

Meeting-report

Investigation of Electron-Beam-Induced Structural Changes in MgCrMnO_4

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Transition metal (TM) oxides, particularly manganese oxide spinels, are currently attracting considerable attention in rechargeable battery research due to their potential application as cathodes for intercalation of multivalent ions, such as Mg^{2+} [1]. However, the electrochemical cycling of these oxide cathodes with Mg^{2+} leads to irreversible structural alterations, resulting in capacity and voltage loss, as reported by multiple studies [2].

Here, we will use in-situ transmission electron microscopy techniques to investigate the electronic and structural changes of MgCrMnO_4 following exposure to electron beam irradiation, utilizing an aberration-corrected scanning transmission electron microscope (STEM) and electron energy loss spectroscopy (EELS). We will illustrate the impact of electron beam irradiation on the observed phase transition, which results in distinct crystalline structures within particles. Although this irradiation does not precisely replicate the structural changes observed in battery cathodes during cycling, it provides valuable insights into the atomic structure changes associated with similar types of transformations.

The high-resolution characterization was carried out using the aberration-corrected JEOL ARM200CF microscope, operated at 200 kV with the emission current set to 14 μA . In STEM mode, a convergence semi-angle of 22 mrad was chosen with an inner detector angle for high angle annular dark field (HAADF) and low angle annular dark field (LAADF) of 75 mrad and 30 mrad, respectively. The microscope is equipped with an Oxford XMAX100TLE EDS detector and a Gatan Continuum GIF spectrometer. A new Gatan ClearView camera was used for in-situ high-resolution TEM imaging. The Protochips Axon Studio software was used to record in-situ video of the structural transformation and dosing rate.

Figure 1 illustrates the process by which electron beam irradiation leads to the creation of a new structure on the surface of a nanoparticle. The images are captured from a video recorded by the Gatan Clearview camera, which has a high frame rate of up to 1600 fps, allowing us to observe the growth process at an atomic scale. The MgCrMnO_4 particle is viewed along the [110] zone axis, and the red boxes in (a) and (b) indicate the area of growth. Figure 2a shows the O *K*-edge, demonstrating the chemical shift of the O *K*-edge pre-peak and the alterations in O-*K* edge EELS fine structure. Figure 2b shows the Mn *L*-edges, emphasizing the chemical shift of the *L* edges. The changes in energy difference between the Mn *L*₃ edge and the O pre-peak, as well as the Mn *L*₃/*L*₂ peaks, indicate changes in the Mn oxidation states resulting from the observed phase transition.

In this contribution, we will compare our in-situ observation to previous studies on MgCrMnO_4 , where phase transitions from a spinel to a rocksalt structure were examined [3]. We will show that structural changes occur not only at the surface of the material, but also result in the growth of the crystal into various crystalline structures. These changes are correlated with the particle size and electron beam dose. Comprehending the dynamics of these phase transitions and their correlation with various parameters can assist us in optimizing the synthesis process to prevent their occurrence. [4]

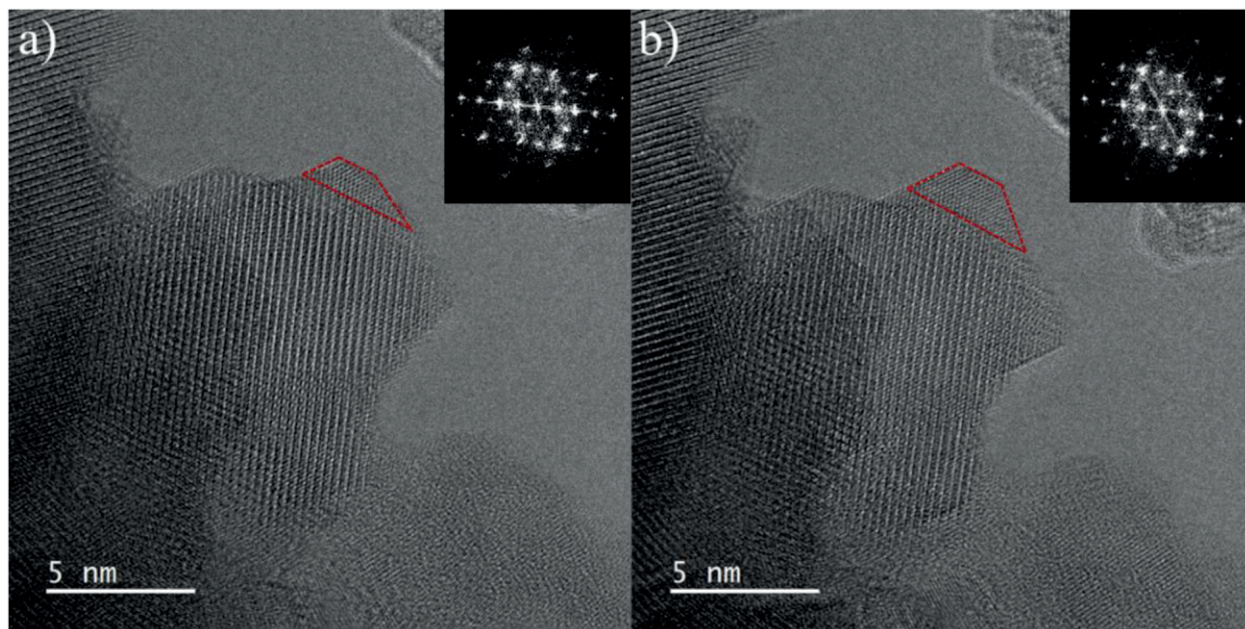


Fig. 1. TEM images show the crystal growth of MgCrMnO_4 particles with embedded red boxes, progressing from image (a) to (b). The time gap between the two images is about 7 minutes. The FFT corresponds to the entire particle, showing the [110] zone axis.

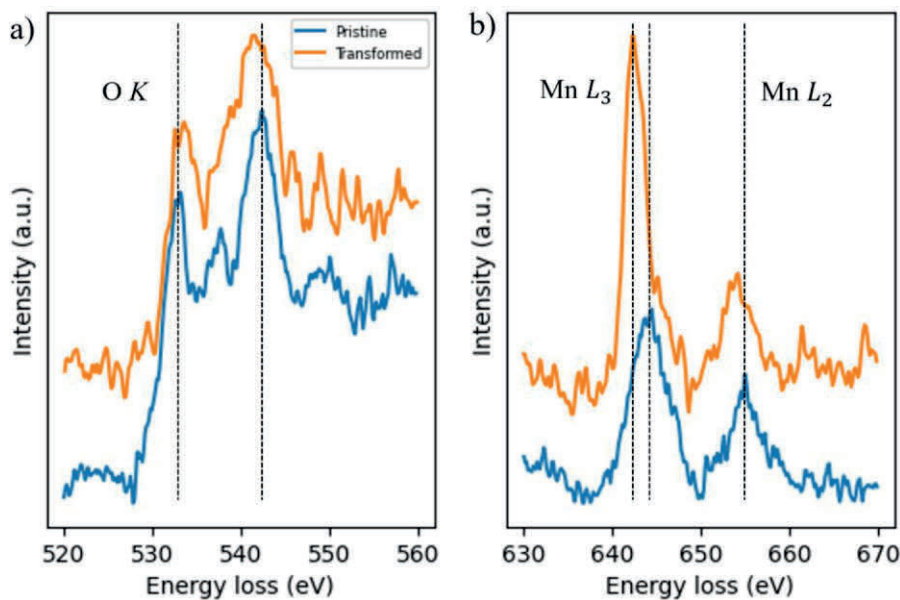


Fig. 2. Examining the MgCrMnO_4 particles both before and after their structural transformation using electron energy loss spectroscopy. (a) Core-loss spectra of O K-edge, (b) core-loss spectra of Mn L-edges.

References

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4. The authors acknowledge support from the National Science Foundation (NSF-CBET 2312359) and by the Army Research Office under Grant Number W911NF-23-1-0225. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing the official policies, either expressed or implied, of the Army Research Office or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation herein.