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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) LiMn2O4 spinel and related ceramic materials are used as cathodes. Structural changes during (dis-)charging are monitored in-situ with XRD, XANES, EXAFS, and ASAXS. Upon charging with lithium, manganese oxide undergoes a phase transformation (Verwey 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 Incoherent X-ray Scattering (RIXS) data on relevant Li-compounds are presented. 3) Comparison of Mn (L2, L3) absorption and K-β spectroscopy data reveal that the surface of the spinel primary particles is affected by electrode preparation, prior to any electrochemical cycling. 4) Mn-L emission spectroscopy on cathode sliced sections allows depth resolved analysis of charge relaxation in the electrode. This poster gives a summary of 2 years of research involving the ALS, APS, and SSRL.

Introduction

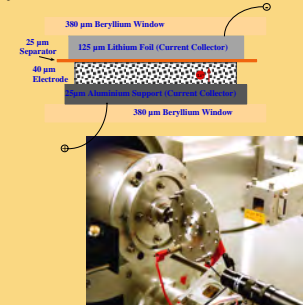
Knowledge of structural changes in electrodes is essential for engineers to optimize battery performance, since those changes may account for the failure of batteries. Structural changes in batteries can be monitored using in-situ electrochemical and X-ray techniques. In the present study, X-ray diffraction and spectroscopy were carried out on lithium manganese oxide LiMn₂O₄ using a spectro-electrochemical battery cell. In manganese oxide based electrodes, the Mn³⁺ is the Jahn-Teller ion which causes a tetragonal Jahn-Teller distortion [1] of Mn-O octahedra in the unit cell of LiMn₂O₄. By deeply discharging the battery, excess lithium is inserted into the crystal with the result that manganese is being reduced from an average valence of 3.5 to a valence of 3. The enhanced presence of Mn³⁺ causes - via the Jahn-Teller effect - a phase transformation in the spinel from cubic to tetragonal (Verwey transition, [2]). We have monitored this transition with XRD and EXAFS. Our recent efforts to utilize anomalous scattering in small angle scattering [3] were also extended to XRD. Attempt was made to utilize anomalous scattering in order to distinguish different phases. More exotic techniques like X-ray Raman and RIXS were used to detect the elusive lithium.

X-ray Electrochemical in-situ cell

A 40 μm thick LiMn₂O₄ electrode, mixed with 10% carbon and cast on aluminum foil, assembled in a spectro-electrochemical cell with beryllium windows, together with separator, electrolyte and lithium counter electrode (Fig.1). A portable potentiostat was used to lithiate the manganese oxide electrode at a constant current of 50 μA, at potentials between 3.05 and 1.5 Volts.

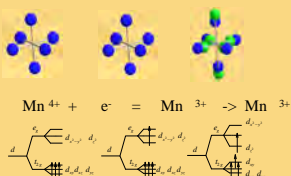


Figs. 1: Upper left: Disassembled cell after usage - polypropylene plate with lithium foil, soaked separators, O-ring, and stainless steel plate with O-rings and electrode assembly (black disk) in its center. Lower left: Front view of polypropylene plate, showing O-rings, beryllium plate covered with kapton tape; assembled cell, ready for use. Unique cell design permits long term experiments without contamination of the cell interior (> 7 days). Middle: Potentiostat, Laptop and digital Multimeter, displaying 2.97 open circuit potential of in-situ cell in SSRL BL 2-1 hutch. Right: Cell assembled at BL 2-1 diffractometer and wired to potentiostat.



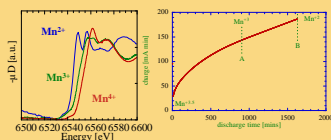
Jahn-Teller Effect

The occupies the d³ ion (Mn⁴⁺) to a d⁴ ion (Mn³⁺) and occupies the e_g level, if the splitting ΔE between t_{2g} and e_g is smaller than the exchange interaction. The split of the ground state degeneracy goes along with a tetragonal distortion of the octahedral coordination polyeder, ΔE being the driving force [1].



in-situ XANES

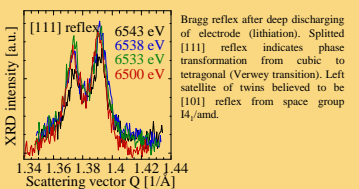
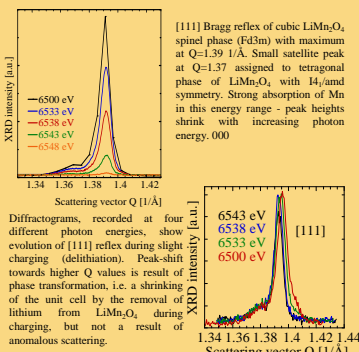
Determination of oxidation state of the Mn during battery cell operation at SSRL synchrotron BL 2.1



Left: XANES at Mn K-edge taken in-situ during deep discharge (red: cell at open circuit, LiMn₂O₄, V₀=3.05 Volt; green: Li₂Mn₂O₄; blue: over(dis)charged, Mn³⁺). Chemical shift of spectra towards lower energies indicates change of valence state of Mn (reduction) and is used for chemical calibration [4]. Spectra also used for determination of atomic form factor f(E) for ASAXS. Right: evolution of charge.

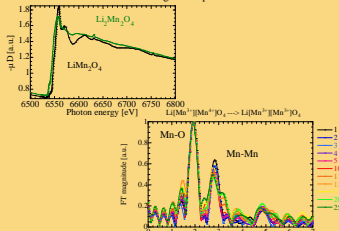
Anomalous in-situ X-ray Diffraction

XRD with photon energies near the absorption edge



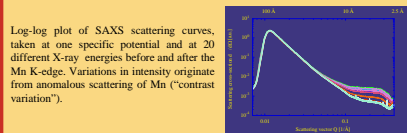
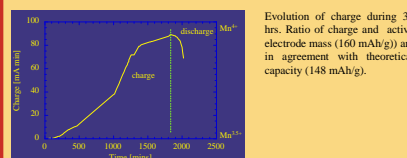
in-situ EXAFS

EXAFS spectra of LiMn₂O₄ and Li₂Mn₂O₄ reveal that structural changes coincide with the reduction of manganese upon electrochemical lithiation.

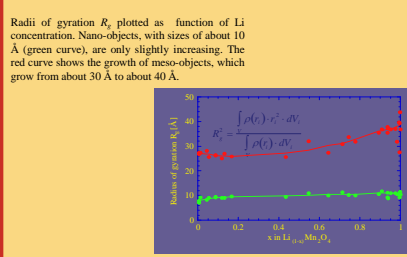


Fourier transformed EXAFS of Li_{23/40}Mn₂₀O₄₀ for 1 ≤ n ≤ 25 recorded in-situ during lithiation. Average distance between Mn and O atoms is about 1.9 Å and does not change significantly. Average distance between adjacent Mn atoms is about 2.9 Å in LiMn₂O₄. Upon lithiation, major peak shifts from 2.9 Å to 2.7 Å, but intensity of a shoulder at 3.2 Å becomes more significant, indicative to major structural changes.

in-situ Anomalous Small Angle Scattering

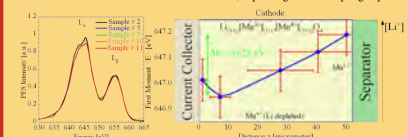


Radii of gyration R_g plotted as function of Li concentration. Nano-objects, with sizes of about 10 Å (green curve), are only slightly increasing. The red curve shows the growth of meso-objects, which grow from about 30 Å to about 40 Å.



Depth Profiling with Mn L_{2,3} Emission

Electrode of 50 micron thickness after cycling was sliced into 20 sections by using sequential, repetitive steps with Kapton tape. Tapes with Li₂Mn₂O₄ were subject to photoemission at the Mn L lines. Changes in peak height and statistical momentum are attributed to different oxidation states of Mn, depending on the sampling depth.

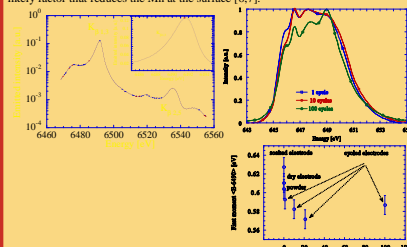


Spectra of several slices were subject to momentum analysis and revealed concentration variation of Mn species along the thickness of the electrode. Potential relaxation of charge states after cycling might be a potential cause [8].

Bulk/Surface Sensitivity

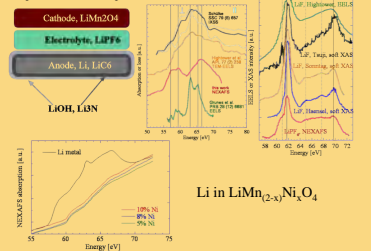
- Mn K-β_{1,3} Emission vs. Mn L₂ (2p) Absorption -

NMR data gave an inconclusive picture on changes of the LiMn₂O₄ during electrochemical treatment. Parallel studies with bulk-sensitive hard (K-β emission) and surface-sensitive soft (L-edge) X-ray spectroscopy revealed that the surface of the LiMn₂O₄ primary particles becomes already reduced during electrode fabrication, prior to any electrochemical treatment. Binding with carbon is the likely factor that reduces the Mn at the surface [6,7].



Where does the Lithium go ?

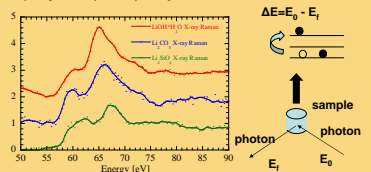
Li is contained in anode, cathode, and electrolyte. Not much known about Li from direct X-ray measurements. Too few electrons. Here some reference compounds NEXAFS spectra [11].



Li (1s) absorption edge at 54.7 eV. Signals not easy to make out, in particular not near strongly absorbing environment. Bulk difficult to probe. Li metal and Li-rich compounds can be measured.

Lifting Light Element info out of Bulk

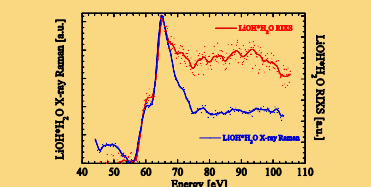
X-ray Raman spectroscopy with hard X-rays (large penetration depth) allows to probe light elements like Li or C with bulk sensitivity, and is in some way complementary to X-ray absorption [5].



Li uncoupled in terms of X-ray experiments. NEXAFS spectra of various compounds do not show much differences, although characteristic features can be made out. Similar situation with corresponding X-ray Raman spectra [12].

Resonant X-ray Raman (RIXS)

Photo excitation energy close to the K-edge threshold energy allows for the resonant X-ray Raman effect. RIXS experiments are relatively novel and require 3rd generation synchrotron radiation sources and high resolution analyzers and detectors. Not only light elements are of interest, but also 3d [13]. With an instrumentation resolution of 10-50 meV, interatomic magnetic interactions in relevant systems such as perovskites could be studied, which are important for magnetoresistance and solid oxide fuel cells, for instance.



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