Advances in Battery Engineering, Interface Design, and Characterization Mini-Symposium
Room 319 - Session BT1+AS+CA+TF-ThM

Interface Engineering in Batteries

Moderators: Prof. Dr. Adriana Creatore, Eindhoven University of Technology, **Prof. Alexander Kozen**, University of Vermont

8:00am **BT1+AS+CA+TF-ThM-1 Plasma and Electrochemical Modification of Battery Cathode Surfaces to Enhance Voltage Stability and Thus Energy Density***, Paul Braun,* University of Illinois Urbana-Champaign **INVITED**

The energy density of battery cathodes increases dramatically with increases in voltage. However, higher operating voltages, in particular above 4.3V leads to significant capacity degradation. Because the mechanism of capacity degradation is often a surface-initiated reaction, modification of the exposed surface of the cathode material is a promising approach to increase energy density without adding significant mass or volume to the battery. Two approaches we are investigating to increase the voltage stability of $LiCOO_2$, a common battery cathode material, include surface modification via a plasma process, and electrochemical deposition of a high voltage stable material. Both methods result in a thin layer of high voltage stable material on the surface of the active cathode material. The plasma modification forms a nanoscale layer of disordered rocksalt on the underlying layered $LiCoO_2$ while the electrochemical modification grows a layer of lithiated manganese oxide on the underlying $LiCoO_2$. In both cases, the cyclable energy density of the $LiCoO_2$ is increased significantly.

8:30am **BT1+AS+CA+TF-ThM-3 Interfacial Engineering of Battery Materials using Atomic Layer Deposition***, Neil Dasgupta,* University of Michigan, Ann Arbor **INVITED**

Interfaces and interphases play a critical role in battery performance, both in current state-of-the-art Li-ion batteries (LIBs), as well as next generation battery technologies. Therefore, there are great efforts to understand, control, and improve the properties of battery interfaces and interphases. This quickly becomes a multi-dimensional optimization problem, where the required properties of interfaces span from performance (i.e. fast rate capability), stability (i.e. long calendar life) and compatibility with the adjacent chemical and material phases. To address these challenges, there has been increasing interest in the application of 'artificial interphase' layers, which are typically comprised of nanoscale thin-film coatings along electrode-electrolyte interfaces. From a manufacturing perspective, it is critical that these surface coatings be deposited in a conformal, reproducible, scalable, and low-cost manner.

Towards these goals, our research group has developed a range of surface coating layers for battery applications, both for LIBs with liquid electrolytes, as well as next-generation systems such as Li metal anodes and solid-state batteries. In this talk, I will summarize recent progress towards precise and tunable interfacial control in batteries with both liquid and solid electrolytes, using atomic layer deposition (ALD) as an enabling platform. I will describe the development of advanced ALD chemistries, beyond the binary oxide systems that are typically employed. In LIBs, I will describe how surface coatings can simultaneously enable low-temperature and fast charging of graphite anodes without Li plating. In solid-state battery systems, I will describe the stabilization of cathode/solid electrolyte interfaces, enabling high-voltage cycling above 4.5 V. Finally, I will describe our efforts towards scalable manufacturing of ALD-coated battery electrodes, through the development of atmospheric-pressure spatial ALD technologies.

9:00am **BT1+AS+CA+TF-ThM-5 Atomic Layer Deposition (ALD) Tuned Interfaces for High-Performance Lithium- and Manganese-Rich Cathodes***, Jahnavi Manikantan Sudharma,* Argonne National Laboratory*; Jeffrey Elam,* Argonne National Laboratory, USA

The growing deployment of renewable energy and the rapid expansion of artificial intelligence and machine learning infrastructures place increasingly dynamic demands on modern electrical grids, requiring the need for high-performance, renewable energy-storage technologies. While nickel (Ni)-rich layered oxides remain the state-of-the-art materials for lithium-ion battery cathodes, their reliance on costly and supply-constrained Ni and cobalt (Co), motivates the development of alternative materials. Lithium- and manganese (Mn)-rich (LMR) cathodes offer a compelling solution due to their high energy density and reversible capacities enabled by anionic redox. However, oxygen loss associated with this redox process induces severe surface and interfacial degradation, including electrolyte decomposition, transition-metal migration, and Mn dissolution, which hinder long-term cycling stability of these cathodes. Suppressing Mn dissolution at the surface is still a key challenge. Advancing surface engineering, structural tuning, and electrolyte optimization is therefore critical to unlocking the full potential of LMR cathodes for next-generation energy-storage systems. Atomic layer deposition (ALD) being a self-limiting thin film growth method characterized by the sequential exposure of chemical species, offers a promising strategy to stabilize the interfaces by depositing tailored ultrathin, uniform and conformal coating layers on the surface and thereby mitigating the surface degradation of the cathode. Surface coatings applied through atomic layer deposition (ALD) offer a highly controlled route to stabilize these interfaces; however, the fundamental mechanisms governing how different ALD chemistries interact with LMR surfaces remain poorly understood. In this presentation, I will discuss our recent study combining in situ measurements of ALD chemistries, ex situ thin film characterization, and electrochemical testing of prototype batteries. By systematically investigating ALD coating chemistries including lithium phosphate (Li_3PO_4) and lithium borate ($LiBO_x$), we elucidated how ALD surface reactions govern coating composition, structure, and protective functionality and how this functionality affects cycling performance. These insights will inform rational interface-engineering strategies, enabling the practical deployment of high-energy, cobalt-lean Mn-rich cathodes for next-generation lithium-ion batteries.

9:15am **BT1+AS+CA+TF-ThM-6 Atomic Layer Deposition for Lithium Metal Anode Stability***, Niels Hoogedoorn, Meike Pieters, Cristian van Helvoirt, Mariadriana Creatore,* Eindhoven University of Technology, Netherlands

High-performance lithium-ion batteries (LIBs) are hampered by phenomena such as dendrite growth, electrolyte decomposition and uncontrolled interface formation between electrode and electrolyte. This is especially the case of next-generation battery materials, such as Si-anodes, Li-metal anodes and solid-state electrolytes. To address these challenges, atomic layer deposition (ALD) offers a promising pathway by engineering ultrathin conformal interfacial layers with atomic-scale precision.

In this contribution we present our recent work on ALD processes on lithium metal anodes (LMAs). The studies include: Al_2O_3, LiPO, LiPON and LiF, all developed in a FlexAL ALD-reactor (Oxford instruments). The supercycle approach for the process development of LiPO is highlighted: a novel Li-precursor, Lider™, is combined with an oxygen plasma (O_2*) and trimethyl phosphate (TMPO). The films are free of carbon impurities, despite that, during the subcycle of Lider + O_2*, Li_2CO_3 is detected by XPS in combination with a vacuum transfer unit. We find that a chemical vapour transformation [1] occurs, where the subsequent exposure of Li_2CO_3 to TMPO, leads to the abstraction of carbonate from the film, towards C-free LiPO [2].

Additionally, we discuss the deposition of these ALD layers on LMAs and their effect on the critical current density (CCD) of the LMAs, tested in a Li | argyrodite | Li symmetric cell. A home- built vacuum transfer module is used to transport the LMAs between a glovebox and the ALD reactor, where the ALD layers are processed at 120 °C. The CCD is the maximum electrical current per unit area that the anode can withstand before reaching failure, typically caused by lithium dendrite induced shorting. Depending on the material, and layer thickness, the ALD layers improve the CCD by more than 40%. For example, in the case of 10 Al_2O_3 cycles, the maximum sustainable current density increases from 2.4 mA/cm^2 to 3.4 mA/cm^2, thereby demonstrating enhanced stability against dendrite shorting. These results illustrate how engineering ALD interface layers can improve the CCD of LMAs and mitigate challenges in LMA stability. Moreover, these studies propose CCD measurements as screening approach of ALD chemistry and processing conditions towards their implementation and testing in full LIB cells.

[1] M. Y. Young et al., *J. Phys. Chem. C*2019, *123,* 9,23783.

[2]M. J. Pieters et al., *J. Phys. Chem. C*2026, 130, 15, 5458.

9:30am **BT1+AS+CA+TF-ThM-7 Buffer Layer Oxidative Polymerization to Stabilize Li Metal Anodes for Lithium Ion Batteries***, Amit K. Datta, Blaine D. Kelly, Dilan M. Gamachchi, Indeewari M. Karunarathne, Campbell A. Sweet, Andrew C. Meng, Matthias J. Young,* University of Missouri

Li metal anodes promise an order of magnitude higher energy density than conventional graphite anodes in Li ion batteries, however, the practical use of Li metal as an anode remains limited by several factors such as unstable interfacial reactions, continuous electrolyte decomposition, and dendritic Li growth, leading to rapid cell failure. Oxidative Molecular Layer deposition (oMLD) offers the ability to deliver thin film polymer coatings with

electronic, ionic and chemical properties of interest for improving stability of Li metal anodes, but oMLD employs harsh oxidants that are not compatible with Li metal substrates. In this work, we demonstrate an approach we term buffer layer oxidative polymerization (BLOP), to enable the delivery of oMLD coatings onto Li metal. We investigate three BLOP derived polymer coatings on Li metal: polyhydroquinone (pHQ), poly(2,5-dimercapto-1,3,4-thiadiazole) (pDMCT), and poly(p-phenylenediamine) (pPDA). These three coatings were selected as representative classes of coatings based on their electronic and ionic conductivity differences: pHQ exhibits both Li ion conductivity and electronic semiconductivity, pDMCT shows only Li ion conductivity and pPDA shows anionic conductivity and electronic semiconductivity. Galvanostatic charge-discharge measurements in Li-Li symmetric cells show differences in the stability enhancement among the different coatings, with a clear benefit for BLOP vs. oMLD and MLD. Electron microscopy on these coatings helps understand the crosslinking depth achieved from BLOP coatings generated by different organic monomers. Overall, this work demonstrates the oxidative synthesis of multiple polymeric thin films directly on Li metal without degrading the substrate and identifies that coatings with Li ion conductivity and electronic semiconductivity show improved Li metal stability over the alternatives.

9:45am **BT1+AS+CA+TF-ThM-8 Modulation of Anode-Free Sodium Battery Interfaces through Atomic Layer Deposition of NaF***, **Jonathan Thurston,*** *Aaron Melemed, Neil Dasgupta,* University of Michigan

Sodium-based batteries are a promising alternative to lithium-ion technologies due to the higher earth abundance and lower cost of sodium. Furthermore, when Na metal electrodes are used in an “anode-free” configuration, the theoretical energy density is competitive with that of lithium-ion systems. However, the effects of the current-collector surface chemistry on the subsequent Na plating/stripping and solid electrolyte interphase (SEI) composition remains limited.

In this study, we synthesize an “artificial SEI” of NaF using atomic layer deposition onto the surface of Cu current collectors (CCs). Thermal ALD of NaF is successfully demonstrated using sodium *tert*-butoxide and ammonium fluoride precursors. We investigate the impact of the NaF surface layers on the subsequent morphology of deposited sodium using electron microscopy. A multi-modal suite of near-edge X-ray absorption spectroscopy (NEXAFS), X-ray photoelectron spectroscopy (XPS), and infrared spectroscopy (IR) are used to characterize the composition and structure of the resulting SEI as a function of depth and battery cycling. Our results show that the NaF layer encourages more homogenous plating with controlled nucleation sites, while bare Cu CCs have more sporadic nucleation sites for Na metal and a more dendritic mossy plating morphology. Additionally, electrochemical impedance spectroscopy (EIS) and chemical state identification indicate that a more stable SEI is formed in the first few cycles for NaF-coated Cu CCs, while an evolving SEI is observed for uncoated Cu CCs. Our work demonstrates the importance of surface layers in anode-free battery current collectors, while investigating the dynamic nature of the SEI composition and structure throughout cycling.

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