Thin Film Division
Room A105 - Session TF2-TuA
Thin Films for Battery and Photovoltaic Applications

Moderators: Richard Vanfleet, Brigham Young University, **Matthias Young**, University of Missouri

4:40pm **TF2-TuA-8 Optimization and Structural Characterization of ITO Thin Fims for Photovoltaic Applications***, F. Ali,* Metallurgical and Materials Engineering, The University of Alabama*; D. Li,* Electrical and Computer Engineering, Tne University of Alabama*; **Subhadra Gupta**,* Metallurgical and Materials Engineering, The University of Alabama

We have optimized the processing and annealing of sputtered indium-tin oxide (ITO) thin films for solar cell applications by DC magnetron sputtering. The effects of process parameters such as deposition power, reactive gas flow percentage, annealing temperature and time, as well as film thickness, on the sheet resistance and transmission of the ITO films was systematically studied, using a Design of Experiments. Additionally, structural characterization of the deposited films was performed using various techniques, including X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), four-point probe, UV-VIS spectrometry, and atomic force microscopy (AFM). TEM analysis revealed grain boundaries, crystallinity, and d-spacing of ITO thin film. The grain size was calculated with the help of the Scherrer equation. The XRD spectra of the ITO films revealed a polycrystalline structure with preferred (222) orientation of the ITO film. The SEM image of the ITO target gives information about the morphology of the racetrack after sputtering. The topography and surface roughness were evaluated by atomic force microscopy (AFM). A sheet resistance of 10 ohms/sq. and transmission of over 90% over 400-700 nm wavelengths was achieved. Perovskite solar cells fabricated with these optimized ITO electrodes showed promising properties.

5:00pm **TF2-TuA-9 Isolating Battery Components to Understand How Processing Affects Interface Formation***, **Victoria Castagna Ferrari**[1], G. Rubloff, D. Stewart,* University of Maryland, College Park

Interfaces dominate the performance of electrochemical systems, from interphase formation to charge transfer impedances, and they require careful study to understand. We have undertaken a broadly applicable approach to isolating components of a solid-state battery (SSB) to analyze them using non-destructive electrochemical impedance spectroscopy (EIS), and systematically build up to the full device. We then apply this knowledge to the matter of spontaneous Li transfer from LiPON to V_2O_5 during the sputtering process, which was also seen in other electrode/electrolyte pairs but is poorly studied.

Using sputtering and *in vacuo* shadow mask exchange, we fabricated an array of 16 batteries (Si/LiPON/LiV_2O_5) in parallel with auxiliary devices with isolated materials and interfaces on a single 3 in Si wafer. The reproducibility of the SSBs was confirmed by electrochemical testing, and the interfaces were evaluated from EIS measurements of the auxiliary devices. Equivalent circuit models for each device were built, ensuring that the components were all physically correlated to a material property or to (non)faradaic reactions of the interface. Interface reaction dynamics were evaluated as the applied voltage was swept over the normal working range of the SSB. The parameters obtained from these auxiliary circuit models were used to build a complete and accurate electric circuit for the SSB.

To evaluate the effect of the sputtering process on the interfaces, two model systems were used offering different conditions. Ultra-thin layers (10-20 nm) of either Li_2O or LiPON were sputtered on top of V_2O_5 using a non-reactive Ar working gas, or reactive N_2, respectively. EIS measurements of the models revealed the presence of an electron blocking LiPON layer, and the absence of a Li_2O layer above the V_2O_5. Furthermore, the properties of the Li_2O/V_2O_5 sample were similar to the lithiated LiV_2O_5 previously measured. An XPS depth profile confirmed that the V_2O_5 was fully lithiated after sputtering Li_2O, while only a fractional lithiation occurred after sputtering LiPON. DC polarization measurements and spectroscopy ellipsometry showed that the interfaces have distinct optical and electronic properties that might indicate interphase formation.

This work presents a materials-agnostic platform for investigating the interfaces in a SSB using non-destructive electrochemical techniques. The auxiliary devices are created in parallel with the SSB, ensuring a 1:1 comparison. Overall, this work presents a comprehensive approach to investigate the interfaces in SSBs, including chemical and physical reactions, and provides insights into improving the interfaces of thin films in SSBs.

5:20pm **TF2-TuA-10 Towards Dual Lithium-Ion and Electronically Conductive Polymer Coatings by MLD***, **Nikhila Paranamana**[2], A. Datta, X. He, M. Young,* University of Missouri, Columbia

Lithium ion batteries (LIBs) employing solid electrolyte offer potential advantages in safety and shelf life over current LIBs made with liquid electrolyte. However, undesired reactions occur between electrode active materials and the solid electrolyte, forming interphase layers that block Li^+ ion transport and degrade cell performance. To prevent these interphase reactions while maintaining battery operation, protective coatings are of interest which provide both electronic conductivity and Li^+ ion conductivity. Recent work has demonstrated the use of molecular layer deposition (MLD) to form electrically conducting poly(3,4-ethylenedioxythiophene) (PEDOT), anion-conducting polypyrrole (PPy), and cation conducting lithicone-glycerol (LiGL). However, MLD coatings that conduct both lithium ions and electrons have proven challenging to synthesize. In this work, we report on recent efforts to form MLD films of polyhydroquinone that are cation-conductive and electronically-conductive. We employ in-situ quartz crystal microbalance (QCM) studies during MLD growth to understand the growth mechanisms, as well as ex-situ spectroscopic ellipsometry (SE), electrochemical impedance spectroscopy (EIS), and electrochemical characterization to identify the material properties. We also report early work applying these coatings to nickel rich $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (NMC) cathode material to be used in solid electrolyte LIBs with the $Li_{10}GeP_2S_{12}$ (LGPS) solid electrolyte to understand how these protective coatings affect interphase layer formation in this system.

5:40pm **TF2-TuA-11 Initiated Chemical Vapor Deposition Stabilized Current Collectors for Anode-Free Lithium Metal Batteries***, **Ramsay Blake Nuwayhid**, J. Yeom, G. Waller, R. Carter, C. Love,* U.S. Naval Research Laboratory

Anode-free Li-metal batteries (AFLBs) offer a substantial enhancement in energy density over conventional graphite anodes. However, their realization is hindered by heterogeneous and irreversible Li plating/stripping from the Cu current-collector, resulting in the buildup of resistive solid-electrolyte interphase (SEI) species leading to poor cycling efficiencies. In this work, we employ initiated chemical vapor deposition (iCVD) polymeric coatings to create a stable interface between the Cu and liquid-electrolyte. The capability to deposit conformal polymer films at the nanoscale makes iCVD an attractive technique to passivate the reactive and complex Cu/liquid-electrolyte interface. We apply nanoscale coatings (5-100 nm) of poly(1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane) (pV4D4) to Cu current-collectors and evaluate their electrochemical performance in Li/Cu coin-cells. The cycling behavior reveals an overall cycling enhancement dependent on pV4D4 thickness. Moderate thicknesses (20 nm) resulted in a coulombic efficiency >90% for 100 cycles, more than double that of uncoated Cu. Through SEM and XPS analysis, it is determined that the cycling improvement is attributed to the uniform plating morphology of Li and the prevention of deleterious SEI component growth from the liquid-electrolyte. For ultrathin coatings (5 nm), a marginal improvement to bare Cu is observed and thick coatings (>100 nm) suffer from poor kinetics due to pronounced insulating effects of the dielectric pV4D4 film. Two distinct mechanisms are observed for Li plating/stripping for sufficient pV4D4 passivation; (1) moderate coatings (20 nm) function as a solid-electrolyte with Li plating beneath the layer and (2) thick coatings (>100 nm) function as a nucleation layer with Li plating on top of it. Overall, this work provides the mechanistic understanding of iCVD pV4D4 layers on Li plating/stripping and demonstrates the promising capability of iCVD to operate as stable interlayers in Li metal batteries.

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

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

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