Understanding the Surface Structure of LiMn$_2$O$_4$ Spinel Cathodes with Aberration-Corrected HAADF STEM and EELS

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As global energy consumption continues to rise, the importance of energy storage becomes increasingly important. Energy density, rate-capability, and cyclability must continually improve. This constant struggle for advancement is seen most easily in the high-density, electrical energy storage market, which is dominated by lithium-ion batteries. One of the most promising chemistries in lithium-ion batteries is LiMn$_2$O$_4$ (LMO), a spinel cathode material which has the advantage of both a high energy density and a high rate capability, but this chemistry is plagued with cyclability problems. In the LMO system the main contributor to cycling degradation is the Mn disproportionation reaction ($2Mn^{3+} = Mn^{2+} + Mn^{4+}$) which creates soluble Mn^{2+} that is lost to solution. This loss of active material from LMO leads to capacity degradation. In order to understand exactly how LMO loses active material from its surface, it is crucial to determine the surface's atomic structure. This is because the surface structure dictates how the electrolyte will interact with the cathode.

In this paper, we use a combination of high-angle annular dark-field (HAADF) aberration-corrected scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) to identify the atomic surface structure and composition of LMO. We confirm the underlying spinel structure and for the first time we find, in as-processed LMO, a surface structure composed of Mn$_3$O$_4$ and a lithium-rich Li$_{1+x}$Mn$_2$O$_4$ subsurface layer which occurs as a result of the surface reconstruction. These conclusions are reached based on Mn oxidation state and oxygen content mapping with EELS as well as structural identification with HAADF STEM and STEM simulations. The presence of Mn^{2+} at the surface provides direct evidence of the Mn disproportionation reaction which has only been indirectly proven, until now. We have also identified that oxygen loss is the mechanism by which the surface reconstruction occurs. This solid understanding of the interface between the cathode and the electrolyte gives us insight into mitigating the undesired surface reactions that occur in the LMO system. Through these pioneering experiments we have gained a deeper understanding of interfacial phenomena in LMO which will be of central importance for all types of lithium-ion chemistries and continue to push the evolution of portable, electrical energy storage.
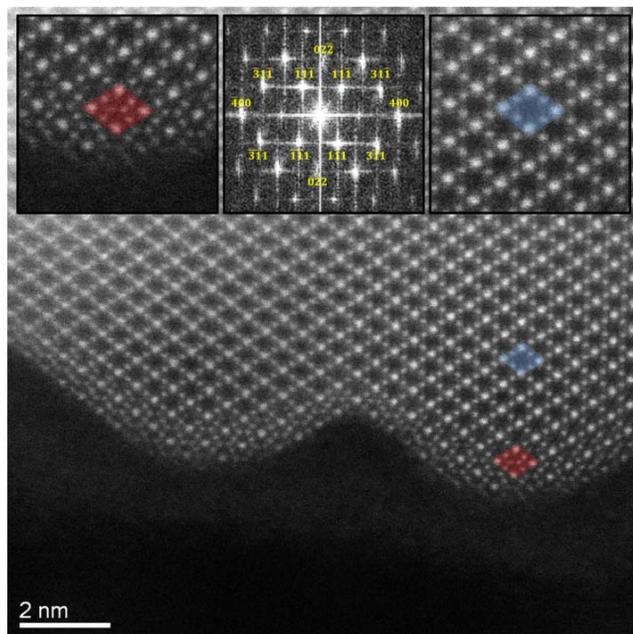
Figure 1. HAADF STEM image of LMO viewed along the [110] zone axis. LMO diamonds (blue) are found in the bulk while Mn_3O_4 (red diamond) is visible at the surface. The insets in the image show a higher magnification of the bulk (top right) and surface (top left). An FFT of the full image (top center) is included to indicate the crystal orientation.
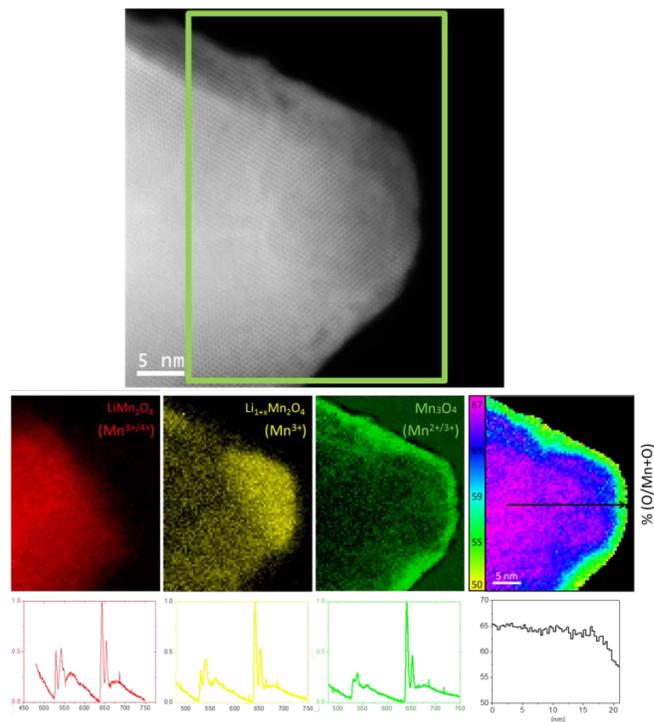
Figure 2. HAADF STEM image of an LMO particle (top). The green rectangle in the STEM image shows the area from where an EELS spectrum image was acquired. The colored maps (red, yellow, and green) and corresponding colored spectra below each image, represent the location of different Mn valence states within the nanoparticle. The oxygen content relative to Mn extracted from the O-K and Mn $L_{2,3}$ edges is shown (middle right). The black arrow shows where the relative oxygen percentage (bottom right) was extracted. The ratio is determined by the number of oxygen atoms to the total number of atoms in the sample.