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

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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, which are based on high rate intercalation reaction of lithium, and more recently, sodium ions into nanostructured and microstructured porous materials, offer efficient electrochemical energy storage [1]. The rate and efficiency of such intercalation reactions are of fundamental importance to the chemists because they permit to design and tailor new host structures for intercalation batteries. Because of the amorphous, ill-crystalline state led by these materials during the intercalation/release processes, X-ray Absorption Spectroscopy (XAS) is the technique of choice for retrieving structural and electronic information. The use of EXAFS spectroscopy in the field of battery materials has been recently reviewed [2].

XAFS experiments have been conducted at ELETTRA [3] on cathode materials using the *operando* mode. This allows to check the structural and electronic reversibility of the battery system while at least one full galvanostatic cycle is performed. XAS data have been recorded on vanadiumoxide materials, lithium rich materials and Prussian Blue-like cathodes for Li batteries.

Typically, a large amount of data is recorded during these experiments. For instance, the study of the charge or the discharge process of a battery produces something like 100–300 spectra, depending on the experimental conditions (data acquisition protocol and battery discharge rate). A chemometric approach can be used to analyze such an amount of data and to obtain a complete understanding of the cell dynamic during the electrochemical process. Among some different chemometric techniques, the application of the Multicurve Resolution Analysis - Alternate Least Squares (MCR-ALS) has been demonstrated to be very useful in the study of XAS spectra on battery systems [4]. 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 without needing any preexisting model or *a priori* information about the system. Once the species have been hypothesized, a common EXAFS analysis can be performed for the structural identification of the selected species in a given range of existence.

The potentiality (and weaknesses) of the MCR-ALS analysis of XAS spectra will be presented in this contribution.

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[1] J. B. Goodenough, Y. Kim, *Chem. Mater.* **2010**, *22*, 587
[2] M. Giorgetti, *ISRN Materials Science* **2013**, Art. No. 938625.
[3] G. Aquilanti, M. Giorgetti, R. Dominko, L. Stievano, I. Arčon, N. Novello, L. Olivi, *J. Phys. D: Applied Physics* **2017**, *50*, Art. No. 074001
[4] P. Conti, S. Zamponi, M. Giorgetti, M Berrettoni, W. H. Smyrl, *Anal. Chem.* **2010**, *82*, 3629.

[5] M. Giorgetti, A. Mignani, G. Aquilanti, P. Conti, M. Fehse, L. Stievano, *J. Phys. Confer. Ser.* **2016**, *712*, Art. No. 012127.