



	Experiment title: Structure of the electrode/electrolyte interface in advanced Li-ion batteries	Experiment number: MA-2351
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Report:

The aim of experiment MA-2351 was to get structural and chemical information on the formation and evolution of the solid electrolyte interphase (SEI) in graphite anodes used in Li-ion batteries.

The SEI is formed during the first electrochemical cycles and acts as a barrier between the electrolyte solution and the electrode. Presently, the evolution of thickness and composition of the SEI, as well as its dependence on electrode materials and morphology, is largely unknown.

Nonetheless, it plays a major role in how lithium ions move into the electrodes (ionic transport and alloying kinetics) and how the electrons interact with the lithium (electron transport at the surface).

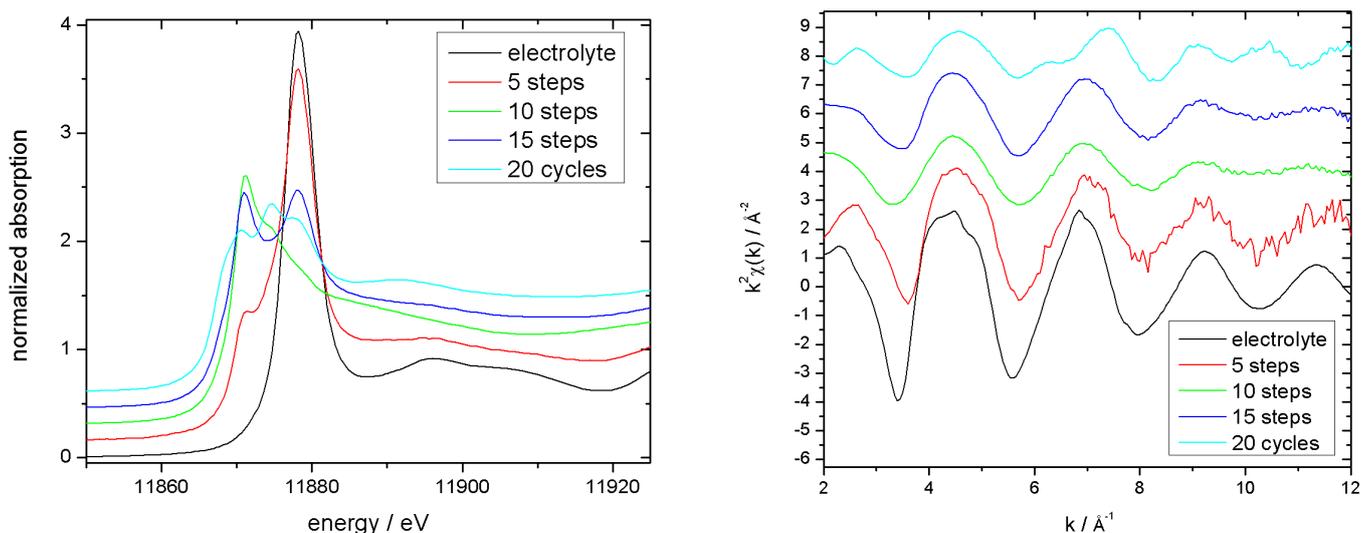
In this first experiment, ex-situ measurements were performed on a set of graphite electrodes prepared at our home laboratories using a mixture of $\text{LiAsF}_6/\text{LiPF}_6$ (which has similar conductivity and chemistry to the commercially used LiPF_6) as electrolyte. XAS measurements were collected at the As K-edge (11867 eV) to probe the SEI. We had initially proposed to investigate the SEI by performing measurements at the electrode interface in grazing incidence geometry, but samples suitable for measurements in grazing incidence geometry (roughness < 1nm) could not be produced and would not be of immediate interest for real applications.

However, we have found that SEI interfaces (thickness 10-100 nm) are formed on powders of the active electrode material (aggregates of graphite nanoparticles) and this allowed us to probe the SEI by measuring the bulk electrodes used in real/commercial batteries. Standardized charge/discharge protocols (CCCV) were

applied to each electrode and four different samples, representing typical stages of the SEI formation and battery lifetime were produced. The liquid electrolyte was then accurately removed using standard procedures and the anodes having developed a SEI coating at the interface were stored under controlled conditions (Ar atmosphere). Standard transmission measurements could not be performed, due to the low As concentration in the electrode (only from the thin SEI interface). Nonetheless, XAS measurements were possible in fluorescence mode and data with a good signal to noise ratio in both the XANES and EXAFS region were collected in reasonable acquisition times.

All the measurements were performed at room temperature. Standard compounds (metal As, As_2O_3 , As_2O_5 and the liquid electrolyte (mixture $\text{LiAsF}_6/\text{LiPF}_6$) were also measured in transmission mode as references.

In the figures below, we report spectra collected at different steps of the first electrochemical cycle and after 20 lithiation/delithiation cycles. The spectra show clear differences in both the XANES and EXAFS region.



The elaboration of the collected data has just started but some preliminary analysis clearly showed that:

- the As content in the electrodes (related to the SEI thickness) increases with the number of cycles (this is not evident from the figures above, as the XANES spectra were normalized for a better comparison).
- the oxidation state of As atoms incorporated in the SEI thin coating formed on the graphite electrodes changes during the formation of the SEI. In particular, there is a progressive reduction of As and its oxidation state changes already at the very early stages of the SEI formation (after 5 steps)
- there is a clear change of the local structure around As atoms as the SEI formation progresses.

Within the same experiment, we have also performed preliminary measurements on ZnFe_2O_4 electrodes. Measurements were collected at the As K-edge as well as the Zn and Fe K-edges. Concerning the As K-edge, results are very similar to those obtained for graphite electrodes. We have also observed clear changes of the Fe and Zn oxidation state. This will be the subject of a new proposal.

This research is part of the SIRBATT (FP7 project [1]) scientific program whose main aim is to study and improve the stability of the SEI through cooperation between electro-chemists, physicists, material scientists and technological companies.