

**Experiment title:**

Structural changes in Fe-doped ZnO anode material for rechargeable Li-ion batteries: In situ XAS determination of the dopant structural environment and oxidation state.

Experiment number:

08-01-962

Beamline:

BM08

Date of experiment:

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Shifts:

18

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*Helmholtz Institute Ulm, Karlsruhe Institute of Technology, ULM (Germany)***Report:**

The aim of experiment 08-01-962 was to investigate the Fe and Zn oxidation state and local structure in Fe-doped ZnO when used as anode material for rechargeable Li-ion batteries. We have recently investigated the structure of pristine $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}$ by a combination of XRD and XAS measurements at both the Fe and Zn K-edge [1] and some of us showed that this compound provides enhanced electrochemical performances such as reversible specific capacities of more than 900 mAh g^{-1} and excellent rate capabilities compared to pure ZnO [2]. For the present experiment, several anodes were prepared in which the active material (carbon coated $\text{Zn}_{0.9}\text{Fe}_{0.1}\text{O}$) was deposited on a thin carbon paper to allow measurements in transmission mode. The first part of the experiment was dedicated to ex-situ measurements. Eight anodes were dis-/charged in a three-electrode-cell and recovered at different stages of charge corresponding to different levels of lithium incorporation in the anode (Fig. 1a). The cycled electrodes removed from the cells in a glove box under Ar atmosphere were sealed within PE foil to avoid chemical reactions due to air exposure.

XAS spectra were measured on the full set of samples at both the Fe and Zn K-edge in transmission mode. In Fig 1b/1c, we report spectra collected on representative anodes (fresh, fully lithiated and delithiated electrodes). The spectra show remarkable differences in both the XANES and EXAFS region.

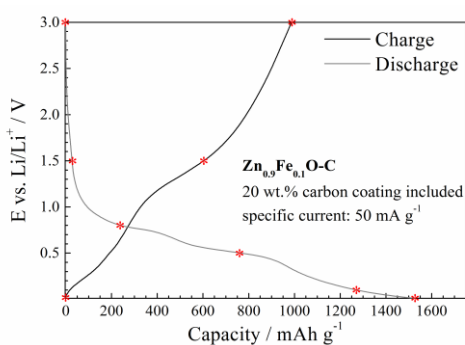


Fig. 1a: 1st galvanostatic cycle

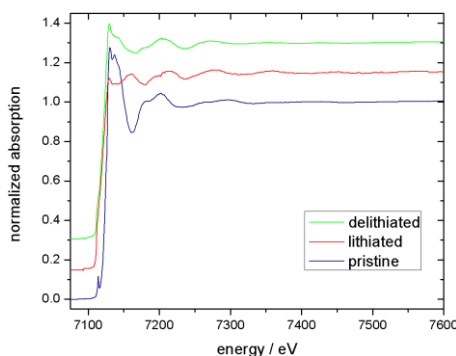


Fig. 1b: XAS at Fe K-edge

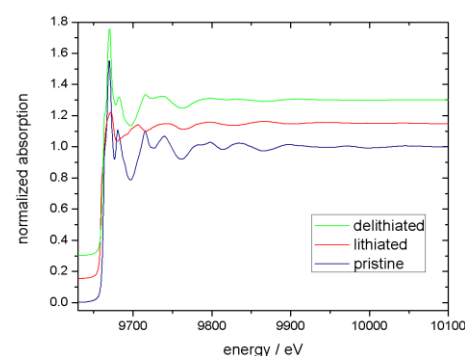


Fig. 1c: XAS at Zn K-edge

The collected data are under elaboration but both XANES/EXAFS data clearly show that a) the oxidation state of both Fe and Zn changes upon lithiation and the reduction is not fully reversible; b) the local structure of both Fe and Zn changes during the redox reaction and the initial wurtzite structure with Fe incorporated in Zn tetrahedral sites is not fully recovered in the cycled electrodes.

Within the same experiment 08-01-962, we tested also the feasibility of in situ XAS measurements on such electrodes operating in a two-electrode-cell configuration. Fig. 2 shows a scheme of the cell, which assembly was optimized for the in situ collection of XAS spectra in transmission mode, and a picture of the cell mounted inside the BM08 experimental chamber. The experiments were done using a CH Instrument 660B Electrochemical working station remotely controlled from the control room.

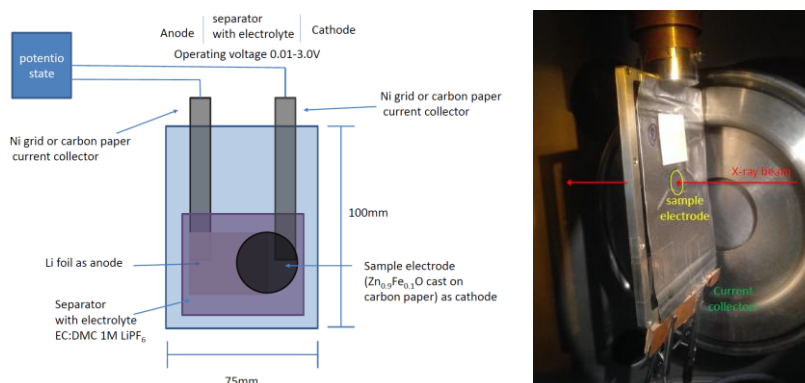
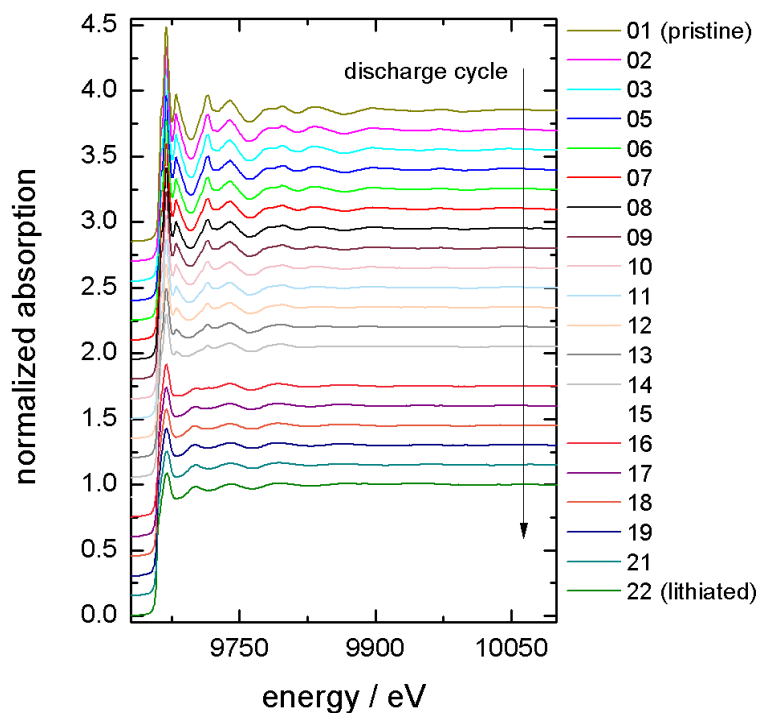


Fig. 2: Scheme and picture of the cell used for in situ XAS experiments

Two sets of in-situ measurements were collected at both the Fe and Zn K-edge along a full charge/discharge cycle. In Fig. 3, the spectra collected at the Zn K-edge while discharging the cell are shown exemplarily.

The charge/discharge cycle lasted about 20 hours and the collection of each spectrum took around 40 minutes. We proved the possibility to collect good quality spectra in transmission mode through the electrochemical cell, even at the Fe K-edge for which the absorption jump is in the order of 0.1 (because of the low Fe content, 10 at% and active material mass loading $< 8 \text{ mg/cm}^2$) and the total absorption by the cell (coffee bag, separator, current collectors, etc) is much higher.



We have observed that both Fe and Zn are electrochemically active but their transformations occur at different potentials, i.e., the reduction of Fe occurs already at the very beginning of the discharge cycle. However, we could not follow the very early stages of the Fe reduction by cycling a cell at very low discharge rate due to the lack of beamtime within this experimental session. After this first successful in situ experiment, we will apply for new beamtime for a more systematic in-situ investigation on cells operating at fixed voltage conditions in order to follow the oxidation state of Fe at discrete amounts of Li insertion into the anode.

[1] G. Giuli, A. Trapananti, F. Mueller, D. Bresser, F. d'Acapito, S. Passerini (2014), submitted manuscript
 [2] D. Bresser, F. Mueller, M. Fiedler, S. Krueger, R. Kloepsch, D. Baiter, M. Winter, E. Paillard, S. Passerini *Chem. Mater.*, 2013, 25 (24), pp 4977–4985