ALD Applications
Room Halla Hall - Session AA1-WeA

Battery Applications I

Moderators: Wei-Min Li, Jiangsu Leadmicro Nano-Equipment Technology Ltd., **Keith Wong**, Applied Materials

1:30pm **AA1-WeA-1 ALD Young Investigator Award Finalist: Atomic Layer Deposition and Molecular Layer Deposition for Li and Na Metal Anodes***, Yang Zhao,* University of Western Ontario, Canada

Li-metal batteries (LMBs) and Na-metal batteries (NMBs) are considered as the promising next-generation battery systems to replace conventional Li-ion batteries (LIBs) due to their high theoretical energy density [1]. For LMBs and NMBs, Li metal and Na metal are the ultimate choices for achieving high energy density due to their high specific capacity, low electrochemical potential, and light weight. However, as alkali metals, both Li and Na metal anodes suffer from serious challenges including 1) Li/Na dendrite formations and short circuits; 2) Low Coulombic efficiency and poor cycling performance; and 3) Infinite volume changes.

In this presentation, I will introduce our research that contributed to the design of artificial interfaces for Li and Na metal anode using atomic layer deposition (ALD) and molecular layer deposition (MLD) techniques [2-3]. i) Developing ionic conductive protective layers for Li and Na metal anodes. A two-step strategy is developed to obtain the smooth and stable LiAlOx and NaAlOx artificial layer for Li and Na metal anodes by the post-lithiation process, respectively. [4]. ii) Nano-alloy structure to the nano-laminated structure for Li and Na metal anodes. Through tailoring the compositions of the hybrid interfaces, we realize the nano-alloy structure to the nano-laminated structure. [5]. iii) An organic-rich or an inorganic-rich interface? We demonstrate the controllable fabrication of the hybrid artificial SEI for Li metal anode with different organic-inorganic ratios. Three typical compositions were realized: organic-rich interface, organic-inorganic-balanced interface and inorganic-rich interface. The different organic-inorganic ratios of the hybrid interfaces result in the tuning of the mechanical properties, lithiophilicity, diffusion kinetics and Li dendrite formation of the Li metal anode [6]. iv) A new hybrid protective layer for the Na metal anode. A metal-doped hybrid polyurea (PU) film with tunable composition, sodiophilic sites and improved stiffness was fabricated by introducing Zn or Al as crosslinkers into the polymer chains and adopted as an artificial SEI for Na metal. Compared to bare Na and pure PU-coated Na, the Na metal anode coated with the metal-doped PU film exhibits significantly improved electrochemical performance [7]. All these ideas have also been further applied to solve the practical issues for different Li and Na metal battery systems.

[1] Energy Environ. Sci., 2024, 17, 442-496

[2] Chem. Soc. Rev., 2024,53, 5428-5488

[3] Chem. Soc. Rev., 2021, 50, 3889-3956

[4] Small, 2022, 18, 2203045

[5] Adv. Mater., 2023, 35, 2301414

[6] Adv. Fun. Mater., 2024, 2406426

[7] Adv. Mater., 2024, 2406837

1:45pm **AA1-WeA-2 Low Temperature Spatial Atomic Layer Deposition of LiF Films for Li-Ion Batteries***, Joost van Himste,* SparkNano, Netherlands*; Niels Hoogendoorn,* Eindhoven University of Technology, The Netherlands*; Jamie Greer,* Air Liquide Advanced Materials, Germany*; Nicolas Blasco,* Air Liquide Advanced Materials, France*; **Paul Poodt,*** SparkNano, and Eindhoven University of Technology, Netherlands

Lithium fluoride (LiF) thin films have gained significant attention as protective/passivating layers for Li-ion battery electrodes due to their wide electrochemical stability window and excellent chemical stability. When deposited using highly conformal methods like atomic layer deposition, LiF can effectively coat the complex, porous structures of battery electrodes to improve their electrochemical performance and stability.

Several combinations of Li precursors and co-reactants for LiF deposition have been explored in the literature. However, these processes often require high deposition temperatures and yield films with notable contamination from oxygen (O), carbon (C), or silicon (Si). Furthermore, the low volatility and reactivity of many Li precursors, combined with the use of greenhouse gas- and PFAS-based or otherwise hazardous co-reactants (e.g., SF_6, CF_4, or HF), pose challenges to the applicability, sustainability, and scalability of reported ALD processes.

To address these limitations, we present a newly developed plasma-enhanced spatial ALD process employing a novel Li precursor named LIFA (Air Liquide Advanced Materials). This approach eliminates the need for greenhouse gas-, or otherwise hazardous co-reactants. Pure LiF films have been successfully deposited at temperatures ranging from 100°C to 200°C, making the process compatible with deposition on Lithium metal anodes. The films exhibit a growth per cycle of 0.04–0.05 nm/cycle and a refractive index of 1.36–1.39 at 633 nm. Characterization via XPS, XRD, and SEM confirms that the films are polycrystalline, highly pure, free of C and O contamination, and stable in ambient conditions.

These LiF films demonstrate excellent conformality on porous substrates and have been applied to various anode and cathode materials, including graphite, silicon, and LMNO, where they have shown significant improvements in electrochemical performance. Additionally, we outline our approach to scaling up the process for industrial-scale manufacturing using high-speed, atmospheric-pressure roll-to-roll spatial ALD. The combination of this sustainable and efficient LiF deposition process with high-speed spatial ALD presents a promising avenue for the mass production of high-performance Li-ion batteries.

2:00pm **AA1-WeA-3 ALD Young Investigator Award Finalist: Advancing Nickel-Rich Layered Oxide Cathodes via Atomic-Scale Synthesis and Surface Engineering***, **Jin Xie,*** ShanghaiTech University, China

Nickel-rich layered oxides ($LiNi_xCo_yMn_{1-x-y}O_2$, NCM) offer high energy density for lithium-ion batteries, yet challenges in synthesis control, structural stability, and interfacial compatibility limit their performance. This work integrates two strategies focused on atomic layer deposition (ALD) to overcome these obstacles and enable next-generation cathode materials.

First, we improve the mechanical stability of layered oxides through surface atomic coatings and controlled nucleation during high-temperature solid-state synthesis. Solid-state synthesis of layered oxides requires precise control over nucleation and grain growth. We demonstrate that an Al_2O_3 coating, which transforms into lithium aluminate during synthesis, acts as a low-interfacial-energy nucleation template. This approach promotes rapid and uniform nucleation at reduced temperatures, as evidenced by solid-state NMR and in situ synchrotron XRD. The resulting Ni-rich cathodes feature densely packed, fine primary particles, enhancing mechanical strength and structural integrity, as confirmed by in situ compression tests.

Second, we improve the surface stability of layered oxides through surface coatings that suppress surface decomposition during high-temperature solid-state synthesis. High temperatures are necessary for forming well-ordered layered structures but can lead to Li/Ni mixing and rock-salt phase formation. By applying a conformal oxygen-affine coating, we stabilize the surface layered structure during high-temperature lithiation. This prevents surface decomposition, preserves lithium-ion pathways, and reduces phase separation during cycling. The optimized cathodes exhibit excellent rate capability and cycle stability.

By leveraging intermediate phases, conformal coatings, and doping strategies, we address synthesis challenges in Ni-rich cathodes. Coupled with advanced characterization, our work paves the way for high-energy, high-power, and mechanically robust battery materials—bridging fundamental insights with industrial-scale production for improved lithium-ion batteries.

References:

1. Promotion of the nucleation of ultrafine Ni-rich layered oxide primary particles by an atomic layer-deposited thin film for enhanced mechanical stability. Nano Lett. 2023, 23, 5770-5778.

2. Pinning the surface layered oxide structure in high temperature calcination using conformal atomic layer deposition coating for fast charging cathode. Adv. Funct. Mater. ASAP, 2423888.

2:15pm **AA1-WeA-4 Unveiling the Unconventional ALD Chemistry of Trimethylaluminum (TMA) on Battery Materials***, **Donghyeon Kang**, Kyobin Park, Jeffrey Elam,* Argonne National Laboratory

Trimethylaluminum (TMA) is a cornerstone precursor in atomic layer deposition (ALD), widely employed for depositing aluminum-based coatings. It reacts with H_2O, HF-pyridine, and H_2S to generate Al_2O_3, AlF_3, and Al_2S_3 by ALD, respectively, following well-established ALD mechanisms. These processes enable ultra-thin Al-based coatings on various substrates, particularly energy storage materials such as battery cathodes, anodes, and solid electrolytes.

Our research explores the unconventional ALD chemistry of TMA on reactive metal substrates, solid-state electrolytes, and battery cathode materials. Notably, on Li-metal anodes, TMA deviates from conventional ALD pathways, forming a carbon composite layer instead of the expected Al_2O_3. This unexpected behavior stems from the inherent reactivity between TMA and Li metal, challenging established ALD paradigms. Additionally, we reveal TMA's interactions with Li-based impurities on solid-state electrolytes and battery cathode surfaces, leading to the formation of protective coatings with beneficial properties. Despite TMA's extensive use, these reactions have remained largely unexplored.

In this presentation, we will unveil our findings using in situ quartz crystal microbalance (QCM), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Raman spectroscopy, and *ab initio* calculations. Furthermore, we will discuss the implications of these discoveries for battery material surface treatments, highlighting their potential for scalable industrial applications.

2:30pm **AA1-WeA-5 Novel Li-Precursor for Interface Engineering in Li-Ion Batteries***, **Meike Pieters**, Cristian van Helvoirt, Lina Bartel, Niels Hoogendoorn, Mariadriana Creatore,* Eindhoven University of Technology, The Netherlands

Ultra-thin coatings (< 5 nm) on Li-ion battery (LiB) electrodes are essential to reduce interface degradation reactions, and improve the performance and lifetime of next-generation LiBs. ALD is a precise and scalable technique to apply these coatings conformally on 3D electrodes. So far, LiO^tBu has been widely adopted as Li-precursor, but it requires a high source temperature (130-180°C). Out of the few other known Li-precursors, only LiHMDS can be used at lower source temperature (60-90°C), but it can lead to Si impurities, which we reported in recent work [1].

Here we address the application of the novel Li-precursor *Lider* developed by Air Liquide, for a wide range of materials, of interest in the field of LiBs: Li_2CO_3, Li_3PO_4, and LiF. *Lider* is Si-free and can be used at a low source temperature of 85°C, but it does not react with H_2O. An O_2 plasma (O_2*) as co-reactant leads to saturation behavior with a GPC of 0.25 Å at 150°C, but the GPC decreases with increasing temperature. XPS and XRD demonstrate that Li_2CO_3 is grown with a (002) orientation, and that the film density of 2.0 g/cm^3 is close to the theoretical density of Li_2CO_3 (2.1 g/cm^3). This suggests that LiOH reacts to Li_2CO_3 during the deposition, presumably due to CO_2 formed in the O_2* step, and not upon air exposure, since the films are air-stable. O_3 as co-reactant results in a higher GPC of 0.35 Å. The film density decreases upon air exposure, and XRD shows no diffraction peaks, which could be due to incorporation of (air sensitive) Li_2O and/or LiOH, which suppresses the Li_2CO_3 crystallinity [2]. This comparison suggests that O_3 may be preferred over O_2* as co-reactant when C incorporation is undesired, e.g. in Li-containing ternary oxides.

The O_2* and O_3-based *Lider* processes are combined with TMPO to grow LiPO. The film composition depends on the co-reactant: O_2* results in a more Li-rich film than O_3. Interestingly, no C impurities were observed in both films. We hypothesize that carbonates are abstracted from the film as CO_2 when exposed to TMPO, similar to the reaction occurring during TMA exposure [3].

Finally, LiF is grown with SF_6* as co-reactant. The GPC is 0.3 Å at 150°C but LiF can be grown at temperatures as low as 50°C, which makes this process compatible with Li metal. XPS shows a Li:F ratio of ~0.8 and low bulk C levels of ~1 at.%. The films are crystalline with a preferred (100) orientation.

Given the range of chemistries attainable by the usage of *Lider*, this contribution will also address applications of the above-mentioned materials in LiBs.

[1] Pieters et al., J. Phys. Chem. C 2024, 128

[2] Hornsveld et al., RSC Adv. 2017, 7

[3] Young et al., J. Phys. Chem. C 2019, 123

2:45pm **AA1-WeA-6 Oxidative Molecular Layer Deposition of Polypyrrole on High Surface Area Powder Substrates for Li-ion Battery Applications***, **Brandon Woo**, Jaime DuMont, Markus Groner, Casey Christopher, Drew Lewis, Jessica Burger, Greg Pach, Wyatt Blevins,* Forge Nano*; Malachi Noked, Ortal Shalev,* Bar Ilan University, Israel*; Arrelaine Dameron,* Forge Nano

Oxidative molecular layer deposition (oMLD) of conjugated polymer films offers a unique solution to many of the interfacial material challenges present in Li-ion batteries. Polypyrrole encapsulated Si anode materials, for example, has the potential to alleviate the volume change of Si, improve the material conductivity, and enhance cyclic stability. Versus solution-based polymerization processes, oMLD can enable molecular-level control of polymer thickness through layer-by-layer growth via sequential surface reactions of monomer(s) and oxidant(s).[1] [2] [3]

In this talk, we demonstrate the successful transfer of the $SbCl_5$/pyrrole oMLD process from wafers to high surface area powder batches, both in fluidized bed and rotary bed particle-ALD reactors with particle diameters as small as 50 nm. The surface area of these powders is thousands of times larger than that of silicon wafers. The scale up to high surface area powders was achieved via controlled high volume precursor delivery, good powder mixing, monitoring of the process with in-situ mass spectroscopy and various external analysis techniques. LECO carbon and nitrogen analysis confirmed an inverse relationship between temperature and purge times with the growth per cycle. ICP-OES allowed for the tracking of both Cl and Sb impurities. Raman spectroscopy confirmed the presence of signature polypyrrole vibrational modes such as the C=C backbone stretching and C-H in plane deformation. TEM analysis confirmed the particles were conformally and uniformly encapsulated. This work represents a significant advancement of the oMLD process in generating new-composite materials for various energy related applications.

[1] Kim, et. Al. Journal of Vacuum Science & Technology A 40, 063401 (2022)

[2] Wyatt, et. Al. ACS Applied Polymer Materials 2022 4 (8), 6156-6168 (2022)

[3] Wyatt, et. Al. Chem. Mater. 35, 1, 154–162 (2023)

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