The role of X-ray absorption spectroscopy for the *operando* characterization of batteries: research highlights at the beamline XAFS at synchrotron Elettra

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The dynamic processes and complexities that govern electrochemical energy storage in batteries are best studied under simulated operating conditions. Similarly, research into new high performance electrode materials requires a better understanding of the electrochemical reaction mechanisms that take place during the charge/discharge process. When performing operando experiments, there is an implicit expectation that the data will provide an accurate representation of the reaction behaviour found under normal operating conditions. In fact, operando avoids some of the disadvantages of sample transfer that are inherent in typical ex situ measurements. Alteration of air- or moisture-sensitive species is avoided, as well as the occurrence of relaxation reactions that could occur when the circuit is open and induce a transformation of the initial cycled material. The entire study can be carried out on a single test cell, thus suppressing the effects of uncontrolled differences in a series of cells, which is necessary for a stepwise ex situ study of the electrochemical mechanism. In addition, an operando X-ray absorption spectroscopy (XAS) experiment allows the structural and electronic reversibility of a battery system to be checked during at least one full cycle. For all these reasons, ex situ studies of electrode materials are complemented by operando measurements using complementary tools such as X-ray diffraction and/or spectroscopic techniques such as XAS.

XAS is a synchrotron-based technique that measures the X-ray absorption coefficient as a function of energy above the absorption edge of a selected element [4]. In addition to being chemically selective, it is sensitive to dilute elements and requires small sample volumes for analysis. As a local probe XAS is applicable to all states of matter, including crystalline solids, amorphous and liquid states, allowing the accurate study of a wide variety of materials. The X-ray absorption near edge structure (XANES) part provides information on the oxidation state and site symmetry of the photoabsorber. The extended x-ray absorption fine structure (EXAFS) part of the spectrum probes short-range order, namely bond distances, coordination numbers and, to some extent, the chemical identity of nearest neighbours.

I will show some recent examples of studies under realistic application conditions on advanced batteries using XAS.These include Li-ion batteries, where a multi-angle approach has revealed the role of the different cathode components during charging and discharging of the battery. In addition, studies on post-Li-ion batteries such as Li-S and Zn-air batteries will be shown.