ALD Applications
Room Plaza ABC - Session AA1-TuA

Batteries II (1:30-3:30 pm)/Emerging Apps III (4:00-5:00 pm)

Moderators: Ganesh Sundaram, Ultratech, Andy Sun, University of Western Ontario, Canada, Erik Østreng, Picosun Oy, Nicholas Strandwitz, Lehigh University

1:30pm **AA1-TuA-1 Highly Improved Performance of High Voltage ALD Coated Cathodes Showing Minimal Capacity/Voltage Fade at 4.8V,** ***Lamuel David****, D Mohanty,* Oak Ridge National Laboratory*; K Dahlberg,* Xalt Energy LLC*; D King,* Forge Nano (a PneumatiCoat Company)*; D Wood III,* Oak Ridge National Laboratory

Energy density of current lithium-ion batteries (LiBs) based on layered $LiMO_2$ cathodes (M=Ni, Mn, Co) needs to be improved significantly for widespread electric vehicle use in the automotive industry. In this work, we show that atomic layer deposition (ALD) of LiPON on Ni-rich NMC and Li-Mn-rich (LMR) NMC active particles substantially improves LIB performance even when cycled at increased upper cutoff voltage (UCV). Our results show that LiPON coatings prevented capacity degradation and decreased voltage fade when cycling at 1C-1C rate at UCV of 4.8 V. These samples also exhibited exceptional rate performance with 5x improvement (160 mAh/g) in capacity for NMC and 3x improvement (210 mAh/g) in capacity for LMR NMC when the particles were coated with LiPON. Electrochemical impedance spectroscopy (EIS) confirmed that LiPON-coated materials exhibited a significantly lower increase in the charge transfer component of impedance during cycling. The ability to mitigate surface related degradation mechanisms of these materials as demonstrated in this report provides insight into enhancing performance of high-voltage and high-energy LIBs.

1:45pm **AA1-TuA-2 Physical and Electrochemical Effects of Post-deposition Annealing on Atomic Layer Deposited Al_2O_3 Coatings on $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$,** ***David Jackson****, T Kuech,* University of Wisconsin-Madison

A systematic study investigating the effects of annealing on atomic layer deposited (ALD) Al_2O_3 coated Li-ion battery cathodes was performed. $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC) cathode powders were ALD coated at 100 °C, annealed from 300 to 700 °C, and then used to fabricate coin cells to investigate the electrochemical effects of the treatment. Analyses have shown that cell properties vary as a function of annealing temperature, and that the resulting electrochemical behavior and the cathodic solid-electrolyte interphase formed during cycling are significantly correlated.

Cells were characterized using charge-discharge cycling at 5C and C/5 rates, electrochemical impedance spectroscopy, charge endpoint slippage analysis, pre-assembly and postmortem X-ray photoelectron spectroscopy, and an elevated temperature storage test. It was observed that Al diffusion into the NMC bulk activates around 500 °C anneal temperature, where the Al atoms overcome a kinetic barrier allowing to them leave the surface Al_2O_3 layer. While efficiency of the cells during 5C rate cycling is higher in the unannealed samples, the starting capacity is also reduced, with Li likely being sequestered in the coating layer. At the highest temperature, 700 °C, the surface is similar to an Al "surface doped" NMC due to diffusion. This Al-doped surface leads to the highest self-discharge of all samples, though charge capacity retention in C/5 cycling is among the highest of all samples.

In samples annealed at 500 °C, an anomalous high charge slippage occurred between the first two cycles, indicating the presence of parasitic reactions. Postmortem XPS analysis of these samples show relatively high amounts of LiF formed in the SEI during cycling. Some connection between LiF formation and high charge slippage indicate the presence of uniquely active surface species formed during the initial stages of Al diffusion into the bulk.

These results demonstrate a new parameter that may be utilized to further control properties of ALD coated battery materials beyond that currently established with the well-studied Al_2O_3 coatings.

2:00pm **AA1-TuA-3 Novel Mechanism of Atomic Layer Deposition Al_2O_3 on $LiMn_2O_4$ for High Capacity Lithium-ion Batteries,** ***Lin Chen,*** Illinois Institute of Technology; Argonne National Laboratory*; R Warburton,* Purdue University*; K Chen,* Northwestern University*; J Libera,* Argonne National Laboratory*; M Hersam,* Northwestern University*; J Greeley,* Purdue University*; J Elam,* Argonne National Laboratory, USA

Previous studies demonstrated that Al_2O_3 coatings prepared by atomic layer deposition (ALD) improved the capacity of $LiMn_2O_4$ (LMO) cathodes for lithium ion batteries. This improvement was attributed to a reduction in surface area and diminished Mn dissolution. However, here we propose a different mechanism for ALD Al_2O_3 on LMO based on in-situ and ex-situ investigations coupled with density functional theory calculations. We discovered that Al_2O_3 not only coats the LMO, but also dopes the LMO surface with Al leading to changes in the Mn oxidation state as revealed by in-situ mass spectrometry and infrared spectroscopy as well as ex-situ X-ray photoelectron spectroscopy. Different thicknesses of Al_2O_3 were deposited on nonstoichiometric $LiMn_2O_4$ for electrochemical measurements. The LMO coated using one cycle of ALD Al_2O_3 (1 × Al_2O_3 LMO) yielded a high initial capacity, 16.4% larger than its uncoated LMO counterpart in full cells. The stability of 1 × Al_2O_3 LMO is also much better as a result of greatly stabilized structure with Al-doping. Furthermore, 4 × Al_2O_3 LMO demonstrates remarkable capacity retention, nearly reaching 100% at 0.5 C for 200 cycles while uncoated LMO only retains 78.2%. Stoichiometric $LiMn_2O_4$ was also evaluatedwith similar improved performance achieved. All superior results, accomplished by great stability and reduced Mn dissolution, is thanks to the synergetic effects of Al-doping and ALD Al_2O_3 coating. This new understanding offers a viable avenue to tune the performance of other Mn-containing, high capacity cathodes by employing $LiMn_2O_4$ as amodel system.

2:15pm **AA1-TuA-4 Atomic Layer Deposition of Superionic Solid-State Electrolytes for Lithium Batteries,** ***Xiangbo Meng,*** University of Arkansas*; J Connell, P Lopes, J Libera,* Argonne National Laboratory, USA*; K Zavadil,* Sandia National Laboratory*; J Zhang,* Pacific Northwestern National Laboratory*; J Elam,* Argonne National Laboratory, USA

Rechargeable lithium batteries are very promising energy storage devices for portable electronics, transportation, and smart grids. As an important component of lithium batteries, liquid electrolytes currently are widely utilized, serving as a lithium-ion conductor but an electrical insulator. The direct contact between the electrodes and the liquid electrolyte, however, causes undesirable electrochemical reactions the ubiquitous formation of solid electrolyte interphases (SEIs). SEIs differ in quality with the coupling selection of anodes, cathodes, and liquid electrolytes, but always adversely consume lithium and liquid electrolytes. On the other hand, the flammable nature of liquid electrolytes poses serious safety concerns in lithium batteries. Among various potential solutions, solid-state electrolytes are highly regarded.

Aimed at developing new superionic solid-state electrolytes, we recently explored two individual processes for binary Li-S and Al-S compounds, respectively, using atomic layer deposition (ALD). By combining the two ALD processes and tuning their cycle ratio, we then synthesized a series of ternary compounds of lithium aluminum sulfides, i.e., Li_xAl_yS. The subsequent impedance measurements verified that the resultants Li_xAl_yS films are promising solid-state electrolytes with tunable ionic conductivities up to over 10^{-4} S/cm, 1000 times higher than the LiPON counterparts reported previously. We further characterized the growth and properties of the ALD Li_xAl_yS films using *quartz crystal microbalance*, *inductively coupled plasmamass spectrometry*, and *X-ray photoelectron spectroscopy*. In addition, we also investigated the surface chemistry for the Li_xAl_yS ALD using in-situ *Fourier transform infrared spectroscopy*. Very interestingly, the resultant Li_xAl_yS films demonstrated an exceptional performance in inhibiting the growth of lithium dendrite structures in lithium batteries.

2:30pm **AA1-TuA-5 Cubic Garnet $Li_7La_3Zr_2O_{12}$ Solid Lithium Electrolyte by ALD,** ***Eric Kazyak****, K Wood, K Chen, A Bielinski, A Davis, T Thompson, J Sakamoto, N Dasgupta,* University of Michigan

Lithium-conducting solid-state electrolytes (SSEs) are a promising platform for achieving the high energy density, long-lasting, and safe rechargeable batteries needed for a wide range of applications. By eliminating the need for flammable and unstable liquid electrolytes, SSEs dramatically reduce the risk of fire while enabling high voltage and energy density chemistries including Li metal. In particular, the ceramic oxide material cubic garnet $Li_7La_3Zr_2O_{12}$ (LLZO) is a promising option due to its stability and high ionic conductivity. Two major challenges to commercialization are manufacturing of thin layers and creating stable, low-impedance, interfaces with both anode and cathode materials. Atomic Layer Deposition (ALD) has recently been demonstrated as a powerful method for depositing both solid electrolytes and interfacial layers to improve stability and performance at electrode-electrolyte interfaces in battery systems. The self-limiting reactions afford the ability to conformally coat arbitrary geometries for 3D batteries, powders, and porous cathodes, an important advantage over the current state-of-the-art LiPON solid electrolyte and previous approaches for thin-film LLZO.

In this study, we present the first reported ALD of the pentenary oxide Al-doped LLZO. Constituent binary processes are successfully combined in a thermal ALD process at 225°C to deposit high purity, dense amorphous LLZO films. The cycle-by-cycle growth of the multi-component film is quantified by in situ quartz crystal microbalance (QCM) measurements. We demonstrate the ability to tune composition within the amorphous as-deposited film, anneal to achieve the desired cubic garnet phase, and characterize the annealed films via *in situ* synchrotron XRD during annealing. The ability to conformally coat high aspect ratio structures of arbitrary composition with ultrathin layers of dense, amorphous LLZO is shown, demonstrating the potential for integration into 3D battery architectures, including porous electrode structures. Approaches to overcome Li loss and phase segregation during annealing are demonstrated and discussed.

The film exhibits preferential orientation when annealed on single crystal substrates, and the cubic-tetragonal phase transition was observed at ~500°C, significantly lower temperature than reported for bulk synthesis methods. By tuning the composition and annealing conditions, the resulting film can be tuned from pure-phase $La_2Zr_2O_7$ pyrochlore, a high temperature thermal barrier material with several commercial applications, to high purity tetragonal LLZO or high phase-purity cubic LLZO, the superionic solid electrolyte material.

2:45pm **AA1-TuA-6 Improving Interfacial Stability of Sulfide-Based Lithium-Ion-Conducting Solid Electrolytes with ALD***, **Jasmine Wallas**, A Heist, S Lee, S George,* University of Colorado - Boulder

Rechargeable solid state Li-ion batteries may revolutionize energy storage. Solid state Li-ion batteries also have the potential for better safety, cycling performance, SEI stability and energy density than liquid electrolyte Li-ion batteries. However, solid electrolytes generally suffer from low ionic conductivity and/or poor interfacial stability. In this work, we demonstrate that the interfacial stability of solid electrolytes can be improved with ALD coatings.

$Li_{10}GeP_2S_{12}$ is a sulfur-based ceramic electrolyte with extremely high ionic conductivity of ~10^{-2} S cm^{-1}. This ionic conductivity is comparable with liquid electrolytes at room temperature. However, $Li_{10}GeP_2S_{12}$ solid electrolyte suffers from interfacial instability with Li metal. Contact with Li metal leads to substantial electrolyte decomposition and the formation of a resistive interphase. However, Al_2O_3 ALD coatings can greatly increase the interfacial electrochemical stability.

In this work cells were composed of symmetric Li electrodes with $Li_{10}GeP_2S_{12}$ solid electrolyte (see supplemental Figure 1). The $Li_{10}GeP_2S_{12}$ solid electrolytes were coated with various numbers of Al_2O_3 ALD cycles. The Li metal was then pressed into the $Li_{10}GeP_2S_{12}$ solid electrolyte. The thickness of the Al_2O_3 ALD coating was varied to optimize interfacial stability. Internal cell resistance measurements were used to monitor the formation of the resistive interphase. The experiments were conducted at 60°C.

The uncoated $Li_{10}GeP_2S_{12}$ solid electrolyte developed extremely high internal resistance and reached the defined failure point (>1000 Ω) within the first 40 hours of the test (see supplemental Figure 2). The Al_2O_3 ALD coatings substantially increased interfacial stability and maintained lower internal resistance. The $Li_{10}GeP_2S_{12}$ solid electrolyte coated with 25 Al_2O_3 ALD cycles increased the chemical stability and extended the time to the failure point to 400 hours (see supplemental Figure 2). The lifetime of the Al_2O_3 ALD-coated $Li_{10}GeP_2S_{12}$ solid electrolyte is more than a factor of 10 longer than the uncoated $Li_{10}GeP_2S_{12}$ solid electrolyte.

3:00pm **AA1-TuA-7 Atomic Layer Deposition of Solid-State Electrolytes for All-Solid-State Lithium Ion Batteries***, **Biqiong Wang**, J Liu, Y Zhao, A Lushington, R Li, T Sham, X Sun,* University of Western Ontario, Canada

The development of batteries with higher energy density, longer cycle lives, and assured safety levels have been the pressing need to satisfy the stringent demands of portable electronic devices, electric vehicles and grid-energy storage systems. [1] Replacement of the conventional liquid electrolytes with solid-state electrolytes (SSEs) will not only eliminate the inherent safety issues but also provide more flexibility in battery design and management. [2] Atomic layer deposition (ALD) offers exclusive advantages of highly controllable thin film depositions especially on high-aspect ratio three-dimensional substrates. [3, 4] In our group, various SSEs have been developed by ALD including Li_3PO_4, lithium silicate, lithium silicophosphate, $LiTaO_3$, and $LiNbO_3$. [5-7] All of the as-deposited thin films presented acceptable ionic conductivity, among which Li_3PO_4 exhibited the best value of 3.3x 10^{-8} S/cm at room temperature (Figure S1). Nevertheless, the electrochemical properties of materials by ALD have shown deviations from those obtained by other methods. Synchrotron-based spectroscopy, including X-ray Photoemission Spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS), were performed to study their detailed electronic structures. Insightful information on both local chemical environment and structures can be extracted. Further analysis of the spectra can give semi-quantitative information. In Figure S2, Nb L-edge X-ray absorption near edge spectra (XANES) show that Nb in the Li_xNb_yO systems by ALD exists as Nb5+ in an octahedron structure with oxygen. While introducing more Li content by controlling the ALD subcycle number of Li, the higher degree of the splitting of the double feature due to the crystal field splitting indicates a probable more distorted local structure in the thin films. To summarize, developing SSE by ALD is indispensable to building reliable high-energy-density batteries. Fundamental studies of the ALD materials are crucial to revealing the growth mechanisms and the correlations between electronic structures and electrochemical properties, shedding lights on future designs of SSEs by ALD.

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3:15pm **AA1-TuA-8 Highly Stable WS_2 Thin Film Anode Grown by Plasma-enhanced Atomic Layer Deposition (PEA LD) for Na-ion Battery***, **Dip Nandi**,* Yeungnam University, Republic of Korea*; S Yeo,* Yonsei University, Republic of Korea*; M Ansari,* Yeungnam University, Republic of Korea*; H Kim,* Yonsei University, Republic of Korea*; T Song, S Kim,* Yeungnam University, Republic of Korea

Plasma-enhanced atomic layer deposited (PEALD) tungsten sulfide (WS_2) thin film was used as an anode in sodium-ion battery (NIB) without any carbon and binder. Thin films of WS_2 were directly grown using an alternate exposure of $W(CO)_6$ and H_2S plasma at a relatively low temperature of 350 ^{o}C using shower-head type ALD reactor without any post sulfurization process. The stoichiometric presence of W and S in the as-deposited films was observed from Rutherford backscattering spectroscopy (RBS) analysis. The films were crystalline in nature with (002) orientation as revealed by the transmission electron microscopy (TEM) analysis. For NIB application, the WS_2thinfilms were directly grown on stainless steel (SS) current collector and used as an electrode without any further modification. Coin cells were then fabricated and tested in a half-cell configuration against Na. The electrochemical reactions during cathodic as well as anodic sweep were studied using cyclic voltammetry (CV) measurements. Reversible conversion and intercalation reactions were evident from the CV which was repeatable in nature after 1st cycle. Improved electrochemical reactivity of the ALD grown thin film against Na^+ ion could be observed from this CV measurement. Films with five different thickness using different ALD cycles were used for charge-discharge cyclic measurements. Cells with ALD-WS_2 as an anode showed high electrochemical stability up to 200 charge-discharge cycles with more than 95% Coulombic efficiency. Different current rates were also used for cyclic measurements to show the suitability of these ALD grown thin film anodes for a wide range of portable electronic appliances.

4:00pm **AA1-TuA-11 ALD-Tin Oxide as Impermeable Electron Extraction Layers for Temperature Stable Roll-to-Roll-Compatible Perovskite Solar Cells***, **Lukas Hoffmann**,* University of Wuppertal, Germany*; K Brinkmann,* University of Wuppertal*; J Zhao, T Hu,* Nanchang University, China*; D Schlamm, J Malerczyk, T Becker, D Theirich,* University of Wuppertal*; S Olthof, K Meerholz,* University of Cologne*; H Gargouri,* Sentech Instruments, Germany*; B Cheng, Y Chen,* Nanchang University, China*; T Riedl,* University of Wuppertal

Organo-lead halide perovskite-based solar cells (PSCs) reached power conversion efficiencies (PCE) beyond 20% within the past years [1]. Nevertheless, the decomposition of the active material in the presence of water or elevated temperatures and follow-up corrosion of e.g. metal electrodes are showing to be one of the big issues to overcome before commercialization [2].

Here we demonstrate the use of tin oxide (SnO_x) grown by ALD, which is electrically conductivity and shows outstanding permeation barrier properties [3], as electron extraction layer (EEL) and concomitant permeation barrier against moisture and decomposition products of methylammonium lead iodide perovskites, perovskite solar cells with outstanding long-term stability can be achieved [4]. Specifically, the tin oxide layers in this study were fabricated by Tetrakis(dimethylamino)tin and different oxidants (water, ozone, O-plasma) at low temperatures (80°-100°C) in low and atmospheric pressure ALD. Strikingly, the solar cells based on SnO_x remain stable over 4500 hours at elevated temperatures as well as in ambient air, whereas devices based on other EELs, without sealing properties, degrade to roughly 50% of their initial efficiency within 100 h. Moreover, SnO_x enables the design of ITO-free semitransparent electrodes based on ultra-thin metal layers (e.g. $SnO_x/Ag/SnO_x$)[5]. Based thereon, semi-transparent perovskite solar cells with about 70% average transmittance in the near-infrared region (λ > 800 nm) and an average transmittance of 17% in the visible region (λ = 500-750 nm) have been realized [5]. For SnO_x as EEL, we unravel the critical importance of the of the oxidant used in the growth of the SnO_x, e.g. the use of ozone is essential for optimizing the fill factor of the solar cells by minimizing the potential barrier in the SnO_x-perovskite boundary layer. These results provide a general avenue to design PSCs incorporating indium-free transparent top- and bottom electrodes based on corrosion sensitive metals [6]. Finally, tin oxide growth by spatial ALD at atmospheric pressure is presented and its compatibility to replace its low-pressure analogs is shown. With this findings, an all-step roll-to-roll fabrication of highly stable, indium-free PSCs could be realized.

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4:15pm **AA1-TuA-12 Nano-Structured Ceramic ALD Coatings to Stabilize SiC Against Reaction in High Temperature Steam***, **Amanda Hoskins,** A Coffey, C Musgrave, A Weimer,* University of Colorado - Boulder

Silicon Carbide (SiC) is an ideal material for many high-temperature applications due to its resistance to thermal shock and high thermal conductivity. However, SiC degrades in water-rich environments limiting its applications in extreme oxidative environments such as combustion engines, heat exchangers, and high temperature reactor materials. Current deposition methods for environmental barrier coating (EBCs) such as plasma spraying and aerosol spraying generate micron-scale films with inherent grain boundaries and cracks. Atomic layer deposition (ALD) generates nano-scale films that are dense, crack-free, and chemically bonded to the surface without the use of excess precursor. We have found that the application of mullite nanostructured films grown with ALD significantly improves the oxidation resistance of SiC in extreme environments with a film much thinner than standard applications. In addition to mullite, we have targeted a variety of high temperature coating materials chosen based on thermal properties, structural characteristics, and stability in oxidative environments. We have grown ALD layers of our desired materials on high surface area SiC particles using a fluidized bed particle ALD reactor. Using thermogravimetric analysis, it has been shown that these coatings improve the oxidation resistance of SiC by up to 64% at 1000^{o}C. We have applied density functional theory (DFT) to model the performance of these mullite coatings in an oxidative environment. Computational modeling of oxygen diffusion through mullite and other candidate materials allows identification of promising coatings to further extend the lifetime of SiC. We expect to use this understanding to develop more advanced stabilizing coatings for SiC and the myriad of other applications that require high-temperature oxidation resistant materials.

4:30pm **AA1-TuA-13 Mechanical, Physical, and Electrical Properties of Plasma-Enhanced Atomic Layer Deposition of TiVN***, **Mark Sowa,*** Ultratech*; N Strandwitz, L Ju,* Lehigh University*; A Kozen,* U.S. Naval Research Laboratory*; B Krick,* Lehigh University

Specific ternary transition metal nitrides are known for their excellent mechanical, electrical, and chemical properties. TiVN thin films for hard, wear-resistant coating applications have been deposited by sputtering[1,2] and arc ion plating[3]. Compared to pure TiN and VN, TiVN films of intermediate stoichiometry are reported to be harder (H = 32.1GPa for $Ti_{0.77}V_{0.23}N$ vs H = 20.2GPa for TiN and H = 5.6GPa for VN) and stiffer (E = 410GPa for $Ti_{0.87}V_{0.13}N$ vs E = 395GPa for TiN and 307GPa for VN).[4] Plasma-enhanced atomic layer deposition (PEALD) of TiN has been extensively studied[5,6,7] and PEALD VN has also been reported[8]. We will report on PEALD $Ti_xV_{1-x}N_y$ (x = 0 to 1) films deposited using tetrakis(dimethylamido)titanium and tetrakis(ethylmethylamido)vanadium with N_2 plasma. Stoichiometry has been varied through control of the TiN:VN deposition cycle ratio. Analyses include spectroscopic ellipsometry(thickness and optical properties), four point probe(resistivity), XPS(stoichiometry and impurities), XRD(crystallinity), XRR(density and thickness), and sliding wear testing(tribological properties).

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