## ALD Applications
## Room Ybor Salons I-IV - Session AA2-TuA

## ALD for Batteries and Energy Storage
**Moderator: Neil Dasgupta**, University of Michigan

4:00pm **AA2-TuA-11 Fabricating Artificial Electrode Electrolyte Interfaces for Lithium Batteries***, Sara Pakseresht, Princess Stephanie Llanos, Filipp Obrezkov, Ville Mikkulainen,* ***Tanja Kallio****,* Aalto University, Finland **INVITED**

With the growing need to increase the energy density of lithium batteries (LIBs), numerous studies have focused on developing high-capacity electrodes capable for operation at a wide potential range. Yet, extending the potential range often compromises the cycling stability because of accelerated mechanochemical ageing of the electrode active materials. Here, various coatings are applied via ALD or MLD on lithium battery electrodes to mitigate premature capacity fade. Focus is on investigating their attributes and effect of the coatings on the performance of high voltage positive electrode materials, particularly $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811), and lithium negative electrode. Additionally, some light is shed on the synthesis of the coatings.

Such coatings as lithium titanate, titanium terephthalate and lithium fluoride are investigated on NMC811 to understand attributes of coatings, or artificial cathode electrolyte interfaces, with different chemical and physicochemical features. Due to the complex interplay of the degradation mechanisms at the crystal structure, particle, and electrode levels, *operando* XRD and dilatometry are combined with ex-situ characterization techniques to have an in-depth understanding of the mechanism of enhancement received by these coatings. The multiscale analyses show that electrodes with coated NMC811 experience more reversible variations and the applied coating improves the cycle life by suppressing various ageing processes.

As for the negative electrodes, highly reactive metallic lithium offering high capacity and most negative lithium redox potential is considered. Electrochemical measurements complemented with o*perando* dilatometry and optical measurements enable optimizing coating thicknesses to achieve a tradeoff between mechanical and chemical durability.

The reaction mechanism during ALD is studied by in-situ near atmospheric pressure XPS. Different reaction mechanisms between the NMC811 substrate and the utilized organometallic precursors are revealed. These measurements also yield information on the active role of lithium metal during the evolution of the coating.

4:30pm **AA2-TuA-13 Beyond Conventional ALD: Investigating Standalone Chemical Vapor Transformation Precursors for Battery Cathode Functionalization***, **Donghyeon Kang**, Jeffrey Elam,* Argonne National Laboratory

Atomic layer deposition (ALD) is a cornerstone technique for stabilizing battery interfaces, typically involving the sequential application of a metal precursor and a co-reactant to grow protective thin films. However, the inherent reactivity of battery cathode surfaces—often covered by native impurities like lithium carbonate (Li2CO3)—presents an opportunity to bypass traditional binary cycles. This study investigates the use of standalone vapor-phase precursors as a direct functionalization strategy, eliminating the need for a secondary pulse while achieving superior interfacial control.

We explore a series of aluminum (Al), phosphorus (P), and boron (B) precursors to determine their efficacy as "transforming" agents. Unlike standard ALD growth, these precursors react directly with the surface layer, converting detrimental impurities into beneficial, lithium-conducting interphases. This process effectively "cleans" the cathode surface while simultaneously depositing a sub-nanometer protective skin in a single, self-limiting step.

The reaction mechanisms are elucidated through **in situ FTIR spectroscopy**, which provides real-time evidence of carbonate consumption and the simultaneous emergence of Al-O, P-O, or B-O vibrational modes. These surface-sensitive insights are corroborated by **XPS** depth profiling and **ab initio calculation**, confirming the transformation of the cathode-electrolyte interface (CEI). Our findings demonstrate that standalone precursor exposure is a scalable and efficient alternative to conventional ALD, offering a streamlined pathway for the surface engineering of high-capacity battery materials.

4:45pm **AA2-TuA-14 Tackling Issues of Transition Metal Oxide Cathodes Using Sulfide Coatings***, **Xiangbo Meng**, Kevin Velasquez Carballo, Taohedul Islam,* University of Arkansas

Transition metal oxides (e.g., layered $LiNi_xMn_yCo_zO_2$) are among the most promising cathodes for next-generation lithium-ion batteries (LIBs) and beyond, but suffer from a series of structural and interfacial issues. In addressing these issues, surface modification has been proved being facile and effective. In this regard, atomic layer deposition (ALD) has emerged and offered some unrivaled benefits in coating quality and process.[1-3] In the past years, we have been investigating various coating materials [4-7] while recently, we first discovered that sulfides are very unique as coatings materials.[8-10] They can react with oxygen released from lattices of transition metal oxide cathodes, transform into sulfates, and thereby protect electrolytes from oxidation. Furthermore, the resultant sulfates as coatings still play multiple important roles in enhancing cathode performance: (1) strengtheners to maintain mechanical integrity and reduce microcracking of cathodes; (2) robust interfaces to mitigate undesirable interfacial reactions and alleviate the formation of cathode electrolyte interphase (CEI); (3) protective layers to hinder transition metal ions from dissolution, (4) structural stabilizers to suppress unfavorable phase transformation; and (5) physical barriers to inhibit crosstalk between the cathodes and anodes and to protect anodes from degradation. As a consequence, we demonstrated that sulfides are excellent surface coatings, which could dramatically improve the performance of transition metal oxide cathodes. Thus, our studies have greatly widened the search of surface coatings and provided new solutions for next-generation LIBs and beyond.

**References:**

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5:00pm **AA2-TuA-15 Atomic Layer Deposition Tuned Surface Chemistry for Advanced Lithium and Manganese Rich Cathodes***, **Jahnavi Manikantan Sudharma**, Kyobin Park, Sungjoon Kim, Subhadip Mallick, Jason Croy, Donghyeon Kang, 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.

5:15pm **AA2-TuA-16 Comparing Al-phosphate ALD on $LiMn_2O_4$ and $SiO_2$,** ***Lowie Henderick****, Christophe Detavernier, Jolien Dendooven,* Ghent University, Belgium

Although lithium ion batteries (LIB) have already significantly improved, undesirable side-reactions at the electrode-electrolyte interface hamper further performance gains. Atomic layer deposition (ALD) is a promising route to improve performance via deposition of a protective coating, where materials ranging from inert (e.g. $Al_2O_3$ and Al-phosphate) to more conductive coatings (e.g. $TiO_2$ or LiPON) are being explored. ALD processes for protective coatings are typically characterized on standard native $SiO_2$/Si substrates and then blindly copied to the LIB electrode material. However, in situ studies have shown that the surface reactions during initial ALD cycles on battery electrodes can differ markedly from those observed on native $SiO_2$/Si substrates. For instance, it was shown that $Al_2O_3$ deposition leads to Al doping at the electrode surface[1], altering its performance. Such effects should be more properly addressed and understood if one aims to fully optimize the LIB electrode. In this work, the deposition of Al-phosphate on a $LiMn_2O_4$ (LMO) electrode is studied with in-vacuo XPS and EDX using two different ALD processes. Both processes are well understood on $SiO_2$, but their initial growth on a LIB electrode has not yet been addressed. On the one hand, a plasma enhanced ALD process is used consisting of TMP plasma–$O_2$ plasma–TMA. For this process, a 5 times higher growth rate is observed on LMO during 30 cycles compared to $SiO_2$. It was found that, while there is saturating growth on $SiO_2$, continuous polymerisation takes place on LMO due to the reactivity of the electrode surface, forming a thick phosphate-rich layer with an equivalent thickness growing beyond 15 nm after prolonged exposure (fig. 1). This highlights a significant process difference, where CVD is observed on LMO even though ALD was expected based on the process characterization on $SiO_2$. On the other hand, a TMP vapour–$O_2$ plasma–TMA–$O_2$ plasma process is used for which more ALD-like (self-limiting) growth can be observed on LMO. Nevertheless, based on in-vacuo XPS, it can be seen that the peak areas of the coating are approximately 70% higher during the initial cycles on LMO compared to $SiO_2$ (fig.2), suggesting substrate specific growth. Next to this, the P-to-Al concentration ratio also significantly differs (fig.3), further indicating a clear substrate dependency. This work highlights the importance of proper LIB interface engineering. Only by studying the deposition directly on the relevant battery electrode material, the initial growth can be fully characterized and the interface can be engineered towards next generation LIB performance. [1] Chen,L. et al., Chem, 2418 – 2435 (2018)

5:30pm **AA2-TuA-17 Unravelling the Mechanism of $Al_2O_3$ Atomic Layer Deposition on $Li_6PS_5Cl$ for All-Solid-State Batteries***, Kyobin Park, Donghyeon Kang, Taewoo Kim, Vepa Rozyyev, Anil Mane, Hacksung Kim, Francisco Vargas, Zachary Hood, Peter Zapol, Justin Connell,* ***Jeffrey Elam****,* Argonne National Laboratory

Sulfide superionic conductors with the argyrodite structure (e.g., $Li_6PS_5Cl$, LPSCl) are extremely promising for all solid-state batteries, but poor atmospheric stability and high interfacial reactivity limit their widespread adoption. Coating LPSCl powders with ultrathin, metal oxide coatings using atomic layer deposition (ALD) mitigates these problems, protecting LPSCl against atmospheric degradation[1] and reducing reactivity with Li metal, yielding more stable cycling[2]. Despite significant promise, the ALD mechanism is unknown, hampering the development of new coating chemistries.

In this study, we elucidate the mechanism for $Al_2O_3$ ALD on LPSCl using trimethyl aluminum (TMA) and $H_2O$ by combining *in situ* Fourier transform infrared spectroscopy measurements and *ex situ* solid-state magic angle spinning nuclear magnetic resonance, UV Raman spectroscopy, and X-ray photoelectron spectroscopy measurements with density functional theory calculations. We determine that ALD $Al_2O_3$ nucleates promptly via TMA reaction with native -OH, -SH, and $PS_3$-OH groups to form transient C-Al-O(S) species that are rapidly hydrolyzed during the subsequent $H_2O$ exposure. This reversible transformation maintains surface nucleophilicity and prevents sulfide decomposition. The resulting layer-by-layer growth leads to highly conformal $Al_2O_3$ coatings on LPSCl.

This detailed understanding of ALD surface reactions provides critical insights guiding the selection of future ALD chemistries with greater enhancement in cycling performance.

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