

## Understanding the Chemical and Relevant Phase Evolutions of Lithium-Based Electrode Materials Using Atomic-Resolution Electron Energy Loss Spectroscopy

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The recent development and implementation of aberration correctors and monochromators, along with the new emerging detectors, have largely improved the detection limit of modern scanning transmission electron microscopes (STEMs). The high spatial and energy resolution of the STEM-EELS (electron energy-loss spectroscopy) technique provides researchers the capability of obtaining chemical and bonding information of the materials in a very localized manner, making it possible to extract correlated phase information. The application of advanced analytical TEM characterization in energy storage materials has opened up an effective way of understanding the fundamental questions related to materials' performance. In this work, the benefit of high-resolution EELS technique in analyzing the chemical and phase evolutions of Li-based cathode materials for lithium-ion batteries (LIBs) during the electrochemical process is discussed.

Herein, we implement atomic-resolution STEM-EELS analysis to the LIB cathode materials at different cycling conditions using a FEI Titan 80-300 Cubed S/TEM equipped with two Cs-correctors (probe and image forming lenses), a monochromator, and a Quantum GIF spectrometer with a newly-installed K2 camera. Along with high-resolution EELS, high-angle annular dark-field (HAADF)-STEM imaging was used to obtain the chemical and structural information from the Li-based cathode materials before and after electrochemical cycling.

Cathode materials with layered  $\text{Li}_{1+x}(\text{NiMnCo})_{1-x}\text{O}_2$  ( $0 \leq x \leq 1/3$ ) and  $\text{LiM}_2\text{O}_4$  spinel structures have been studied in this work to understand the localized chemical and relevant phase evolutions before and after cycling. For instance, the Li-rich high-energy  $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$  (HENMC) cathode material, where excess Li is added to the transition metal (TM) layers in order to enhance the energy density, have a complex, and yet still debated, structure that is different from the conventional layered  $\text{LiMO}_2$  trigonal phase. The presence of the "continuous dotted contrast" partial plane in the TM layers that having the "TM-TM dumbbell" ordering (with excess Li) of HENMC could be easily misinterpreted, since such continuous atomic-ordering can be observed from both the  $C2/m$  monoclinic phase and  $R\bar{3}m$  trigonal phase. Using atomic-resolution EELS, we have been able to reveal that there is no chemical variation between the planes exhibiting this peculiar contrast and the "dumbbell" regions. Combined with detailed image analysis, the results demonstrate that the change in the local atomic ordering is arising from the presence of three-dimensional stacking faults rather than the existence of  $R\bar{3}m$  trigonal phase [3]. Furthermore, atomic-resolution STEM-EELS mapping has been used to reveal the TM segregation at single (or few atomic) planes at surfaces, as well as changes in the local electronic structure in thin (few atomic) layers of impurity phases present in the cathode internal structure or formed during surface modification [4], one example is illustrated in Figure 1. Such features are critically important to understand the materials' behavior during the electrochemical process.

In terms of cycling-induced evolution, surface degradation has been widely considered to correlate with

the performance decay of the LIB cathodes. Using high spatial- and energy-resolution EELS, we have obtained energy-loss near-edge fine structures (ELNES) of the TM cations during Li intercalation-deintercalation. By acquiring reference spectra and performing statistical analysis, the results demonstrate that the localized change in the oxidation state of cations, and the correlated phase evolution near the surface of the cathode materials, can be mapped effectively at different cyclic states [1-2]. Our work shows that the surface evolution of cathodes, *e.g.* layered Li(NiMnCo)O<sub>2</sub> or spinel LiMn<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub>, (Figure 2) can be initiated during the first Li-deintercalation process. Meanwhile, our findings demonstrate that the degree of surface degradation shows variations depending on the cycling conditions and the composition of the materials. For the Li-rich HENMC cathode, however, a bulk-evolution-dominated degradation process was discovered using high-resolution STEM-EELS combined with other bulk sensitive techniques [3]. Furthermore, significant change in the electronic structure have been detected from the lithium and oxygen K-edges when probing from the active material into the cathode-electrolyte interphase (CEI) [5].

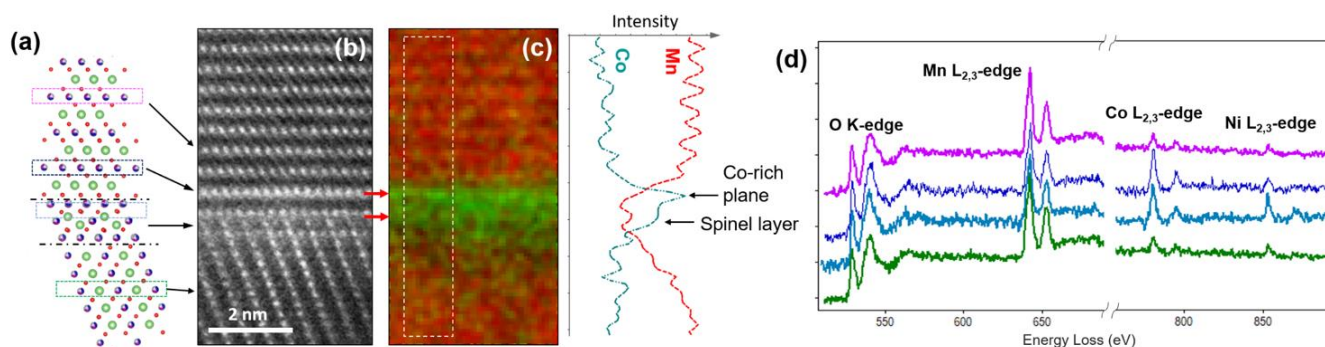
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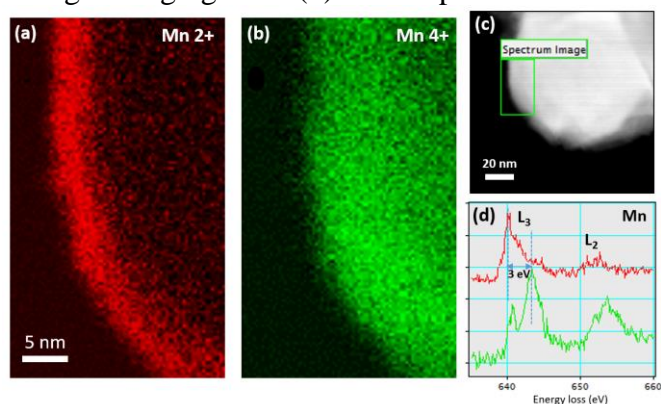
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**Figure 1.** High-resolution STEM-EELS mapping showing the TM segregation at the impurity phase in pristine Li-rich cathode material. (a) atomic model for the HAADF image shown in (b), where green spheres: Li; purple: TM; red: O. (c) EELS mapping of Co (green) and Mn (red), and the intensity profile showing Co segregation. (d) EELS spectra obtained from lattice planes highlighted in (a).



**Figure 2.** Valence maps for a delithiated LiMn<sub>2-x</sub>Cr<sub>x</sub>O<sub>4</sub> particle showing the surface reduction of Mn.