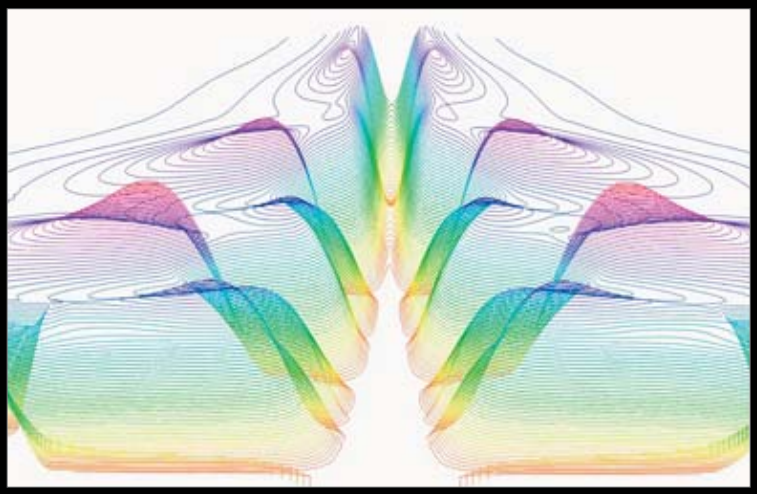
Nanoscale excitations in emergent materials

NEEM 2015



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Augusto Marcelli
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SEI growth and characterization by soft XAS in nanostructured Li batteries anodes

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Solid electrolyte interface (SEI)[1] formation during batteries charge and discharge cycles was monitored at the atomic level as a function of time by using XAS [2], a chemical sensitive and short range probe, and by selectively tuning the detection depth by collecting electrons, total and partial yield, and photon fluorescence yield. X-ray absorption experiments have been conceived and realized to study the modification of the signals related to the various atomic species in ZFO-C electrodes selected at different states of charge during the first Li insertion process and thickness and composition of the SEI layer with anisotropic growth depending on the nanostructuration of the anodes and on their characteristic coating.

Introduction

$ZnFe_2O_4$ Li-ion batteries (LIBs) represent a reliable, affordable, and safe energy storage technology for use in portable application. However, performances and durability of the cells are strongly influenced by the characteristics of the solid electrolyte interphase (SEI), [1–3] Materials and methods: Composite electrodes were prepared by using Na-carboxym-ethylcellulose (CMC, Sigma-Aldrich) binder dissolved in deionized water (5:95 wt/wt). ZFO and SuperP carbon (MMM-Carbon), previously mixed and ground in an agate mortar were added to the binder solution resulting in a slurry with a ZFO:SuperP:CMC composition equal to 75:20:5 (mass ratio) and electrodes preparation as reported in ref. [4].

Figure 1 reports the equilibrium capacity (Q) versus OCV (E) profile as acquired by GITT. The profile is consistent with previous findings [5] and describes the Li uptake by ZFO active material, leading to LiZn, Fe, Li_2O as final products of the mixed conversion/alloying processes, superimpose to the irreversible Li storage by the carbonaceous matrix, which leads to the formation of the SEI upon electrode surface. The discharge capacity is about 1200 mAh g^{-1}

which allows to estimate about 20% first-cycle capacity loss for irreversible processes with respect to the nominal reversible capacity (1000 mAh g^{-1}).
Specific points in Figure 1, marked as (A) (B), (C), (D), correspond to capacity and potential values of the electrodes that later underwent ex situ XAS characterization. The (A) point corresponds to the fresh electrode.

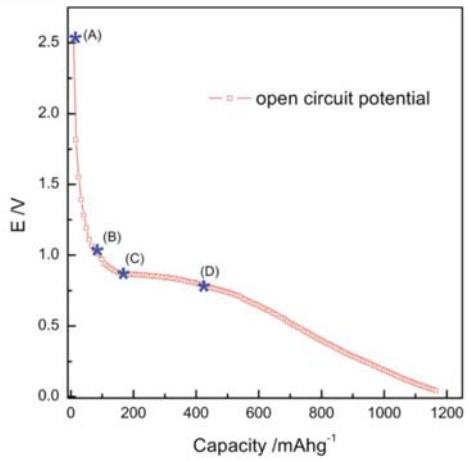

Figure 1: Open-circuit potential (E) vs. specific capacity (Q) of the ZFO-C vs. Li half-cell investigated during first Li uptake.

Samples characterization by XAS
Soft XAS experiments were performed in a wide photon energy range (50-1100 eV) at the BL8.1 BEAR end-station of the ELETTRA synchrotron facility in Trieste (Italy). All XAS spectra were collected in total electron yield (TEY) mode (i.e., drain current mode) up to the carbon K-edge (286 eV) while at higher photon energy the photon emission signal (fluorescence yield) was also collected. The thickness evolution of the SEI can be monitored by the fading of the Zn and Fe signal of the ZFO nanoparticles being covered by the SEI layer as reported in Fig. 2. A possible model of growth is reported in Fig. 3 together with SEM image of the SEI; the latter is found to grow preferentially over the active ZFO-C particles, and as reported already in ref. [4].
Changes are associated with the SEI layer growing on the two electrode-active materials. In particular, the SEM image in Figure 3 does not show a thick SEI layer growing all over the electrode when ZFO-C is concerned. The SEI is found to grow preferentially over the active ZFO-C particles, in agreement with present findings by XAS. The absence of a thick SEI layer covering the electrode allows the easy movement of Li^+ ions into the electrode pores facilitating the (de)lithiation process.

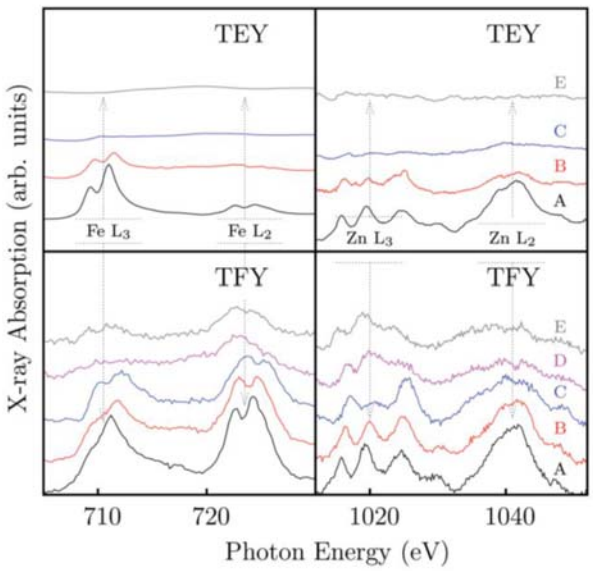

Figure 2. Left panel: total electron (TEY, top) and fluorescence (TFY, bottom) yield XAS spectra at Fe (left) and Zn (right-hand) L-edges for the ZFO-C electrodes under consideration (A–E, see text and previous figures). The intensity trends reflect the evolution of the SEI upon the electrodes.

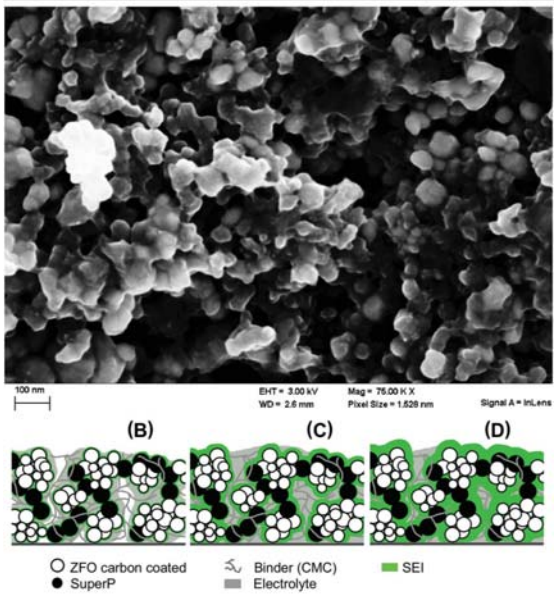

Figure 3: The SEM image shows the surface of a cycled electrode (10 full charge/discharge cycles) evidencing the absence of the SEI on the electrode surface.

Conclusions

The main conclusions that can be drawn by this work can be thus summarized as follows: 1) the evolution of the SEI takes place already during the first steps of the charging process and its thickness reach about 40 nm at about 1/3 of the full capacity, with a stable total thickness up to 20 working cycles; 2) the XAS technique is found to be very effective providing an estimate of the local thickness of the SEI, and indicates that the SEI grows preferentially around the ZFO nanoparticles.

References

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