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Understanding the Surface Structure of $LiNi_{0.45}Mn_{1.55}O_4$ Spinel Cathodes with Aberration-Corrected HAADF STEM

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In order for Li-ion batteries to mature to a level useful for integration into the current or future energy infrastructure, basic problems such as cyclability, cost and rate capability must be overcome. $LiNi_{0.5}Mn_{1.5}O_4$ (LNM), a spinel cathode material, has the advantage of being both cost-effective and a high-rate capable material, but it is plagued with cyclability problems. In the LNM system the main contributor to cycling degradation is the high operating voltage which leads to solid-electrolyte interphase (SEI) formation. We find that excess-Mn doping of this material ($LiNi_{0.5-X}Mn_{1.5+X}O_4$ where x=0.05) leads to increased cyclability through natural passivation [1]. To understand the exact role that excess Mn plays in the passivation of this cathode material, it is crucial to determine the surface's atomic structure. This is because the surface structure determines how reactive the cathode will be with the electrolyte during oxidation and reduction cycles.

In order to understand how excess-Mn LNM reacts with the electrolyte, it is critical to understand the different phases that form in this system. In this regard, aberration-corrected HAADF STEM was used to identify the surface and bulk structures in the excess-LNM system. HAADF STEM confirms the spinel structure (Fig. 1) and shows good agreement with STEM simulations in the bulk. Near the surface however, other phases are observed. These include a rock-salt structure which is expected from x-ray diffraction (XRD) results and a new phase, defined here as "ring-type structure", because of the characteristic rings that are formed within the first few atomic surface layers. All three phases are observed near the surface, however only the spinel is found within the bulk of the particles. Also, the rock-salt phase and ring phase do not necessarily have to exist in close proximity to one another even though they are found near each other in Fig. 1. This is evidenced in Fig. 2 where only the spinel and ring phases are present. HAADF STEM enables a detailed characterization of these phases and has led to an important understanding of the cycling degradation mechanisms in the excess-Mn LNM system. In turn, this work enables us to develop a well-suited cathode material for future energy storage that will potentially spur the evolution of the future sustainable energy landscape.

References:

[1] J. Song et al., Chem. Mater. 24 (2012), 3101.

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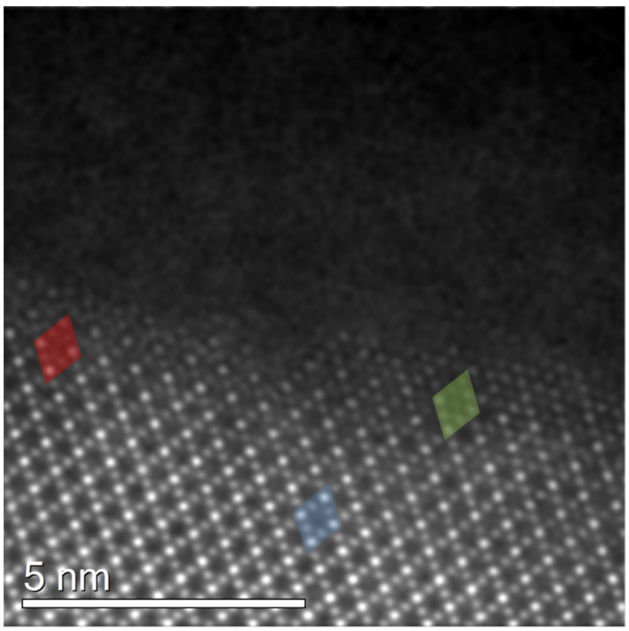

Figure 1. HAADF STEM image of $LiNi_{0.45}Mn_{1.55}O_4$ along the [110] zone axis. Shown in the figure are the normal spinel phase (blue), the rock-salt phase (green) and the ring phase (red). The image has been deconvoluted for clarity.

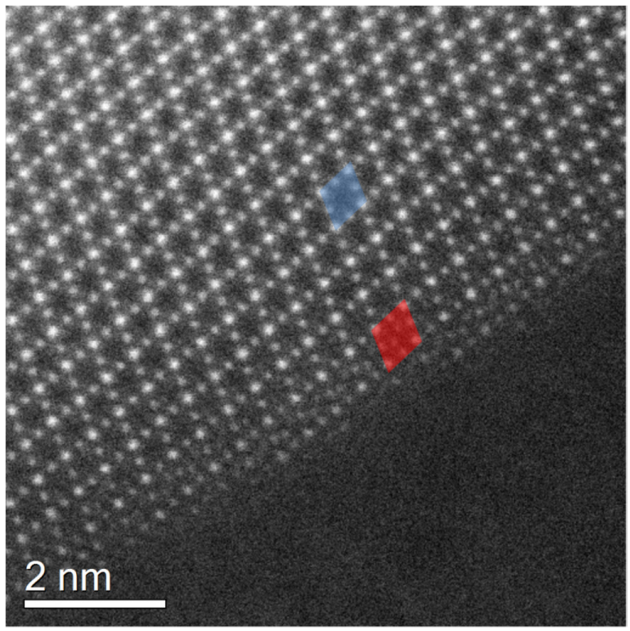

Figure 2. HAADF STEM image of $LiNi_{0.45}Mn_{1.55}O_4$ along the [110] zone axis. Observed are the normal spinel phase in the bulk (blue) and the ring phase at the surface (red). No rock-salt phase is observed in this image.

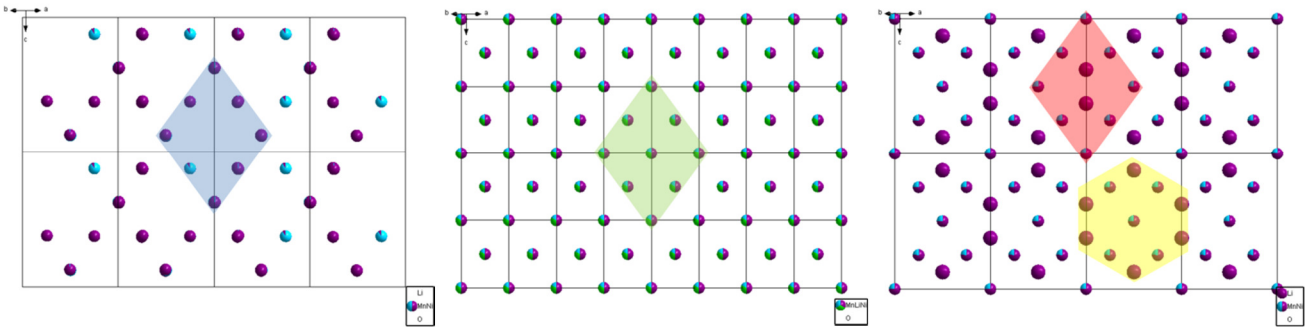

Figure 3. Structural models of the ordered spinel (left), rock-salt phase (center) and ring phase (right) oriented along the [110] zone axis. Observed in the left image is the blue diamond, which is characteristic of the spinel structure because there are no transition metals in the diamond's center region. In the rock-salt phase contrast is observed in the center of the normal spinel diamond indicating the presence of a transition metal in the once unoccupied octahedral site. In the ring phase the normal spinel diamond is filled with two transition metals occupying the tetrahedral sites normally reserved for Li. The yellow region indicated in the right figure is the characteristic ring observed in this phase. The blue atoms in the figures above represent Ni, the purple atoms are Mn, and green represents Li. Multicolored atoms indicate a fractional occupancy in those sites.

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