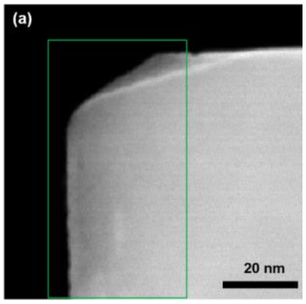
A Guide to Using Electron Microscopy to Reveal the Degradation Mechanisms of Battery Electrodes

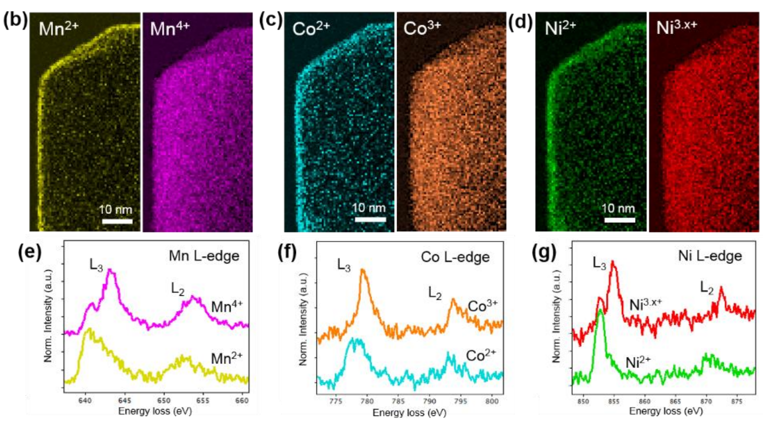
This work was completed in a collaborative network between academia and industry with specific interest from General Motors.

Problem: Understanding the degradation and failure mechanisms of different Lithium (Li+) ion battery cathodes.

The Solution: Study the structural and chemical evolution of the cathode materials using electron microscopy techniques in both two- and three-dimensions.

- Focused ion beam (FIB)/scanning electron microscopy (SEM) was used to reconstruct, at the micron- and nano- scale, the three-dimensional structure of the cathodes to understand the structural degradation during battery cycling.
- Electron energy loss spectroscopy (EELS) was used to examine the charge compensation process of cathode material, i.e. valence change of transition metals during battery charging/discharging.
- Scanning transmission electron microscopy (STEM) combined with EELS and nano-beam electron diffraction was used to understand the effect of short-term and long-term electrochemical cycling on the phase transformations and surface degradation of the cathode material at the atomic-scale.
- A specialized TEM vacuum holder was used to transfer samples from the glove box to the TEM to prevent air exposure, as the delithiated cathode materials are air sensitive.





Valence maps of a charged (4.1 V) $LiNi_xMn_yCo_{1-x-y}O_2$ particle. (a) STEM image showing the region-of-interest (ROI), (b-d) valence maps of Mn, Co and Ni, respectively, with, the corresponding reference spectra shown in (e-g).

> Industrial companies are concerned with the performance of batteries, for example, energy and power density, lifetime, and safety issues. By using our techniques [electron microscopy], we can understand from a fundamental perspective, the degradation mechanisms of the cathode materials, which is of great importance for the future design of electrodes as it allows us to enable improved cycling performances.
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> *Dr. Hanshuo Liu, McMaster 2018*

The Results:

- **Understanding the charge compensation mechanism of battery materials:** The transition metals responsible for the charge compensation during Li+ ion insertion and extraction from the cathode material was determined for different voltages of the charge/discharge process by examining the oxidation state of the cathode transition metals.
- **Increasing the battery lifetime:** Irreversible phase transformations and Li+ loss within the cathode material occurred during the battery's first use and proceeded throughout its lifetime, which has been found to be detrimental to the batteries' operation if an inactive phase was formed.
- **Performance improvements:** Three-dimensional structural investigation has revealed the detachment between the active material and the binder phase of the cathode after long-term use, thus leading to a decreased performance over time. This method can be used to evaluate the microstructural evolution of different battery cathodes.

Instruments Used:

Zeiss NVision FIB/SEM, FEI Titan 80-300 LB, FEI Titan 80-300 HB, TEM vacuum holder

References:

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