ALD Applications
Room Halla Hall AB - Session AA2-WeA

Battery Applications II
Moderators: Il-Kwon Oh, Ajou University, **Junjie Zhao**, Zhejiang University

4:00pm **AA2-WeA-11 Novel Atomic and Molecular Layer Deposition Processes for Robust Battery Interfaces***, **Xiangbo Meng**, Kevin Velasquez Carballo, Kang Lu, Aiying Shao,* University of Arkansas

Adopting lithium metal (Li) as anodes and nickel (Ni)-rich lithium nickel manganese cobalt oxides ($LiNi_xMn_yCo_zO_2$, NMCs, $x \geq 0.6$, $x + y + z = 1$) as cathodes, the resultant Li||NMC lithium metal batteries (LMBs) could be twice higher in energy (up to 500 Wh/kg) but 50% lower in cost ($100/kWh) than that of LIBs, holding great promise to replace LIBs for the applications of portable electronics, electric vehicles, and aircrafts. Unfortunately, such a compelling technology has been hindered from commercialization due to some serious interfacial issues related to the Li anodes and NMC cathodes. Aimed at addressing these challenges, we recently have developed a series of novel coatings via atomic and molecular layer deposition (ALD and MLD). ALD and MLD share several unique merits but are complementary in their target materials. They have emerged as two new techniques of interface engineering of rechargeable batteries in the past decade.[1-5] They both could deposit conformal and uniform coatings over complex shapes of different substrates, operate at low process temperature, and accurately control coating thickness. Through adopting different precursors, ALD exclusively deposits inorganic films while MLD specially grows organic or hybrid films. For the issues of Li anodes and NMC cathodes, we particularly designed function-oriented coatings via ALD and MLD. Using our ALD and MLD processes, very encouragingly, both the surface-coated Li anodes and NMC cathodes have exhibited remarkable improvements in their electrochemical performance. Our studies have further shown that the combination of these coatings can synergistically maximize their benefits to achieve higher performance of Li||NMC LMBs, enabling a cell capacity fading 10 times slower than that of bare Li||NMC cells and a capacityretention improvement over 60%after 500 charge/discharge cycles. In this talk, we will introduce these novel coatings and their compelling effects. Particularly, we would like to explain the underlying mechanisms related to their benefits. Thus, our studies have not only opened new areas of surface coatings but also demonstrated their technical feasibility for developing high-performance LMBs.

References:

1. *Adv. Mater.* **2012,** 24, (27), 3589-3615.
1. *Energy Storage Materials* **2020,** 30, 296-328.
1. *J. Mater. Chem. A* **2017,** 5, 10127-10149.
1. *J. Mater. Chem. A* **2017,** 5, (35), 18326-18378.
1. *J. Mater. Res.* **2021,** 36, 2-25.

4:15pm **AA2-WeA-12 Atomic Layer Deposition of Al_2O_3 and ZrO_2 Coatings on Single-Crystal NCM Cathodes: A Parametric Study for Enhanced Lithium-Ion Battery Performance***, **Sung Eun Jo**, Wooseong Kim, Hyongjune Kim,* Pohang University of Science and Technology (POSTECH), Republic of Korea*; Jungwoo Park,* POSCO Holdings, Republic of Korea*; Jihwan An,* Pohang University of Science and Technology (POSTECH), Republic of Korea

Atomic Layer Deposition (ALD) has emerged as a powerful technique for surface modification of battery materials, offering unparalleled control over coating thickness and conformality at the atomic scale. This study investigates the application of ALD-deposited Al_2O_3 and ZrO_2 coatings on single-crystal $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NCM622) cathodes to enhance the performance and durability of lithium-ion batteries.

Single-crystal $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NCM622) cathodes have garnered significant attention due to their superior structural stability and reduced surface area compared to their polycrystalline counterparts. These characteristics contribute to improved cycling performance and reduced side reactions with the electrolyte. However, single-crystal NCM materials still face challenges, particularly at high voltages and during long-term cycling, necessitating surface modification strategies to mitigate these issues.

This study investigates the application of Atomic Layer Deposition (ALD) to deposit ultrathin Al_2O_3 and ZrO_2 coatings on single-crystal NCM622 cathodes, aiming to address their inherent limitations while preserving their advantages. We systematically explored coating thicknesses of 10, 30, and 100 nm for both materials.

Electrochemical performance of bare, Al_2O_3-coated (10 and 30 ALD cycles), and ZrO_2-coated (10 cycles) single-crystal NCM622 cathodes, focusing on capacity retention, degradation rates, and the impact of coating thickness. While Al_2O_3 coatings showed poor longevity, retention stability diminishes with increasing thickness due to kinetic limitations. In contrast, ZrO_2 coatings at 10 cycles offer a balanced approach, combining moderate capacity retention with robust degradation resistance (after 30cycles, 3.4% increase). Optimizing ALD cycles for minimal thickness (≤10 cycles) is critical for maximizing the performance of NCM cathodes.

4:30pm **AA2-WeA-13 Role of the Precursor'S Stability for ALD Lithium-Containing Films***, **Nicolas Massoni**, Manon Letiche, Sylvain Poulet,* CEA/LETI-University Grenoble Alpes, France*; Katharina Märker, Pierre-Alain Bayle,* CEA-University Grenoble Alps, IRIG, France*; Névine Rochat,* CEA/LETI-University Grenoble Alpes, France*; Olivier Hernandez,* Nantes Université, CNRS, Institut des Matériaux de Nantes Jean Rouxel, IMN, France*; Messaoud Bedjaoui,* CEA/LETI-University Grenoble Alpes, France

Lithium-based layers play key roles in developing nanostructured energy storage systems. As such, ultrathin lithium phosphorous oxynitride LiPON deposited by Atomic Layers Deposition is incorporated as solid-electrolyte for on-chip microsupercapacitors [1-2]. In this way, fundamental understanding of precursors chemistry and stability could be beneficial to control thermal ALD process. In this work, we will focus on the use of Lithium hexamethyldisilazide (LiHMDS) and Diethylphosphoramidate (DEPA) precursors. Both precursors are maintained in canisters at 90°C (DEPA) and 70°C (LiHMDS). Their ageing time in the canisters was considered. New and aged precursors were characterized by Thermogravimetry (TGA), infrared spectroscopy (FTIR), Powder X-Ray Diffraction (PXRD), Nuclear Magnetic Resonance (NMR) and Pyrolysis coupled with Gas Chromatography Mass Spectrometry (PY-GCMS). The growth per cycle, stoichiometry and ionic conductivity of LiPON films were followed.

It was found that new and aged LiHMDS kept the same thermal behavior and the same structure, till 200 days of use. Hence, there was no proof of significate degradation of LiHMDS with storage duration. On the contrary, new and aged DEPA showed differences. The TGA curves progressively changed from one steep mass loss at 220°C to two partial mass losses occurring between 200°C and 320°C. FTIR spectra showed that the amine group of the aged DEPA disappeared after 60 days of storage. NMR data confirmed a deep modification of the P-N-H_2 chain. A possible polymerization of DEPA monomers might take place. Furthermore, yellow spots were observed in the inner bottom of the DEPA's storage canister. A SEM/EDX analysis revealed deposits enriched with phosphorous. These first measurements pointed out that DEPA has degraded in the canister. The PY-GCMS data confirmed a congruent total evaporation for new DEPA, contrary to new LiHMDS. Its vapor was made of two third of gaseous LiHMDS and one third by a lighter unknown compound.

Shortly, a mass spectrometer will be plugged to the reactor to complete the study by the understanding of the LiPON growth mechanism.

[1] Gölert et al, 2017, https://doi.org/10.1016/j.nanoen.2017.01.054

[2] Sallaz et al, 2024, https://doi.org/10.1021/acselectrochem.4c00022

4:45pm **AA2-WeA-14 Closing Remarks and Awards in Tamna Hall A***,*

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