	Experiment title: Evolution of the Solid Electrolyte Interphase in advanced Li-ion electrodes probed by ex-situ and in-situ XAS	Experiment number: MA-2716
Beamline: BM08	Date of experiment: from: 25/11/2015 to: 01/12/2015	Date of report: 03/03/2016 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Alessandro PURI	
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Report:

The aim of the present experiment was to investigate the formation and evolution of the solid electrolyte interphase (SEI) in carbon coated ZnFe_2O_4 anodes for Li-ion cells both ex-situ and in-operando conditions by x-ray absorption spectroscopy (XAS). The evolution of thickness and composition of the SEI layer during the first charge/discharge cycles and along the cell life time (several cycles) plays a major role in how lithium ions move into the electrodes and how the electrons interact with the lithium. In a previous experiment (MA-2351), ex-situ XAS measurements were successfully performed on a set of graphite and carbon coated ZnFe_2O_4 anodes. A solution of 0.5 M LiPF_6 + 0.5 M LiAsF_6 (which has similar conductivity and chemistry to the commercially used LiPF_6) in EC:DMC 1:1 v/v was used as electrolyte to probe the SEI layers which are formed on powders of the active electrode material, by measuring XAS at the As K-edge (11867 eV). Within the present beamtime activity, we intended to use the same strategy to complete previous activities (ex-situ measurements) and further explore the SEI formation and evolution under in-operando conditions.

For ex-situ measurements, four samples were prepared in the de-lithiation half cycle and other three electrodes were recovered after 20, 50 and 200 charge/discharge cycles to follow the SEI stability during lithium de-insertion (to complete the previously studied lithiation stage) and after several charge/discharge cycles. The beamline ran smoothly and XAS measurements were collected in fluorescence mode (due to the low As concentration in the electrode, only from the thin SEI interface) by using a 12 elements high purity Ge detector to collect data with a good signal to noise ratio in reasonable acquisition time (~4 hours/sample).

As an example, in Figure 1 we report the XANES spectra collected on anodes recovered after 20, 50 and 200 lithiation/delithiation cycles. The elaboration of the collected data is in progress but the spectra show clear differences, mostly on the ratio of the different As species (As^{2+} , As^{3+} , As^{5+}). The preliminary interpretation confirms the previously suggested [1] instability of the SEI layer by the re-oxidation of the electrolyte related phases within the SEI after many cycles.

To study the evolution of the SEI layer in a non-equilibrium condition following the real-time structural evolution, the experiment was proceeded with in-situ XAS measurements. An ECC-OPTO spectro-electrochemical cell equipped with a kapton window to collect XAS measurements in fluorescence mode was installed on the BM08 second experimental chamber (Figure 2) and connected to a potentiostat-galvanostat (Bio-Logic).

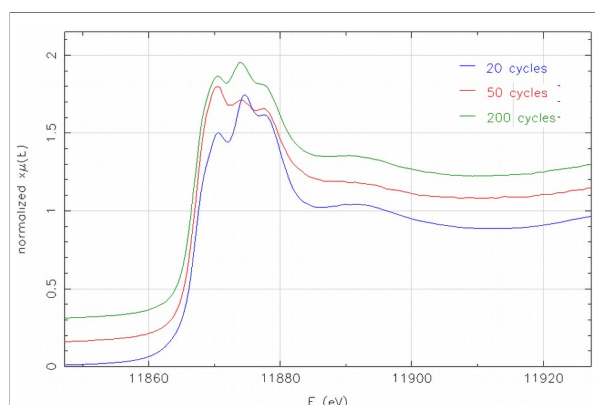


Fig 1: As K-edge XANES spectra collected *ex-situ* on anodes recovered after 20, 50 and 200 lithiation/delithiation cycles at 2C rate.

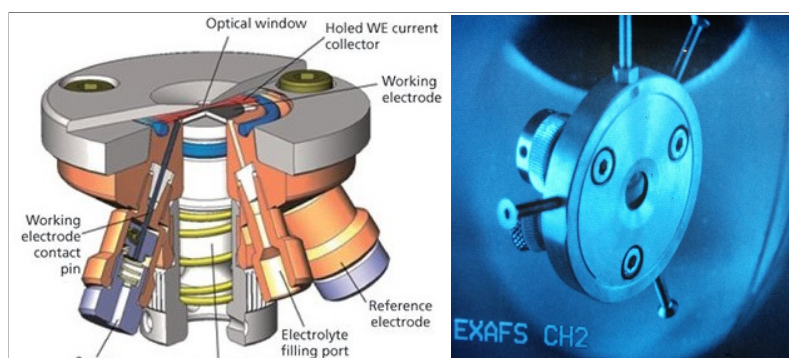


Fig 2: Left) The schematics of the electrochemical cell (ECC-OPTO from EL-CELL GmbH) used for the *in operando* XAS measurements. Right) Picture of the cell mounted in the experimental chamber of the LISA-BM08 beamline (connection cables to the potentiostat unplugged).

For these measurements, ZnFe_2O_4 based anodes were fabricated with high active material loading, specifically calculated to completely attenuate the As fluorescence signal from the liquid electrolyte, then allowing us to probe only the As signal from SEI layers which are formed on the grains of the active electrode material. Since this signal was expected to have a much lower intensity than the fluorescence lines from Zn and Fe from ZnFe_2O_4 , we have used a Silicon Drift (SDD) detector for fluorescence detection due to its wide dynamic range and Al filters to reduce the contribution from Zn/Fe. Unfortunately, we had several failures of the tested cells possibly related to the high loading of active material with respect to standard electrodes, that hampered the successful completion of a full charge/discharge cycle. Moreover, due to the porous nature of the electrodes (consisting of large agglomerates of nanoparticles), the signal from the electrolyte was not completely attenuated and, although the new phases associated with the SEI formation were visible, the strong signal related to the electrolyte makes a precise analysis of the SEI evolution rather difficult. For future experiments aimed at following the process of SEI formation *in-operando* conditions by XAS at the As K-edge, a new cell/electrodes design has to be adopted.

In the final part of the experiment, carbon coated ZnFe_2O_4 anodes, with low concentration of the active material optimized to collect XANES measurements at the Fe K-edge in fluorescence mode were also tested to follow the evolution of oxidation state and structural environment of Fe during the very early stages of lithiation and during the formation of the SEI structure. The cell worked smoothly in this case and the preliminary results evidence a change of the Fe oxidation state towards the metallization of the Fe. Since measurements were collected in fluorescence mode and at a relatively low speed lithium insertion, the remaining beamtime was not sufficient to collect spectra during a full charge/discharge cycle and to measure in the full EXAFS range. A new proposal has just been submitted focused on XAS measurements at both the Fe and Zn K-edges by using a cell (standard pouch cell) suitable for measurements in transmission mode.

We acknowledge the invaluable assistance of the whole BM08 staff to setup the experiment and the ESRF for providing beamtime and access to the Electrochemistry Laboratory.

[1] S. J. Rezvani, M. Ciambezi, R. Gunnella, M. Minicucci, M. A. Muñoz, F. Nobili, M. Pasqualini, S. Passerini, C. Schreiner, A. Trapananti, A. Witkowska, and A. Di Cicco, *J. Phys. Chem. C* **120**, 4287 (2016)