

XAS study of the Lithium storage mechanism in transition metal doped ZnO anodes

Trapananti A.¹, Giuli G.², Bresser D.^{3,4}, Mueller F.^{3,4}, Eisenmann T.^{3,4}, Passerini S.^{3,4}
angela.trapananti@unicam.it

- (1) School of Science and Technology, Physics Division, University of Camerino, Camerino, Italy
- (2) School of Science and Technology, Geology Division, University of Camerino, Camerino, Italy
- (3) Helmholtz Institute Ulm (HIU), Ulm, Germany
- (4) Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Li-ion batteries (LIB) are the state-of-the-art power sources for portable electronics. Nonetheless future large scale applications such as, for instance, electric vehicles require novel cathode and anode materials with enhanced energy and power density along with long term cycling stability. For the anode site, a new class of materials, combining the conversion and alloying reaction mechanisms in one single active compound has gathered continuously increasing interest. Within these materials, transition-metal-doped zinc oxide has been reported as a very promising alternative anode material for Li-ion batteries [1]. The introduction of Fe or Co into the wurtzite structure results into an enhanced reversible capacity exceeding 900 mAh/g (almost three times higher than in pure ZnO) and improved cycling stability even at high rate. The further optimization of such class of materials requires the understanding of the electrochemical (de-)lithiation reaction mechanism at the atomic scale.

Within this contribution we report a detailed XAS investigation of $Zn_{1-x}Fe_xO$ and $Zn_{1-x}Co_xO$. Samples were prepared through sucrose assisted wet chemical synthesis. X-ray absorption spectroscopy (XAS) has been used to probe oxidation state and local structural environment of the transition metals on the pristine material [2,3] as well as on anodes measured both *ex-situ* and in *operando* during galvanostatic cycling [4].

The present study provides a full characterization of the different crystalline but also amorphous and nanocrystalline phases that commonly form upon Li-uptake/release and fundamental insight into the mechanism of the conversion/alloying reaction in this class of materials. During discharge, the reduction of Zn and its alloying with Li has been observed, concurrently with the formation of non-alloying metallic Fe/Co nanograins. A significant fraction of Zn reversibly oxidizes during charge. Such enhanced reversibility compared with pure ZnO could be related to the advantageous influence of the dopant on the highly reversible conversion-alloying lithium storage of such class of materials.

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