

Oxidation state changes of Mn in lithium battery electrodes during electrode preparation

Artur Braun ^{a)}, Uwe Bergmann ^{b)}, Hongxin Wang ^{b,c)}, Pieter Glatzel ^{b)}, Tobias Funk ^{b)},
Michael C. Tucker ^{d)}, Stephen P. Cramer ^{b,c)}, and Elton J. Cairns ^{a,d)}

^{a)} Environmental Energy Technology Division, E.O. Lawrence Berkeley National Laboratory, Berkeley, CA 94720

^{b)} Physical Biosciences Division, E.O. Lawrence Berkeley National Laboratory, Berkeley, CA 94720

^{c)} Department of Applied Science, University of California, Davis, CA 95616

^{d)} Dept. of Chemical Engineering, University of California, Berkeley, CA 94720

INTRODUCTION

Lithiummanganate (LiMn_2O_4) was studied with X-ray absorption and emission spectroscopy. Particular attention was paid to changes in the spectra of samples during the electrode manufacturing and cell assembly processes, as well as to electrodes, operated for various numbers of cycles. Results reveal consistently that changes in the oxidation state of the manganese occur even between preparation of the electrode and assembly into the cell, prior to charging and discharging. Also, from the evolution of the spectra we can conclude that during cycling the manganese is being oxidized towards a more Mn^{4+} -like species, regardless a subsequent electrochemical reduction.

EXPERIMENTAL

LiMn_2O_4 was prepared from a stoichiometric mixture of Li_2CO_3 (J.T. Baker) and MnO_2 (Japan Metals, CMD). The mixture was fired at 850°C in air for 20 hours, then removed from the furnace and cooled down in ambient atmosphere.

Electrodes were prepared by dispersing above mentioned spinel, acetylene black (Shawinigan), graphite (Timcal), and poly(vinylidene fluoride) (PVDF, Elf Atochem) (90:2:4:4) in n-methyl pyrrolidinone (NMP, Aldrich). For the electrodes to be used for X-ray studies, a smaller quantity of the dispersion was cast onto aluminium foil and dried at 150°C for 40 minutes, resulting in a final electrode thickness of approximately 50 μm . Electrodes were punched out and dried overnight at 100°C under vacuum before being transferred to a helium-filled glovebox for cell assembly. Cells were prepared by sandwiching a spinel electrode against a lithium foil with Celgard 3401 (DuPont) separator and flooded with 1M LiPF_6 in ethylene carbonate/dimethyl carbonate (1:2) (EM Industries) electrolyte in a stainless steel Swagelok union. Cell cycling was performed using an Arbin battery tester. Cells were cycled between 3.3-4.4V at a C/15 rate, with 30 minute open circuit periods between half cycles. After cycling, all samples were returned to a nominal composition of $\text{Li}_x\text{Mn}_2\text{O}_4$ by discharging to 3.05V and letting the current decay to less than $0.1\mu\text{A}/\text{mg}$. Electrochemical lithium extraction was achieved by charging to 4.4V and letting the current decay to less than $0.1\mu\text{A}/\text{mg}$. After electrochemical preparation, electrode samples were washed with acetonitrile to remove excess electrolyte.

K-Beta emission spectroscopy was performed at the Stanford Synchrotron Radiation Laboratory (SSRL) at beamline 10.2 with a homebuilt high-resolution spectrometer (7). The excitation energy was set constant to 11,000 eV. $K_{\beta(1,3)}$ and $K_{\beta(2,5)}$ emission spectra were recorded in the range from 6465 eV to 6555 eV. All spectra were normalized to their integrated intensity. For further data analysis, the first moment $\langle E \rangle$ of the emitted intensity of the $K_{\beta(1,3)}$ band was determined in the range from $E_a=6485$ eV to $E_b=6495$ eV:

L-edge absorption spectroscopy on samples from the same batch was performed at the Advanced Light Source (ALS) in Berkeley at beamline 4.0.2, using the total electron yield technique to record absorption spectra in the energy range from 640 eV to 665 eV. The manganese L(III) absorption edge is found at about 645 eV. The spectra were normalized to their maximum peak height. Integration was carried out from 643 eV to 655 eV.

We point out that due to the small penetration depth of these low energy photons (1 micron for manganese oxide) and the even smaller mean free path of electrons in solids (about a few nanometer), this technique can be considered as surface sensitive, while the K_{β} spectroscopy is predominantly bulk-sensitive.

RESULTS

K_{β} Spectroscopy:

Figure 1 displays the emission spectra of the spinel powder (solid line) and of an electrode (dashed line), which had been charged to 4 Volt. The $K_{\beta(1,3)}$ spectrum of the charged electrode is shifted to a somewhat lower energy than the spectrum of the powder. This indicates that the manganese in the partially charged electrode is present at a higher average valence than in the powder. As a general rule in our K_{β} experiments, a shift of about 0.28 eV accounts for one valence unit.

For a better view, the $K_{\beta(1,3)}$ region is magnified and shown in the inset. We have also analyzed an electrode sample which was soaked with electrolyte and then dried, as well as samples which were charged and discharged between 4.3 Volts and 3.05 Volts for 1, 10, 21, and 100 cycles. The moment analysis results are summarized and displayed in Figure 2, which shows the first moment $\langle E \rangle$ versus the number of cycles.

For cycles 1, 10 and 21 a systematic decay of $\langle E \rangle$ is obvious, which means that the manganese is being oxidized towards Mn^{4+} as a result of cycling, although the electrode was discharged to 3.05 Volts for all samples. This reduced first moment is not recovered after the sample is cycled for a 100 times. On the other hand, we observe during the stages "powder \rightarrow electrode \rightarrow soaked electrode", that the manganese in the sample is being reduced, because their corresponding $K_{\beta(1,3)}$ emission spectra are shifted towards higher energies. These stages are noted accordingly for the samples, which are assigned 0 cycles in Figure 2.

L-edge XANES Spectroscopy:

The findings from the bulk-sensitive x-ray emission experiment at 6.5 keV are in general verified by the more surface-sensitive XANES at 650 eV. Figure 3 displays the X-ray near edge spectra (XANES) of the powder, dry electrode and electrolyte soaked electrode. The L(III) absorption edge is located at about 645 eV.

The edge position of the powder sample is found at a slightly higher energy than the edge of the dry electrode sample. The soaked electrode sample has its edge at the lowest energy. Note that in absorption spectroscopy, the adsorption edge of an oxidized species is shifted towards a somewhat higher energy

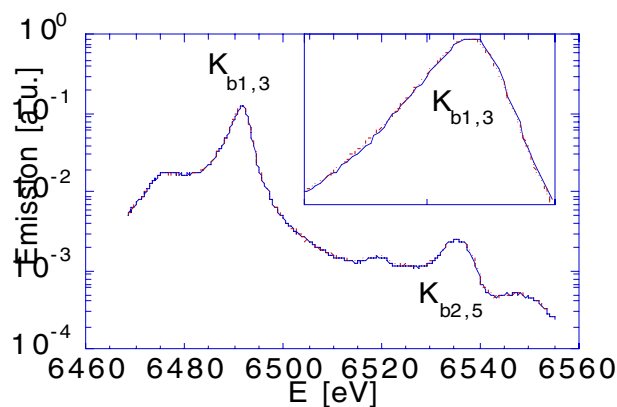


Figure 1. K-Beta emission spectra of manganese from a powder sample (solid line) and an electrode (dashed line) kept at 4 Volt. The inset shows a magnification of the K-Beta 1,3 peak.

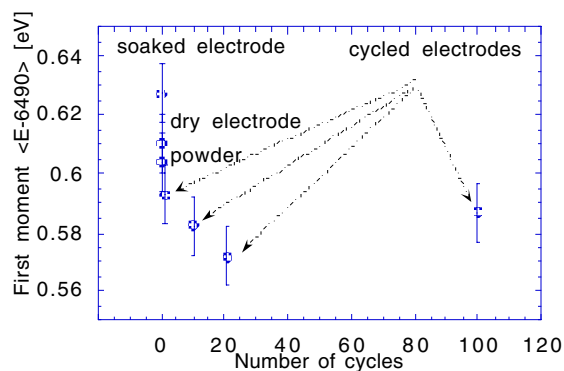


Figure 2. Moment analysis of the intensity arising from the $K_{\beta(1,3)}$ transition in the range 6485 – 6495 eV.

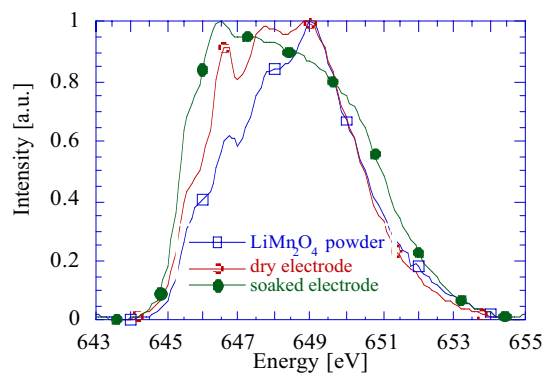


Figure 3. Manganese L-edge absorption spectra of powder, dry electrode, and soaked electrode. Shown are the L(III) edges.

than that of the reduced species. Even more pronounced is the position of the intensity maximum of either spectrum, which reflects the fact that the manganese in the samples is reduced during electrode/cell processing.

The first moment $\langle E \rangle$ of the powder sample (Figure 5) represents the largest value among all samples so far. The soaked and dry electrodes have a smaller value of $\langle E \rangle$, which means that the manganese they contain has become reduced. The sample cycled only once and discharged to 3.05 Volt has a value for $\langle E \rangle$ even lower than the non-cycled sample (XANES shown in Figure 4). However, upon further cycling (10 and 100 cycles), the $\langle E \rangle$ values increase again, indicating that the manganese in the samples is becoming oxidized towards a Mn^{4+} valence.

DISCUSSION

The fact that the manganese becomes partially reduced during electrode processing could have its origin in the addition of carbon and polymer to the spinel powder or exposure to organic electrolyte. The reduction inferred so far should be located at the surface of the spinel grains, because this is the interface between reductive agents (carbon, polymer, organic electrolyte solvent) and the electrode active material. Considering the X-ray emission and absorption spectra, we find that the more surface sensitive L-edge experiment reflects valence changes even more pronounced than the bulk sensitive emission experiments at higher X-ray energies. This result is consistent with the picture that reduction of manganese during electrode preparation occurs at the surface of the spinel grains. The remaining oxidized manganese Mn^{4+} during and after cycling may have its origin in structural fatigue of the spinel material, as reported for instance by Thackeray et al. (8).

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Principal investigator: Stephen P. Cramer, Physical Biosciences Division, Ernest Orlando Lawrence Berkeley National Laboratory. Email: cramer@cramer.batnet.com. Telephone: (510)495-2052

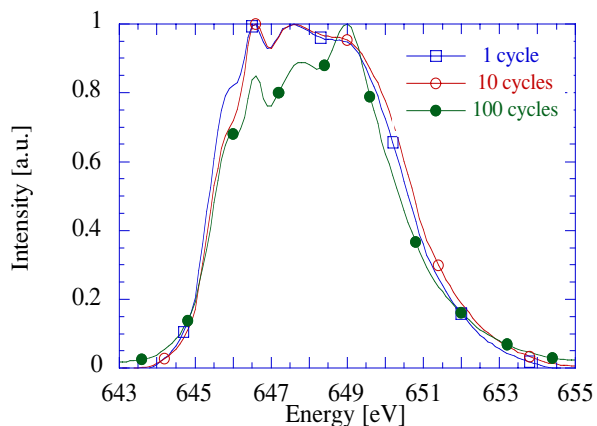


Figure 4. Manganese L-edge absorption spectra of cycled electrodes (1, 10, and 100 cycles). Shown are the L(III) edges.

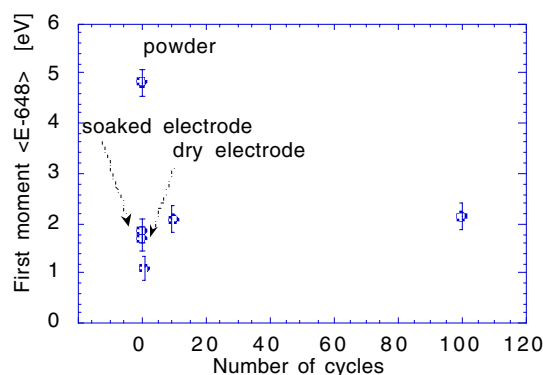


Figure 5. Moment analysis of the absorption arising from the L(III)-edge transition in the range 643 – 655 eV.