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

Solid-State Batteries

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

8:15am **BT+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 **BT+AS+CA+TF-FrM-3 Unravelling the Mechanism of Al2O3 Atomic Layer Deposition on Li_6PS_5Cl 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., Li_6PS_5Cl, LPSCl) are extremely promising for all solid-state batteries, but poor atmospheric stability and high interfacial reactivity limit their widespread adoption. Coating LPSCl powders with ultrathin, metal oxide coatings using atomic layer deposition (ALD) mitigates these problems, protecting LPSCl against atmospheric degradation[1] and reducing reactivity with Li metal, yielding more stable cycling[2]. Despite significant promise, the ALD mechanism is unknown, hampering the development of new coating chemistries.

In this study, we elucidate the mechanism for Al_2O_3 ALD on LPSCl using trimethyl aluminum (TMA) and H_2O 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 Al_2O_3 nucleates promptly via TMA reaction with native -OH, -SH, and PS_3-OH groups to form transient C-Al-O(S) species that are rapidly hydrolyzed during the subsequent H_2O exposure. This reversible transformation maintains surface nucleophilicity and prevents sulfide decomposition. The resulting layer-by-layer growth leads to highly conformal Al_2O_3 coatings on LPSCl.

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 **BT+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/cm^2) 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 **BT+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 **BT+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 $LiNi_xMn_yCo_zO_2$ (NMC)/$Li_7La_3Zr_{2-x}Ta_xO_{12}$ (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.

10:00am **BT+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 (V_2O_5) 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 V_2O_5, 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 V_2O_5. We wanted to address the roughness of the LiPON/V_2O_5 interface by altering the fabrication steps to form a smooth interface, but unintentionally reduced the V_2O_5 to a VO_2 phase.

This smooth interface was achieved by sputtering amorphous V_2O_5 thin films in Ar/O_2 environment, then coated with LiPON, and subjected to post-deposition annealing in N_2 gas environment at 300 ◦C. The N_2 gas environment for the post-deposition annealing would crystallize the V_2O_5 and preserve the LiPON composition. We tracked the formation of a VO_2 phase, which was not observed for N_2 annealed V_2O_5 without LiPON, which remains VO_2 free. We used electrochemical cycling to probe the presence and evolution of the VO_2 phase, illustrating VO_2 reaction peaks instead of characteristic crystalline V_2O_5 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 V_2O_5 phases. Systematic variation of LiPON sputtering parameters and annealing conditions, while holding LiPON thickness constant, reveal processing regimes that drive VO_2 formation versus preserving V_2O_{-5}. Ultimately, preserving the morphological benefits of a smooth LiPON/ V_2O_5 interface while constraining VO_2 formation, providing guidance for designing desired application-specific vanadium-oxide phases.

Author Index

Bold page numbers indicate presenter

— A —
Ambriz-Vargas, Fabian: BT+AS+CA+TF-FrM-7, 1
Amisi, Austine: BT+AS+CA+TF-FrM-7, **1**
— B —
Braun, Paul: BT+AS+CA+TF-FrM-4, **1**
— C —
Carden, Peyton: BT+AS+CA+TF-FrM-1, 1
Cho, En Ju: BT+AS+CA+TF-FrM-5, 1
Connell, Justin: BT+AS+CA+TF-FrM-3, 1
— E —
Elam, Jeffrey: BT+AS+CA+TF-FrM-3, **1**
— H —
Hernandez, Raquel-Garza: BT+AS+CA+TF-FrM-7, 1
Hood, Zachary: BT+AS+CA+TF-FrM-3, 1
— K —
Kang, Donghyeon: BT+AS+CA+TF-FrM-3, 1
Kim, Hacksung: BT+AS+CA+TF-FrM-3, 1
Kim, Taewoo: BT+AS+CA+TF-FrM-3, 1
— L —
Lan, Kai-Wei: BT+AS+CA+TF-FrM-5, 1
— M —
Mane, Anil: BT+AS+CA+TF-FrM-3, 1
— P —
Park, Kyobin: BT+AS+CA+TF-FrM-3, 1
Perry, Nicola: BT+AS+CA+TF-FrM-5, 1
— R —
Rozyyev, Vepa: BT+AS+CA+TF-FrM-3, 1
Rubloff, Gary: BT+AS+CA+TF-FrM-8, 2
— S —
Stewart, David: BT+AS+CA+TF-FrM-8, 2
— T —
Tapia-Aracayo, Leopoldo: BT+AS+CA+TF-FrM-8, **2**
— V —
Vargas, Francisco: BT+AS+CA+TF-FrM-3, 1
— W —
Westover, Andrew: BT+AS+CA+TF-FrM-1, **1**
— Z —
Zapol, Peter: BT+AS+CA+TF-FrM-3, 1