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Understanding the Surface Structure of $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$ by Aberration-Corrected STEM and EELS

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Abstract

$\text{Li}[\text{Mn}_2]\text{O}_4$ (LMO) is a well-known cathode material for Li-ion batteries, but it is plagued with cyclability problems associated with the surface disproportionation of Mn ($2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$) and consequent loss of Mn^{2+} to the organic liquid electrolyte during electrochemical cycling.

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_3O_4 and a lithium-rich $\text{Li}_{1+x}\text{Mn}_2\text{O}_4$ subsurface layer which occurs as a result of the surface reconstruction.

In addition, we have applied an aqueous acid treatment, a non-aqueous chemical delithiation, and an oxygen plasma treatment to LMO in order to understand how this surface reconstruction is affected by chemical treatments. We find that Mn_3O_4 is a robust surface phase in the $\text{Li}_{1-x}[\text{Mn}_2]\text{O}_4$ system regardless of the chemical treatment and level of lithiation. The surface Mn_3O_4 phase is cubic whereas bulk Mn_3O_4 undergoes a cooperative Jahn-Teller distortion to tetragonal symmetry. Thicker Mn_3O_4 surface layers are tetragonal.

References

- [1] J. Song et al., Chem. Mater. 24 (2012), 3101.
- [2] C. Amos, M. Roldan, M. Varela, J. Goodenough, P. Ferreira, "Revealing the Reconstructed Surface of $\text{Li}[\text{Mn}_2]\text{O}_4$ ", Nanoletters, 16, (2016), 2899.

Figures

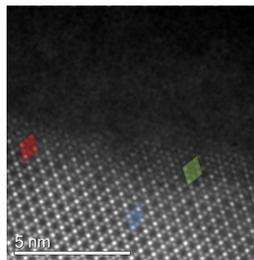


Figure 1. HAADF STEM image of $\text{LiNi}_{0.45}\text{Mn}_{1.55}\text{O}_4$ along the [110] zone axis. Shown in the figure are the normal spinel phase (blue), the rock-salt phase (green) and the ring phase (red).

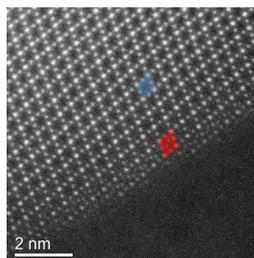


Figure 2. HAADF STEM image of $\text{LiNi}_{0.45}\text{Mn}_{1.55}\text{O}_4$ along the [110] zone axis. Observed are the normal spinel phase in the bulk (blue) and the ring phase at the surface (red). No rock-salt phase is observed in this image.