

Understanding the Superior Performance of $\text{LiNi}_{0.5-x}\text{Mn}_{1.5+x}\text{O}_4$ Spinel Cathodes with Advanced Electron Microscopy

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Currently, batteries are the primary source of electrical energy storage used in electric vehicles (EVs), hybrid electric vehicles (HEVs), and plug-in hybrid electric vehicles (PHEVs). These batteries are plagued with high cost, high toxicity, low energy density, and low performance both in terms of cyclability and discharge rate. The spinel cathode material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNM) has the potential to remedy all of these problems with the added benefit of a high operating voltage. LNM is comprised of cost-effective, low-toxicity elements and a high theoretical energy density, but this material has cyclability problems of its own. We find that excess Mn doping of this material ($\text{LiNi}_{0.5-x}\text{Mn}_{1.5+x}\text{O}_4$ where $x=0, 0.05, \text{ and } 0.08$) 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 surface structure is one of the main contributors to reduced cyclability in electrochemical systems.

In this regard, advanced electron microscopy (EM) techniques such as aberration-corrected high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) as well as diffraction STEM (D-STEM), a technique developed in our lab [2] that allows 1-2 nm spatial resolution electron diffraction, are used in this study to identify the surface and bulk atomic structures. HAADF STEM (Fig. 1a) reveals the [110] zone axis of the spinel structure (Fig. 1b) and shows good agreement with STEM simulations in the bulk (Fig. 1c). The surface (Fig. 2a), however, is observed to transition towards a rock-salt phase (Figs. 2b,c), as seen by the bright contrast in the center of the "diamonds" (circled in Fig. 2a). These results are corroborated with D-STEM (Fig. 2) which indicates a rock-salt structure nearer the surface (Fig. 3a), transitioning to disordered spinel FD-3M (Fig. 3b) between the surface and the bulk, and finally revealing the ordered spinel P4_132 (Fig. 3c) space group in the bulk of the particle. It is found that this thin layer of rock-salt-impurity structure is created under certain doping levels and thermal conditions. This rock-salt structure helps protect the cathode from reacting with the electrolyte. The excess Mn helps stabilize this structure and allows Ni, the active redox couple in the LNM spinel, to migrate to unoccupied octahedral sites within the spinel and therefore transforms the surface structure to a passive rock-salt phase.

These advanced EM results are compared with x-ray diffraction data (XRD) and time-of-flight secondary ion mass spectroscopy (TOF-SIMS) and cross correlated with traditional electrochemical techniques. Interestingly, STEM and D-STEM reveal surface structures in some of the samples that do not present themselves in traditional XRD results, which indicate the importance of these techniques. This increased understanding of the Mn passivation mechanism leads to optimized synthesis and composition of the $\text{LiNi}_{0.5-x}\text{Mn}_{1.5+x}\text{O}_4$ system and, therefore, a high performance cathode material that will potentially spur the development of next-generation transportation technology.

References:

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

[2] K. J. Ganesh et al., *Microsc. Microanal.* 16 (2010), 614.

[3] This work was supported by a NASA Office of the Chief Technologist's Space Technology Research Fellowship and the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under award number DE-SC0005397. The STEM work was supported by a grant from the National Institute on Minority Health and Health Disparities (G12MD007591) from the National Institutes of Health.

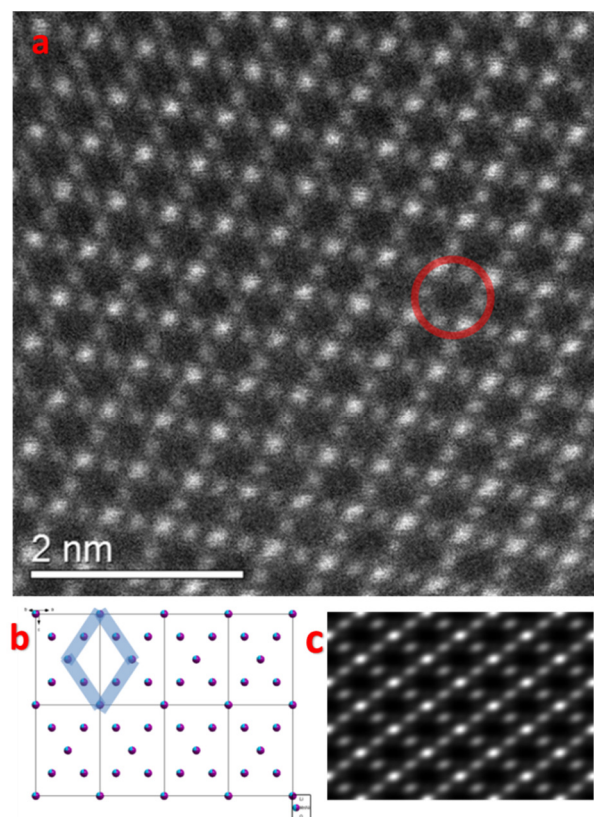


Figure 1. (a) HAADF STEM image of the bulk materials in excess Mn LNM down the [110] zone axis and (b) corresponding structure with (c) a STEM-simulated image.

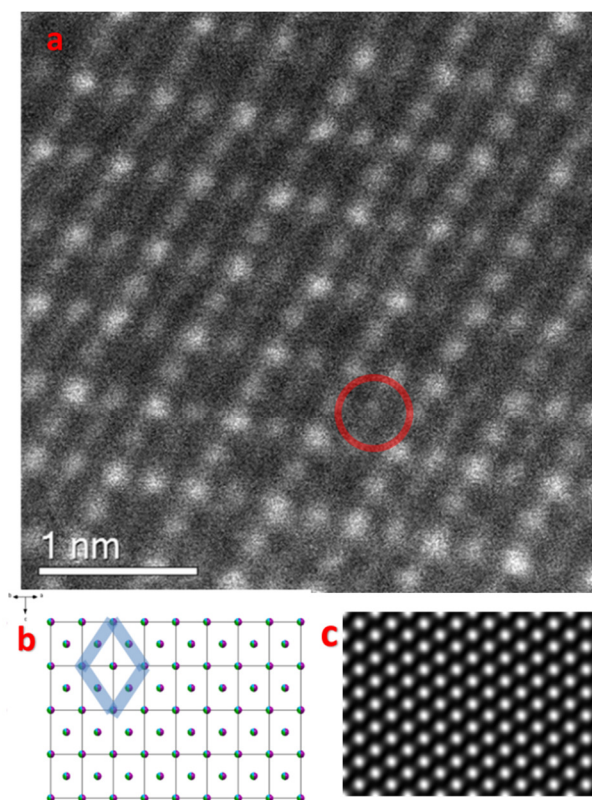


Figure 2. (a) HAADF STEM image of the surface materials in excess Mn LNM down the [110] zone axis and (b) a rock salt NiO structure with (c) a STEM-simulated image.

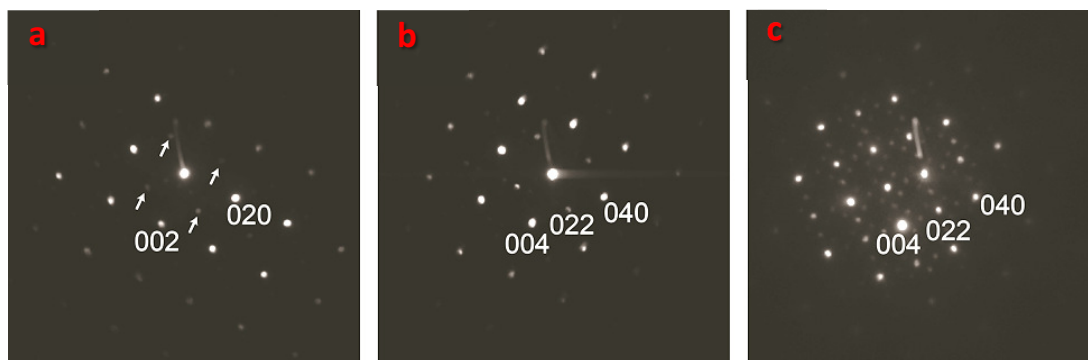


Figure 3: D-STEM patterns on the [100] zone axis collected from (a) the edge of a particle indexed as rock-salt, (b) between surface and bulk indexed as disordered-spinel, and (c) bulk indexed as ordered-spinel. The arrows point to faint spinel-reflection in the rock-salt pattern.