

TEM Analysis of Multivalent Ion Battery Cathode

Bilash KC¹, Jinglong Guo¹, Robert Klie¹, D. Bruce Buchholz², Guennadi Evmenenko², Jae Jin Kim³, Timothy Fister³ and Brian Ingram³

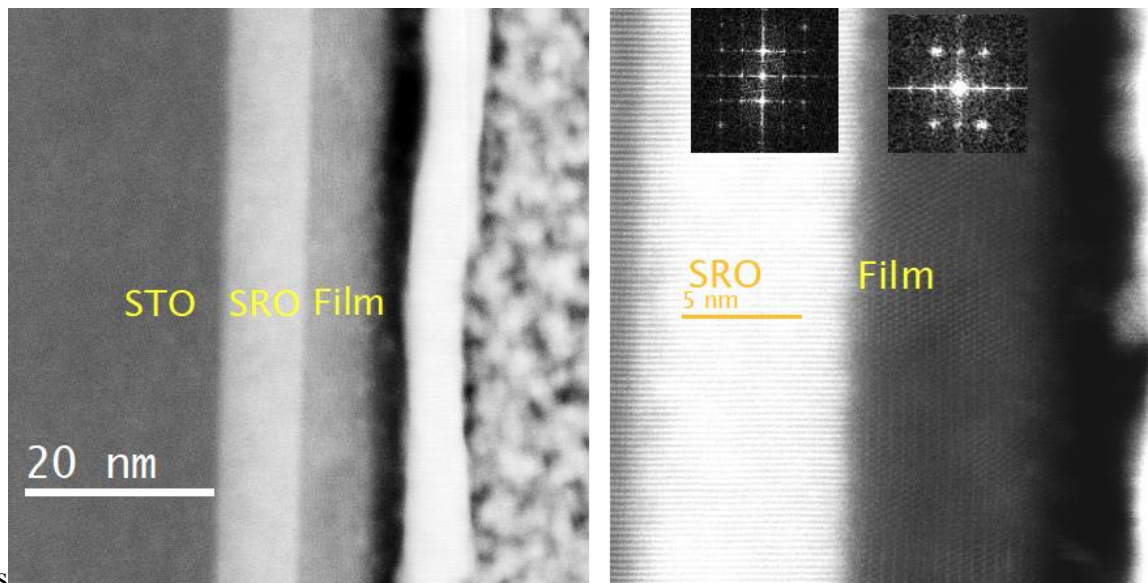
¹University of Illinois at Chicago, Chicago, Illinois, United States, ²Northwestern University, Evanston, Illinois, United States, ³Argonne National Lab, Lemont, Illinois, United States

The rechargeable batteries as of today are predominantly Li-ion batteries (LIBs) [1]. LIBs capacity, however, is intrinsically limited by the monovalency of Li⁺ ions. The increasing demand for rechargeable batteries with high energy and power density has led to exploration of several alternatives to LIBs, such as multivalent Mg ion batteries. Since Mg²⁺ ions are comparable in size to Li⁺ ions and can store twice the charge upon intercalation than Li⁺, Mg ion battery is an attractive option for high energy density [2]. However, due to difficulty of Mg intercalation into the host, need for suitable combination of electrolyte and cathode structure need to be identified [3]. Drawing upon the success of LiMn₂O₄, the spinel oxide Mn₂O₄ host is examined as suitable intercalation structure for Mg²⁺ with higher theoretical capacity (270 mAh/g for MgMn₂O₄) [4]. Although many studies have shown signs of reversible Mg intercalation, the amount of Mg intercalation have been very low and non-uniform and is plagued by limited understanding of various phenomena such as intercalation sites, Mg-Mn inversion, high migration barriers [5]. Moreover, most of these studies are based on polycrystals or powder samples which are difficult to interpret. By isolating a specific orientation, single-crystal cathodes allow for detailed characterization of surfaces and interfaces, defects concentrations, depth profiling of chemical and structural changes to examine the (de)intercalation process of Mg ions.

In this contribution, we will describe our atomic-resolution characterization study of Mg intercalation in single-crystal thin-film Mn₂O₄ host structures. Single-crystal LiMn₂O₄ thin films were grown on SrTiO₃ with SrRuO₃ as conductive buffer layer using pulsed laser deposition. The films and buffer layer follow epitaxial relationship of LiMn₂O₄ (111) // SrRuO₃ (111) // SrTiO₃ (111) out of plane. Li ions were deintercalated by charging to 4.3 V leaving behind Mn₂O₄ framework. Mn₂O₄ was then used as host cathode structure with Mg anode and 0.05 M Mg(TPFA)₂ (Magnesium Perfluoroalkoxyaluminate) in triglyme electrolyte build into custom designed X-ray transmission cell for electrochemistry of Mg ions intercalation, and discharged from 4.3V to 2.0 V. SrRuO₃ maintained conductivity and crystallinity within the cycling voltage range of 2.0-4.3 V

Figure 1a) and b) show images of ~ 10 nm of delithiated LMO and subsequently Mg intercalated Mg-Mn₂O₄ film taken along the [110] zone axis using JEM-ARM200CF scanning transmission electron microscope (STEM) at UIC. JEM-ARM200CF is probe aberration corrected with a cold field emission source with 0.35eV energy resolution, and spatial resolution of less than 0.08nm for high-angle annular dark field (HAADF) imaging at an acceleration voltage of 200 kV. Oxford Energy Dispersive X-ray Spectroscopy (XEDS) signal was recorded using Oxford X-Max 100TLE SDD X-ray detector. We find that the Mg- Mn₂O₄ film is continuous and maintains good epitaxy close to the interface with the SrRuO₃ buffer layer. However, near the thin film surface, we find an amorphous layer 2-3 nm thick. Figure 2 shows the EDS mapping of the magnesiated film. We find that Mg shows the highest concentration in the

amorphous surface layer and very little Mg was found inside the crystalline film. This difficulty for Mg intercalation in polycrystal and nano powders has been well reported in literature [3,4,5] and initial analysis of single crystal thin films clearly demonstrates the challenge. Detailed examination of the electrochemistry and optimal conditions for Mg intercalation is under investigation.[6]



SSSSS

Figure 1. (a). LAADF image shows SrRuO₃ buffer layer and Mg- Mn₂O₄ layer appear continuous. (b) HAADF image shows SrRuO₃ is epitaxial and Mg- Mn₂O₄ appears polycrystalline. Insets show epitaxial and crystalline nature of SRO and film.

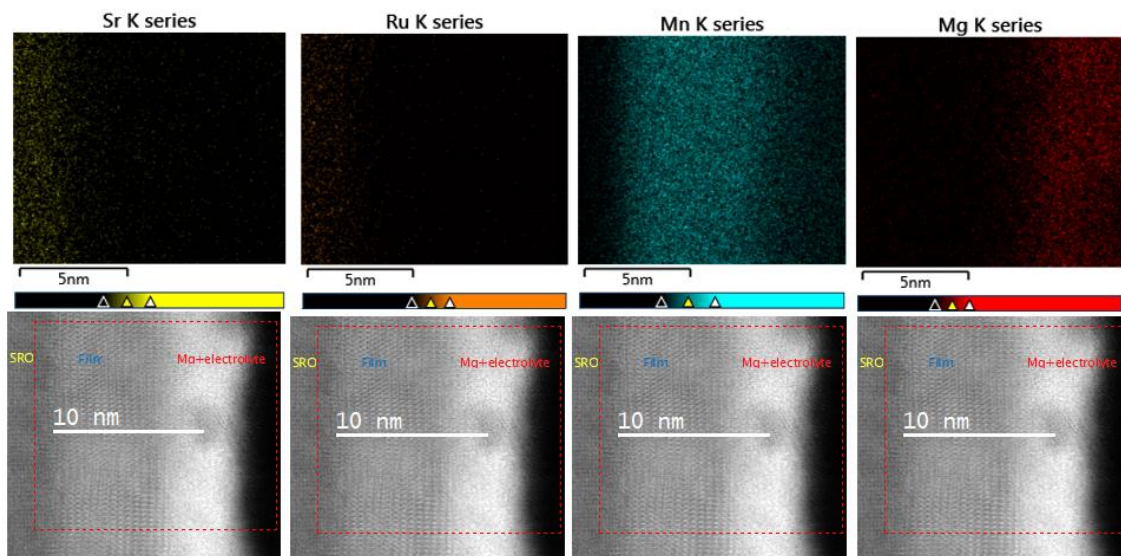


Figure 2. Top layer of the Mg-Mn₂O₄ appear amorphous. Mg is detected in top amorphous layer

References

[1] Manthiram, A., Yu, X., and Wang, S., Nature Reviews Materials **2.4** (2017), p. 16103.

- [2] Yoo, H. D., Shterenberg, I., Gofer, and Y., Gershinsky. *Energy & Environmental Science* **6** (2013), p. 2265-2279.
- [3] E. Levi, Y. Gofer, and D. Aurbach, *Chemistry of Materials* **22** (2010), p. 860
- [4] Ichitsubo, T., Adachi, T., and Yagi, S., *J. Mater. Chem.* **21** (2011), p.11764
- [5] Malavasi, L., Ghigna, P., and Chiodelli, J. *Solid State Chem.* **166.1** (2002), p.171
- [6] This work was support by the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sci