Origin of chemical shift of manganese in lithium battery electrode materials—a comparison of hard and soft X-ray techniques

A. Braun[a,*], HongXin Wang[b,c], U. Bergmann[c], M.C. Tucker[d],
Weiwei Gu[b,c], S.P. Cramer[b,c], E.J. Cairns[a,d]

[a]*Ernest Orlando Lawrence Berkeley National Laboratory, Environmental Energy Technologies, One Cyclotron Road, Berkeley, CA 94720, USA*
[b]*Department of Applied Sciences, University of California at Davis, One Shields Avenue, Davis, CA, 95616, USA*
[c]*Ernest Orlando Lawrence Berkeley National Laboratory, Physical Biosciences, One Cyclotron Road, Berkeley, CA 94720, USA*
[d]*Chemical Engineering Department, University of California at Berkeley, Gilman Hall, Berkeley, CA 94720, USA*

Abstract

L-edge X-ray absorption near edge spectroscopy and K_β emission spectroscopy were applied to monitor ex situ chemical valence changes of manganese in battery electrode materials as they appear during electrode processing and battery operation. We found that significant chemical shifts of the spectra occur already during electrode fabrication, prior to any electrochemical treatment. Employment of these two different techniques allows for the qualitative separation of contributions originating from the surface and from the bulk of the electrode particles. Published by Elsevier Science B.V.

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1. Introduction

The search for environmentally friendly and cheap rechargeable battery electrode materials with a high cycling stability is an ongoing quest. Numerous X-ray spectroscopy studies on as-prepared electrode powders and, to a growing extent, in situ studies of assembled electrodes have been published in the recent years, not least because X-ray spectroscopy permits the determination of the oxidation states of elements present in the electrodes and thus to distinguish between electrochemically active and passive species.

The origins of valency changes in atoms may be manifold, however, and not always caused by the intended electrochemical reactions, but by unintended side reactions, for example. Also, the data obtained by either of the various X-ray techniques applied, need not necessarily be representative for the entire material.

The information depth of X-ray techniques depends directly on the wavelength of the X-rays. While soft X-rays may be very surface sensitive, hard X-rays are predominantly bulk-sensitive. In the present paper, we want to address both of these issues.

During electrode fabrication, the lithium manganese oxide spinel may become reduced by mixing it with carbon-one of the most important reduction agents in technology—and the binder and organic electrolyte. This reduction may be confined to the surface of the spinel particles, since this is the major part exposed to the reduction agents. Neglecting such an effect could result in a misinterpretation of data, in particular when a pronounced surface sensitive technique such as X-ray photoelectron spectroscopy or soft X-ray absorption is applied.

A complex system such as a battery electrode allows for the application of both techniques for various reasons. In particular, the intercalation of lithium ions in the manganese spinel host is a solid state chemical reaction which takes place in the entire spinel particle.

Since a particle size is typically not less than 1 μm, and electrodes made from them are often as thick as 50 μm or even up to 1 mm, a bulk-sensitive technique has to be employed. On the other hand, the spinel particles are exposed to electrolyte and binder and carbon and may chemically react with them, and these reactions are confined to the surface of the particles, while it may remain open how *deep* this surface reaction really may go into the core of the particle.

We have therefore prepared and cycled electrodes and measured the material at various processing stages [2] with X-rays of 650 and 6500 eV photon energy; those are the

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energies for the manganese absorption L-edge and K_β emission lines;

We found that the results exhibit a similar trend for both techniques. But significant differences were also found and could be attributed to surface located reactions.

2. Experimental

2.1. Sample preparation

$LiMn_2O_4$ was prepared from a stoichiometric mixture of Li_2CO_3 and MnO_2 and blended with carbon black, graphite and binder to obtain an electrode, as described in [1]. The oxide particles, as obtained by the sintering method, have a diameter of about 1 μm. Those electrodes were dried for 24 h at 100 °C under vacuum before being transferred to a helium-filled glovebox for cell assembly. $LiPF_6$, dissolved in dimethyl carbonate, was used as an electrolyte. Battery cells were prepared in the helium filled glovebox and then cycled between 3.3 and 4.4 V. One single electrode was soaked with electrolyte for 24 h, but not assembled in a cell. After cycling, the samples were returned to a nominal composition of $LiMn_2O_4$ by discharging to 3.05 V.

After electrochemical preparation, electrode samples were washed with acetonitrile to remove excess electrolyte.

2.2. X-ray spectroscopy

K_β emission spectroscopy was performed at the Stanford Synchrotron Radiation Laboratory (SSRL) at beamline 10.2 with a homebuilt high-resolution spectrometer [3,4]. The excitation energy was set constant to 11,000 eV. $K_{\beta1,3}$ and $K_{\beta2,5}$ emission spectra were recorded in the range from 6465 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 $I(E)$ of the $K_{\beta1,3}$ band was determined in the range from $E_a = 6485$ eV to $E_b = 6495$ eV:

$$\langle E \rangle = \frac{\int_{E_a}^{E_b} I(E)\, E\, dE}{\int_{E_a}^{E_b} I(E)\, dE} \tag{1}$$

The same samples were subject to L-edge absorption spectroscopy 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 to 665 eV [5]. The manganese L_{III} absorption edge is found at about 645 eV. The spectra were normalized to their maximum peak height. Integration as to Eq. (1) was carried out in the energy range from 643 to 655 eV.

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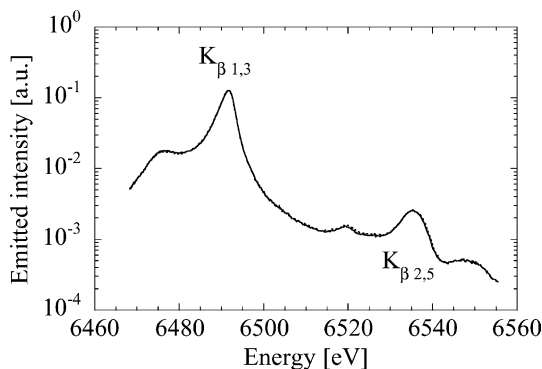

Fig. 1. Manganese K_β emission spectra of a cycled and uncycled electrode.

3. Results

Fig. 1 displays the K_β emission spectra of a cycled electrode (dashed line), which had been charged to 4.4 V and subsequently discharged to 3.05 V, and of the spinel powder (solid line), which had not at all been electrochemically treated.

The spectrum of the cycled electrode is slightly shifted to a somewhat lower energy compared to the spectrum of the powder. This phenomenon is known as the *chemical shift*, because it is caused by a chemical reaction, this is, a reduction or an oxidation, of the element under consideration. For a better view, the $K_{\beta1,3}$ region is magnified and plotted on a linear scale in Fig. 2. The shift indicates that the manganese in the cycled electrode is present at a higher average valency than in the powder, although this electrode had been returned to its original potential of 3.05 V.

Due to the stoichiometry of $LiMn_2O_4$, this is, $Li[Mn^{3+}][Mn^{4+}]O_4$, the average oxidation state of the manganese in the untreated spinel powder is anticipated to be +3.5. In a charged electrode, the oxidation state of the manganese is expected to be +4 [1]. By subsequent discharging, the manganese generally can be returned to its original oxidation state [1].

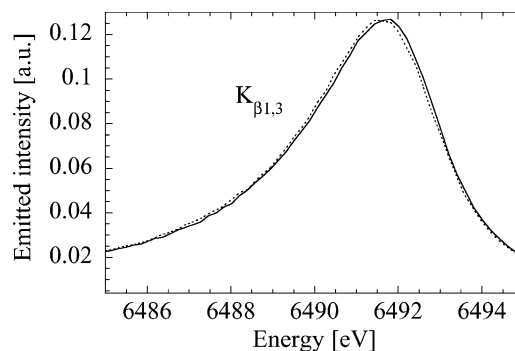We have also analyzed one electrode sample which was soaked with electrolyte and then dried, but not charged or

Fig. 2. Magnified manganese $K_{\beta1,3}$ emission spectra of a cycled (dashed line) and uncycled electrode from Fig. 1.
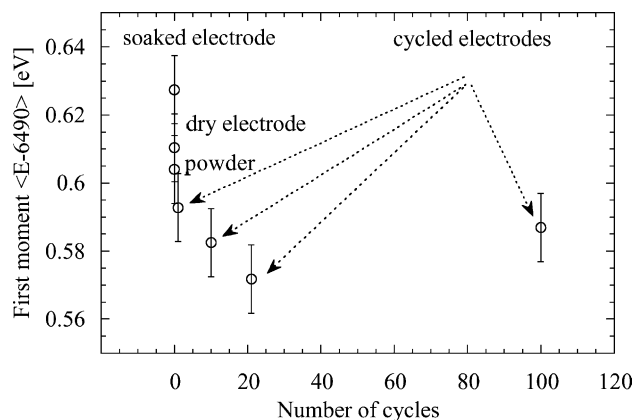
Fig. 3. First momentum $\langle E \rangle$ of electrode samples as obtained from manganese K_β spectra. The spectrum of the cycled electrode is dashed.

discharged. Also, we have studied electrodes which were charged and discharged between 4.4 and 3.3 V for 1, 10, 21, and 100 cycles and thereafter returned to 3.05 V.

To quantify the chemical shift, the spectra were subjected to the momentum analysis, as exercised in the experimental section of this manuscript. The results are summarized and displayed in Fig. 3, which shows the variation of the first moment $\langle E \rangle$ of the emission peak energy versus the number of cycles. For better view, the origin of the abscissa is reset to 6490 eV, so that it displays the difference $\langle E - 6490 \rangle$ eV. The powder, the dry electrode and the soaked electrode are considered as samples which had not been cycled at all and thus be found at 0 cycle in Fig. 3.

For this particular technique, one valence unit accounts for an energy shift of about 0.28 eV, and since a total chemical shift of about 0.034 eV is observed, the valence change of the manganese amounts to 0.12 units from +3.5 to +3.62.

For cycles 1, 10, and 21, a systematic decrease of $\langle E \rangle$ is obvious, indicating that the manganese is being oxidized

towards Mn^{4+} as a result of cycling, although the electrode had been finally discharged to 3.05 V for all samples. This reduced first moment is not recovered after the sample was cycled for a 100 times.

But even those samples which had not been cycled experience valence changes of the manganese during electrode processing. We observe during the process stages *powder → electrode → soaked electrode*, that the manganese in the sample is being reduced, as indicated by their corresponding $K_{\beta 1,3}$ emission spectra which are shifted towards higher energies. These samples were assigned the status zero cycles, which is noted accordingly in Fig. 3.

Taking the error bars into account, the valency shows an overall variation from 0.56 to 0.64. Since in our K_β experiments a shift of about 0.28 eV accounts for one valence unit, and the spectra display an overall chemical shift of 0.08 eV, the valence change is about 0.29 electron charges.

The findings from the bulk-sensitive X-ray emission experiment at 6.5 keV are in general confirmed by the more surface-sensitive XANES at 650 eV, which will be presented now.

Fig. 4 displays the X-ray near edge spectra of the powder, dry electrode and electrolyte soaked electrode. Fig. 5 displays the spectra of the cycled electrodes. The L_{III} absorption edge of the manganese 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 higher energy 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 represents the largest value among all samples so far (Fig. 6). The soaked and dry electrodes have a smaller value of $\langle E \rangle$, which means
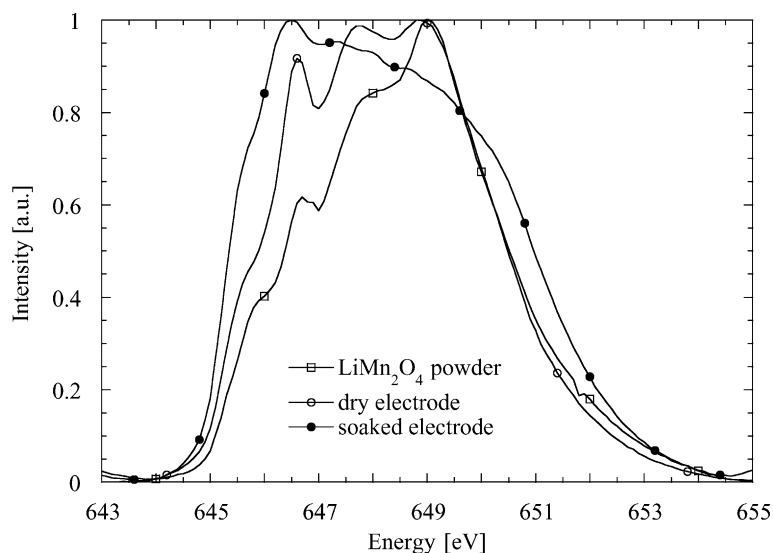

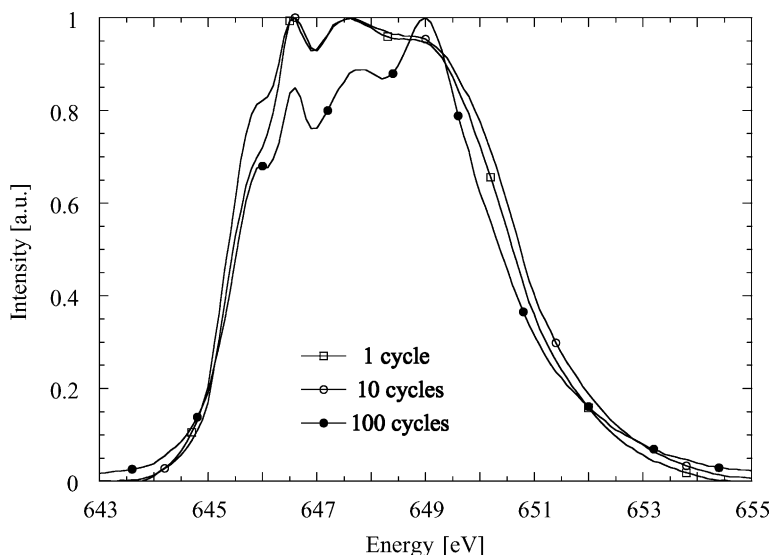Fig. 4. XANES of the uncycled electrode materials.

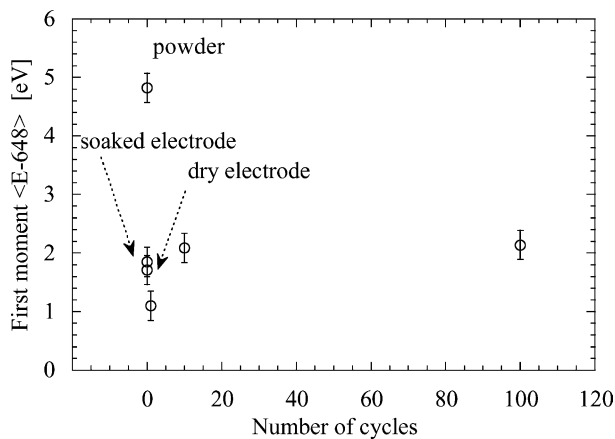Fig. 5. XANES of the cycled electrode materials.

Fig. 6. First momentum $\langle E \rangle$ as obtained from manganese L-edge spectra.

that the manganese they contain has become reduced. The sample cycled only once (Fig. 5) and discharged to 3.05 V has a value for $\langle E \rangle$ even lower than the non-cycled sample (XANES shown in Fig. 4). However, upon further cycling (10 and 100 cycles, Fig. 5), the $\langle E \rangle$ values increase again, indicating that the manganese in the samples is becoming oxidized towards a Mn^{4+} valence.

4. Discussion

In $LiMn_2O_4$, the manganese is present to equal quantities as Mn^{3+} and Mn^{4+}. Upon charging to 4.4 V, about 90% of the lithium is being removed from the spinel lattice, and, therefore, the major part of the manganese is present with the oxidation state Mn^{4+}. Reversely, discharging to 2.5 V inserts more lithium in the spinel lattice so that the manganese is reduced towards Mn^{3+}.

The variation of the average oxidation state upon charging and discharging can be monitored using XANES [1], for

instance. 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 and exposure to organic electrolyte. The reduction inferred so far should be located at the surface of the spinel particles, 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 is confined to the surface of the spinel particles. The occurrence of residual oxidized manganese Mn^{4+} during and after cycling may have its origin in structural fatigue of the spinel material, which has become isolated from the electrochemically active electrode matrix and thus remains in a final oxidized state, as reported for instance by Thackeray et al. [6]. Another potential cause could be due to Li-for-Mn ion exchange, as reported by Blyr et al. [7].

5. Conclusions

We found evidence that the electrode manufacturing process alters the surface of manganese spinel particles in such a way that it is reduced, while its bulk remains predominantly unaffected. Neglecting this effect may result in misinterpretation of X-ray spectroscopic data, in particular when surface sensitive techniques, such as soft X-rays, are employed. This can be even worse, when the bulk manganese experiences significant alterations in its oxidation state, while the oxidation state of the manganese in the surface region would be pinned by the reduction agents in the vicinity of the surface. Often, the only samples that are

considered in a series are the as-prepared spinel powder and cycled electrodes, which were not only electrochemically reduced and oxidized, but who also were blended with electrode typical additives such as carbon, binder and electrolyte.

Acknowledgements

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