In-situ Electrochemical Synchrotron Studies on Lithium Ion Battery Materials

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The lithium ion battery is one archetype of system whose performance and durability have significantly benefitted from of synchrotron radiation studies. Advanced X-ray techniques with synchrotron radiation are demonstrated on lithium battery materials. 1) LiMn\(_{2}\)O\(_{4}\) spinel and related ceramic materials are used as cathodes. Structural changes during (dis-)charging are monitored in-situ with XANES, EXAFS, and ASSAX. Upon charging with lithium, manganese oxide undergoes a phase transformation (Vorhey transition cubic → tetragonal), which is considered a major origin of electrode failure. 2) Lithium, the anode material, has been quite elusive with respect to X-ray characterization. Soft X-ray NEXAFS, X-ray Raman and Resonant X-ray Scattering (RIXS) data on relevant Li-complexes are presented. 3) Comparison of Mn (Li\(_2\)L\(_3\)X) absorption and k-\(_{\text{sp}}\) spectroscopy data reveal that the surface of the spinel primary particles is affected by electrode preparation, prior to any electrochemical cycling. 4) Mn-L\(_3\)M\(_3\) EXAFS spectroscopy on cathode sliced allows deep resolved analysis of charge relaxation in the electrode. This poster gives a summary of 2 years of research involving the ALS, APS, and SSRRL.

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Introduction

Kathedral structural changes in electrodes is essential for engineers to optimize battery performance, since these changes may account for the failure of batteries. Structural changes in batteries can be monitored using in-situ electrochemical and X-ray techniques. For the present study, X-ray diffraction and spectroscopy were carried out on lithium manganese oxide LiMn\(_{2}\)O\(_{4}\), using a synchrotron-based electrochemical cell. In-situ measurements were performed using X-ray diffraction and spectroscopy, which allows for the determination of either k-space phase transitions (of the tetragonal LiMn\(_{2}\)O\(_{4}\)) or of the spinel phase transition. The calcium end member of this system, CaMn\(_{2}\)O\(_{4}\), is a relatively simple structure (space group I\(_{4}\)1/amd) which consists of a distorted face centered cubic (FCC) structure. The unit cell of CaMn\(_{2}\)O\(_{4}\) is the most closely related to the cell of LiMn\(_{2}\)O\(_{4}\). By deeply discharging the battery, excess Li is inserted into the crystal with the result that manganese is being released from an average volume of 3.5 to a volume of 7.5. The reduced presence of Mn\(^{2+}\) ions - in the tetragonal LiMn\(_{2}\)O\(_{4}\) (Vorhey transition) [2], we have monitored this transition. (dis-)charging processes, potential are varied in a specific range to obtain specific phases (with beryllium windows, together with separator, electrolyte and glass windows, together with separator, electrolyte and glass windows, together with separator, electrolyte and glass windows).

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X-ray electrochemical in-situ cell

A set-up with Li(II) electrolyte, in-cell with 0.1 M lithium electrolyte and battery material consisting of a lithium plate with lithium foil, soaked separators, O-ring, and stainless steel tape; assembled using a spectro-electrochemical battery cell. In this paper, we present the application of X-ray absorption spectroscopy to in-situ battery studies, starting with a discussion of the structure of the LiMn\(_{2}\)O\(_{4}\) spinel and the charge/discharge properties of the spinel.

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Where does the Lithium go?

In-situ XANES

Determination of oxidation state of the Mn during battery cell operation at SSRRL synchrotron BL 2.1

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Anomalous in-situ X-ray Diffraction

XRD with photon energies near the absorption edge

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Jahn-Teller Effect

The electron induces the d\(_{\uparrow}\) to d\(_{\downarrow}\) transition and introduces an exchange interaction into the exchange interaction. The split of the ground states results in a distortion of the structure and creation of a coordination polymer. All being ferroic states [2].

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References