

Advances in Battery Engineering, Interface Design, and Characterization Mini-Symposium Room 319 - Session BT1+AS+CA+TF-FrM

Solid-State Batteries

Moderators: Alexander Kozen, University of Vermont, Chuan-Fu Lin, Catholic University of America

8:15am BT1+AS+CA+TF-FrM-1 Grain Structure Control of Evaporated Li Metal Films for Optimized Solid State Batteries, Andrew Westover, Peyton Carden, Oak Ridge National Laboratory, USA **INVITED**

Lithium metal is a critical anode material for next-generation, high-energy batteries. To realize these batteries, the lithium metal must be between thick, depending on the cathode chemistry. Furthermore, lithium metal must have controlled surface chemistry and high purity for optimal performance. Thermal evaporation is one of the most effective methods for producing thin lithium metal films that meet these criteria. In this work, we present our efforts to understand how to produce lithium metal films as thin as , and we explore the ability to fabricate lithium metal thin films with controlled microstructures. We have developed a process to modify the as-deposited lithium metal grain size in evaporated films from . Using these thin films with standard liquid electrolytes, localized high-concentration electrolytes, and solid electrolytes lead to significant differences in the cycling performance of lithium metal films. This work demonstrates the critical importance of microstructure control for realizing next-generation, high-energy lithium metal batteries.

This work was funded by the United States Department of Energy Transportation Technology Office Battery Materials Research Program and German-US Collaboration on Energy Storage under Simon Thompson and Tien Duong.

8:45am BT1+AS+CA+TF-FrM-3 Unravelling the Mechanism of Al₂O₃ Atomic Layer Deposition on Li₆PS₅Cl for All-Solid-State Batteries, Kyobin Park, Donghyeon Kang, Taewoo Kim, Vepa Rozyyev, Anil Mane, Hacksung Kim, Francisco Vargas, Zachary Hood, Peter Zapol, Justin Connell, Jeffrey Elam, Argonne National Laboratory

Sulfide superionic conductors with the argyrodite structure (e.g., Li₆PS₅Cl, LPSCI) are extremely promising for all solid-state batteries, but poor atmospheric stability and high interfacial reactivity limit their widespread adoption. Coating LPSCI powders with ultrathin, metal oxide coatings using atomic layer deposition (ALD) mitigates these problems, protecting LPSCI against atmospheric degradation¹ and reducing reactivity with Li metal, yielding more stable cycling². Despite significant promise, the ALD mechanism is unknown, hampering the development of new coating chemistries.

In this study, we elucidate the mechanism for Al₂O₃ ALD on LPSCI using trimethyl aluminum (TMA) and H₂O by combining *in situ* Fourier transform infrared spectroscopy measurements and *ex situ* solid-state magic angle spinning nuclear magnetic resonance, UV Raman spectroscopy, and X-ray photoelectron spectroscopy measurements with density functional theory calculations. We determine that ALD Al₂O₃ nucleates promptly via TMA reaction with native -OH, -SH, and PS₃-OH groups to form transient C-Al-O(S) species that are rapidly hydrolyzed during the subsequent H₂O exposure. This reversible transformation maintains surface nucleophilicity and prevents sulfide decomposition. The resulting layer-by-layer growth leads to highly conformal Al₂O₃ coatings on LPSCI.

This detailed understanding of ALD surface reactions provides critical insights guiding the selection of future ALD chemistries with greater enhancement in cycling performance.

1. *Acs Materials Letters* **2024**, 6, (12), 5409-5417.
1. *Advanced Materials* **2023**, 35, (21), 13.

9:00am BT1+AS+CA+TF-FrM-4 Engineered Cathode Chemomechanics Enables Ultra-Low Stack Pressure Solid-State Batteries, Paul Braun, University of Illinois Urbana-Champaign

In solid-state batteries, stresses resulting from electrode material chemomechanics are strongly coupled to solid electrolyte-electrode interface failures. Such failures are significant barriers to realization of practical Li metal solid-state batteries. While high external pressures can reduce these failures, the required pressures are impractical, and thus a different approach to reducing interface failures is required. We show that control of cathode chemomechanical stress provides an important path for

realization of solid-state batteries which operate at commercially relevant low (e.g., <1 MPa) stack pressures. Using a series of cathodes with different chemomechanics we provide experimental evidence of the role of electrode chemomechanics in solid-state battery failure. Our model systems reveal that electrode chemomechanics significantly alter Li metal plating and stripping behavior at low stack pressure. We utilize these learnings to build long cycle-life solid-state batteries with practical areal capacity (5 mAh/cm²) operating under a 1 MPa stack pressure and at room temperature. Our findings highlight the importance of controlling positive electrode chemomechanics to realize low stack pressure solid-state batteries.

9:15am BT1+AS+CA+TF-FrM-5 Pulsed Laser Deposition of Solid Electrolytes: How Limited Thermal-Budget Processing Relates to Li-ion Conductivity, Nicola Perry, University of Illinois; En Ju Cho, Kai-Wei Lan, Nicola Perry, University of Illinois Urbana-Champaign **INVITED**

Near-room-temperature, thin-film deposition of air-sensitive Li-ion conductors can enable multilayer solid electrolytes and coatings for high-energy-density batteries and microdevices, compatible with thermally sensitive components. We investigate the capabilities of pulsed laser deposition for fabrication of high-quality layers of low-voltage- and high-voltage-stable solid-electrolyte compositions, including low-melting antiperovskite hydroxyhalides and higher-melting nasicon-structured oxides that contain glass-forming elements. The influence of growth parameters such as temperature, pressure, and laser fluence on stoichiometry, density, roughness, crystallinity, and conductivity is explored. Grazing-incidence nuclear reaction analysis paired with Rutherford backscattering spectrometry provides insight into light-element stoichiometry (e.g. Li, Cl, P) and the expected loss of Li (e.g.) with increasing temperature (given its volatility) and growth pressure (given its mass that enables scattering). Strategies to control stoichiometry of multiple light elements and deposition rates, through composite targets and sequential multi-target deposition, are demonstrated. X-ray reflectometry, grazing-incidence diffraction, and ellipsometry shape the understanding of structural dependence on growth parameters. We also examine the benefit of integrated impedance spectroscopy in the PLD chamber during and after growth to provide insights into transport behavior in a clean (air-free) environment as a function of temperature. We find most compositions benefit from vacuum deposition, but while the antiperovskite hydroxyhalides form single-phase, highly conductive films at room temperature, with phase decomposition and conductivity degradation above ~60 C, the nasicon-structured electrolytes benefit from post-deposition anneals to improve crystallinity and conductivity.

9:45am BT1+AS+CA+TF-FrM-7 Open-Circuit Energy Band Alignment at NMC/LLZTO and LLZTO/Li Interfaces for Solid-State Microbattery Applications, Austine Amisi, Raquel-Garza Hernandez, Fabian Ambriz-Vargas, Centro de Investigaciones en Óptica, Mexico

Stable electrode/electrolyte interfaces are critical for the electrochemical performance and long-term reliability of solid-state microbatteries. This work reconstructs the open-circuit energy band diagram of an all-solid-state LiNi_{0.8}Mn_{0.2}Co_{0.2}O₂ (NMC)/Li₇La₃Zr_{2-x}Ta_xO₁₂ (LLZTO)/Li microbattery stack through band alignment analysis of the NMC/LLZTO cathode–electrolyte and LLZTO/Li electrolyte–anode heterojunctions. Thin-film bilayers were fabricated by RF magnetron sputtering and thermal evaporation. Valence and conduction band offsets (VBOs and CBOs) were experimentally determined using the Kraut method through conventional and angle-resolved X-ray photoelectron spectroscopy (XPS/ARXPS). A VBO of +3.13 ± 0.1 eV and a CBO of -6.00 ± 0.1 eV were measured at the NMC/LLZTO interface, with a large CBO that suggests the formation of an electronically insulating interface that suppresses electrolyte decomposition at the cathode during charging. In contrast, a VBO of +1.92 ± 0.1 eV and a near-zero CBO of +0.08 ± 0.1 eV were determined at the LLZTO/Li heterojunction, indicating an electronically conductive interface that promotes electron accumulation and facilitates LLZTO degradation upon contact with the anode. An electrochemical potential window of 6.00 ± 0.1 eV and an open-circuit voltage of 3.29 ± 0.1 eV were obtained from the reconstructed full-stack band diagram. These results establish a direct link between interfacial band alignment and potential degradation mechanisms and provide critical design guidelines for advancing the operational stability of LLZTO-based solid-state microbatteries.

Friday Morning, November 13, 2026

10:00am BT1+AS+CA+TF-FrM-8 LiPON-Enabled Reduction of V₂O₅ during Fabrication of Thin-Film Ionic Devices, *Leopoldo Tapia-Aracayo, David Stewart, Gary Rubloff*, University of Maryland College Park

Vanadium (V) Oxide (V₂O₅) is a well-researched layered oxide with high capacity (375 mAh/g), often cited for its applications in energy storage, electrochromic, and neuromorphic applications. In the field of thin-film ionic devices, we can sputter Lithium Phosphorus Oxynitride (LiPON) on top of crystalline V₂O₅, creating our electrolyte/electrode stack. This sequence simplifies the fabrication of thin-film ionic batteries as sputtering LiPON can insert Lithium up to 2 Li⁺ per V₂O₅. We wanted to address the roughness of the LiPON/V₂O₅ interface by altering the fabrication steps to form a smooth interface, but unintentionally reduced the V₂O₅ to a VO₂ phase.

This smooth interface was achieved by sputtering amorphous V₂O₅ thin films in Ar/O₂ environment, then coated with LiPON, and subjected to post-deposition annealing in N₂ gas environment at 300 °C. The N₂ gas environment for the post-deposition annealing would crystallize the V₂O₅ and preserve the LiPON composition. We tracked the formation of a VO₂ phase, which was not observed for N₂ annealed V₂O₅ without LiPON, which remains VO₂ free. We used electrochemical cycling to probe the presence and evolution of the VO₂ phase, illustrating VO₂ reaction peaks instead of characteristic crystalline V₂O₅ peaks in the 2.2 V – 4.0 V vs Li⁺/Li window. (Seen in Figure 1). We will discuss how this behavior may be caused by LiPON-enabled reduction pathways at the buried interface. We confirm this reduction is limited to the interface as analysis via Raman identifies lithiated V₂O₅ phases. Systematic variation of LiPON sputtering parameters and annealing conditions, while holding LiPON thickness constant, reveal processing regimes that drive VO₂ formation versus preserving V₂O₅. Ultimately, preserving the morphological benefits of a smooth LiPON/ V₂O₅ interface while constraining VO₂ formation, providing guidance for designing desired application-specific vanadium-oxide phases.

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