrast to the behavior of most anion redox active Li-rich oxides whose TM ions either stop being oxidized or are even reduced during the high-voltage plateau. Principle component analysis and non-negative matrix factorization of XANES spectra reveal the presence of three spectral end members corresponding to the Li₂IrO₃, Li₁IrO₃, and Li_{0.5}IrO₃ compositions, consistent with the two isosbestic points marked in Figure 39b. Linear combination analysis using these end members confirms that the entire spectral evolution is well described by two consecutive, two-phase reactions. The total shift in iridium L₃ WL energy (1.2 eV) is consistent with iridium being oxidized by ~ 1.5 e⁻, accounting for the entire capacity and strongly suggesting LIO exhibits only cationic iridium redox.

To directly assess the contribution of bulk oxygen to the LIO redox mechanism, the team performs soft X-ray absorption spectroscopy (sXAS) at the oxygen K edge of LIO. Transmission and fluorescence yield (FY) detection modes with probing depths of hundreds of nm were employed (see methods). Figure 40a shows the oxygen K edge sXAS-FY and transmission sXAS spectra of LIO during the first electrochemical cycle. The peaks at ~529 eV and 532 eV are ascribed to the unoccupied iridium 5*d*-O 2*p* t_{2g} and e_g^* hybridized states, respectively. The difference plots taken between different states of charge (Figure 40b) clearly show that the intensity of the t_{2g} peak increases and decreases throughout charge and discharge, mirroring the evolution of the

iridium L_3 WL (Figure 40c). Figure 40c shows that the integrated area ratio of the two oxygen K XAS pre-edge peaks follows the same trend in transmission sXAS, which probes the entirety of the particles, confirming that this is a bulk phenomenon. The correlated changes at the oxygen K and iridium L_3 edges indicate redox of a hybridized Ir–O state and are widely accepted as a fingerprint of conventional "TM-O" cation redox.



Figure 39. Reversible redox and phase behavior of Li_{2-x}IrO₃. (a) Capacity-voltage curves of Li_{2-x}IrO₃ galvanostatically measured at a C/12 rate (17.58 mA g⁻¹) in 4.50-2.50 V for the initial three cycles and the stable phases during the two consecutive two-phase reactions of Li_{2-x}IrO₃ occurring at each voltage plateau obtained by combined X-ray diffraction Rietveld refinements and density functional theory calculations. (b) *Operando* transmission X-ray absorption near edge structure spectra of iridium L3 edge for charging (left) and discharging (right) with two isosbestic points (arrows in insets). (c) Shift of the white line energy showing the continuous oxidation/reduction of iridium throughout the whole charge/discharge processes. Error (see methods) was determined to be reasonably small. (d) Linear combination analysis of the three end-members obtained through NMF, consistent with the phase behavior.



Figure 40. Hybridized Ir-O redox in Li_{2-x}IrO₃. (a) soft X-ray absorption spectroscopy (sXAS) fluorescence yield spectra (solid lines) and STXM (scanning transmission X-ray microscopy)-XAS spectra (dashed lines) of oxygen K edge of Li_{2-x}IrO₃ at various states of charge in the first cycle. From bottom to top, pristine (red, A), charged to 3.9 V (yellow, B), charged to 4.6 V (green, C), discharged to 3.7 V after being charged to 4.6 V (olive, D), and discharged to 2.5 V after being charged to 4.6 V (blue, E). (b) Difference plot of sXAS obtained from A showing the hole population evolution of iridium 5*d* -O 2*p* t_{2g} and e_g^* hybridized state. (c) Ratio of the area of iridium 5*d*-O 2*p* t_{2g} peak and iridium 5*d*-O 2*p* t_{2g} peak measured by resonant inelastic X-ray scattering (RIXS), STXM, and sXAS. (d) Oxygen K edge RIXS maps of Li₂IrO₃, LiIrO₃, and Li_{0.5}IrO₃ showing conventional Ir-O cationic redox. The right bottom panel shows the RIXS spectra of each composition at 530.7 eV excitation energy where the anion redox feature is expected to appear.

Patents/Publications/Presentations

Publication

Hong, J., W. E. Gent, P. Xiao, K. Lim, D.-H. Seo, J. Wu, P. M. Csernica, C. J. Takacs, D. Nordlund, C.-J. Sun, K. H. Stone, W. Yang, D. Prendergast, G. Ceder, W. C. Chueh, and M. F. Toney. "Metal-Oxygen Decoordination Stabilizes Anion Redox in Li-Rich Oxides." (2018). Submitted.

Presentations

- Gordon Research Conference Batteries, Ventura, California (February 25, 2018): "Coupling Between Oxygen Redox and Cation Migration Explains Unusual Electrochemistry in Lithium-Rich Layered Oxides"; W. E. Gent, K. Lim, Y. Liang, J. Hong, M. McIntire, Q. Li, S-J. Ahn, J. H. Song, J-H. Park, S-K. Doo, D. Kilcoyne, D. Vine, A. Mehta, S. Ermon, W. Yang, D. Prendergast, M. F. Toney, and W. C. Chueh. Poster.
- Materials Research Society Meeting, Phoenix, Arizona (April 3, 2018); W. C. Chueh.
- Materials Research Society Meeting, Phoenix, Arizona (April 2, 2018); W. C. Chueh.
- California Institute of Technology Department of Applied Physics & Materials Science, Pasadena, California (January 24, 2018); W. C. Chueh.
- Nature Conference on Materials Electrochemistry, Shenzhen, China (January 12, 2018); W. C. Chueh.

TASK 3 – MODELING

Summary and Highlights

Achieving the performance, life, and cost targets outlined in the EV Everywhere Grand Challenge 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 sales 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 are also focused on obtaining the 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, the effort is focused on understanding the working principles of the high nickel layered materials with an aim of understanding structural changes and the 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 addition, focus is paid to the assembling of porous electrodes with particles to predict the conduction behavior and developing tools to measure electronic conduction.

In the area of silicon anodes, the effort is in trying to understand the interfacial instability and suggest ways to improve the cyclability of the system.

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.

Highlight. At LBNL (Cedar's group), the team has developed a fluorinated manganese double redox cathode, $Li_2Mn_{2/3}Nb_{1/3}O_2F$; this material minimized structural changes upon oxidation. Materials cycled in cells demonstrate capacities > 300 mAh/g when cycling between 1.5 V and 5 V.

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) novel disordered, high-rate Li-excess cathodes, (2) new fundamental understanding of the cathode/electrolyte interface and the factors that control the interfacial chemistry and interfacial impedance, (3) critical surface and coating design and optimization strategies that will improve cycling of Li-ion battery cathodes, and finally (4) understanding of the factors that govern stability in nonaqueous electrolytes for Li-ion and Li-S systems.

Project Impact. To enhance the 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 the 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 stability, 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 modelled through coupled classical MD and first-principles methods to accurately capture solvation structure as well as reactivity of liquid system.

Out-Year Goals. Stable interfaces will be determined by focusing initially on degradation mechanisms related to the 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. For the electrolyte development, work will be aimed toward understanding the atomistic interactions underlying the performance of lithium electrolytes specifically elucidating the solvation structure (as a function of salt concentration) and its impact on the stability of different liquid constituent species.

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 modeling of LiAsF₆ in weakly dissociating solvent. Identification of concentration limit causing change in Li⁺ solvation structure between contact-ion-pair and solvent separated species. (Q1, December 2017; Completed)
- Finish modeling of LiPF₆ in weakly solvating solvent. Identification of concentration limit causing change in Li⁺ solvation structure between contact-ion-pair and solvent separated species. (Q2, March 2018; Completed)
- 3. Modeling of dielectric constant of complex Li⁺ electrolytes using MD. (Q3, June 2018; Ongoing)
- 4. *Go/No-Go Decision*: Test algorithm against experimental results to assess whether the project's model can quantitatively capture the change in dielectric behavior as a function of concentration and different solvation structures. If not, change approach. (Q3, June 2018; Ongoing)
- 5. Present simulated kinetic and thermodynamic evaluations of lithiation mechanisms of amorphous silicon and SiO₂. (Q4, September 2018; Completed)

One project goal is to examine the effect of crystalline and amorphous coatings on electrodes. Initial studies will focus on the effects of a native SiO_2 coating on a silicon anode. The project seeks to understand the lithiation kinetics of SiO_2 and the phases formed during lithiation.



Figure 41. Formation energy of crystalline and amorphous (a) lithium silicides and (b) lithium silicates, following lithiation path from silicon and SiO₂, respectively, as seen on the (c) phase diagram.

Figure 41c shows the calculated Li-Si-O phase diagram at low temperature, which is constructed from the calculated formation energies, defined as $E_F = E_{Li_xSiO_2} - xE_{Li} - E_{Si} - E_{O_2}$, for the crystalline and amorphous phases respectively, as a function of lithium content. The convex hull, which constructs the energy envelope of the thermodynamically stable phases, is depicted with lines, and the stable phases as nodes along those lines. The team emphasizes that metastable compounds (for example, those with energies above the convex hull) may be observed experimentally if the energy difference is small compared to the room-temperature driving force for structural reorganization.

Figure 41a shows the binary convex hull for the Li-Si composition line in the phase diagram, where the calculated metastable phases are also indicated. The team notes that the amorphous states exhibit a high degree of metastability, ranging from 10-500 meV/atom; however, the amorphous convex hull follows a similar trend as the crystalline counterparts, as a function of lithium content. This suggests that the relative difference in formation energy between different compositions originates primarily from changes in short-range order Li-Si motifs. As indicated by the dashed line in Figure 41c, SiO_2 is thermodynamically driven to lithiate. The predicted lithiation process passes through ten 3-phase regions consisting of lithium silicides, silicon, and stoichiometric lithium silicates, until the end products Li₂O and Li_xSi are formed. Following this compositional trajectory, the team examines the calculated formation energies of a range of Li_xSiO_y amorphous compositions and compares to the combined energy of the crystalline phases as obtained through the convex hull of the phase diagram (illustrated by the same color scheme in Figure 41c). Similar to the lithiation of silicon, the amorphous structures are metastable as compared to the combination; the overall shape of the lithiation convex hull is similar for both crystalline and amorphous phases. Again, the common trend suggests that the energy differences between the compositions are dominated by the local Li-Si-O environments, rather than longer range interactions, which are not similar in crystalline and amorphous states. The initial charging will extrude silicon, promoting more oxygen-rich silicates. Further charging (lithiation of the anode) will produce various lithium silicides until Li₂O and Li_xSi are formed.

Task 3.2 – Addressing Heterogeneity in Electrode Fabrication Processes (Dean Wheeler and Brian Mazzeo, Brigham Young University)

Project Objective. The project goal is to better understand connections between fabrication conditions and undesired heterogeneity of thin-film electrodes by means of new nondestructive inspection techniques and computer models.

Project Impact. This work will result in new diagnostic and modeling tools for rapidly and conveniently interrogating how well homogeneity has been maintained in electrodes during fabrication and in subsequent cycling. Real-time measurement of heterogeneity will enable manufacturer quality control improvements. The measurement and modeling tools will further enable researchers to compare different electrodes, improve formulations and processes, and anticipate cell performance of new designs.

Approach. Two non-destructive inspection techniques will be developed or improved that will characterize electrochemical and mechanical uniformity of the electrodes. The first tool will be a flexible contact probe on a polymer substrate for rapidly measuring local electrical conductivity across electrodes of any geometry. The second tool will be a new acoustic probe that measures local elasticity and density of the composite film. These two prototyping efforts will be tied together by a particle-based microstructure model that allows prediction and correlation of electrode conductive and mechanical properties with fabrication conditions.

Out-Year Goals. This project was initiated October 2016 and concludes September 2019. Overall goals by fiscal year are as follows:

- 2017. Fabricate first-generation flexible conductivity probe and proof-of-concept of acoustic probe. Improve microstructure model to match experiment.
- 2018. Integrate flex probe with test fixtures suitable for assessment of large or continuous samples. Demonstrate measurement of localized ionic conductivity.
- **2019.** Assess affect of heterogeneity on cell charge and discharge performance. Further improve accuracy and reliability of probe and modeling technologies.

Collaborations. Ram Subbaraman and Jake Christensen (Bosch), Daniel Abraham (ANL), Steve Harris (LBNL), Bryant Polzin (ANL), and Chisu Kim (Hydro-Quebec, HQ) have provided battery materials for analysis. Other collaborations and the transfer of this technology to interested parties are being pursued.

- 1. Integrate flex probe with off-the-shelf CNC positioning system to enable interrogation of large-format electrode films. (Q1, December 2017; Completed)
- 2. Integrate flex probe with prototype rolling apparatus to enable interrogation of continuous-roll electrode films. (Q2, March 2018; Completed)
- 3. *Go/No-Go Decision*: Demonstrate that localized conductivity probe has adequate reliability for continued development. Criteria: Localized ionic conductivity probe can match macroscopic results for a representative electrode sample. (Q3; In progress)
- 4. Quantify the durability of multiple flex probes to validate suitability for industrial use. (Q4; In progress)

Milestone 2 (Complete). The flexible N-line probe has provided opportunity for a more robust way of taking electronic measurements of battery electrode films. With the flex probe integrated into an off-the-shelf CNC machine as a positioning system, the probe becomes more commercially attractive. The second milestone was to develop a proof-of-concept rolling probe, allowing for interrogation of continuous-roll electrode films without compromising integrity of the films.

Using 3D printing, a series of designs was realized for the rolling apparatus. The flex probe is embedded along the circumference of the rolling apparatus, which in turn attaches to the head unit of the CNC positioning system, as shown in Figure 42. Use of the CNC positioning system is a preliminary step to simulate a fully continuous rolling apparatus as might be used during roll-to-roll electrode manufacturing. Here the apparatus can complete two full rotations in one test, and therefore take two measurements at intervals on the electrode film.

Figure 43 shows results of a rolling measurement over 40 mm of travel distance. A nonzero current corresponds to the region where the N-line probe is in contact with a Li-ion electrode sample, and therefore allows a conductance to be computed. Figure 43 shows the intermittent contact for 8 repetitions in which the roller is moved back and forth over the same location. The results for conductance show relatively high repeatability. Further work on this apparatus will continue, moving toward a fully automated measurement tool.



Figure 42. Converted Carbide 3D CNC stage with custom rolling N-line probe attachment.



Figure 43. Conductance measurements over 40-mm segment of battery electrode film, showing areas of no, minimal, and good contact. Measurement is repeated eight times with the probe rolled back and forth over the same segment.

Patents/Publications/Presentations

Patent

 Mazzeo, B. A., J. Vogel, D. Wheeler, E. Hardy, and D. Clement. Flexible, Compliant Multiline Microprobes for Measurements of Material Electrical Properties. U. S. Provisional Patent Application No. 62/453,846; filed February 2, 2017.

Publications

- Dallon, K., J. Yao, D. Wheeler, and B. Mazzeo. "Characterization of Mechanical Properties of Battery Electrode Films from Acoustic Resonance Measurements." *Journal of Applied Physics* 123 (2018): 135102.
- Forouzan, M., B. Mazzeo, and D. Wheeler. "Modeling the Effects of Electrode Microstructural Heterogeneities on Li-ion Battery Performance and Lifetime." Submitted to *Journal of The Electrochemical Society* (2018).

Presentations

- Gordon Research Conference on Batteries, Ventura, California (2018): "Variations in Microstructure and Conductive Properties of Porous Li-Ion Electrodes"; D. Wheeler.
- International Battery Seminar & Exhibit, Fort Lauderdale, Florida (2018): "Measurement and Origins of Conductivity Variations in Commercial Li-Ion Electrode Films"; B. A. Mazzeo.

Task 3.3 – 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 define 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 chemical, structural, and dynamical properties and of the electrode micro- and nano- structure on the formation and evolution of the SEI layer and 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). Prof. G. Somorjai (UC Berkeley) and Prof. Shahbazian Yassar (UIC) have also contributed to the project.

- 1. Complete analysis of effects of Li-substrate interactions on lithium deposition. (Q1, FY 2018; Completed)
- 2. Complete study of SEI reactions over lithium deposits. (Q2, FY 2018)
- 3. Complete analysis of operating conditions on dendrite growth. (Q3, FY 2018)
- 4. Complete evaluation of co-deposition effects. Establish comparisons with experimental trends. (Q4, FY 2018)

Chemistry of Lithium Plating. The team investigated the reactions and electronic distribution taking place when a lithium ion (bare, with one or more solvent molecules, or coupled with the salt anion) is in contact with a Li-metal surface. They carried out density functional theory (DFT) calculations to determine whether the reduction of the lithium cation takes place on the surface. The team observed that the anion or solvents are reduced first. However, when the cation is reduced, a large accumulation of electrons (much more than needed to reduce a single cation) takes place in the vicinity of the site where the cation is reduced. This accumulation of electrons should induce further reduction of other species, including electrolyte components but also other cations. The team studied the effect of surface defects, and the presence of a nucleating SEI, on the deposition of reduced lithium. When the lithium ion arrives to the top of the SEI (represented by a monolayer of Li_2CO_3), it is not reduced. Instead, there is a driving force for lithium diffusion toward the surface, where it is reduced, and similar accumulation of electrons takes place. The team suggests that this extreme reactivity of the lithium surface and the subsequent uneven distribution of electrons in the lithium metal are the origin of the dendrite nucleation. These phenomena occur when the deposition is on a Li-metal foil or on the current collector (after a thin film of lithium is deposited). Thus, a comprehensive solution to the problem of the dendrite formation must arise from controlling such reactions. The team is analyzing various scenarios for accomplishing this goal. A manuscript has been submitted that extensively discusses these findings.

Surface Films Due to Li-Metal Dissolution and SEI Nucleation. The buildup of the SEI layer was studied using classical MD to analyze possible reactions and rearrangements taking place at the electrolyte/Li-metal anode interface. The simulations with different electrolytes indicate that a porous phase develops immediately above the anode surface, which contains not only decomposed species due to electron transfer from the lithium surface, but also intact electrolyte molecules. Over the porous phase, two additional surface films are formed: the nest and the disperse phases. The nest phase has an amorphous matrix structure of connected lithium atoms separated by nanochannels, through which the intact electrolyte and other products of its decomposition such as ethylene (molecules and radical anions) diffuse. In the disperse phase (the top layer in contact with the electrolyte), lithium atoms in a higher oxidation state are connected in networks nucleating SEI blocks such as Li₂O and LiF, or more complex structures. A manuscript has been submitted.

Dendrite Growth under an Electric Field. The team simulated dendrite growth by testing a few charge distributions in a nanosized square representing a crack of the SEI, which is where the electrolyte solution comes into direct contact with a LiSi alloy anode. Depending on the selected charge distributions, the dendrites grow when an external field is applied. The team found that dendrites grow when strong variations of charge take place on the surface of the crack. The results were published.

Lithium Electrodeposition in Intercalated Electrodes. A mesoscale Kinetic Monte Carlo model was developed linking rates of reduction of lithium ions and diffusion of lithium atoms into the anode and electrolyte and surface diffusion to operating conditions and material properties. The critical events determining electrodeposition occur at the anode-electrolyte interface. If the rate of lithium diffusion into the anode is about the same order as the rate of reduction of lithium ions on the anode surface, lithium atoms accumulate on the anode surface as a film. There are two electrochemical reactions occurring on the anode surface: reduction on the graphite anode, and reduction on the deposited lithium film. The rate of lithium reduction on the graphite anode is large compared to that on the surface. In the absence of surface diffusion of lithium atoms on the electrodeposited film, if the reduction reaction on the graphite anode dominates compared to the reaction on the lithium film, the morphology of the film deposited is that of a uniform layer. On the other hand, if the reduction reaction on the lithium film dominates, a dendritic morphology is obtained. If the diffusion of the lithium atoms on film is included, the morphology of the electrodeposited film changes from dendritic to columnar or mossy. Surface diffusion is a key component in the morphology of the electrodeposited film. The effect of the surface diffusion rate was investigated: if the rate of diffusion is small, the film is irregular due to diffusion of lithium atoms into the anode, but the morphology is mostly flat. At larger rates of surface diffusion, the film growth is mostly vertical. A manuscript was submitted.

Patents/Publications/Presentations

Publications

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Presentation

 U. S.-Germany Workshop on Energy Storage, Washington, D. C (March 26–27, 2018): "Interfacial Phenomena at Si Anodes: Effects of Surface Chemistry & Structure, and Electrolyte Composition"; Perla B. Balbuena. Task 3.4 – Electrode Materials Design and Failure Prediction (Venkat Srinivasan, Argonne National Laboratory)

Project Objective. The project goal is to develop a continuum-based mathematical model to (i) investigate the impact of SEI layer on the growth of dendritic protrusions, and (ii) elucidate the deposition mechanism and deposit morphology observed on top of the carbon substrate in Li-S battery cathodes. Mechanical stiffness and transport mechanism of lithium through the SEI layer can significantly affect the nucleation of dendritic protrusions on top of Li-metal anodes. Effectiveness of protective layers in preventing the growth of lithium dendrites can also be studied by using this methodology. Next-generation, high-energy-density Li-S batteries experience limited capacity due to cathode surface passivation because of the precipitation of Li-sulfides during the discharge process. Understanding the morphology of precipitates can significantly help to develop strategies that can minimize the surface passivation and improve the practical specific capacity of Li-S batteries. The main focus will be to develop microscale models capable of successfully capturing the multiscale multiphysics phenomena that occurs during Li-metal and Li-sulfide deposition processes.

Project Impact. Based on the work conducted as part of this project, better understanding of the different mechanisms responsible for degradation in Li-metal anodes and Li-S batteries can be developed. Based on these understandings, different strategies can be devised to minimize the impact of degradation mechanisms and enhance the performance and lifetime of next-generation Li-ion batteries.

Out-Year Goals. At the end of this project, mathematical models will be developed that can capture the impact of diffusivity, conductivity, transference number, solubility, and mechanical stiffness of various species on the morphology of lithium and Li-sulfide deposits on top of Li-metal and carbon substrates, respectively.

Collaborations. This project has no collaborations this period.

Milestones

Incorporate SEI Layer in Li-Metal Dendrite Model

- 1. Incorporate SEI layer in lithium dendrite growth model and analyze its influence on growth of dendritic protrusions. (Q1, December 31, 2017; Completed)
- 2. Evaluate the impact of mechanical properties and thickness of SEI layer on propensity for dendrite growth. (Q2, March 31, 2018; Completed)

Mathematical Model for Sulfur Redistribution

- 3. Develop a model to examine the precipitation process of lithium sulfide during battery discharge. (Q3, June 30, 2018; In progress)
- 4. Develop a mathematical model to describe surface morphology evolution in sulfur cathode. (Q4, September 30, 2018; In progress)

Incorporate SEI Layer in Lithium Metal Dendrite Model: Evaluate the Impact of Mechanical Properties and Thickness of SEI Layer on Propensity of Dendrite Growth

Last quarter, the project demonstrated that internal heterogeneity of thin SEI could lead to formation of lithium dendrites. Here, the impact of thick SEI layers and their mechanical stiffness on the growth of lithium dendrites has been studied. Internal heterogeneity of transport properties within the SEI leads to development of non-uniform current distribution and formation of lithium nuclei. The computational mesh is shown in Figure 44a, where heterogeneity within the SEI layer has been assumed to exist at the left edge (highlighted). Enhanced transport of ions through this imperfection leads to formation of lithium nucleus. However, presence of a stiff SEI layer is expected to prevent the growth of any inhomogeneity. To capture the suppression of lithium dendrites by the SEI layer, a two-step computational mechanism has been adopted. (i) Based on the amount of lithium deposited, the lithium electrolyte interface is deformed. This produces excessive compression in electrolyte. (ii) Next, the stress in lithium is relaxed, and the compressed electrolyte is allowed to push the lithium (with dendritic protrusion) back to equilibrium. This two-step mechanism ensures the evolution of compressive stresses within both lithium and electrolyte. Figure 44b-c demonstrates the distribution of potential and concentration, respectively, within the electrolyte, under specific operating conditions.



Figure 44. (a) Computational mesh used to understand growth of dendritic protrusions under the presence of SEI layer. Internal heterogeneity of the SEI at the left boundary leads to faster transport of reacting species, which eventually leads to growth of dendritic protrusions. (b) Potential distribution within the electrolyte during operation under specified conditions. (c) Concentration distribution within electrolyte under the same operating condition specified above the figures. Larger gradients of both potential and concentration are observed within the SEI.

Figure 45a demonstrates that increasing SEI thickness helps to prevent growth of dendritic protrusions. Decrease in dendritic protrusion height with increasing SEI stiffness has been demonstrated in Figure 45b. Figure 45c shows that higher surface energy density helps to stabilize the growth of dendrites, but the impact is more pronounced at lower current densities. Development of a model that captures the impact of SEI thickness and stiffness on dendrite growth fulfills this quarter's milestone.



Figure 45. (a) Growth of dendritic protrusions with time under applied current density of 100A/m². Increasing thickness of a stiff SEI layer helps to prevent dendrite growth. (b) Height of the dendritic protrusion with increasing SEI stiffness. Increase in applied current density helps to grow the dendritic protrusion. (c) Increasing surface energy density between lithium and electrolyte helps to suppress the dendritic protrusion. However, the impact of surface energy density minimizes at extremely high currents of operation (~100 A/m²).

BMR Quarterly Report

Patents/Publications/Presentations

Presentation

 232nd Fall Meeting of The Electrochemical Society, National Harbor, Maryland (October 2017): "Impact of Electrolyte Transference Number on Lithium Dendrite Growth Process"; Pallab Barai, Kenneth Higa, and Venkat Srinivasan.

Task 3.5 – First-Principles Calculations of Existing and Novel Electrode Materials (Gerbrand Ceder, Lawrence Berkeley National Laboratory)

Project Objective. The main project objectives are as follows: (1) develop very high-capacity, layered cathodes with high structural stability (> 250 mAh/g) and high surface stability; (2) clarify the role that Li-excess and cation disorder play in capacity and structural stability; (3) develop predictive modeling of oxygen charge transfer and oxygen loss, and find ways to make oxygen redox beneficial in terms of increase capacity; and (4) develop materials with engineered surface passivation that does not lead to impedance increase.

Project Impact. The project will lead to insight in how Li-excess materials work and ultimately to higher capacity cathode materials for Li-ion batteries. The project will help in the design of high-capacity cathode materials that are tolerant to TM migration.

Out-Year Goals. Future goals include the following: (1) develop higher capacity Li-ion cathode materials, and novel chemistries for higher energy density storage devices, and (2) guide the field in the search for higher energy density Li-ion materials.

Collaborations. This project collaborates with K. Persson (LBNL), C. Grey (Cambridge), G. Chen (LBNL), and B. McCloskey (UC Berkeley).

- 1. Assess, through modeling, the viability of fluorination of disordered-rocksalt cathodes to reduce the oxygen activity. (Q1, FY 2018; Completed)
- 2. Synthesize one partially fluorinated cathode material and demonstrate fluorination through NMR, TEM, XRD, or other characterization tool. (Q2, FY 2018)
- 3. Demonstrate viability of reducing TM valence in Li-excess materials to create higher capacity (for example, use Mn^{2+} or V^{3+} or more Ni^{2+}). (Q3, FY 2018)
- 4. Demonstrate capacity > 200mAh/g in a novel fluorinated disordered rocksalt. (Q4, FY 2018)

High-energy-density cathode employing oxygen redox is attracting much attention. However, anion activity causes oxygen loss near the surface of the particles. In turn, this results in creation of high impedance surface layers and large polarization of the voltage profile, leading to poor cycling performance. To minimize structure changes after oxygen oxidation, the team developed fluorinated manganese double redox cathode based on Mn^{2+}/Mn^{4+} . Through the combined strategy of high valent cation (Nb⁵⁺, Ti⁴⁺) substitution and O²⁻ replacement



Figure 46. X-ray diffraction, scanning electron microscopy, and scanning transmission electron microscopy energy dispersive X-ray spectroscopy mapping from Li₂Mn_{2/3}Nb_{1/3}O₂F.

by F⁻, the team achieved maximum TM redox and bypassed the negative effect of oxygen oxidation [Lee et al. *Nature* 556 (2018): 185].

The project developed Li-Mn-Nb-O-F (LMNOF) and Li-Mn-Ti-O-F (LMTOF) systems by mechanochemical ball-milling. XRD, SEM, and STEM energy dispersive X-ray spectroscopy (EDS) were applied to confirm that the particle is a disordered rocksalt structure with homogenous fluorination (Figure 46). NMR was further examined to estimate that fluorination is effectively incorporated into the bulk.

Galvanostatic charge-discharge tests were carried out in LMNOF and LMTOF materials within different voltage windows and rates. Using fluorination and

high-valent cation substitution, the team developed, for the first time. Mn-based Li-excess cathodes that achieve ultrahigh (> 300 mAh/g)capacity and energy density (~ 1000 Wh/kg) within the voltage window of 1.5-5.0 V at 10 mA/g (Figure 47). Mn^{2+}/Mn^{4+} through redox combined with a limited use of oxvgen redox.



Figure 47. Electrochemical performance of Li-Mn-Nb-O-F (LMNOF).

The team also studied the redox mechanism by combination of *ex-situ* XRD and XAS of manganese and oxygen K edge, and successfully proved the usage of reversible Mn^{2+}/Mn^{4+} redox with partial overlap with oxygen redox at high voltage. With DFT calculations, the team found this overlap between oxygen redox and manganese redox came from fluorination and the large lattice constant of the materials (Figure 48).



Figure 48. A schematic band structure of Li₂Mn_{2/3}Nb_{1/3}O₂F.

Task 3.6 – 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 mm-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 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. Compare lithium morphology obtained from experiments and modeling. *Go/No-Go Decision*: Determine if effect of SEI on dendrite growth should be modeled implicitly or explicitly. (Q1, December 30, 2017; *Go*)
- Identify electronic pathway of lithium dendrite growth inside Li₇La₃Zr₂O₁₂ (LLZO). (Q2, March 31, 2018; Completed)
- 3. Identify Li-ion pathway of lithium dendrite growth inside LLZO. (Q3, June 30, 2018; In progress)
- 4. Develop multiphase multigrain phase-field model that incorporates mechanical and electrochemical driving forces for lithium dendrite growth in polycrystalline solid electrolyte. (Q4, October 31, 2018; In progress)

Liquid Electrolyte

Using the newly developed implicit lithium morphology model, the impact of surface energy, exchange current, and anisotropy on lithium morphology was investigated. It was found that the most effective way to form



Figure 49. Lithium dendrite morphology change with relative exchange current.

smooth surface morphology during the lithium electrodeposition process is by reducing the relative exchange current, I0 (Figure 49).

To vary I0 experimentally, electronically conductive carbon coatings and ionically conductive Li_{1.5}Al_{0.5}Ge_{1.5}P₃O₁₂ solid

electrolyte coatings were deposited on lithium electrode via DC and radio frequency (RF) magnetron sputtering systems, respectively. The thickness of the carbon layer was measured to be about 65 nm from a profiler. Figure 50 shows the voltage profiles of Li-Li symmetrical cells cycled in ether-based electrolyte (0.4 M LiNO₃ + 0.6 M LiTFSI in DOL:DME=1:1, vol%) with a current density of 1 mA cm⁻² and a capacity density of 4 mAh cm⁻². This aggressive capacity density was applied to quickly examine the effect of carbon coating. Prolonged cycle life was achieved in lithium electrodes coated with carbon. Two mechanisms are proposed: (1) the SEI layer formed in carbon layer acts a protective layer to lithium by reducing the

lithium-electrolyte reactions; and (2) the carbon layer could improve the uniformity of current distribution. On the other hand, no improvements of cycling performance were found with the 245-nm thick solid electrolyte LiAlGePO coating. SEM observation shows that lithium was deposited above and below the LiAlGePO coating. More efforts on developing Li-ion conductive coatings are under way.



Figure 50. Improved cycle life with carbon-coated lithium electrode.

Solid Electrolyte

The driving force for the metallic lithium formation in solid electrolyte is still puzzling, considering the large band gap of bulk cubic Li₇La₃Zr₂O₁₂ (c-LLZO) and the preference of lithium being ionic in oxides. DFT-based electronic structure calculation and analysis revealed that additional surface states exist in the bandgap of the (110) surface of c-LLZO and tetragonal LLZO (t-LLZO), but not in the (100) surface of Li₂PO₂N (Figure 51). Excess electrons would be trapped on LLZO surfaces, either around the lanthanum atoms on the surface of c-LLZO or dispersed on the nonstoichiometric surface of t-LLZO. It is also thermodynamically favorable for the excess electrons on lanthanum to reduce Li+ forming metallic Li0. In contrast, the excess electrons will be localized on oxygen or nitrogen underneath the surface in Li₂PO₂N, making Li+ hard to be reduced. Thus, the pore and crack surfaces in c-LLZO provide a possible electron pathway for metallic lithium formation, and the t-LLZO interlayer observed at the Li/c-LLZO interface should not stop metallic lithium formation due to its similar lithium nucleation tendency as c-LLZO. Furthermore, the team proposes, based on the calculation results, that an interlayer of Li₂PO₂N (ALD Lipon) at the Li/c-LLZO interface would be more efficient and defect tolerant to suppress lithium dendrite formation.



Figure 51. Compare the density of states between bulk and slabs.

Patents/Publications/Presentations

Publications

- Wang, A. P., S. Kadam, H. Li, S. Q. Shi, and Y. Qi. "Review on Modeling of the Solid Electrolyte Interphase (SEI) for Lithium-Ion Batteries." *npj Computational Materials* 4, id. 15 (2018). Invited review.
- Yulaev, A., V. Oleshko, P. Haney, J. Liu, Y. Qi, A. A. Talin, M. Leite, and A. Kolmakov. "From Microparticles to Nanowires and Back: Radical Transformations in Plated Li Metal Morphology Revealed via *In Situ* Scanning Electron Microscopy." *Nano Letters* 18, no. 3 (2018): 1644–1650.
- Li, Y. S., and Y. Qi. "Transferable SCC-DFTB Parameters for Li-Metal and Li-Ions in Inorganic Compounds and Organic Solvents." *Journal of Physical Chemistry C* (2018). Submitted.
- Tian, H. K., B. Xu, and Y. Qi. "Computational Study of Li Nucleation Tendency in LLZO and Rational Design of Interlayer Materials to Prevent Li Dendrites." *Journal of Power Source* (2018). Submitted.
- Cheng, Q., L. Wei, Z. Liu, N. Ni, Z. Sang, B. Zhu, W. Xu, L-Q. Chen, W. Min, and Y. Yang, "*In-Operando*, Three Dimensional, and Simultaneous Visualization of Ion Depletion and Lithium Growth by Stimulated Raman Scattering Microscopy." *Nature Communications* (2018). Submitted.

Presentations

- Spring ACS National Meeting, New Orleans, Louisiana (March 20, 2018): "Simulation of Lithium Ion Transport through the Complex Electrode/SEI/Electrolyte Interface"; Yue Qi and Yunsong Li. Invited talk.
- International Battery Seminars, Fort Lauderdale, Florida (March 29, 2018): "Advanced Electrode Materials for Next Generation Lithium Ion Batteries"; X. Xiao. Invited talk.
- Materials Research Society (MRS) Spring Meeting, Phoenix, Arizona (April 5, 2018): "Phase-Field Method of Li Dendrite Formation during Electrodeposition"; Z. Liu, L. Chen, Y. Qi, X. Xiao, Q. Zhang, and L-Q. Chen. Invited talk.
- MRS Spring Meeting, Phoenix, Arizona (April 5, 2018): Computational Study of Li Nucleation Tendency in LLZO and Rational Design of Interlayer Materials to Prevent Li Dendrites"; H. K. Tian, B. Xu, and Y. Qi.

Task 3.7 – First-Principles Modeling and Design of Solid-State Interfaces for the Protection and Use of Lithium-Metal Anodes (Gerbrand Ceder, UC 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 *ab initio* molecular dynamics (AIMD) and nudged elastic band (NEB) calculations. Simultaneously, a robust framework will be developed to identify factors controlling Li-dendrite propagation within solid electrolytes and interfacial products by accounting for irregularities, defects, and grain boundaries, 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 electro-chemical stability and high ionic conductivity. DFT is used to calculate bulk elastic constants of materials, surface energies, and interface de-cohesion energies of grain boundaries; 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 electro-chemical 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 metal-electrolyte electrochemical-mechanical interface model. (Q1, FY 2018; Completed)
- 2. Stability screening of candidate material for good SSE. (Q2, FY 2018; Completed)
- 3. Determine critical stress conditions that yield fracture in ceramic electrolytes during lithium deposition. (Q3, FY 2018; In process)
- 4. Lithium conductivity screening using AIMD and NEB method to screen for materials with high lithium mobility. (Q4, FY 2018; On target)

The project developed a model for the electrochemical stability of potential solid electrolyte material, based on the framework for stability analysis of electrode/electrolyte interface. The team embedded the high component phase diagrams to the calculation of electrochemical stability, as shown in Figure 52; LGPS is used as an

example to describe details of this method. According to current computational results, for the same element M in Li-M-X (X = O or N)ternaries, nitrides exhibit better stability against lithium metal than their oxide counterparts. The team attributes this effect of nitrides to their more covalent M-N bonding that stabilizes M from being reduced by lithium metal. In terms of decomposition against products lithium metal, Li-metal oxides would form electron conductive phase such as Li-M alloys, making the interface decomposition non-passivating, while in contrast. for N-rich Li-metal often self-passivating.



nitrides, the nitride/lithium interface is Figure 52. Grand potential phase diagram used in electrochemical stability calculation.

Study of Contact Loss of Interface of Li-Metal Anode and Solid Electrolyte. Experimental work has shown that external pressure on a solid-state battery and the interfacial contact quality between lithium metal and solid



Figure 53. Mechanical model to study contact loss and surface roughness.

electrolyte will affect the overall capacity of battery. To quantify the relation between external pressure and interfacial contact, and understand how the contact loss will lead to the formation of dendrites, the team built the model shown in Figure 53. As shown, the contact between Li-metal anode and solid electrolyte usually is not perfect. To study the inhomogenous deposition caused by this imperfect contact, the team constructed a simplified model to study the relation between surface roughness and interfacial contact. They found that because of existance of roughness, a stress and lithium deposition concentration will develop and cause further crack of the solid electrolyte.

Task 3.8 – Large-Scale *Ab Initio* Molecular Dynamics Simulations of Liquid and Solid Electrolytes (Lin-Wang Wang, Lawrence Berkeley National Laboratory)

Project Objective. The project goal is to use large-scale AIMD simulations and other computational approaches to study the discharging mechanism in Li-S battery, especially for polysulfur 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. One major issue is solvation of Li₂S_n molecules in the electrolyte. The team is working to find the solution to this problem by both understanding the Li_2S_n -electrolyte interaction and discovering better cathode materials for optimal Li₂S_n-cathode binding. Specifically, the team seeks to: (1) develop reliable methods that combine classical force field (CFF) simulations with *ab initio* calculations to study thermal dynamic properties of Li_2S_n in different electrolytes, as well as interactions with different species within the electrolytes; and (2) study Li₂S_n interaction with different cathode materials, especially for 2D cathode materials consisted 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, thermodynamically, the Li_2S_n will not be dissolved in the electrolyte. To study the Li_2S_n -electrolyte interaction, the team needs to accurately calculate the molecule entropy inside the solvent, which is a challenging task. The team plans to combine CFF with ab initio calculations for that study. To study Li_2S_n and cathode interaction, the team will calculate the phase diagrams of the systems with different number n and will hence obtain the binding energies and voltages at every step of the discharging process.

Project Impact. Making the Li-S battery a commercial reality will have a major impact in 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.

Out-Year Goals. In the outgoing years, the team will further develop computational methods for more accurate entropy and interaction energy calculations for the electrolyte. This is a critical capability to study the battery system. The team 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 and using curved amorphous structures to increase capacity. The key is to investigate all the effects and competitions of different reactions.

Collaborations. The project will collaborate with Gao Liu's group for cathode design. It has also collaborated with Prof. Feng Pan of Beijing University for lithium battery research in general.

- 1. Set up the Li_2S_n calculation with charge polarization model (CPM) solvent model without explicit solvent molecule. (Completed).
- Carry out Li₂S_n/cathode structure calculations using CPM solvent model, with different cathode structures. (In progress).
- 3. Continue the Li_2S_n calculation with explicit solvent molecules; carry out direct CFF and AIMD simulations.
- 4. Continue calculation of Li₂S_n/cathode binding energies and phase diagrams, discovering new adequate cathode materials and morphologies.

The team finished a study using 2D phosphorene oxides (POs) as lithium cathode material. This is under the design principle of using light element 2D material as lithium battery cathode. Four surface oxidization states $(P_4O_1, P_4O_2, P_4O_3, and P_4O_4)$, are evaluated as potential cathode for sealed Li-oxygen battery. Project simulations reveal several findings. (1) By forming maximum Li-O bonds, lithium can be tightly chemisorbed on the surface of POs with large binding energy ranging from -2.32 to -3.72 eV and charge transfer of $\sim 0.9 e$ from lithium to oxygen. (2) The diffusion of lithium on POs is strongly anisotropic, as the barrier along the armchair direction is nearly two times higher than that along the zigzag direction. The barrier dramatically decreases to 0.2 eV with increasing oxidization, indicating a high diffusivity. (3) For P_4O_4 cathode, the thermodynamically stable, fully discharged product has a stoichiometry of Li: P: O = 1:1:1, achieving a specific capacity of 570.56 mAh/g, an average OCV of 2.55 V, and an energy density of 1457 Wh/Kg. The energy density can be further increased by considering solvent effects. More polar cyclic EC solvent brings in larger energy density enhancement than less polar linear 1,2-dimethoxyethane (DME). (4) Semiconductor-to-metal transition occurs within POs after lithium adsorption, facilitating the electrical transport in POs-based battery. A combination of strong lithium adsorption, high diffusivity, and good conductivity makes POs a great candidate for future fully-sealed Li-oxygen battery. Figure 54 shows the stability study of the Li_xP₄O_y. AIMD is used to test the structural stability. As one can see, if x is less than or equal to y, the system is stable. On the other hand, when x is larger than y, the system becomes unstable. The paper describing this work has been accepted by the Journal of Materials Chemistry A.



Figure 54. The snapshots from *ab initio* molecular dynamics simulation at room temperature. When the number of lithium (green ball) is larger than the number of oxygen (red ball), the system becomes unstable.

Using the project's newly developed implicit solvent model, the team studied use of 2D hexaaminobenzene, as Li-S battery anode. 2D hexaaminobenzene is consisted with a carbon-nitride sheet with carbon in a benzene

ring and nitrogen atom binding with TM. The team has studied the system with TM manganese. Such a system can absorb S_8 molecule, which in turn can serve as Li-S battery cathode. The team shows that the system can absorb lithium and be able to prevent dissolvation of lithium sulfate cluster. When fully charged, the energy capacity of the system can be around 1300 Wh/Kg. The team also recalibrated the theoretical Li₂Sn cluster energy in the solvent electrolyte. This is shown in Figure 55. In the literature, the team found that often insufficient solvent energy is included in the Li₂S_n cluster calculated result, and sometimes lithium metal cluster, instead of lithium crystal, is used as the lithium reference energy.



Figure 55. The calculated energy diagram of $\rm Li_2Sn$ clusters including solvent effects.

Patents/Publications/Presentations

Publications

- Yang, L., J. Zheng, M. Xu, Z. Zhuo, W. Yang, L.W. Wang, L. Dai, J. Lu, K. Amine, and F. Pan. "Short Hydrogen Bonds on Reconstructed Nanocrystal Surface Enhance Oxygen Evolution Activity." ACS Catalysis 8 (2018): 466.
- Duan, Y., B. Zhang, J. Zheng, J. Hu, J. Wen, D. J. Miller, P. Yan, T. Liu, H. Guo, W. Li, X. Song, Z. Zhuo, C. Liu, H. Tang, R. Tan, Z. Chen, Y. Ren, Y. Lin, W. Yang, C. M. Wang, L. W. Wang, J. Lu, K. Amine, and F. Pan. "Excess Li-Ion Storage on Nanocrystal Reconstructed Surface to Boost Battery Performance." *Nano Letters* 17 (2017): 6018.
- Wu, J., and L. W. Wang. "2D Frameworks C2N as a Potential Cathode for Lithium Sulfur Batteries: An *Ab Initio* Density Functional Study." *Journal of Materials Chemistry A* 6 (2018): 2984.
- Li, Y., F. Ma, and L. W. Wang. "Phosphorene Oxides as Promising Cathode Material for Sealed Non-Aqueous Li-Oxygen Battery." *Journal of Materials Chemistry A* (2018). doi: 10.1039/C8TA01218K.

Task 3.9 – *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 the 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 extreme 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, Vincent Battaglia's for cell assembly for 3-Omega studies and Robert Kostecki's for pristine battery active material growths for TDTR studies.

- 1. TDTR measurements of ideal battery samples. (Q1, FY 2018; Completed)
- 2. 3-Omega sensing and heating lines fabricated, and metrology developed. (Q2, FY 2018; Completed)
- 3. Electrochemical cells with 3-Omega sensors integrated on the electrodes. (Q3, FY 2018; On schedule)
- 4. *Go/No-Go Decision*: Baseline *in operando* thermal diagnostics and measurement with 3-Omega technique performed. (Q4, FY 2018; On schedule)

Quarter 2 Milestone – Completed. The project successfully developed the in-house 3-Omega metrology, fabricated heating and sensing lines, and evaluated the efficacy of the system on test samples spanning two orders of magnitude in thermal conductivity (k) and four orders of magnitude in thickness. The project's custom built 3-Omega metrology is shown in Figure 56. The system can hold the sample at a controlled temperature of $T_{ambient} \pm 70^{\circ}$ C. All data collection is fully automated. The team tested the system by measuring k of SiO₂ and silicon. They measured k of a bulk silicon wafer (450μ m), of bulk glass (1 mm), and of 300-nm and 1- μ m thick glass films thermally grown on a silicon wafer. Examples of 3-Omega sensors fabricated on different samples are shown in Figure 57. The team measured an average k of glass across all samples of 1.07 ± 0.05 W/m-K. This value agrees with literature and shows that the team can measure k accurately for both bulk samples and thin films. They measured an average k of silicon of 147 ± 5 W/m-K, again in agreement with literature. Combined, these results show that the project's system is capable of measuring thermal conductances as high as 3.5 MW/m²-K and for material layers varying from bulk down to hundreds of nm thick. These specifications meet and exceed the anticipated requirements for the future battery cell thermal measurements.



Figure 56. Custom-built, fully automated 3-Omega thermal conductivity measurement system in the Principal Investigator's lab.



Figure 57. Control samples used to test the 3-Omega system with heating and sensing lines fabricated. (left) Bulk 1-mm glass. (middle) 300-nm thick glass layer thermally grown on a silicon wafer. (right) plain undoped bulk 450-µm silicon wafer.

Task 3.10 – Multi-Scale Modeling of Solid-State Electrolytes for Next-Generation Lithium Batteries (Anh Ngo, Larry Curtiss, and Venkat Srinivasan, Argonne National Laboratory)

Project Objective. This project is part of a multi-scale modelling 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 and Monte Carlo simulations. The calculations will be used to determine properties of the electrode with the solid electrolyte as well as in grain-boundary 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 Venkat Srinivasan at ANL.

- 1. AIMD of the interface structure of the LLZO solid electrolyte lithium anode and Monte Carlo simulations of LLZO grain boundaries. (Q2, FY 2018; Completed)
- 2. Calculations of Young's modulus at grain-interior and grain-boundary region for LLZO solid electrolytes as a function of applied electric field. (Q3, FY 2018; Initiated)
- 3. Calculations of exchange current density at the electrode-electrolyte interface. (Q4, FY 2018; Initiated)

The use of ceramic solid electrolytes to create all solid-state batteries can enable the use of lithium metal by preventing unstable propagation of lithium dendrites, therefore enhancing safety and decreasing capacity fade. The interfaces between lithium metal and solid electrolyte must be stable to enable the 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. This project is carrying out DFT and Monte Carlo calculations on LLZO interfaces with lithium metal and on grain boundaries within LLZO. As an initial part of this study, the team investigated the seven possible surfaces of LLZO to determine which surface is most stable. Since the LLZO surface can have different terminations, the team also investigated four different terminations: lithium, lanthanum, zirconium, and oxygen. The calculations were carried out with the Perdew-Burke-Ernzerhof (PBE) functional with a plane wave basis. A summary of the results is given in Figure 58 for 28 possible surfaces. The lowest energy surface was found the (100)surface with lithium termination. which had a surface to be energy of 0.8 J/m^2 (Figure 58). In addition, another four lithium terminated surfaces [(011), (101), (110), (111)] had low energies. The zirconium terminated surfaces are generally quite high in surface energy.

Based on the LLZO surface studies, an interfacial supercell between lithium anode and LLZO was then built. The stability of the interface between lithium electrode and the lowest energy LLZO surface [(100) lithium terminated] was investigated with AIMD simulations. A11 production runs of AIMD trajectories were obtained after 5 ps of thermal equilibration. The team then carried out calculations for the barrier of the Li-ion migration from LLZO electrolyte into lithium anode to determine the Li-ion transport using DFT. Several barriers were calculated for Li-ion migration and found to be around 0.65 eV. The calculated structure of the interface and the Li-ion migration barrier will be used for calculation of exchange current density for input into continuum level modeling of the LLZO/Li interface.



Figure 58. Surface energies from density functional theory calculations of different crystalline faces of LLZO and different terminations.

To establish the atomic structure/stoichiometry of LLZO grain boundaries, Monte Carlo simulations were conducted using a large-scale atomic/molecular massively parallel simulator (LAMMPS) with soft Butler-Volmer (BV) potentials and about 15000 atoms. The calculations have provided the structures of four low angle grain boundaries [$\Sigma_3(112)$, $\Sigma_5(210)$, $\Sigma_5(310)$, $\Sigma_9(221)$]. They reveal that the equilibrium composition near the $\Sigma_3(112)$ grain boundary in LLZO is enriched with lithium. The structure of the grain boundaries will be used to calculate various properties such as exchange current density, Li-ion conductivity, and mechanical properties that are needed for the continuum level modeling of dendrite growth.

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, the 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 μ m 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 Task takes a broad look at this challenge for both solid-state batteries and batteries continuing to use liquid electrolytes. For the liquid electrolyte batteries, steady improvement has been realized by PNNL researchers through use of dual lithium salts and organic additives to the typical organic solvent electrolytes to impede lithium corrosion and roughening. Now, Massachusetts Institute of Technology is investigating halide and other additives to form self-healing SEI coatings. Engineered coating and 3D-anode structures continue to offer promising results. These include application of various 2D coating materials under investigation at Stanford University and use of 3D-copper-foam structures at University of Pittsburgh. An increasing number of programs are turning to various composites of polymer and ceramic electrolytes to address mechanical and ion transport challenges. ORNL is continuing investigation of spray-coated composite polymer electrolytes, while UT Austin and PNNL are also initiating work in this direction. A breakthrough is needed to promote facile Li-ion transport between the ceramic and organic polymer or liquid electrolytes. Two highly successful programs using ceramic solid electrolytes, specifically the LLZO garnets, were completed. Both demonstrated a great decrease in the area specific resistance (ASR) of the garnet-Li interface, reaching values of just a few ohms. This was accomplished variously using coating to promote wetting, treatments to ensure the surface is free of flaws and contamination, or higher interface areas to decrease the current density. As the ASR decreased, the interface adhesion and the critical current density achievable without forming Li-metal shorts increased. Fundamental aspects of this work on inorganic solid electrolytes are being continued by ANL researchers and others. The last project is focused on the properties of lithium metal itself. Past work using nanoindentation showed that lithium plating under high currents can exert large stresses at the lithium SEI. Following this, ORNL with Michigan Technological University and University of Michigan will initiate work to create lithium stability maps to understand conditions where the lithium morphology becomes difficult to control. Each of these projects involves a collaborative team of experts with the skills needed to address the challenging materials studies of this dynamic electrochemical system.

Highlights. Progress for this quarter is summarized below. The approaches to stabilizing the Li-metal anode are varied and encompass the following: new formulations of the electrolyte solutions to promote more stable and efficient lithium plating; the addition of robust barrier coatings at the lithium surface to block dendrites; and the use of ceramic and polymer solid electrolytes to confine the lithum. Each path offers some improvement.

With liquid electrolytes:

- Various polyethylene and polypropylene separators with ceramic or polymer surface coatings were evaluated with two different electrolyte solutions. A maximum CE (86%) was realized with the LiTFSI-LiBOB/EC-EMC electrolyte with little variation due to the different coatings. Results suggest that the separators are not stable with lithium metal, particularly in presence of a LiPF₆ salt or ceramic coating.
- DFT simulations along with XPS studies provide concrete evidence of the spontaneous formation of LiF on the surface of lithium metal. This is enhanced by addition of FEC to the electrolyte and may form the basis for passivating and self-healing monolayer coatings.
- Polymer blends were electrospun to form mats used as separators. These mats were saturated with a liquid electrolyte of LiTFSI in DOL/DME and evaluated for Li/Li cycling with no noticeable lithium dendrite growth at 200 cycles.
- As ionic liquids based on Pry13-TFSI or Pry14-TFSI with dissolved lithium salts appear to be stable with lithium, attempts were made to prepare hybrid electrolytes of the salt mixtures with inorganic fillers and polymers. So far preparing uniform mixtures proved to be difficult without addition of an organic solvent.

Forming barrier materials at the lithium surface:

• Nano-diamond coatings were found to be effective barriers to lithium dendrite growth. These ultra-strong interface layers were fabricated as a double layer to circumvent the effect of local defects. Improved performance was demonstrated with cycling of a Li-S cell.

Performance with solid electrolytes:

- Polymer and composite polymer+ceramic electrolytes prepared by spray coating onto the cathode were incorporated into full batteries with LiFePO₄ and lithium electrodes and cycled 50-75°C. The ceramic-polymer interface continues to dominate the cell resistance.
- Impedance studies of different LLZO ceramic electrolytes in Li//Li cells indicates that the Ta-doped LLZO was stable for several days, while the Nb-doped LLZO showed a dramatic increase in impedance over the same period.
- Nanoindentation was used to measure the creep displacement for the Lipon glass electrolyte. Although the technique needs to be refined, the creep displacement accommodated by Lipon is about five times larger than that for the fused silica reference material. This creep behavior may alleviate stresses at the Li/Lipon interface.

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

Project Objective. The project objective is to enable lithium metal to be used as an effective anode in rechargeable Li-metal batteries for long cycle life at a reasonably high current density. The investigation in FY 2018 will focus on effects of various lithium salt mixtures, inorganic fillers and polymer types on ionic conductivity, lithium CE, Li-anode morphology, and battery performances in terms of long-term cycling stability at room temperature and elevated temperatures and at various current density conditions, rate capability, and low-temperature discharge behavior. The compatibility of such electrolytes with 4-V NMC cathode will 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 their practical applications. 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 for PHEVs as required by the EV Everywhere Grand Challenge.

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 Chongmin Wang, PNNL, on characterization by TEM/SEM.

- 1. Develop a lithium salt mixture that has an ambient melting temperature and an ionic conductivity over 1 mS/cm. (Q1, December 31, 2017; Completed)
- 2. Investigate effects of inorganic fillers and polymers on hybrid composite electrolytes. (Q2, March 31, 2018; Completed)
- 3. Develop an inorganic/polymeric hybrid composite electrolyte with ionic conductivity over 1 mS/cm and lithium CE over 99%. (Q3, June 30, 2018; Ongoing)
- Achieve over 300 cycles for 4-V Li||NMC batteries with ~ 2 mAh/cm² cathode loading. (Q4, September 30, 2018; Ongoing)

This quarter, the project investigated the stability of conventional polymer separators with Li-metal anode in the presence and absence of electrolytes under low voltages. The separators are polyethylene (PE) and polypropylene (PP) without and with surface coatings of ceramic (Al_xO_y), Siloxy polymer, and polyvinylidene fluoride (PVDF); the electrolytes are 1 M LiPF₆ in EC-EMC (4:6 by wt.) (always with trace amount of HF) and 0.6 M LiTFSI + 0.4 M LiBOB in EC-EMC (4:6 by wt.) (without HF). The average lithium CE was measured using Li||Cu cells with five separators and two electrolytes. As shown in Figure 59, the average lithium CE values for the LiPF₆/EC-EMC electrolyte vary largely from different separators. However, the average lithium CE values for the LiTFS-LiBOB/EC-EMC electrolyte are nearly the same for the four separators (PE, PP, Siloxy-PP, and PVDF-PP), although it is slightly lower for Al_xO_y -PE. Li||Li symmetric cells demonstrate

that PP and PVDF-PP show unstable and high polarization with cycling in the LiPF₆/EC-EMC electrolyte; however, both of them show stable and low polarization in the LiTFSI-LiBOB/EC-EMC electrolyte, while Al_xO_y-PE shows slightly higher but still stable polarization. The AFM images of these cycled separators indicate that PP separator has very good morphological and textual maintenance; however, the other four separators have large change in morphology, and there are plenty of small particles on the surface. The FTIR and XPS characterizations indicate that the separators are stable with Li-metal anode if there is no LiPF₆-based electrolyte, but the coating layers are unstable either with lithium metal or with the lithium metal and the electrolyte. PE separator is most stable with Li-metal anode as well as electrolytes. Ceramic coating is not stable with Li-metal anode.





The team also tested the electrochemical stability of the salt mixtures of (LiTFSI-LiFSI)_{0.2}-IL_{0.8} where the ILs are Pyr13-TFSI and Pyr14-TFSI. Both salt mixtures show good stability on Li-metal electrode and have an oxidation potential of ~ 5.0 V versus Li/Li⁺ on platinum and about 4.4 V on aluminum. When adding the inorganic fillers (Al₂O₃ and SiO₂) and polymers (PEO and PVDF) into the above salt mixtures in the effort of preparing the hybrid polymer composite electrolytes, it was found that without the aid of proper organic solvents, it was difficult to make uniform mixtures of salt(s), polymer and/or inorganic fillers by simply heating and stirring the mixtures at the melting or softening temperatures of the components, so the membranes of the hybrid polymer composite electrolytes could not be made. Later, the team added a certain amount of organic solvent [acetonitrile, DMC, DME, N-N-dimethylacetamide (DMAc)] into the above salt/polymer/filler mixtures to make slurries. It was found that DMAc is a good solvent to dissolve both PEO and PVDF at high content and allow the addition of salt mixtures at high content as well. However, the solvent DMAc was unable to be completely removed even after drying at 100°C under vacuum for 24 h. Currently, the electrochemical performances of the salt/polymer/filler mixtures with trace amount of DMAc are under test, and the preparation of the salt/polymer/filler membranes without solvent are under development.

Patents/Publications/Presentations

Publications

- Li, X., J. Tao, D. Hu, M. H. Engelhard, W. Zhao, J.-G. Zhang,* and W. Xu.* "Stability of Polymeric Separators in Lithium Metal Batteries in a Low Voltage Environment." *Journal of Materials Chemistry A* 6 (2018): 5006–5015. Doi: 10.1039/c7ta11259a.
- Li, X., J. Zheng, X. Ren, M. H. Engelhard, W. Zhao, Q. Li, J.-G. Zhang,* and W. Xu. "Dendrite-Free and Performance-Enhanced Lithium Metal Batteries through Optimizing Solvent Compositions and Adding Combinational Additives." *Advanced Energy Materials* (2018). doi: 10.1002/aenm.201703022.
- Li, X., J. Zheng, M. H. Engelhard, D. Mei, Q. Li, S. Jiao, N. Liu, W. Zhao, J.-G. Zhang,* and W. Xu.* "Effects of Imide-Orthoborate Dual-Salt Mixtures in Organic Carbonate Electrolytes on the Stability of Lithium Metal Batteries." ACS Applied Materials & Interfaces 10 (2018): 2469–2479. doi: 10.1021/acsami.7b15117.

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 and deliver cells to DOE-specified laboratories for testing and evaluation.

Collaborations. This project collaborates with 24M Technologies Inc. (18 cm²/80 cm² pouch cell fabrication and tests).

- 1. Demonstrate Li-Li asymmetric cell using halide additives that outperforms additive-free cell according to criteria in Q3 and Q4. (Q1, December 2017; Completed)
- 2. Deliver structural and chemical characterization results for baseline halide films on lithium metal. (Q2, March 31, 2018; Completed)
- 3. Deliver structural and chemical characterization results for self-healed halide films on lithium metal. (Q3, June 30, 2018; Ongoing)
- 4. Establish quantitative theoretical criteria for effectiveness and reproducibility in dendrite-suppression experiments. (Q4, September 30, 2018)
- 5. *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)

This quarter, results are reported for DFT simulations of reactions between fluorinated compounds and lithium metal to guide electrolyte design. The results show concrete evidence of a self-forming mechanism. XPS characterization results for baseline halide films on lithium metal are also reported.

The team performed DFT calculations to study the effectiveness of the fluorinated electrolytes to self-form LiF as the primary solid electrolyte component. The DFT calculations were used to determine the thermodynamic decomposition products of fluorinated electrolytes reacting with lithium metal. The team chose the lithium (100) surface to perform the DFT calculations as it is the most stable surface of lithium. This means that the (100) surface will tend to be the predominant surface on lithium foil and also that all other surfaces will be more reactive with the target compounds compared to (100). The DFT calculations were done using the grid-based plane augmented wave (GPAW) method. The team used the PBE exchange correlational functional for the DFT calculations. This quarter, the team explored the reactivity of EC, FEC, LiPF₆, LiTFSI, and LiFSI with lithium metal.



Figure 60. Density functional theory simulation showing the decomposition of FEC additive on a Li-metal surface in the presence of $LiPF_6$ salt.

From the DFT calculations, the team sees that FEC and LiFSI form LiF spontaneously on the lithium (100) surface, as shown in Figure 60. LiPF₆ and LiTFSI salts are stable against lithium (100) surface and only adsorb on the surface. Interestingly, the team finds that EC is chemically stable against the lithium (100) surface, but decomposes in the presence of LiPF₆ salt to form lithium organic salts. These DFT results are consistent with XPS measurements of the surface of Li-metal electrodeposited from LiPF₆ EC/DMC and LiPF₆ FEC/DMC electrolytes (Figure 61). A much higher LiF concentration is observed at the surface in the presence of FEC.



Figure 61. X-ray photoelectron spectroscopy studies of the SEI formed in LiPF₆ EC/DMC and LiPF₆ FEC/DMC electrolytes.

To investigate whether the chemical reactions are self-limiting, the team also performed similar DFT calculations of these additives on a lithium (100) surface initially covered with a mono-layer of LiF. The team observes that all compounds are stable and do not decompose in these simulations. This clearly shows that a mono-layer of LiF is sufficient to passivate the lithium surface. These pathways will give the team further insight on the stable composition of the SEI formed on lithium. With these results, the project has completed the quarter's milestone.
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 $\ge 2000 \text{ mAh/g}$ ($\ge 10 \text{ mAh/cm}^2$), ~ 1000 cycles, CE loss $\le 0.01\%$, 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 is a veritable challenge. If overcome, it 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 the use of Li-free cathodes, opening myriad possibilities to push the envelope in terms of cathode capacity and battery energy density.

Out-Year Goals. This project comprises three major phases to be successfully completed in three years:

- Year 1 Synthesis, characterization, and scale up of suitable porous foams (PF) for use as current collectors for lithium anodes and Li-ion conductor (LIC) materials to prepare multilayer porous foams (MPF).
- Year 2 Development of Li-rich structurally isomorphous alloy (SIA) anodes. Generation of composite multilayer anodes (CMAs).
- Year 3 Advanced high-energy-density, high-rate, extremely cyclable cell development.

Collaborations. The project will collaborate with Dr. Moni Kanchan Datta and Dr. Oleg I. Velikokhatnyi (University of Pittsburgh) as co-PIs. It will collaborate with Dr. A Manivannan (Global Pragmatic Materials) for XPS analysis. It will also collaborate with Dr. D. Krishnan Achary (University of Pittsburgh) for solid-state magic angle spinning NMR (MAS-NMR) characterization and Dr. J. R. Gaines (Kurt Lesker) for thin-film system fabrication and characterization.

- 1. Synthesis of MPFs exhibiting: specific capacity ≥ 1000 mAh/g (≥ 4 mAh/cm²), > 400 cycles without cell failure), and initial CE of ≥ 95% with ≤ 0.05% loss per cycle. (Q1, October 2017; Ongoing)
- 2. Perform first-principles investigations into identifying electronically and ionically conductive materials capable of acting as SIA compositions over a range of lithium compositions. (Q1, October 2017; Ongoing)
- 3. Fabrication and characterization of suitable thick electrodes for 10-mAh cell configurations. (Q1, October 2017; Ongoing)
- 4. Synthesis and testing of SIA electrodes. (Q3, April 2018; Ongoing)
- 5. Optimization of MPFs to improve capacity and stability for scaling. (Q4, July 2018; Ongoing)

To stabilize the Li-metal battery system, work this quarter focused on modifying the nucleation and growth of lithium metal on the current collector. The first approach was to develop a composite polymer electrolyte (CPE) that would control Li-ion flux and inhibit dendritic growth. CPE separators were accordingly fabricated by electrospinning which polymer-blends, after electrospun mats were punched to vield individual separators. The were separators soaked in traditional liquid electrolyte (50:50 DOL:DME by volume, 1.0M LiTSFI. 0.1 M LiNO₃) before assembling symmetric Li/Li coin cells. No additional liquid electrolyte was added beyond that used to activate the CPEs. Figure 62 shows the potential-time curves for the two different CPEs (called CPE 3 and



Figure 62. Voltage-time curve for symmetric Li/Li cells using composite polymer electrolytes. (~ 200 cycles)



Figure 63. Scanning electron microscopy images of lithium metal after cycling in symmetric Li/Li cells with separators shown above; (left) cell with CPE 3, and (right) cell with composite polymer electrolyte 6. (After ~ 200 cycles)

CPE 6) after cycling for ~ 200 cycles in symmetric Li/Li cells. The SEM images collected on the Li-metal foil after ~ 200 cycles confirm the absence of dendrites (Figure 63).

The second approach has been to alter the Li-metal surface structure and control the nucleation and growth by creating preferential nucleation and growth sites. Figure 64 shows the nucleation potential as a function of current density for many of the modified lithium surfaces (S1, S2, and S3). The SEM images of some of these Li-metal surfaces were provided in the previous report. It is observed that large modifications in the engineered surface area (S1, S3) of the structures created on the surface of the lithium metal helps to lower the nucleation potential. On the other hand, creation of small modification of the surface architecture (S2) creates an undesired roughness and surface characteristics that actually increase the nucleation potential compared to the unmodified Li-metal surface. Study of full-cell testing and cycling stability of the surface modified lithium metal is in progress and will be discussed in later reports.



Figure 64. Nucleation potential for various surface modified Li-metal foils at different current densities.

Task 4.4 – Nanoscale Interfacial Engineering for Stable Lithium-Metal Anodes (Yi Cui, Stanford University)

Project Objective. This study aims to render Li-metal anode with high capacity and reliability by developing chemically and mechanically stable interfacial layers between lithium metal and electrolytes, which is essential to couple with sulfur cathode for high-energy, Li-S batteries. With the nanoscale interfacial engineering approach, various kinds of advanced thin films will be introduced to overcome issues related to dendritic growth, reactive surface, and virtually "infinite" volume expansion of Li-metal anode.

Project Impact. Cycling life and stability of Li-metal anode will be dramatically increased. The success of this project, together with breakthroughs of sulfur cathode, will significantly increase the specific capacity of lithium batteries and also decrease cost, thereby stimulating the popularity of EVs.

Out-Year Goals. Along with suppressing dendrite growth, the cycle life, CE, and current density of Li-metal anode will be greatly improved (that is, no dendrite growth for current density up to 3.0 mA/cm², with CE greater than 99.5%) by choosing the appropriate interfacial nanomaterial along with rational electrode material design.

- 1. Further improve the efficacy of Li-metal protection layers. (Q1, December 2017; Completed)
- 2. Improve the CE > 99.2%. (Q2, FY 2018; Completed)
- 3. Demonstrate > 800 cycles of Li-metal anode with stable host and interphase. (In progress)

Interfacial engineering is among the essential means to answer the formidable challenges of Li-metal anode caused by its unstable SEI. This approach relies on the introduction of an artificial scaffold on the current collector to reinforce the spontaneously formed SEI layer, and ideally the two can move together during battery cycling without fracturing and side reactions. To fulfill the goal, several exacting requirements are imposed for the interfacial layer design. (1) It needs to be absolutely stable against lithium, which precludes most of the polymeric and inorganic coatings explored so far as the ideal candidates. (2) A high elastic modulus and compact structure is especially desirable, for the mechanical strength of lithium interface can play the key role in retarding dendrite propagation. (3) A certain degree of flexibility is required to accommodate the volume change of electrode during cycling. (4) It shall enable homogenous Li-ion flux without local hot spots. (5) The interfacial layer needs to be designed with low electrical conductivity and weak binding to the substrate such that lithium deposition could solely take place underneath the film. Considering the requirements, diamond, a material well-known for its highest bulk modulus, chemical inertness, and electrically insulating nature, is ideal for Li-metal protection.



Figure 65. Fabrication process of nanodiamond interfacial layer for lithium metal.

considerations are put into material fabrication to render diamond compatible as interfacial layer; by subtly choosing the correct substrate together with graphene oxide (GO) as a release layer, polycrystalline nanodiamond thin film with long-range homogeneity but only weak adhesion to the substrate can be obtained

for lithium deposition to occur underneath. Notably, an extremely high modulus of over 200 GPa was obtained via nanoindentation test on the nanodiamond interfacial layer, which is the highest value from real measurement reported so far among the artificial coatings for lithium metal. Importantly, a unique doublelayer film design was proposed for the first time to circumvent the adverse effect of local defects, which was often the failure mechanism of singlelayer Li-metal interfaces developed previously.

The multi-fold advantages of the double-layer nanodiamond interface, the average Li-metal anode CE over 10 cycles can be as high as 99.4% at a current density of 1 mA cm⁻² and an areal capacity of 2 mAh cm⁻², and performance can be well-sustained during prolonged cycling. Prototypical Li-S cells were also constructed. With ~ 250% excess lithium, more than 400 stable cycles can be obtained at a current density of 1.25 mA cm⁻², corresponding to an average lithium anode CE of above 99%.

This quarter, the project presents an ultrastrong interface constructed with high-quality nanodiamonds for lithium metal that is rationally designed to strictly satisfy all above-mentioned requirements. The nanodiamond interface was synthesized by microwave-plasma chemical vapor deposition, and detailed



Figure 66. (a) The Coulombic efficiency (CE) of bare copper and nanodiamond electrode cycled at varying current densities and capacities. (b) CE measured according to the method developed by Aurbach and co-workers. (c) Long-term cycling of bare copper and nanodiamond electrode. (d) Cycling performance of the prototypical Li-S cells at 0.5 C.

Patents/Publications/Presentations

Publication

Liu, Y., Y.-K. Tzeng, Y. Cui, et al. "A Rationally-Designed Ultrastrong Double-Layer Nanodiamond Interface for Stable Lithium Metal Anodes." Submitted.

Task 4.5 – 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. This project does not seek discovery of new electrolytes; rather, the goal is to study combinations of well-known electrolytes. The project emphasizes investigation of polymer-ceramic interfaces formed as bilayers and as simple composite mixtures where effects of interface properties can be readily isolated. In general, the ceramic phase is several orders of magnitude more conductive than the polymer electrolyte, and interfaces can contribute an additional source of resistance. Using finite element simulations as a guide, composites with promising compositions and architectures are fabricated and evaluated for Li-transport properties using AC impedance and DC cycling with lithium in symmetric or half cells. General design rules will be determined for wide application to other solid electrolyte combinations.

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. Yiman Zhang and Dr. Xi Chen. Dr. Jihua Chen (ORNL) assisted with electron microscopic characterization and Dr. Rose Ruther (ORNL) with Raman spectroscopy. Electrolyte powders are obtained from Ohara Corporation and Prof. Sakamoto (University of Michigan).

- 1. Fabricate a full battery using aqueous spray coating for both the composite electrolyte and cathode incorporating a protected Li-metal anode. (Q4 FY 2017 stretch goal; Completed)
- 2. Accurately determine the polymer/ceramic electrolyte interface resistance for PEO and Ohara. Revisit effect of DMC on interface ASR. (Q1, FY 2018; Completed detailed report next quarter)
- 3. Minimize interface ASR by chemical and mechanical treatment with a goal of < 100 ohm. (Q2, FY 2018; ongoing as ASR is > 100 ohm)
- 4. Move beyond model materials like Ohara and PEO, to include polymer gels. Identify promising polymer ceramic systems with interfacial ASR less than 10 ohm. (Q3, FY 2018)
- 5. Assess the feasibility of slurry spray coating to form the thin membrane of new materials. (Q4, FY 2018)

In last quarter's effort on full battery fabrication, the project identified a number of problems that led to limited cycling. This quarter, the project achieved dramatically improved full battery cycling performance by tackling these problems. The team first tried to mitigate the catholyte drying problem by supplying liquid catholyte to the cathode with a layer of glass fiber fully soaked with EC-DMC-LiPF₆ (1.2M). In this design, the cell had excess catholyte, but was not flooded. However, this approach did not work. The team thus decided to use the solid polymer catholyte in the cathode to completely eliminate the catholyte drying problem. The team chose PEO+LiTFSI for its relatively high ionic conductivity and good adhesion to contacting particles.

To enhance adhesion of the solid electrolyte and prevent deleterious reactions between Ohara ceramic and lithium, a bilayer electrolyte consisting of a layer of composite electrolyte (50 vol% Ohara ceramic powder in PEO+LiTFSI, CPE) and a layer of polymer electrolyte (PEO+LiTFSI, PE) was used to construct the full cell. The cycling performance was dramatically improved compared to the first quarter's designs. The working full cell consisted of LiFePO₄ cathode, polymer catholyte, bilayer electrolyte (or single layer PE as control) and lithium anode. The discharge/charge capacity and voltage profile are shown in Figure 67. All the cells are still under testing. Next quarter, the team will further optimize cell design.

Polymer-ceramic-polymer electrolyte (trilayer) cell was constructed to assess the interfacial resistance between the polymer and ceramic electrolyte. Due to unreproducible results obtained by spray coating



Figure 67. (upper panel) Discharge and charge capacity as a function of cycle number for three all solid-state cells. (lower panel) The discharge and charge voltage profile at cycle 5 is shown for three cells.

from PEO+LiTf aqueous solutions followed by drying at 100°C, the team changed the spray coating carrier solvent to acetonitrile and drying condition to 40°C. The interfacial resistance between dry polymer electrolyte PEO+LiTf and sintered Ohara plate at 30°C was 6.5 K Ω , using the modified method. The team infused the trilayer cell with DMC vapor in a sealed container and measured the interfacial resistance between DMC-plasticized polymer electrolyte and Ohara plate. The interfacial resistance was not effectively reduced (Figure 68). A new approach to minimize interfacial resistance will be sought next quarter.



Figure 68. Nyquist plots of (a) Ohara plate, (b) PE and PE infused with DMC, (c) trilayer and trilayer infused with DMC, and (d) Arrhenius plot of interfacial resistance (with and without DMC), resistance of PE (with and without DMC), and resistance of Ohara plate.

Patents/Publications/Presentations

Publication

 Pandian, Amaresh Samuthira, X. Chelsea Chen, Jihua Chen, Bradley S. Lokitz, Rose E. Ruther, Guang Yang, Kun Lou, Jagjit Nanda, Frank M. Delnick, and Nancy J. Dudney. "Facile and Scalable Fabrication of Composite Polymer-Ceramic Electrolyte with High Ceramic Loadings." *Journal of Power Sources* 390 (2018): 153–164.

Presentation

 APS March Meeting 2018, Los Angeles, California (March 5–9, 2018): "Study of Ion Conductivity and Chain Dynamics in Polymer-Ceramic Composite Electrolytes"; X. Chelsea Chen, Amaresh Samuthira Pandian, Naresh Osti, Frank Delnick, and Nancy Dudney.

Task 4.6 – 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 the SEI layer formation and the 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 a 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 Karim Zaghib at HQ.

- 1. Test the cyclability of plating of metallic lithium through a conventional polymer/ceramic or ceramic Li⁺ electrolyte. (Q1, FY 2018; Ongoing)
- Test relative energies of Cu⁺/Cu⁰ redox couple and energy of plating/stripping of lithium on/from copper. (Q2, FY 2018; Ongoing)
- 3. Test plating/stripping of metallic lithium on a carbon-coated copper current collector with different electrolytes. (Q3, FY 2018)
- 4. Demonstrate a low-cost, 3V cell with a copper current collector as cathode. (Q4, FY 2018)

The team has tested the relative energies of the Cu^+/Cu^0 redox couple and its reversibility during an electrochemical reaction. Half cells, with lithium as the anode and copper as the cathode, were assembled. The team tested several polymer electrolyte membranes such as an Al₂O₃-incorporated LiTFSI:PEO (1:2 weight ratio) membrane, a LiTFSI/Cu(ClO₄)₂-dissolved PEG/PVDF gel polymer membrane, and the bilayer of these two. All the cells were tested at 60°C.

Galvanostatic cycling showed clear contrasts of these polymer electrolyte membranes in their electrochemical performance. First, the PEO-based solid electrolyte showed poor CEs during the cycling (Figure 69): ~ 20% for the initial 30 cycles and later saturated to ~ 95% after cycling. Since the starting membrane does not have any copper salts, the electrochemically fed Cu⁺ ions diffuse out from the copper cathode to the anode side due to the concentration gradient, which is the reason for the initial irreversibility. With a sufficient Cu⁺ concentration in the electrolyte after cycling, the redox reaction becomes more reversible.

Second, the copper ions were introduced to the Li^+ gel polymer electrolyte membrane, and that was used as the separator. It turned out that the cell quickly lost reversible capacities owing to side reactions (for example, copper deposition and the corresponding SEI formation) at the anode (lithium) surface. Therefore, third, the team has combined these two membranes as a multi-layer separator: the PEO membrane on the anode side for protection, and the gel polymer on the cathode side. Figure 70 shows the charge/discharge voltage curves of the cell. The cycling is reproducible, but the CEs were consistently as low as ~ 70%. The team attributed this result to an interfacial contact issue; as the anodic copper dissolution proceeds, the surface of the copper foil becomes porous, and the physical contact becomes deteriorated. In this multi-membrane cell, the team did not observe the capacity increase with cycling, as in the case of the PEO membrane cells.

To solve the problem, the team has introduced a thin film of succinonitrile ($C_4H_4N_2$; m.p. 57°C) to the copper surface. It was expected that the succinonitrile melt could fill the porous interface and promote the Cu^+/Cu^0 redox at 60°C. Figure 70 shows the charge/discharge voltage curves of the cell. The cycling is reproducible, and the CEs were as high as ~ 100%. Although the charge polarization was increased, the reversibility was greatly improved. The team is in the process of minimizing the polarization.



Figure 69. Charge/discharge voltage curves of the Cu/Al₂O₃-filled LiTFSI:PEO membrane/Li cell at the 5 (blue), 50 (green), and 100 (red) cycles and 60° C.



Figure 70. Charge/discharge voltage curves of the Cu/LiTFSI+Cu(CIO₄)₂-dissolved PEG-PVDF gel polymer membrane/Al₂O₃-filled LiTFSI-PEO membrane/Li cells with (red) and without (blue) succinonitrile at the cathode interface and 60° C.

Task 4.7 – Advancing Solid-State Interfaces in Lithium-Ion Batteries (Nenad M. Markovic and Larry 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. It will establish collaboration with Jeff Sakamoto at University of Michigan.

- 1. Development of new synthesis and characterization methods for controlled deposition of lithium on crystalline LLZMO (M = Nb, Ta, Al) materials on the appropriate substrate. (Q1, FY 2018; Completed)
- 2. Use electrochemical methods to investigate the efficiency as well as charge-discharge cyclability for selected LLZMO materials; Characterize the interface stability of lithium in contact with LLTO solid electrolyte with different orientation. (Q2, FY 2018; Completed)
- 3. Development of chemical- and physical-based synthesis method to make amorphous $Li_2S-P_2S_5$ (~ 10^{-3} S/cm at room temperature) and LLZMO solid electrolytes with fast ionic transport of lithium and to elucidate the chemical interaction of lithium with such a glass material. (Q3, FY 2018)
- 4. Introduce new experimental and computational tools for characterizing *ex situ* and *in situ* interaction of lithium and LiCoO₂ with amorphous solid electrolytes. (Q4, FY 2018)

LLZO Interface Stability Correlation with Impedance. The impedance spectra are composed of the total resistance of the LLZO bulk and grain boundaries, as well as the LLZO-electrode interfacial resistance. One of the biggest challenges in pairing LLZO with a lithium anode is the high interfacial resistance; it is well known that a Li₂CO₃ oxidation layer decreases the wettability by lithium and increases the impedance of LLZO/Li interface. The project previously reported two methods of removing the LLZO surface oxidation layer and studied its interfacial stability. The first method is polishing with sand paper inside a glove box. LLZO surfaces prepared in this manner still have some Li₂CO₃ remaining and are only slightly reduced by lithium metal. The second method is heating in UHV to 500°C, which totally removes the Li₂CO₃ layer, allowing the lithium metal to fully wet the LLZO surface and resulting in the lowest interfacial impedance. However, improved contact between lithium and LLZO also increases the extent of chemical reaction at the interface, with the interfacial stability exhibiting a dopant dependence. Among all three doped LLZMO samples (M = Al, Ta, and Nb), Nb-doped LLZO exhibits the most reduction at the interface, whereas Ta-doped LLZO is relatively stable. This observed chemical instability directly correlates with the time-dependent impedance measured using Li-Li symmetric coin cells assembled with both vacuum-deposited lithium and lithium foil present on both sides of heated LLZO samples. A significant



Figure 71. The impedance spectrum of Nb- (top) and Ta- (bottom) doped LLZO_lithium symmetric cells at room temperature.

increase in impedance for Nb-doped LLZO takes place over several days at open circuit (Figure 71), while Ta-doped LLZO exhibits only a negligible change, consistent with the observed differences in reactivity between Nb- and Ta-doped LLZO with lithium metal.

LLTO Orientation-Dependent Interfacial Stability. $Li_{0.33}La_{0.55}TiO_3$ (LLTO) is a perovskite solid electrolyte with a tetragonal structure and ionic conductivity of ~ 6.8×10^{-4} S/cm at room temperature. Its commercial

application is mainly limited by instability against the lithium anode, as titanium in the structure is reduced in contact with lithium metal. To better understand the effect of crystal orientation on the stability of the LLTO/Li interface, (100), (110), (112) and (001)-oriented epitaxial LLTO films (~ 200-nm thick) were deposited on SrTiO₃ and NdGaO₃ substrates by PLD. Metallic lithium was then sputtered on these surfaces, which were then transferred under argon to the Advanced Photon Source at ANL to characterize the extent of titanium reduction in the bulk (~100 nm) via hard X-ray photoelectron spectroscopy (HAXPES). Before lithium sputtering, the titanium is purely in +4 valence state for all film orientations. Partial reduction of titanium from +4 to +3 was observed after sputtering lithium, with the degree of reduction varying significantly between orientations (Figure 72). Among all four orientations, LLTO(001) is the most unstable, with $\sim 33\%$ titanium reduced in the bulk, whereas the LLTO(100) film has only ~ 13% titanium reduced in the bulk, making it the most stable. This result suggests that lithium can migrate along the c-axis in the LLTO structure, enabling a more extensive reduction, which is consistent with theoretical calculations.



Figure 72. Titanium 2p hard X-ray photoelectron spectroscopy core level spectra after lithium sputtering show reduction of titanium. The amount of titanium reduced differs with orientation.

Task 4.8 – 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. A new project objective will be to understand the evolution of lithium metal upon 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. For the initial one-year effort, 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.

- 1. Characterize *in situ* changes in lithium anode from a single stripping/plating half cycle. (FY 2017; Ongoing)
- 2. Identify two experimental tools to probe the defect structure of lithium created under cycling. (Q2, FY 2018; Completed)
- 3. Cycle lithium under conditions expected to create different defect structures and morphologies to begin creation of stability maps. (Q3, FY 2018)
- Design and construct stability diagrams to map the evolution of the defects structure and morphology for lithium metal under a variety of cycling conditions and with different model solid electrolytes. (Q4, FY 2018)

As the subcontracts to work toward study of lithium defect formation were not completed, efforts this quarter included the wrap up of publications and ground work for studies of the defect formation in lithium metal. Experimental tools to characterize defect formation in lithium metal during electrochemical cycling across the SEI will include acoustic spectroscopy, nanoindentation, and neutron imaging using Li-isotope labeling. Figures 73-75 illustrate expected behaviors.

Acoustic echo techniques have been used to detect the onset of Li-metal deposition as dendrites in LLZO. Using a different geometry, the project plans to look at defects formed at the interface of lithium during plating and stripping. An exaggerated view of the voids and acoustic signal expected to form at the positive electrode when the current is high and stack pressure low is shown in Figure 73. Beam time has been awarded to R. Garcia and J. Sakamoto for neutron imaging during lithium transport across LLZO. Lithium migration along the grain boundaries may be detectable and correspond to an inhomogeneous lithium distribution at the electrode interfaces. Imaging showing the ⁶Li ⁷Li exchange under a DC current flow is shown in Figure 74. For nanoindentation, the load displacement curves may show abrupt and discontinuous behavior when the indenter enters the region of lithium defect-rich due to plating of lithium at the interface, as shown in Figure 75.



Continuing earlier preliminary study, E. Herbert investigated the creep behavior of the Lipon solid electrolyte. Previous work published by the group indicates Lipon may have unique time-dependent deformation mechanisms capable of relieving a significant fraction of the mechanical stresses that develop at electrode interfaces. To examine the possible mechanisms, nanoindentation creep experiments were performed at four discrete indentation depths and three temperatures. The experiment utilized a dynamic test method to determine the average creep displacements. The large scatter bars are an unfortunate consequence of utilizing the dynamic method. However, despite the high noise level, the average creep results are believed to be reliable. The creep displacement accommodated by Lipon is approximately five times that of fused silica, suggesting that Lipon's creep behavior may alleviate stress at the lithium interface.



Figure 76. Creep in fused silica (a) and Lipon (b) at 25°C. Creep displacement measured during a 60 s interval over which the applied load was held constant upon reaching the targeted indentation depth of 50, 100, 400, or 650 nm.

Patents/Publications/Presentations

Publications

- Herbert, E. G., P. S. Phani, N. J. Dudney, and S. A. Hackney. "Nanoindentation of High Purity Vapor Deposited Lithium Films: The Elastic Modulus." *Journal of Materials Research*. In press.
- Herbert, E. G., S. A. Hackney, N. J. Dudney, V. Thole, and P. S. Phani. "Nanoindentation of High Purity Vapor Deposited Lithium Films: A Mechanistic Rationalization of Diffusion-Mediated Flow." *Journal of Materials Research*. In press.
- Herbert, E. G., S. A. Hackney, N. J. Dudney, V. Thole, and P S. Phani. "Nanoindentation of High Purity Vapor Deposited Lithium Films: A Mechanistic Rationalization of the Transition to Dislocation-Mediated Flow." *Journal of Materials Research*. In press.
- Wang, M., and J. Sakamoto. "Correlating the Interface Resistance and Surface Adhesion of the Li Metal-Solid Electrolyte Interface." *Journal of Power Sources* 377 (2018): 7–11.

Presentations

- Gordon Research Conference Integrating Theory, Synthesis, Characterization, and System Validation for the Battery of Tomorrow, Ventura, California (February 2018): "Time-Dependent Mechanical Behavior of LiPON"; Violet Thole,* Erik G. Herbert, and Nancy J. Dudney. Poster.
- Gordon Research Conference Integrating Theory, Synthesis, Characterization, and System Validation for the Battery of Tomorrow, Ventura, California (February 2018): "Coupling between the Mechanical Behavior of Lithium and Device Performance"; Erik G. Herbert. Invited presentation.

TASK 5 – SULFUR ELECTRODES

Summary and Highlights

Advances in Li-ion technology have been stymied by challenges involved in developing high reversible capacity cathodes and stable anodes. Hence, there is a critical need for development of alternate battery technologies with superior energy densities and cycling capabilities. In this regard, Li-S batteries have been identified as the next flagship technology, holding much promise due to the attractive theoretical specific energy densities of 2,567 Wh/kg. In addition, realization of the high theoretical specific capacity of 1,675 mAh/g corresponding to formation of Li₂S using earth-abundant sulfur renders the system highly promising compared to other available cathode systems. Thus, the research focus has shifted to developing Li-S batteries. This system, however, suffers from major drawbacks, as elucidated below:

- Limited inherent electronic conductivity of sulfur-based and sulfur-compound-based cathodes;
- Volumetric expansion and contraction of both the sulfur cathode and lithium anode;
- Soluble polysulfide formation/dissolution and sluggish kinetics of subsequent conversion of polysulfides to Li₂S, resulting in poor cycling life;
- Particle fracture and delamination resulting from the repeated volumetric expansion and contraction;
- Irreversible loss of lithium at the sulfur cathode, resulting in poor CE; and
- High diffusivity of polysulfides in the electrolyte, resulting in plating at the anode and consequent loss of driving force for lithium diffusion (that is, drop in cell voltage).

These major issues cause sulfur loss from the cathode, leading to mechanical disintegration. Additionally, surface passivation of anode and cathode systems results in a decrease in the overall specific capacity and CE upon cycling. Consequently, the battery becomes inactive within the first few charge-discharge cycles. Achievement of stable, high capacity Li-S batteries requires execution of fundamental studies to understand the degradation mechanisms in conjunction with devising engineered solutions.

This Task addresses both aspects with execution of esoteric, fundamental in situ XAS and in situ electron paramagnetic resonance (EPR) studies juxtaposed with conducting innovative applied research comprising use of suitable additives, coatings, and exploration of composite morphologies as well as appropriate engineered strategies. Both ANL and LBNL use X-ray based techniques to study phase evolution and loss of CE in S-based and S-Se-based electrodes, primarily by the former during lithiation/delithiation while understanding polysulfide formation in sulfur and oligomeric PEO solvent by the latter, respectively. Work from PNNL, University of Pittsburgh, and Stanford demonstrates high areal capacity electrodes exceeding 4 mAh/cm². Following loading studies, PNNL performed *in situ* EPR to study reaction pathways mediated by sulfur radical formation. Coating/encapsulation approaches adopted by University of Pittsburgh and Stanford comprise flexible sulfur wire electrodes coated with LIC by University of Pittsburgh, and TiS₂ encapsulation of Li₂S in the latter, both ensuring polysulfide retention at sulfur cathodes. BNL work, on the other hand, has focused on benchmarking of pouch-cell testing by optimization of the voltage window and study of additives such as LiI and LiNO₃. Ab initio studies at Stanford and University of Pittsburgh involve calculation of binding energies, diffusion coefficients, ionic conductivities, and reaction pathways determination, augmenting the experimental results. Similarly, AIMD simulations performed at TAMU reveal multiple details regarding electrolyte decomposition reactions and the role of soluble polysulfides on such reactions. Using kinetic Monte Carlo simulations, electrode morphology evolution and mesostructured transport interaction studies were also executed. Studies at PNNL suggest that proper control of electrode porosity/thickness is essential for obtaining high-energy Li-S batteries.

Porosity shows strong dependence on calendering pressure because of low tap densities of electrode components such as sulfur and carbon. Increasing the calendering-pressure from 0.2 to 1.5 ton (T) leads to rapid decrease of electrode porosity, resulting in improvement of electrode volumetric energy density.

Measured electrode volumetric energy density increased from 650 Wh L⁻¹ for as-cast electrode (120- μ m thick) to 1300 Wh L⁻¹ for electrode compressed to 60 μ m. Additionally, Pennsylvania State University has shown use of dimethyl disulfide as a functional co-solvent, demonstrating its ability to show an alternate electrochemical reaction pathway for sulfur cathodes by formation of dimethyl polysulfides and lithium organosulfides as intermediates and reduction products. Further, University of Wisconsin has conducted high-performance liquid chromatography (HPLC)-MS studies and has determined the distribution of polysulfides at various discharge and recharge reactions. UT Austin, at the same time, has shown that by integrating polysulfide-filter-coated separators fabricated with cellulose nanofiber (CNF), the cells retain 50% of the initial capacity after storing for one year and exhibit a low self-discharge rate of only 0.14% per day.

Each of these projects has a collaborative team of experts with the required skill set needed to address the EV Everywhere Grand Challenge of 350 Wh/kg and 750 Wh/l and cycle life of at least 1000 cycles.

Highlights. This Task reports the following project highlights for this quarter:

- Dr. Khalil Amine, ANL, used high concentration electrolytes to suppress polysulfides dissolution during charge/discharge. Using a S/MC-70% composite sulfur cathode and 5M LiTFSI/DME+ANL-2 electrolyte, an initial capacity of 1222.3 mAh/g and CE of 95% were demonstrated for over 60 cycles.
- Dr. Donghai Wang, Pennsylvania State University, has used poly [sulfur-random-1, 3-diisopropenylbenzene (PSD-90)] as electrolyte additive to suppress dendrite formation on the anode during plating/stripping. Upon adding 8 wt% PSD-90 to the electrolyte, a stable lithium cycling was achieved in symmetric Li/Li cells with > 99% CE.
- By using a carbon material with a hierarchically ordered mesoporosity and high-level heteroatom (nitrogen) -doping, Dr. Deyang Qu, University of Wisconsin at Milwaukee, and Dr. Xiao-Qing Yang, BNL, were able to achieve a sulfur loading of 69 wt%, demonstrating stable cycling performance with 95% capacity retention for over 20 cycles. It was demonstrated that the carbon materials with balanced porosity and N-doping level could effectively increase the conductivity of sulfur and alleviate the "shuttle effect" while exhibiting high specific capacity, good rate performance, and superior cycling stability.

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_xSe_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 (S 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 Chunsheng Wang of UMD, Dr. Yang Ren and Dr. Chengjun Sun of Advanced Photon Source at ANL, and Dr. Larry Curtiss at ANL.

- 1. Exploration of novel siloxane-based electrolytes for Li-Se and Se-S systems. (Q1, FY 2018; Completed)
- 2. Development of high-performance Li/Se-S batteries using optimized siloxane-based electrolytes. (Q2, FY 2018; Ongoing)
- 3. In operando XAS study on the working mechanism of siloxane-based electrolytes. (Q3, FY 2018)
- 4. Computational modeling on the working mechanism of siloxane-based electrolytes. (Q4, FY 2018)

Last quarter, the project used high-concentration electrolytes to suppress polysulfides/polyselenides dissolution during charge/discharge. This quarter, the team furthered work on rational design of cathode structures to achieve better electrochemical performance and increase active material loading in the composite, thus allowing increase in the overall energy density.

Although high-concentration electrolyte is able to suppress polysulfides dissolution, it suffers from high viscosity, which leads to sluggish Li⁺ diffusion kinetic and thus lowers electrochemical performance. Macroporous carbons have been the least utilized for Li/S cells owing to their open architecture, which is highly ineffectual at containing soluble polysulfides. However, if the macroporous carbon is coupled to the high-concentration electrolyte, the Li⁺ diffusion rate can be significantly increased, and the lithium polysulfides can be also remained at the cathode.

Figure 77 shows the SEM images of macroporous carbon used for high-loading Se-S systems. As shown, the particle size of the macroporous carbon is around tens of micrometer, but the surface of macroporous carbon is highly porous. The macroporous carbon used in this work has a main pore size of around 40 nm and a high pore volume of



Figure 77. (a) low and (b) high magnification scanning electron microscopy images of a microporous carbon as host for high loading sulfur systems.



Figure 78. (a) Charge/discharge curves and (b) cycle performance of sulfur/highly porous carbon composite with a sulfur loading of 70 wt% in 5M LiTFSI/DME+ANL-2 at C/10.

6 cc/g. This could enable a high sulfur loading and also a high tap density for sulfur/carbon composite, both of which can lead to higher volumetric energy density. The team has thus successfully prepared a sulfur/macroporous carbon (S/MC-70%) composite with a sulfur loading of 70 wt% by the melt-diffusion strategy. Figure 78a-b shows the charge/discharge curves and cycle performance of S/MC-70% composite using 5M LiTFSI/DME+ANL-2 as electrolytes. Two discharge plateaus (2.3 V and 2.0 V versus Li/Li⁺) can be seen during discharge, corresponding to the reduction from amorphous sulfur to polysulfides and further lithium sulfide; a main charge plateau related to the re-formation of sulfur at around 2.3 V can be clearly observed. The initial discharge capacity is about 1222.3 mAh/g with the initial charge capacity at 1165.8 mAh/g, leading to a high initial CE of 95%. This could be a good indicator of limited polysulfide shuttle. The S/MC-70% cathode also shows minimal capacity fading during charge/discharge. After 60 cycles of charge/discharge, the reversible capacity of S/MC-70% was maintained above 800 mAh/g. The good electrochemical performance of S/MC-70% can be attributed to the synergistic effect of high-concentration electrolytes and macroporous carbon structure.

Next quarter, the team will further investigate and report the interplay between cathode structures and electrolytes to unravel the physics behind the electrochemical performance.

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. Alternative anode will be explored to address the lithium anode issue. 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. Xiao-Qing Yang (BNL), Dr. Deyang Qu (University of Wisconsin at Milwaukee), Dr. Xingcheng Xiao (GM), and Dr. Jim De Yoreo (PNNL).

- 1. Study of electrolyte compatibility with different carbon host materials and binders and their effects on reversible sulfur utilization. (Q1, December 31, 2017; Completed)
- 2. Design and demonstration of an electrochemical cell by using ceramics Li⁺ conductive separator for focused cathode or anode mechanism study for Li-S. (Q2, March 31, 2018; Completed)
- 3. Study failure mechanism of Li-S cell under lean amount of liquid electrolyte by decoupling the interference of lithium anode using liquid/solid electrolyte hybrid cell. (Q3, June 30, 2018; In progress)
- 4. Develop functionalized separators to suppress polysulfide shuttle and improve interfacial stability of lithium anode. (Q4, September 30, 2018; In progress)

Understanding the failure mechanisms of sulfur cathodes is critical to improve performance of Li-S batteries; however, study on the failure mechanism in these batteries is complicated by interferences of the Li-metal anode. Due to the lack of a stable SEI protection layer, lithium metal continuously reacts with electrolyte, which not only builds up a thick lithium interphase layer, but also consumes electrolytes quickly. Similarly, lithium also reacts with soluble polysulfides chemically, resulting in irreversible sulfur loss and low CE (shuttle reactions). Apparently, interactions of lithium metal with either electrolyte or polysulfide are the leading causes



Figure 79. (a) Section view of the hybrid cell design, (b) electrochemical impedance of In-SE-In and In-SE-LE-Li (5 mv, 10^{5} - 10^{-1} Hz). (c) charge/discharge curves of LiIn-SE-LE-S. (0.1C, V_{InLi} vs. V_{Li}= 0.6V).

of capacity fading or cell failure, which also makes a clear understanding of sulfur cathode and electrolyte reactions more complicated.

This quarter, the team designed a generic hybrid cell that can be used to decouple the interferences of lithium anode for focused studies of sulfur cathodes, including rational cathode architecture, and sulfur reaction mechanisms at different electrolyte/sulfur ratios. To achieve this goal, the methodology is to realize cathode operation with liquid electrolyte (LE) to mimic reactions in conventional Li-S batteries, while the anode is all-solid-state to eliminate any interferences from lithium metal. Figure 79a depicts a section view of the overall design. To completely block "cross-talk" of lithium with either electrolyte or polysulfides, a rigid and dense garnet solid electrolyte (SE) was

employed to separate the cathode and anode chambers. Sealing mechanism of the cell is guaranteed by three O-rings and meticulously designed sealing parts. This enables durable testing of setup outside of the glove box.

A key challenge to be addressed is how to stabilize SE-Li interface to enable high current operation of the SE without any short circuit. The team used LiIn instead of pure lithium as the anode, and the interface was enhanced by nanometer gold coating, which easily forms Au-In alloy upon contacting with indium. The above design was carefully optimized and verified in In-SE-In symmetric cell test. As shown in Figure 79b, without LE, the In-SE-In symmetric cell shows the typical impedance response of only SE, corresponding to ionic conductivity of 0.6 mS/cm. The absence of interfacial processes indicates excellent contact between SE and indium with help of a gold layer. When lithium and LE are used to form an In-SE-LE-Li cell, a nearly identical bulk resistance is identified. This indicates a well-maintained SE pellet and proper sealing of the system; otherwise, an obvious decrease of resistance will be observed if the SE cracks or if there is liquid leakage.

Meanwhile, one additional semicircle was observed at lower frequency through impedance fitting, suggesting the presence of SE/liquid interface. Hence, chemical compatibility of SE and liquid electrolyte needs to be carefully studied and addressed. The indium electrode was lithiated electrochemically by capacity control, forming LiIn, and the LiIn-SE-LE-S cell was assembled subsequently. In Figure 79c, the cell shows a high sulfur utilization of 1350 mAh/g absence of shuttle in the following charging process by using excess amounts of electrolyte (E/S > 10); this excludes any crossover of LE, and thus proves the functionality of the hybrid cell design. Based on the design, mechanism study of sulfur cathodes is focused on rational cathode architecture design, electrode wetting process, sulfur utilization, and reversibility at different electrolyte/sulfur ratios without any interference of the lithium anode.

Patents/Publications/Presentations

Publications

- Liu, J., D. Lu, J. Zheng, P. Yan, B. Wang, X. Sun, Y. Shao, C. Wang, J. Zhang, and J. Liu. "Minimizing Polysulfide Shuttle Effect in Lithium Sulfur Batteries by Anode Surface Passivation." ACS Applied Materials & Interfaces. Under revision.
- Lu, D., Q. Li, J. Liu, J. Zheng, Y. Wang, S. Ferrara, J. Xiao, J. Zhang, and J. Liu. "Enabling High Energy Density Cathode for Lithium-Sulfur Batteries." Under review.

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.

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: In situ X-ray, Dr. Michael Toney, and
- Stanford: Professor Nix, mechanics; and Professor Bao, materials.

- 1. Establish a standard procedure to quantitatively compare the polysulfide adsorption capability of candidate materials. (FY 2017, July 2017; Completed)
- 2. Quantitatively approximate the polysulfide adsorption amount of candidate materials. (Q1, FY 2018, October 2017; Completed)
- 3. Elucidate different adsorption mechanisms and probe possible adsorption species. (Q2, FY 2018, January 2018; Completed)
- 4. Develop multi-functional sulfur cathode binder capable of controlling the polysulfide shuttling and facilitating Li-ion transport. (Q3, FY 2018, April 2018; Completed)
- 5. Demonstrate the flame-retardant property of binder to improve safety and propose flame-retardant mechanism. (Q4, FY 2018, July 2018; Ongoing)
- 6. Build *in situ* characterization platform to monitor nucleation/dissolution of sulfur/Li₂Sn. (Q1, FY 2019, October 2018; On schedule)

In the last report, the project elucidated different adsorption mechanisms and probed possible adsorption sulfide species, and provided a useful strategy to screen for suitable candidate materials and design of long cycle life Li-S batteries. This quarter, the team develops an aqueous inorganic polymer, ammonium polyphosphate (APP), as a novel multifunctional binder to address the issues existing in Li-S batteries. The strong binding affinity of the main chain of APP with lithium polysulfides blocks diffusion of polysulfide anions and inhibits their shuttling effect. The coupling of APP with Li-ion facilitates ion transfer and promotes the kinetics of the cathode reaction.

APP is commercially used as a food additive, emulsifier, and fertilizer available at large scale and low cost (Figure 80a). Here, the project employs it as a multifunctional binder. The absorptivity of APP and commonly used PVDF binder toward LiPSs was quantitatively evaluated by adding different masses of binder with the same total surface area into a DOL/DME (1:1, v:v) solution containing 0.005 M Li₂S₆. After adsorption and rest for 4 h, there is no obvious color change of the polysulfide solution after adsorption by PVDF, suggesting weak adsorption of polysulfide (Figure 80b). In sharp contrast, APP demonstrates significant polysulfide adsorption capability, and the color of the polysulfide solution changes from yellow to nearly colorless, indicating strong interaction between Li_2S_6 and APP binder. To further probe the polysulfide trapping ability of different binders, the supernatant liquid of the three bottles after adsorption was analyzed by ultraviolet-visible (UV-vis) absorption spectroscopy, and the concentration variation of Li_2S_6 solution before and after adding various binders is shown in Figure 80c. All samples exhibited a broad absorption region between 250 and 350 nm, and the characteristic peaks located around 260, 280, 300 and 340 nm can be attributed to S_6^{2-} species. Compared with pristine Li₂S₆ solution, the peak intensities of the solution soaked with PVDF decreased slightly, while the absorption peak intensities of the APP solution decreased much more sharply. The APP binder adsorbs roughly twice as much polysulfide as the PVDF binder, as indicated by the much lower concentration of Li_2S_6 remaining in the solution and demonstrating the strong affinity of the S_6^{2-} species to the APP binder.

To clarify the enhancement of binding strength by inorganic APP polymer, first-principles simulations were carried out on the adsorption of Li-S species on APP and PVDF. The binding energies between the LiPS species and two polymers are computed to evaluate the interaction strength between them, which can be expressed as $E_{b} = E_P + E_{LiS} - E_{P-LiS}$ (E_{P-LiS} , E_P and E_{LiS} are the total energies for the adsorption system, isolated polymer and isolated Li-S species, respectively). The Li-S species chosen for simulation are Li₂S, Li₂S₂, Li₂S₄, Li₂S₆, and Li₂S₈, which can cover the whole lithiation process and represent all of the typical species in the fully-lithiated, middle-lithiated, and under-lithiated stages. The chemical structures as well as adsorption conformations are illustrated in Figure 80d-g. The binding strengths of various LiPS species on two kinds of polymer binders are demonstrated in Figure 80h. It can be clearly seen that APP polymer can induce binding energies in the region of 2.16-2.30 eV, much higher than those of PVDF (0.58-0.74 eV).

Important requirements for binders include good swelling in the electrolyte to maintain electrolyte immersion and high viscosity to enable good mechanical properties of the electrode. To determine the electrolyte uptake ability of the two binders, the swelling ratios of APP and PVDF are tested at different times and shown in Figure 80i. APP binder exhibits an electrolyte uptake of around 40% after 10 min, much higher than the uptake of PVDF binder with limited values of 20% measured after 30 min. APP binder's higher uptake suggests that it can effectively adsorb and maintain electrolyte in the electrode structure to improve ion accessibility and reaction kinetics.



Figure 80. (a) Commercially available ammonium polyphosphate (APP) used as fertilizer. (b) Digital image of the Li_2S_6 (0.005 M) captured by polyvinylidene fluoride (PVDF) and APP in DOL/DME solution. (c) Ultraviolet-visible absorption spectra of Li_2S_6 solution before and after the addition of PVDF and APP. Chemical structures of (d) APP and (e) PVDF binders. Adsorption conformations and binding strengths for Li_2S_6 on (f) APP and (g) PVDF polymers. (h) Binding strengths for APP and PVDF with various Li-S species. (i) Swelling ratios of the APP and PVDF binders.

Task 5.4 – Addressing Internal "Shuttle" Effect: Electrolyte Design and Cathode Morphology Evolution in Lithium-Sulfur Batteries (Perla Balbuena, Texas A&M University; Partha Mukherjee, Purdue University)

Project Objective. The project objective is to overcome the Li-metal anode deterioration issues through advanced Li-anode protection/stabilization strategies including (1) *in situ* chemical formation of a protective passivation layer and (2) alleviation of the "aggressiveness" of the environment at the anode by minimizing the polysulfide (PS) shuttle with advanced cathode structure design.

Project Impact. Through formulation of alternative electrolyte chemistries as well as design, fabrication, and test of improved cathode architectures, it is expected that this project will deliver Li/S cells operating for 500 cycles at efficiency greater than 80%.

Approach. A mesoscale model including different realizations of electrode mesoporous structures generated based on a stochastic reconstruction method will allow virtual screening of the cathode microstructural features and the corresponding effects on electronic/ionic conductivity and morphological evolution. Interfacial reactions at the anode due to the presence of polysulfide species will be characterized with *ab initio* methods. For the cathode interfacial reactions, data and detailed structural and energetic information obtained from atomistic-level studies will be used in a mesoscopic-level analysis. A novel sonochemical fabrication method is expected to generate controlled cathode mesoporous structures that will be tested along with new electrolyte formulations based on the knowledge gained from the mesoscale and atomistic modeling efforts.

Out-Year Goals. By determining reasons for successes or failures of specific electrolyte chemistries, and assessing relative effects of composite cathode microstructure and internal shuttle chemistry versus that of electrolyte chemistry on cell performance, expected results are as follows: (1) develop an improved understanding of the Li-S chemistry and ways to control it, (2) develop electrolyte formulations able to stabilize the lithium anode, (3) develop new composite cathode microstructures with enhanced cathode performance, and (4) develop a Li-S cell operating for 500 cycles at an efficiency greater than 80%.

Collaborations. This is a collaborative work combining first-principles modeling (Perla Balbuena, TAMU), mesoscopic-level modeling (Partha Mukherjee, Purdue University), and synthesis, fabrication, and test of Li/S materials and cells (Vilas Pol, Purdue University). Balbuena also collaborates with M. Vijayakumar from PNNL.

- 1. Elucidate effects of PS migration and reduction at the anode on overall performance. (Ongoing)
- 2. Investigate charge reactions of nucleating Li₂S structures. (Ongoing)

Chemical Interactions of Li-Anode and Electrochemical Complexations in Li-Sulfur Cells. During electrochemical operation of a Li-sulfur cell, sulfur is present in different forms in the electrolyte phase. Each of these species can reach the Li-metal anode due to the shuttle effect. Since the lithium metal is quite reactive, it can reduce the sulfur species arriving at anode. This reduction, being chemical in nature, does not contribute to electrochemical capacity and gives rise to a capacity defect. Figure 81a compares the electrochemical response of two cells with and without these deleterious reactions at the anode. The speciation also changes, and in turn the cell potential profile changes its form. Each dissolved sulfur and long-chain/medium-chain PSs can partake in these reactions. Based on the availability of the species, various elemental reactions are active at different stages in electrochemical operation (Figure 81b). The reduction of a medium-chain PS (for example, Li_2S_4) forms a solid species on the Li-metal surface. This constitutes an irreversible capacity loss. In contrast, the reactions involving higher-chain PS (for example, Li_2S_6) and dissolved sulfur reduce them to lower oxidation states; however, the products are still present in the electrolyte phase, and this sulfur may not be irreversibly lost (referred to as the reversible capacity defect in Figure 81c).



Figure 81. Anode chemical reactions and electrochemical interactions at 1C. (a) With chemical redox reactions at lithium anode, capacity decreases as well as qualitative nature of the potential profile changes given concurrent changes in speciation. (b) The dominant mode of chemical reduction at Li-metal anode correlates the form of sulfur present at that instance. (c) This capacity defect has both reversible and irreversible components.

Essentially, these chemical interactions at Li-metal anode are composed of two mechanisms: transport of electrolyte species and chemical reduction. The kinetics of these reactions are dependent on interfacial characteristics and temperature. On the other hand, transport interactions are identified by electrode composition (for example, sulfur loading), microstructure (for example, porosity), and electrolyte evolution. The importance of these factors is being investigated.

Charge Reactions of Nucleating Li₂S Structures. The *ab initio* simulation method was used to study the delithiation process of ultra-small Li₂S nanoparticles represented by a Li₂₀S₁₀ cluster. It was found that although the overall delithiation is an oxidation reaction, local reductions and disproportionation reactions were observed. Long-chain PSs can be found as intermediate products. However, these PSs can be firmly bonded to insoluble S^{2-} via lithium atoms as mediators. The charge and discharge voltages were also estimated based on the energy profiles of changing lithium content in the cluster. The charge process only requires 0.37 V overpotential. Although the discharge voltage of the Li₂₀S₁₀ particle is only 1.26 V, it can still deliver a theoretical specific energy density about 1480 Wh/kg of Li₂S. During the charging process, polarons can form in the ultra-small particles, providing charges to support oxidation reactions. This is the first study that probes reactions during the delithiation of an ultra-small Li₂S nanoparticle. It is still unclear if small nanoparticles would agglomerate during charge/discharge processes. Agglomeration of nanoparticles can increase the charge transport distance and slow down the kinetics. In addition, the electrolyte also plays a significant role in the Li-S electrochemical system. An interesting and important remaining question that will be pursued is whether side reactions may happen between the electrolyte and the nanoparticle, and then result in chemical degradation. The study was published in *Physical Chemistry Chemical Physics*.

Patents/Publications/Presentations

Publications

- Beltran, Saul Perez, and Perla B. Balbuena. "Formation of Multi-Layer Graphene Domains with Strong Sulfur-Carbon Interaction and Enhanced Sulfur Reduction Zones for Lithium-Sulfur Battery Cathodes." *ChemSusChem.* In press.
- Liu, Zhixiao, Huiqiu Deng, Wangyu Hu, Fei Gao, Shiguo Zhang, Perla B. Balbuena, and Partha P. Mukherjee. "Revealing Reaction Mechanisms of Nanoconfined Li₂S: Implications for Lithium-Sulfur Batteries." *Physical Chemistry Chemical Physics*. In press.
- Mistry, A., and Partha P. Mukherjee. "Electrolyte Transport Evolution Dynamics in Li-Sulfur Batteries." Under review.

Presentations

- The Minerals, Metals, and Materials Society (TMS) 147th Annual Meeting and Exhibition, Phoenix, Arizona (March 2018): "Analysis of Discharge Reactions and Electrolyte Effects at the Cathode of Li/S Batteries"; Saul Perez Beltran, Ethan Kamphaus, Jaebeom Han, and Perla B. Balbuena.
- The Minerals, Metals, and Materials Society (TMS) 147th Annual Meeting and Exhibition, Phoenix, Arizona (March 2018): "Mechanistic Understanding of Transport-Mechanics Interactions in Li-S Cathodes"; A. Mistry and Partha P. Mukherjee.

Task 5.5 –Investigation of Sulfur Reaction Mechanisms (Deyang Qu, University of Wisconsin at Milwaukee; Xiao-Qing Yang, Brookhaven National Laboratory)

Project Objective. The primary objectives are (1) to conduct focused fundamental research on the mechanism of "shuttle effect" inhibition for the rechargeable Li-S batteries, and (2) to develop electrode and electrolyte systems that can mitigate "shuttle effect" so low self-discharge and long cycle life can be achieved. Special attention will be paid to the following: investigating chemical interactions between additives and dissolved polysulfides, management for solubility of polysulfide ions, formation of SEI layer and dead lithium on surface of lithium anode, and exploration of electrode and cell designs. Through such investigations, the Li-S chemistry will be studied systematically, and scientific understanding of the inhibition mechanism for "shuttle effect" can be well utilized to guide system engineering design. The goal is to develop a practical rechargeable Li-S battery to meet the challenges of powering next-generation EVs beyond Li-ion technologies.

Project Impact. With the unique *in situ* electrochemical-HPLC/MS technique developed in this program, the mechanisms of all reactions in a Li-S cell can be revealed. The interactions between additives and the soluble polysulfides can be investigated in real-time toward mitigation of "shuttle effect." The results will guide development of sulfur cathode and Li-S designs for EVs.

Approach. This project will use *in situ* electrochemical-MS, 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.

One-Year Goals. The one-year goals include the following: (1) complete preliminary investigations of the inhibition mechanism for the "shuttle effect" and evaluation of "shuttle effect" inhibitors, and (2) complete preliminary design and tests of sulfur-containing electrodes and electrolytes.

Collaborations. The PI, Deyang Qu, is the Johnson Control Endowed Chair Professor; thus, the University of Wisconsin at Milwaukee and BNL team have close collaboration with Johnson Controls' scientists and engineers. This collaboration enables the team to validate the 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 Control 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. Complete the investigation and determination of the possible chemical reactions between dissolved polysulfide ions with the materials in a Li-S cell, both active and non-active during the storage, and thus the stability of battery components. (Q1, December 31, 2017; Completed)
- 2. Complete tabulating the list of materials to be tested as the inhibitive additives to mitigate "shuttle effect"; start the tests and develop understanding of the mechanism of such effects. (Q2, March 31, 2018; Completed)
- 3. Complete testing the inhibitive additives; start to explore and design sulfur-containing electrode materials. (Q3, FY 2018)
- 4. Complete the preliminary engineering design and test for the new sulfur-containing electrode materials. (Q4, FY 2018)

This quarter, the project started to synthesize new materials for sulfur cathode. The main purpose is to localize the dissolved polysulfide ions in the cathode matrix. The team is exploring to bond the polysulfide species on the backbone materials, either modified carbon or polymers through chemical bonds.

A carbon material with hierarchical-ordered mesoporosity and high-level heteroatom (nitrogen) doping were synthesized. Sulfur was loaded in the mesocarbon; the sulfur content was determined to be ~ 69% wt%. Figure 82 shows the performance of the cathode made by sulfur loaded N-doped mesocarbon. Good cyclic performance was demonstrated. The team found that the synthesis conditions can substantially change



Figure 82. The cyclic performance and Coulombic efficiency for electrodes synthesized under different conditions.

performance, as shown in Figure 82. The team investigated effects of porosity and nitrogen doping on the electrochemical performances of the composite as the cathodes in Li-S batteries. It was demonstrated that carbon materials with balanced porosity and nitrogen-doping level could effectively increase conductivity of sulfur and also alleviate the "shuttle effect" and exhibit high specific capacity, good rate performance, and superior cycling stability.

The second approach to localize polysulfide

species was to bond them on a polymer backbone. Figure 83 shows the monomers used to construct the polymer backbone; sulfur was chemically bonded on the polymer chains. Figure 84 shows the first 20 cycles of a polymer-S composite electrode with lithium anode. Table 4 summarizes the performance of six groups of a polymer-S electrode with different polymer backbones.



Figure 83. The monomers used to synthesis polymer-S composite electrodes.



Figure 84. Twenty cycles of a polymer-S composite cathode with lithium anode.

Table 4. Performance of	f six groups of	f a polymer-S	electrode with	different
polymer backbones.				

Туре	1st Capacity (mAh/g)	20 th Capacity (mAh/g)	Retention after 20 cycles (%)
1	661.5	494.8	74.8
2	565.3	368.3	65.1
3	477.8	327.0(17 th cycle)	68.4 (17 th cycle)
4	341.8	184.5	54.0
5	828.1	506.7	61.2
6	1633.2	1551.3	95.0

Task 5.6 – Statically and Dynamically Stable Lithium-Sulfur Batteries (Arumugam Manthiram, University of Texas at Austin)

Project Objective. The project objective is to develop statically and dynamically stable Li-S batteries by integrating polysulfide-filter-coated separators with a protected Li-metal anode through additives or a modified Li₂S cathode with little or no charge barrier during first charge. The project includes demonstration of electrochemically stable cells with sulfur capacities of > 1000 mA h g⁻¹ and cycle life in excess of 500 cycles (dynamic stability) along with positive storage properties (static stability) at > 70 wt% sulfur content and ~ 5 mg cm⁻² loading.

Project Impact. The combination of polysulfide-filter (PS-filter)-coated separator, Li-metal-protection additives, and Li₂S cathode modifications offers a viable approach to overcome the persistent problems of Li-S batteries. This project is systematically integrating the basic science understanding gained in its laboratory of these three aspects to develop the Li-S technology as the next-generation power source for EVs. The project targets demonstrating cells with sulfur capacities of over 1000 mA h g⁻¹ and cycle life in excess of 500 cycles along with good storage properties at high sulfur content and loading that will make the Li-S technology superior to the present-day Li-ion technology in terms of cost and cell performance.

Approach. Electrochemical stability of the Li-S cells is improved by three complementary approaches. The first approach focuses on establishment of an electrochemically stable cathode environment by employing PS-filter-coated separators. The PS-filter coatings aim to suppress the severe polysulfide diffusion and improve the redox capability of Li-S cells with high-sulfur loadings. The study includes an understanding of materials characteristics, fabrication parameters, electrochemical properties, and battery performance of the PS-filter-coated separators. The second approach focuses on electrode engineering from two aspects. First, investigation of a Li-metal anode with coating- and additive-supporting approaches is aimed at improving the safety of Li-S cells. Second, research on activated-Li₂S cathode with little or no charge-barrier will promote performance and safety of the C-Li₂S cells. Integration of the first two approaches would create statically and dynamically stable Li-S batteries for EVs.

Out-Year Goals. The overall goal is to develop statically and dynamically stable Li-S batteries with custom cathode and stabilized anode active materials. In addition to developing a high-performance battery system, a fundamental understanding of the structure-configuration-performance relationships will be established. Specifically, the optimization of the electrochemical and engineering parameters of PS-filter-coated separators aims at comprehensively investigating different coating materials and their corresponding coating techniques for realizing various high-performance custom separators. The developed PS-filter-coated separators can be coupled with pure sulfur cathodes with high-sulfur loading and content. Multi-functional PS-filter-coated separators, high-loading sulfur cathodes, stabilized-Li-metal anodes, activated-Li₂S cathodes, and novel cell design are anticipated to provide an in-depth understanding of the Li-S battery chemistry and to realize statically and dynamically stable Li-S batteries.

Collaborations. There are no collaborative activities this quarter.

- 1. Develop Li-metal anodes with high electrochemical stability. (Q1, December 2017; Completed)
- 2. Develop Li₂S cathodes with low activation barrier and polarization. (Q2, March 2018; Completed)
- 3. Demonstrate high-loading coin cells and pouch cell prototypes. (Q3, June 2018; Ongoing)
- 4. *Go/No Go Decision*: Study cost and environmental impact assessment of the technology. (Q4, September 2018; Ongoing)

This quarter, the project has demonstrated a shell-shaped carbon architecture for developing pure lithium sulfide (Li_2S) cathodes with superior cell-design parameters and electrochemical characteristics. The key concept of the Li_2S core – carbon shell electrode aims to encapsulate the insulating Li_2S and its redox products within the

conductive shell to facilitate good electron/ion accessibility and limit the irreversible loss of the active material. To realize the best cell-design specification, the core-shell Li₂S cathode was initially carefully evaluated in relation to the critical cell-design parameters, such as the loading and content of Li₂S in the cathode and the electrolyte amount in the cells. Accordingly, the project's cells present the highest Li₂S loading of 8 mg cm⁻² (a value five times higher than the average value in the literature) with 100% Li₂S content (63 wt%, including all cathode components), as shown in Figure 85a, and the lowest electrolyte/Li₂S (E/L) ratio of 9/1 (a value that is five times lower than the average value in the literature, Figure 85b).

Even with such strict cell-design parameters, Figure 85c demonstrates that the core-shell Li_2S cathodes achieve a high peak chargestorage capacity of 601 mA h g⁻¹ and keep a



Figure 85. Cyclability (a) with various electrolyte/Li₂S (E/L) ratios from 45 to 9 μ L mg⁻¹ at a fixed sulfur loading of 8 mg cm⁻² and (b) with various Li₂S loadings from 2 to 8 mg cm⁻² at a fixed E/L ratio of 9/1. E/L ratio and Li₂S loading of, respectively, 45 μ L mg⁻¹ and 2 mg cm⁻², are the average values reported in published Li₂S papers. (c) Cell performances at various cycling rates.

high reversible capacity of 540 mA h g⁻¹ after 200 cycles at C/14 rate. Such enhanced battery performance demonstrates (i) superior Li₂S utilization with the highest areal, gravimetric, and volumetric capacities, (ii) high capacity retention of 90%, and (iii) enhanced rate performance from C/14 – C/3.5 rates.

Besides this progress, the project conducted a comprehensive literature analysis of all Li_2S research articles to show progress in the field. Figure 86 summarizes the cell-design parameters used and the remaining cell-design deficiencies in the literature, and, most importantly, evidences the accomplishments of the project's cathode design. The analytical results shown could provide a meaningful guideline for designing high-performance rechargeable batteries with practical cell-assembly metrics.



Figure 86. Literature analysis based on all Li₂S papers in the literature (references R1 - R55) and the project's work: (a) loading and content of Li₂S, (b) charge-storage capacity and Li₂S loading [the values in parentheses refer to the electrolyte/Li₂S (E/L) ratio and cycle life], and (c) gravimetric capacity and areal capacity.

Patents/Publications/Presentations

Publications

- Chung, S.-H., L. Luo, and A. Manthiram. "TiS₂-Polysulfide Hybrid Cathode with High Sulfur Loading and Low Electrolyte Consumption for Lithium-Sulfur Batteries." ACS Energy Letters 3 (2018): 568–573.
- Chung, S.-H., and A. Manthiram. "Designing Lithium-Sulfur Batteries with Practically Necessary Parameters." *Joule* 2 (2018): 1–15.

Presentations

- University of Central Florida, Orlando, Florida (January 19, 2018): "Electrical Energy Storage: Next Generation Battery Technologies"; A. Manthiram. Invited.
- National Alliance for Advanced Transportation Batteries (NAATBatt) Annual Meeting and Conference, San Antonio, Texas (March 21, 2018): "Next Generation Battery Chemistries"; A. Manthiram. Invited.

Task 5.7 – 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. The use of these high-performance Li-metal 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 second year, the team will develop the 2nd generation of organo- $\text{Li}_x S_y$ lithium protection layers with tuned functionality: (1) finding appropriate composition, (2) developing appropriate synthesis and fabrication methods, and (3) optimizing organic components in a protection layer to further improve CE and Li-S battery performance.

Out-Year Goals. Work will progress toward development of the 2^{nd} generation of organo-Li_xS_y lithium protection layers with tuned functionality. Characterization, performance, and compatibility tests on materials and systems will be conducted. Uniform and dendrite-free lithium deposition under the protection of the 2^{nd} generation of organo-Li_xS_y lithium protective layers will be demonstrated, and CE will be further improved.

Collaborations. There are no active collaborations.

- 1. Development of the 2nd generation of organo-Li_xS_y lithium protection layers with tuned functionality. Conduct characterization and performance tests on the materials. (Q1, FY 2018; Completed)
- 2. Demonstrate uniform and dendrite-free lithium deposition under protection of the 2nd generation of organo-Li_xS_y lithium protective layers. (Q2, FY 2018; Completed)
- 3. Optimize the 2^{nd} generation of organo-Li_xS_y lithium protective layer and demonstrate lithium anodes cycling with ~ 98.8% CE for ~ 200 cycles. (Q3, FY 2018)
- 4. Demonstrate lithium anodes with optimized 2^{nd} -generation organo-Li_xS_y lithium protective layer and ~99.2% CE for ~ 300 cycles. (Q4, FY 2018)

For the protection of the Li-metal anode, [poly(sulfur-random-1, 3-diisopropenylbenzene (PSD)], which contains the sulfur chains and aromatic-based organic components, is used for fabrication of organo- $\text{Li}_x S_y$ lithium protection layers. The PSD with 90 wt% sulfur (PSD-90) exhibited the best cycling performance. The content of PSD-90 as additives in the electrolyte affects the lithium plating/stripping cycling performance. As shown in Figure 87, comparing the lithium plating/stripping performance of using electrolyte containing 2 wt%, 5 wt%, 8 wt%, and 10 wt% of PSD-90, the team found that the cycling life is improved with increasing content of PSD-90 additive until reaching 8 wt%. When the content of PSD-90 in the electrolyte increases to 10 wt%, the cycling life deteriorates.



Figure 87. Cycling performance of cells using electrolytes containing different contents of single-ion conducting polymers.

Therefore, the **PSD-90** was investigated as additive the electrolyte to suppress growth lithium dendrites and of enhance CE. The control electrolyte used was 1 M LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) and 4 wt% LiNO₃ in DOL/DME (1:1, v:v). The electrolyte containing 8 wt% PSD-90 was used in the following study. Figure 88 shows SEM images of the deposited lithium after 10 cycles at a current density of 2 mA cm⁻² and a deposition capacity of 2 mA h cm^2 . For the control electrolyte, both the top (Figure 88a-b) and the cross-section view (Figure 88c)

show typical dendritic and fluffy structure, indicating dendritic and mossy lithium grows on the whole electrode. When 8 wt% PSD-90 was added in the electrolyte, the deposited lithium shows a continuous, uniform, and highly packed morphology not accompanied by any dendritic and mossy lithium (Figure 88d-e). The cross-section view displays the compact structure without any dendrite observed at the interior of the lithium layer (Figure 88f).



Figure 88. Morphologies of lithium metal deposited onto stainless-steel substrates. Scanning electron microscopy images of lithium metal deposited onto bare stainless-steel substrates in the control electrolyte (a-c), and the electrolyte containing 8 wt% PSD-90 (d-f) at a current density of 2 mA cm⁻² and a deposition capacity of 2 mA h cm⁻² after 10 cycles of lithium plating/stripping.

Even after 100 cycles of lithium plating/stripping, the deposited lithium still exhibits very smooth, uniform surface and compact interior without any growth of lithium dendrites (Figure 89a-b). The growth of the compact and dendrite-free lithium should be ascribed to the property change of the SEI layer in the presence of the PSD-90 additive. In comparison to lithium morphologies using PSD-90 as additive, a large amount of typical dendritic and fluffy structure is observed using the control electrolyte at both surface and interior of the deposited lithium layer after 100 cycles (Figure 89c-d).



Figure 89. Scanning electron microscopy images of the deposited lithium after 100 cycles at a current density of 2 mA cm⁻² and a deposition capacity of 2 mA h cm⁻². (a, b) Top view and cross-section view of deposited lithium using the electrolyte containing 8 wt% PSD-90. (c, d) Top view and cross-section view of deposited lithium using the control electrolyte.

Patents/Publications/Presentations

Publication

 Gao, Y., Y. M. Zhao, Y. C. Li, Q. Q. Huang, T. E. Mallouk, and D. H. Wang. "Interfacial Chemistry Regulation via a Skin-Grafting Strategy Enables High-Performance Lithium-Metal Batteries." *Journal of the American Chemical Society* 139, no. 43 (2017): 15288–15291.
Task 5.8 – Materials and Cell Design Optimization for Lithium-Sulfur Battery Technology (Hong Gan, Brookhaven National Laboratory)

Project Objective. Develop a low-cost battery technology for PEV application utilizing the Li-S electrochemical system by incorporating new materials (cathode, electrolyte, additives), consistent with DOE's long-term goals.

Project Impact. The Li-S battery system has gained significant interest due to its low material cost potential (35% cathode cost reduction over Li-ion) and its attractive 2.8x (volumetric) to 6.4x (gravimetric) higher theoretical energy density compared to conventional Li-ion benchmark systems. Commercialization of this technology requires overcoming several technical challenges. This effort will focus on improving the cathode energy density, power capability, and cycling stability by introducing optimized multifunctional cathode additives (MFCA) and multifunctional electrolyte (MFE) and conductive carbon host. The primary deliverable of this project is to boost the sulfur utilization and further improve the energy efficiency and the energy density at the cell level for Li-S battery technology.

Approach. In the past 3 years, the team successfully completed the project "*Multi-Functional Cathode Additives (MFCA) for Li-S Battery Technology.*" The layer structured TiS_2 has been identified as the true MFCA for Li-S cells, which is conductive electronically, active electrochemically, and with ability to adsorb polysulfide. By incorporating all the improvements—including the TiS_2 additive, the formulation optimization, the new binder and new carbon host for high sulfur loading, the electrode processing optimization, the electrode density control, and the electrolyte fill weight control—2032 coin cells with > 4 mAh delivered capacity with excellent cycle life have been demonstrated. This year, the team will build on previous work by incorporating MFE studies, in addition to the cathode material studies to further optimize Li-S cell performance.

Out-Year Goals. To address the system level interactions, one area of research will be the electrolyte and electrolyte additives, since electrolyte is a critical component in the Li-S battery for polysulfide dissolution, lithium anode SEI protection, and cathode interface reaction control. The project will continue to look into electrolytes with reduced polysulfide solubility, and the electrolytes/additives with ability to improve sulfur utilization to achieve long cycle life and high energy-efficiency. Improvement of sulfur utilization and the delivered energy density at the electrode level will also be achieved by introducing the 2D-nano-sheet TiS_2 with reduced particle size and increased Brunauer–Emmett–Teller (BET) surface area for maximized polysulfide– TiS_2 interaction, and by introducing the new carbon host of high pore volume and high BET surface area with controlled particle size distribution for high sulfur loading.

Collaborations. This project collaborates with Dong Su (BNL), Xiao Tong (BNL), Qin Wu and Yu-chen Karen Chen-Wiegart (SBU, BNL), Amy Marschilok (SBU), Kenneth Takeuchi (SBU), and Esther Takeuchi (SBU, BNL).

- 1. Electrolyte with low polysulfide solubility. (Q1, December 2017; Completed)
- 2. Electrolyte additive investigation for improved sulfur utilization. (Q2, March 2018; Completed)
- 3. Proof-of-concept testing of 2D TiS₂ as MFCA in sulfur electrode. (Q3, March 2018; Initiated)
- 4. Alternative high pore volume and high BET surface area carbon host investigation. (Q4)

One major challenge for the Li-S battery system is inefficient utilization of sulfur. Although the sulfur theoretical specific capacity is 1674 mAh/g, delivered capacity in the real cell is much lower—typically in the range of 50-70% of the theoretical. The focus this quarter was to

investigate the impact of electrolyte on the 2.1V voltage plateau discharge efficiency.

Sulfur Utilization Assessment. Li-S cell discharge has two voltage plateau regions, as shown in Figure 90. The Region I corresponds to the high ordered soluble polysulfides formation with 0.5 electrons per sulfur atom. In Region II, the soluble polysulfides are converted into insoluble sulfides, Li_2S_2 and Li_2S , with a total of 1.5 electrons per sulfur atom. In theory, the specific sulfur capacity of the Region II should be 3 times the capacity in Region I. Careful examination of the Li-S cell data indicates the sulfur utilization deficiency is strongly linked to the Region II discharge.

Effect of Electrolyte on Region II Sulfur Utilization. The region II sulfur utilization is affected by low Li_2S conductivity and its deposition morphology. The team discovered that electrolyte could have significant impact on sulfur utilization at this voltage



Figure 93. Morphology of discharged cathode.

plateau, possibly due to influence on Li_2S nucleation and the deposition distribution. Figure 91 shows the voltage profile of Li-S coin cells discharged under the identical

conditions, except the electrolytes—New Electrolyte versus the control electrolyte (1.0M LiTFSI /DOL:DME = 1:1 + 0.4M LiNO₃). The cell with New Electrolyte significantly extends the 2.1 V voltage plateau capacity and thus affords much higher sulfur utilization (85.8% versus 64.4%). Furthermore, when the New Electrolyte is used to test a sulfur electrode with improved conductive carbon host (Figure 92), the sulfur utilization is increased further to almost quantitative (1650 mAh/g sulfur) when compared to the cell with control electrolyte (98.6% versus 82.3%). Quantitative sulfur utilization with high sulfur loading electrode (~ 6 mg/cm² or 10 mAh/cm²) has never been reported. Preliminary investigation indicates the difference in morphology of the discharged cathodes



Figure 90. Li-S cell discharge voltage profile.



Figure 91. Electrolyte effect on sulfur utilization.



(Figure 93) with more porosity observed in New Electrolyte. Additional research is under way to fundamentally understand the underlying mechanism. The 2D TiS_2 sheet preparation as polysulfide adsorbing additive for Li-S batteries is initiated. Results will be reported next quarter.

Patents/Publications/Presentations

Publication

 Sun, Ke, Avi K. Matarasso, Ruby M. Epler, Xiao Tong, Dong Su, Amy C. Marchilok, Kenneth J. Takeuchi, Esther S. Takeuchi, and Hong Gan. *Journal of Electrochemical Society* 165, no. 3 (2018): A1–A8.

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.
- Limited cyclability of the battery associated with instability of the electrolyte and other battery components.
- 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. PNNL researchers will investigate new approaches to improve stability of Li-metal anode in Li-O₂ batteries and develop thick carbon/catalyst composite air electrodes for practical 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. Thick carbon/catalyst composite air electrodes based on carbon nanotubes (CNTs) and transient metal oxides such as RuO_2 and with $\geq 4 \text{ mg/cm}^2$ areal loading will be developed. At ANL, new cathode materials and electrolytes for Li-air batteries will be developed for Li-O₂ batteries with long cycle life, high capacity, and high efficiency. The state-of-the-art characterization techniques and computational methodologies will be used to understand the charge and discharge chemistries. Success of this project 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 the performance of Li-S batteries and other energy storage systems based on chemical conversion processes.

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

Project Objective. The project objective is to develop rechargeable lithium-oxygen (Li-O₂) batteries with long-term cycling stability. The team has found that the corrosion of Li-metal anode is a critical degradation mechanism of Li-O₂ batteries. Realization of very high energy density of Li-O₂ batteries strongly depends on the stability of Li-metal anodes. In FY 2018, the focus will be on protection of Li-metal anodes for Li-O₂ batteries. Several approaches, including *in situ* and *ex situ* methods will be used to study the corrosion of Li-metal anode in Li-O₂ cells under different treatment/protection conditions.

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 *in situ* formation of a stable SEI layer before Li-O₂ cell operation through various electrolyte formulations and treatment protocols and *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. Thick carbon/catalyst composite air electrodes based on CNTs and transient metal oxides such as RuO₂ and with ≥ 4 mg/cm² areal loading will be developed. The lithium anodes 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, energy-dispersive X-ray spectroscopy (EDX), 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 Chongmin Wang of PNNL on characterization of cycled air electrodes by TEM/SEM.

- 1. Investigate electrolyte additives to form stable SEI layer on Li-metal anode of Li-O₂ batteries. (Q1, December 31, 2017; Completed)
- 2. Develop inorganic/polymeric composite hybrid electrolyte membranes to protect Li-metal anode in Li-O₂ batteries. (Q2, March 31, 2018; Completed)
- Develop thick air electrodes of at least 4 mg/cm² areal loading for Li-O₂ batteries. (Q3, June 30, 2018; Ongoing)
- 4. Evaluate cycling performance of Li-O₂ batteries with protected Li-metal anode and thick air electrode. (Q4, September 30, 2018; Ongoing)

This quarter, the project synthesized an inorganic/polymeric composite membrane composed of Li_{6.75}La₃Zr_{1.75}Ta_{0.25}O₁₂ (LLZTO), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), and PVDF by a facile method to protect Li-metal anode in PVDF and LiTFSI Li-O₂ batteries. (7:3 weight ratio) were first dissolved in N.N-dimethylformamide (DMF) with a polymer concentration of 10 wt% followed by mechanical stirring to obtain a homogeneous solution. LLZTO was then added into the homogeneous solution with a LLZTO to PVDF weight ratio of 1:10. The mixture was then cast with a doctor blade on a clean PTFE plate. Finally, the free-standing solid LiTFSI-LLZTO-PVDF composite thin (LLP) membranes (~ $20 \mu m$ in thickness) were obtained after further drying under vacuum at 80°C for 24 h to remove the DMF solvent, as shown in Figure 94a-b. The effect of LLP hybrid protective membrane on Li-O₂ cell performance was investigated. Compared to the limited cycle life of the Li-O₂ cells without Li-metal protection membranes (Figure 94c-d), the addition of LLP protective membrane on Li-metal anode surface in Li-O₂ cells largely enhanced Li-metal stability upon cycling, leading to more stable operation of



Figure 94. (a, b) Optical images of as-prepared free-standing thin composite LiTFSI-LLZTO-PVDF (LLP) membrane with good flexibility. Cycling performance of Li-O₂ cells composed of carbon nanotube air-electrode and lithium anode without LLP membrane (c, d), or with LLP membrane (e, f) cycled at 0.1 mA cm⁻² under a limited capacity of 1,000 mAh g⁻¹.

Li- O_2 cells (Figure 94e-f) due to significantly decreased contact area between lithium metal and electrolyte. Thus, it has been proved that this kind of inorganic/polymeric composite membrane composed of LLZTO, LiTFSI, and PVDF facilitates Li-metal protection in Li- O_2 cell, which is beneficial for cycling improvement of high-energy Li- O_2 battery.

Patents/Publications/Presentations

Publication

 Liu, B., W. Xu, and J.-G. Zhang*. "Stability of Li Metal Anode in Li-Air Batteries." Invited book chapter for *Wiley* Publishing Group, Germany; 2018, in press.

Task 6.2 – Lithium-Air Batteries (Khalil Amine and Larry 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 the performance of Li-air batteries. The project impact will be to develop new electrolytes and cathode materials that are stable and can increase cycle life and improve efficiency of Li-air batteries.

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 the 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. Kah Chun Lau (University of California at Norridge), Prof. Yiying Wu (Ohio State University), Dr. Dengyun Zhai (China), and Reza Shahbazian-Yassar (UIC).

- 1. Investigation of highly uniform Pt₃Co nanoparticles in biphasic nitrogen-doping cobalt@graphene heterostructures as cathode materials. (Q1, FY 2018; Completed)
- 2. Computational studies of dependence of stability and composition of discharge products in Li-O₂ batteries on ether-based electrolytes. (Q2, FY 2018; Completed)
- 3. Use of highly uniform small iridium clusters supported on reduced graphene oxide to study formation of Ir₃Li alloys for lithium-superoxide-based batteries. (Q3, FY 2018; Initiated)
- 4. Investigation of dependence of discharge composition on type of ether used in electrolytes from experimental studies. (Q4, FY 2018; Initiated)

The disproportionation rate for lithium superoxide to form lithium peroxide and oxygen depends on several factors. Understanding these factors is important for designing cathode and electrolyte materials for Li-O₂ batteries for optimal performance. One factor involved in disproportionation is the rate at which O₂ molecules leave the surface of lithium superoxide. The kinetic stability of crystalline and amorphous LiO₂ was previously investigated using DFT calculations for the barrier for O₂ elimination from a surface in a vacuum (Lu et al., *Nature* 2016). The DFT results indicated that the barrier for O₂ to leave a clean surface into a vacuum is ~ 0.9 eV based on a low energy LiO₂ surfaces. For an amorphous surface, the barrier is less (~ 0.3 eV) than for the crystalline surface.

The presence of an electrolyte in contact with the LiO_2 surface should make O_2 desorption more difficult and increase the barrier and, thus, the lifetime of LiO_2 in a $Li-O_2$ discharge product. The team has carried out calculations for the barrier of the dissolution of O_2 from a crystalline surface of lithium superoxide into an

electrolyte to determine the effect on disproportionation. The calculations have been done for three different electrolytes: tetraglyme (TEGDME), dimethoxyethane (DME), and dimethylsulfoxide (DMSO). The dissolution barriers were calculated by DFT, as shown in Figure 95 for TEGDME. The barriers are 1.51, 1.66, and 1.82 eV for TEGDME, DME, and DMSO, respectively. The increase in barriers compared to the calculated barrier (0.9 eV) in vacuum indicate that the lifetime of lithium superoxide would increase significantly in the presence of an electrolyte at the surface. This is consistent with the project's previous experimental studies, which indicated that the presence of a TEGDME-based electrolyte decreases the disproportionation of lithium superoxide formed using an Ir-rGO cathode compared to when it is aged for 24 hours in vacuum. Characterization of the sample by Raman and charge potential shows a significant increase in disproportionation in the vacuum, indicating kinetics plays an important role in stabilizing the LiO₂ as found in the team's calculations. In experimental work that has been initiated, the team is examining the effect of electrolytes other than TEGDME on the disproportionation of lithium superoxide.



Figure 95. Density functional theory calculations: (top) structure of TEGDME solvent at a (111) LiO_2 surface; (bottom) barrier for dissolution of O_2 into the TEGDME.

Patents/Publications/Presentations

Publication

Halder, Avik, Hsien-Hau Wang, Kah Chun Lau, Rajeev S. Assary, Jun Lu, Stefan Vajda, Khalil Amine, and Larry A. Curtiss. "Identification and Implications of Lithium Superoxide in Li-O₂ Batteries." ACS *Energy Letters* 3 (2018): 1105–1109. doi: 10.1021/acsenergylett.8b00385.

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 the 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 350 Wh/kg cell with more than 50 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 that can be incorporated into the consortium.

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. Scale up the synthesis capacity of high-Ni-content NMC to 500 g; Incorporate cathode surface modification in coin cells with greater than 2 mAh/cm² loading. (Q1, December 2017; Completed)
- 2. Establish the high-nickel NMC coin cell properties using the materials synthesized by the team and supplied by other sources; Develop stage 1 pouch cell testing protocols and provide updated component parameters toward 350 Wh/kg; Establish baseline properties of Li-S coin cells using parameters required to reach 350 Wh/kg. (Q2, March 2018; Completed)
- 3. Provide feedback on characterization of new materials and concepts by the characterization team; Develop procedures to identify lithium anode failure in coin cells and pouch cells. (Q3, June 2018; In progress)
- 4. Establish coin cell performance with 30% weight reduction in the anode current collector; Develop and implement methods to improve and understand cycle and calendar life limitations of pouch cells. (Q4, September 2018; In progress)

This period, the second milestone for FY 2018 was completed. The properties and performances of the high-Ni NMC materials synthesized by the Battery500 team and supplied by other sources have been tested and thoroughly studied. The stage 1 pouch cell testing protocols and updated component parameters toward 350 Wh/kg have been developed. Baseline properties of Li-S coin cells using parameters required to reach 350 Wh/kg have been established.

The FY 2018 first quarter review was held in Berkeley, California. The PIs, postdocs, and students of the Battery500 Consortium team presented 13 talks and 17 posters. Two posters were rewarded as best posters of the review meeting. The active involvement of the young scientists in the review meeting resulted in many interesting discussions during and after the review meeting, as well many post-meeting collaborative research activities.

In addition, the Battery500 Consortium PIs delivered more than 30 invited talks this quarter and had 18 papers published or accepted for publication in peer-reviewed journals.

Consortium members held about 12 technical teleconferences for scientific information exchange along with four working group teleconferences for managing the consortium project.

The technical part of this report is organized under the three keystone projects, as shown below.

Keystone Project 1: Materials and Interfaces

High-Ni NMC. This quarter, the team addressed three critical questions on the high-Ni NMC: (i) environmental sensitivity, (ii) impact of thick electrodes on capacity and capacity retention, and (iii) a recommendation on the NMC beyond 622.

- (i) A moist environment was shown to be detrimental to the capacity of high-Ni NMCs, as shown in Figure 96a for a 94% nickel sample. The capacity decreases with time and has lost more than 50% of its capacity after 30 days. The addition of a little aluminum helps ameliorate these major losses, but does not completely eliminate the losses. This is consistent with the reports on NCA and indicates that all these high-Ni materials must be handled carefully in a dry atmosphere.
- (ii) Two NMC-622 thick electrodes were provided by Maxwell Technologies: Maxwell24 (19% porosity, 95% active material ratio, 24 mg/cm² areal active mass loading, and 75-µm thickness) and Maxwell30 (31% porosity, 94% active material ratio, 30 mg/cm² areal mass loading, and 100-µm thickness). The Maxwell24 shows the better capacity retention (Figure 96b) and has a higher rate capability, possibly due to its greater density that might lead to a higher electrode overall electronic conductivity.
- (iii) A comparison of NMC-811, NMC-622, and NCA showed that 811 was overall superior to 622 in capacity, capacity retention, and rate capability (Figure 96c). Although NCA showed the highest capacity at rates of 2C and greater, its capacity retention at the desired rates from C/5 to 1C was the lowest. Thus, Keystone 1 is recommending that NMC-811 with some aluminum doping be the cathode of choice for the next year.



Figure 96. (a) First-cycle charge/discharge voltage profiles of LiNi_{0.94}M_{0.06}O₂ at fresh and after exposure to a moist atmosphere for 14 and 30 days. (b) Cycling performance of Maxwell24 and Maxwell30, two cycles at C/10, then third through fiftieth cycle at C/3, 2.8-4.4 V. (c) Comparison of rate capability and capacity of NMC-811, NMC-622, and NCA, 12 mg/cm².

Sulfur. A novel inorganic binder, APP, has been designed that combines several attractive properties for high-performance Li-S batteries including the following: (1) moderate binding strength to maintain integrity of the electrode material; (2) strong affinity with LiPSs via chemical interactions to suppress the dissolution of LiPSs since the main chain of the inorganic polymer binder can be highly polarized chemical bonds, which can bind LiPSs more efficiently; (3) flame-retardant property to improve safety, a property that conventional organic polymer binders do not have; (4) facilitation of Li-ion transport to accelerate redox chemistry and promote the reaction kinetics; and (5) water solubility for environmentally friendly processing. The sulfur cathode applying this inorganic polymer binder demonstrated good electrochemical performance with a high-rate capacity of 520 mAh g⁻¹ at 4C and excellent cycling stability of ~ 0.038% capacity decay per cycle at 0.5C for 400 cycles. Even with a high sulfur loading of 5.6 mg cm⁻², the electrode still exhibits good cycling performance with reversible discharge capacities reaching 530 mAh g⁻¹ at 0.5C rate after 200 cycles.

Lithium. A range of electrolytes was studied to achieve the 300 Wh/kg Li||NMC-622 cells reported last quarter. The preferred one is a localized high-concentration electrolyte consisting of 1.2 M lithium bis(fluorosulfonyl)imide (LiFSI) in a mixture of DMC/bis(2,2,2-trifluoroethyl) ether (BTFE) (1:3 by mol). This electrolyte enabled stable, dendrite-free cycling of Li-metal anodes with high CE of up to 99.2%. Moreover, it exhibits excellent anodic stability even up to 5.0 V and greatly enhances the cycling performance of Li-metal batteries. A Li||NMC-622 cell using this electrolyte retained > 97% capacity after 600 cycles at 1C rate (ca. 1.6 mA cm⁻²), corresponding to a negligible capacity decay of < 0.005% per cycle (Figure 97). Currently, a flame-retarding LHCE based on flame-retardant triethyl phosphate (TEPa) can enable the Li||NMC-811 cells to cycle stably for more than 50 cycles in 1 Ah, 350 Wh/kg pouch cells. This new electrolyte can enable safe operation of high-energy Li-metal batteries for practical applications.



Figure 97. Cycling stability and efficiency of Li||NMC-622 cells with different electrolytes at C/3 charge and 1C discharge rates after two formation cycles at C/10 in the voltage range of 2.8~4.4 V at 30°C. CC/CV charging. Conventional: 1 M LiPF₆ in EC/EMC; HCE: 3.2M LiFSI in DMC; and LHCE: 1.2 M LiFSI in DMC-BTFE.

Keystone Project 2: Electrode Architecture

The goal of Keystone 2 is to design, model, fabricate, and characterize the effect of electrode architecture on electrode and cell performance in support of reaching the project of 500 Wh/kg cell specific energy. Included in this keystone are architectured design of thick cathodes (UCSD), Li-metal electrode architectures (PNNL and Stanford), inorganic electrolytes (UT Austin) and polymer electrolytes (Stanford), and electrode performance modeling (UW).

This quarter, UCSD continued its effort in optimizing fabrication of thick cathodes as well as evaluation of electrodes with exceptionally low porosities. Figure 98 shows that binder choice is critical for achieving high-quality electrodes with uniform carbon coating on the particle surface. The copolymer, PVDF-HFP, which absorbs organic solvents more readily, results in a much less uniform coating of carbon than PVDF-HSV, a homopolymer. Under similar processing conditions and polymer loading (2%), the later results in highly uniform distribution of carbon on the oxide surface, while the former has carbon aggolomerization.



Figure 98. Scanning electron microscopy images of NMC-811 electrodes fabricated with two different binders, PVDF-HFP copolymer and PVDF-HSV 900 homopolymer.

The better carbon distribution in the PVDF homopolymer sample resulted in clear advantage in electrochemical performance. Figure 99 shows the electrode reaching > 200 mAh/g of discharge capacity at the first discharge. At C/3, the discharge capacity is still over 190 mAh/g. This recipe was extended for the fabrication of an electrode with a loading of 30 mg/cm². The electrode showed similar performance to the 19 mg/cm² sample: at C/10, the capacity is ~ 200 mAh/g and and at C/3, 195 mAh/g. These results indicate that high-quality electronic conduction is of primary importance at these moderate rates.



Figure 99. Galvanostatic cycling curves of the two electrodes shown in Figure 98. The better distribution of carbon clearly led to the higher capacity and smaller resistance for the PVDF-HSV sample. First three cycles, C/10; fourth to fifth cycles, C/3. Electrode loading is 19 mg/cm².

In the area of Li-metal architecture, the Stanford team previously demonstrated that 2D atomic crystal layers of hexagonal boron nitride (h-BN) can be used as interfacial protection layers for Li-metal anodes. However, it is difficult to grow pristine, electrode-scale, high-quality BN due to defects that form and the small grain sizes. Here, the team demonstrates the selective ALD of LiF on defect sites of h-BN prepared by chemical vapor deposition. The LiF deposits primarily on the line and point defects of h-BN, thereby creating seams that hold

the h-BN crystallites together. The selective deposition allows us to visualize the location of defects in h-BN using SEM, AFM, and TEM. The chemically and mechanically stable hybrid LiF/h-BN film successfully suppresses lithium dendrite formation during both the initial electrochemical deposition onto a copper foil and the subsequent cycling. Lithium metal that is deposited on the LiF/h-BN-protected current collector is highly dense and nearly free of void spaces, with its density matching that of bulk lithium. The protected lithium electrodes exhibit good cycling behavior with more than 300 cycles at relatively high CE (>95%) in an additive-free carbonate electrolyte, as compared to the unprotected lithium anodes that had rapidly decaying CE and overall mossy lithium morphology.



Figure 100. Schematics (top) of LiF deposition on h-BN to heal the defects. This approach enables dense, void-free Li-metal cycling (a, bottom). In contrast, lithium deposits on bare copper surface in a carbonate-based electrolyte is dendritic and porous (b, bottom).

In summary, the consortium continues to make advancements in both cathode and Li-anode architectures. Recent work on multiple cathode samples shows the importance of achieving highly uniform electronic conductivity to achieve desired rate and cycling stability under the targeted moderate rate of cycling, C/3. Progress in Li-metal protection highlights the need for defect-free interfacial layers to realize dense, dendrite-free cycling.

Keystone Project 3: Cell Fabrication, Testing, and Diagnosis

Distinct focal points this quarter were on refining modeling architectures to advance understanding of Li-metal electrodes and thick electrode architectures, developing and conducting early evaluation of higher specific energy Li||NMC pouch cell designs, identifying means to increase cycle life, and performing advanced scientific diagnostics of Li-metal electrodes. With respect to the modeling activities, the Battery500 team performed 2D modeling of novel electrode architectures to understand the effect of architecture design and material parameters on Li-ion transport and, thus, overall rate performance. In conjunction with developing this modeling framework, the team also focused on developing codes that enable simulations to be performed in a computationally efficient manner. The result of the new codes is that simulations are faster and more robust than simulations run on commercial software. A continuum model that captures the dynamics of lithium deposition and stripping during repeated cycling was also developed, which includes a moving boundary representation to the standard Butler-Volmer method.

To date in FY 2018, cells with a specific energy of 340 Wh/kg have been developed using a Li-metal anode and a high Ni-NMC cathode. Thus far, cells have demonstrated at least 50 cycles. The ability to extend life was also a key area of research. Combined methods looking to more distinctly control pressure and initial conditioning of lithium have extended cycle life from just over 50 cycles with no control to over 225 cycles (still cycling) for a cell with a design of 310 Wh/kg. Analysis on the calendar life of LilNMC cells has begun. For both pouch and coin cells, the electrochemical characterization standard methods for evaluation are also in place.

With respect to diagnostics analysis, lithium metal deposited from different electrolytes was analyzed using a newly developed cryogenic-FIB-SEM (Cryo-FIB-SEM). This method significantly minimizes beam damage to the lithium sample. For investigations, roughly ~5 μ m of lithium was deposited from two different electrolytes. From the top view, the conventional carbonate electrolyte (1 M LiPF₆ in EC-DMC) generates needlelike dendrites with highly porous surface (Figure 101a). In contrast, close-packed large lithium particles with dense surface are formed in LiTFSI-FM: CO₂-Additive01 electrolyte (Figure 101b). From the cross-section view, the Li-metal film from the conventional electrolyte has porous structure, with large voids resulting in a thickness of ~10 μ m (Figure 101c). On the contrary, use of LiTFSI-FM: CO₂-Additive01 electrolyte forms a dense lithium deposit with a thickness of 5.2 μ m. The dense deposition formed in liquefied-gas-based electrolyte prevents dendrite formation and severe electrolyte consumption from SEI formation.



Figure 101. Cryogenic–focused ion-beam–scanning electron microscopy images of the plated lithium at the first cycle, and the corresponding cross-section images when the cells are cycled in (a/c) 1 M LiPF₆ EC: DMC, and (b/d) 0.1 M LiTFSI in fluoromethane: CO₂19:1 with 0.1 M Additive01.

Patents/Publications/Presentations

Publications

- Zhou, G., K. Liu, Y. Fan, M. Yuan, B. Liu, W. Liu, F. Shi, Y. Liu, W. Chen, J. Lopez, D. Zhuo, J. Zhao, Y. Tsao, X. Huang, Q. Zhang, and Y. Cui. "An Aqueous Inorganic Polymer Binder for High Performance Lithium-Sulfur Batteries with Flame-Retardant Properties." ACS Central Science 4 (2018): 260–267.
- Alvarad, J., M. Schroeder, O. Borodin, E. Gobrogge, M. Olguin, M. Ding, M. Gobet, S. Greenbaum, Y. S. Meng, and K. Xu. "Solvent-Salt Synergy Offers Fresh Pathway to Unlock Next Generation Li-Ion Chemistries." *Materials Today*. Accepted 2018.
- Whittingham, M. S., F. Omenya, and C. Siu. "Solid State Ionics The Key to the Discovery, Introduction and Domination of Lithium Batteries for Portable Energy Storage." *Solid State Ionics* 318 (2018): 60–68. doi: <u>https://doi.org/10.1016/j.ssi.2018.01.007</u>.
- Hu, E., X. Wang, X. Yu, and X.-Q. Yang. "Probing the Complexities of Structural Changes in Layered Oxide Cathode Materials for Li-Ion Batteries during Fast Charge–Discharge Cycling and Heating." Accounts of Chemical Research 51 (2018): 290–298. doi: https://doi.org/10.1021/acs.accounts.7b00506.
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- Li, W., X. Liu, H. Celio, P. Smith, A. Dolocan, M. Chi, and A. Manthiram. "Mn vs. Al in Layered Oxide Cathodes in Lithium-Ion Batteries: A Comprehensive Evaluation on Long-term Cyclability." *Advanced Energy Materials* 8 (2018): 20173154.
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- Xue, L., H. Gao, Y. Li, and J. B. Goodenough. "Cathode Dependence of Liquid-Alloy Na–K Anodes." Journal of the American Chemical Society 140 (2018): 3292–3298.
- You, Y., H. Celio, J. Li, A. Dolocan, and A. Manthiram. "Stable Surface Chemistry against Ambient Air of Modified High-Nickel Cathodes for Lithium-Ion Batteries." *Angewandte Chemie International Edition* (2018). doi: <u>https://doi.org/10.1002/anie.201801533</u>.
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- Li, Y., X. Chen, A. Dolocan, Z. Cui, S. Xin, L. Xue, H. Xu, K. Park, and J. B. Goodenough. "Garnet Electrolyte with an Ultra-Low Interfacial Resistance for Li-Metal Batteries." *Journal of the American Chemical Society* (2018). doi: <u>https://doi.org/10.1021/jacs.8b03106</u>.
- Li, Y., H. Xu, P. Chien, N. Wu, S. Xin, L. Xue, K. Park, Y. Hu, and J. B. Goodenough. "A Stable Perovskite Electrolyte in Moist Air for Li-ion Batteries." *Angewandte Chemie International Edition*. Accepted.

- Chen, S., J. Zheng, D. Mei, K. S. Han, M. H. Engelhard, W. Zhao, W. Xu, J. Liu, and J.-G. Zhang. "High-Voltage Lithium Metal Batteries Enabled by Localized High Concentration Electrolytes." *Advanced Materials* 30 (2018): 1706102.
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- Hu, G., C. Shen, L.-Z. Cheong, S. Wang, S. Huang, J.-G. Zhang, and D. Wang. "Direct Observation of Lithium Dendrite Growth by Operando EC-AFM." *Small Methods* 2 (2018): 1700298.
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Presentations

- Gordon Research Conference on Batteries, Ventura, California (2018): "High Energy and Sustainable Sodium Organic Battery Using Sodium Rhodizonate"; M. Lee, J. Hong, J. Lopez, Y. Sun, D. Feng, K. Lim, W. C. Cheuh, M. F. Toney, Y. Cui, and <u>Z. Bao</u>. Invited.
- Gordon Research Conference on Batteries, Ventura, California (2018): "Enhanced Cycling Stability of Sulfur Electrodes through Effective Binding of Pyridine-Functionalized Polymer"; Y. Tsao, Z. Chen, S. Rondeau-Gagné, Q. Zhang, H. Yao, S. Chen, G. Zhou, C. Zu, Y. Cui, and <u>Z. Bao</u>. Invited.
- Nature Conference on Materials Electrochemistry: Fundamental and Applications, Shenzhen, China, (January 13–15, 2018): "High-Nickel Layered Oxides for Lithium-Ion Batteries: Intricacies of Bulk and Surface Chemistry"; <u>A. Manthiram</u>. Invited keynote talk.
- University of Central Florida, Orlando, Florida (January 19, 2018): "Electrical Energy Storage: Next Generation Battery Technologies"; A. Manthiram. Invited.
- International Battery Association Meeting, Jeju, South Korea (March 11–16, 2018): "High-Nickel Layered Oxide Cathodes: Delineating the Intricacies and Their Mitigation"; A. Manthiram. Invited keynote talk.
- NAATBatt Annual Meeting and Conference, San Antonio, Texas (March 21, 2018): "Next-Generation Battery Chemistries"; A. Manthiram. Invited.
- University of Houston Mechanical Engineering Distinguished Lecture, Houston, Texas (March 29, 2018):
 "Electrochemical Reactions: Energy Storage and Beyond"; P. Liu. Invited.
- Nature Conference on Materials Electrochemistry: Fundamentals and Applications, Shenzhen, China (January 13, 2018): "Design Solution Chemistries to Form Solid Electrolytes"; P. Liu. Invited.
- U. S.-Germany Energy Storage Workshop, Washington, D. C. (March 26, 2018): "High Efficiency Lithium Metal Batteries Enabled by Localized High Concentration Electrolytes"; J.-G. Zhang. Invited.
- Nature Conference on Materials Electrochemistry: Fundamentals and Applications, Shenzhen, China (January 13–15, 2018): "Nanoscale Design and Cryogenic Electron Microscopy for Energy Storage"; Yi Cui. Keynote.
- Seminar, Peking University School of Materials Science at Shenzhen, China (January 14, 2018): "Nanotechnology for Energy, Environment, and Textile"; Yi Cui. Invited.
- Seminar, Dalian Institute of Chemical Physics, Dalian, China (January 16, 2018): "Nanotechnology for Energy, Environment, and Textile"; Yi Cui. Invited.
- Seminar, Dalian Institute of Technology, Dalian, China (January 19, 2018): "Nanotechnology for Energy, Environment, and Textile"; Yi Cui. Invited.
- Seminar, University of California at Irvine (February 2, 2018): "Nanotechnology for Energy, Environment, and Textile"; Yi Cui. Invited.

- Stanford Energy Seminar, Stanford University, Stanford, California (February 12, 2018): "Pathways of Batteries towards Sustainable Electric Transportation and Stationary Storage"; Yi Cui. Invited.
- Seminar, Tsinghua University, Beijing, China (March 5, 2018): "Nanotechnology for Energy, Environment, and Textile"; Yi Cui. Invited.
- Seminar, General Motors, Warren, Michigan (March 16, 2018): "Materials Design for High Energy Batteries towards Electric Transportation"; Yi Cui. Invited.
- American Chemical Society Spring Meeting, New Orleans, Louisiana (March 18–22, 2018): "Nanoscale Design and Cryogenic Electron Microscopy for Energy Storage"; Yi Cui. Invited.
- International Battery Seminar, Fort Lauderdale (March 26–29, 2018): "Emerging Materials Selection and Design for Batteries with High Energy Density, Ultralong Cycle Life, and Excellent Safety"; Yi Cui. Invited.
- U.S.-Germany Energy Storage Workshop, Washington, D. C. (March 26–27, 2018): "Materials Design of Li-Metal Host and Interface and Characterization with Cryo Electron Microscopy"; Yi Cui. Invited.
- International Battery Seminar and Exhibit, Fort Lauderdale, Florida (March 2018): "Building Next-Generation Rechargeable Lithium Metal Batteries"; J. Xiao and J. Liu. Invited.
- International Association Battery Association, Jeju, South Korea (March 11–16, 2018): "Building the Next Rechargeable LI Batteries"; J. Liu. Invited.
- 2018 Advanced Automotive Battery Conference, Mainz, Germany (January 29–February 1, 2018):
 "Developing High Energy Rechargeable Lithium Metal and Lithium Sulfur Batteries"; J. Liu. Invited.
- Nature Conference on Materials Electrochemistry, Shenzhen, China (January 13–15, 2017): "Innovation and Integration in Energy Materials and Energy Technologies"; J. Liu. Invited.
- Munich Battery Discussion Meeting, Munich, Germany (February 19, 2018): "Role of Strain and Defects in Classical Layered Oxides and Lithium Rich Layered Oxides – Pushing the Limit of Intercalation"; Y. Shirley Meng. Invited.
- International Battery Association (IBA), Jeju Island, South Korea (March 16, 2018): "New Insights on the Structure of Electrochemically Deposited Li Metal and Its Solid Electrolyte Interphase via Cryogenic FIB & TEM"; Y. Shirley Meng. Keynote.
- Joseph Priestley Society Symposium, Philadelphia, Pennsylvania (January 11, 2018): "New Energy Storage Technologies for Enabling Renewables"; M. Stanley Whittingham. Invited.
- Nature Conference on Materials Electrochemistry, Shenzhen, China (January 13, 2018): "The Development of the Li-Ion Battery and Related Energy Storage Technologies and Future Trends"; M. Stanley Whittingham. Plenary.
- International Coalition for Energy Storage & Innovation, Dalian, China (January19, 2018): "The Development and Future Directions of Lithium Intercalation Batteries"; M. Stanley Whittingham. Keynote.
- *NAATBatt Annual Meeting*, San Antonio, Texas (March 20, 2018): "The Past and the Future of Lithium-Ion Battery Technology"; M. Stanley Whittingham. Invited.