ALD of Thin-Film Na_xMn_yO Cathode Materials for Sodium Ion Batteries

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In recent years, sodium ion batteries have been of increasing interest due to the limited availably 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 O_3 precursor doses are used to form MnO_x, while Na^{t}OBu and H_2O 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 O_3 exposures for saturation. Correspondingly, the growth rates of MnO_x using 6 s and 300 s O_3 doses were measured to be 0.76 Å/cycle and 1.62 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 NaO^{t}Bu 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.