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$_2$MnO$_3$ 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 LiMnO$_2$ (M = Ni and Co) and Li$_2$MnO$_3$. The strength and limitation 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$_2$MnO$_3$ 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$_2$MnO$_3$ component, even if present in small amount, but certainly represents an issue with regard to cost. It has been reported that Li[Li$_{0.2}$Ni$_{0.16}$Mn$_{0.56}$Co$_{0.08}$]O$_2$ , which can be indicated as 0.6 Li$_2$MnO$_3$: 0.4LiMn$_{0.3}$Ni$_{0.13}$Co$_{0.13}$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 °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, N₂ and He in order to have 10%, 70% and 95% of absorption in the I₀, I₁ and I₂ 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 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[Li₀.2Ni₀.16Mn₀.56Co₀.08]O₂ 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]. E₀ values have been found to be displaced by several eV respect to the edge inflection point. The utilized S₀² 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 indicate 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 LiPF₆ in EC/DMC.](image-url)
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 reports the 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.** 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.

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 Ni⁴⁺-O. This confirms that Ni²⁺/Ni⁴⁺ 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 Co²⁺/Co³⁺ and Ni²⁺/Ni⁴⁺ 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 $\sigma_{Mn-Mn}$ and $CN_{Mn-Mn}$ (third shell). It is seen that at the 95% confidence level two structural configuration indicated as A ($\sigma_{Mn-Mn}=0.003$ and $CN_{Mn-Mn}=4.5$) and B ($\sigma_{Mn-Mn}=0.007$ 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, $Li[Li_{0.2}Ni_{0.16}Mn_{0.68}Co_{0.06}]O_2$ 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.

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