

Atomic-scale Insights of Cation Diffusion into Multivalent Battery Cathodes

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In early 2021, General Motors announced that it will end the production of its cars, trucks, and SUVs with diesel- and gasoline-powered engines by 2035. This and other similar trends of transition necessitates the widespread deployment of high energy charge storage system and the integration of more renewable energy into the grid. Currently, Li-ion batteries have been serving the majority of the demand of rechargeable energy sources. However, the long-term concerns of high cost, limited reserves of lithium/cobalt, and safety of Li-ion batteries have driven the researchers to search for alternative energy storage solutions. Among them, multivalent cations such as Mg^{2+} , Ca^{2+} , Zn^{2+} , Ni^{2+} , Al^{3+} are considered as potential candidates for beyond Li-ion batteries considering not only their ability to transfer more than one electron thereby facilitating higher energy density but also the possibility of using corresponding metals as the anode of the battery system for their energy density and improved safety.¹⁻³

Despite tremendous efforts in the field, the progress towards the development of multivalent battery systems is often hindered by a lack of suitable cathode chemistries that show good reversibility of ion intercalation. The main challenge to overcome is sluggish solid-state diffusion for multivalent ions and the desolvation of solvent ligands at the cathode surface.¹ It appears that the sluggish intercalation chemistry during electrochemical cycling is mostly due to structural changes and phase transitions hindering the mobility and reversibility of the cations.^{4,5} Hence, the systematic and thorough understanding of those intercalated structures at the atomic-scale is necessary if multivalent ion-based batteries are to be turned from laboratory cells into a commercial product.

In this contribution, we will provide insights into the atomic-level structure and spectroscopy of the multivalent cathodes after discharge, which are mostly undetectable during bulk characterization. In particular, structural changes in $MgCrMnO_4$ after Mg discharge and $FePO_4$ after Ca discharge are explored by employing atomic-resolution imaging and electron energy loss spectroscopy. All the electron-microscopy studies were performed in an aberration-corrected JEOL JEM-ARM200CF, equipped with a cold field emission gun, operated at 200 kV. Furthermore, battery cathode samples were prepared inside an Ar-filled glovebox to avoid any chance of sample degradation by air exposure. Results show that Mg intercalation into $MgCrMnO_4$ spinels results in the formation of a rocksalt surface layer, while Ca intercalation into polyanionic compounds proceeds via a core-shell process. These results guide battery scientists to better select and design the components of the battery to optimize the performance of the system.

Figure 1 shows atomic resolution images of pristine and Mg discharged $MgCrMnO_4$ (Mg discharged after the extraction of Mg). Close analysis of the discharged particle shows two distinct crystallographic phases; spinel in region I, having a diamond-shaped unit cell, whereas a defective rocksalt on region II showing empty tetrahedral sites (8a; Wyckoff notation) and occupied octahedral sites (16c; Wyckoff notation), which are empty in the region I. Furthermore, the contrast of the atomic columns across various columns is almost homogenous in region II indicating a defective rocksalt phase on the particle's surface upon Mg discharge.

Atomic-resolution images and EELS spectroscopy of the Ca discharged FePO_4 are summarized in Figure 2. As illustrated in Figs 2(a,b), results show that Ca mostly intercalates on the surface of the particle showing 1) diminishing trend of Ca L edge signals and 2) gradual decrease of Fe^{2+} and increase of Fe^{3+} from the surface to the bulk of the particle. Furthermore, the annular bright-field image of the Ca discharged FePO_4 clearly shows the decrease in the atomic contrast of the expected Ca atomic columns from the surface to the bulk of the particle. These results demonstrate the core-shell pattern of Ca intercalation into FePO_4 .⁶

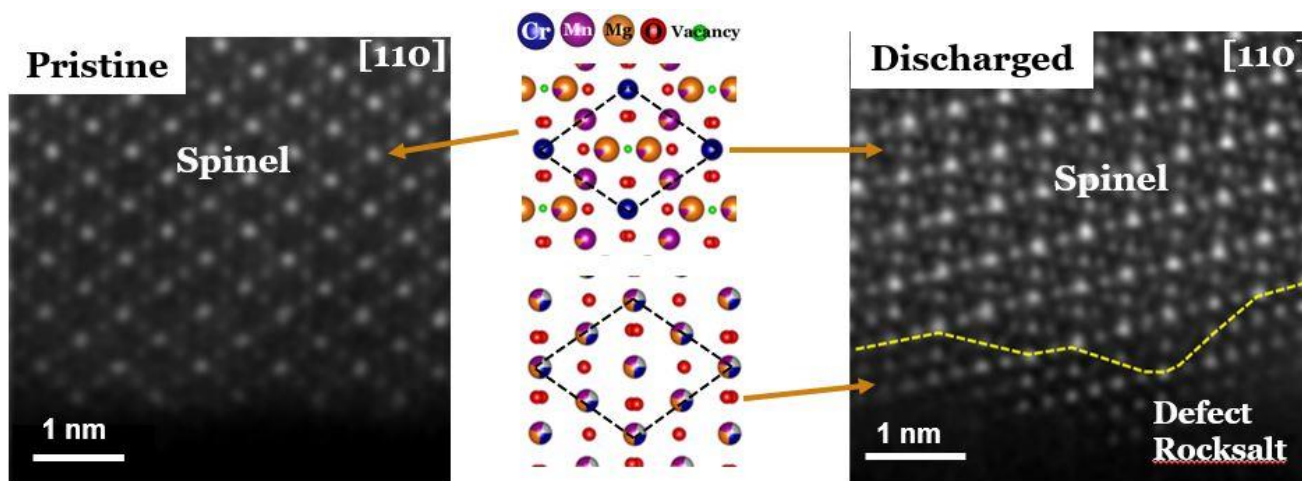


Figure 1. Figure 1: STEM-HAADF images of pristine and Mg discharged MgCrMnO_4 showing spinel phase in pristine materials, whereas defect rocksalt phase on the surface of the discharged structure.

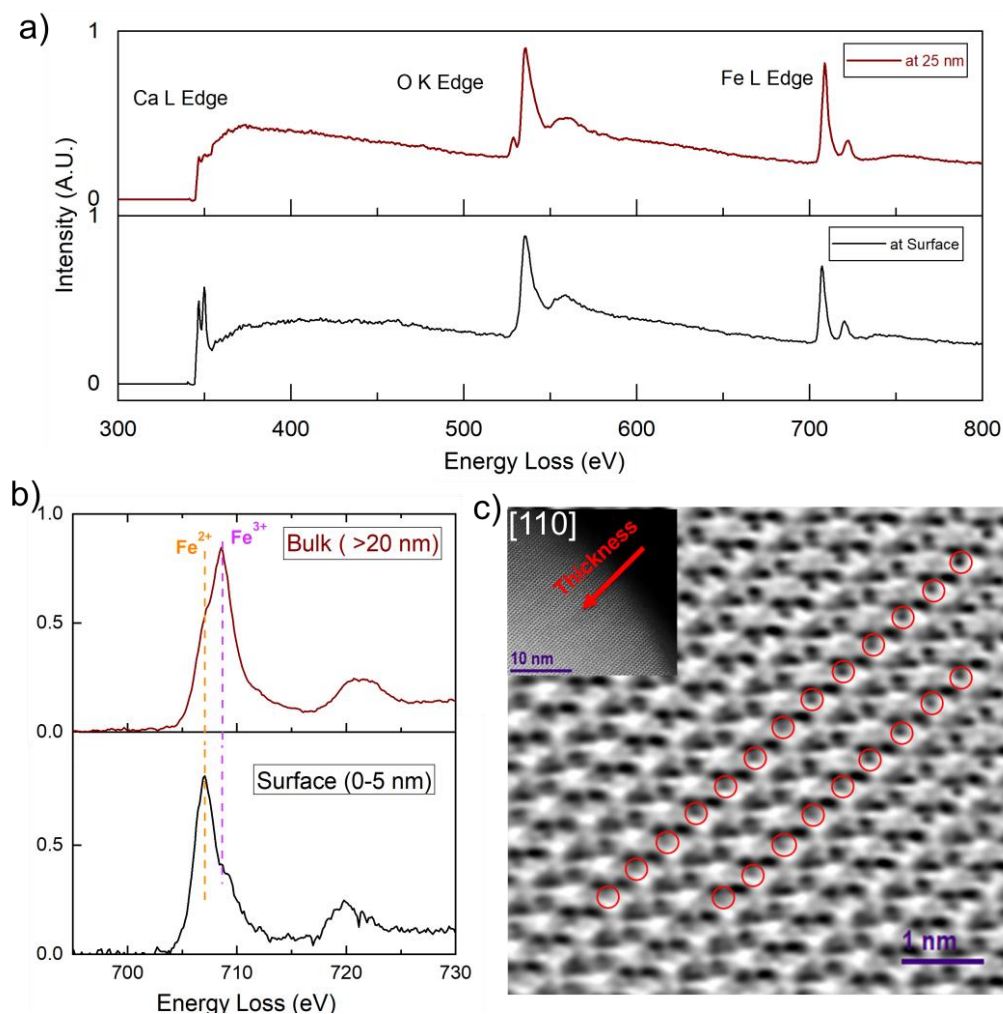


Figure 2. Figure 2: EEL spectra and STEM-ABF image of Ca discharged FePO₄ showing the core-shell pattern of Ca intercalation. (a) EEL spectra from surface and bulk showing prominent Ca signals from the surface, signals diminished with an increase in thickness. b) Magnified view of the Fe L-edge showing mostly Fe²⁺ on the surface and Fe³⁺ on the bulk. c) STEM-ABF image showing the decrease in the atomic contrast of Ca columns with an increase in thickness.

References

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