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Li ion nanowire batteries and their *in situ* characterization in the TEM

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The ability to measure the morphological, chemical, and transport characteristics with nanoscale resolution in electrochemical energy storage devices is critical for understanding the complex interfacial reactions and phase transformation that accompany cycling of secondary batteries. In this talk I will describe the use of an all-nanowire Li ion battery for *in situ* characterization of charge and discharge reactions. The nanowire batteries (NWBs) consist of a metalized core, a $LiCoO_2$ cathode, LiPON solid electrolyte, and a thin film Si anode. Measuring several micrometers in length and several hundred nanometers in diameter, the NWBs can be readily imaged and analyzed in transmission electron microscopes (TEM, STEM). We use focused ion beam milling and electron beam induced deposition to separate the cathode and anode and fabricate Pt contacts to a NWB. *In situ* electrical cycling of NWBs in TEM reveals that the most of the structural changes due to cycling happens in the electrolyte layer especially near the cathode/electrolyte interface. Electrical response from a single NWB was measured in the sub-pA range. For NWBs with the thinnest electrolyte, approximately 100 nm, we observe rapid self-discharge, along with void formation at the electrode/electrolyte interface, indicating electrical and chemical breakdown. The analysis of the NWB's electrical characteristics reveals space-charge limited electronic conduction, which effectively shorts the anode and cathode electrodes. When the electrolyte thickness is increased, the self-discharge rate is reduced substantially and the NWBs maintain a potential above 2 V. Our study illustrates that at reduced dimensions the increase in the electric field can lead to large electronic current in the electrolyte effectively shorting the battery even when the electrolyte layer is uniform and pinhole free. The scaling of this phenomenon provides useful guidelines for design of 3D Li ion batteries.