VIDEO ARTICLE

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On the Dynamics of Battery Materials Revealed by Operando XRD and XAS

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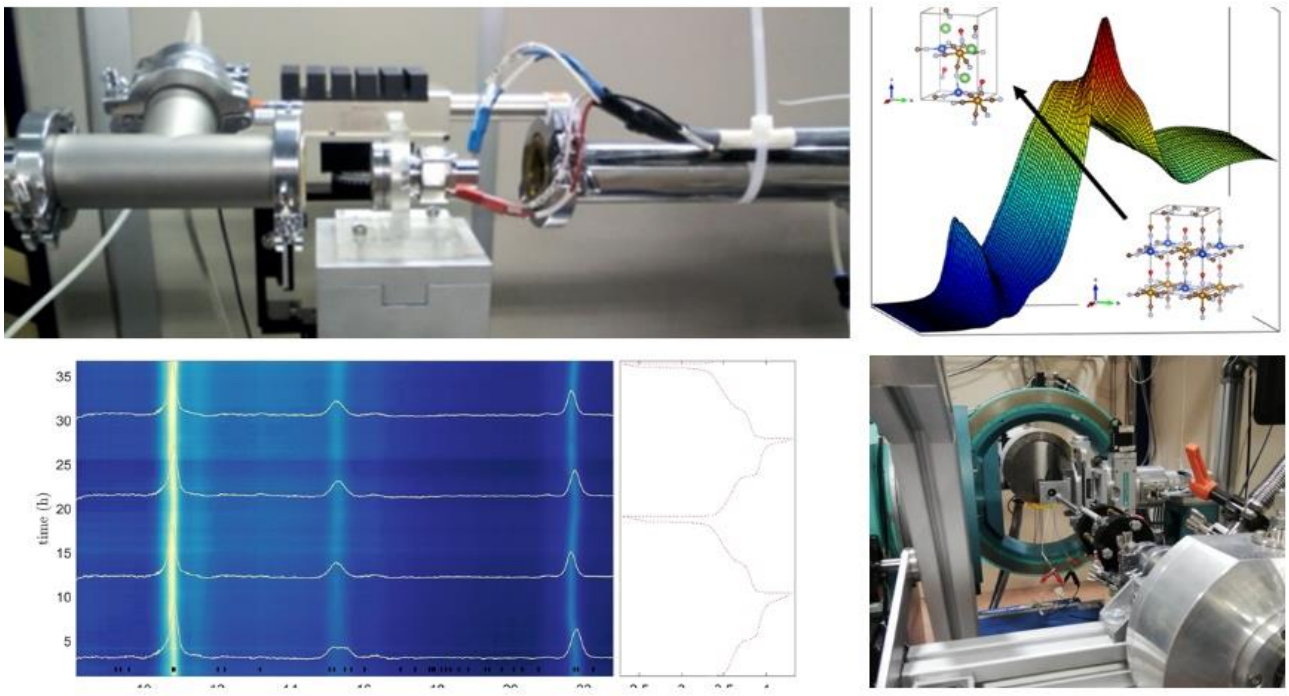
Graphical Abstract

Operando XRD and XAS experiments at Elettra.



Abstract

Affordable energy is a crucial factor for sustainable economic growth. The electrochemical energy storage plays a major societal role due to its widespread technological applications. Host nanostructured materials have a crystal structure with insertion sites, channels and/or interlayer spacings allowing the rapid insertion and extraction of lithium ions with generally little lattice strain, making them useful as electrode materials for batteries. Dynamic processes occurring in batteries can be studied by *operando* modality, which provide a realistic representation of the electrochemical

reactions occurring at the electrodes, allowing to check the structural and electronic reversibility of a battery system while at least one full cycle is performed. For all these reasons, *ex situ* studies, which reflect a given state of charge (SOC) of electrode materials are complemented by *operando* measurements using complementary techniques such as X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). X-ray absorption spectroscopy is a synchrotron radiation based technique that provide both electronic and structural information on a selected atom. Operando synchrotron radiation x-ray powder diffraction (SR-XRPD) experiments allow monitoring the periodic structure of a material during the intercalation/release process of ions. The potentiality of the joint XAS-XRD approach in the newly proposed Prussian blue analogues (PBA) cathodes materials for rechargeable batteries is here highlighted, giving emphases on the copper hexacyanoferrate, copper nitroprusside, and manganese hexacyanoferrate. As an example, manganese hexacyanoferrate (MnHCF) is made of earth-abundant elements by a safe and easy synthesis and features high specific capacities at a higher potential than other PBAs. Na-rich MnHCF was tested in both Li- and Na-ion organic electrolytes in a post-Li strategy perspective and investigated using XAS and XRPD. Both Fe and Mn sites are involved in the electrochemical process, and the high delivered capacity (>130 mAh g^{-1}) results from a reversible evolution in the metallic centers' oxidation states (Fe^{3+}/Fe^{2+} and Mn^{2+}/Mn^{3+}). Along with the Mn^{2+}/Mn^{3+} oxidation, the Mn local environment experiences a substantial yet reversible Jahn–Teller (JT) effect, detected by the spectroscopic technique: the EXAFS shows a substantial and reversible basal contraction (10%) in the charged states due to the equatorial Mn-N bonds' shortening (2.18 Å → 1.96 Å). Furthermore, operando XRD highlights a non-cooperative JT (NCJT) distortion. The lattice volume expands only by 2% upon electrochemical alkali-ion removal and insertion, which contrasts with EXAFS-retrieved Mn−N distances. This apparent disagreement underlines the capability of the PBA open framework to mitigate and disperse the pronounced variation of the JT-active Mn3+, granting overall stability to the structure. XANES. The dynamic of the ions insertion/release electrochemical reaction was further investigated by analysing the full XAS dataset by a multivariate curve resolution with alternating least squares algorithm (MCR-ALS), with the intent to assess the number of species involved and their evolutions during the electrochemical process.

Keywords: Batteries; X-ray absorption; X-ray diffraction; operando.

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Biography of Presenting Author

Marco Giorgetti is an Associate Professor at the University of Bologna and the local coordinator of the Erasmus Mundus Joint Master degree in "Advanced Spectroscopy in Chemistry" since 2014, and coordinator of several Erasmus exchange university of Bologna - European universities (Lille, Leipzig, Madrid, Montpellier). He was member of the Peer Review Committee of synchrotron SOLEIL, France. He has coordinated more than 30 projects in synchrotron radiation facilities. Marco received his Ph.D. in Chemical Sciences (1998) in Italy and held a two-years post-doc position at the University of Minnesota, Minneapolis (1998-2000). The research activity of Prof. Marco Giorgetti covers the field of the structural and electronic characterization of materials and solutions by core level spectroscopies, such as X-ray absorption spectroscopy, applied electrochemistry, sensors, synthesis and characterization of materials for advanced batteries. He had pioneered the in-situ characterization of energy material by the x-ray absorption technique since 1998, with emphasis on improvement in data analysis and data interpretation. He is author about 100 papers published on international journals, 30 Large Scale Facility (LSF) reports, 9 book chapters, 7 highlights, about 20 seminars around the world including schools and workshops, and about 85 communications at scientific meetings, including 30 oral communications. He has spent several periods abroad including France, Germany, USA. He has been an Erasmus teacher in France, and currently teaching in the field of instrumental analysis and advanced analytical techniques. Marco has supervised more than 20 graduate students and more than 10 undergraduates, 4 PhDs. He is in the editorial board of Batteries (MDPI).

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