In situ Nanoscale Imaging and Spectroscopy of Energy Storage Materials

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Rechargeable lithium ion batteries have become a vital electrical energy storage technology that finds applications ranging from portable electronic devices to electric vehicles. During electrochemical cycling, there are degradation mechanisms at play that affect performance characteristics, leading to a reduction in cycle-life and overall device failure. These mechanisms can be pinpointed to nanoscale structural and chemical changes that occur at the electrode/electrolyte interface or at interfaces within the electrode; therefore, it is important to understand these processes at the nanoscale and within a liquid battery electrolyte during electrochemical cycling. Understanding these complex electrochemical processes has been challenging; however, continued advances in *in situ* electrochemical scanning transmission electron microscopy (ec-STEM) has demonstrated the feasibility to perform quantitative electrochemical measurements [1] that can be directly correlated with dynamic imaging of solid electrolyte interface (SEI) formation [2-3] and lithium metal dendrite formation mechanisms [4-6].

In the first part of this study, we show how *in situ* ec-STEM is being used to investigate the mechanisms of lithium metal deposition from a 1.2M $LiPF_6$ EC:DMC battery electrolyte using imaging and spectroscopy [4]. Figure 1a shows a sequence of annular dark-field (ADF)-STEM images that capture the initial stages of lithium metal dendrite nucleation and growth on the edge of a glassy carbon working electrode during cyclic voltammetry experiments below -3.0V vs. Pt_{pseudo} reference electrode. In ADF-STEM images, the lithium dendrites are dark compared to the background because they are less dense than the surrounding electrolyte. The Li dendrites grow with a globular morphology during a sequence of bursts, whereby newly formed lithium metal deposits are passivated by the SEI followed by additional growth events associated with localized regions of SEI breakdown. Figure 2a shows ADF-STEM images of the lithium dendrites in the liquid cell filled with the 1.2M $LiPF_6$ EC:DMC electrolyte. When the liquid is displaced, the same globular lithium dendrites collapse, and we observe a contrast reversal as the dendrites become brighter compared to background; this results from electron scattering through the denser lithium compared to the silicon nitride membrane and the glassy carbon working electrode (refer to Figure 2b). Electron energy loss spectroscopy confirmed that the deposits are lithium metal and that their surface is composed of inorganic compounds commonly found in the SEI (Figure 2c). The EEL spectra reveal a Li metal plasmon peak at 7.5eV and a characteristic LiF spectral feature on the Li K-edge at 55eV.

In the second part of this work, we show how EELS is used to track the oxidation changes of battery electrodes within the liquid cell since electrode materials undergo changes in oxidation states during lithiation and delithiation [7]. For these experiments, radio frequency magnetron sputtering was used to deposit a thin layer of $LiMn_2O_4$, a commonly used battery cathode material, directly onto the silicon nitride membrane of the cell. Simultaneous low-loss and core-loss EEL spectra were acquired with and without the presence of dimethyl carbonate (DMC) in the liquid cell (Figure 3c). The low-loss portion of the EEL spectra confirms the presence of the DMC within the liquid cell and aides in the quantification of fluid layer thickness. If the fluid layer thickness is small, it is possible to extract and analyze the Mn $L_{2,3}$-edge for quantification of the Mn oxidation state using the "white-line" intensity ratio method. We

measure mixed $Mn^{3+/4+}$ oxidation in the as-deposited $LiMn_2O_4$, which shifts to a lower oxidation state when DMC is present in the cell, suggesting that $LiMn_2O_4$ can be prone to electron beam induced chemical reduction when immersed in a battery electrolyte during *in situ* experiments. Further efforts are underway to explore how additives and electrochemical cycling protocols can be applied to suppress Li dendrite nucleation and growth and how STEM-EELS can be used to image and analyze evolving structural and chemical changes within battery electrodes within the *in situ* ec-STEM platform [8].

References:
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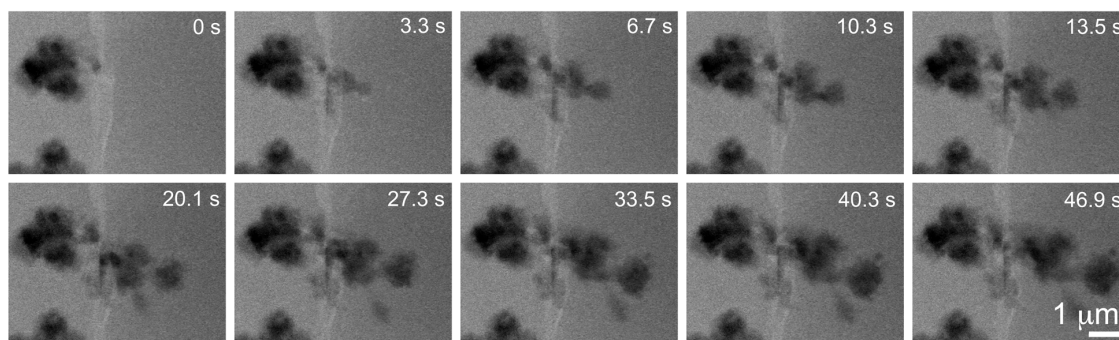
Figure 1. Sequence of ADF-STEM images showing the initial stages of lithium dendrite nucleation and growth from a glassy carbon working electrode from 1.2M $LiPF_6$ EC:DMC electrolyte [4].
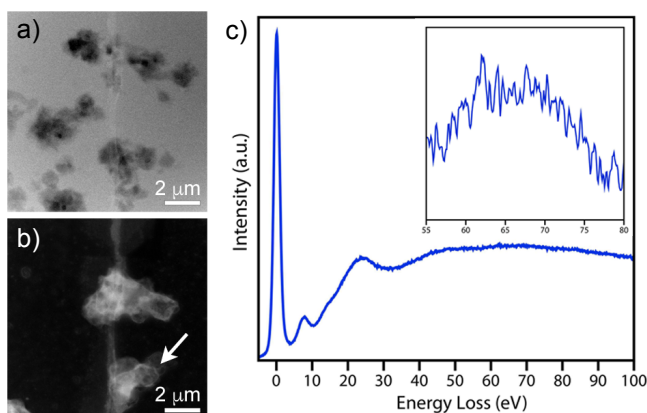
Figure 2. a) ADF STEM image of Li dendrites immersed within 1.2M $LiPF_6$ EC:DMC. b) ADF STEM image of Li dendrite without electrolyte. c) EEL spectra from marked region in b revealing characteristic feature s of a Li plasmon at 7.5 eV and LiF at 55 eV [4].
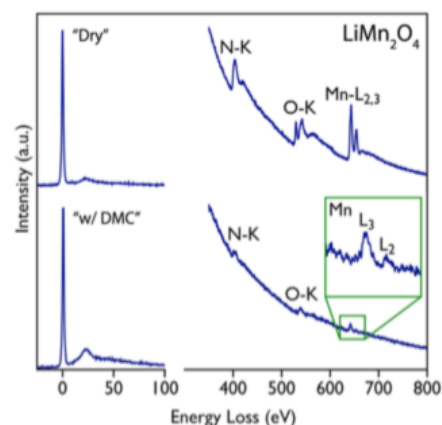
Figure 3. Experimental low-loss and core-loss EEL spectra of RF magnetron sputtered and annealed $LiMn_2O_4$ thin film within the *in situ* ec-STEM liquid cell. Data acquired from the ''dry'' cell (top spectra) and with DMC solvent (lower spectra) [7].