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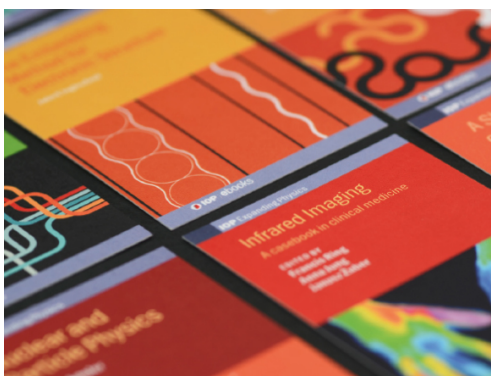
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Structural and electronic studies of metal hexacyanoferrates based cathodes for Li rechargeable batteries

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Abstract. *Operando* XANES and EXAFS spectra on the newly prepared Fe hexacyanocobaltate active material for positive electrodes in lithium batteries have been recorded at the XAFS beamline of Elettra using a suitable *in situ* cell. In this way, it was possible to follow in detail the main structural and electronic changes during the charge and discharge processes of the battery. The use of a chemometric approach for data analysis is also underlined.

1. Introduction

The development of low-cost, efficient storage of off-peak electric power and of electrical energy generated by energy sources other than fossil fuels is a global priority. Rechargeable batteries offers efficient electrochemical energy storage and batteries based on lithium technology has been used in several devices [1]. At present, the searching for new materials with sufficiently large interstitial spaces for the fast intercalation/release process of Li^+ and other cations is one of the most interesting chemical challenges. Metal hexacyanoferrates (*Mhcf*) represent an interesting class of intercalation materials, with high void space, which can be a viable and low-cost alternative to conventional electrodes based on metal oxides. Manganese hexacyanoferrate has been used in Na batteries, delivering a reversible capacity of 120-130 mAh/g for in the first 30 cycles [2]. Wessels *et al.* proposed application of *Mhcf* as electrode material in aqueous batteries [3], the copper analogues has been proposed by Asakura for lithium batteries, investigating the specific role of the Fe and Cu site during the lithium insertion [4]. Aqueous zinc-ion battery based hexacyanoferrate has been recently reported [5], whereas Kurihara and Moritomo studied the structural and electronic properties of a Mn and Co hexacyanoferrate [6] family of cathodes for Li batteries. This paper deals with the study by X-ray absorption spectroscopy (XAS) [7] of the modification of the structural and electronic properties of the iron(II) hexacyanocobaltate analogues while used as positive electrode materials for lithium rechargeable battery.

2. Experimental

The sample was prepared by co-precipitation method at 40 °C [8] resulting in a stoichiometric $\text{K}_{0.44}\text{Fe}_{1.56}\text{Co}(\text{CN})_6$ material. The electrode was obtained by tape casting a slurry containing the pure



active material (80%), 10% polyvinylidene fluoride (PVDF) and 10% carbon black in NMP (N-methylpyrrolidone) on a flat teflon surface. The mass loading of the electrode was about 2.5 mg/cm^2 of active materials. *Operando* X-ray absorption (XAS) spectra were recorded at Elettra (Basovizza, Italy) at the XAFS beamline [9]. A suitable electrochemical cell for the *operando* measurements, which work in transmission geometry, was charged and successively discharged at C/30 rate (insertion of a mole of Li per mole of active material in 30 hours). The storage ring was operated at 2.0 GeV in top-up mode with a typical current of 300 mA. The data were recorded alternatively at the Fe K-edge (7112 eV) and Co K-edge (7709 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 of 30% with respect to the maximum of the rocking curve. Internal reference of Fe and Co foils were used for energy calibration in each scan. Spectra were collected with a constant k-step of 0.03 \AA^{-1} with 3s/point acquisition time from 6850 to 7700eV (Fe K-edge) and from 7550 to 8320eV (Co K-edge).

XAS spectra were calibrated using the Athena program [10]. The pre-edge background was removed by subtraction of a linear function extrapolated from the pre-edge region, and the XANES spectra were normalized at the unity by extrapolation of the atomic background. The EXAFS analysis has been conducted by using the GNXAS software package [11]. E_0 values were found to be displaced by several eV respect to the edge inflection point. S_0^2 values were found to be 0.70 and 0.74 for Fe and Co, respectively.

3. Results and Discussion

From the structural viewpoint iron hexacyanocobaltate (Fehcc) materials, as per the complete series of metal hexacyanoferrates, are based on three dimensional -Co-C-N-Fe- network, $Fm\bar{3}m$ (No.225), where both metals occupy the octahedral 4a Wyckoff position and water molecules are present at interstitial sites (see the sketch inside Figure 1). Alkali-metals, such as Li⁺ or Na⁺, are placed at the 8c site to guarantee neutrality, and of course can be removed and inserted during an electrochemical reaction process. Figure 1 displays the charge and discharge curve as obtained during the *operando* XAS experiment. During the charge the K⁺ cation is extracted from the hexacyanocobaltate structure making feasible the Li⁺ insertion in the successive discharge. Overall we have recorded 73 spectra at both Fe and Co K-edge, 42 during the charge and 28 in the subsequent discharge, this number enables a very close monitoring of the local charge and structure modification upon the potassium release and the lithium insertion process. The charge curve displays a curved-shape behavior during the registration of the first 15 spectra which may indicate an activation process of the active material, most probably related to the irreversible dehydration of the starting material.

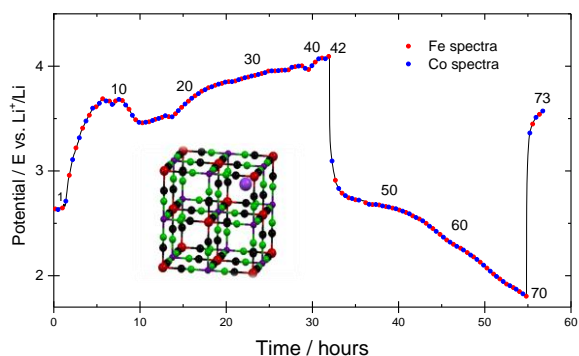


Figure 1. Voltage profile of the charge and discharge curves of Fehcc cathode, as obtained during the *operando* XAS experiment. The battery has delivered 77 and 59 mAh/g during charge and discharge, respectively. Numbers indicate the i^{th} spectrum during the experiment. 42 spectra during charge and 28 during discharge have been recorded. Reference and counter electrode: Li. electrolyte: 1 M LiPF₆ in EC:PC:3DMC (ethylene carbonate, propylene carbonate, dimethylcarbonate)

Figure 2 panel (a) shows a selection of the XANES spectra during the first charge and the successively discharge. A dramatic change of the spectra in the rising portion of the edge, the edge and on the main peak are observed. This suggests a relevant electronic and local structure modification of

the Fe environment during the first charge (spectra 1-42). An almost opposite behavior is observed during the discharge process, spectra 42-70. Figure 2(b) compares the pristine (black), the charged electrode (blue) and the discharged (red) XANES curves. The curve moves towards higher energy during charge and therefore Fe^{2+} is oxidized and, successively, reduced in the subsequent discharge. This process is not fully reversible. In fact, even though the threshold energy is set back to the initial point after the discharge, other characteristics such as the edge feature B, the main peak C and the resonance D are different. Overall, this experiment points out that the Fe is electroactive but a different local atomic arrangement is present after one full redox cycle. A complete different behavior is observed at the Co site, as shown in the panel (c): the XANES spectrum of the pristine material (1st) appears the same of the charged (42th) spectrum) and discharged (70th) electrode. The local and electronic structure of cobalt does not change during the electrochemical process, and is thus completely inert in this range of investigated electrochemical potentials.

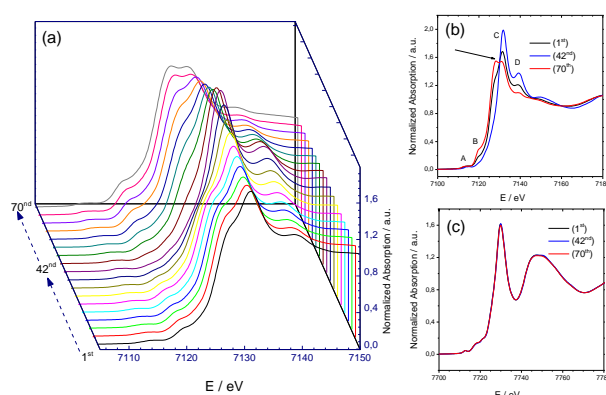


Figure 2. (a) Selection of Fe K-edge XANES spectra obtained during the *operando* XAS experiment. They are indicated spectra # 1, 4, 9, 13, 18, 22, 27, 31, 36, 42, 46, 50, 54, 58, 63, 67, 70. (b) Comparison of the normalized XANES spectra at the Fe K-edge for the pristine, the charged and discharged electrode. The arrow indicates the presence of an isosbestic point. (c) Corresponding normalized XANES spectra at the Co K-edge.

A chemometric approach can be used to obtain a more complete understanding of the cell dynamic during the electrochemical process. Among some different chemometric techniques, the application of the Multicurve Resolution Analysis (MRC) has been demonstrated to be very useful in the study of XAS spectra on battery systems [12]. Following this approach not only the number of species but also the existence range of the various species involved during the electrochemical approach can be revealed. Fig 3a shows the concentration profiles obtained by this analysis. They support the presence of three species during the overall electrochemical cycle (charge and discharge). Generally speaking, species 1 converts to species 2 during the first charge and species 2 converts to species 3 after the subsequent discharge. In addition, there is a sub-range where each species exists almost exclusively. This is the case of species 2, which is present after the first charge (spectrum 42th), and species 3 which forms after the subsequent discharge (spectrum 70th). Interestingly, the pristine electrode does not completely matches with species 1, but only to about 80%. Also, the situation concerning the first 15 spectra is quite stable and different to the other ranges where, typically, there is a progressive conversion of one species to the other. This is in agreement to the behaviour of the first 15 points of the charge curve presented in Fig. 1.

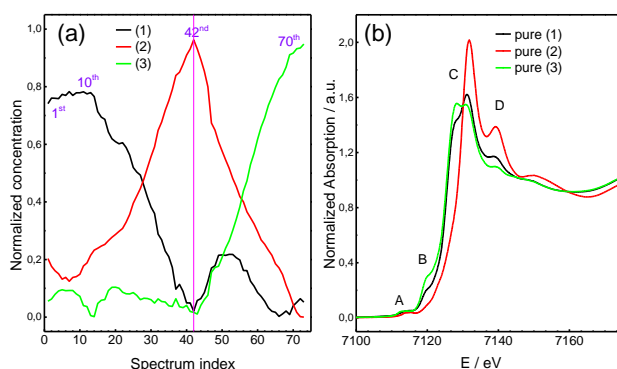


Figure 3. MRC Analysis computed using XANES data at the Fe K-edge. (a) concentration profiles and (b) corresponding pure spectra. Three species can be observed during the overall electrochemical process (charge and discharge).

Figure 3b displays the XANES spectra of the pure species computed by the MRC analysis. The curves are rather similar to the experimental ones displayed in the Figure 2b, especially for species 2 and 3, which agree to the 42th and 70th spectra, respectively. In addition, the pure species 1 is slightly different to the 1st experimental spectrum: the rising edge feature B and the peak maximum C are more intense.

The shape of the curve of Fig. 3a also suggests that when a relative concentration of two species is the same, like the crossing points 28th and 56th, an isosbestic point should be present in the experimental spectra. Indeed, Fig. 2b confirms the appearance of such a condition at about 7130 eV, marked by an arrow. In summary, this underlines the capability of the present chemometric analysis to study *operando* XAS experiments.

A preliminary EXAFS data analysis computed by multiple-edge approach [8] on the experimental raw data at both Fe and Co K-edges has evidenced some structural variation of the Fe-N-C-Co structural unit. The analysis was conducted on a selected number of samples, indicated by the MRC analysis. These fits suggest that the Fe-N distance is almost the same during the first discharge, from 2.06(1) to 2.04(1) Å and sets back to the value of 2.05(1) Å in the 70th spectrum. On the contrary, the corresponding Fe-N Debye-Waller factor is strongly influenced by the electrochemical process. A higher value is observed for spectrum 10th, indicating higher structural disorder, but a progressive decrease is then observed from 0.008(2) to 0.003(1) Å² during the full charge (K⁺ removal, spectrum 42th). The subsequent lithium insertion takes place with an increase of the structural disorder, and the value of 0.008 Å² is restored. At the Co site, the Co-C bond length is the same in all investigated spectra, and the same holds true for the corresponding Debye-Waller factor. Concerning the Fe-N-C-Co structural unit, both angles Fe-N-C and N-C-Co are subject of small deviation from the perfect linearity during charge. The latter could be studied because of the strong four-body Multiple Scattering effects usually observed in these materials [13].

4. Conclusions

The experiment carried out in this work concerned the structural and electronic characterisation of the iron hexacyanocobaltate as positive electrode material for secondary Li battery. It has revealed that Fe is the electroactive metal contributing to the charge balance, by giving activity of the Fe³⁺/Fe²⁺ couple, whereas the Co site is electrochemically inert. Emphasis was also devoted to the combined use of chemometry to the *operando* XAS experiment at the Fe K-edge.

5. Acknowledgements

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