

SYMPOSIUM ET01

Solid-State Batteries—Materials, Interfaces and Performance
November 26 - November 29, 2018

Symposium Organizers

Liwei Chen, Suzhou Institute of Nanotech and Nanobionics, CAS
Liangbing Hu, University of Maryland
Jennifer Rupp, Massachusetts Institute of Technology
Venkataraman Thangadurai, University of Calgary

* Invited Paper

SESSION ET01.01: Session I
Session Chairs: Liwei Chen and Liangbing Hu
Monday Morning, November 26, 2018
Hynes, Level 3, Room 310

8:00 AM ET01.01.01

Mechanism of High Ionic Conduction Paths in Composite Solid Electrolyte Feifei Shi and Yi Cui; Material Science and Engineering, Stanford University, Stanford, California, United States.

As one of the most promising next-generation batteries, all-solid-state lithium battery is well known for its superior advantage of high energy density and nonflammability, as well as its intrinsic drawback poor ionic conductivity of solid electrolyte. Therefore, it is crucial to understand the ion conduction mechanism in solid electrolyte for optimized design to enhance ionic conductivity. Recently, composite solid electrolyte with aligned interface has been reported to achieve one order of magnitude enhancement on ionic conductivity. However, the mechanism accounting for the enhanced ionic conductivity at solid/solid interfaces remains unclear.

Here we unveil the diffusion path of the lithium in the composite electrolyte by tracking labeled lithium isotope, characterizing polymer crystal structure with both hard and soft X-ray diffraction, and mapping the electronic structure of lithium by electron spectroscopy. Further understanding of the correlation between interface structure and ion conduction mechanism has been obtained, which enables new solid electrolyte design with better ionic conductivity.

Acknowledgement:

The work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the US Department of Energy under the Battery 500 Consortium program.

8:15 AM ET01.01.02

State-of-Charge-Dependent Space-Charge-Layer Formation in Solid-State Batteries Michael W. Swift and Yue Qi; Michigan State University, East Lansing, Michigan, United States.

As all-solid-state lithium ion batteries develop as an alternative to traditional liquid-electrolyte cells, a thorough theoretical understanding of the driving forces behind battery operation is needed. We present a model of potential profiles in a generic all-solid-state battery, and apply the model to the Li/LiPON/Li_xCoO₂ system. The potentials yield valuable information about lithium distribution and transport, including the nature of electrical double layers which form at interfaces. The results suggest design rules to minimize interfacial lithium barriers and optimize device performance.

8:30 AM ET01.01.03

Mapping LLZO Grains and Grain Boundaries Through a Simple Thermal Etching Technique Masumi Sato, Regina Garcia-Mendez and Jeff Sakamoto; University of Michigan, Ann Arbor, Michigan, United States.

LLZO is one of the most promising solid-state electrolytes due to its electrochemical and chemical stability against metallic Li and high ionic conductivity (1 mS cm⁻¹) at room temperature. However, it has been reported that Li metal still propagates along LLZO grain boundaries above a critical current density (CCD) (1).

It is known that the chemistry of grain boundaries and grains are typically different. In this study, we assume the same is true for polycrystalline LLZO. We hypothesize that grain boundaries etch faster than grains, thus enabling a technique to visualize and study the microstructure of LLZO. The proposed technique does not requiring extensive sample preparation such as what is required for electron backscattering diffraction (EBSD). Variables such as temperature, dwell time, atmosphere and flow rate were tuned to optimize the thermal etching method while maintaining phase purity, e.g., not decomposing LLZO grains.

Al-LLZO pellets were densified by rapid induction hot pressing, followed by grinding and polishing. Surface heat treatment was conducted to reduce the concentration of Li₂CO₃ and LiOH layers that readily form after LLZO is exposed to air (2) before thermal etching. Scanning Electron Microscope (SEM) was used to see the grain boundaries and determine the grain size of the surface of the thermal etched LLZO pellets and X-Ray Diffraction to analyze phase purity. EBSD was conducted to confirm that the features observed in thermally etched LLZO surface correspond to grain boundaries. Additionally, TGA-Mass Spectrometry was used to correlate the mass loss to the chemistry of the volatilized compounds during thermal etching of LLZO. Furthermore, Electrochemical Impedance Spectroscopy (EIS) measurements were conducted to evaluate that the ionic conductivity of LLZO remains unchanged after completing the thermal etching process.

It is believed that the thermal etching method developed and optimized in this work can be used as a simple technique to examine the microstructure of LLZO and perhaps other polycrystalline electrolytes.

References

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8:45 AM ET01.01.04

Bottleneck of Diffusion and Inductive Effects in $\text{Li}_{10}\text{Ge}_{1-x}\text{Sn}_x\text{P}_2\text{S}_{12}$ Thorben Krauskopf, Sean P. Culver and Wolfgang G. Zeier; Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen, Gießen, Germany.

Solid state electrolytes are currently being intensively investigated for the possible application in solid-state batteries.¹ Among all known solid Li^+ conductors, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) is one of the most promising candidates due to its unrivaled high ionic conductivity of 12 mS cm^{-1} and successful implementation into solid state batteries.^{2,3} Therefore, there is a great interest to further optimize the Li^+ mobility and to reduce the costly germanium content using different doping strategies in related structures. Unfortunately, increasing the Sn fraction in $\text{Li}_{10}\text{Ge}_{1-x}\text{Sn}_x\text{P}_2\text{S}_{12}$ leads – counter to chemical intuition – to a reduction in the ionic conductivity.⁴

The present work reveals the structural and lattice dynamical reasons for the observed behavior.⁵ Solid solutions of $\text{Li}_{10}\text{Ge}_{1-x}\text{Sn}_x\text{P}_2\text{S}_{12}$ were synthesized and structural changes and their resulting impacts on the Li^+ transport property were investigated using a combination of structural refinements, ultrasonic speed-of-sound measurements and AC impedance spectroscopy. It is shown that while the lattice volume and the c/a ratio of the compounds increase with increasing Sn^{4+} fraction, the ionic conductivity decreases. Taking a deeper look into the local bonding properties reveals that a bottleneck of the diffusion channels along the z -direction tightens. In addition, a softening of the lattice with the more polarizable Sn^{4+} cation was observed similar to other classes of lithium and sodium thiophosphate solid electrolytes.^{6,7} But in this case the softening of the anion backbone leads to stronger $\text{Li}^+ - \text{S}^{2-}$ Coulombic interactions, that can be understood with the concept of inductive effects. Overall this work demonstrates, that chemical intuition can struggle in the understanding of structure property relationships and that a deeper look into the local bonding properties is necessary for the future design of solid electrolytes.

References

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- 5 T. Krauskopf, S. P. Culver and W. G. Zeier, *Chem. Mater.*, 2018, 30, 1791–1798.
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- 7 M. A. Kraft, S. P. Culver, M. Calderon, F. Böcher, T. Krauskopf, A. Senyshyn, C. Dietrich, A. Zevalkink, J. Janek and W. G. Zeier, *J. Am. Chem. Soc.*, 2017, 139, 10909–10918.

9:00 AM *ET01.01.05

Interfacial Effects on Storage and Transport in Batteries Jochaim Maier; Max Planck Institute for Solid State Research, Stuttgart, Germany.

After a brief introduction into the bulk situation, ionic and electronic charge carrier distribution is discussed for various interfaces of interest in batteries (electrode/electrolyte; electrode/passivation layer; passivation layer/electrolyte; boundaries within electrode, electrolyte or passivation phases; solid electrolyte grain boundaries). Modified carrier concentrations are of significant influence on charge transport (conductivity) and transfer (transfer resistance) and hence indirectly for the storage behavior.

However, space charge zones can be also of great significance for the storage directly. The extreme case is met if the abrupt contact of two phases allows for storing Li or Na in a job-sharing way even if none of the two phases allows for storage isolatedly. This is relevant the more so since this storage can be extremely fast. Thermodynamics and kinetics of this storage mode are set out in greater detail [1-4].

Finally, heterointerfaces are also of enormous relevance for the internal circuitry of electrodes. Even for ideal interfaces the distribution topology of electronic or ionic current collecting phases is—as will be discussed in the context of the wiring-length concept—decisive for the network efficiency [5].

References

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9:30 AM *ET01.01.06

Sussing out Important Parameters for Cathode Coatings in All-Solid-State Batteries Lincoln Miara; Samsung Electronics, Burlington, Massachusetts, United States.

Recent computation and experimental works have discovered a remarkable array of materials with superionic conductivities that rival or exceed the conductivity of conventional liquid electrolytes such as Li and Na conducting NASICON-type oxides, Li garnets, sulfides and thiophosphate materials. Unfortunately, the high ionic conductivity often is associated with a penalty of high impedance at interfaces between electrolyte and electrodes; this interfacial impedance can dominate the internal resistance in many systems. High impedance is found both in thiophosphate electrolytes in contact with oxide cathodes and during high temperature processing of oxide electrolytes co-sintered with oxide cathodes. Because of the necessity of maintaining low interfacial impedance for high power applications, we have focused on understanding the reactions occurring at the various interfaces. This talk will focus on the application of cathode coatings discovered by computational thermodynamic methods. Experimental evidences of interfacial products and degradation phenomena gathered via electrochemical, spectroscopic, and TEM analysis will be compared to predictions. We use these results to identify the factors that contribute most to forming stable interfaces and easy processing for use in high voltage all solid state battery systems.

10:00 AM BREAK

10:30 AM *ET01.01.07

Nanoscale Composite Polymer Electrolyte Batteries Yi Cui; Stanford University, Stanford, California, United States.

Solid polymer electrolyte has excellent processibility although its ionic conductivity and mechanical strength needs to be improved. Here I will present our recent progress on nanoscale design of using nanomaterials to form composite polymer electrolyte to improve both ionic conductivity and mechanical strength. Nanomaterials include nanowires and porous anodized alumina. Organic-organic composite electrolyte is also explored. We use successfully these solid electrolytes for Li metal batteries.

11:00 AM ET01.01.08

Fabrication of Advanced Composite Cathodes in All-Solid-State Batteries Using 3D Reconstruction Analysis and Complementary Wet-Based Process [Sungjun Choi](#)^{1,2}, [Wo Dum Jung](#)¹, [Minjae Jeon](#)¹, [Seong-Min Kim](#)¹, [Ji-Su Kim](#)¹, [Byung-Kook Kim](#)¹, [Byoung-In Sang](#)² and [Hyoungchul Kim](#)¹; ¹High-Temperature Energy Materials Research Center, Korea Institute of Science and Technology, Seoul, Korea (the Republic of); ²Department of Chemical Engineering, Hanyang University, Seoul, Korea (the Republic of).

Next-generation Li-ion battery (LIB) applications such as electric vehicles, unmanned aerial vehicles, energy storage systems, and integrated power devices for the Internet of Things require the development of technologies that allow the storage of electrical energy at safer and higher energy densities over a wider range of operating temperatures. In this context, all-solid-state battery (ASSB) technologies have the advantage of eliminating the organic electrolyte from the existing secondary battery in addition to incorporating solid-state materials for all components, thereby meeting all requirements for next-generation LIB applications. The composite cathode of an ASSB composed of various solid-state components (i.e., the active material, electrolyte, conductive additive, and etc.) requires a dense microstructure and highly-percolated solid-state interface different from that of a conventional liquid-electrolyte-based Li-ion battery. Indeed, the preparation of such a system is particularly challenging.

In this study, quantitative analyses of composite cathodes by three-dimensional (3D) reconstruction analysis were performed beyond the existing qualitative analysis, and their microstructures and reaction interfaces were successfully analyzed. Interestingly, various quantitative values of structure properties (such as the volume ratio, connectivity, tortuosity, and pore formation) associated with material optimization and process development were predicted, and they were found to result in limited electrochemical charge/discharge performances. We also verified that the effective two-phase boundaries (TPBs) were significantly suppressed to ~23% of the total TPB, due to component dispersion and packing issues. In addition, we have developed a pore decomposition process (PDP) that tracks the origins of pore structures using quantitative values of a 3D reconstruction structure. The solid electrolyte and cathode active material showed a noticeable difference in the ratio of induced pore volume: 43% of the total pore from solid electrolyte and 56% from active material. To solve the observed problems such as formation of pores, we adopted a wet-synthesis process of sulfide solid electrolyte on fabricating composite cathode. The introduction of a new wet-based solid electrolyte improved the microstructure of the composite cathode by eliminating pores, increasing interfacial contact area, and mitigating inhomogeneous mixing. Therefore, the enhanced microstructure provide a better ionic conduction pathway, resulting in higher electrochemical cell performance. The pore formation, the powder characteristics, and the process optimization of composite cathode are closely related, and the quantitative analysis results from 3D reconstruction process provide relevant insights.

11:15 AM ET01.01.09

Effect of Microstructure on the Critical Current of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [Jeff Wolfenstine](#); Army Research Laboratory, Adelphi, Maryland, United States.

Li-ion conducting solid-state batteries based on a $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) solid-state electrolyte combined with a Li-metal anode have attracted considerable attention because they offer the advantages of higher energy and enhanced safety compared to the current Li-ion batteries. One of the major issues the with Li/LLZO system is determining what LLZO microstructural variables influence the critical current (current at which lithium dendrites/filaments form on charging). For a single-phase material the major microstructural variables are porosity and grain size. For a solid-state electrolyte a high relative density is required thus, the major microstructural variable is the grain size. It is the purpose of this presentation to discuss the effect of grain size (5 to 600 nm) on the room temperature critical current of LLZO and by examining the effect of grain size on ionic conductivity and fracture toughness and determine which of these properties has a major influence on the critical current for hot-pressed high relative density (>97%) $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$.

11:30 AM ET01.01.10

Phase-Field Simulations of Lithium Dendrite Growth with Open-Source Software [Zijian Hong](#) and Venkatasubramanian Viswanathan; Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Dendrite growth is a long-standing challenge that has limited the applications of rechargeable lithium metal electrodes. Here, we have developed a grand potential based nonlinear phase-field model to study the electrodeposition of lithium as relevant for a lithium metal anode, using open-source software package MOOSE. The dynamic morphological evolution under large/small overpotential is studied in 2-dimensions, revealing important dendrite growth/stable deposition patterns. The corresponding temporal-spatial distributions of ion concentration, overpotential and driving force are studied, which demonstrate an intimate, dynamic competition between ion transport and electrochemical reactions, resulting in vastly different growth patterns. Given the importance of morphological evolution for lithium metal electrodes, wide-spread applications of phase-field models have been limited in part due to in-house or proprietary software. In order to spur growth of this field, we utilize an open-source software package and make all files free available online to enable future studies to study the many unsolved aspects related to morphology evolution for lithium metal electrodes.

11:45 AM ET01.01.11

Crosslinked Poly(tetrahydrofuran) as a Loosely-Coordinating Solid Polymer Electrolyte [David Mackanic](#)¹, [Yi Cui](#)² and [Zhenan Bao](#)¹; ¹Chemical Engineering, Stanford University, Stanford, California, United States; ²Materials Science and Engineering, Stanford University, Stanford, California, United States.

Solid polymer electrolytes (SPEs) promise to improve the safety and performance of lithium ion batteries (LIBs). However, the low ionic conductivity and transference number of conventional poly(ethylene oxide) (PEO) based SPEs preclude their widespread implementation. Herein, we introduce crosslinked poly(tetrahydrofuran) (xPTHF) as a promising polymer matrix for “beyond PEO” SPEs. The crosslinking procedure creates thermally stable, mechanically robust membranes for use in LIBs. Molecular Dynamics and Density Functional Theory (DFT) simulations accompanied by ⁷Li NMR measurements show that the lower spatial concentration of oxygen atoms in the xPTHF backbone leads to loosened O-Li⁺ coordination. This weakened interaction enhances ion transport; xPTHF has a high lithium transference number of 0.53 and higher lithium conductivity than a xPEO SPE of the same length at room temperature. We demonstrate that organic additives further weaken the O-Li⁺ interaction, enabling room temperature ionic conductivity of 1.2×10^{-4} S cm⁻¹ with 18 wt.% DMF in xPTHF. In a solid state LIB application, neat xPTHF SPEs cycle with near theoretical capacity for 100 cycles at 70 °C, with rate capability up to 1C. The plasticized xPTHF SPEs operate at room temperature while maintaining respectable rate capability and capacity. The novel PTHF system

demonstrated here represents an exciting platform for future studies involving SPEs.

SESSION ET01.02: Session II
Session Chairs: Liwei Chen and Hong Li
Monday Afternoon, November 26, 2018
Hynes, Level 3, Room 310

1:30 PM ET01.02.01

Band Edge Considerations for Interfacial Stability Between Sulfide Solid Electrolytes and Li Metal Anodes Haesun Park and Donald Siegel; Univ of Michigan, Ann Arbor, Michigan, United States.

Despite their high energy density, Li metal anodes have not been successfully commercialized due to dendritic Li plating during charging. However, recent developments in Li-ion conducting solid electrolytes have rekindled interest in the use of Li metal anodes. In particular, sulfide solid electrolytes (SSEs) are attractive materials due to their high ionic conductivities, low grain boundary resistance, and mechanical strength. However, SSEs are readily reduced by Li metal, calling into question their viability. Here, the interfacial stability between SSE and Li metal anodes is investigated computationally using the concept of band edge alignment. First-principles calculations were performed using many body perturbation theory to evaluate the position of the conduction band minimum (CBM) in various SSEs. These levels are compared with the Li/Li⁺ electrochemical potential in order to evaluate the likelihood charge injection (i.e., reduction) from Li anodes. Our calculations reveal that reduction by Li is preferred for Li₁₀GeP₂S₁₂, Li₁₀SnP₂S₁₂, Li₃PS₄, Li₄GeS₄, and Li₄SnS₄. Although the position of the CBM is sensitive to the surface features of the SSE, varying the surface composition appears to be insufficient to prevent reduction. In addition to predicting CBM positions, the full band gaps of several SSEs were evaluated. Band gap values range from 4.0 eV in Li₁₀SnP₂S₁₂ to 4.8 eV in Li₃PS₄. Finally, we discuss the implications of our findings for interfacial reactions between SSEs and Li metal.

1:45 PM ET01.02.02

New Liquid Synthesis of Solid-State Electrolytes for the Next Generation Batteries Hui Wang, Dominika A. Ziolkowska, William Arnold, Mahendra Sunkara and Thad A. Druffel; University of Louisville, Louisville, Kentucky, United States.

All-solid-state batteries (ASSBs) are intensively studied as next-generation lithium battery systems and have made remarkable progress in recent years. Lithium argyrodites are relatively new and very promising class of sulfide-based lithium ion superconductors. They prove their high ionic conductivities and suitable electrochemical stability. In general, more convenient manufacturing methods for solid state electrolytes synthesis and their coating processing are highly desirable. Since up-to-date melt-quenching and high-energy ball milling methods are the most common laboratory approaches, a study on the solution synthesis method is still a milestone.

In this study argyrodite Li₇PS₆ solid-state electrolyte was synthesized using new liquid synthesis approach. Similarly to the ball-milling methods, the molar ratio can be used to obtain this product, whereas the reaction time and homogeneity of the material is significantly improved. The total time of the preparation does not exceed 3 h. This argyrodite electrolyte has the best conductivity (0.11 mS cm⁻¹ at RT) among argyrodite materials prepared by liquid method, the most probably due to its purity and homogeneity. This material is stable in the electrochemical window up to 5 V. The quick preparation, easy processing, and thin film casting from a liquid phase possibility makes Li₇PS₆ an attractive electrolyte candidate in the all-solid-state battery industry.

2:00 PM *ET01.02.03

New Solid State Na⁺ Ion Conducting Glassy Solid Electrolytes and Their Use in All-Solid-State Sodium Batteries Steve W. Martin; Materials Science & Engineering, Iowa State University, Ames, Iowa, United States.

Recent challenges and problems of explosions and fires with organic liquid electrolyte based batteries has renewed interest in all solid state batteries which replace the highly conducting but also highly flammable and volatile organic liquid electrolyte with an all solid state electrolyte. There are many such solid electrolytes and one of particular interest due to its low cost of manufacturing are glassy solid electrolytes. In this talk, I will give an overview of glassy solid electrolytes with a particular emphasis on highly conducting sulfide-based chemistries and show recent results from our laboratory on using these solid electrolytes in new all solid state sodium batteries in their application for low cost safe high energy density storage for electrical grid application.

2:30 PM ET01.02.04

Epitaxial Li₄Ti₅O₁₂ Thin Film as Model System for Li-Ion Conductivity Francesco Paganì^{1,2}, Evelyn Stilp¹, Reto Pfenninger^{2,3}, Eduardo Cuervo Reyes¹, Arndt Remhof¹, Zoltan Balogh-Michels¹, Antonia Neels¹, Jordi Sastre Pellicer¹, Michael Stiefel¹, Max Döbeli⁴, Marta D. Rossell¹, Rolf Erni¹, Jennifer L. Rupp^{2,3} and Corsin Battaglia¹; ¹Empa-Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland; ²Electrochemical Materials, ETH Zürich, Zürich, Switzerland; ³Department of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ⁴Ion Beam Physics, ETH Zürich, Zürich, Switzerland.

Thin-film all-solid-state batteries provide a model system for the fundamental study of Li-ion transport, defect chemistry [1], and electrochemical stability [2] and find applications in smart cards, sensors, and radio-frequency identification tags [3]. Here we compare the Li-ion conductivity of epitaxial and polycrystalline Li₄Ti₅O₁₂ thin films (≈ 125 nm thick) and investigate the impact of grain boundaries on Li-ion conductivity. Phase-pure epitaxial and polycrystalline Li₄Ti₅O₁₂ thin films were grown on (111) oriented MgO substrates and on polycrystalline MgO, respectively, by pulsed laser deposition. The Li content across the films was quantified by time-of-flight secondary ion mass spectrometry calibrated by elastic recoil detection analysis. Transmission electron microscopy shows that the Li₄Ti₅O₁₂ grows with no strain on the MgO(111) substrate. Using out-of-plane and in-plane X-ray diffraction, we prove epitaxy of Li₄Ti₅O₁₂ on MgO(111) and characterize the polycrystalline film, quantifying texture and estimating an average in-plane grain size lower than 10 nm. Temperature dependent impedance spectroscopy measurements show that the epitaxial film behaves like an ideal Li-ion conductor that can be described by an equivalent parallel RC circuit with a DC conductivity of 1.73×10⁻⁴ S/cm at 300°C and activation energy of 0.79 eV. In contrast, the polycrystalline film exhibits a more complex frequency response, with contributions from the bulk and grain boundary processes, resulting in subdiffusive behavior. We discuss strategies and next steps required to integrate epitaxial anode Li₄Ti₅O₁₂ into a thin-film all-solid-state battery.

References:

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2:45 PM ET01.02.05

Transition Metal Sulfide Nanostructures (CuS, MoS₂) as Conversion Electrodes for Rechargeable All-Solid-State Batteries [Aggunda Lingamurthy Santhosha](#)³, Raimund Koerver², Kilian Pollok¹, Falko Langenhorst¹, Juergen Janek² and Philipp Adelhelm³; ¹Institute of Geosciences, Friedrich Schiller University Jena, Jena, Germany; ²Institute of Physical Chemistry, Justus-Liebig-University Giessen, Giessen, Germany; ³Institute for Technical Chemistry and Environmental Chemistry, Friedrich-Schiller-University, Jena, Germany.

Electrochemical energy storage devices have attracted wide attention for energy conversion and storage. Over the past several decades, the success of the lithium-ion batteries (LIBs) has triggered the revolution of personal electronics and significantly changed our lifestyle. However, further progress in battery technology is still needed and great efforts are devoted to improve energy density, cycle life, cost and safety.

Among the various types of rechargeable batteries for future applications, the all-solid-state configuration using inorganic solid electrolytes (SE) has become a promising option. Research in this field is mainly motivated by the promise to further increase the energy density as well as the safety characteristics compared to today's battery technology. However, all-solid-state batteries still fall short of expectation largely because of limited interface kinetics and interface stability. Moreover, processing of the materials and preparation of the cells needs to be significantly improved to reach higher energy densities and/or lower price compared to conventional cells with liquid electrolytes. In particular, sulfide-based SEs are strongly investigated due to their high ionic conductivity and ductility. The SE Li₃PS₄ (LPS) exhibits an acceptable ionic conductivity of 10⁻³ to 10⁻⁴ mS cm⁻¹ at room temperature as well as low grain boundary resistance even under cold pressing conditions. In our study, we combine LPS with different transition metal sulfides as cathode active materials. The attractiveness of such materials lies in their high specific capacity of their reaction with lithium. The transition metal sulfides react with lithium in a conversion reaction described by the general formula M_nS + (n) Li ↔ aM + Li_nS (M = transition metal, e.g. Mn, Fe, Cu, Ni, Co, Zn, Mo). The performance of the all-solid-state batteries is evaluated with respect to capacity, cycle life and rate capability and reversible capacities of several hundred mAh g⁻¹ are demonstrated. Additionally, the impact of the electrode composition and cathode loading on the cell performance is evaluated. At last, we discuss analogue cells with sodium as charge carrier ion.

3:00 PM BREAK

3:30 PM *ET01.02.06

Atomically-Precise Interfacial Engineering of Solid-State Batteries [Neil P. Dasgupta](#); Department of Mechanical Engineering, University of Michigan, Ann Arbor, Michigan, United States.

Solid-state batteries have experienced a recent explosion in R&D, owing to their potential to improve safety and energy density. However, the requirements on an all-solid-state battery are stringent, as cells must simultaneously incorporate a high ionic conductivity electrolyte, form high performance interfaces against both anode and cathode materials, and exhibit stability against chemical, electrochemical, morphological, and mechanical evolution under a wide range of cycling conditions. In particular, it has been widely recognized that solid-state interfaces present unique challenges compared to traditional liquid electrolytes, including high interfacial impedances, evolution mechanical stresses due to solid-solid interfacial contact with active materials, and (electro)chemical instabilities that can arise from localized gradients in ionic and electronic concentrations.

To address this challenge, our group focuses on gaining new fundamental insights into the coupled phenomena occurring at interfaces, and applied this knowledge to rationally design interfacial chemistry to address the root cause of performance limitations. This is accomplished through a combination of experimental techniques, including *in situ/operando* analysis using optical and x-ray techniques, precise surface/interfacial energy measurements, and design of model interfaces to decouple factors that contribute to electrochemical behavior. Equipped with this knowledge, we employ atomically-precise interfacial modifications to rationally design interfacial chemistry.

In this talk, examples will be presented in both bulk solid-state battery interfaces [1], and thin film electrolytes deposited by Atomic Layer Deposition (ALD) [3,4]. By studying interfacial chemistry across length scales ranging from atoms to millimeters, we have been able to systematically identify the mechanisms of interfacial degradation. At bulk length scales, the coupled chemical/electrochemical/morphological evolution of a range of solid electrolytes will be discussed, including oxides, sulfides, and polymers. The link between surface chemistry, Li wettability, and interfacial impedance are quantitatively evaluated [1]. Trends and tradeoffs are observed in these systems, which represents a systems engineering problem to optimize overall battery performance. To modify these surfaces, ALD of solid electrolytes is demonstrated [2,3], which enables tunability of surface chemistry, morphology, and stability. These ALD electrolytes are demonstrated in both thin-film battery architectures and as interfacial layers against bulk solid electrolytes. Through this interdisciplinary approach of fundamental chemistry and applied engineering, strategies to address future interfacial challenges will be addressed, which will accelerate the pathway from laboratory science to scalable manufacturing.

1. A. Sharafi et al. *Chem. Mater.* **29**, 7961 (2017)
2. E. Kazyak et al. *Chem. Mater.* **29**, 3785 (2017)
3. E. Kazyak et al. *Submitted* (2018)

4:00 PM ET01.02.07

Highly Lithium-Ion-Conducting Halide Electrolytes for 4 V Class All-Solid-State Batteries and Their Conduction Path [Akihiro Sakai](#), Tetsuya Asano, Satoru Ohuchi, Masashi Sakaida, Akinobu Miyazaki and Shinya Hasegawa; Technology Innovation Division, Panasonic, Kadoma, Japan.

We recently reported that the solid halide electrolytes consisting of rightly-selected cations satisfy the high lithium ion conductivity, electrochemical stability, material stability, and deformability: all of which are simultaneously required properties for solid electrolytes for application in all-solid-state batteries (ASSBs).[1] The ionic conductivity of the halide electrolytes surpassed 1 mS/cm. The bulk-type ASSBs fabricated with cold-pressed method exhibited excellent performances: higher than 94 % coulombic efficiency with 4-V class cathode active materials as well as discharge capacity retention higher than 98 % for 100 cycles. These superior material property as well as excellent battery performance indicate that the halide electrolytes are another good candidate for the solid-state electrolyte for ASSB application other than sulfides and oxides.

Here, we will report the identified crystal structures of these halide electrolytes and the ionic conduction path to elaborate the relationship of lithium ionic conductivity and the crystal structure of these halide electrolytes. Interestingly, the crystal structures of these highly lithium-ion-conducting halide materials do not satisfy the "criteria for high ionic conductivity" of sulfide electrolytes which is BCC-like arrangement of anion sublattice. [2] On the other hand, these halide electrolytes consist of nearly close-packed anion sublattice, and yet, still show as high lithium ionic conductivity as 0.1 - 1 mS/cm. The simulated ionic conduction paths understandably indicate that cation-cation coulombic repulsion reduces the available conduction paths and alters the crystallinity-conductivity relationship. These results indicate that the design principles of the halide electrolytes for high ionic conductivity differ from previously reported sulfide or oxide electrolytes.

References:

[1] T. Asano et al., 233rd ECS meeting, May 2018, Seattle.

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4:15 PM ET01.02.08

Flexible Solid-State Ion Conducting Membrane with Garnet Nanostructures Kun Fu; Mechanical Engineering, University of Delaware, Newark, Delaware, United States.

Beyond state-of-the-art lithium-ion battery (LIB) technology with metallic lithium anodes to replace conventional ion intercalation anode materials is highly desirable because of lithium's highest specific capacity (3,860 mA/g) and lowest negative electrochemical potential (~3.040 V vs. the standard hydrogen electrode). In this work, we report for the first time, to our knowledge, a 3D lithium-ion-conducting ceramic network based on garnet-type $\text{Li}_{6.4}\text{La}_3\text{Zr}_2\text{Al}_{0.2}\text{O}_{12}$ (LLZO) lithium-ion conductor to provide continuous Li^+ transfer channels in a polyethylene oxide (PEO)-based composite. This composite structure further provides structural reinforcement to enhance the mechanical properties of the polymer matrix. The flexible solid-state electrolyte composite membrane exhibited an ionic conductivity of 2.5×10^{-4} S/cm at room temperature. The membrane can effectively block dendrites in a symmetric Li | electrolyte | Li cell during repeated lithium stripping/plating at room temperature, with a current density of 0.2 mA/cm² for around 500 h and a current density of 0.5 mA/cm² for over 300 h. The presentation will focus on our recent development of 3D garnet nano structured solid-state electrolyte membrane for Li metal batteries.

4:30 PM ET01.02.09

PEO/Perovskite Composite Electrolyte with Enhanced Li^+ Conductivity Henghui Xu, Yutao Li, Nan Wu and John Goodenough; The University of Texas at Austin, Austin, Texas, United States.

Rapid developments in electric road vehicles and grid energy storage are boosting the development of long-life, high-energy-density lithium-ion batteries (LIBs) with high safety. Replacing the liquid electrolyte in conventional LIBs with solid electrolytes can not only address the limitation of leakage and flammability but also guarantee a long cycle life because of the stable structure of the all-solid-state components. Moreover, LIBs built with solid electrolytes may achieve high energy density by using a Li-metal anode and commercially available cathodes. However, there are no ideal solid electrolytes so far that possess both high Li^+ conductivity and small interfacial resistance. Composite polymer electrolytes (CPE) prepared by incorporating ceramic nanoparticles into polymer matrix have been deemed an effective way to simultaneously enhance ionic conductivity, improve the electrochemical stability, and reduce the critical interfacial resistance between electrodes and electrolytes. Unfortunately, most reported Li^+ conductivities of composite polymer electrolytes are still lower than 1×10^{-5} S cm⁻¹ at room temperature.

We reported a flexible composite polymer electrolyte with an enhanced conductivity of 4×10^{-5} S cm⁻¹ at room temperature by blending a perovskite solid electrolyte with a PEO polymer electrolyte. The addition of perovskite not only helps to reduce the polymer crystallinity and increase the mechanical strength but also constructs a strong bond with the anions in Li salts. As a result, many more lithium ions are released from the Li salts to render a much higher ion conductivity. Surface-sensitive techniques are carried out to directly visualize and probe the stable interphase formed between the CPE and electrodes, which improves the Li^+ transfer across the interface. A symmetric Li/Li cell and an all-solid-state LiFePO_4 cell with the CPE show small overpotentials, high Coulombic efficiencies, and stable cycling performance at 40 °C

4:45 PM ET01.02.10

Garnet Electrolyte Coated with a Single-Li+-Conducting Polymer for All-Solid-State Lithium Batteries Weidong Zhou; Beijing University of Chemical Technology, Beijing, China.

To meet the requirements of high energy density, safety and long cycle life, it is necessary to replace the organic flammable electrolyte and graphite anode of the Li-ion battery by a solid electrolyte and metallic-lithium anode that can be plated/stripped reversibly without lithium-dendrite formation. Garnet electrolyte with a high room-temperature Li-ion conductivity and a good stability against lithium metal suffers from the huge interfacial resistance and fast lithium-dendrite growth. A Li^+ conducting polymer with a high Li^+ transport number of 0.9, which was coated on the surface of garnet electrolyte as an artificial SEI layer, not only reduced the Li metal anode/garnet interfacial impedance but also suppressed the formation and growth of lithium dendrites along the garnet grain boundaries. In all-solid-state Li/LiFePO₄ cells, a high Coulombic efficiency near 100% was achieved for long cycling. These tests show the feasibility of a safe Li-metal rechargeable battery having an appropriate single Li^+ conducting polymer SEI between a ceramic electrolyte and the metallic lithium anode.

SESSION ET01.03: Session III

Session Chairs: Jennifer Rupp and Venkataraman Thangadurai

Tuesday Morning, November 27, 2018

Hynes, Level 3, Room 310

8:15 AM ET01.03.01

The Structure and Conductivity of 3D Superionic Na₃SbS₄ Conductor at Extremely Low Temperatures Hui Wang¹, Yan Chen², Zachary D. Hood^{2,3,4}, Jong K. Keum², Amaresh Pandian², Miaofang Chi², Ke An², Chengdu Liang⁵ and Mahendra Sunkara¹; ¹University of Louisville, Louisville, Kentucky, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ³Georgia Institute of Technology, Atlanta, Georgia, United States; ⁴Electrochemical Materials Laboratory, Massachusetts Institute of Technology, Boston, Massachusetts, United States; ⁵College of Chemical and Biological Engineering, Zhejiang University, Hangzhou, China.

Overcoming the solid-liquid state transition of the liquid electrolyte in state-of-the-art batteries represent a grand challenge for the next-generation energy storage. All-solid-state batteries that employ superionic solid conductor potentially enable the broadening of battery operation in harsh environments, such as under sub-zero temperatures and even lower. The solid electrolyte as the key component requires structural stability, high-efficiency of ion transportation channels, and low activation energy to maintain the fast-ionic conduction against temperature drop. Compared to one-dimensional (1D) conductive chain, a three-dimensional (3D) framework of ion-conduction tunnel is more favorable structure for solid conductors to work at subzero temperature range. The tetragonal Na₃SbS₄ is such a superionic conductor that holds 3D tunnel network for Na-ion transportation and exceptionally low activation energy of 0.205 eV. In this work, we use Na₃SbS₄ as a model system to investigate the structure stability and Na-ion conduction paths of 3D superionic conductor at extreme low temperature (20 K) via cryogenic neutron and X-ray diffractions. Cryogenic *in-situ* neutron and X-ray diffractions reveal that Na₃SbS₄ maintains a stable tetragonal crystal structure and the anisotropic lattice contraction upon cooling. The evolution of S-gate, where Na ions hop through in the 3D transportation network, is found to maintain open sizes in the *xy*-plane, contributing to the low activation energy and impressive

ionic conductivity. The Na-ion transportation network is demonstrated to be directionally accessible at the extremely low temperature, which reveals the mechanism of the superior ionic conductivity at broadened temperature range in the view of structure. These findings provide valuable guidance in the search for materials as promising solid electrolyte in solid-state batteries to fulfill harsh environmental needs.

8:30 AM ET01.03.02

Exploring a New Horizon for Lithium Anodes in Combination with Solid Electrolytes Keita Niitani, Patrick Bonnick, Koji Suto, Timothy S. Arthur and John Muldoon; Toyota Research Institute of North America, Ann Arbor, Michigan, United States.

The holy grail of battery research is the coupling of a metal negative electrode with a high capacity positive electrode to produce a cell with higher energy density than lithium-ion cells. Sulfur cathode has a high theoretical capacity of 1672 mAh g^{-1} and a theoretical energy density of 2500 Wh kg^{-1} in a lithium sulfur (Li-S) battery. Li-S batteries are tormented by several challenges, most notably the dissolution of polysulfide in to the electrolyte during the reduction of sulfur and the growth of lithium dendrite during charging. [1,2,3] A paradigm shift is required to completely block or avoid polysulfide dissolution, one option is to use inorganic solid electrolyte such as lithium thiophosphate in place of the liquid electrolyte. [4,5] Lithium thiophosphate solid electrolyte has a narrow potential window which make thermodynamically incompatible with lithium metal anode. [6] We will discuss how the lithium/solid electrolyte interface and electrolyte structure can dramatically affect the stripping/plating of lithium metal. The challenges associated with using the lithium thiophosphate electrolyte in Li-S battery will also be examined.

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8:45 AM ET01.03.03

Li⁺ Ion Conduction Mechanisms of Li⁺-Doped NaI and Its Electrochemical Properties Reona Miyazaki¹, Isao Sakaguchi² and Takehiko Hihara¹; ¹Nagoya Institute of Technology, Nagoya, Japan; ²National Institute for Materials Science, Tsukuba, Japan.

From the early stage of the research, solid electrolytes for the all-solid-state lithium ion batteries have been developed mainly based on the Li compounds. On the other hand, we have been evidenced that the solid electrolytes can also be fabricated by the doping of Li compounds to “Li-free” compounds like the liquid electrolytes prepared by the dissolution of a given ionic salt into the carrier-free liquid solvents. These types of solid electrolytes are so-called “Co-ionic conductor”, where the small doped guest ions play a major role for the ion conduction in the host materials [1]. From our previous research, it has been shown that both NaI and KI become pure Li⁺ ion conductors via doping 6 mol% of LiBH₄, whose conductivity value exceeds that of LiI [1, 2]. However, the details of the ion conduction mechanisms in NaI-LiBH₄ system, especially for the host Na⁺ ions are not well understood. The purpose of the present work is the investigation of the ion conduction mechanisms in NaI-LiBH₄ systems. The electrochemical stability will be also investigated as a function of the concentration of LiBH₄.

NaI-LiBH₄ systems were fabricated by ball-milling. The given molar ratio of NaI and LiBH₄ (Aldorich Co) were mechanically milled at 400 rpm with 10 pieces of balls in a chrome still pot (45 ml). The total milling time was 5 hours. In order to investigate the conduction mechanism of Li⁺ and Na⁺ ions separately, all-solid-state half-cell was fabricated using the sputtered amorphous Si (*a*-Si) film and 15NaI_LiBH₄ as an anode material and a solid electrolyte, respectively. Li foil was used as a counter electrode. After charging, the half-cell was deconstructed and the Si film was collected in a glove box. Subsequently, the depth profile inside the charged Si film was investigated by SIMS measurement. Cyclic voltammetry was performed using Mo and Li foils as a working and counter electrode, respectively.

During the charging of *a*-Si film, two kinds of plateau regions were observed at around 0.2 and 0.1 V vs. Li⁺/Li, which are the typical lithiation curves for *a*-Si film [4]. From the SIMS measurement inside the charged Si film, it was confirmed that ⁶Li⁺ ions are mainly detected. The steady state charging of Li⁺ ions can be attained by the constant transport of the Li⁺ ions in NaI. Hence, the main conduction carrier in the NaI doped with 6 mol% of LiBH₄ was proven to be the small doped Li⁺ ions. On the other hands, ²³Na⁺ ions were also detected inside the Si film although the signal intensity was three orders of magnitude smaller than that of ⁶Li⁺ ions. The detailed conduction mechanism and electrochemical stability of NaI-LiBH₄ systems will be shown in the presentation.

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9:00 AM *ET01.03.04

Electrochemomechanical Failure in Active Materials and Solid Electrolytes Yet-Ming Chiang; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The pursuit of high energy density and long life in rechargeable lithium batteries has exposed several modes of failure due to electrochemical-mechanical coupling. This talk will discuss specific examples in intercalation cathode and inorganic solid electrolytes, and potential failure-mitigation approaches.

It is now recognized that even active materials with much lower chemical expansion coefficients than the well-known extreme cases (e.g., Si or Sn and their alloys) undergo cycling induced fracture at the secondary particle level. The possible failure modes have been previously classified [1] and studied using macroscopic measurements such as acoustic emission [1,2]. Recently a methodology has been developed for measuring the electrochemical response of single electrode particles and directly observing the electrochemomechanical damage [3]. Applied to NMC333 and NCA particles, it is shown that the resulting single-particle kinetics are a trade-off between surface area increase, and loss of electrical continuity, both due to microscopic fracture at the secondary particle level.

Inorganic solid electrolytes undergo lithium metal penetration via an entirely different failure mode than classical dendrite formation in liquid electrolytes [4]. Although it has been argued that grain boundaries are a weak link along which Li metal preferentially penetrates, we show that even single crystals are highly susceptible to metal penetration from surface defects. Failure criteria such as the existence of a critical overpotential that are related to flaw size and the physical properties of the solid electrolyte can be tested using deliberately introduced surface flaws of controlled size. A new result to be discussed is the impact of field concentration effects at current collector discontinuities.

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9:30 AM ET01.03.05

Degradation Mechanisms of All-Solid-State Li-S Battery with $\text{Li}_6\text{PS}_5\text{Cl}$ [Saneyuki Ohno](#), Georg Dewald, Juergen Janek and Wolfgang G. Zeier; Institute of Physical Chemistry, Justus-Liebig-Universität Gießen, Gießen, Germany.

While the demand for batteries with a high energy density is rapidly growing, the current commercially available Li-ion battery chemistry is approaching a theoretical limit.¹ To overcome this issue, Li-S batteries exploiting the conversion reaction between sulfur and Li_2S have been attracting significant attention as a promising candidate of the next generation batteries.^{2–4} The history of the conventional Li-S battery development has been a fight against the notorious shuttle effect caused by polysulfides dissolved into the liquid electrolyte. However, a concept of all solid state batteries can physically hinder the polysulfide shuttle. Indeed the exhibit no evidence of the shuttle effect the all-solid-state Li-S battery cells, composed of Li-ion conducting thiophosphate (e.g. $\text{Li}_6\text{PS}_5\text{Cl}$), exhibit no evidence of the shuttle effect.

Nevertheless, there are still multiple challenges to achieve a high capacity and its good retention. One of the critical issues is a large capacity loss in the first battery cycle. A poor capacity retention over the long term cycling is another issue. In this study, we elucidated the degradation mechanisms of an all-solid-state Li-S battery employing $\text{Li}_6\text{PS}_5\text{Cl}$ as an electrolyte and achieved a significant improvement of the battery performance based on it. The deeper understanding of the underlying chemistry of the degradation mechanisms will lead to further enhancement of the capacity and cyclability of the all-solid-state Li-S batteries.

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9:45 AM ET01.03.06

Interface Engineering of the Garnet-Based Solid-State Batteries and *In Situ* Neutron Depth Profiling Diagnose [Chengwei Wang](#), Yunhui Gong, Hua Xie, Lei Zhang, Hao Wang, Eric D. Wachsman and Liangbing Hu; University of Maryland, College Park, Maryland, United States.

Garnet-based solid state electrolytes (SSEs) have attracted much attention for their high ionic conductivities and stability with lithium metal anodes. However, the high interfacial resistances between electrodes and garnet SSEs are one of the main challenges to develop all solid state lithium (Li) metal batteries. Herein, we develop several effective techniques to significantly improve Li-garnet interface and lead to an interface resistance as low as $\sim 7 \Omega \cdot \text{cm}^2$. We also develop an effective cathode-garnet interface using a mixed ionic-electronic (MIE) conductor, which enables cycling of all solid state batteries without a liquid or polymer electrolyte interface. The solution-processed two dimensional (2D) layered TiS_2 shows MIE conductivity after slow pre-lithiation, resulting in more than 20 times lower interfacial resistance. The all solid state batteries can work at high temperatures from 100 °C to 150 °C for 400 cycles at current densities up to 1 mA/cm². To reveal the interfacial behaviors of garnet SSE in contact of metallic Li, neutron depth profiling (NDP), a nondestructive and unique Li-sensitive technique, is used to *in situ* monitor Li plating-stripping processes. The NDP measurement has demonstrated the predictive capabilities for diagnosing short-circuits in garnet-based solid state batteries.

10:00 AM BREAK

10:30 AM *ET01.03.07

Dendrite-Free Lithium Metal Batteries Capable of Stable Operation at Elevated Temperature Based on Liquid Organic Electrolytes [Hong Li](#); Chinese Academy of Sciences, Beijing, China.

Rechargeable lithium metal batteries have attracted wide attention due to high theoretical energy density. For practical applications, high-temperature performance of lithium batteries is essential due to complex application environments, in terms of safety and cycle life. However, it's difficult for normal operation of lithium metal batteries at high temperature using current electrolyte systems. Herein, a kind of new electrolyte system is designed by adding two thermal-stable lithium salts together (i.e. LiTFSI and LiDFOB) into carbonate solvents with high boiling/flash point (i.e. EC and PC). Low ratio of LiPF₆ is also added to prevent the corrosion of Al current collector. The results indicate that the new electrolyte system possesses good high-temperature performance, meanwhile, it is beneficial to effectively suppress the formation of lithium dendrite. At a current density of 1.2 mA/cm², LiCoO₂ cathode with 2.4 mAh/cm² shows the capacity retention of 90% after 100 cycles at 80 °C in a lithium metal cell. Such performance is achieved for the first time for rechargeable lithium metal battery using liquid organic electrolyte. The enhanced cycling performance at elevated temperature is ascribed to effective protection of lithium metal by the generation of organic-inorganic composite solid-electrolyte interphase (SEI) on surface of lithium anode, formation of cathode electrolyte interphase (CEI) with high content of LiF on LiCoO₂ cathode and good stability of electrolyte itself. Its the first demonstration of dendrite-free Li metal battery capable of stable operation above 60 °C using liquid organic electrolyte. The improved cycling performance at elevated temperature based on the new electrolyte system is ascribed to effective protection of Li metal by the generation of organic-inorganic composite SEI on surface of Li anode, formation of CEI with high content of LiF on LiCoO₂ cathode and good stability of electrolyte itself. In addition, *in situ* solidification is also introduced to this system to form a solid electrolyte, which can improve the interfacial solid/solid contact significantly during cycling.

11:00 AM ET01.03.08

Interface Reverse Design in Solid-State Batteries for Metal Electrode Protection Yaosen Tian^{1,2}, Yingzhi Sun¹, Daniel Hannah², Yihan Xiao¹, Hao Liu³, Karen W. Chapman³, Shou-hang Bo² and Gerbrand Ceder^{1,2}; ¹Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; ²Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; ³Argonne National Laboratory, Argonne, Illinois, United States.

Recent years have witnessed the increasing demand for high-quality, safe, and low-cost rechargeable batteries. Metal-based solid-state batteries are particularly promising in this regard, where extremely high energy densities can be attained by utilizing metallic Li/Na anodes, and the use of a ceramic solid-state electrolyte membrane enables greatly enhanced battery safety. However, most solid-state electrolytes react with lithium and sodium metals, causing a continuous increase of the cell impedance and thus battery degradation. Therefore, passivation reaction with Li/Na metal is required for the electrolyte to achieve a relatively stable interface.

Herein, we present a 'reverse design' strategy to improve the stability of the interface between solid-state electrolytes and metal anodes. Using the advanced first-principles computational tools developed in our previous work, we identify a protective hydrate coating for solid electrolytes that would lead to the generation of passivating decomposition products upon contact of the electrolyte with metal electrodes. A significantly improved interface stability with the metal electrode of a hydrate-coated solid-state electrolyte is observed, compared with that of its non-hydrated counterpart. The buried interface between the surface-treated solid-state electrolyte and the metal electrode was characterized using *post-operando* synchrotron X-ray depth-profiling, providing spatially resolved evidence of the multilayered phase distribution in the metal-based symmetric solid-state cell. The experimental results are consistent with our theoretical predictions. In addition, we propose a general strategy of interface reverse design and discuss the possible pretreatment of the solid-state electrolyte using other chemicals.

11:15 AM ET01.03.09

Investigating the Effects of Lanthanum Concentration in Ta-Doped Li₇La₃Zr₂O₁₂ Solid Electrolyte Joseph M. Valle and Jeff Sakamoto; University of Michigan–Ann Arbor, Ann Arbor, Michigan, United States.

Solid electrolytes based on the garnet crystal structure have shown promise in the push to develop electrochemical cells utilizing lithium metal anodes due to their high lithium conductivity and stability against metallic lithium. One of these solid electrolytes is cubic phase lithium lanthanum zirconium oxide (LLZO). The critical doping of LLZO with tantalum at the zirconium site has been shown to stabilize the highly conductive cubic LLZO phase at room temperature Li_{6.5}La₃Zr_{1.5}Ta_{0.5}O₁₂. This critical doping has been shown to provide an optimal amount of lithium vacancies to stabilize the cubic phase without transitioning to the less conductive tetragonal phase of LLZO. While much work has been done to investigate the doping and charge balancing on the zirconium site, comparatively little focus has been paid to the lanthanum site. The effects of the sub stoichiometric use of lanthanum on the crystal structure of LLZO have yet to be characterized.

In this work, lanthanum content is varied in the LLZO structure Li_{6.5}La_{2+x}Zr_{1.5}Ta_{0.5}O₁₂ from x=0 to x=1.2. X-ray diffraction and electrochemical impedance measurements were performed in order to correlate the effect of lanthanum deficiency on crystal structure and electrochemical properties of LLZO. A linear increase in lattice parameter is observed until the stoichiometric composition (x=1.0) is achieved. An increase in conductivity is also observed ranging from .41mS/cm² at x=0.2 to .72mS/cm² at x=1.2.

11:30 AM ET01.03.10

Garnet and Anti-Perovskite Solid Electrolytes—Atomic-Scale Studies on Li-Ion Conduction, Surface Structures and Grain Boundaries Saiful Islam; University of Bath, Bath, United Kingdom.

Major advances in solid-state lithium batteries require the discovery and characterization of solid electrolyte materials. It is clear that a complete understanding of such materials requires greater fundamental knowledge of their underlying structural, ion transport and interface properties on the atomic- and nano-scales. For example, grain boundary effects on Li-ion transport are not fully understood. This talk will highlight recent studies [1-3] in two related areas: the influence of grain boundaries on Li-ion conduction in the Li-rich anti-perovskite Li₃OCl and the particle morphologies and lithium segregation to surfaces of the garnet Li₇La₃Zr₂O₁₂. A combination of advanced materials modelling techniques has helped us gain new insights into these complex materials, which are valuable in developing strategies to optimize their electrolyte properties.

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11:45 AM ET01.03.11

Very High Lithium Diffusion in LiTi₂(PS₄)₃ Through Energy Landscape Frustration Geoffroy Hautier¹, Davide Di Stefano¹, Anna Miglio¹, Koen Robeyns¹, Yaroslav Filinchuk¹, Marine Lechartier², Anatoly Senyshyn³, Hiroyuki Ishida⁴, Stefan Spammenberger⁵, Bernhard Roling⁵, Denise Prutsch⁶, Daniel Rettenwander⁶, Martin Wilkening⁶ and Yuki Kato²; ¹Université catholique de Louvain, Louvain-la-Neuve, Belgium; ²Toyota Motor Europe, Zaventem, Belgium; ³Technische Universität München, München, Germany; ⁴Toray Research center, Otsu, Japan; ⁵Marburg University, Marburg, Germany; ⁶TU Graz, Graz, Austria.

Solid-state materials with fast high ionic diffusion are necessary to many technologies including all-solid-state Li-ion batteries.

In this work, we demonstrate that LiTi₂(PS₄)₃ (LTPS) exhibits the largest Li-ion diffusion coefficient ever measured in a solid. We use extensive characterisation (neutron, X-ray diffraction, impedance and NMR) as well as theoretical studies to study the lithium diffusion in LTPS. We show for instance with recent X-ray data that the Li mobility is so high that low temperature is needed to freeze and observe the lithium ions positions. We rationalise the exceptional performances of this new superionic conductor through the concept of frustrated energy landscape. The absence of regular and undistorted lithium site to occupy leads to low energy barrier for diffusion as well as an exceptional pre-factor. We discuss how this frustration could be present in previously known ionic conductors and be used to search and design new structural families of superionic conductors.

1:30 PM ET01.04.01

Fast Ion Transport Tunnels in Solid-State Crystalline Electrolytes [Yan Chen](#)¹, Hui Wang² and Ke An¹; ¹Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²University of Louisville, Louisville, Kentucky, United States.

Fast solid ionic conductor electrolytes are key enablers of all-solid-state batteries, which potentially possess high energy density and diminish safety concerns during battery operation in large scale energy storage system. Compared to liquid electrolytes, low ionic conductivity is one of the critical issues in solid electrolyte development. Understanding its origin of potential high ionic conductivities provides insight of designing better electrolytes. The ionic transportation efficiency in solid crystals depends on the accessible tunnels in the structure as well as the active vacancy for ion hopping. Via neutron and X-ray diffraction, the ionic transport tunnels, from one-dimension to three-dimension, can be revealed in typical oxide- and sulfide-base light ionic (Li^+ , Na^+) conductors. The directions of the ionic transport have strong correlation with the lattice symmetry and the atomic arrangement in those solid conductors. The effective ion tunnel and the active vacancy quantity can be altered by neighboring aliovalent dopants, which is manipulated for optimal ionic conductivity in the solid electrolyte. The tunnel accessibility is also influenced upon temperature change, due to the tuned framework structure. The evolutions of the tunnel size and the anisotropic oscillation of charge carrier ions indicate the possible dimensional change of the transport pathway network. Moreover, the directional conduction is found to correlate with the anisotropic physical properties, demonstrated by the uneven coefficients of the thermal expansion along different crystallographic axes. These correlations of conduction tunnel provide valuable guidance in materials searching for solid conductors with superior performance in varied environments. The results of the anisotropic thermal-strain response correlated with ionic transport also provide consideration of the physical compatibility in the design of all-solid-state batteries.

1:45 PM ET01.04.02

Incorporating Two-Dimensional Materials in Semi-Solid Electrolytes for Fast Charge Li-Ion Batteries [Ramin Rojacee](#)¹, Salvatore Cavallo^{1,2}, Santosh Mogurampelly³, Bill Wheatle⁴, Venkat Ganesan⁴ and Reza Shahbazian-Yassar¹; ¹Mechanical and Industrial Engineering Department, University of Illinois at Chicago, Chicago, Illinois, United States; ²Department of Energy-DENERG, Politecnico di Torino, Torino, Italy; ³Institute for Computational Molecular Science (ICMS) and Temple Materials Institute (TMI), Philadelphia, Pennsylvania, United States; ⁴Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas, United States.

Poor electrochemical stability and low ionic conductivity trigger of prime importance for the development of new-generation of lithium-ion batteries. Solid electrolytes have been attracted significant attention owing to their superior safety and potential for boosting specific energy density. Here, we report a new type of semi-solid electrolytes with two-dimensional materials embedded in ternary polymer electrolyte. The developed electrolyte has a high electrochemical stability of 5.5 V vs. Li/Li^+ . We report a high ionic conductivity of $4 \times 10^{-3} \text{ S.cm}^{-1}$ at ambient temperature and significantly low interfacial resistance over the long period of time of 600 h overpotential cycling tests. The developed electrolyte is capable of fast charging with great capacity retention benefiting due to unique atomic arrangement of 2D material additive. FTIR, Raman, and NMR characterizations revealed the higher concentration of the free cations will be present in the electrolyte by about 30% upon addition of designated 2D material nanosheets. The layered 2D material lowers the binding energy for hopping the ions through the electrolyte to allow improved storage capacity and power density. We hypothesize that 2D materials introduce unique properties to the electrochemical behavior of the electrolyte and boost the ionic conduction through the electrolyte by providing efficient pathways for local ion transport through the structure and can be a great candidate for novel lithium polymer batteries. MD Simulation studies confirmed our experimental achievements and suggested that the f-BP nanosheets facilitate Li^+ ion movement by lowering the required energy to dissociate cations and move along the electrolyte.

2:00 PM *ET01.04.03

Advanced Sulfide Solid Electrolyte by Core-Shell Structural Design—Theory and Experiment [Xin Li](#); Harvard University, Cambridge, Massachusetts, United States.

Ceramic sulfide solid electrolyte can show high lithium conductivity, while the voltage stability was reported as an issue in many previous literatures. We show in this talk a new way to improve the voltage stability of sulfide solid electrolyte materials by microstructure modification of the electrolyte materials. The improved battery performance and voltage stability are shown by electrochemical test. A combination of first principle simulation and transmission electron microscopy imaging techniques are used to understand the principle behind the phenomenon. Specifically, sulfide Li-Si-P-S has been synthesized, characterized and tested to show an improved voltage stability window up to 3.1 V and quasi-stable voltage window up to 5V due to the microstructure modification. This is far beyond the limited voltage stability of these sulfides around 1.7 – 2.1 V as predicted by DFT simulation. We further from a combined thermodynamic modeling and DFT simulation understand the principle behind this promising result. A new design principle and theory is proposed and discussed systematically for tuning the voltage stability of solid electrolyte, giving the guidelines for the design of advanced sulfide electrolytes.

2:30 PM *ET01.04.04

Electrochemical Characterization of All-Solid-State Battery with $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolyte [Kiyoshi Kanamura](#); Tokyo Metropolitan University, Tokyo, Japan.

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is the promising electrolyte due to its high chemical stability against Li metal and high ionic conductivity. All solid state battery has been fabricated by using LLZO. However, the cell performance is not so good. This is due to a high impedance of the prepared cell. The resistance of solid electrolyte is the largest among resistances in the cell. In addition, the interfacial impedance between cathode or anode and solid electrolyte is not easily decreased. The interface between Li metal anode and LLZO solid electrolyte pellet is large due to poor contact. The contact has been improved by using an interlayer between Li metal and LLZO. A thin gold layer prepared by sputtering method has been employed as the interlayer. The thickness was about 50 nm. The gold layer reacted with Li to form alloy. During this alloying process, the good connection was formed. A cathode material is usually powder sample. The interfaces between cathode material and LLZO sheet and LCO powder and solid electrolyte powder in the cathode layer exist in all solid state battery. In this study, the cathode layer was formed by aero-sol deposition process (AD). The aero-sol of LCO was deposited on the LLZO sheet. Li_3BO_3 is one solid electrolyte with low melting temperature and $10^{-8} \text{ S cm}^{-1}$ conductivity. The core (LCO)-shell (LBO) type particle was prepared for AD deposition process. The prepared composite particle was deposited on LLZO sintered pellet which thickness was 500 μm . By using AD process, the uniform cathode layer was fabricated on the LLZO. The discharge and charge behavior of the fabricated cathode layer was investigated at constant current of 0.1 C rate. The discharge capacity was 55.5 mA h g^{-1} . The all solid state battery was not so good. In order to improve the electrochemical behavior of the cell, a heat treatment process was employed. LBO can be melted at 700 °C. Therefore, the temperature for heat treatment was determined to be 750 °C. Several cells prepared by heat treatment at 750 °C were examined to observe their electrochemical performance. The cathode layer prepared at 750 °C exhibited good performance. The highly reversible discharge and charge behavior was obtained. The discharge capacity was 140 mA h g^{-1} which was near to the expected one. The rate capability of the cell was measured. At 0.2 C rate, the discharge capacity was 50 mA h g^{-1} . With increasing discharge and charge current, the capacity was decreased. The cell impedance was evaluated with electrochemical AC impedance measurement at various temperatures. Before the heat

treatment, the cell had a large impedance. After the heat treatment, the cell impedance decreased. The heat treatment is very effective to reduce the interfacial resistance of the cathode layer in all solid state battery. However, further improvements are necessary. The thickness of the solid electrolyte should be decreased and the conductivity of the cathode layer should be increased.

3:00 PM BREAK

3:30 PM *ET01.04.05

Construction of Flexible Interfacial Layer for Solid-State Li Batteries Yong Yang; Xiamen Univ, Xiamen, China.

Solid-state batteries (SSBs), one of the most promising energy storage devices for next generation, have now been extensively developed due to their high safety and long cycle life. Here, the interfacial layers between solid electrode and solid electrolyte is one of most important features for the design of solid-state lithium batteries. Normally, the interfacial layer should be stable, highly conductive for Li ions, and flexible to tolerate the big volume changes during charging/discharging process.

In this presentation, I will present some examples we have used in this lab to build up such thin but important interfacial layer, making the highly efficient Li dissolution/deposition possible. For example, we proposed an ultra-simple and effective strategy to enhance the interfacial connection between garnet SSEs and Li metal just by drawing a graphite-based soft interface with a pencil. Both experimental analysis and theoretical calculations confirm that the reaction between graphite-based interfacial layer and metallic lithium forms a lithiated connection interface with good lithium-ionic and electronic conductivity. Compared to the reported interfacial materials, the graphite material provides a soft interface with better ductility and compressibility. With the improvement by this soft interface, the impedance of symmetric Li cells significantly decreases from 1350 to 105 Ω cm² and the cell can cycle for over 1000 hours at a current density of 300 mA/cm² at room temperature. In addition, some examples to construct an intimate solid electrolyte interface (SEI) in sulfide-based electrolyte by using ionic liquids will be also presented.

4:00 PM ET01.04.06

Simulations of Varying Li-Ion Vacancy Concentrations in Lithium-Oxyhalide Anti-Perovskites Reveal the Effects of Correlated Motion on Diffusion Zerina Mehmedovic, Vanessa Wei, Andrew Grieder and Nicole Adelstein; San Francisco State Univ, San Francisco, California, United States.

Introduction: Our simulations are designed to answer the long-standing question in solid-state batteries: how to increase Li-ion conductivity in solid electrolytes through engineering the structure and chemistry of the anion sub-lattice. Understanding the mechanism behind lithium ion diffusion in promising solid electrolytes, such as lithium-oxyhalide anti-perovskites, can provide design principles for new battery materials. Our *ab-initio* molecular dynamics (AIMD) simulations of Li₃OCl with Li vacancy concentrations between 0.5 and 2% reveal the origin of complex interactions between vacancies and new insights into the effect of correlated motion on the diffusion mechanism. Previous simulations of Li₃OCl compute conductivities that are much lower than measured experimentally [1] and our simulations show that finite size effects are part of the problem.

Methods: *Ab-initio* molecular dynamics were performed on a 4x4x4 supercells using VASP. The size of the supercell (320 atoms) allows for realistic vacancy concentrations and reducing finite size effects. The supercells had at least one and up to four Li⁺ vacancies. Maximally Localized Wannier Functions were used to calculate the dynamic polarization of anions and their effect on Li⁺ diffusion, which is a novel technique that we developed for analyzing solid electrolytes [2]. As is standard, the diffusion coefficient for each compound was determined using the mean squared displacement. The 'binding energy' of Li⁺ vacancies is calculated and lattice screening is separated into the strain and electronic effects.

Results: We discovered new collective diffusion mechanisms in Li₃OCl and that finite size effects plague most AIMD simulations. For example, simulating two Li⁺ vacancies (0.5% concentration) increases diffusion because the negatively charged vacancies "push" each other along. The largest vacancy concentration we simulated was 2%, which gave the highest diffusion due to disordering of the Li-sublattice, rather than a "push" mechanism. Vacancies can interact up to 7 Å from each other, with strain effects dominating 5 Å or closer. Vacancies communicate through the lattice, especially through polarization of anions. The dynamics of the anion polarization can be quantified easily in a nudged-elastic-band calculation and is still important even in AIMD. Thus, diffusion may be controlled by changing the polarizability of the anions, such as creating Br and F alloys with Li₃OCl.

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4:15 PM ET01.04.07

Tuning Charge Diffusion in Polyethylene Oxide-Based Electrolytes Using Secondary Sites—Insights from Molecular Dynamics Simulations Arthur France-Lanord, Yanming Wang, Tian Xie and Jeffrey C. Grossman; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Solid-state polymer electrolytes (SPEs) constitute a promising technology for energy storage applications. In addition to a more flexible form factor, batteries using such electrolytes have the potential to be safer, less expensive, and greener than the current liquid-based standard technology. However, hindered by their low ionic conductivity, SPEs can only operate under limited conditions. The improvement of SPEs requires a deeper understanding of ion transport in polymer networks, where modeling and computation can play an important role. Here, through classical molecular dynamics simulations, we investigate charge diffusion in SPEs consisting of a mixture of polyethylene oxide (PEO) based polymers and lithium bis(trifluoromethane)sulfonimide (LiTFSI) salt. By varying the chemical structure of the polymer, we alter the ion-polymer binding strength, which allows us to explore various ionic transport mode. Importantly, this study reveals the delicate balance between ionic association on one hand, and ionic crosslinking on the other hand.

4:30 PM ET01.04.08

Two-Dimensional Boron Nitride-Protected Solid Electrolyte for Rechargeable Lithium Metal Batteries Qian Cheng¹, Aijun Li^{1,2} and Yuan Yang¹; ¹Program of Materials Science and Engineering, Department of Applied Physics and Applied Mathematics, Columbia University, New York, New York, United States; ²School of Earth and Space Sciences, Peking University, Beijing, China.

Solid-state lithium batteries can improve the battery safety and energy density compared with conventional Li-ion batteries. However, a lot of solid electrolytes with low cost and high ionic conductivities can be reduced by the anode in lithium battery systems (e.g. lithium, graphite). Here, we introduce a novel strategy, in which chemically and mechanically robust two-dimensional boron nitride (BN) film was deposited onto the surface of solid electrolyte (e.g. Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃, LATP) to prevent reduction of solid electrolyte from lithium. The lithium symmetric cells with BN protected LATP/liquid hybrid electrolyte can cycle up to 700 hours with a current density up to 0.5 mA/cm², and full cell utilizing LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂/LATP/BN/Li can cycle 100 times without apparent decay at a current density of 0.3 mA/cm². In contrast, LATP/liquid hybrid electrolyte can only be cycled for 40 cycles with fast capacity fading. Meanwhile, with PEO coated on both sides of LATP/BN, all-solid-state Li/LiFePO₄ cells show a good cycling ability, further demonstrating excellent protection on solid electrolytes. This research provides a universal strategy to protect solid electrolytes of small electrochemical windows against

lithium metal, leading to notable improvement of stability and cycling ability.

4:45 PM ET01.04.09

Fabrication of Ultrathin Films of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ with Tunable Surface Morphology by Spray Pyrolysis [Zachary D. Hood](#)¹, Yuntong Zhu¹, Lincoln Miara² and Jennifer L. Rupp^{1,3}; ¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Samsung Research America, Advanced Materials Lab, Burlington, Massachusetts, United States; ³Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Garnet-based lithium solid electrolytes are expected to improve next-generation energy storage technology in electric vehicles and portable electronics on the basis of energy density, safety, cost, amongst other parameters. Yet many of these solid electrolytes, such as $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), were previously difficult to process into thin films between 200 nm and 5 μm in thickness using solution-based techniques. Several vacuum-based^{1,2} and sol-gel-derived^{3,4} methods shown success in making thin garnet-based solid electrolyte films with relatively high ionic conductivity ($\sim 10^{-6}$ - 10^{-5} S/cm at room temperature), yet better methods are desired to improve the bulk resistance of the electrolyte and overall cost of production. Therefore, the exploration of scalable fabrication techniques is of special importance to develop thin films of garnet-based solid electrolytes that hold high ionic conductivity and compatibility with high-capacity cathodes. In this work, we developed a novel method of fabricating thin films with controllable thicknesses of garnet-based LLZO solid electrolytes using spray pyrolysis. We show that the crystallization and the phase transformation can be modulated to lower temperatures (< 750 °C) by tuning the concentration of cations and the boiling point of the solvents used in the spray solution. Also, by altering the chemistry of the spray solution and the post-annealing conditions, we show that the surface roughness can be modulated while still maintaining dense and continuous membranes of LLZO. Our results highlight a new opportunity for manufacturing garnet-based solid electrolytes with tunable electrochemical surface areas, and the insights from this work are expected to serve as fundamental guidelines for future optimization of thin film superionic garnet-based materials for next-generation lithium metal batteries.

Acknowledgements

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SESSION ET01.05: Poster Session I
Session Chair: Liwei Chen
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET01.05.01

Li^+ Ion Conduction Properties and Electrochemical Properties of Sodium Bromide Doped with Li^+ Ions [Masatoshi Shomura](#), Reona Miyazaki and Takchiko Hihara; Nagoya Institute of Technology, Nagoya-shi, Japan.

Lithium-ion batteries (LIBs) has been used for portable device because of their high operating voltage. All-solid-state LIBs, where conventional liquid electrolytes are substituted with the solid electrolytes have been attracted much attention as the next generation batteries. The solid electrolytes are required to have the high Li^+ conductivity, electrochemical stability. From the early stage of the research, the solid electrolytes have been developed based on the Li compounds.

On other hand, solid electrolytes can be fabricated not only from the Li compounds but also prepared via doping of Li compounds into "Li-free solid solvents". It has been reported that KI and NaI act as the pure Li^+ conductors via doping of 6 mol% of LiBH_4 [1][2]. In this study, new solid electrolyte is synthesized via doping of LiBH_4 and/or LiBr into NaBr in order to expand the material selectivity for the Li-free solid solvents. Furthermore, the Li^+ ionic conductivity and electrochemical stability will be compared with those of NaLiBH_4 system.

A given molar ratio of NaBr , LiBH_4 and LiBr were mixed by ball milling using an air tight chrome steel pot (45 ml) and 10 pieces of balls (10 mm in diameter). The crystal structures and microstructures of the prepared samples were characterized by XRD measurement and SEM observation, respectively. For the electrochemical measurement, the powder sample was pelletized at ca. 150 MPa for 1 min, resulting in the pellet with the diameter of 10 mm and thickness was ca. 1 mm. The electrical conductivities were measured between 303 K to 423 K by AC impedance method. Cyclic voltammogram was obtained using Mo and Li foils as working and counter electrodes, respectively. All the experiments were conducted in an Ar atmosphere.

From XRD patterns of NaBr-LiBH_4 systems, the diffraction peaks of rock-salt type structure were mainly observed and peak positions of NaBr-LiBH_4 system were shifted from those of NaBr . It means that the lattice size of NaBr-LiBH_4 system was changed from that of NaBr . Hence, it can be said that NaBr and LiBH_4 formed solid solution. Because ion radii of $\text{Li}^+(\text{BH}_4^-)$ is smaller (larger) than that of $\text{Na}^+(\text{Br}^-)$, the doping of Li^+ ions into NaBr lattice cannot be identified only from the variation of the lattice parameters. In order to identify the Li^+ doping into NaBr more specifically, NaBr-NaBH_4 system where Li^+ ions are not included were prepared and their lattice parameters were also evaluated as a function of BH_4^- anion ratio. It was confirmed that the lattice parameters of NaBr-LiBH_4 system are smaller than those of NaBr-NaBH_4 system with the same anion ratio. Therefore, it was suggested that host Na^+ ions are substituted by guest Li^+ ions. The detailed results of XRD measurement, SEM observations and electrochemical properties will be presented at the meeting.

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ET01.05.02

Solid Polymer Electrolyte from Polytetrahydrofuran-Epoxy Copolymers for Lithium-Ion Conduction Francielli S. Genier¹, James Baena², Jiayue Wang¹, Saïd Biria¹ and Ian Hosein¹; ¹Syracuse University, Syracuse, New York, United States; ²Cazenovia High School, Cazenovia, New York, United States.

High performance batteries are central components to the development of safe, clean and affordable energy storage systems. For this reason, the replacement of the liquid or gel electrolyte with a solid polymer material, namely a solid polymer electrolyte (SPE), has been a research area of intense interest. Solid electrolytes have the potential to enable higher energy densities and address concerns over the volatility and flammability of currently used organic solvents. Of the numerous polymer systems under investigation, SPEs produced through crosslinking are quite attractive owing to their high conductivity and excellent mechanical stability. Commonly, crosslinking is achieved through free-radical initiated reactions involving end-functionalized monomers or oligomers. This approach is limited by the available polymer precursors, often necessitating deliberate end-functionalization of the molecules to carry out the reaction. Hence, the formation of crosslinks from molecules in their native form would be more cost-effective and straightforward. In this work, a novel crosslinked solid polymer electrolyte was developed through the copolymerization of polytetrahydrofuran (PTHF) and a cycloaliphatic epoxide (referred as Epoxy) under visible light, without previous functionalization. In particular, these chemicals were employed due to PTHF's potential to achieve high conductivity and the thermal and mechanical stability associated with cycloaliphatic epoxides, creating a stable, solid crosslinked material. The crosslinked samples were evaluated for their ionic conductivity, thermal stability, crystallinity and mechanical stiffness. They presented conductivity on order of 10^{-5} to 10^{-3} S/cm, similar to previously reported electrolytes, now with the manufacturing benefits from the photocuring process, which is energy-efficient and less thermally stressful to the substrate materials. Thermogravimetric analysis of the electrolytes indicated stability at battery operating temperatures, and differential scanning calorimetry demonstrated the material's amorphous behavior over a wide temperature range. The electrolytes also showed excellent mechanical stiffness. Further studies on 2032 coin cell batteries will be presented and discussed. This work represents a new route for cleaner and safer energy storage devices with potential for a broad variety of applications.

ET01.05.03

Synthesis and Characterization of a New Lithium Chloro-Thiophosphate as a Solid State Ionic Conductor Zhantao Liu¹, Jue Liu², Sylvio Indris³, Wenqian Xu⁴, Shan Xiong¹, Xuetian Ma¹, Lufeng Yang¹ and Hailong Chen¹; ¹Georgia Institute of Technology, Atlanta, Georgia, United States; ²Neutron Scattering Division, Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee, United States; ³Karlsruhe Institute of Technology–Institute for Applied Materials, Karlsruhe, Germany; ⁴X-ray Science Division, Argonne National Laboratory, Argonne, Illinois, United States.

Solid state Li^+ and Na^+ conductors have attracted great interest as the electrolyte for all-solid-state batteries. Compared with conventional batteries using liquid organic electrolytes, all-solid-state batteries with non-flammable solid electrolyte have significant advantages in safety. Among known solid-state Li^+ conductors, sulfide-based electrolytes are superior in ionic conductivity than oxide conductors and a number of sulfides with different chemical compositions and crystal structures have demonstrated conductivities comparable to liquid electrolytes [1].

Here we report the synthesis, structural characterization and ionic transport study of a novel lithium chloro-thiophosphate compound, $\text{Li}_{15}\text{P}_4\text{S}_{16}\text{Cl}_3$. $\text{Li}_{15}\text{P}_4\text{S}_{16}\text{Cl}_3$ can be synthesized in pure phase with facile solid state reaction method under relatively low temperature. The crystal structure of $\text{Li}_{15}\text{P}_4\text{S}_{16}\text{Cl}_3$ is characterized with using neutron and synchrotron x-ray powder diffraction techniques, indicating it has an I-43d cubic space group. The ionic conductivity was measured by electrochemical impedance spectroscopy at different temperatures. At 30 °C, $\text{Li}_{15}\text{P}_4\text{S}_{16}\text{Cl}_3$ exhibited an ionic conductivity of 4.2×10^{-7} S/cm. The lithium ion transport in $\text{Li}_{15}\text{P}_4\text{S}_{16}\text{Cl}_3$ was also studied by multiple solid-state NMR methods, including pulsed field gradient and variable temperature NMR. The discovery of this new compound provide a new crystal structure that can serve as a foundation for the design of more sulfide ionic conductors with high conductivities.

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ET01.05.04

Rapid Li Spin Dynamics in the Interfacial Regions of the Nanocrystalline Solid Electrolyte LiBH_4 Stefan Breuer¹, Marlena Uitz¹, Denise Prutsch¹ and Martin Wilkening^{1,2}; ¹Institute for Chemistry and Technology of Materials, Graz University of Technology, CD-Laboratory for Lithium Batteries, Graz, Austria; ²Alistore-ERI European Research Institute, Graz, Austria.

Currently, all-solid-state batteries with ceramic electrolytes and lithium metal anodes, for example, represent an attractive alternative to conventional Li-ion batteries. So far many materials have been reported as promising candidates for such systems.^{1,2} Their dynamic properties and electrochemical stabilities are feverishly studied to identify those materials that may indeed replace flammable liquid electrolytes.

LiBH_4 , especially when available in a nanocrystalline form, belongs to one of these promising solid electrolytes.² Besides its good compatibility with metallic lithium it shows a high ionic conductivity above 113 °C making it a suitable candidate for high-temperature solid-state batteries.³ In general, nanostructured ceramics, if prepared by high-energy balling from the coarse-grained counterparts, are composed of crystalline grains surrounded by structurally disordered interfacial regions. These areas are considered to be responsible for increased ion dynamics in these materials.

The aim in this work was to separately study the diffusivity of the fast Li ions in the large volume fraction of interfacial regions from an atomic scale point of view. Therefore, we used nuclear magnetic resonance (NMR) to record purely diffusion-induced ^7Li NMR spin-lattice relaxation magnetization curves. Indeed, the transients are composed of two components. We attribute the fast relaxing component to the highly mobile Li ions in the interfacial regions. These ions showed much lower activation energies than those in the crystalline grains. NMR line shapes, recorded under static conditions, corroborated this point of view.⁴

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ET01.05.05

Investigation of Interfacial Reactions Between a NASICON Type Solid Electrolyte and Lithium John Lewis¹, Francisco Javier Quintero Cortes¹, Matthew G. Boebinger¹ and Matthew McDowell^{1,2}; ¹School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; ²George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Solid-state electrolytes have been predicted to prevent dendritic growth of lithium metal anodes due to the mechanical properties of ceramic solid electrolytes. However, cell failure when using lithium metal has been observed with various solid electrolyte materials. A well-known example is the

growth of lithium through the bulk of the garnet-type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) electrolyte, despite its thermodynamic stability and high shear modulus. An alternative to LLZO is the NASICON family of solid electrolytes, which offers comparable conductivities and mechanical properties. The disadvantage of these materials is that they are chemically unstable against lithium metal, and they typically react upon contact to form a high-impedance interface. While the chemical reaction between NASICON material $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP) and lithium was recently shown to cause mechanical and thermal failure, comprehensive understanding of the electrochemical reaction mechanism and phase transformation process at the Li/LAGP interface has not been attained. This knowledge is key for stabilizing NASICON-based batteries for long lifetimes. Here, we investigate the reactions between LAGP and lithium using various electrochemical and ex situ/in situ analytical techniques. In symmetric electrochemical cells, the extent of reaction and distribution of the reacted region throughout the solid electrolyte is found to be strongly dependent on the applied current density. Cell failure is ultimately governed by a dramatic increase in impedance due to mechanical fracture of the solid electrolyte. Multiple characterization techniques reveal that the reacted phase is amorphous, in contrast to the crystalline reaction products predicted to exist by prior density functional theory calculations. Both ex situ and in situ electron microscopy demonstrate that LAGP experiences a volume expansion during reaction, which likely drives fracture of the ceramic. These results demonstrate that the thermodynamic instability of LAGP against lithium alters the failure mechanism when compared to a stable material such as LLZO, and they suggest that NASICON-type materials could be used within viable solid-state devices with additional engineering to stabilize interfaces.

ET01.05.06

Diffusion Mechanism in the Superionic Conductor $\text{Li}_4\text{PS}_4\text{I}$ Studied by First-Principles Calculations [Karsten Albe](#), Sabrina Sicolo and Constanze Kalcher; TU Darmstadt, Darmstadt, Germany.

$\text{Li}_4\text{PS}_4\text{I}$ was recently discovered as a novel crystalline lithium ion conductor by applying a soft chemistry approach. It adopts a tetragonal structure type suggesting a three-dimensional migration pathway favorable for a high conductivity [S.J. Sedlmaier, *Chem. Mater.* 29 (2017) 1830]. In order to shed light on the full potential of this material, we performed a theoretical study of $\text{Li}_4\text{PS}_4\text{I}$ in the framework of density functional theory. After creating a structural model that accurately accounts for the partial occupancies determined by diffraction experiments, we performed molecular dynamics simulations, unraveled the diffusion mechanisms and calculated diffusion coefficients and the activation barrier for diffusion. The results of the theoretical study on both a crystalline and a glassy supercell imply that $\text{Li}_4\text{PS}_4\text{I}$ is in fact a superionic conductor with a much higher conductivity than reported so far.

ET01.05.07

Effect of Cell Volume on Li^+ Diffusion in Ordered and Disordered LLZO Systems [Andrew Grieder](#)¹, Tae Wook Heo², Nicole Adelstein¹, Brandon Wood² and Prateek Mehta³; ¹San Francisco State University, San Francisco, California, United States; ²Lawrence Livermore National Laboratory, Livermore, California, United States; ³University of Notre Dame, Notre Dame, Indiana, United States.

The garnet $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ is a promising candidate as a solid electrolyte due to its stability and fast lithium diffusion. A lithium deficient system $\text{Li}_{6.75}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) was studied using classical molecular dynamics simulations to investigate the effect of cell size on ordered and disordered LLZO systems. The disordered systems serve as a proxy for grain boundaries, which are thought to impede Li^+ conductivity in polycrystalline materials. We find that the disordered system has regions with more free volume where Li^+ gets trapped. Results from the simulations with ordered cell volumes confirm that more free volume in the system decreases the rate of diffusion.

Activation energies and diffusion pre-factors were extracted from Arrhenius plots of diffusion at temperatures ranging from 500 K to 2000 K for systems with volumes ranging from 92% to 108% of the experimental cell volume. The activation energies were found to decrease for smaller cell sizes even though there is less space for Li^+ to jump. The activation energies for the disordered systems were found to be higher than the ordered systems. The pre-factor and activation energy of the ordered system increase stepwise when cell volume is 106% of the experimental cell volume indicating a change in diffusion mechanism at this volume. The results from different cell volumes of ordered and disordered systems provides insight into diffusion around and through grain boundaries for the LLZO system.

ET01.05.08

Kinetics and Chemical Analysis of the Crystallization Process of $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ Thin Films Deposited by a Sol-Gel-Derived Wet Chemistry Method [Yuntong Zhu](#)¹, Zachary D. Hood¹, Lincoln Miara², Kunjoong Kim¹, Juan Carlos Gonzalez-Rosillo¹ and Jennifer L. Rupp^{1,3}; ¹Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Advanced Materials Lab, Samsung Research America, Burlington, Massachusetts, United States; ³Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Garnet-based solid-state batteries exhibit several exceptional properties, including its wide electrochemical stability window, high room temperature Li-ion conductivity, and good thermal stability, rendering it as one of the most promising candidates for next-generation electrochemical energy storage devices. While many studies have detailed bulk garnet-based electrolytes such as $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), the preferred choice for future electric vehicles is thin films as it can effectively reduce the bulk resistance of the electrolyte layer, and therefore, improve the energy density of the battery. Several studies have demonstrated a promising room temperature ionic conductivity of LLZO thin films using vacuum-based deposition techniques, such as pulsed laser deposition (PLD)¹ and sputtering². Only a few groups have demonstrated the possibility to synthesize LLZO thin films using scalable wet chemical methods such as sol-gel-derived spin coating³ and dip coating⁴ which are of essence for mass-manufacturing. Amongst these techniques, there is still a lack of understanding in the kinetics of the LLZO phase formation via wet chemistry routes. In this study, LLZO thin films are prepared via a sol-gel-derived wet chemistry method. The crystallization and phase transitions of the LLZO thin films during annealing processes were studied by *in situ* Raman spectroscopy and differential scanning calorimetry (DSC). Furthermore, X-ray photoelectron spectroscopy (XPS) was used to study the surface chemistry of the films during the phase transformation processes. Our results reveal that the as-deposited films undergo several phase transformation processes and the pure garnet phases can be obtained in an attractive low-temperature range. Additionally, we investigated the effect of precursor composition on the phase transformation. This work provides a better understanding of the LLZO phase formation through wet chemistry synthetic methods and offers valuable insight for the design and synthesis of electrolytes for all-solid-state lithium batteries.

Acknowledgments

This work was sponsored by Samsung Electronics.

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SESSION ET01.06: Session V
Session Chairs: Neil Dasgupta and Hong Li
Wednesday Morning, November 28, 2018
Hynes, Level 3, Room 310

8:00 AM ET01.06.01

Anion Dynamics as One of the Key Drivers for Ultrafast Diffusion in Superionic Hydro-Polyborate Salts of Lithium and Sodium Mirjana Dimitrievska^{1,2}, Wan Si Tang¹, Patrick T. Shea³, Kyoung E. Kweon³, Joel B. Varley³, Vitalie Stavila⁴, Brandon C. Wood³ and Terrence J. Udovic¹; ¹National Institute of Standards and Technology, Gaithersburg, Maryland, United States; ²National Renewable Energy Laboratory, Golden, Colorado, United States; ³Lawrence Livermore National Laboratory, Livermore, California, United States; ⁴Sandia National Laboratories, Livermore, California, United States.

The disordered phases of solid lithium and sodium polyborate-based salts, such as closo-borate ($B_{12}H_{12}^{2-}$, $B_{10}H_{10}^{2-}$, $CB_{11}H_{12}^{-}$, and $CB_9H_{10}^{-}$) and nido-borate ($B_{11}H_{14}^{-}$, $7-CB_{10}H_{13}^{-}$, $7,8-C_2B_9H_{12}^{-}$, and $7,9-C_2B_9H_{12}^{-}$), possess superb superionic conductivities making them intriguing molecules for use in organometallic catalysis and as electrolyte anions in metal-ion battery technologies. This dramatically high conductivity (e.g., $\sim 0.03 \text{ S cm}^{-1}$ for $NaCB_9H_{10}$ at 297 K) is enabled by the emergence of a vacancy-rich cation sublattice and possibly further aided by the concomitant onset of high reorientational mobility (typically $>10^{10}\text{-}10^{11}$ reorientational jumps s^{-1}) of the quasi-spherical anions. Furthermore, these superionic-conducting phases can be better stabilized at device-relevant temperatures via additional strategies such as ball-milling and anion-mixing.

Neutron scattering techniques are invaluable for elucidating the dynamical nature of the reorienting anions with these hydrogenous materials. Obtaining any detailed fundamental understanding of the reorientational dynamics of these complex anions requires appropriate experimental probes, such as neutron scattering fixed window scan analysis (FWS) and incoherent quasielastic neutron scattering (QENS).

In this work, FWS, QENS, and ab initio molecular dynamics calculations are combined to probe anion reorientations and their mechanistic connection to cation mobility over a broad range of timescales and temperatures.^{1,2} The relationship among the reorientational behaviors and mobilities of the different divalent and monovalent polyhedral anions within the various disordered salt structures obtained from these techniques and the unusually rapid cation translational diffusion properties will be discussed. It is found that anions do not rotate freely, but rather transition rapidly between orientations defined by the cation sublattice symmetry. Furthermore, there appears to be a correlation between reorientational mobility of the anions and the diffusion rates of the cations. The results suggest that synergy between the anion reorientational dynamics and the cation-anion interaction significantly accounts for the high cationic conductivity observed in these salts.

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8:15 AM ET01.06.02

Understanding the Effect of Interlayers at the Thiophosphate Solid Electrolyte/Lithium Interface for All-Solid-State Li Batteries Lingzi Sang¹, Ralph G. Nuzzo² and Andrew Gewirth²; ¹University of Alberta, Edmonton, Alberta, Canada; ²University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

All-solid-state Li-ion batteries afford possibilities to enhance battery safety while improving their energy and power densities. Current challenges to achieving high performance all-solid-state batteries with long cycle life include shorting resulting predominantly from Li dendrite formation and infiltration through the solid electrolyte (SE), and increases in cell impedance induced by SE decomposition at the SE/electrode interface. In this work, we evaluate the electrochemical properties of two interlayer materials, Si and $Li_xAl_{(2-x/3)}O_3$ (LiAlO), at the $Li_7P_3S_{11}$ (LPS)/Li interface. Compared to the Li/LPS/Li symmetric cells in absence of interlayers, the presence of Si and LiAlO both significantly enhance the cycle number and total charge passing through the interface before failures resulting from cell shorting. In both cases, the noted improvements were accompanied by cell impedances that had increased substantially. The data reveal that both interlayers prevent the direct exposure of LPS to the metallic Li, and therefore eliminate the intrinsic LPS decomposition that occurs at Li surfaces before electrochemical cycling. After cycling, a reduction of LPS to Li_2S at the interface when a Si interlayer is present; LiAlO, which functions to drop the potential between Li and LPS, suppresses LPS decomposition processes. The relative propensities towards SE decomposition follows from the electrochemical potentials at the interface which are dictated by the identities of the interlayer materials. This work provides new insights into the phase dynamics associated with specific choices for SE/electrode interlayer materials and the requirements they impose for realizing high efficiency, long lasting all-solid batteries.

8:30 AM ET01.06.03

Mechanical Properties and Nucleation of Nano-Sized Li Electrodeposited in a Solid-State Battery Michael Citrin¹, Heng Yang¹, Wenpei Gao³, Simon Nieh², Xiaoqing Pan³, Joel Berry⁴, David J. Srolovitz⁴ and Julia R. Greer¹; ¹California Institute of Technology, Pasadena, California, United States; ²Front Edge Technology, Baldwin Park, California, United States; ³University of California, Irvine, Irvine, California, United States; ⁴University of Pennsylvania, Philadelphia, Pennsylvania, United States.

Li metal is the most energy dense anode material for Li-based rechargeable batteries, with a theoretical specific capacity of 3860 mAh/g^1 . Its use in commercial batteries has been largely limited by the formation of dendrites during cycling in liquid electrolytes, leading to early cell death. It has been theorized that a sufficiently strong and stiff solid electrolyte can mechanically suppress dendrite formation and growth². Gaining a fundamental understanding of the mechanics of Li dendrite nucleation, strength, and stiffness as a function of microstructure and crystallographic orientation is essential to successfully implement solid electrolytes in Li metal batteries.

We investigated nucleation and growth of Li in a commercial all solid-state thin film Li free battery with a LiPON solid electrolyte³. We conducted electrochemical cycling experiments *in-situ*, inside a scanning electron microscope (SEM). We observed that during charging, Li preferentially nucleated from the LiPON-Cu interface by rupturing through the Cu film along the topological landscape that reflects the domain boundaries of the underlying

LiCoO₂ cathode. Continuum electrochemical simulations of Li ion transport suggest that Li is driven to these preferential nucleation sites by the local electrostatic potential that concentrates at the domain boundaries.

We observed Li nuclei with varying morphologies: micron-sized spheres, ~200 nm diameter fibers, and ~300 nm to 1 micron-diameter pillars. We conducted *in-situ* uniaxial compression experiments in an SEM on electroplated pillars with diameters between 350 nm and 1 μm and aspect ratios of about 3:1, which revealed an average elastic modulus of 6.56 ± 3.03 GPa and an average yield strength of 15.4 ± 8.57 MPa, over an order of magnitude higher than the material's bulk polycrystalline strength⁴. No size effect was observed, in contrast to the ubiquitous "smaller is stronger" size effect present in single crystalline metallic pillars created by Ga⁺ focused ion beam (FIB) milling⁴. The strengths observed were about an order of magnitude smaller than those measured from FIB-milled single crystalline Li pillars⁴. To understand the difference between observed and reported strengths, we conducted electrochemical charging *in-situ* inside a transmission electron microscope (TEM) on a thin lamella extracted from the solid-state battery to investigate the microstructure of the Li. This work enables laying out a parameter space for stiffness and strength of Li as a function of its deposition process, electrolyte, microstructure and orientation. The results have significant implications for lithium dendrite suppression using robust solid electrolytes for the next generation of lithium metal secondary batteries.

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8:45 AM ET01.06.04

Ice-Templated Ceramic/Polymer Composite Electrolyte for Solid-State Batteries Xue Wang^{1,2}, Haowei Zhai¹ and Yuan Yang¹; ¹Columbia University, New York, New York, United States; ²Harbin Institute of Technology, Harbin, China.

Composite solid electrolyte is attractive as it combines high ionic conductivity of ceramic electrolyte and excellent mechanical properties of polymer electrolyte. For maximizing the ionic conductivity of composite electrolyte, one ideal structure is vertically aligned ceramic particles in the polymer matrix. Here, by using the ice-templating method, we report a vertically arranged wall structure of high ionic conductive Li_{1.5}Al_{0.5}Ge_{1.5}(PO₄)₃ (LAGP) ceramic particles combined with polyethylene oxide (PEO) polymer. The vertical LAGP walls with the shortest lithium-ion transporting path were gathered by the force of the ice crystal growth. Filling PEO in the space between LAGP walls could achieve flexible composite electrolyte and lower interfacial resistance with electrode surfaces. This as-synthesized solid-state composite electrolyte had a conductivity as high as 1.5×10^{-4} S/cm at room temperature, which was even more significant at high temperature with excellent stability. LiFePO₄/LAGP-PEO/Li full cell was also assembled to test its electrochemical performance; the capacity only decayed ~8% after more than 130 cycles. This research successfully utilizes the ice-templated vertically aligned structure in ceramic/polymer composite electrolyte for solid-state batteries, with comprehensively enhanced battery performance. It could provide new design and application strategy for further composite electrolyte study.

9:00 AM *ET01.06.05

Examining the Low Voltage Stability of Li_{6.25}Al_{0.25}La₃Zr₂O₁₂ (LLZO) Regina Garcia-Mendez and Jeff Sakamoto; Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan, United States.

The band gap of bulk Li_{6.5}Al_{0.25}La₃Zr₂O₇ (LLZO) was reported to be 5.87 eV with its band edges positioned above and below the electrochemical potential of Li metal and high voltage cathodes (~5 V), respectively. From a quantum mechanical perspective, this unprecedented wide stability window could enable a paradigm shift in secondary Li batteries whereby the electrolyte does not decompose against the anode and cathode¹. However, it has been observed that the Li-LLZO interface is destabilized at high Li plating current densities resulting in Li metal penetration. In this study, we hypothesize for the first time that Li metal penetration could result from a quantum mechanical instability rather than an electrochemical or mechanical instability. To analyze this phenomenon, all-solid-state cells consisting of separate working and reference electrodes were used to measure the stability of the Li-LLZO interface at and below 0 V vs Li/Li⁺. Unlike typical tests that vary the current and measure the resulting potential, this study controls the potential and measures the current. At low underpotentials, the Li-LLZO interface exhibits Ohmic behavior. However, at greater underpotentials, deviation from Ohmic behavior is observed, which we believe it is an indicator of a threshold voltage; above which the Li Fermi level is above the conduction band minimum and below which the Li Fermi level is pushed into the conduction band. This study will analyze and interpret the consequences of the latter. Furthermore, galvanostatic tests were conducted in three electrode Li-Li symmetric cells, in which current densities were increased from 0.1 to 2 mA cm⁻² on the Li plating side. It was found that the current density of 0.5 ± 0.1 mA cm⁻² at which the drop in voltage was observed in galvanostatic conditions is comparable to the 0.6 ± 0.1 mA cm⁻² current density at which the threshold voltage occurs in the voltage sweep tests. At this macroscopic scale, no electric field dependence was observed. In this study, we propose a hypothesis to explain why relative soft Li metal can penetrate a relatively hard ceramic electrolyte. The mechanism could be governed by quantum mechanical aspects; an explanation that has not been considered before. The results of this work could help better understand Li-solid electrolyte interface and how to increase the rate at which solid-state batteries are cycled.

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9:30 AM ET01.06.06

Materials Design for Highly Conductive Polymer Electrolyte by Machine Learning Assisted Coarse-Grained Molecular Dynamics Yanning Wang, Tian Xie, Arthur France-Lanord, Jeremiah Johnson, Yang Shao-Horn and Jeffrey C. Grossman; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Solid polymer electrolytes (SPEs) are considered as promising building blocks for the next-generation lithium-ion batteries. However, current SPEs have yet to be incorporated into real-world applications, due to their low ionic conductivity. This motivates the development of advanced computational models, for better understanding the ionic transport mechanisms and fast exploring the high-dimensional material parameter space, towards designing highly conductive SPE materials. Here we develop a coarse-grained molecular dynamics (CGMD) model with parameters calibrated by full atomistic simulations. The model captures both the ion motion and the polymer conformational evolution during the transport process, from which the conductivity and transference number are extracted. Adopting the Bayesian optimization (BO) algorithm, conductivity optimization is conducted by automated CGMD simulations in iterations, for screening influential factors, such as the size of molecules and the strength of intermolecular interactions, on the conduction of the polymer-salt system. This research sheds light on the mechanisms of ionic transport in polymers, and provides useful guidance for designing innovative SPE materials.

9:45 AM ET01.06.07

Sol-Gel Processed Amorphous $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ as Solid Electrolyte Yubin Zhang and Yan Wang; Worcester Polytechnic Institute, Worcester, Massachusetts, United States.

Amorphous $\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ (LLTO) has been proved to be a promising candidate for electrolyte in All-Solid-State-Battery (SSB), amorphous LLTO thin films were also synthesized by sol-gel process in our previous work. The ionic conductivities of amorphous LLTO thin films were 4.5×10^{-6} , 6.9×10^{-6} , 1.3×10^{-5} , and 3.8×10^{-5} S/cm at 30°C, 50°C, 70°C, and 90°C, respectively. However, the inner relationship among the ionic conductivity, structure and mechanism of Li ion transfer is still unrevealed. In this study, we successfully prepared amorphous LLTO thin film and amorphous LLTO powder via similar sol-gel procedure, moreover, differences were introduced during the sintering process. XRD and SEM were applied to demonstrate the morphology change with different annealing conditions. In addition, the ionic conductivities of the thin film prepared were measured sequentially. With the accumulation of annealing time, the ionic conductivity of LLTO thin film raised from 2.32×10^{-8} S/cm to 9.01×10^{-6} S/cm, then dropped back to 1.65×10^{-9} S/cm at 30°C. Whereas the activation energy of lithium ion transferring is approximately constant, from which proved the lithium ion transfer in LLTO is dynamic-controlled. It gave us an optimized synthesis condition of LLTO thin film in the meantime for future investigation.

10:00 AM BREAK

10:30 AM *ET01.06.08

Li-Ion and Na-Ion Solid State Electrolytes for Solid-State Batteries Linda F. Nazar, Laidong Zhou, Kavish Kaup, Zhizhen Zhang and Erika Ramos; University of Waterloo, Waterloo, Ontario, Canada.

All-solid state Li-ion batteries (ASSBs) have emerged as very attractive alternatives to conventional liquid electrolyte cells for automotive transportation, owing to their enhanced safety and higher energy densities. Similarly, low-cost solid state Na-ion batteries may prove an excellent alternative for grid storage. ASSBs are founded on high performance fast-ion conducting electrolytes, and in the important search for new materials, alkali thiophosphates are a particularly promising class of materials owing to their ductility and good mechanical properties. This presentation will focus on several new alkali fast ion conductors within this class recently developed in our laboratory, and the understanding of superionic conductivity in these materials using a combination of structural elucidation via single crystal X-ray/powder neutron diffraction, ion conductivity via impedance studies, and *ab initio* molecular dynamics simulations. We correlate crystal structure with ionic conductivity in a range of our newly developed fast ion Li and Na conductors to understand how changes in composition and vacancy population affect the conductivity and activation energy. These considerations lead to an overarching understanding of the relative importance of interstitial alkali ion site occupation for ion migration, and the factors that govern thermodynamic (meta)stability.

11:00 AM ET01.06.09

Li Transport Induced Phase Transitions in Epitaxial LiCoO_2 Thin Films Yingge Du, Zhenzhong Yang, Phuong-Vu Ong, Le Wang and Peter V. Sushko; Pacific Northwest National Laboratory, Richland, Washington, United States.

Structurally ordered materials exhibit a broad range of structural, physical, and ion transport properties, which can be further tuned or even drastically transformed by means of judicious elemental doping, strain, and defect engineering. This talk will highlight our most recent effort aiming to modify LiCoO_2 through heteroepitaxy for tunable Li^+ transport, which have profound implications in energy conversion and storage devices. We will present the epitaxial growth and *in situ* TEM studies of LiCoO_2 with or without overlayers to understand the Li transport processes across the epitaxial interfaces, and device failure mechanisms. We show that while orienting Li containing planes of LiCoO_2 can effectively tune the Li ion transport characteristics, allowing Li incorporation into the overlayers across the interface, it does not modify its stability against Li metal (mimicking a Li dendrite), which preferentially attack the LiCoO_2 crystal structure along the [001] direction, enabling to Li propagation across Li-containing planes.

11:15 AM ET01.06.10

Lithium-Metal Anode Protection—From Liquid to Solid-State Batteries Chunpeng Yang and Liangbing Hu; University of Maryland at College Park, College Park, Maryland, United States.

High-energy lithium metal batteries are among the most promising candidates for next-generation energy storage systems. With a high specific capacity and a low reduction potential, the Li metal anode has attracted extensive interest for decades. Dendritic Li formation, uncontrolled interfacial reactions, and huge volume effect are major hurdles to the commercial application of the Li metal anodes. In this talk, I will introduce our approaches to protect Li metal anodes from liquid batteries to solid-state batteries. We designed advanced host structures with nanoseeded nucleation sites for Li anode, ion-conductive protecting layers for Li metal anode, and so on. The strategies in liquid batteries improve the performance and safety of Li metal anodes in liquid electrolytes significantly. Superior to the liquid electrolytes, solid-state electrolytes are considered able to inhibit problematic Li dendrites and build safe solid Li metal batteries, but their utilization is mainly hindered by the poor interface between the solid electrolyte and electrodes. We introduce a solid-state Li anode hosted in a 3D garnet-type ion-conductive framework with bottom-deposited Cu. The Li anode is plated within the solid garnet framework from the bottom Cu layer and shows a dendrite-free deposition behavior, effectively averting the dendrite penetration issue. Owing to the 3D ion-conductive host, the volume change and interface contact problem of the Li anode have been significantly mitigated, realizing a high-capacity and safe Li metal anode for solid-state high-energy-density batteries.

11:30 AM ET01.06.11

Dominating Factors Controlling The Ion Conductivity of $\text{Na-}\beta''\text{-Alumina}$ Ceramic Electrolytes Marie-Claude Bay^{1,2}, Meike V. Heinz¹, Nicola Zanon³, Ulrich F. Vogt^{1,2} and Corsin Battaglia¹; ¹Empa—Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland; ²Albert-Ludwigs-University Freiburg, Freiburg i. Breisgau, Germany; ³FZSoNick SA, Stabio, Switzerland.

Ceramic $\text{Na-}\beta''\text{-alumina}$ is a fast solid-state sodium-ion conductor at elevated temperature (0.2 S/cm at 300 °C) and thus favored as electrolyte in high-temperature batteries (Na/NiCl_2 , Na/S) [1]. Furthermore it is gaining attention as interesting candidate for all-solid-state batteries (1 mS/cm at room temperature) [2]. Although known since the 1970s, processing of $\text{Na-}\beta''\text{-alumina}$ into a dense material with high ion conductivity is challenging, in particular due to significant Na loss during sintering. Ion conductivity values reported in the literature vary by a factor of 100 [3]. While these variations are generally ascribed to microstructure and composition, conclusive studies identifying the relevant parameters are lacking.

Depending on sintering temperature and sintering time, we obtain samples with conductivities between 0.04 and 0.37 S/cm at 300°C from identical starting powders. We identify the average grain size as the dominating factor controlling ion conductivity for densely sintered samples. For an average grain size between 1 and 6 μm , we obtain conductivities between 0.17 and 0.27 S/cm. The influence of porosity in under-sintered, highly porous samples is well accounted for by Archie's law and results in lower ion conductivity down to 0.04 S/cm at 68 % density. The overall Na content remains constant within experimental uncertainties. However, we observe evidence in X-ray diffraction that the local sodium concentration inside the grains increases with increasing sintering temperature. We present a model to predict the influence of grain size on the ion conductivity and effective activation energies of grain and grain-boundary phases. Our insights into microstructural factors controlling ionic conductivity such as grain size and density are instrumental for the

successful integration of Na-β''-alumina ceramic electrolytes into next-generation batteries.

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11:45 AM ET01.06.12

Kinetic Monte Carlo Simulations of Solid State Battery Materials Steffen P. Grieshammer^{1,2}; ¹Helmholtz-Institut Münster, Forschungszentrum Jülich GmbH, Münster, Germany; ²Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany.

Ionic conductivities of solid state materials are of crucial importance for the efficiency of solid state batteries. Quantum chemical methods, such as density functional theory (DFT), have become a useful tool to predict structural and electronic properties of solid state materials as well as the migration paths of the ionic charge carriers. In ideal materials with dilute concentration of defects the macroscopic ionic conductivity can be derived analytically from the microscopic energy barrier of ion motion. However, at non-dilute concentration of defects, the motion of ions is correlated and depends on the local environment due to the interactions of the defects. In this case the ionic conductivity is determined by the inhomogeneous energy landscape of ion migration and can be simulated by the Kinetic Monte Carlo (KMC) method.

In this talk, the simulation of the ionic conductivity of solid state materials for battery applications is presented. DFT calculations are performed to derive migration energies and defect interaction energies, which are used to model the energy landscape for the migrating ions. The energy models are applied in an in-house KMC code to simulate the ionic conductivity depending on composition and temperature.

Simulations are performed for oxygen ion conductors like doped ceria and melilite structured oxides, which are potential electrolytes in rechargeable oxide batteries.

In doped ceria, the conductivity is influenced by the interaction of oxygen vacancies with dopant ions leading to a 'trapping' next to the dopant ions and 'blocking' of the migration paths. In melilite structured oxides, different migration paths with different energies exist for oxygen interstitials and migration energies are additionally shifted depending on the local arrangement of cations. The effects of these local environments on the conductivity are investigated here.

Simulations are extended to lithium ion conducting materials for application in solid state Li-ion batteries including both electrolytes and electrodes. In particular, the ionic conductivity of Li-intercalation electrodes changes with the charge state of the battery and the advantages and challenges of the KMC method to predict these changes are discussed with regard to selected examples.

SESSION ET01.07: Session VI

Session Chairs: Liwei Chen and Jennifer Rupp
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room 310

1:30 PM ET01.07.01

The Structural and Compositional Factors that Control the Li-Ion Conductivity in LiPON Electrolytes Valentina Lacivita², Nongnuch Artrith¹ and Gerbrand Ceder^{2,1}; ¹Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; ²Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Amorphous or glassy materials are ubiquitous in rechargeable battery devices. Therefore, understanding the structural and chemical factors affecting the ionic transport in such materials is key for battery technology. However, the complexity of amorphous systems makes this task very challenging. We addressed this question using *ab initio* computational models. Specifically, in this presentation we report atomistic-level insight into the mechanisms underlying the mobility of Li⁺ in amorphous LiPON (lithium phosphorus oxynitride) thin-film electrolytes. These materials have been known for more than twenty years for their outstanding electrochemical performance which combines good ionic conductivity at room-temperature (around 2-3 μS/cm) and compatibility with Li metal anode. Despite the importance of LiPON electrolytes, no conclusive explanation has yet been given for their electrochemical behavior. Our work fits in this context revealing for the first time how structure and chemistry interplay to influence the Li-ion mobility in amorphous LiPON. We show that the conductivity benefits from both amorphization of the phosphate framework and nitrogen doping. In particular, the N doping involves 1(N):1(O) substitutions (apical N) as well as 1(N):2(O) substitutions promoting the condensation between phosphate units (bridging N). We find that the ratio between apical and bridging N changes with the Li:P content, correlating with the conductivity trends experimentally observed and also well reproduced by our models. This detailed understanding of the structural mechanisms that affect Li⁺ mobility should be useful in optimizing the conductivity of LiPON and other amorphous Li-ion conductors. *This work was supported by the ARPA-E IONICS program, U.S. Department of Energy, award DE-AR0000775.*

1:45 PM ET01.07.02

Fabrication of All-Solid-State Lithium-Ion Battery Using Inorganic-Organic Hybrid Solid Electrolyte Jong Heon Kim and Hyun-suk Kim; Chungnam National University, Daejeon, Korea (the Republic of).

Lithium ion battery is considered to be the most promising battery technology currently available because it exhibits relatively high energy density compared to other chemical batteries. Normally, conventional lithium ion battery using organic liquid electrolyte exhibits relatively high ionic conductivity, but has some disadvantages such as safety problem, short lifetime, high cost and low power density. All-solid-state thin film battery is one of the ways to solve these problems, and safety is improved by using non-flammable solid electrolyte. It also has long lifetime, high energy density and less requirements on packaging. However, in spite of these many advantages, the low ionic conductivity of the material itself and the interfacial resistance between the electrode and the solid electrolyte are major problems to overcome for commercial application.

In this work, we studied inorganic-organic hybrid electrolyte with polyethylene oxide (PEO) based polymer and lithium phosphorus oxynitride (LiPON) of oxide based ceramics to reduce the interfacial resistance between the solid electrolyte and the electrodes. LiNi_{0.5}Mn_{1.5}O₄ and Li₄Ti₅O₁₂ were used for cathode and anode, respectively, and all the layers were fabricated on a stainless steel substrate as a thin film. Polymer electrolytes were fabricated by

electrospinning system and all other thin films were fabricated by sputtering system. The thickness, microstructure and surface morphology were examined using transmission electron microscopy and scanning electron microscopy. The crystal structure was identified by X-ray diffraction. The ion-conductivity was measured by an AC impedance method. The electrochemical properties were studied with charge-discharge cycling test and cyclic voltammetry.

2:00 PM *ET01.07.03

On Applications of Li-Garnets in Energy Storage and Sensing Devices Michal Struzik^{1,2}, Reto Pfenninger^{3,2} and Jennifer L. Rupp^{2,4}; ¹Warsaw University of Technology, Warszawa, Poland; ²DMSE, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ³Department of Materials, ETH Zürich, Zurich, Switzerland; ⁴EECS, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Technological and social advancement stimulates a need for clean and sustainable production of energy, its storage and efficient utilization, that will ensure energetic safety of the society of tomorrow. Most popular, nowadays, energy storage technology, based on components consist of lithium conducting polymers and liquids, suffer from limited power densities available, limited miniaturization potential and safety, due to dendrites growth of Li pathways in the electrolyte. New possibilities for safe energy storage devices arise with a development of new generation of highly conducting Li⁺ electrolytes, such as Li-La-Zr-O system, showing pure ionic conductivity of ca. 10⁻³ Scm⁻¹ at room temperature, good structural, thermal and chemical stability and compatibility with many of high capacity electrode materials. Li⁺ conducting ceramics can be employed not only as the electrolytes for batteries, but also can be utilized as electrolytes for potentiometric gas sensors for i.e. CO₂ detection and monitoring. The flexibility of applications and perspectives of functionalization of one electrolyte material with different sets of electrodes to define multiple functionalities is in focus of this work.

We discuss on the ceramic processing of Li₇La₃Zr₂O₁₂ based solid electrolytes and their structural and electrical properties by the means of X-Ray Diffraction, Raman Spectroscopy and Impedance Spectroscopy. Further, we employ Li-garnet electrolytes in all-solid-state battery cells and discuss their performance with emphasis on the interfacial effects. Further we turn on to gas sensing of Li-garnets. We report on the fabrication of potentiometric gas sensor for CO₂ levels monitoring and we perform an experimental evaluation of its performance in a simulated environment. We discover quick response times of ca. 60 s at working temperatures of ca. 300°C, which is faster than similar systems based on NASICON electrolytes.

2:30 PM BREAK

3:30 PM ET01.07.04

Grain Boundary and Dopant Engineered Ultra-Dense Garnet Towards Stable High Current Cycling Lei Zhang, Chengwei Wang, Dennis McOwen, Jack Gritton, Liangbing Hu and Eric D. Wachsman; University of Maryland, College Park, Maryland, United States.

High capacity and high rate are the two major requirements for the next generation Li ion batteries. Among all candidates, solid state Li metal battery utilizing solid electrolyte is promising. Garnet type Li ion conductor has been the most widely studied material system due to its high conductivity and stability with Li metal. Aside from high capacity, the high rate cycling with Li garnet solid electrolyte is hard to achieve. Previous reports on cycling failure pointed out Li dendrite growth at grain boundaries. However, a close examination at those reports reveals that the microstructure in their ceramics is not satisfactory. Small grain, clean grain boundary and high relative density are the three key factors that guarantee ceramics to have good mechanical properties. Herein, an ultra-dense garnet pellet was fabricated by controlling grain size and grain boundary phase. The high relative density (>99%) grants the pellet to be translucent. Nano indentation results show the improved mechanical property of ultra-dense garnet to conventional pressed-sintered garnet. Besides good mechanical property, electrochemical stability of dopants in Li garnet is another requirement. Nb, Ta and Al doped garnet were compared. It is found that Ta doped garnet has the best electrochemical stability. Nb doped garnet can be reduced upon Li metal coating. Al doped garnet is vulnerable to Li dendrite formation. Together with the grain boundary engineering and dopant engineering, stable long-term high-current cycling was proved to be achievable.

3:45 PM ET01.07.05

New Insights into the Most Promising Solid Electrolytes Daniel Rettenwander^{1,2}, Günther Redhammer³ and Martin Wilkening^{1,2}; ¹Institute for Chemistry and Technology of Materials, Technical University of Graz, Graz, Austria; ²Christian Doppler Laboratory for Lithium Batteries, Technical University of Graz, Graz, Austria; ³Department of Chemistry and Physics of Materials, University of Salzburg, Salzburg, Austria.

Much scientific attention is devoted to the development of all-solid state batteries (ASSB) as important and superior alternative to electrochemical cells relying on aprotic liquid electrolytes. Among promising solid electrolytes Li-oxide garnets, NASICON (Na-ion Super Ionic CONductor), and LiRAP (Li-Rich Anti-Perovskites) attracted most attention having the potential to realize those future energy storage technologies, due to there extremely high ionic conductivities and exceptional high stability versus low or high voltage electrode material. Despite all the research already performed, however, many questions remain unanswered. In particular, these include the fundamental ones concerning structure, stability, Li ionic conductivity and diffusivity. Herein, we will show, *e.g.*, that (i) the acentric cubic garnet structure is the thermodynamically favored modification of Ga-stabilized LLZO at room temperature with improved chemical and electrochemical properties, (ii) the variation in the phase behavior and ionic transport reported for "NASICON"-based solid electrolytes is related to the preparation history, and (iii) that Li₄(OH)₃Cl and variants of Li_{3-x}(OH)_xCl, with x > 0, are so far the only thermodynamically stable LiRAPs having experimental proof.

4:00 PM ET01.07.06

Discovery of New Oxide and Sulfide Compounds as Electrolytes for All-Solid-State Li-Ion Batteries Shan Xiong¹, Xingfeng He², Zhantao Liu¹, Zhensong Ren³, Shuo Chen³, Yifei Mo³ and Hailong Chen¹; ¹Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; ²Materials Science and Engineering, University of Maryland, College Park, Maryland, United States; ³Physics, University of Houston, Houston, Texas, United States.

All-solid-state batteries (ASSBs) are considered as a promising alternative to conventional Li-ion batteries owing to their good safety properties and potentially higher volumetric energy density. Multiple challenges now exist in the development of ASSBs, including the lack of good solid electrolytes with high conductivity, good electrochemical stability and mechanical compatibility. Here we report recent progresses in our research group in the design and discovery of new oxide and sulfide based lithium ion conductors. Lithium tantalum oxosilicate was identified through a computation assisted search and screening with using ab initio molecular dynamics (AIMD). While the stoichiometric compound is expected to be an ionic insulator, a number of aliovalent ion doped compounds were predicted to have very high Li⁺ conductivities. A group of zirconia doped lithium tantalum oxosilicate were successfully synthesized and tested. The 12.5% Zr doped samples showed encouraging ionic conductivity of >10⁻⁵ mS/cm at room temperature. Meanwhile, a group of lithium chloro-thiophosphate compounds were also experimentally identified assisted by in situ X-ray diffraction investigations. The new compounds have a novel crystal structure that have never been reported previous. The structure of both sulfides and oxides new compounds were characterized with using synchrotron X-ray diffraction and neutron diffraction. The conduction mechanisms were investigated combining AIMD computation, electrochemical impedance spectroscopy and solid state NMR experiments.

4:15 PM ET01.07.07

Resolving the Amorphous Structure of Lithium Phosphorus Oxynitride (Lipon) Andrew S. Westover¹, Valentina Lacivita², Andrew Kercher¹, Nathan Phillip¹, Guang Yang¹, Gabriel Veith¹, Gerbrand Ceder^{2,3} and Nancy J. Dudney¹; ¹Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²Lawrence Berkeley National Laboratory, Berkeley, California, United States; ³Material Science, University of California, Berkeley, Berkeley, California, United States.

Lithium phosphorus oxynitride or Lipon solid-state electrolytes are at the center of the search for solid-state Li metal batteries. Key to the performance of Lipon is a combination of high Li content, amorphous character, and the incorporation of N into the structure. Despite the material's importance, our work presents the first study to fully resolve the structure of Lipon. In order to resolve the structure structural models were first developed using a combination of *ab initio* molecular dynamics. In this presentation we compare simulated neutron pair distribution functions (PDF), and infrared spectroscopy (IR) of the Lipon with the experimental PDF and IR data. For both techniques we see exceptional agreement between the simulated and experimental results. Although details of the modeling efforts will be presented in a separate talk, some of the key findings show that N forms both bridges between two phosphate units and non-bridging or apical N. The model further shows that as the Li content is increased the ratio of bridging to apical N shifts from being predominantly bridging at Li contents around 2.5:1 Li:P to only apical N at higher Li contents of 3.38:1 Li:P. Furthermore, the simulations show that Li hopping events are faster in the vicinity of bridging N. This crossover from bridging to apical N appears to directly correlate and explain both the increase in ionic conductivity with the incorporation of N and the ionic conductivity trends found in our own experimental results and across the literature.

This work was supported by the ARPA-E IONICS program, U.S. Department of Energy, award DE-AR0000775.

4:30 PM ET01.07.08

Vertically-Aligned and Continuous Ceramic-Polymer Interfaces in Composite Solid Polymer Electrolytes for Enhanced Ionic Conductivity Xiaokun Zhang¹, Yong Xiang¹ and Yi Cui²; ¹University of Electronic Science and Technology, Chengdu, China; ²Stanford University, Stanford, California, United States.

Among all solid electrolytes, composite solid polymer electrolytes, comprised of polymer matrix and ceramic fillers, garner great interest due to the enhancement of ionic conductivity and mechanical properties derived from ceramic-polymer interactions. Here, we report a composite electrolyte with densely-packed, vertically-aligned, and continuous ceramic-polymer interfaces, using surface-modified anodized aluminum oxide as the ceramic scaffold and polyethylene oxide as the polymer matrix. The fast Li⁺ transport along the ceramic-polymer interfaces was proven experimentally for the first time, and an interfacial ionic conductivity higher than 10⁻³ S/cm at 0 °C was predicted. The presented composite solid electrolyte achieved an ionic conductivity as high as 5.82×10⁻⁴ S/cm at the electrode level. The vertically-aligned interfacial structure in the composite electrolytes enables the viable application of the composite solid electrolyte with superior ionic conductivity and high hardness, allowing Li-Li cells to be cycled at a small polarization without Li dendrite penetration.

SESSION ET01.08: Poster Session II
Session Chairs: Jennifer Rupp and Venkataraman Thangadurai
Wednesday Afternoon, November 28, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

ET01.08.01

Role of Lattice Polarization and Rotation on Lithium Diffusion in Li₁₀GeP₂S₁₂ (LGPS), β-Li₃PS₄ (LPS), and Li₁₀GeP₂O₁₂ (LGPO) Solid Electrolytes from *Ab Initio* Molecular Dynamics Alex T. Hall¹, Nicole Adelstein¹, Nima Leclerc², Joel B. Varley³ and Leonid Kahle⁴; ¹San Francisco State University, San Francisco, California, United States; ²Cornell University, Ithaca, New York, United States; ³Lawrence Livermore National Laboratory, Livermore, California, United States; ⁴Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland.

The search for a solid electrolyte in order to create a safe, long-lasting, all-solid battery has been extensive, but the fundamentals of lithium diffusion are still not completely understood. One of the fastest conducting electrolytes that has been identified is Li₁₀GeP₂S₁₂ (LGPS), though this electrolyte faces challenges to incorporation in batteries due to instability with the electrode interface. While significant computational research has been done on LGPS, nuances of the mechanisms governing ion diffusion are still unknown. Insight into the extraordinary conductivity of LGPS will enable the engineering and search for new electrolyte materials. Polarization of anions and (P/Ge)S₄ tetrahedra as well as rotation of tetrahedra were studied in order to elucidate the difference in conductivity between the LGPS, β-Li₃PS₄ (LPS), and Li₁₀GeP₂O₁₂ (LGPO) solid electrolytes. Experimentally, LPS has orders of magnitude lower ionic conductivity than LGPS, but a very similar composition and structure. These analyses allow quantification of the effects of electronic structure (polarization) and rotation on lithium diffusion. Polarization and rotation events were extracted from Density Functional Theory Molecular Dynamics (DFT-MD) simulations. Detailed analysis of the DFT-MD simulations revealed correlation of both tetrahedral rotation and polarization with lithium ion diffusion. Expansion of the unit cell in LGPS was found to facilitate the rotation of PS₄ tetrahedra in addition to increasing lithium ion diffusion. In contrast, expansion of the LPS unit cell did not affect tetrahedral rotation in a meaningful way. Anion polarization was found to correlate with lower lithium ion diffusion in LPS. The polarization of oxygen in LGPO, a structural isomer of LGPS, is calculated to study the effect of anion polarizability.

ET01.08.02

Microstructural Characterization of Cathodes in Sulfide-Based All-Solid-State Batteries via Tomographic Techniques Sungjun Choi, Wo Dum Jung, Ji-Su Kim, Hyoungchul Kim, Byung-Kook Kim and Hae-Weon Lee; Korea Institute of Science and Technology, Seoul, Korea (the Republic of).

The all-solid-state lithium-ion batteries (LIBs) have drawn increasing interests and demands as the next-generation rechargeable batteries for electric vehicles and energy storage devices since they have much more potentials (e.g., higher safety, reliability, power density, and design flexibility) than conventional LIBs. However, we all know that any further advances in all-solid-state LIBs are not possible without solving the current raising issues of all-solid-state LIBs, such as low lithium-ion conductivity, structural instability, and high resistance of electrode/electrolyte interface. Recently, sulfide-based all-solid-state LIBs are exhibiting the best performance approaching to the commercialization stage with various material advantages (e.g., excellent lithium-ion conductivity, room-temperature formability, and so on). Despite the comprehensive studies to develop high-performance sulfide-based all-solid-state LIBs, the fundamental understanding of crystallographic structure and elemental distribution for materials used in sulfide-based all-solid-state LIBs has been lacking.

Here we present the recent advances of structural and elemental analysis in sulfide-based all-solid-state LIBs using vacuum-transferred transmission electron microscopy (TEM) and 3-D tomography techniques. According to the high-speed energy dispersive X-ray spectroscopy and selected area

diffraction analysis implemented in TEM, we verified the crystallographic results of bulk XRD analysis, and the microscopic elemental distribution of a composite cathode structure were successfully analyzed. Employing the atom probe tomographic technique, in addition, we properly reconstructed the cathode structure, and unveiled the 3-D distribution of each element (including lithium-ion) in the all-solid-state composite cathode. We believe these research activities lead to the promising technological advances and provide new guidelines in developing the sulfide-based all-solid-state LIBs for the next-generation rechargeable batteries.

Acknowledgement: This work was supported by the Dual Use Technology Program of the Institute of Civil Military Technology Cooperation granted financial resources from the Ministry of Trade, Industry & Energy and Defense Acquisition Program Administration (17-CM-EN-11).

ET01.08.03

Improved Interface Between Lithium-Rich Anti-Perovskite Electrolyte and Cathode for Developing Solid-State Lithium Batteries Shuai Li¹, Jinlong Zhu², Xujie Lv², Li Huang¹, Yonggang Wang¹, Ruqiang Zou³ and Yusheng Zhao¹; ¹South University of Science and Technology, Shenzhen, China; ²Center for High Pressure Science and Technology Advanced Research, Shanghai, China; ³Peking University, Beijing, China.

Lithium ion batteries have shown great promise in electrical energy storage with enhanced energy density, capacity, and cycling lifetimes. However commercial liquid electrolytes consisting of lithium salts dissolved in organic solvents are toxic, corrosive or flammable. Solid electrolytes with superionic conductivity can avoid those shortcomings, so that for safe application. Meanwhile, the mechanical property of solid electrolyte enable it to prevent the risk of lithium dendrites, thereby to achieve high energy density. Here we present a novel class of solid electrolyte materials with three-dimensional conducting pathways based on lithium-rich anti-perovskites (LiRAP). Our previous work shows its high ionic conductivity, low activation energy, and high stability with lithium metal. LiRAP also serves as solid electrolyte functionally in a half battery with LTO and lithium metal, running at elevated temperature. The new LiRAP materials can be readily manipulated via chemical, electronic, and structural means to boost ionic conductivity and serve as high-performance solid electrolytes. Furthermore, by transition metal doping, as TM-LiRAP, this material can serve as cathode in lithium battery. This creative idea is promoted by the fact that the solid-solid interface is an critical issue in solid batteries. Therefore a seamless interface with bi-layered LiRAP electrolyte and TM-LiRAP cathode is designed, and preliminary test evidenced this concept. The enhanced compatibility between LiRAP based electrolyte and cathode, in the aspects of crystal lattices, chemical compositions, thermal evaporation coefficient and volume change during cycling, could improve the solid state interface and hence the battery performance. These results could be quite helpful for the R&D of solid state lithium batteries.

ET01.08.04

Enhanced Performance of Dopamine Modified $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ /PEO Composite Electrolyte for Solid-State Battery Huang Zeya and Chang-An Wang; Tsinghua University, Beijing, China.

Solid state electrolyte with high ionic conductivity and low interfacial resistance as well good stability is essential for the application of solid state battery. The Ta doped garnet-type solid state electrolyte - $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ (LLZTO) has high ionic conductivity and wide electrical window. However, it is not easy to be assembled into batteries due to lack of flexibility. Polymer electrolytes such as poly(oxyethylene) (PEO) have good flexibility, but the room temperature conductivity is low. The PEO has relative narrow electrochemical window and poor thermal stability. The composite electrolyte where the LLZTO particles are dispersed in the PEO has enhanced electronic conductivity, electrochemical stability, thermal stability, and good processability. The addition amount of LLZTO is an important factor affecting the performance of the composite electrolyte. A high ceramic/polymer ratio will significantly increase the proportion of high-speed channel for ion transport in the composite electrolyte and thus achieve better electrical performance. However, the increase in the proportion of ceramics will bring about problems of particle agglomeration, uneven dispersion, and deterioration of mechanical properties. These problems are caused by the compatible of polymer and ceramic due to their difference in surface energy. In this paper, LLZTO was modified by dopamine to improve the wettability of LLZTO and PEO, so that more than 80wt% of LLZTO can be uniformly dispersed in 20% of PEO/LiTFSI polymer electrolyte. Because of the wetting nature of dopamine, the composite electrolyte has good adhesion with both positive and negative electrodes, which will improve the interfacial contact and thus decrease the resistance. The composite electrolyte with 80wt% LLZTO coated with dopamine in PEO was synthesized by solvent casting method. Electrochemical performance tests showed that after dopamine modification, the conductivity at room temperature (20 °C) increased from 2×10^{-5} S/cm to 4×10^{-5} S/cm, and the interface resistance between the composite electrolyte and metallic lithium decreased from $490 \Omega \cdot \text{cm}^2$ to $191 \Omega \cdot \text{cm}^2$. The thermal stability and electrochemical stability of the composite electrolyte have also been improved. These results showed that the performance of PEO-LLZTO composite electrolyte can be improved by dopamine modification.

ET01.08.05

Combined DFT and Semi-Continuum Modelling of Space-Charge Regions in Li_3OCl Solid Electrolytes Georgina Wellock, James A. Dawson, Pieremanuele Canepa, Saiful Islam and Benjamin J. Morgan; University of Bath, Bath, United Kingdom.

Over recent decades, lithium-ion batteries have become the dominant power source for portable devices due to their high energy densities and low self-discharge rates. Despite this success, there are safety concerns regarding the use of lithium ion batteries in applications such as electric vehicles and grid scale storage, due to their use of flammable organic liquid electrolytes.¹

Lithium rich anti-perovskites, such as Li_3OX , where X is a halide ion, are a promising family of solid electrolytes with the potential for improved safety in commercial lithium-ion batteries. In polycrystalline Li_3OX , the presence of grain boundaries can strongly affect the transport of lithium ions, due to local changes in atomic structure and associated electrostatic potentials, and therefore affect measured ionic conductivities. Although there has been recent work investigating the effect of grain boundaries on lithium transport in Li_3OX anti-perovskites, this is still not fully understood.²

A key mechanism by which grain boundaries affect ionic transport is through the formation of space-charge regions. Charged defects, such as lithium vacancies, are expected to segregate to, or from, grain boundaries, which produces a net local charge. This charge interacts with the surrounding crystal regions, where the bulk defects are depleted or accumulated in so-called “space-charge” regions to restore equilibrium. Because these space-charge regions can have defect concentrations that strongly differ from the bulk crystal, they can strongly enhance or decrease the ionic conductivity of the sample. Grain boundary effects on space charge formation and ionic conductivity in Li_3OX , and many other lithium-ion solid electrolytes, are not fully understood, especially on the atomic scale.^{3,4}

Considering Li_3OCl as a model polycrystalline electrolyte, we have calculated explicit defect positions and segregation energies using density functional theory. We have then used these positions and segregation energies to perform self-consistent semi-continuum 1D Poisson-Boltzmann calculations, to predict equilibrium defect concentrations, electrostatic potentials, and resistivities at grain boundaries and their adjacent space-charge regions.

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ET01.08.06

PEO/NASICON Composite Electrolyte with a Low Interfacial Resistance Nan Wu, Yutao Li, Henghui Xu and John Goodenough; The University of

Texas at Austin, Austin, Texas, United States.

Compared to current commercial available lithium ion batteries, solid-state batteries are emerging as an attractive energy storage device because of their high safety, reliability and high energy density when paired with lithium metal anode. Rigid ceramic electrolytes have a high ion conductivity, but exhibit a very high interfacial resistance due to the discrete contact with electrodes. Soft polymer electrolytes enable a good contact with electrodes with a low interfacial resistance, but their conductivity is too low. Incorporating rigid ceramic electrolytes into soft polymer electrolytes matrix simultaneously enhances ionic conductivity and reduces the interfacial resistance between electrodes and electrolytes.

Here we demonstrated a PEO/NASICON composite electrolyte with a high conductivity of 10^{-3} S cm⁻¹ at 60 °C. When used as a solid electrolyte in Li symmetric cell, the as-prepared PEO/NASICON composite membrane exhibits a very low interfacial resistance. Surface analyses were carried out to probe the mechanism of the low interfacial resistance. Our results show that an interphase was formed between the lithium metal anode and the composite electrolyte, which may account for symmetric cells with low resistance and high stability. Furthermore, a LFP/PEO-NASICON/Li cell was assembled to demonstrate its feasibility for practical applications.

ET01.08.07

TEM Single-Particle Analysis of Solid-State Electrolyte with Mobile Biasing Probe Nikhilendra Singh², Timothy S. Arthur², Julio A. Rodriguez Manzo¹, Daan H. Alsem¹ and Norman Salmon¹; ¹Hummingbird Scientific, Lacey, Washington, United States; ²Toyota Research Institute of North America, Ann Arbor, Michigan, United States.

Solid-state electrolytes are an alternative to liquid-based electrolytes, when it comes to improving the safety of batteries and their energy density. However, large impedances at solid-state electrolyte-electrode interfaces remain a challenge.

Obtaining reliable electrochemical information from individual solid-state particles is difficult; particles can have nanoscale dimensions and ionic current paths cannot be confined to a single particle unless the electrodes are touching only the particle of interest. However, understanding single-particle effects is paramount to optimize the functionality of assemblies—ion insertion rates can vary at subparticle length scales [1]. This challenging characterization need, however, can be addressed with a purpose-designed in-situ transmission electron microscope (TEM) sample holder with biasing capabilities and a mobile electrode probe. With this TEM platform, a static sample can be approached with a biasing sharpened probe—usually a few tens of nanometers in diameter—to create an electrical circuit, where the contact point can be chosen with high spatial resolution. With the right control electronics, ionic currents in the order of picoamps can be measured while, simultaneously, all TEM-related characterization techniques (high-resolution imaging, electron-based spectroscopy, electron diffraction, etc.) can be applied to study the particle and its interfaces. This approach has been used to investigate, for example, the switching of oxide resistive memories [2], anode materials for batteries [3,4], and the conductance through rows of atoms [5,6].

Here, we present an in-situ TEM study of solid-state electrolyte particles under load. Micron-sized particles were contacted with a mobile probe and cyclic voltammograms were obtained. Ionic currents in the order of picoamps were measured and, simultaneously, electrochemical induced structural changes—within particles and at interfaces—were imaged. Our results show clear correlations between gathered electrochemical data and structural transformations. This approach can be used to study any solid-state electrolyte-electrode configuration, provided that the electron irradiation-induced effects are taken into consideration.

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ET01.08.08

Analyzing the Role of Li Transport in Achieving High Critical Current Densities in Li₇La₃Zr₂O₁₂ Michael Wang and Jeff Sakamoto; University of Michigan, Ann Arbor, Michigan, United States.

The development of cubic Li₇La₃Zr₂O₁₂ (LLZO) for physically stabilizing the Li-electrolyte interface has shown potential for safe, high energy-density Li-ion batteries in recent years. Despite its high elastic modulus and hardness, it has been observed that Li metal filaments can propagate through LLZO above a certain critical current density (CCD). Currently, reported values for CCD are still well below the current density regimes relevant to electric vehicles, and therefore, there is a need to increase the CCD and understand the mechanisms of Li propagation in LLZO. This study utilizes a combination of recently developed processing methods from the literature in order to achieve low Li-LLZO interface resistance and consistently high CCDs close to 1 mA/cm² at room temperature in Al-stabilized LLZO. The relationship between CCD and temperature is examined. By analyzing the flux of Li⁺ at the Li-electrolyte interface, it is hypothesized in this study that the CCD may be heavily influenced by the rate of Li transport (diffusivity) in the metal electrode. The results presented here demonstrate optimistic improvements toward improving the rate capabilities of LLZO solid state batteries and provide further insight on the potential role of Li diffusivity in determining the CCD.

ET01.08.09

Mechanochemical Assembly of 3D Mesoporous Conducting-Polymer Aerogels for High Performance Hybrid Electrochemical Energy Storage Luhua Cheng^{1,2}, Xiaosong Du¹, Yadong Jiang¹ and Alexandru Vlad²; ¹State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China (UESTC), Chengdu, China; ²Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Louvain-la-Neuve, Belgium.

Functional and structural tailoring of three-dimensional (3D) conducting polymer nanoarchitectures is a promising route but remains challenging to develop high-performance electrodes for electrochemical energy storage. Herein, we design poly(3, 4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) 3D mesoporous aerogel electrodes through a simple and original one-pot mechanochemical processing route. The hierarchical structure of neat PEDOT:PSS aerogels displays a highly interpenetrated porous conductive network with a record high active surface area of 470 m² g⁻¹ amongst the class of conducting polymer architectures. Robust structural and electrochemical performances are achieved with high gravimetric, areal and volumetric capacitance metrics of 120 F/g, 2.5 F cm⁻², and 124 F cm⁻³, respectively, as the result of a mixed hybrid faradaic - capacitive charge storage mechanism. Moreover, these performances are attained in organic based electrolytes, reported so far to be incompatible or hinder the electrochemical activity of PEDOT:PSS. We undermine the fundamentals of the electrochemical operation in these electrodes and show that the electrolyte chemistry and the aerogel morphology particularly impact the charge storage performances demonstrating the superiority of the mesoporous architecture for charge transfer and ion exchange. Asymmetric cells are built having a specific capacitance of 40 F/g based on the total mass of electrodes and a good cyclic stability with 90%

capacitance retention after 1000 charge and discharge cycles. This study offers a new route to enhance the electrochemical properties of conducting polymers and provides suggestive insights for developing high performance polymer electrode materials for electrochemical energy storage.

ET01.08.10

Construction of Neural Network Potential to Study Ion Migration Under Applied Voltages Takanori Moriya¹, WenWen Li², Koji Shimizu¹, Emi Minamitani¹ and Satoshi Watanabe^{1,3}; ¹Department of Materials Engineering, The University of Tokyo, Bunkyo-ku, Japan; ²Research Center for Computational Design of Advanced Functional Materials, National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan; ³Research and Service Division of Materials Data and Integrated System, National Institute for Materials Science, Tsukuba, Japan.

A new memory device that can be switched between high and low open-circuit voltages, Vol-RAM, has recently been proposed [1]. Vol-RAM has a laminated structure of Li, amorphous solid electrolyte Li_3PO_4 and Au, and may be able to achieve higher performance than other memory devices in terms of power consumption and integration. Elucidation of microscopic elementary processes during its operation is strongly desired for practical application. Since it has already been found that the Li ion distribution in Li_3PO_4 and $\text{Li}_3\text{PO}_4/\text{Au}$ interface differs between the two voltage states, the next important issue that should be clarified is the behavior of Li ions in Li_3PO_4 under applied voltages, in other words, under electric fields. First-principles molecular dynamics (MD) simulations would be powerful to study this, but are computationally expensive. On the other hand, the computational cost of MD simulations using empirical potentials is cheap, but determination of their functional forms and parameters to achieve sufficient reliability is extremely difficult. Considering this situation, we have been trying to tackle with this issue using the high-dimensional Neural Network (NN) potential [2], which is expected to achieve high reliability and low computational cost simultaneously. Since the NN potential of Li_3PO_4 has already been constructed in our previous study [3], we focus on the inclusion of the effects of voltage application in the NN potential in the present study. Using simulations within the density functional theory with VASP package, we examined the dependence of the forces acting on atoms on the structure and applied electric field, and found the followings. First, the change in the force acting on the atom is proportional to the electric field. Second, the proportional coefficient shows a strong correlation with Born effective charge. Third, the Born effective charge correlates with the features of the local atomic structure. These results suggest that NN to predict the Born effective charge from the atomic arrangement information can be constructed, and the NN potential taking account of the effect of applied electric fields can be constructed using the NN for the Born effective charge. We have already constructed a preliminary NN for the Born effective charge, though its accuracy is insufficient. Its improvement is in progress.

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SESSION ET01.09: Session VII
Session Chairs: Eric Wachsman and Bilge Yildiz
Thursday Morning, November 29, 2018
Hynes, Level 3, Room 310

8:00 AM ET01.09.01

Microstructural Exploration of Solid-State Electrolytes for Dendrite Suppression—Towards a Reliable Mechanical and Electrochemical Performance Xiaomei Zeng¹, Andrew J. Martinolich², Kimberly A. See² and Katherine T. Faber¹; ¹Applied Physics and Materials Science, California Institute of Technology, Pasadena, California, United States; ²Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, United States.

The garnet-type oxide $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) is one of the most promising candidates as a solid-state electrolyte in lithium ion batteries, due to its unique combination of high ionic conductivity (up to ~ 1.8 mS/cm), and good chemical and electrochemical stability with lithium metal or lithium-containing compounds. The high mechanical strength and shear modulus of LLZO were believed to be adequate for suppressing the formation of lithium dendrites, which is a major challenge in lithium ion battery design. However, recent research reported that the flaws in the polycrystalline microstructure, such as the grain boundaries and interconnected pores, still serve as pathways for lithium dendrite formation and lead to short-circuit in the battery. These boundaries and pores produce dendrite nucleation sites at the electrode/electrolyte interface and their propagation within the electrolyte.

Though numerous studies have been conducted to modify the electrode/electrolyte interface to achieve uniform current distribution and suppress the nucleation of dendrites, limited effort has been devoted to optimizing the LLZO microstructure to obtain a robust electrolyte. In this work, we systematically explored the parameters controlling densification and grain growth of LLZO during synthesis. It was discovered that particle agglomeration is responsible for the formation of large cavities and interconnected pores along grain boundaries. The grain size was found to be limited by powder size and moisture content on the powder surface. Through high energy ball milling and freeze drying, nanoscale powders without agglomeration were successfully obtained, which sinter into dense LLZO electrolyte with a relative density $> 97\%$ and a grain size > 200 μm . This combination of large grain size and strong grain boundary without interconnected pores significantly enhances the mechanical and electrochemical reliability of the electrolyte. As a result, lithium dendrites were effectively suppressed under high current density > 0.5 mA/cm². This type of robust electrolyte is critical for the development of all-solid-state batteries to have reliable cyclic performance.

8:15 AM ET01.09.02

Probing the H^+ and Li^+ Ion Mobility in $(\text{Li}_{6.25-x}\text{H}_x\text{Al}_{0.25})\text{La}_3\text{Zr}_2\text{O}_{12}$ Through Comprehensive Neutron Scattering and Advanced Electron Microscopy Xiaoming Liu¹, Yan Chen¹, Cheng Ma², Zachary D. Hood¹, Hui Wang³, Ke An¹, Jeff Sakamoto⁴, Yongqiang Cheng¹, Niina Jalarvo¹ and Miaofang Chi¹; ¹Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²University of Science and Technology of China, Hefei, China; ³University of Louisville, Louisville, Kentucky, United States; ⁴University of Michigan—Ann Arbor, Ann Arbor, Michigan, United States.

Though liquid-based lithium-ion batteries are ubiquitous to our daily life, they are reaching their theoretical limits in terms of their energy and power densities. New battery configurations are urgently needed to meet the requirements for large-scale applications, especially in applications where the power densities are relatively high (e.g. electric vehicles, grid energy storage systems, etc.). Aqueous lithium batteries are considered to be one of the most promising solutions due to their low cost, high rate capability, and their prospect in utilizing metallic lithium, the solid-state anode with highest theoretical capacity and lowest electrochemical potential. Recently, it was reported that the garnet-based $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) shows excellent structural stability towards exposure to aqueous solutions with a large range of pH value, with Li^+ ions being partially substituted by H^+ , demonstrating its promise to be used as a separator to stabilizing Li metal in aqueous lithium batteries. However, the mobility of Li^+ and H^+ ions in protonated LLZO ($\text{H}_x\text{-LLZO}$), that critically determine the performance of LLZO, has yet to be investigated. This shortfall is largely due to the challenges in differentiating the diffusion of

the two ions. In this work, we successfully reveal not only the structural evolution after ion exchange in H_x -LLZO, but also the mobility of H^+ and Li^+ ions by combining high-resolution scanning transmission electron microscopy (STEM), neutron diffraction, and electron energy loss spectroscopy. Our results show that the H^+ ions in H_x -LLZO are largely immobile at temperatures less than 200 °C while the Li^+ ions remains mobile in the structure. The activation energy of Li^+ ions in protonated LLZO is about 20.08 kJ/mol at room temperature, which is $\sim 1.5\times$ that of pristine LLZO, indicating a reasonable Li^+ ion conductivity in H_x -LLZO. Our results highlight the potential of LLZO as a separation layer to protect metallic lithium anode in aqueous lithium batteries.

8:30 AM *ET01.09.03

Direct Growth of 3D Host on Cu Foil for Stable Lithium Metal Anode [Xiaogang Han](#)¹, Fei Shen¹ and Xuchun Gui²; ¹Xi'an Jiaotong University, Xi'an, China; ²Sun Yat-sen University, Guangzhou, China.

Due to light-weight and high specific capacity, lithium (Li) metal anode has been regarded as the “Holy Grail” for lithium-ion based batteries. However, the issues of mossy and dendritic Li formation and infinite volume expansion, leading to low Coulombic efficiency and poor cycling performance, retards Li metal anode application in practice. Effort should be done to address the issues in order to the application of Li metal anode. In this study, we report a novel design to stabilize Li metal anode by growing porous carbon nanotube (CNT) sponge directly on Cu foil, (C-host@Cu), where CNT sponge as host and Cu foil as current collector. The intrinsic porous feature of CNT sponge meets the requirements for an outstanding Li host: 1) high porosity to accommodate infinite volume change of Li; 2) low local current density to suppress Li dendrite formation; 3) stable and electrically conductive framework for Li deposition during long-term cycles; 4) strong seamless attachment to the current collector. The as-designed 3D host Li metal anode exhibits stable cycling performance with high Coulombic efficiency $\sim 99\%$ at a current density of 1 mA/cm² over 250 cycles. In contrast, the bare Cu electrode presents a mossy-like morphology with a low Coulombic efficiency $\sim 60\%$ after 150 cycles. The results reveal that the effective confinement of Li deposition in this unique 3D host successfully suppresses the growth of Li dendrites.

9:00 AM *ET01.09.04

Simulations of Ionic Transport in Disordered and Correlated Solid Polymer and Amorphous Ceramic Electrolytes [Boris Kozinsky](#)^{1,3}, Chris Ablitt^{2,3}, Mordechai Krombluth³, Jonathan Mailoa³ and Nicola Molinari¹; ¹Harvard University, Cambridge, Massachusetts, United States; ²Imperial College London, London, United Kingdom; ³Bosch Research, Cambridge, Massachusetts, United States.

Materials design for next-generation solid-state Li-ion batteries require atomistic-level understanding of ionic transport mechanisms and the required ingredients and design principles for enabling high ionic conductivity in solid-state materials at room temperature. Strong ion-ion interaction, geometric frustration, disorder and collective motion are emerging as common themes in recent investigations of super-ionic materials. In this talk we present recent efforts to gain mechanistic understanding of the influence of correlation, disorder and frustration on ionic transport in solid polymer and ceramic materials. We find that ionic dynamics in polymer electrolytes is strongly influenced by the host polymer dynamics and the strong coupling between mobile component species and the host polymer. In the domain of inorganic electrolytes, the success of LiPON thin films indicates promise of amorphous materials, which are known to have different transport properties than their crystalline counterparts. Using atomistic simulations of ion dynamics, we analyze ionic transport mechanisms in the presence of disorder, using insights to develop design rules for optimizing structure and composition of glassy electrolytes.

9:30 AM ET01.09.05

Electrochemical Characterization of Ionic Liquid Electrolytes for Printed Secondary Zinc-Manganese Dioxide Batteries [Bernard Kim](#)¹, James W. Evans² and Paul K. Wright¹; ¹Mechanical Engineering, University of California, Berkeley, Berkeley, California, United States; ²Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States.

Ionic liquids are room temperature solutions of cations and anions that have emerged as possible electrolyte materials for batteries due to their wide thermal and electrical potential stability windows relative to conventional electrolytes [1]. In the case of zinc-based batteries, their use has been shown to enable reversible cycling with traditional electrode materials, unlike cycling in aqueous electrolytes [2]. Furthermore, their extremely low vapor pressure allows for integration with a polymer to form a printable, monolithic gel polymer electrolyte which can function both as a mechanical separator as well as an ion conductor [3].

However, the vast array of possible cation and anion pairs making up each ionic liquid as well as each pair's compatibility with supporting metal salts reveals a significant challenge in characterizing material combinations for optimal performance in full cells. Specifically, this work seeks to identify optimal ratios of ionic liquid, supporting metal salt, and gel polymer in order to maximize redox currents as well as mitigate losses associated with repeated cycling.

This work is conducted in two parts. The first part determines the diffusion coefficient of Zn^{2+} and the peak currents, solution resistance, and redox potentials of Zn/Zn^{2+} in solutions of only ionic liquid and zinc salt. The second part determines the solution resistance and characterizes the reversibility of gel polymer electrolytes with varying compositions of ionic liquid, zinc salt, and polymer binder. Cyclic voltammetry and electrochemical impedance spectroscopy are used to determine constant values and characterize material compositions.

Ionic liquids with smaller cations demonstrate higher peak currents in cyclic voltammograms, but they also exhibit narrower potential stability windows with higher rates of unwanted reactions within the Zn/Zn^{2+} redox window. Gel polymer electrolytes demonstrate good reversibility for at least 50 cycles and solution resistances comparable with the pure ionic liquids.

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9:45 AM ET01.09.06

A Mechanism for Lithium Metal Penetration Through Solid Electrolytes—Atomic Simulations for Grain Boundary Softening [Seungho Yu](#) and Donald Siegel; University of Michigan—Ann Arbor, Ann Arbor, Michigan, United States.

Models based on linear elasticity suggest that a solid electrolyte with a high shear modulus will suppress ‘dendrite’ formation in batteries that use metallic

lithium as the negative electrode. Nevertheless, recent experiments find that lithium can penetrate stiff solid electrolytes through microstructural features such as grain boundaries. This failure mode emerges even in cases where the electrolyte has an average shear modulus that is an order of magnitude larger than that of Li. Adopting the solid electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) as a prototype, here we demonstrate that significant softening in elastic properties occurs in nanoscale regions near grain boundaries. Molecular dynamics simulations performed on tilt and twist boundaries reveal that the grain boundary shear modulus is up to 50% smaller than in bulk regions. We propose that inhomogeneities in elastic properties arising from microstructural features provide a mechanism by which soft lithium can penetrate ostensibly stiff solid electrolytes.

10:00 AM BREAK

10:30 AM *ET01.09.07

All-Solid-State Li-Ion Microbatteries Using Functionalized Self-Organized Titania Nanotubes Thierry Djenizian; Ecole des Mines Saint-Etienne, Gardanne, France.

Lithium-ion batteries (LIBs) are widely used to power portable devices, microelectronics, vehicles, etc. With many advantages such as high surface area and improved charge transport, self-supported 3-D nanostructured metal oxides such as titania nanotubes (TiO_2 nts) are promising electrode materials for LIBs and their impact is particularly significant when considering the miniaturization of energy storage systems and the development of 3D microbatteries.

This talk will review the concept and fabrication of all-solid-state Li-ion microbatteries using TiO_2 nts as negative electrode [1-7]. Effects of material selection and processing on the performance and reliability are presented as a means to develop conceptual guidelines to understand and improve microbattery designs. Fundamentals such as electrode reactions, lithium ion diffusion and the conformal electrodeposition mechanism of polymer electrolytes onto the nanostructured electrodes will be presented. The fabrication of a full 3D microcell showing high electrochemical performance will be presented and the development of the next generation of 3D microbatteries will be discussed.

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11:00 AM ET01.09.08

LiSnZr(PO₄)₃: NASICON-Type Solid Electrolyte for Lithium Batteries Sunil Kumar, Tanvi Pareek and Sushmita Dwivedi; Metallurgy Engineering and Materials Science, Indian Institute of Technology Indore, Indore, India.

Safety issues associated with the high flammability and volatility of organic electrolytes used in commercial rechargeable lithium-ion batteries has led to significant attention to ceramic-based solid electrolytes. In this work, $\text{LiSnZr(PO}_4)_3$ (LSZP) ceramics were fabricated via a sol-gel route and were characterized for their properties using the X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, and electrochemical chemical impedance spectroscopy. Rietveld refinement of synchrotron X-ray diffraction data confirmed the room temperature crystal structure of $\text{LiSnZr(PO}_4)_3$ as rhombohedral (R-3c space group). The Zr 3d, Sn 3d, P 2p, Li 1s and O 1s, core level X-ray photoelectron spectra associated with different valence states on the LSZP sample were deconvoluted. Surface morphology, densification, and the ionic conductivity of ceramics sintered at various temperatures were investigated. LSZP ceramics sintered at 1273 K exhibited an excellent room temperature bulk ionic conductivity of about $10^{-4} \text{ S.cm}^{-1}$ and associated activation energy $\sim 0.36 \text{ eV}$ in the temperature range of 300 – 500 K. DC polarization study confirmed the conductivity of LSZP ceramics as predominantly ionic. Distinct relaxations observed in dielectric and modulus formalisms and the temperature dependence thereof are also discussed.

11:15 AM ET01.09.09

Fluorinated Solid Electrolyte Interphase Enables Highly Reversible Solid-State Li Metal Battery Xiulin Fan, Xiao Ji, Fudong Han, Jie Yue, Ji Chen and Chunsheng Wang; University of Maryland, College Park, College Park, Maryland, United States.

Solid-state electrolytes (SSEs) have received great interest in recent years due to the escalating demands for the next-generation high energy battery technologies. However, the facile formation of the Li dendrite in the SSEs with much lower critical current density of only 1/10 of the conventional non-aqueous electrolytes hindered the possible commercialization of the high energy SSE Li metal batteries. Herein, we describe a simple and efficient strategy to stabilize the Li metal anode in the SSE batteries by in situ forming an efficient LiF-rich solid electrolyte interphase (SEI) layer between the SSE and the Li metal. This LiF-rich SEI layer not only effectively blocks electron leakage but also efficiently facilitates Li transport along the interface and suppresses the penetration of Li dendrite into the SSE.

11:30 AM ET01.09.10

Electro-Chemo-Mechanical Stability of Solid-State Battery Interfaces Giovanna Bucci^{2,3}, Peter K. Hart¹, Yet-Ming Chiang³ and Craig Carter³; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Energy Storage, Bosch, Sunnyvale, California, United States; ³Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Despite the progress in achieving high solid-electrolyte bulk conductivity, the rate capability of many all-solid-state batteries (ASSBs) remains poor. This is typically ascribed to various interfacial phenomena, including chemo-mechanical instability of composite electrodes and unstable metallic lithium interfaces. Such mechanisms are difficult to ascertain and characterize experimentally. Fracture in solid Li-ion conductors represents a barrier for Li transport, and accelerates the decay of rate performance. Therefore, mechanical degradation is linked to the battery power-density. Low porosity solid-state composite electrodes are generally more prone to mechanical degradation if not designed to accommodate intercalation-induced deformations.

We present a quantitative analysis of mechanical reliability of composite electrodes. We quantify the mechanical stress caused by chemical expansion and contraction of electrode particles and identify two main degradation mechanisms. First, the formation of micro-cracks within the solid electrolyte (SE) is expected to reduce the SE effective ionic conductivity [1, 2, 4]. Second, interfacial delamination reduces internal contact and may become the kinetic

bottleneck to achieve high power density [5].

Our analyses lead to guidelines for the engineering of particle size, volume ratio of active material, interfacial cohesion and the electrolyte mechanical properties [2-5]. The impact of mechanical degradation on an electrode's transport properties will also be discussed. In particular, we illustrate, via random-walk analysis, how micro-cracking of solid-Li-ion conductors increases the cell tortuosity, especially in densely packed microstructures [4, 5]. Finally, we explore the interplay of surface geometry and interfacial resistance in the Li-metal cells. Electric field magnification at the tip of surface defects and grain boundaries may lead to a largely non-uniform current density and localized Li-plating. Strategies for current density regularization are investigated. For instance, mechanical confinement causes pressure to rise within the Li metal filling a crack. Exploiting stress-potential coupling, such pressure can prevent further plating and divert deposition away from the crack tip. The model predicts the limiting conditions that hinder Li plating at the crack tip and prevent further electrolyte's fracturing.

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SESSION ET01.10: Session VIII

Session Chairs: Neil Dasgupta and Venkataraman Thangadurai
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room 310

1:30 PM ET01.10.01

Intrinsic Improvement of LLZO Solid-State Electrolyte to Suppress Li Dendrite Formation Yulia Arinicheva¹, Juliane F. Nonemacher², Fadli Rohman³, Maria Meledina³, Chih-Long Tsai¹, Alexander Schwedt³, Joachim Mayer³, Jürgen Malzbender², Dina Fattakhova-Rohlfing¹, Olivier Guillon¹ and Martin Finsterbusch¹; ¹Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research Materials Synthesis and Processing (IEK-1), Jülich, Germany; ²Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research: Microstructure and Properties of Materials (IEK-2), Jülich, Germany; ³Central Facility for Electron Microscopy, RWTH Aachen University, Aachen, Germany.

After the unexpected discovery of similar metal dendrite issues in dense ceramic electrolytes as in conventional liquid ones, the key factors governing the Li dendrite formation e.g. in LLZO are still not fully understood. Possible factors include lithium ion diffusion kinetics at grain boundaries, influenced by microstructure [1, 2] and density [3], as well as inhomogeneous contact between LLZO solid electrolyte and Li electrodes, leading to high contact resistance. Multiple strategies can be employed to reduce the contact resistance: first, the surface can be treated in order to remove LiOH/Li₂CO₃-contamination [4], second, the effective contact area can be increased [5] and third, surface defects can be reduced [6], and finally, the surface can be coated to increase the wettability [7-9].

To elucidate the interdependence of the various possibilities, the present work focuses on the effect of doping, microstructure, surface properties and density of the Li_{6.6}La₃Zr_{1.6}Ta_{0.4}O₁₂ solid state electrolyte on its electrochemical performance, especially the resistance to dendrite penetration. Al-doped and Al-free LLZO:Ta precursor powders with larger ($\approx 5 \mu\text{m}$) and nano-sized particles were synthesized via solid-state synthesis and solution-assisted solid-state synthesis, respectively. LLZO:Ta pellets with high density (>99% of the theoretical density), high conductivity ($8 \cdot 10^{-4} \text{ S/cm}$) and various grain sizes were obtained for both precursor powders by hot pressing. The grain size dependence of mechanical properties (fracture toughness, micro hardness, Young modulus), ionic conductivity, cycling stability, stability in contact with humid air on microstructure was investigated. The conductivity was separated into grain and grain boundary contributions. Activation energies of polycrystalline conductivity for the samples with larger and smaller grains were determined. Lower interfacial resistances and better cycling behaviour was found and attributed to surface quality and mechanical properties of the material.

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1:45 PM ET01.10.02

Structure and Ion Transport at Polymer-Ceramic Electrolyte Interface Xi C. Chen, Amaresh Samuthira Pandian, Xiaoming Liu, Robert Sacchi, Gabriel Veith and Nancy J. Dudney; Oak Ridge National Lab, Oak Ridge, Tennessee, United States.

Composite solid electrolytes consisting of a polymer electrolyte and a ceramic electrolyte are promising in meeting the challenging requirements to stabilize lithium metal anode to achieve high energy density. The requirements include high ionic conductivity, high shear modulus, good chemical stability and adhesion with metallic lithium. When the components act synergistically, composite electrolytes may overcome the intrinsic weaknesses of single component electrolytes such as brittleness of ceramic electrolytes and low shear modulus of polymer electrolytes. However, composite electrolytes with high ceramic loadings suffer from low ionic conductivity due to a large interfacial resistance for ion transport.[1, 2] The origin of this interfacial resistance is not well-understood.

This work focuses on understanding ion transport at the interface between polymer electrolyte and ceramic electrolyte. Polymer-ceramic-polymer electrolyte (trilayer) cell is constructed to study the interfacial resistance between the polymer and ceramic electrolyte. Sintered ceramic plate from Ohara corporation is sandwiched between two thin layers of polymer electrolyte (poly(ethylene oxide) + lithium triflate salt) obtained by spray coating. The interfacial resistance is determined by analyzing the impedance spectra of single layer ceramic plate, single layer polymer electrolyte and the trilayer sample. We discovered that at 30 °C, the interfacial resistance is as high as 10000 Ohm. As an effort to decrease the interfacial resistance, plasticizers such

as tetraethylene glycol dimethyl ether (TEGDME) and dimethyl carbonate (DMC) are infused into the polymer electrolyte of the trilayer cell. Both plasticizers enhance the ionic conductivity of the polymer electrolyte but have limited effects on facilitating ion transport across the polymer-ceramic interface. The structure of polymer electrolyte at the polymer-ceramic interface is examined with depth-profiling infrared spectroscopy and neutron reflectometry in order to shed light on the origin of this large interfacial resistance.

Acknowledgements:

This work was primarily supported by the U. S. Department of Energy (DOE-EERE), Vehicle Technologies Office (Advanced Battery Materials Research, Tien Duong). We thank Brion Hoffman, Ohara Corporation, for supplying ceramic electrolyte powders.

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2:00 PM *ET01.10.03

Structure, Chemistry and Charge Transfer Resistance of the Interface Between Garnet Solid Electrolyte and Oxide Cathodes [Bilge Yildiz](#), Gulin Vardar, Younggyu Kim and Yet-Ming Chiang; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

All-solid-state batteries promise significant safety and energy density advantages over liquid-electrolyte batteries. The interface between the cathode and the solid electrolyte is an important contributor to charge transfer resistance. Strong bonding of solid oxide electrolytes and cathodes requires sintering at elevated temperatures. Knowledge of the temperature dependence of the composition and charge transfer properties of this interface is important for determining the ideal sintering conditions. To understand the interfacial decomposition processes and their onset temperatures, model systems of LiCoO₂ (LCO) thin films deposited on cubic Al-doped Li₇La₃Zr₂O₁₂ (LLZO) pellets were studied as a function of temperature using interface-sensitive techniques. X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS), and energy-dispersive X-ray spectroscopy (EDS) data indicated significant cation interdiffusion and structural changes starting at temperatures as low as 300 C. La₂Zr₂O₇ and Li₂CO₃ were identified as decomposition products after annealing at 500 C by synchrotron X-ray diffraction (XRD). X-ray absorption spectroscopy (XAS) results indicate the presence of also LaCoO₃, in addition to La₂Zr₂O₇ and Li₂CO₃. Based on electrochemical impedance spectroscopy, and depth profiling of the Li distribution upon potentiostatic hold experiments on symmetric LCO|LLZO|LCO cells, the interfaces exhibited significantly increased impedance, up to 8 times that of the as-deposited samples after annealing at 500 C. Our results indicate that lower-temperature processing conditions, shorter annealing time scales, and CO₂-free environments are desirable for obtaining ceramic cathode-electrolyte interfaces that enable fast Li transfer and high capacity.

2:30 PM ET01.10.04

Fracture Toughness Improvements and Lithium Metal Penetration in Nanocomposite Ceramic Electrolytes Maria C. Ramirez, Mok Yun Jin and [Brian W. Sheldon](#); Brown University, Providence, Rhode Island, United States.

The relatively low fracture toughness of ceramic solid electrolytes can significantly limit battery performance and reliability. While small dimensions are generally needed for faster ion transport, these length scales also restrict the approaches that can be used to improve fracture resistance. Nanoscale reinforcements are thus a logical option for improving the fracture resistance of ceramic electrolytes. Graphene oxide and reduced graphene oxide have been successfully used to reinforce a variety of polymer and engineering ceramics, where significant changes in the elastic modulus and toughness have been obtained with relatively low volume fractions. In the present work, we explore the reinforcement capability of small amounts of graphene oxide added to oxide-based lithium ion conductors. Standard electrochemical measurements were used to measure ionic and electrical conductivities. Fracture toughness measurements on both large and small scale specimens were then employed, to provide detailed information about the mechanical properties of these materials.

2:45 PM ET01.10.05

Effects of Electrochemical Cycling on the Mechanical Behavior of High Purity Lithium [Erik G. Herbert](#)¹, Stephen A. Hackney¹, Nancy J. Dudney² and Fereshteh Mallakpour¹; ¹Michigan Technological University, Houghton, Michigan, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Nanoindentation experiments have been performed in high purity vapor deposited and electrochemically cycled lithium. At a homologous temperature of 0.66, the measured hardness is found to depend significantly on the indentation depth and strain rate, and is studied as a function of cycling conditions. The experimental observations are rationalized in terms of lithium's evolving dislocation density, Nabarro-Herring and Harper-Dorn creep and dislocation mediated flow. In well-annealed, low dislocation density lithium, it is surmised that dislocation motion is initiated by the activation of a Frank-Read source. Prior to dislocation motion, the plastic deformation is taken to be controlled by self-diffusion to the free surface and/or preexisting dislocations. Collectively, the proposed rationalizations provide a novel framework to better understand the complex relationship between electrochemical cycling, the dislocation density and the mechanisms that control pressure within submicron scale defects at the lithium/solid electrolyte interface. Moreover, the experimental observations and mechanistic rationalizations provide new insight into the mechanisms capable of causing mechanical failure of a solid electrolyte.

3:00 PM BREAK

3:30 PM *ET01.10.06

Beyond Dendrites, Cycling Li-Metal Across Garnet at High Current Densities [Eric D. Wachsmann](#); Maryland Energy Innovation Institute, University of Maryland, College Park, Maryland, United States.

Solid-state Li-batteries (SSLiBs) have the potential to be a transformational and intrinsically safe energy storage solution. However, their progress has been limited by high solid-solid interfacial impedance and numerous reports of Li-dendrites and a corresponding "critical current density". By first modifying the garnet surface to enable Li-metal to wet it and then fabricating garnet-electrolytes into tailored tri-layer microstructures to form electrode supported dense thin-film (~10µm) solid-state electrolytes we have been able to overcome these limitations. The microstructurally tailored porous garnet scaffold support increases electrode/electrolyte interfacial area, overcoming the high impedance typical of planar geometry SSLiBs resulting in an area specific resistance (ASR) of only ~2 to 7 Ωcm² at room temperature. The unique garnet scaffold/electrolyte/scaffold structure further allows for charge/discharge of the Li-metal anode and cathode scaffolds by pore-filling, thus providing high depth of discharge ability without mechanical cycling fatigue seen with typical electrodes. Moreover, the scalable multilayer ceramic fabrication techniques, without need for dry rooms or vacuum equipment, provide for dramatically reduced manufacturing cost.

The fabrication of supported dense thin-film garnet electrolytes, their ability to cycle Li-metal at high current densities with no dendrite formation, and results for Li-metal anode/garnet-electrolyte based batteries with a number of different cathode chemistries will be presented.

4:00 PM ET01.10.07

Enhancing Stability Between Garnet Electrolyte and Li Metal Electrode with a Metal Carbide Coating Fengyu Shen, Marm Dixit, Wahid Zaman and Kelsey B. Hatzell; Vanderbilt University, Nashville, Tennessee, United States.

Overcoming large interfacial resistances at electrode|electrolyte interfaces is a major challenge facing all-solid-state batteries. To alleviate this challenge, there has been a significant push toward manufacturing and processing monolayer thin films and coatings at solid electrolyte interfaces [1, 2]. Typically, atomic layer deposition has been the manufacturing approach used within the solid electrolyte community. While effective, this process increases the cost of processing solid electrolytes [1, 3]. Herein, we explore a facile coating process where colloidal low-dimensional metal carbide materials are deposited on the solid electrolyte with a spray coater. The effects of spray coating sub-micron scale metal carbide coatings directly on $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) electrolytes to decrease the interfacial resistance are investigated. Electrochemical characterization reveals that the growth rate of interfacial resistance for the coated LLZO is almost one order of magnitude smaller than that of the bare LLZO. The wettability of Li on LLZO electrolyte is enhanced and a greater electrochemical window is obtained. The critical current density is improved 2x with the metal carbide coating at room temperature and the capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{LLZO}/\text{Li}$ cell is stabilized. Thus, this work demonstrates a facile and scalable way of coating ceramic electrolytes for low interfacial resistances.

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4:15 PM ET01.10.08

Intercalation Induced Mechanical Failure of Olivine Compounds Ananya Renuka Balakrishna¹, Christian Henriksen², Kai Xiang¹, Dorthe B. Ravnsbæk², Ming Tang³, Craig Carter¹ and Yet-Ming Chiang¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²University of Southern Denmark, Odense M, Denmark; ³Rice University, Houston, Texas, United States.

When electrodes fail mechanically, it affects a battery's capacity, rate capability and lifetime. In ion storage compounds, mechanical failure typically occurs after ion intercalation changes the electrode's volume. These volume changes increase the elastic energy stored in electrodes. Sometimes, electrodes crack to relieve this stored elastic energy. Electrode cracking can be mitigated by reducing the electrode particle size [1], by doping electrode compounds [2] and by operating at low overpotentials [3]. Our recent experiments show that when crack propagation is suppressed, olivine compounds such as NaFePO_4 and $\text{NaMn}_y\text{Fe}_{(1-y)}\text{PO}_4$ release their stored elastic energy by forming a disordered phase [4].

Here, we identify the critical particle size at which electrode cracking and amorphization are suppressed. To that end, we use olivine compounds, such as LiFePO_4 , NaFePO_4 , $\text{LiMn}_y\text{Fe}_{(1-y)}\text{PO}_4$, and $\text{NaMn}_y\text{Fe}_{(1-y)}\text{PO}_4$, as model systems. We compute the elastic energy stored in electrodes analytically as a function of particle size and lattice strain. Furthermore, we compare the electrodes' stored energy with the energy required to form new surfaces (fracture) or a disordered phase (amorphization). This analysis results in a narrow range of particle sizes at which olivine compounds neither crack nor amorphize. The present research provides insight into the effects of scaling, lattice strains, and glass-former conditions on the mechanical stability of intercalation electrodes.

References

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4:30 PM ET01.10.09

Rational Design of Nanostructures in Solid Polymer Electrolyte Snehashis Choudhury and Lynden Archer; Cornell University, Ithaca, New York, United States.

Metal based batteries that comprise of a reactive metal anode like lithium, sodium or potassium are the future of energy storage devices because of their high volumetric and gravimetric energy density. However, these batteries fail by three distinct modes – chemical instability due to internal reactions, morphological instability due to uneven electrodeposition and hydrodynamic instability due to convective flows at the vicinity of electrode-electrolyte interface. Both liquid based, and solid-state electrolytes have their individual advantages and disadvantages in mitigating these issues. In this work, we show that solid-polymer interphases based on crosslinked polymer networks can essentially possess qualities from both of these worlds. We find that by tuning the thermodynamic interactions between the polymer network and oligomer diluents, one can control the bulk properties like ion transport and mass transfer rate. Thus, it is possible to design solid-like electrolyte-phases where the electroconvective flows can be inhibited, while maintaining high ionic conductivity. We further show that these polymer networks act as excellent interfacial layer for lithium metal electrode to inhibit dendrite growth and side reactions. On pairing with high voltage cathodes, the lithium metal battery exhibit over 250 cycles of stable operation even at high current densities.

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Organic Radical Thin-Film Batteries with Solid-State Electrolyte Roland Roesch^{1,2}, Philip Zimmer^{1,2}, Raik Zacharias^{1,2}, Tina Mede^{1,2}, Ulrich S. Schubert^{2,1} and Harald Hoppe^{1,2}; ¹Center for Energy and Environmental Chemistry Jena (CEEC Jena), FSU Jena, Jena, Germany; ²Laboratory of Organic and Macromolecular Chemistry (IOMC), FSU Jena, Jena, Germany.

All-solid state thin film batteries with organic radical polymer electrodes, such as TEMPO (2,2,6,6-tetramethyl-4-piperidiny-N-oxyl radical) [1] and TCAQ (tetracyano-9,10-anthraquinonedimethane) [2] are demonstrated. These electrodes as well as the solid-state electrolyte were cast from solution respectively liquid-phase, which was enabled by use of orthogonal solvent systems. The thickness of all functional films within this device as well as the

solid-state electrolyte were systematically varied in order to understand performance limiting factors, such as limited charge or ionic conductivity. For analysis of the same, impedance spectroscopy was applied. Finally, charging and discharging kinetics are presented and linked with an optimized device layout.

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