Solid Electrolyte interface formed on metal alloy oxide nanoparticles via lithiation

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Transition metal oxide nanoparticles offering Li-ion storage through the combined conversion-alloying mechanism are interesting anode materials for lithium ion batteries due to their enhanced capacity compared to the conventional anode materials.

It is well known that the Li-ion anode materials often operate outside the voltage stability window of the electrolyte components. However, the electrolyte decomposition may lead to the formation of a protective layer at the interface of these nanoparticles with the electrolyte, called SEI (solid electrolyte interphase), which enable the reversible Li^+ ion storage. [1]. The reductive decomposition of the electrolyte results in the formation of several compounds which can be present either in the whole SEI layer (e.g., LiF) or solely on the surface (e.g., LiC_x). The electronic insulation property of the SEI layer prevents the further reduction of the electrolyte salt and solvents, while its ionic conductivity allows the Li^+ ion storage, i.e., the battery performance [2]. Improved performance (lower irreversible capacity) of the batteries employing such anode materials can be achieved if the complex set of chemical reactions could be rationalized and optimized. Hence, the detailed understanding of the nature and composition profile of the SEI layer formed on such nanoparticles, improving the understanding of the role of different components, may enhance the functionality of the Li ion battery electrodes.

We applied X-ray absorption spectroscopy (XAS) at the C, O, Li and F K-edges to study the composition of this superficial layer (SEI) on carbon coated $ZnFe_2O_4$ prototypical nanoparticles [3] during the first lithiation-delithiation cycle, and after several cycles. XAS spectra taken from samples at different stage of lithiation and delithiation. The line-shape evolution was also tracked at distinct stages before and during Li insertion. We demonstrate that apart from conventional SEI layer formed in these electrodes, a reversible superficial alkyl layer ($ROCO_2Li$) is formed within the lithiation process which can partly be responsible for the higher capacity of these materials.

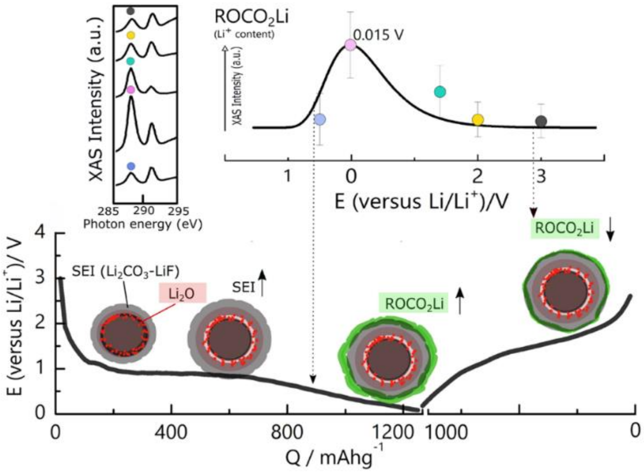

Figure 1: Trend of Li storage in the superficial SEI layer (below 0.7 V) by alkyl lithium carbonates as monitored by the corresponding intensity of the $ROCO_2Li$ component at the XAS C K-edge [4].

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