

## Operando studies of cathode materials for Li-ion batteries using XAS and Mossbauer spectroscopy

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Li-ion batteries are currently considered as most versatile and reliable solution for efficient energy storage and conversion, but researches still needed to meet application requirements. Improvement of the electrode materials used in the Li-ion batteries is crucial to enhance their performance, but such it requires comprehensive insight on the electrochemical processes involved.

Obtaining the most reliable and adequate information about the Li insertion/extraction processes in the electrode material implies the *operando* studies. *Operando* XAS is a perfect method to probe the changes in the electronic and atomic structure of the material during charge/discharge. *Operando* Mossbauer spectroscopy, in turn, is extremely efficient and robust for Fe-containing electrode materials.

Since most of the materials used in Li-ion cells are extremely sensitive to the oxygen and moisture, in our Research Center we have successfully developed the specific cell for *operando* studies. Design with the separate spring-loaded anode allows the work with electrode layers of variable thickness, which gives the single cell suitable for the *operando* measurements with XAS, XRD and Mossbauer spectroscopy. Cell is equipped with ultra X-Ray transparent conductive glassy carbon windows to work with laboratory X-Ray sources.

The viability of such approach was proved by our study of mixed d-metal olivines (general structure  $\text{LiFe}_{1-x}\text{M}_x\text{PO}_4$ ), which are now considered as promising cathode materials for Li-ion rechargeable batteries since they keep benefits from both d-metal components while having increased stability over the commercially used single d-metal cathodes. In this study we investigated a set of Co and Mn doped  $\text{LiFePO}_4$  samples obtained by mechano-assisted and solvothermal synthesis by the Group of Materials for Lithium-ion Batteries of the Institute of Solid State Chemistry and Mechanochemistry SB RAS [1,2].

The *ex situ* K-XANES spectra for Fe and Mn in the samples, obtained by different synthesis techniques are identical so we can conclude that the local atomic and electronic structure of d-metals are the same and are not responsible for the

previously observed difference in electrochemical performance. This difference most likely comes from the morphology of the particles obtained and properties of the carbon coating, which differ between synthesis methods.

As it was expected, during *operando* measurements Fe K-XANES spectra changes significantly depending on a cell SOC. It is remarkable that the changes in the first cycle are only partially reversible and initial and final spectra differ in shape and energy position, meaning that there might be irreversible structure changes or additional phases formation. In the second and subsequent cycles all changes are fully reversible.

In the first cycle Fe oxidation state (obtained from the absorption edge position) changes during the whole charge process and only on the Fe redox plateau on the discharge. In the second cycle, Fe oxidation state changes only on the Fe redox plateau during both charge and discharge. To further study the changes in Fe oxidation state during cycling we performed a principle component analysis for the series of *operando* Mossbauer spectra. Resulting data indicates that the reversible Fe<sup>2+</sup>/Fe<sup>3+</sup> transition occurs, but only 50-60% of Fe ions are involved in this process, which may be due to the almost doubled cathode coating thickness compared to the *operando* XANES experiment.

- [1] N.V. Kosova et al, 2014, J. Mater. Chem. A, 2, 20697
- [2] N.V. Kosova et al, 2012, Solid State Ionics, 225, 564–569