

Microstructural changes in cathodic LiCoPO₄ thin films during electrochemical cycling

Yumi H. Ikuhara, Xiang Gao, Yoshihiro Sugawara, Craig A. J. Fisher,
Akihide Kuwabara, Hiroki Moriwake, and Yuichi Ikuhara

*Nanostructures Research Laboratory, Japan Fine Ceramics Center,
Atsuta, Nagoya, Aichi 456-8587, Japan*

E-mail: yumi@jfcc.or.jp

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 LiMn₂O₄^{1,2)}. In this study we extend these techniques to novel cathode material LiCoPO₄.

Olivine-structured LiCoPO₄ is an attractive cathode material for all-solid-state batteries because it has a high theoretical redox potential vs Li/Li⁺ of 4.8 V and a high theoretical specific capacity of around 167 mAh/g³⁾. In this study we fabricated thin films of LiCoPO₄ 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.⁴⁾

STEM observations showed that LiCoPO₄ 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 bulk⁴⁾.

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 PO₄ tetrahedra was found to occur near the film's surface, consistent with degradation of LiCoPO₄ during electrochemical cycling. These two factors are likely a major cause of the observed capacity fading when LiCoPO₄ is used as the cathode material in secondary batteries because distortion of the surface structure blocks for Li⁺ ion insertion, and Co²⁺ ions on Li⁺ sites block the one-dimensional Li⁺ migration pathways.

References:

- [1] Y. H. Ikuhara, et al., J. Phys. Chem. C 118 (2014) 19540–19547.
- [2] X. Gao, et al., Adv. Mater. Interfaces 1 (2014) 1400143.
- [3] K. Zaghbi, et al., J. Power Sources 232 (2013) 357-369.
- [4] Y.H. Ikuhara, et al., J. Mater. Chem. A 5 (2017) 9729-9738.

Acknowledgement:

This work was partially supported by Toyota Motor Corporation.