

ALD Applications

Room On Demand - Session AA3

Energy: Batteries and Energy Storage

AA3-1 Revealing the Control of Lithium Plating Microstructure Derived from ALD-Grown TiO₂, Solomon Oyakhire, W. Huang, Y. Cui, S. Bent, Stanford University

Lithium (Li) metal batteries are desirable as rechargeable storage devices due to their high energy density; however, their practical implementation is hindered by the difficulty in controlling the Li metal plating microstructure. Artificial solid-electrolyte interphases (SEIs) have shown the potential to curtail the electrochemical instabilities of lithium, and atomic layer deposition (ALD) is commonly employed for the synthesis of thin-film artificial SEIs such as Al₂O₃ and alucone. However, these films quickly become delaminated because of their innate resistance to the cyclic shuttling of Li ions, resulting in marginal improvements in cell performance.

While previous ALD studies have focused on directly coating the top of Li metal with thin-film artificial SEIs, we adopt a different approach, situating the ALD film beneath Li metal and directly on the copper current collector. We show that by depositing TiO₂ directly on the Cu current collector, we can control the deposition morphology of Li in the widely studied ether-based electrolyte - 1M LiTFSI in a 1:1 mixture of 1,3 dioxolane and 1,2 dimethoxyethane, with 1 weight percent LiNO₃ as an additive. By optimizing the thickness of TiO₂, we reveal that lithium nucleates into large deposits atop the TiO₂ film under significantly reduced overpotential, resulting in a reduction in contact surface area with the electrolyte and an increase in cell performance. We report substantial improvements in cycling efficiency with an average Coulombic efficiency of 96% after 150 cycles at a current density of 1 mA cm⁻² in Li/Cu cells. In comparison to the unmodified cells, voltage profiles for the champion TiO₂-modified cell display negligible loss in charge capacity in the mid and late-stage electrochemical cycles, indicating an improvement in the reversibility of lithium stripping and plating. Using X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDS), we establish that lithium plates atop TiO₂, rather than beneath it, suggesting that the presence of TiO₂ supports the enhanced reversibility of Li stripping and plating. Also, we utilize coulometry and cryogenic transmission electron microscopy (cryo-TEM) measurements to establish that prior to its nucleation, Li reacts with TiO₂ to form an amorphous Li_xTiO₂ complex. We propose that this complex serves as a lithiophilic layer that promotes the coalescence of large lithium particles and improves cell performance.

AA3-2 Li, N co-controlled Lithium Phosphorous Oxy-nitride(LiPON) Coating for Three Dimensional Thin Film Solid-state Batteries (3D TSSBs) using ALD, Ha Yeon Kwon, S. Hong, T. Park, Hanyang University, Korea

Recently, various types of solid electrolytes have been studied due to the stability problem of liquid electrolytes.[1] At the same time, three-dimensional thin film solid-state batteries for microbatteries is in the spotlight due to reduced device size. LiPON is the most commonly used solid material for implementing 3D TSSB. LiPON is chemically stable by having a wide electrochemical window and can be applied on flexible substrates with amorphous phase. [2], [3] Unfortunately, LiPON does not have high ionic conductivity among all solid electrolytes. To compensate this point, existing studies have conducted studies to increase ion conductivity by controlling the composition of LiPON. Existing studies have noted that ion conductivity increases with increasing N content of LiPON. However, there were several problems in the process of adjusting the N content. [4], [5], [6] In this study, Li, N composition of LiPON was co-controlled by adjusting ALD super cycle of the LiPON and LiN. By simultaneously adjusting Li and N content, the ion conductivity of LiPON is improved. In addition, a very uniform 3D TSSB can be produced by depositing LiPON using ALD. Details of experimental methods and results will be presented.

References [1] *Renew. Sust. Energ. Rev.*, 81 (2018): 1427-1452., [2] *ACS Appl. Mater. Interfaces* 7.42 (2015): 23685-23693. [3] *J. Am. Chem. Soc.*, 140.35 (2018): 11029-11038. [4] *ECS Solid State Lett.*, 5 (1) A14-A17 (2002) [5] *Solid State Ionics* 186 (2011) 29-36 [6] *Chemistry of Materials* 27.15 (2015): 5324-5331.

AA3-3 Rational Modification of LiMn₂O₄ Surfaces by Controlling the Acid-Base Surface Chemistry of Atomic Layer Deposition, D. Kang, Argonne National Laboratory, USA; R. Warburton, Purdue University, USA; A. Mane, Argonne National Laboratory, USA; J. Greeley, Purdue University, USA; Jeffrey Elam, Argonne National Laboratory, USA

Next-generation energy storage devices demand superb control over interfaces. Atomic layer deposition (ALD) coatings can suppress undesirable electrochemical reactions between lithium ion battery (LIB) cathode surfaces and the organic liquid electrolyte. However, our limited understanding of ALD cathode coatings restricts our ability to predict which coating/cathode combinations will succeed. In this study, we performed a combined theoretical-experimental study of a model coating/cathode system aimed at elucidating synthesis-structure-property relationships. We selected five ALD Al precursors exhibiting a range of Lewis acid-base properties to establish trends in the ALD Al₂O₃ chemistry on LiMn₂O₄. Density functional theory calculations deduced a correlation between the Lewis acidity of the ligands and the ALD thermochemistry. X-ray photoelectron spectroscopy and *in situ* infrared spectroscopy measurements supported these predictions and further revealed how the Al precursors modify the LiMn₂O₄ atomic and electronic surface structure. Finally, coin cell electrochemical measurements established the link between materials properties and device performance. We discovered that while the Mn oxidation state is strongly influenced by the Lewis acidity of the precursor ligand, the surface coverage and thickness of the Al₂O₃ coating are a more representative descriptor of the electrochemical performance measured in coin cell experiments.

AA3-6 ALD of Thin-Film Na_xMn_yO Cathode Materials for Sodium Ion Batteries, Nikhila Paranamana, M. Young, University of Missouri, Columbia

In recent years, sodium ion batteries have been of increasing interest due to the limited availability of lithium resources for the production of lithium-ion batteries. Because of its abundance in the earth's crust and similar chemical properties to lithium, sodium is viewed as an attractive alternative to lithium. Unfortunately, sodium ion batteries suffer from materials instability issues that limit cycling performance. For example, sodium manganese oxide (Na_xMn_yO) is a promising cathode material for sodium ion batteries but suffers from chemical and structural degradation during electrochemical cycling. Unfortunately, it is difficult to understand the origins of Na_xMn_yO degradation because the local behavior at the Na_xMn_yO surface cannot be observed *in situ* within assembled battery cells. In this work aim to enable the study of the degradation processes in Na_xMn_yO by creating model thin film Na_xMn_yO using atomic layer deposition (ALD). We report on the ALD growth Na_xMn_yO using alloys of MnO_x and NaOH ALD chemistries. Mn(thd)₃ and O₃ precursor doses are used to form MnO_x, while Na⁺OBu and H₂O doses are used to form NaOH. We examine the effect of mixing these ALD chemistries in varying ratios on the growth behavior and final material composition and structure, and characterize the optical and electrochemical properties of the resulting films. In particular we identify that NaOH facilitates nucleation of MnO_x, and identify slow oxidation processes requiring >300 s O₃ exposures for saturation. Correspondingly, the growth rates of MnO_x using 6 s and 300 s O₃ doses were measured to be 0.12 Å/cycle and 0.42 Å/cycle, respectively. The Na_xMn_yO alloy growth proceeds with a linear growth rate of 8.88 Å/supercycle. Additionally, our studies suggest that at high MnO_x content, the Na⁺OBu exposure yields a bulk sub-surface reaction with MnO_x. This work expands upon previous work and contributes to growing understanding of the ALD-growth of alkali-containing ternary oxides.

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