Time-resolved Atomic-scale Chemical Imaging of the Dynamic Phase Transformation in Li-rich Layered Cathode Materials Induced by Electron-beam Irradiation

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The layered lithium transition-metal (TM) oxides such as the lithium-rich, manganese-rich oxides (e.g., Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ (LNMO)), are of great interest as cathode materials for secondary (rechargeable) lithium ion batteries [1-3]. The materials however have several known issues including gradual voltage fade and irreversible capacity loss upon charge-discharge cycling, attributed to a permanent, irreversible phase transformation on the surfaces during the electrochemical charge-discharge cycling. The materials also are known to be prone to radiation damage by high-energy electron beams. Furthermore, the phase transformations induced by electron beam are found to be identical to those reported due to the charge-discharge cycling, as observed recently by aberration-corrected scanning transmission electron microscopy (STEM) using the techniques such as Z-contrast or HAADF imaging and atomic-scale chemical STEM EDS mapping [4,5]. However, due to the long acquisition time (> few hundreds of seconds) required for atomic-scale EDS mapping as well as highly sensitive nature of the materials to high-energy electron beam, the studies so far have not able to reveal critical local transient structure involved in the phase transformation. The information is critical to advancing our understanding of the transformation mechanism and electrochemistry.

Recently, we have developed a novel atomic-scale STEM EDS chemical imaging technique that reduces the acquisition time to as little as one second, a reduction of more than 100 times [6]. The technique consolidates the x-rays sparsely scattered over a large area (~10 nm^2) into a smaller, single unit cell area using lattice-vector translations, producing the averaged chemical maps for the crystal. In this study, the new capability is used to investigate dynamic structure transformation in LNMO under the influence of electron beam irradiation. By capturing a series of time-lapsed chemical maps, we are able to show for the first time clear atomic-scale evidence of preferred Ni-mobility in LNMO phase transformation, revealing important new insights into the kinetic mechanisms [6].

LNMO (a monoclinic unit cell, a=0.4926nm, b=0.8527nm, c=0.5028nm, and β=109.22^{o}) exhibits a layered structure composed of repeating TM layer, O layer and Li layer as shown Fig.1a. A HAADF image taken from the crystal without electron beam pre-exposure is shown in Fig.1b. The bright layers with a lattice spacing of 0.474nm, i.e., (001) plane, correspond to positions of the TM layer, the middle point between TM layers is the Li layer. Three sequential EDS datasets were taken from the same specimen area with a collection time of ~4.5 sec for each dataset. Figs. 1c, 1d, 1e shows chemical maps of Mn K and Ni K x-rays extracted by the lattice-vector translation method from the three datasets, respectively. The difference amounts to approximately 4.5 seconds of electron beam exposure. The result indicates that the phase transformation progresses as Ni atoms jump preferentially (relative to Mn atoms) into the Li sites once the sites are vacated. It is clear that traditional mapping processes, requiring 100X more electron exposure, would miss this subtle, but important phenomenon. The observations

enable a better understanding of the structural evolution mechanism in the Li-rich layered oxides during the electrochemical cycling [6, 7].

References:

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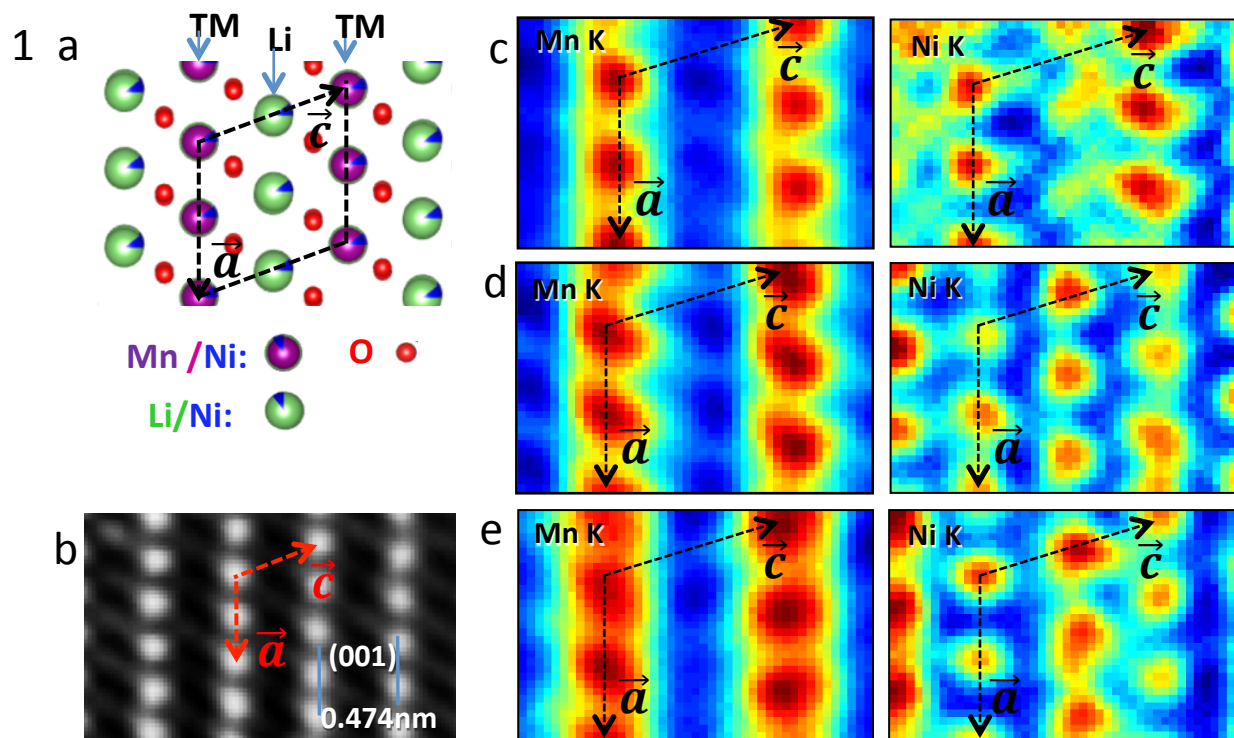
Figure 1. Time-resolved atomic-scale chemical imaging study of the phase transformation in Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ (LNMO). (a) Projected LNMO structure in [010] direction; (b) HAADF image taken in [010] direction from an area without electron beam pre-exposure; (c-e) x-ray chemical maps of Mn K (left) and Ni K (right), obtained by using the lattice-vector translation method from three EDS spectral imaging datasets acquired sequentially from the same area (4.46 nm×6.69 nm), with a collection time of ~4.5 sec each. LNMO has a monoclinic unit cell (*a*=0.4926 nm, *b*=0.8527 nm, *c*=0.5028nm, and β=109.22°) with space group *C2/m*. Vectors $\vec{a}$ and $\vec{c}$ indicate the *a*- and *c*-axis of the unit cell. A FEI Titan^{TM} G2 80-200 STEM with a Cs probe corrector and ChemiSTEM^{TM} technology operated at 200 kV was used in this study.