

**Surface Modification of Li-Mn-Rich****Li<sub>1.2</sub>Ni<sub>0.13</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>O<sub>2</sub> Cathode Material by Atomic Layer Deposition**Xiaofeng Zhang,<sup>a</sup> Ilias Belharouak,<sup>a\*</sup> Yu Lei,<sup>b</sup> Xiangbo Meng,<sup>b</sup> Rui Xu,<sup>a</sup> Jeffrey W. Elam<sup>b</sup><sup>a</sup>Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave, Argonne, IL 60439, USA, Email: [belharouak@anl.gov](mailto:belharouak@anl.gov)<sup>b</sup>Energy System Division, Argonne National Laboratory, 9700 S. Cass Ave, Argonne, IL 60439

Lithium- and manganese-rich (LMR) oxides,  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$  (M = Mn, Ni, and Co), are promising cathode materials in terms of safety and energy density for Li-ion batteries in the era of electrified transportation and portable electronics. To improve the rate capability of this type of materials, a porous morphology is normally adopted. However the cycling stability of the cell will be challenged due to the enlarged surface area of the active materials. Recently, it has been demonstrated that surface modification using fluorine or phosphate can enhance the resistance against undesired electrode-electrolyte reactions, and consequently improve the cycle life and rate performance of the cells. Despite these improvements, the coating film thickness, composition, uniformity and conformity of the coatings can not be controlled at ease, in particular at larger scales. Atomic layer deposition (ALD) is an advanced technique to grow conformal ultrathin films with atomic layer thicknesses utilizing sequential and self-limiting surface chemical reactions.<sup>[1]</sup> ALD has been utilized to coat anode materials,<sup>[2]</sup> cathode materials,<sup>[3]</sup> and electrodes<sup>[4]</sup> for Li-ion batteries. Specifically, enhanced electrochemical performance had been reported in the case of Al<sub>2</sub>O<sub>3</sub> coated LiCoO<sub>2</sub>,<sup>[5]</sup> LiNi<sub>1/3</sub>Mn<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub><sup>[6]</sup> and Li<sub>1.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>O<sub>2</sub>.<sup>[7]</sup> However, the full cell performance with the ALD coated cathode materials has not been thoroughly studied. In this paper, we will compare the Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> ALD coatings on the full cell performance of porous Li<sub>1.2</sub>Ni<sub>0.13</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>O<sub>2</sub> powders at various test conditions. The reactivity of the surface coated species will be also discussed.

Ultrathin Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> films were deposited on the Li<sub>1.2</sub>Ni<sub>0.13</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>O<sub>2</sub> powder surfaces in a viscous-flow ALD reactor, using trimethylaluminum (TMA) and titanium isopropoxide (TTIP) precursors, respectively. The surface coated Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> were characterized using an aberration-corrected JEOL JEM-ARM200CF scanning transmission electron microscope (STEM) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) with Al K $\alpha$  radiation (1486.7 eV). The electrochemistry of the ALD coated Li<sub>1.2</sub>Ni<sub>0.13</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>O<sub>2</sub> was studied using 2032 coin cells with Li foil or meso-carbon-micro-bead (MCMB) as the anode.

The ALD coated Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> films on the Li<sub>1.2</sub>Ni<sub>0.13</sub>Mn<sub>0.54</sub>Co<sub>0.13</sub>O<sub>2</sub> porous powder have two distinguished surface morphologies regarding to uniformity, conformity and smoothness. A higher first cycle coulombic efficiencies and improved cycling stability were attained for the ALD coated samples, which were due to the protective effect of the surface films against electrode-electrolyte reactions, in particular at the high voltages. The full cell and high-temperature performance will be discussed in the paper.

**References:**

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