Thin Films
Room 115 - Session TF1-TuA
Thin Films for Energy Applications II: Batteries

Moderators: Adriana Creatore, Eindhoven University of Technology, **Mark Losego**, Georgia Institute of Technology

2:30pm **TF1-TuA-2 Surface Chemistry of Plasma Exposure on Sulfide Solid Electrolytes**, ***Alexander Kozen***, University of Vermont; *Y. Wang, D. Fontecha, G. Rubloff, S. Lee,* University of Maryland, College Park

Sulfide solid state electrolytes (SSEs) are considered one of the most promising materials to replace liquid electrolytes in next-generation batteries due SSEs astonishing ionic conductivities. However, the high reactivity of sulfide SSE materials precludes direct contact with Li metal anodes. One approach to stabilize the sulfide SSEs is passivating the sulfide interface with thin films of stable chemical species, forming an artificial solid electrolyte interphase (ASEI) layer. Ideal passivation materials for the anode/SSE interface are generally comprised of Li_3N or LiF species, which are stable at Li metal potentials. Here, we investigate the impact of plasma treatment on sulfide SSEs, as well as deposition of plasma-based ASEI materials using atomic layer deposition (ALD).

I will discuss the implications of Ar, N_2, and NH_3 plasma exposures on sulfide solid electrolytes (LGPS, LPSCl) and the resulting surface chemical changes as determined by in-vacuo x-ray photoelectron spectroscopy (XPS) measurements. N_2 and NH_3 plasma exposure can cleave Li_2S surface bonds and replace them with Li_3N surface species, however due to a lack of Li available at the surface this coverage is limited to ~30% and cannot form complete ASEI layers. Additionally, I will report the changes in electrochemical behavior of these pellets in Li/SSE/Li symmetric cells. Due to the incomplete surface coverage of Li_3N species, the surface nitride passivation is reduced and still allows deleterious reactions to occur after contact with Li metal. These results indicate that for complete Li_3N surface coverage, additional Li species must be available on the sulfide SSE surface before plasma treatment. I will also discuss the initial stages of ALD ASEI layer deposition on the sulfide SSE materials and evaluate their protection efficacy.

2:45pm **TF1-TuA-3 Tuning the Composition and Structure of High Mobility Nasicon-Type Thin Films Through Atomic Layer Deposition**, ***Daniela R. Fontecha***[1], University of Maryland College Park; *A. Kozen,* University of Vermont; *D. Stewart, G. Rubloff, K. Gregorczyk,* University of Maryland College Park

Fast Li^+ ion conducting thin film solid state electrolytes (SSEs) by atomic layer deposition (ALD) enable high power density, fast time constants, and high operating frequency regimes in solid state ionic devices. However, the ionic conductivity of thin film SSEs fabricated by ALD has been limited by material development challenges, phase purity concerns when dealing with tertiary and quaternary systems, and challenges related to crystallinity. These complexities require careful consideration of the material system, precursor selection, process parameters, and post-annealing conditions to realize ideal ALD thin-film SSE materials with ionic conductivities $>10^{-6}$ S/cm. Bulk oxide SSEs, such as $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) have a NASICON-type crystal structure, show high ionic conductivity when crystalline (10^{-3} S/cm), demonstrate air & water stability, and a high voltage stability window. ALD synthesis of LATP can be broken down into well-known constituent processes (e.g., Li_3PO_4, Al_2O_3, TiP_2O_7) which can be combined with respect to stoichiometric ratios.

LATP can be considered Al-doped $LiTi_2(PO_4)_3$ (LTP), in which Al^{+3} ions partially replace Ti^{+4} ions in the NASICON-type structure. This facilitates fast Li^+ ion conduction through the 3D network. With that in mind, an ALD process for LTP was first developed by alternating between Li_2O and TiP_2O_7 sub-processes. The Li_2O sub-process uses lithium *tert*-butoxide (LiO^tBu) as the lithium source and water to complete the surface reaction. The TiP_2O_7 sub-process uses titanium (IV) isopropoxide (TTIP) as the titanium source, trimethyl phosphate (TMP) as the phosphorous source, and water. The growth rate of LTP was measured to be 0.4 Å/cycle at 300 ^{o}C. By adjusting the ratio between Li_2O and TiP_2O_7 cycles, the Li concentration in LTP can be tuned between 8.4-34.3 at % Li.

A NASICON-type crystalline structure is achieved by post-annealing the LTP films between 650 ^{o}C – 850 ^{o}C. The ideal annealing temperature was found to be a function of Li-ion concentration. The resulting measured ionic conductivity of partially crystalline LTP thin films is $3.6x10^{-5}$ S/cm at 80 ^{o}C. In this talk, we will discuss the complex issues related to process parameters, stochiometric tunability, and the resulting ionic conductivity when exploring ternary and quaternary LTP/LATP metal phosphates phase space.

3:00pm **TF1-TuA-4 Unlocking Novel Chemistry in Atomic Layer Deposition: Transformative Insights from Trimethylaluminum Interactions with Battery Materials**, ***Donghyeon Kang***, *A. Mane, J. Elam,* Argonne National Laboratory

Trimethylaluminum (TMA) stands as a keystone in atomic layer deposition (ALD), widely esteemed for its role in crafting aluminum-based coatings across diverse applications. Notably, TMA is used to produce Al_2O_3 with H_2O, AlF_3 with HF-pyridine, and Al_2S_3 with H_2S, adhering to well-defined ALD mechanisms. These processes have permeated various substrates, leading to ultra-thin Al-based coating layers, particularly within the realm of energy storage materials such as battery cathodes, anodes, and solid electrolytes.

Our research group has embarked on a profound exploration of TMA's ALD chemistry, unveiling captivating interactions with reactive metal substrates, solid-state electrolytes, and battery cathode materials. Interestingly, when subjected to Li-metal anodes, TMA deviates from conventional ALD pathways, engendering a carbon composite layer atop the Li metal. This unconventional behavior arises from the inherent reactivity of both TMA and Li metal, diverging from established ALD paradigms. Moreover, our investigations reveal TMA's propensity to engage with Li-based impurities on solid electrolyte and cathode surfaces, yielding protective layers with beneficial attributes. Astonishingly, despite TMA's extensive utilization, this phenomenon has eluded prior scrutiny.

In this presentation, we unveil our findings on the intricate chemistry between TMA and battery materials (Li-metal, cathode, solid electrolytes) elucidated through in-situ quartz crystal microbalance (QCM), high-resolution X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and Raman spectroscopy studies. Furthermore, we demonstrate the transformative potential of these discoveries in the realm of battery materials surface treatment, offering tantalizing prospects for streamlined industrial applications.

3:15pm **TF1-TuA-5 Mapping Lithium Diffusion in Thin-Film V_2O_5 using Raman Spectroscopy**, ***Daniel MacAyeal***, University of Vermont; *L. Tapia-Aracayo, S. Caverly, D. Stewart, G. Rubloff,* University of Maryland; *A. Kozen,* University of Vermont

Understanding lateral diffusion of lithium in thin-film solid-state battery (SSB) materials is critical to improving SSB performance, stability, lifespan, and architecture. Using model test structures of sputtered V_2O_5/W/LiPON, we use Raman spectroscopy peak shifts to map Lithium concentration in V_2O_5. We evaluate the diffusion of lithium from LiPON layers into thin-film V_2O_5, measure the impact of different sputter deposition process conditions on lateral lithium diffusion, and investigate the effects of post-annealing the fabricated test structures. We will discuss the benefits of front versus back-side Raman spectroscopy for analyzing masked devices and correlate Raman spectroscopy mapping to XPS data to confirm compositional accuracy. Additionally, we will discuss the impact of electrochemical cycling at C/10 on lateral Lithium diffusion for symmetric V_2O_5/LiPON/V_2O_5 devices. Lastly, we will discuss the important implications of the lateral spacing limitations of clustered SSB devices due to lateral diffusion and propose architectural design rules based on this diffusion behavior for optimized device performance.

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[1] **TFD James Harper Award Finalist**

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