

The Role of Aberration-Corrected STEM in the Characterization of Oxide Cathode Materials

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The development of next-generation batteries for use in advanced applications (such as hybrid electric vehicles) continues to be a sought-after goal and thus a relevant research topic, in particular with respect to Li-ion and multivalent-ion batteries. In the case of Li-ion, their full potential has yet to be reached given their inherent cycling performance issues, such as voltage instability and capacity fading. On the other hand, by extending battery technology to include multivalent ions, it is proposed that such systems can surpass the energy storage capabilities of Li-ion technology, hence the impetus to identify materials which can accommodate (de)intercalation of such multivalents.

The present contribution will discuss a variety of oxide cathode materials in the context of scanning transmission electron microscopy (STEM) analysis. Specifically, these materials require characterization of chemical compositions/gradients, electronic structure (ion valence), structural disorder/rearrangements, and in the largely-unknown realm of multivalent ions: whether or not intercalation has actually occurred. Thus, STEM-based methods are quickly becoming the most promising characterization tools, with techniques available which include the direct imaging of both heavy and light elements, and both energy-dispersive X-ray (EDX) and electron energy loss (EEL) spectroscopies.

Two Li-based cathode materials will be discussed: a Mn-rich spinel and the monoclinic Li_2MnO_3 . Nanocrystalline spinel particles were engineered with an Al-rich passivating epitaxial shell [1] to curb the common issue of degradation at the electrolyte/electrode interface; as such, the STEM will focus on directly imaging the shell in low angle annular dark field (LAADF) to confirm its epitaxial nature and composition analysis via EDX, as presented in Fig. 1. Li_2MnO_3 will be discussed in its pristine, electrochemically cycled, and in-situ electron beam irradiated states [2]; the latter allows for single particle tracking of the dynamic processes occurring upon Li and O loss from the material. In this case, the focus will be on tracking structural evolution (and hence the use of annular bright field (ABF) STEM) as well as the Mn valence and O loss via high-resolution EELS (Fig. 2).

Additionally, multivalent-based cathodes will be discussed. For these cases, generally a combinatorial approach is required, consisting of LAADF/ABF imaging, EELS to determine valence, and high-spatial-resolution EDX spectroscopy to determine the nature of intercalation; furthermore, in some cases, the imaging voltage may change between 80/200 kV, depending on the desired output. It is important to note that much of the above analysis would not be possible without the use of advanced STEM instruments, outfitted with both EEL and EDX capabilities. In the present case, the UIC aberration-corrected JEOL JEM-ARM 200CF STEM instrument, capable of 0.73 Å spatial and 0.35 eV energy resolution, equipped with a large angle silicon drift EDX detector, was employed [3].

References

[1] C. Kim, P.J. Phillips, L. Xu, A. Dong, R. Buonsanti, R.F. Klie, J. Cabana, *Chem. Mater.* **27** (2015) 394–399. [2] P.J. Phillips, H. Iddir, D.P. Abraham, R.F. Klie, *Appl. Phys. Lett.* **105** (2014) 113905.

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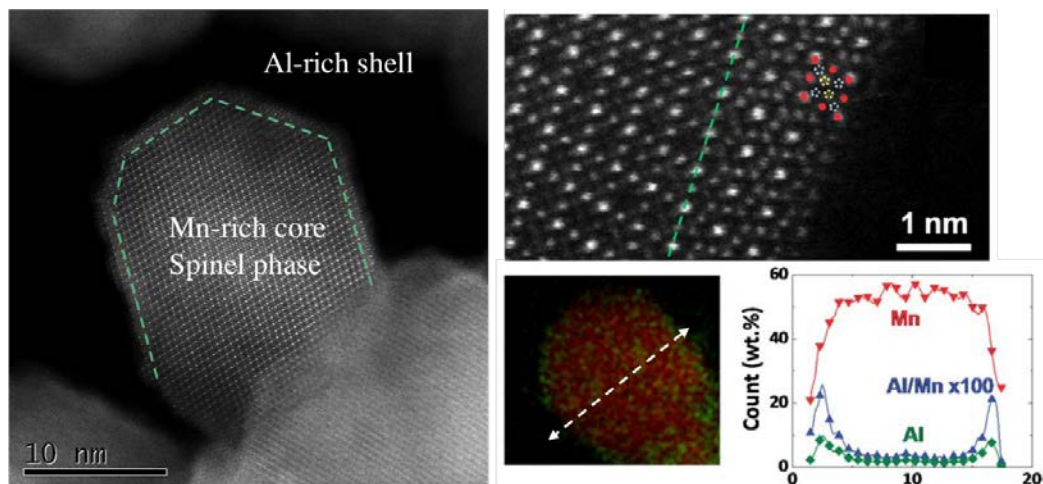


Figure 1: LAADF STEM image of the core-shell nanocrystals (left), along with a higher magnification view of the epitaxial shell (right); the Mn atomic positions are indicated with solid red spheres, while O and Li atomic positions are represented by hollow blue and yellow spheres, respectively, in the spinel structure. The Li site would not show intensity in this LAADF view, indicative that there are heavier elements present (Al). Finally, an EDX map and line scan of a core-shell nanoparticle, showing Al enrichment at the surface (shell).

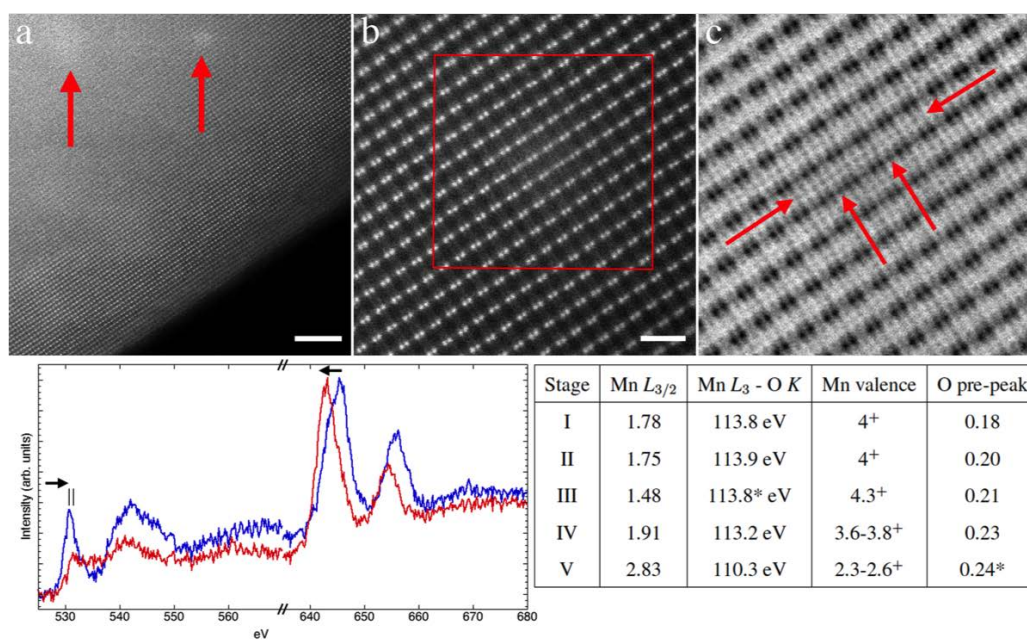


Figure 2: a) LAADF image showing two pockets of damage formed during electron beam irradiation; LAADF (b) and ABF (c) of a damaged region, showing anomalous intensity in what would be Li positions in the pristine oxide (arrowed); this is indicative of Mn moving into the Li sites. EELS O K- and Mn L-edge results form a moderately damaged (blue) and a severely damaged (red) region, with severely damaged material showing a decrease in the Mn valence and the presence of O vacancies; the table at right summarizes EELS results from various stages of damage, I being the pristine material, V being the most severely damaged (red EELS curve).