ALD Applications
Room Grand Ballroom E-G - Session AA2-TuM
ALD for Batteries I

Moderators: Neil P. Dasgupta, University of Michigan, Noemi Leick, National Renewable Energy Laboratory

10:45am **AA2-TuM-12 Atomic Layer Deposition of Glassy Lithium Borate-Carbonate Electrolytes for Solid-State Lithium Metal Batteries***, E Kazyak, A Davis, S Yu, K Chen, A Sanchez, J Lasso, T Thompson, A Bielinski, D Siegel,* ***Neil P. Dasgupta,*** University of Michigan

Solid electrolytes could enable significant improvements in the energy density, cycle life, and safety of next-generation battery chemistries. The ability to fabricate thin electrolyte films with high ionic conductivity and electrochemical stability on complex architectures has been a bottleneck to realizing a wide range of 3D structured thin-film and bulk batteries. Recent progress in ALD for solid electrolytes has shown great promise, and there is significant interest in realizing materials with even higher conductivities and stability with Li metal anodes in order to dramatically enhance the energy density of ALD-based batteries. In addition, ALD films with high ionic conductivity and good stability could be used for interfacial engineering of bulk-type solid and liquid based batteries to improve stability and safety.

This work demonstrates a novel ALD process for glassy lithium borate-carbonate thin films with ionic conductivities above 10^{-6} S/cm at 298K [1]. This is the highest reported value to date for any ALD-deposited solid electrolyte. The composition, structure, and stability of the films are characterized with X-ray photoelectron spectroscopy and a range of electrochemical measurements. These experiments are compared with those calculated with Density Functional Theory and Molecular Dynamics to elucidate the origins of the high ionic conductivity and excellent stability. The film properties are studied as a function of ALD deposition temperature, showing tradeoffs between process conditions and performance, and demonstrating the precise control afforded by the ALD process. The optimized film remains an ionic conductor when in contact with metallic Li, with no measurable changes after several weeks, and displays stable cycling when paired with a thin-film cathode and Li metal anode. This new ALD material and process represents a pathway towards interfacial engineering of both thin-film and bulk solid-state batteries, enabling stable cycling against Li metal anodes.

1) Kazyak, E.; Chen, K. H.; Davis, A. L.; Yu, S.; Sanchez, A. J.; Lasso, J.; Bielinski, A. R.; Thompson, T.; Sakamoto, J.; Siegel, D. J.; Dasgupta, N. P. *J. Mater. Chem. A* **2018**, *6*, 19425–19437.

11:00am **AA2-TuM-13 ALD Interlayers for Stabilization of $Li_{10}GeP_2S_{12}$ Solid Electrolytes Against Li Metal Anodes***,* ***Andrew Davis,*** University of Michigan*; K Wood,* National Renewable Energy Laboratory*; R Garcia-Mendez, E Kazyak, K Chen, J Sakamoto,* University of Michigan*; G Teeter,* National Renewable Energy Laboratory*; N Dasgupta,* University of Michigan

Solid-state batteries based on high-ionic-conductivity solid electrolytes are a promising technology to increase battery lifetime and capacity, and reduce safety concerns associated with flammability. In recent years, sulfide solid electrolytes such as $Li_{10}GeP_2S_{12}$ (LGPS) have achieved ionic conductivities comparable to or higher than that of traditional liquid electrolytes. Despite these promising breakthroughs, realization of sulfide solid-state batteries with high capacities and energy densities has proved elusive. This can be attributed to the narrow electrochemical stability window of sulfide electrolytes, which leads to undesirable reactions at the electrode/electrolyte interface against both high voltage cathode materials and Li metal anodes. This forms an unstable solid electrolyte interphase (SEI), which dramatically degrades battery performance. Artificial SEIs made of ALD interlayers have recently been explored as a method of increasing stability of the Li metal/solid electrolyte interface. ALD allows for conformal, pinhole free coating of the LGPS which protects the surface from direct contact with lithium metal while facilitating Li-ion transport across the interface.

In this study, we explore the impact of ALD interlayers at the LGPS-Li metal interface, in order to gain a deeper fundamental understanding of the dynamic evolution of the SEI. A multi-modal characterization approach was performed that combined electrochemical measurements*, operando* X-ray photoelectron spectroscopy (XPS), *in-situ* auger spectroscopy, scanning electron microscopy (SEM), and optical microscopy. This allowed for quantitative evaluation of the time-dependent degradation of the interface, which occurs due to the evolution of a variety of decomposition by-products. ALD coated samples exhibited significantly less decomposition of the LGPS interface. *Operando* XPS was used to correlate the distinct decomposition products that correspond to increases in overpotential [1]. Auger, SEM and optical mapping of the surface shows spatial inhomogeneities that lead to preferential Li plating and corresponding $Li_{10}GeP_2S_{12}$ breakdown. These observations were rationalized in the context of bulk solid-state batteries employing Li metal anodes, demonstrating the advantages and challenges associated with ALD modification of solid-state battery interfaces.

K. N. Wood, K. X. Steirer, S. E. Hafner, C. Ban, S. Santhanagopalan, S.-H. Lee, G. Teeter, *Nature Communications* **9**, 2490 (2018).

11:15am **AA2-TuM-14 ALD and MLD on Lithium Metal – A Practical Approach Toward Enabling Safe, Long Lasting, High Energy Density Batteries***,* ***Andrew Lushington,*** Arradiance*; Y Zhao, L Goncharova, Q Sun, R Li, X Sun,* University of Western Ontario, Canada

Global warming and rising levels of atmospheric CO_2 have resulted in a rapid search for alternative energy sources. Among the possible portable energy storage systems available, lithium-based batteries have the highest theoretical energy density. Unfortunately, current battery technology is approaching its limits and research toward alternative battery chemistries with higher energy density, such as Li-S, Li-O_2 and all solid-state batteries, is required to meet future energy storage demands. However, these next-generation batteries require the use of a pure Li-metal anode .[1] Li-metal has a high specific capacity of 3860 mAh g^{-1}, a value 10x greater than the standard graphite anode (370 mAh g^{-1}) used today. Unfortunately, Li-metal is highly reactive and forms a high surface area mossy-like reaction product with the electrolyte, known as the solid electrolyte interface (SEI). The uncontrolled growth of this SEI rapidly consumes liquid electrolyte, drying up the battery and causing it to quickly fail. This problem is further exacerbated by dendrite growth which can short circuit the battery, posing a significant safety threat.[2] One effective strategy for mitigating these problems is to use Atomic layer deposition (ALD) and molecular layer deposition (MLD) to coat the surface of electrodes. This strategy has been shown to help form a stable SEI layer and improve battery longevity.[3]

Herein we compare the stripping and plating behavior of Li-metal coated using 3 different ALD and MLD films. Galvanostatic cycling revealed that MLD coated electrodes vastly outperform ALD coated ones. We use Gravimetric Intermission Titration Technique (GITT) to carefully analyze the voltage behavior of coated electrodes and disseminate the key MLD film properties that enable the formation of a stable SEI layer. Additionally, electrode morphology was examined using scanning electron microscopy along with Rutherford backscattering spectroscopy to reveal the composition of the SEI. To further demonstrate the practicality of MLD coated Li-metal, full cell batteries using lithium iron phosphate and carbon-sulfur as a cathode was performed. This presentation provides the necessary fundamental understanding of the hurdles that face the commercialization of lithium metal anodes and how ALD/MLD can be used to address these challenges.

1. Lin, D., Liu, Y. & Cui, Y. Reviving the lithium metal anode for high-energy batteries. *Nat. Nanotech.* **12**, 194–206 (2017).

2. Palacín, M. R. & De Guibert, A. Batteries: Why do batteries fail? *Science.***351**, (2016).

3. Zhao, Y. et al. Robust Metallic Lithium Anode Protection by the MLD Technique. *Small Methods.***2(5)**, 1700417 (2018).

11:30am **AA2-TuM-15 Synergistic Effect of 3D Current Collectors and ALD Surface Modification for High Coulombic Efficiency Lithium Metal Anodes***,* ***Kuan-Hung Chen****, A Sanchez, E Kazyak, A Davis, N Dasgupta,* University of Michigan

Improving the performance of Li metal anodes is a critical bottleneck to enable next-generation battery systems beyond Li-ion. However, stability issues originating from undesirable electrode/electrolyte interactions and Li dendrite formation have impaired long-term cycling of Li metal anodes. In this work, we demonstrate a bottom-up fabrication process using templated electrodeposition of vertically aligned Cu pillars, which are subsequently coated by an ultrathin layer of ZnO by atomic layer deposition (ALD) to form a to form core-shell geometry with precise thickness control [1]. Transmission electron microscopy (TEM) analysis was performed to show the uniform thickness and core-shell geometry on the pillar surface. We demonstrate the application of these core-shell 3-D architectures as an efficient current collector for Li metal electro-deposition and dissolution. By rationally tuning geometric parameters of the 3D current collector architecture, including pillar diameter, spacing, length, and ALD shell thickness, the morphology of Li plating/stripping upon cycling can be controlled.

We further demonstrate the mechanistic role of the ZnO shell on current collector surface, which facilitates the initial Li nucleation, and influences the morphology and reversibility of subsequent cycling. The improved nucleation is correlated with increased wettability of molten Li metal, which is quantitively evaluated using a sessile drop test inside of an argon glovebox. The resulting core-shell pillar architecture allows for the geometry and surface chemistry to be decoupled and individually controlled to optimize the electrode performance. Leveraging the synergistic effects of the optimized 3D geometry and ALD surface modification, we have demonstrated cycling of Li metal anodes with Coulombic efficiency of 99.5%, which is among the highest reported values to date for any Li metal anode. The results from this work thus provide a pathway toward high-efficiency and long-cycle life Li metal batteries with reduced excess Li loading.

[1] K.-H. Chen, A. J. Sanchez, E. Kazyak, A. L. Davis, N. P. Dasgupta, *Adv. Energy Mater*. **9**, 1802534 (2019).

11:45am **AA2-TuM-16 Atomic Layer Deposition FeS@CNT from Elemental Sulfur as an Electrode for Lithium-Ion batteries***, **Hongzheng Zhu**, J Liu,*
University of British Columbia, Canada

Iron sulfide (FeS) is regarded as an attractive anode material for high-performance LIBs because of its high lithium storage capability, natural abundance, and ecofriendly. However, FeS suffer from low reversible capacity and large volume change (200%) during charging and discharging process, resulting in mechanical degradation of cracking and loss of electrical connection with current collectors and then rapid capacity loss [1]. In order to overcome these problems, we choose ALD (Atomic Layer Deposition) method to deposit a controllable thin layer on CNT to building 3D nanostructured electrode for Li-ion batteries [2-3]. In this work, ALD method are chosen to realize thickness and size control of FeS, and CNTs are applied for replacing traditional carbon black to further improve the electrical conductivity and excellent physical support for the electrodes. In most of the metal sulfide ALD processes, film was deposited by using H_2S as the source of sulfur. However, H_2S is a flammable, corrosive, and highly toxic gas, and its incorporation in the ALD technology presents several serious technical challenges. Therefore, the aspiration for a new route of FeS by ALD process seems particularly strong. It is known that sulfur-based ALD processes have been reported for copper sulfide thin films recently [4]. But there is no report on FeS sulfur-based ALD process.

Here, we present a simple ALD process for the deposition of FeS thin films by using elemental sulfur as sulfur source, and test its performance in Li-ion batteries, as a highly viable solution to the challenges discussed above. The XPS spectra of the Fe 2p and S 2p regions are shown in figure a and b for FeS thin film with ALD deposited temperature at 180 °C. The Fe 2p3/2 peaks located at 710.6 and 713.0 eV belong to Fe^{2+} of FeS, which is a solid evidence for the existence of FeS. However, the FeS might partially be oxidized to $FeSO_4$. From the S 2p region in figure b, S 2p3/2 at binding energies 169.1 and 170.2 eV are belonging to SO_4^{2-}, which is the proof of FeS oxidation. Figure c shows the growth rate of FeS is ≈5.2 Å per cycle. The cyclic voltammograms (CVs) of the FeS electrode are shown in Figure d. The strong peak at 0.7 V is attributed to the decomposition of the electrolyte and formation of a solid electrolyte interlayer (SEI) in the first cathodic scan. The peak at 1.7 V in the second cathodic scan is related to the reversible interaction of Li^+ with FeS: $2FeS + 2Li + 2e^- = Li_2FeS_2 + Fe$. In the anodic sweep, the oxidation peak appear obviously at 2.5 V is attributed to the oxidation of Fe and the delithiation process of Li_2FeS_2 to form $Li_{2-x}FeS_2$.

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