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Local structure modification in lithium rich layered Li-Mn-O cathode material

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Abstract. X-ray absorption spectroscopy (XAS) is applied to study the local geometry of Co, Ni, and Mn sites in a new high voltage cathode for lithium batteries. The material is a solid solution between Li_2MnO_3 and $Li_{(x)}Mn_{0.4}Ni_{0.4}Co_{0.2}O_2$. The XAS technique has permitted to check the local atomic structure and charge associated with the metals in a series of electrodes with different lithium concentration x, obtained during the first charge operation, and compared to the first discharge and a successive charge. The ex-situ XAS investigation on the initial activation of the cathode material (first charge) can be described by two separated reaction of $LiMO_2$ (M = Ni and Co) and Li_2MnO_3. The strength and limitations of the EXAFS approach in these materials is underlined.

1. Introduction

Batteries are currently being developed to power an increasingly diverse range of application, from cars to microchip [1]. Among the cathode materials, layered transition metal oxides have been investigated extensively. $LiCoO_2$ is the most important commercial material because of its very good electrochemical performance, despite its major drawbacks such as high cost, toxicity and safety problems [2]. Solid solution of layered cathode materials such as the combination of Li_2MnO_3 and $LiMO_2$ (M= Mn, Co, Ni..) have been shown as promising candidates for cheaper, higher capacity and safer cathodes for lithium batteries [3]. The presence of cobalt reduces the electrode polarization and improves the activation of the Li_2MnO_3 component, even if present in small amount, but certainly represents an issue with regard to cost. It has been reported that $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$, which can be indicated as $0.6\ Li_2MnO_3\cdot0.4LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$, delivers an initial capacity of about 250 mAh/g within the potential range extending from 2.0 to 4.8V [4]. A new high voltage layered $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.08}]O_2$ cathode material, synthesized by co-precipitation method followed by high temperature annealing at 900 ^{o}C, displays a capacity of 270 mAh/g (first cycle) at even high rate of charge with a reduction of the use of cobalt in the active material [5]. We present here the ex-situ XAS investigation [6] of the lithium-rich cathode material, $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.08}]O_2$ at different state of charge (SOC), in order to gain an understanding of the role of the three metal sites in the electrochemical redox process occurring during the initial activation. An extensive XANES and a detailed pre-edge study of such electrodes [7] during the first charge has revealed that the manganese is not taking part in the electrochemical oxidation process and a complete Ni^{2+}/Ni^{4+} and a partial Co^{3+}/Co^{4+} redox processes occur. The present paper focuses on the EXAFS characterization of the

same electrode at Mn, Ni and Co K-edges. We anticipate that the results of the EXAFS fittings has been found to be correlated to the XANES analysis.

2. Experimental

X-ray absorption Spectroscopy (XAS) spectra have been recorded at Elettra (Basovizza, Italy) at the XAFS beamline [8]. The storage ring was operated at 2.0 GeV in top up mode with a typical current of 300 mA. The data were recorded at the Mn K-edge (6539 eV), Co K-edge (7709 eV) and Ni K-edge (8333 eV) in transmission mode using an ionization chamber filled with a mixture of Ar, N_2 and He in order to have 10%, 70% and 95% of absorption in the I_0, I_1 and I_2 chambers, respectively. The white beam was monochromatized using a fixed exit monochromator equipped with a pair of Si (111) crystals. Harmonics were rejected by detuning one of the two crystal of the monochromator of 30% with respect to the maximum of the rocking curve. Internal reference of Mn, Co, and Ni foils were used for energy calibration in each scan. Spectra were collected with a constant k-step of 0.03 Å^{-1} with 3s/point acquisition time from 6330 to 7700 eV (Mn K-edge); from 7550 to 8320 eV (Co K-edge) and from 8150 to 9500eV (Ni K-edge).

The preparation of Li[Li$_{0.2}$Ni$_{0.16}$Mn$_{0.56}$Co$_{0.08}$]O$_2$ electrodes for the ex-situ XAS measurements is as follows: 10 pellets of Li-half cell were prepared (d=13mm) and cycled with C/10 (20 mA/g) to a certain potential, *e.g.*, certain capacity. The cells were then rested for a fixed amount of time before open circuit voltage (OCV) of each cell was checked. Afterwards they were disassembled, the electrodes washed with dimethyl carbonate (DMC), dried and sealed.

The EXAFS analysis has been conducted by using the GNXAS package [9]. E_0 values have been found to be displaced by several eV respect to the edge inflection point. The utilized S_0^2 values were 0.69, 0.76 and 0.84 for Mn, Co, and Ni, respectively according to the literature [10].

3. Results and Discussions

Figure 1 shows the voltage profile of the cell during charge-discharge operation. The numbered points in the curve indicates predetermined states of charge (SOC) at which cells were prepared for the XAS measurements. Point 1 represents the fresh, unchanged electrode, point 2 to 4 corresponds to the extraction of ~83, 103, 200 mAh/g capacity, and point 5 represents a fully charged electrode at 4.8V corresponding to the full ~347 mAh/g practical capacity of the electrode. Point 8 represents a fully discharged electrode at 2.6 V after one complete cycle. Point 9 and 10 were taken on the second charge process.
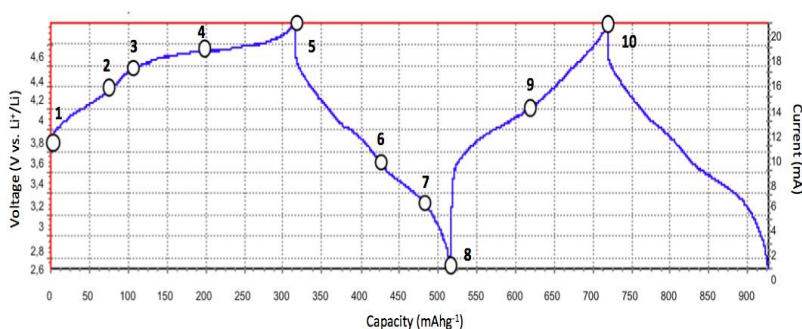

Figure 1. Voltage profile of two successive charge and discharge curves of Li-rich NCM at 20mA/g. Representative points of 1-10 in the process of XAS measurements are indicated. Reference and counter electrode: Li. electrolyte: 1 M LiPF$_6$ in EC/DMC.

The active material, Li[Li$_{0.2}$Ni$_{0.16}$Mn$_{0.56}$Co$_{0.08}$]O$_2$, is an equimolar solid solution of monoclinic *(C2/m)* Li$_2$MnO$_3$ and hexagonal layered *(R3m)* LiMn$_{0.4}$Ni$_{0.4}$Co$_{0.2}$O$_2$. Structurally speaking the presence of two phases can make the EXAFS analysis difficult. A structural model based on the hexagonal layered structure works well for Ni and Co, whereas a mixed phase should be considered for the Mn K-edge data. Because of the observed Li$_2$MnO$_3$ activation step [7] during the first charge (sample 1 to 5) with concomitant conversion of the monoclinic component to the hexagonal one, we have used the hexagonal structural model for the EXAFS analysis at the Ni, Co K-edges (all samples) and Mn (samples 5 to 10), whereas modifications for samples 1-4 in the case of Mn K-edge data were applied.

The structural differences between the two phases, at the local domain probed by EXAFS, arises in the Mn-Mn interactions of the second shell (three in the monoclinic vs. six in the hexagonal layered structure). Figure 2 displays an example of the EXAFS data analysis at the Mn K-edge of sample 6. The quality of the fits is good. The only frequency missing, and not added in the fitting procedure, is the one ascribable to the Mn-Mn pair at distance higher than 5 Å (Fig 2b).
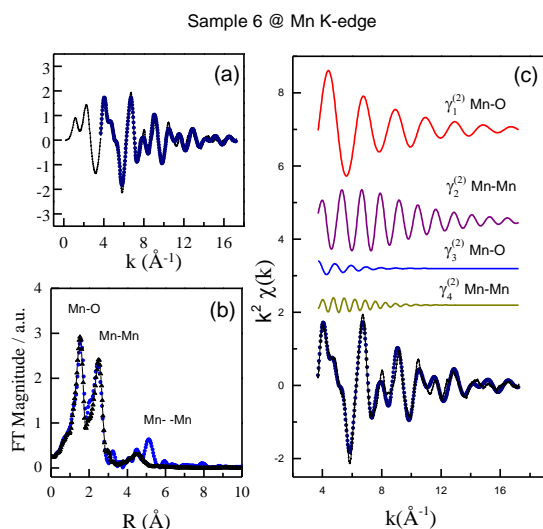

Figure 2. Best fit for sample 6 at the Mn K-edge as an example, in terms of EXAFS signal (a), the corresponding FT (b), and details of the single EXAFS contribution (c).
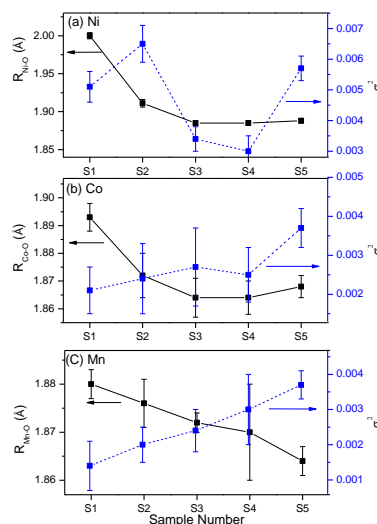
Figure 3. M-O first shell best fit results and corresponding Debye Waller. The error bars are also indicated. They have been calculated by the CONTOUR plots.

Figure 3 reports the M-O first shell best fit results and corresponding Debye Waller at the three metal edges, for the first charge. The first shell of Ni shortens dramatically (by about 0.12 Å for the Ni-O distance) and also for Co (by about 0.03 Å, coordinated by six oxygen atoms). The corresponding Debye Waller factors generally increase during the lithium release process (first charge), indicating an increase of the structural disorder around the Ni and Co site. The Mn-O first shell distance exhibited only minor changes (about 0.02 Å). The corresponding EXAFS Debye Waller factor has revealed a large increase of the structural disorder. This phenomenon is in good agreement with the pre-edge analysis [7]. Overall these findings agree well with the proposed mechanism of initial Li_2MnO_3-like domain activation to a hexagonal phase, which is retained during subsequent cycling.

EXAFS confirms that the manganese is not fully redox active in this material but, instead, assists only to a low extent in the overall redox reaction. As seen, a large decrease of the Ni-O first shell distance was observed. This bond distance is about 1.88 Å in sample 3, 4, and 5, which agrees with the one observed in similar electrodes [9] for Ni^{4+}-O. This confirms that Ni^{2+}/Ni^{4+} is the most reacting electrochemical couple during the first activation process. Data for samples 6 to 10 (not reported in figure 3) agrees with a reversible structural modification for both Co^{2+}/Co^{3+} and Ni^{2+}/Ni^{4+} electrochemical couple.

The use of Contour plots in the parameter error determination, depicted in Figure 4, suggests a further consideration. Among the few examples shown in the figure for samples 5 and 10, where parameters have been selected among those having strong correlation, in order to reflect the highest error, the last two at the bottom (in blue) involving the coordination number of the Mn--Mn in the second shell, deserve a particular attention. This parameter is highly relevant because it allows a direct comparison of the two possible phases of the lithium manganese oxide cathode. This number is expected to be three in the monoclinic case and six in the hexagonal layered structure case. As seen

from the figure, this relevant parameter has a strong correlation when considered against the EXAFS Debye Waller. This means that the two fitting models, namely A (hexagonal like) and B (monoclinic plus hexagonal) in the figure, are statistically of the same quality and both possible. In our case we have kept the coordination number fix to 6. In another test, both parameters were allowed to float, and the results indicated a coordination number close to 6. In other cases [11] there has been a speculation to the ability of the EXAFS to discriminate among the two different phases. The work presented here suggests to take into account about these pitfalls while investigating the structures of the lithium based manganese oxide cathode materials.
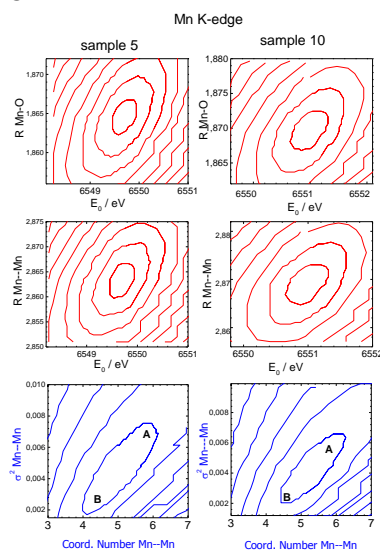

Figure 4. Examples of two-dimensional section of the parameter space (contour plots) for the error parameter determination, for Mn K-edge EXAFS data (sample 5 and 10). These plots were selected among the parameters having strong correlation to reflect the highest error. This evaluation provides only statistical errors on EXAFS refined parameters. The inner elliptical contour corresponds to the 95% confidence level. The parameters errors have been indicated in Figure 3. The two plots at the bottom have been obtained by left floating both σ^2_{Mn-Mn} and CN_{Mn-Mn} (third shell). It is seen that at the 95% confidence level two structural configuration indicated as A (σ^2_{Mn-Mn}= 0.003 and CN_{Mn-Mn} = 4.5) and B (σ^2_{Mn-Mn}= 0.007 and CN_{Mn-Mn} = 6) can be considered equivalent at the 95% confidence level.

4. Conclusions

EXAFS data at Mn, Ni, and Co K-edges of the lithium rich, cobalt poor, $Li[Li_{0.2}Ni_{0.16}Mn_{0.56}Co_{0.08}]O_2$ layered material at different state of charge provided new insights on the mechanism of the lithium release and insertion in their first stages of battery life.

5. Acknowledgements

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