doi:10.1017/S1431927620015846
Microsc. Microanal. 26 (Suppl 2), 2020

Electron-beam-induced Spinel to Defect Rocksalt Phase Transition in $MgCrMnO_4$

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Recent progress in the field of scanning/transmission electron microscopy (S/TEM) has resulted in intense electron probes (10^6 Acm^{-2}) providing an ultra-high spatial (e.g. sub-Å) and energy (3 meV) resolution, with a previously unattainable signal-to-noise ratio [1]. However, this intense electron probe can alter the specimen, causing a massive atomic displacement and/or excitations followed by significant structural and chemical transformations depending upon the materials under irradiation [2]. Consequently, for structural characterization, electron beam damage precludes us from attaining atomic-resolution imaging or spectroscopy, resulting in drastic changes to the structure/chemistry of materials inadvertently. Hence, radiation damage, if unchecked, is becoming a major limiting factor in the TEM field, necessitating a cautious interpretation of the results.

Battery materials are widely known to be highly beam sensitive materials. Within the basic science battery community, efforts are now focusing on the discovery of electrode materials beyond Li-ion, including the search for cathodes and anodes that are appropriate for multivalent batteries. Several theoretical and experimental studies have revealed that transition-metal oxide spinels constitute a class of materials that provide possible host structures for favorable multivalent ion intercalation due to their three-dimensional pathways of migration, offering a diversity of favorable intercalation sites [3]. Initial studies have demonstrated low levels of Mg (de)intercalation into the spinel cathodes [4]. It was suggested that the sluggish intercalation chemistry during electrochemical cycling is due to structural changes and phase transitions hindering the Mg mobility and reversibility [5]. However, the atomic-scale mechanism of the (de)intercalation and causes of these phase transitions are largely unknown.

In this contribution, we will demonstrate the formation of a spinel to rocksalt phase transition in $MgCrMnO_4$ nanoparticles, a potential cathode for multivalent batteries, by employing atomic-resolution imaging and electron energy loss spectroscopy. The particles are exposed to an intense electron beam (approximate dose of 10^6 $e^-/Å^2$) and both the structural and electronic changes induced by the electron beam are observed. Our results show that the spinel structure is transformed to a defective rocksalt structure on the $MgCrMnO_4$ particle, due to the migration of the cations. Although electron irradiation is not a substitute for electrochemical cycling, these types of in-situ analyses help in understanding the possible structural transformation as a result of (de)intercalation across the cathodes.

Figure 1a) shows two distinct regions in the $MgCrMnO_4$ structure: structurally transformed, highly beam-damaged (region I), and neighboring area in pristine phase (region II). A higher magnification image of both the regions and their atomic models are shown in Fig 1b) and c). Careful analysis of the two regions within the image shows that the structure is spinel in region II containing a diamond-shaped pattern, whereas, the new structure in region I is defective rocksalt showing empty tetrahedral sites (8a; Wyckoff notation) and occupied octahedral sites (16c; Wyckoff notation), which is empty in region II. Furthermore, the contrast of the atomic columns across various columns is almost homogenous and the unit cell corresponding to the new structure is half of the diamond-shaped spinel unit cell. This suggests that spinel $MgCrMnO_4$ changed into a defective rocksalt on the particle surface upon electron beam irradiation.

Electron energy loss (EEL) spectra from the two regions [Fig 2a) and b)] further verifies two distinct phases showing notable differences in the oxygen pre-peak intensity and manganese white line intensity ratio. [6]

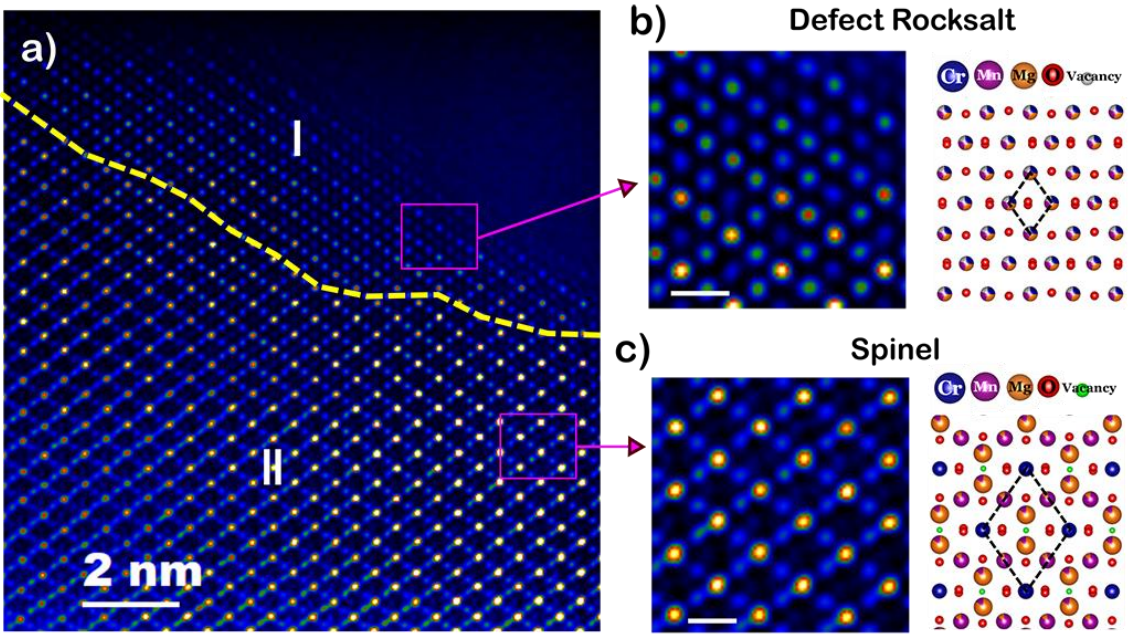
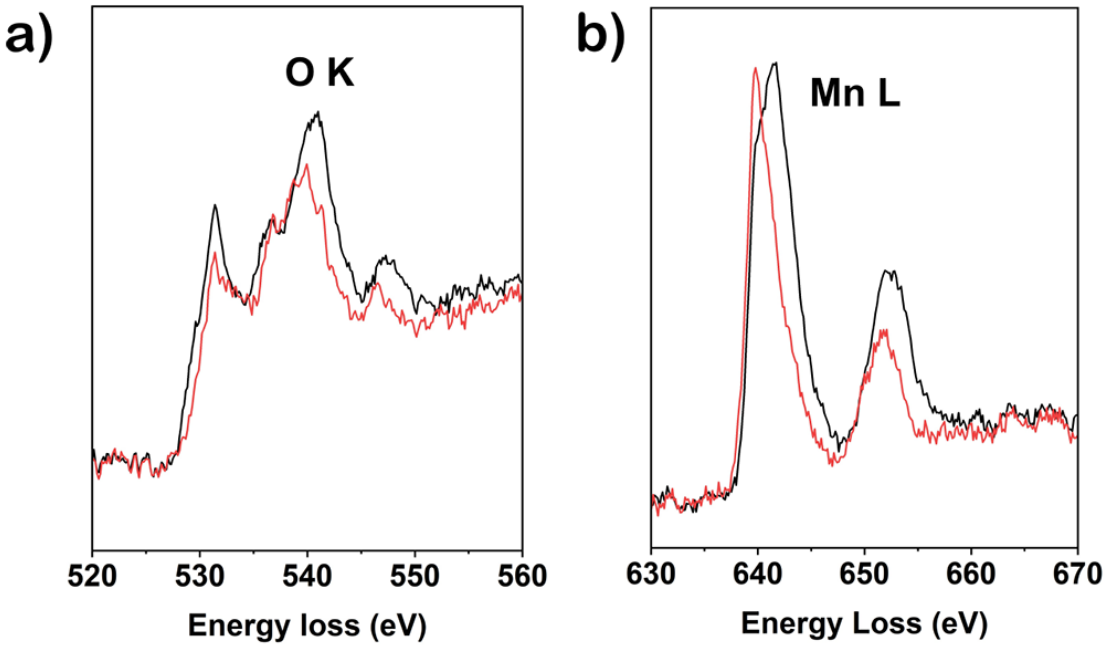


Figure 1. Atomic-resolution image of MgCrMnO4 nanostructure. a) Filtered STEM-HAADF image of the particle showing defect rocksalt (region I) and spinel (region II) phases, b) and c) higher magnification images of the defect rocksalt and spinel phases respectively with their corresponding model. Scale bar in fig b,c is 0.5 nm.



https://doi.org/10.1017/S1431927620015846 Published online by Cambridge University Press

Figure 2. EEL spectra of oxygen (a) and manganese (b) corresponding to the two distinct phases: spinel (black) and rocksalt (red).

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6. This work was supported by the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U.S. Department of Energy, Basic Energy Sciences.