

# Microstructural changes in cathodic LiCoPO<sub>4</sub> thin films during electrochemical cycling

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Rechargeable batteries with high energy density and high cell voltage are urgently needed to power fully electric and hybrid-electric vehicles. Multilayer Li-ion batteries made from solid-state components are a promising technology for these applications, but their successful development rests on a thorough understanding of the effect of microstructure on battery performance. In particular, cathode-electrolyte interfaces, where many of the key electrochemical reactions take place, are known to affect charge/discharge rates, cyclability, and battery lifetime. Synthesis of cathodic films by chemical solution deposition and their characterization using atomic-resolution scanning transmission electron microscopy (STEM) has proven to be a powerful strategy for analyzing Li-battery cathodes such as LiMn<sub>2</sub>O<sub>4</sub><sup>1,2)</sup>. In this study we extend these techniques to novel cathode material LiCoPO<sub>4</sub>.

Olivine-structured LiCoPO<sub>4</sub> is an attractive cathode material for all-solid-state batteries because it has a high theoretical redox potential vs Li/Li<sup>+</sup> of 4.8 V and a high theoretical specific capacity of around 167 mAh/g<sup>3)</sup>. In this study we fabricated thin films of LiCoPO<sub>4</sub> on Au-coated monocrystalline sapphire substrates using a chemical solution deposition method. Each film's microstructure, crystal structure, and heterointerface with the substrate were analyzed using STEM and electron energy loss spectroscopy (EELS) methods both before and after electrochemical cycling with a standard liquid electrolyte up to 5 V.<sup>4)</sup>

STEM observations showed that LiCoPO<sub>4</sub> crystals in the as-deposited thin films were highly oriented. STEM observations and EELS analysis also showed that cation exchange defects formed during the first deintercalation-intercalation cycle, with higher concentrations in the surface regions than in the bulk<sup>4)</sup>.

Comparison of EELS spectra from the film before and after cycling also revealed how the electronic states of the atoms in different regions of the film were affected. In addition to cation exchange, oxygen loss and disruption of PO<sub>4</sub> tetrahedra was found to occur near the film's surface, consistent with degradation of LiCoPO<sub>4</sub> during electrochemical cycling. These two factors are likely a major cause of the observed capacity fading when LiCoPO<sub>4</sub> is used as the cathode material in secondary batteries because distortion of the surface structure blocks for Li<sup>+</sup> ion insertion, and Co<sup>2+</sup> ions on Li<sup>+</sup> sites block the one-dimensional Li<sup>+</sup> migration pathways.

## References:

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