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## XAFS studies on battery materials: data analysis supported by a chemometric approach

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### Abstract

The large amount of data collected during a typical *operando* X-ray absorption fine structure (XAFS) experiment and the interest to thoroughly investigate and comprehend a redox process occurring in a Li-ion battery need an advanced data analysis approach. In this context, multivariate curve resolution (MCR) has gained attention as chemometric technique that allows the identification of the number of the species and their existence range without any *a priori* information on the studied system. The call for an advanced data treatment is answered by a joint XAFS-MCR approach, able to unveil the local structural dynamics of the selected species, providing a quick and efficient data interpretation.

### Keywords

XAFS; EXAFS; MCR-ALS; Li-ion battery; Operando

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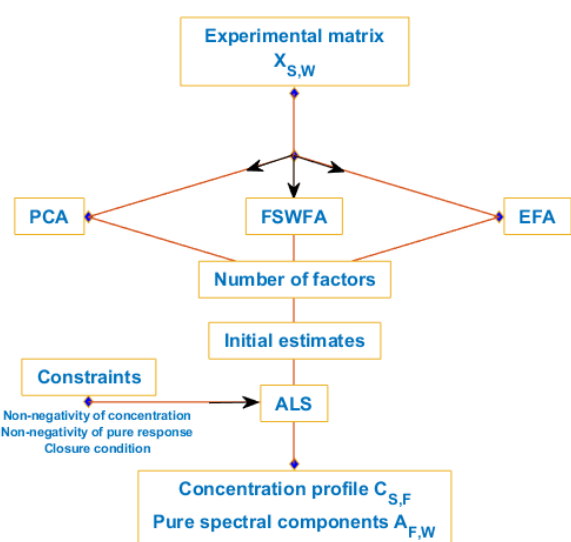
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## 1. Introduction

The development of reliable, low-cost, sustainable storage of electrical energy generated by sources other than fossil fuels is a global priority. Rechargeable batteries, which are based on high rate intercalation reaction of lithium ions into nano- and micro- structured porous materials, offer efficient electrochemical energy storage.[1] The structural and electronic evolution of such hosts is of fundamental importance to design advanced tailored materials, making X-ray absorption fine structure (XAFS) the technique of choice for retrieving this information.[2] During a typical *operando* XAFS experiment, a large amount of data can be acquired, calling for a suitable strategy to data treatment: to this purpose, a joint XAFS-chemometric approach on large datasets allows an efficient and in-depth investigation of the (de)lithiation process. By recording the electrochemical response relatively slowly compared to the spectral data collection, it is possible to build an experimental data matrix ( $X_{S,W}$ ) where each row is a XAFS spectrum in a very narrow potential range. Multivariate curve resolution refined by alternating least squares (MCR-ALS) provides an additive bilinear model of pure contributions without any preexisting model or *a priori* information on the system, decomposing the experimental matrix in a product of two matrices to which chemical meaning can be attributed,[3,4] as it follows (Eqn. 1):

$$X_{S,W} = C_{S,F} A_{F,W} + E_{S,W} \quad (1)$$

where  $C_{S,F}$  is the column matrix of the concentration profile,  $A_{F,W}$  is the row matrix of the X-ray absorption near edge structure (XANES) spectra of pure species and  $E_{S,W}$  is the matrix of the residue.



Scheme 1. MCR-ALS analysis diagram

diagram (Scheme 1) is reported to visualize the steps involved in the MCR-ALS analysis.

MCR-ALS technique has been applied in several fields, for instance in chromatography,[9] and on in situ XAFS data on catalysis.[10,11] The first example of a joint XAFS-MCR approach dates back to 2010,[4] when Conti *et al.* studied Cu-doped vanadium pentoxide ( $Cu_{0.1}V_2O_5$ ) for its attractive properties as insertion host for Li-ions batteries. Although the compound was known since years among the scientific community, the actual reaction mechanism occurring during charge was unclear. The mechanism was demonstrated to involve an intermediate species, which was further identified through EXAFS analysis. Here we present a combined XAFS-MCR analysis approach carried out on battery systems to disentangle the electrochemical reaction

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mechanism. To this purpose, we have selected three case studies: iron hexacyanocobaltate (FeHCC), copper hexacyanoferrate (CuHCF), and vanadium pentoxide ( $V_2O_5$  ARG-like) cathodes.

## 2. Experimental

X-ray absorption spectroscopy experiments for FeHCC and CuHCF cathodes were performed at the XAFS beamline of Elettra Sincrotrone in Basovizza (Italy).[12]. Data collection was carried out during the first charge/discharge cycle in the  $1.8 < E < 4.0$  V and  $2.0 < E < 4.3$  V vs.  $Li^+/Li$ , respectively. The data were recorded in transmission mode either at Fe, Co and/or Cu K-edges. The energies were defined by assigning the first inflection point of the spectra of the metallic foil of Fe, Co and/or Cu to 7112, 7709 and 8979 eV, respectively. An internal reference of Fe, Co and/or Cu foil was used for energy calibration in each scan. Experiments for  $V_2O_5$  ARG-like were performed at the V K-edge at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory using the beamline X11 A. [4] Data collection was carried out in transmission mode while discharging from open voltage circuit (OCP) value (3.3 Volts) to 1.5 V vs.  $Li^+/Li$ . The energy was defined by assigning the first inflection point of the spectra of a vanadium foil. The extended X-ray absorption fine structure (EXAFS) analysis was performed by using the GNXAS package[13,14] that takes into account the multiple scattering (MS) theory. The theoretical signal is calculated *ab initio* and contains the relevant two-body  $\gamma^{(2)}$ , three-body  $\gamma^{(3)}$ , and four-body  $\gamma^{(4)}$  MS terms,[15]. A typical structure of hexacyanoferrates[16] was used as structural model for the FeHCC and CuHCF MS signals calculation. The MCR-ALS analysis was performed by taking into account the XANES portion of the XAFS spectrum exclusively. The Unscrambler [17] and homemade routines based on Parvus [18] was used in data treatment.

## 3. Results and discussion

FeHCC and CuHCF [19] belong to the Prussian blue analogues (PBAs) class of materials, which are characterized by a high versatility towards several ions and a low-strain insertion/extraction capability. The EXAFS analysis consisted in this case of a multiple edge refinement, *i.e.*, a simultaneous fitting at both structural metal edges (Fe, Co for FeHCC and Cu, Fe for CuHCF). The structural information is thus obtained by using two independent measurements, enhancing the reliability and accuracy of the result. On the other side, the MCR-ALS analysis was accomplished only at the Fe and Cu K-edge for FeHCC and CuHCF, respectively, because of the higher variability along the W columns of the experimental  $X_{S,W}$  matrix. This can be considered a peculiarity of this class of materials where the metal site linked to the N end of the cyanide group has been found more electroactive than the other metal (linked to the C site) and therefore its spectra during the electrochemical process change dramatically. Despite (i) being structurally very similar displaying both a cubic lattice and a cell parameter of roughly 10 Å, and (ii) being processed in the same way as cathodes for Li-ion batteries, the respective redox mechanisms are different. According to Figure 1a, FeHCC displays during charge a transformation that can be approximated to the conversion of species 1 to species 2, except for the initial part ascribed to a dehydration process, thus explaining the flat concentration profile (therefore  $K^+$  ions are not extracted in this plateau); however, in the following discharge process the system does not react reversibly going back to species 1, instead it evolves to species 3. This fact, though, can be rationalized by the fact that  $K^+$  ions are released during charge and  $Li^+$  ions are inserted during the subsequent discharge.

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Unlike CuHCF material (Figure 1b), shows a completely reversible interconversion between species 1 and 2 ( $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$ , respectively), featuring a 100% relative concentration of species 2 at the end of the charge. This fact can anticipate a good cyclability of this material during the electrochemical performance recording.

Figure 1c highlights the potentiality and the weaknesses of the MCR-ALS approach while a limited number of spectra is considered. The cathode material was the  $\text{V}_2\text{O}_5$  ARG-like which has been studied during discharge, by considering only 25 spectra along the lithiation process. This material belongs to the class of  $\text{V}_2\text{O}_5$  gel for lithium intercalation batteries, can be considered a highly interconnected porous material with very thin solid walls and shows a unique lithium intercalation behavior [20]. By looking at the concentration profile plot, two exclusive species are gradually interconverted during discharge, being present in equal concentration between spectra 12-13. Eventually, a gradual interconversion of pristine and discharged species has been evidenced, notwithstanding the reduced number of recorded spectra which causes a less clear picture in the concentration profile plot.

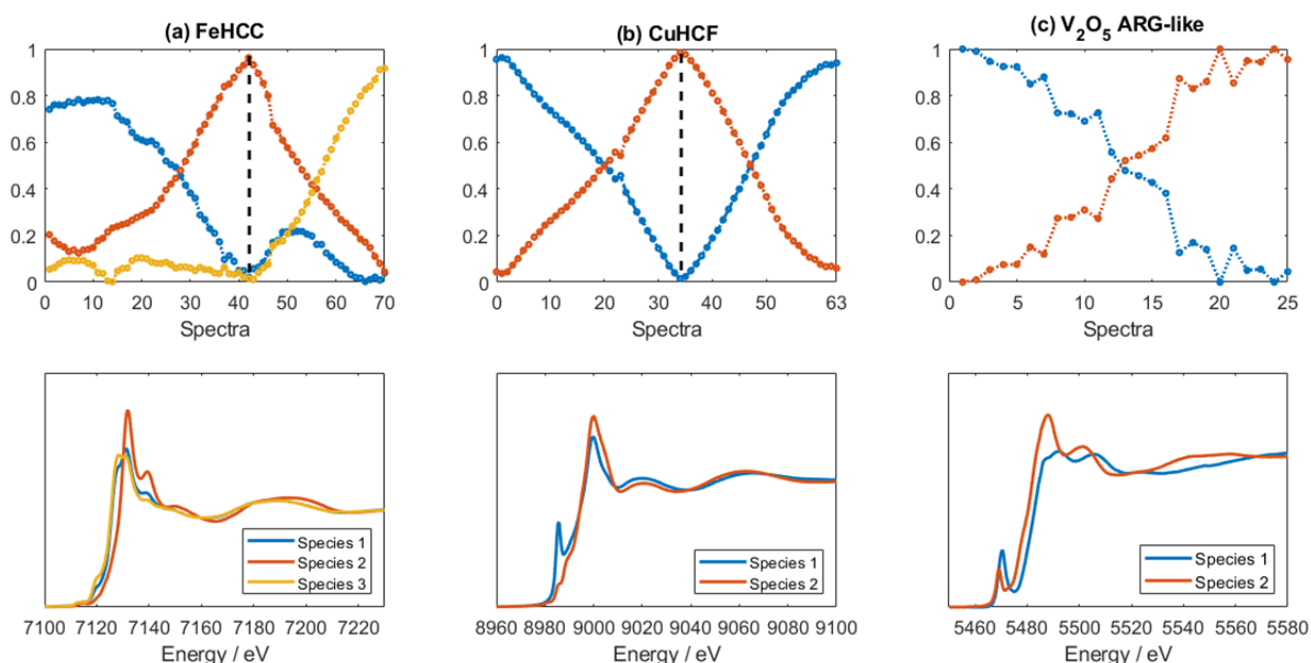


Figure 1. Concentration profiles (top layer) and pure spectral components (bottom layer) for (a) FeHCC, (b) CuHCF, and (c)  $\text{V}_2\text{O}_5$  ARG-like as obtained by the MCR-ALS analysis. The dashed lines in panels a, b separate the charge from the discharge.

#### 4. Conclusions

In the reported examples, the XAFS-MCR combination allowed the identification of the different species and the pure spectral components in the explored range of reaction coordinate, which is the potential in an electrochemically driven process such as the one involving a battery charge and discharge. The concentration profile also indicates the reaction paths of the different redox

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processes. This joint approach has been demonstrated to have a wide potentiality in retrieving the local structural dynamics of selected cathode materials, allowing a quick and efficient data interpretation which would be otherwise time consuming.

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