

Supporting Information

Improved Cycle Life and Stability of Lithium Metal Anodes through Atomic Layer Deposition Surface Treatments

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Experimental Section

ALD coatings were carried out in a Savannah S200 (Ultratech) ALD reactor with trimethylaluminum (TMA) and water as precursors. Pre-cycles of water were pulsed to provide a more reactive surface for the TMA to react with. Lithium metal was coated at 100°C using TMA pulses of 0.1s, water pulses of 0.02s, and a carrier gas flow rate of 10 SCCM Argon. Lithium Foil (Alfa) .75mm thick was punched by hand into 17mm discs and cleaned in anhydrous pentane with a vortex mixer for 30 seconds immediately prior to treatment and/or assembly into coin cells. Determining the exact growth rate of ALD Al₂O₃ on Li metal is very difficult, as standard film thickness measurement techniques (ellipsometry, x-ray reflectivity, cross-sectional TEM) are not possible at the current moment due to the air instability of lithium metal. Therefore, the number of ALD cycles performed (which we know exactly) is reported, rather than listing a film thickness. However the growth rate on (100) silicon was measured at 1.0 Å/cycle was measured using a Woollam M-2000DI spectroscopic ellipsometer.

Coin cells were assembled in an Argon glovebox (mbraun) with coin cell shells, spacers, and wave springs purchased from MTI INC. After coating, lithium was immediately assembled into coin cells using 45µL 1M LiPF₆ in 1:1 EC/DMC (Soulbrain) and an MTI coin cell crimping press taken up to 1000psi 3 times, relaxing between each time. The cells were symmetrical Li/Electrolyte-Separator/Li, allowing simplified investigation of behavior of the anode material. Cells were uncrimped using a disassembly die in the same MTI crimping press and electrodes were removed for further characterization after rinsing with DMC.

Cell cycling was done with a C-2001A (Landt Instruments) using coin cell holders at room temperature. Charge rates were normalized based on electrode area to current densities at $1\text{mA}/\text{cm}^2$. High-resolution electrochemical characterization, including 2-electrode Electrochemical Impedance spectroscopy, was conducted with a Gamry interface 1000. EIS was conducted in a frequency range of 0.1mHz-1MHz at a DC voltage of 0V (Li/Li+) with an applied AC current between -10uA-10uA. Morphology was observed using field emission scanning electron microscopy (SEM) on an FEI Nova Nanolab. Chemical composition was measured using X-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra XPS. In order to transfer the air-sensitive battery electrodes between the glovebox and the XPS, a custom sample-transfer enclosure was used that was opened inside of the XPS after pumping down to a fine vacuum.

Scalability of ALD for Battery Research:

Nearly all pure, Li metal is processed and formed in a dry, oxygenated environment. Similarly, most of today's Li ion battery fabrication is completed in dry rooms. While, ALD has not been widely adopted by the battery community yet, it is currently used in large scale manufacturing in both front-end and back-end processing in the semiconductor industry, and being developed at the start-up level for commercialization for applications in Li-ion battery materials¹. Therefore, it is well within the range of capabilities for this technique to be part of a future roll-to-roll battery fabrication process in a dry room environment.

1. Poodt, P. *et al.* Spatial atomic layer deposition: A route towards further industrialization of atomic layer deposition. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **30**, 010802 (2012).