ALD Applications
Room Halla Hall - Session AA2-WeA

Battery Applications II

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

4:15pm **AA2-WeA-12 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

4:30pm **AA2-WeA-13 Enabling Uniform Lithiation in Solid-State Synthesis by Preventing Pre-Matured Surface Grain Coarsening Through Grain Boundary Engineering**, ***Yifan Wu***, *Jin Xie,* ShanghaiTech University, China

Solid-state reactions are a foundational and widely used method for synthesizing inorganic solid materials, especially metal oxide ceramics. In typical processes, solid precursors are mixed and heated to high temperatures to induce heterogeneous reactions forming new phases. However, solid-state diffusion-driven phase transitions at elevated temperatures often introduce structural inhomogeneity. For example, Li-ion battery cathodes such as $LiTMO_2$ (TM = Ni, Mn, Co) are commonly produced via high-temperature reactions involving $TM(OH)_2$ precursors and lithium sources (e.g., LiOH) in oxidative atmospheres. This complicated non-equilibrium reaction also suffers inherent heterogeneity arises from insufficient solid state lithium diffusion.

While previous studies emphasize optimizing lithium diffusion and particle growth, the intrinsic heterogeneity in solid-state calcination calls for more advanced control strategies. In this work, we found that early-stage formation and coalescence of primary layered particles on polycrystalline $Ni_{0.9}Co_{0.05}Mn_{0.05}(OH)_2$ ($NCM(OH)_2$) hinder lithium diffusion, resulting in structural non-uniformity and reduced electrochemical performance. To overcome this, we developed a conformal WO_3 coating via atomic layer deposition (ALD), which effectively regulated lithium transport and suppressed particle coarsening at grain boundaries during calcination. In situ high-temperature X-ray diffraction (XRD) revealed that the WO_3 layer shifted the early-stage reaction from growth-dominated to nucleation-dominated, thus maintained the grain boundary integrity and improved reaction homogeneity. Scanning transmission electron microscopy (STEM) analysis confirmed that rocksalt phases and voids formed in the uncoated product which is signatures of poor lithium diffusion, and they were absent in the WO_3-coated product. As a result, the modified cathode delivered significantly improved performance (92.9% capacity retention after 200 cycles, vs. 78.7% for the pristine sample) under 2.8V-4.4V charging/discharging cycles.

This work advances the understanding of early-stage solid-state reactions and provides a pathway to achieve homogeneity in high temperature solid-state reactions for next-generation cathode materials through grain-boundaries engineering by ALD technique.

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

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