Deleterious Phase Transitions in Lithium Intercalation Electrodes

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The stability of intercalation compounds used as electrodes in lithium batteries is one of the most important factors contributing to high capacity and long cycle life. Both anode and cathode materials undergo undesirable phase transformations when the limits of reversible insertion or deinsertion are exceeded. The changes may be rapid, or may only occur during long-term storage in extreme states of charge or discharge. All of the commonly used cathode materials, for example, are unstable with respect to loss of oxygen or reaction with electrolyte components if overcharged. Other, subtler, changes may result from dissolution of transition metals from an oxide lattice or conversion to an inactive phase or mixture during overdischarging. Similarly, anode intercalation compounds and alloys may lose some reversibility due to overcharging or even partially dissolve from overdischarging.

Overcharging of the spinel cathode $LiMn_2O_4$, for example, causes significant charges in its intercalation behavior (Fig. 1). Extraction of manganese ions at potentials above 4.5 V is believed to contribute to the transformation. Oxygen loss may also occur, especially in the electrolyte breakdown regime (in this example, above 4.8 V).

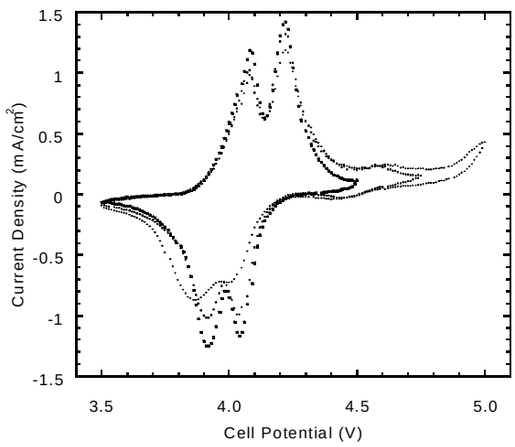

Figure 1. Deterioration of $LiMn_2O_4$ electrode due to overcharging.

The results of investigations of such transformations using X-ray diffraction, vibrational spectroscopy and microbalance techniques on composite and thin-film electrodes will be presented.

This work was supported by the Office of Science, Basic Energy Sciences, Chemical Sciences Division of the United States Department of Energy under contract No. DE-AC03-76SF00098.