## 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 $Li_6PS_5Cl$ 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***[1], 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 **BT1+AS+CA+TF-FrM-4 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.

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 $LiNi_xMn_yCo_zO_2$ (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

[1] **JVST Highlighted Talk**

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.

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