

Unusual Structural Transformation in LiMn_2O_4 Cathode Revealed by Atomic-Scale STEM Characterization

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The rapid development of portable electronics and hybrid electric vehicle (HEV) markets promotes the research of electric energy storage systems. Among them, lithium-ion batteries (LIBs) have attracted intense attention, due to their high energy density and long cycle lifetime. The demand for higher energy density LIBs facilitate the study of various electrode materials. Performance optimization of electrode materials necessitates information about structural evolution of electrode materials at an atomic scale. However, limited understanding for the structural evolution of electrode materials at atomic resolution, especially the Li ions distribution and arrangement at the atomic level, underlying electrochemical process substantially hinders our exploration of reaction mechanism and further performance optimization.

The annular-bright-field (ABF) imaging in aberration-corrected scanning transmission electron microscopy (STEM) allows simultaneous imaging of light and heavy elements, providing an unprecedented opportunity to probe the nearly equilibrated local structure of electrode materials after electrochemical cycling at atomic resolution. A JEM-ARM200F STEM operated at 200 kV and equipped with double aberration-correctors for both probe-forming and imaging lenses was used to perform ABF and high angle angular dark-field (HAADF) imaging with the acceptance semiangle 12~25 mrad and 90-370 mrad, respectively.

The most interesting cathode materials for lithium-ion batteries are spinel LiMn_2O_4 and its derivatives, e.g., $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, due to their low cost and nontoxicity. However, the cycling performance of these cathode materials degrades due to structural distortion during electrochemical cycling, particularly at elevated temperatures. We investigated the atomic-level surface structure of LiMn_2O_4 by heat-treatments in various atmospheres, finding similar surface spinel-to layered structural transformation only for LiMn_2O_4 heat-treated in argon atmosphere for a few minutes (Figure 1). It suggested that the spinel-to-layered transformation is made possible via migration of Mn ions from octahedral sites to lithium tetrahedral sites, forming an intermediate LiMn_3O_4 structure, followed by a further shift of some of Mn ions from the LiMn_3O_4 back to the octahedral sites to form the layered-like structure. The distortion of the surface regions can be extended to the whole bulk by heat-treatment for 300–600 min, ultimately enabling us to identify the bulk-level structure as layered Li_2MnO_3 (Figure 2). This work demonstrates the critical role of Mn^{3+} in controlling the kinetics of the structural transformation in spinel LiMn_2O_4 and suggests heat-treatment in argon as a convenient method to control the surface oxygen loss and consequently reconstruct the atomic-level surface structure [2].

References:

[1] Ben *et al*, *Acs Appl. Mater. Inter.* **9** (2017), p. 35463.

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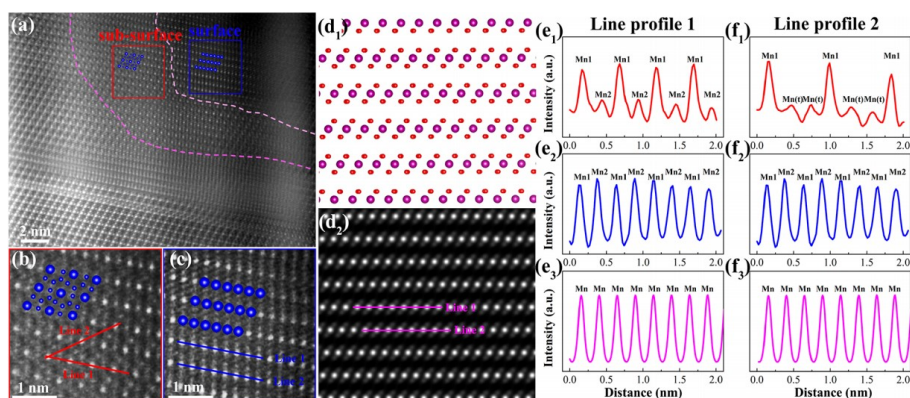


Figure 1. (a) Typical STEM-HAADF image of high-voltage cycled LMO (16th cycle, fully charged). (b, c) Enlarged images of the surface and subsurface regions, corresponding respectively to the red and blue boxes in panel (a). (d1) Crystal structure of the layered (e.g., Li_2MnO_3 , C2/m) viewed along the [100] direction. Mn atoms (purple) occupy octahedral sites. O atoms are depicted in red. (d2) Corresponding simulated STEM-HAADF image. (e, f) Line profiles corresponding to the red lines in panel (b), blue lines in panel (c), and black lines in panel (d), respectively. (Schematic lattice structures are overlaid in panels a–c.)

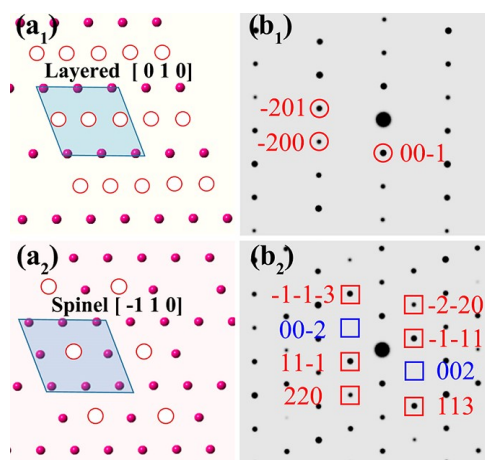


Figure 2. Schematics showing the Mn sublattice in (a1) layered structure, e.g. Li_2MnO_3 (C2/m) viewed along the [0 1 0] direction and (a2) spinel LMO (Fd-3m) viewed along the [1-1 0] direction. (b1) Simulated electron diffraction patterns corresponding to the layered structure and (b2) the spinel structure.