ALD Applications
Room Grand Ballroom H-K - Session AA1-TuM

ALD for Batteries

Moderators: Prof. Dr. Hyeontag Jeon, Hanyang University, Prof. Markku Leskela, University of Helsinki, Finland

8:00am **AA1-TuM-1 Nanoscale Surface Engineering for Battery Electrode and Solid Ionic Electrolytes*, Chunmei Ban,*** CU Boulder **INVITED**

This presentation will discuss the effects of using atomic/molecular layer deposition (ALD/MLD) in stabilizing surface/interface of battery electrode materials and facilitating ion diffusion at the surface of ionic conducting materials. ALD and MLD have proven themselves to be the best methods to grow continues, conformal and pinhole-free ultrathin films for high-aspect-ratio microstructures and nanomaterials. Thus, ultrathin oxides layers (<5nm) have been used to protect surface of electrode materials from liquid electrolytes, leading to the greatly improved battery cycling performance of lithium-ion electrodes. In addition, surface coatings via ALD/MLD have been recently applied to ionic conducting materials to increase wettability and electrochemical stability. This talk will summarize recent studies on surface modification using ALD/MLD for electrodes and solid-state electrolytes, to correlate the electrochemical properties of the coated electrochemical materials with chemistry of coating materials. Electrochemical analysis will be used to study how the modified surfaces alter charge transfer and electrochemical reactions at the electrode surface or at the electrode-electrolyte interface. Furthermore, we will combine electrochemical diagnosis with spectroscopic studies to investigate the structural and morphology evolution of the coating materials during electrochemical processes, present insights in design of surface coatings and their applications in solid-state batteries.

8:30am **AA1-TuM-3 Enabling Fast Charging of Lithium-ion Batteries by Coating of Graphite with ALD**, *E. Kazyak, K. Chen, Y. Chen, T. Cho,* ***Neil P. Dasgupta,*** University of Michigan, Ann Arbor

Increasing the achievable charging rate of lithium-ion batteries (LIBs) is critical to the widespread commercialization of electric vehicles (EVs). The primary factor limiting the fast-charge ability of state-of-the-art LIBs is the propensity for Li metal to plate out on the graphite surface during charging.[1] The poor reversibility of Li metal in LIB electrolytes leads to rapid capacity fade, consumption of the electrolyte (cell drying), and possibly even short-circuit from dendrites penetrating the separator. This problem is exacerbated in high-energy density cells with thicker electrodes, leading to energy-power tradeoffs.

To prevent/mitigate these effects, in this study[2] we implement an atomic layer deposition (ALD) surface coating on calendered graphite anodes. We demonstrate that this artificial solid electrolyte interphase (a-SEI) that outperforms the natural SEI in fast-charging ability. The large majority of the previous ALD coatings that have been investigated as electrode coatings for LIBs have been binary metal oxides that have very low ionic conductivity. In contrast, the ALD coating used here is a lithium borate-carbonate (LBCO) solid electrolyte. This ALD single-ion conductor has previously been shown to exhibit ionic conductivities above 2*10^{-6} S/cm and excellent electrochemical stability, including with Li metal.[3]

Here we demonstrate that in comparison to uncoated control electrodes, the LBCO a-SEI coating: 1) eliminates natural SEI formation during formation cycles, 2) decreases interphase resistance by >75% compared to that of the natural SEI, and 3) extends cycle life under 4C-charging conditions, enabling retention of 80% capacity after 500 cycles (compared to 12 cycles in the uncoated control) in pouch cells with >3 mAh-cm^{-2} loading. Not only is this a promising approach to enable fast-charging of LIBs, but it also challenges the prevailing thinking that mass-transport limitations in the liquid electrolyte must be addressed to enable fast charging. In the future, this opens up new possibilities for engineering of LIB interfaces for performance enhancements beyond improved stability and cycle life.

References

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8:45am **AA1-TuM-4 Aluminum Doping of Lithium Phosphate using Atomic Layer Deposition***, **Daniela Fontecha**, K. Gregorczyk, A. Kozen, G. Rubloff,* University of Maryland, College Park

Metal phosphate glasses developed by ALD have been used for a variety of applications in microelectronics. Lithium phosphate deposited by ALD is relevant in solid-state battery (SSB) applications as a Li-ion conducting thin film that is compatible with many Li-ion battery chemistries, enabling the passivation of reactive interfaces between solid-state cathode and electrolyte films. It has also been shown that lithium aluminum phosphate (LAP) is a promising protection layer for cathode materials in SSBs. This work explores the impact of Al-doping of lithium phosphate in terms of its structural, chemical, and Li$^+$ ion conducting properties with a new ALD synthesis method for thin film applications.

The constituent ALD process for crystalline Li_3PO_4 (LPO) utilizes lithium tert-butoxide (LiO^{t}Bu), water, and trimethyl phosphate (TMP) at 300 ^{o}C with a growth rate of 0.8 Å/cycle and ionic conductivity of 1.3x10^{-9} S/cm. Trimethyl aluminum (TMA) and water are then used to insert aluminum into the LPOfilm by cycling between 1 cycle of TMA + water and **[n]** cycles of LPO (n = 30-120) to produce a film with Al content between 1-4 %. This work shows that the ionic conductivity of LAPincreases to 4.0x10^{-8} S/cm – one order of magnitude higher than that of LPO– due to the role aluminum plays in cross-linking phosphate groups even at these low Al concentrations. Deposition temperatures ranging from 250 – 300 ^{o}C show growth rates from 0.8 to 0.9 Å/cycle, respectively. The TMA + water pulse appears to have a minimal effect on the overall growth rate, which indicates compatible precursor chemistry between hydroxylated TMA and LiO^{t}Bu.XPS O 1s high resolution spectra of LAP films show an increase in bridging oxygen content with a shift in the bridging oxygen peak to lower binding energies suggesting the increase of Al-O-P bonding. The presence of P-O-P and Al-O-P binding states as well as GIXRD results showing some loss of crystallinity in as-deposited LAP compared to LPO suggest that there is cross-linking between phosphate groups at low Al-doping levels. We find that deposition temperature is a critical factor in controlling resultant film morphology with films deposited at 300 ^{o}C exhibiting an additional peak at 28.3^o 2θ. This peak lies between crystalline Li_3PO_4 and $AlPO_4$ peaks seen in literature, suggesting that at higher deposition temperatures, a mixture of crystalline LPO and $AlPO_4$ phases develops. In this talk, thin film processing of LAP is discussed along with materials characterization of a new Li-ion conducting thin film by ALD.

9:00am **AA1-TuM-5 Developing High-Performance Nickel-Rich Cathodes of Lithium-ion Batteries via Atomic Layer Deposition***, **Xiangbo Meng**, X. Wang, K. Velasquez Carballo, A. Shao,* University of Arkansas*; Y. Liu, H. Zhou,* Argonne National Laboratory*; X. Xiao,* Brookhaven National Laboratory

$LiNi_xMn_yCo_zO$ (NMCs, x + y + z =1) are promising for next-generation lithium-ion batteries (LIBs) and emerging lithium metal batteries (LMBs), featuring their higher capacity and lower cost than those of $LiCoO_2$. In particular, the advantages of NMCs in capacity and cost become more evident with increased Ni content. In other words, the higher the Ni content is, the higher the capacity is and the lower the cost is. With the increasing Ni content, however, the issues of NMCs become more challenging, exhibited as performance fading and safety risk. The issues include residual lithium compounds, irreversible phase transition, oxygen release, transition metal dissolution, and microcracking. They can further cause interface problems and electrolyte degradation and eventually lead to cell failure. This is particularly evident for Ni-rich NMCs (x ≥ 0.6).

In searching for solutions to these issues, surface coating remains as an important technical strategy and has proven effectiveness. In the past decade, atomic layer deposition (ALD) has emerged as a new surface coating process and has been attracting an ever-increasing attention for addressing issues of various battery systems.[1-4] Its advantages lie in multiple aspects: (1) uniform and conformal coating, (2) moderate process temperature, and (3) the only capable technique enabling coatings over either prefabricated electrodes or battery powders. In addressing the issues of Ni-rich NMCs, we have been intensively investigating various surface coatings via ALD, including binary oxides, ternary Li-containing oxides, binary sulfides, and ternary Li-containing sulfides.[5-8] Our efforts revealed that these coatings commonly could inhibit interface reactions, mitigate microcracking, and suppress irreversible phase transition. Among them, Li-containing compounds could enable better ionic conductivity while sulfide coatings could offer some unique protective effects through scavenging oxygen released from NMC lattices. Our original discovery on sulfide coatings is particularly significant, for it opens a new research direction on surface coatings of rechargeable batteries and paves a novel technical avenue for achieving high performance of NMCs and the like in LIBs and LMBs.

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5. Wang, X.*, et al.*, *Nanotechnology* (2021) **32** (11), 115401

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8. Wang, X.*, et al.*, *Journal of Energy Chemistry* (2022) **69**, 531

9:15am **AA1-TuM-6 Molecular-Layer-Deposited Zincone Films Induce the Formation of LiF-Rich Interphase for Lithium Metal Anodes*, Wei-Min Li,*** Jiangsu Leadmicro Nano-Technology Co., Ltd., China*; S. Chang, A. Li,* Nanjing University, China

Lithium (Li) metal has been recognized as the promising anode material for rechargeable batteries because of its high theoretical capacity of 3,860 mAh g^{-1} and the lowest electrode potential (−3.04 V v.s. the standard hydrogen electrode (SHE)). However, Li metal usually forms a fragile solid electrolyte interphase (SEI), which is not sufficiently dense to passivate the surface of Li metal. During stripping and plating, the SEI cannot suppress the side reaction between Li metal and electrolyte. The poor SEI may also induce the heterogeneous deposition of Li, leading to the formation of notorious dendrites. The uncontrolled Li dendrites not only consume cyclable Li but also accumulate irreversible "dead lithium" owing to the loss of electric connection. Coulombic efficiency (CE) is then dramatically reduced. At a fixed loading, the deliverable capacity decays rapidly. In addition, Li dendrites may cause safety issues such as short circuits and catastrophic cell failures, which hinders the practical application of Li metal batteries.

In this work, we report a zincone (ZnHQ) MLD technology and its application for induced LiF-rich SEI on a copper nanowire (CuNW) anode. Zincone is a zinc-based hydroquinone (HQ) where Zn replaces hydrogen of HQ. As shown in **Figure 1a**, the hydroxyl (-OH) modified Cu is grafted with HQ during the MLD. Diethylzinc further reacts with the hydroxyl groups of grafted HQ to yield ZnHQ. HQ is selected as the backbone molecule because it is relatively stable upon lithiation and a single chain of ZnHQ has a terminal oxygen, which can serve as the nucleophilic group to attack Li bistrifluoromethanesulfonimide (LiTFSI) upon negative polarization. The resultant LiF-rich SEI (**Figure 1b, c**) can facilitate Li ion diffusion and suppress the dendritic Li growth that is usually induced on a pristine Cu (**Figure 1d, e**). More importantly, zinc atoms can facilitate the deposition of Li metal owing to the lithiophilicity.

Furthermore, the high surface area of porous scaffold and CuNWs reduces the local current density and prolongs the Sand's time. As a result, the CuNW@ZnHQ electrode demonstrates superior cyclability for over 7000 h at a capacity of 1 mAh cm^{-2} and can maintain more than 300 h at a high loading capacity (15 mAh cm^{-2}). In addition, CuNW@ZnHQ is paired with NCM523 at a capacity of 3.2 mAh cm^{-2} with excellent cyclability of 90% capacity retention for 1000 cycles. This work provides an alternative approach to developing nanoscale interfacial coatings for Li metal and demonstrates that the zincone MLD strategy may serve as a potential technology for next-generation high-energy Li metal anodes.

9:30am **AA1-TuM-7 Deconvoluting the Impacts of Lithium Morphology and SEI Stability on Battery Cyclability Using ALD-Grown Thin Films*, Sanzeeda Baig Shuchi,*** *S. Oyakhire, Y. Cui, S. Bent,* Stanford University

The establishment of a fossil-fuel-free world strongly depends on electrification. The Li-ion battery, a universal mode of electrochemical energy storage, is reaching the theoretical limit, creating an urgency to produce more efficient batteries for next-generation applications. A more energy-dense battery configuration is the anode-free Li metal battery (LMB), in which Li is directly plated on and stripped from the Cu current collector (CC).

Electrodeposited Li morphology and solid electrolyte interphase (SEI) are the two most crucial performance modulators in LMBs. The literature has shown that low surface area morphology and anion-derived SEIs are desired for improved performance. However, it is difficult to deconvolute the individual impact of low surface area morphology and anionic SEI species on performance as they coexist and are correlated. We demonstrate a novel interface engineering approach to deconvolve the effects of Li morphology and SEI stability using atomic layer deposition (ALD). First, we modify the Cu CC surface using two thin films with distinct characteristics: resistive, acidic HfO_2; and conductive, acidic ZnO, using TDMAHf-H_2O and DEZ-H_2O precursors.

We leverage ALD to precisely vary the thickness of the nanofilms and establish that increasing the film resistance results in improved performance due to resistance-derived Li morphology. In addition, the HfO_2-modified CCs performed better than the ZnO-modified CCs, consistent with their relative resistivities. To decouple the impact of SEI species from morphology, we preform the SEI before cycling using a simple potential hold step for these two acidic metal oxide films, each of which has different electric properties. We find that with increasing film thickness, the preformed SEI has more anionic species due to the surface acidity of the thin films. Despite being anion-rich, the preformed SEI does not improve performance, which we attribute to its evolution into an organic-rich SEI during plating. Moreover, the impact of the preformed SEI was statistically insignificant during long-term cycling while the role of resistance became more evident.

In conclusion, the results indicate that morphological control is more successful for improved battery cyclability due to the inherent challenges with preformed SEI preservation. Correspondingly, the results suggest that resistance of the ALD-grown thin films is more important than surface acidity for CC modification. We show this resistance-derived Li morphology and performance enhancement in three different electrolytes with at least a twofold increase in cycle life along with improved capacity retention in practical anode-free pouch cells.

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