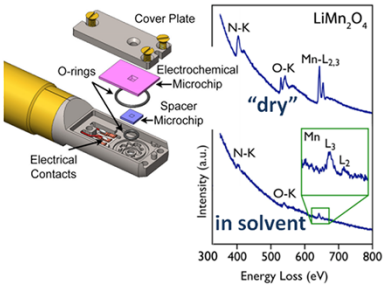
Quantitative Electron Energy Loss Spectroscopy through Liquid Layers



Schematic of liquid cell EELS and core-loss EEL spectra from $LiMn_2O_4$ acquired in the cell either "dry" or in the solvent (dimethyl carbonate).

Work performed as User Project at the Center for Nanophase Materials Sciences, ORNL

Scientific Achievement

Quantitative electron energy loss spectroscopy (EELS) determines the oxidation state of battery electrode materials within a battery solvent (*in situ* liquid cell TEM).

Significance and Impact

Tracking oxidation state changes in Li-ion battery electrodes is essential to understanding electrochemical redox processes and the mechanisms controlling cycle life and capacity fade. This work presents a method to determine oxidation states of electrode materials within liquid environments using core-loss EELS $L_{2,3}$ white-lines.

Research Details

- Low-loss and core loss spectra are acquired simultaneously for $LiMn_2O_4$ in the battery solvent dimethyl carbonate.
- The $L_{2,3}$ white-line intensity ratio determines the mixed $Mn^{3+/4+}$ oxidation state in $LiMn_2O_4$.

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Narrative Highlight Text:
EELS results from liquid cell microscopy demonstrate the ability to obtain quantitative chemical information from battery electrode materials during *in situ* ec-S/TEM experiments. We show that the oxidation state of TMs in thin film battery electrodes can be directly determined using either peak fitting or the white-line intensity ratio method even when the materials are exposed to an organic battery electrolyte solvent. These results have important implications for future in situ ec-S/TEM experiments, with an achievable goal to use ''closed-form'' in situ electrochemical liquid cells to cycle battery materials within organic battery electrolytes, track electrochemical redox processes and image structural changes during electrochemical cycling. The influence of electron dose on chemical modifications of the electrode and electrolyte must be understood and accounted for, in order to separate electron beam effects from quantifiable EELS measurements. Understanding the evolution of battery materials at the nanoscale can lead to an improved understanding of electrode degradation mechanisms for a wide range of electrochemical energy storage and conversion systems.

Reference:
"Probing Battery Chemistry with Liquid Cell Electron Energy Loss Spectroscopy"
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