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The impact of defects on the EC performance of LiFePO₄ batteries - an EELS and NEXAFS study

M.E. Schuster¹, D. Teschner¹, F. Girgsdies¹, M.G. Willinger¹, J. Tornow¹, N. Ohmer², D. Samuelis²
J. Popovic^{2,3}, M.-M. Titirici³, R. Schlögl¹

¹Fritz-Haber-Institute der Max-Planck Gesellschaft, Anorganische Chemie, Berlin, Germany

²Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany

³Max-Planck-Institut für Kolloid- und Grenzflächenforschung, Potsdam, Germany

manfred@fhi-berlin.mpg.de

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The olivine-structured LiFePO₄ is considered as a highly promising cathode material for lithium battery due to its high operating voltage (~3.5 V vs. Li/Li⁺) and its large theoretical gravimetric capacity (~170 mAh/g). Further advantages such as its low cost, safety advantages and non-toxicity are faced by major drawbacks such as low electron conductivity and the one-dimensionality of the Li⁺ diffusion [1]. The performance of the cathode material strongly depends on the transport of Li into and out of the host material and its actual charging state in the host matrix.

In particular, reversibility in the intercalation of Li is crucial for achieving high performance of LiFePO₄; additionally, a stable structure is auspicious for long-term stability upon cycling. A correlation between electrochemical performance and the morphology and nanostructure of the LiFePO₄ is recognized, however still poorly understood. The structural and morphological heterogeneity of the synthesized material hampers to establish such a correlation by means of integral methods, while local characterization techniques are required. It will be shown in this work that electron microscopy characterization is especially suitable to establish such correlation.

By means of cross section preparation and by tuning the acceleration voltages in the TEM, small and big particles are separately characterized. Those results are compared with that obtained by integral methods such as XRD and NEXAFS. Modifications of the crystal structure as function of the particles size were investigated in this work by means of HRTEM and XRD, while changes in the electronic structure between Fe²⁺ and Fe³⁺ were studied by EELS and NEXAFS of the Fe L_{3,2} edge. To study the mobility of Li in and out the surface and bulk region as function of the particles size, LiFePO₄ cathode materials at several charging and discharging stages were investigated by a combination of local (EELS) and integral (NEXAFS) methods. Variation on the surface and in the bulk of the fresh and cycled samples were accessed by TEY and FY NEXAFS measurements.

A comparative analysis of the completely charged sample by means of Fe L_{3,2} edge EELS for particles with significantly different particle size is depicted in Figure 1. The lithiated phase and delithiated phase of LiFePO₄ differ in the onset of the O K-edge, due to the formation of a pre-edge peak upon Li removal. This feature is related to unoccupied states with strong oxygen 2p character in FePO₄ and appears at around 528 eV [1]. Additionally, changes in the oxidation state of iron can be observed as a shift of the Fe L₃ peak maximum position. It can be clearly seen that the L₃ edge position shifts to higher energy losses as the sample thickness increases, indicating that Li is removed more easily from the bigger crystallites compared to the smaller LiFePO₄ nanoparticles.

HRTEM analysis revealed a higher defect content for the small crystallites while the crystalline structure of the several 100 nm big crystals seems to be unaffected by the cycling procedure. A turbostratic arrangement was found in the nanosized LiFePO₄ crystals hindering the mobility of the Li atoms during the charging/discharging process. This is especially crucial for the case of the olivine structured LiFePO₄ as the Li mobility is limited to one dimensionality.

In conclusion, this work [3] shows that turbostratic alignment of layers and therefore higher defect content is responsible for irreversible hosting of Li in the structure of small particles. This work is of relevance to optimize conditions for hydrothermal synthesis of LiFePO₄ battery materials towards formation of huge (several 100 nm – μm) sized crystallites which show reversible intercalation behavior.

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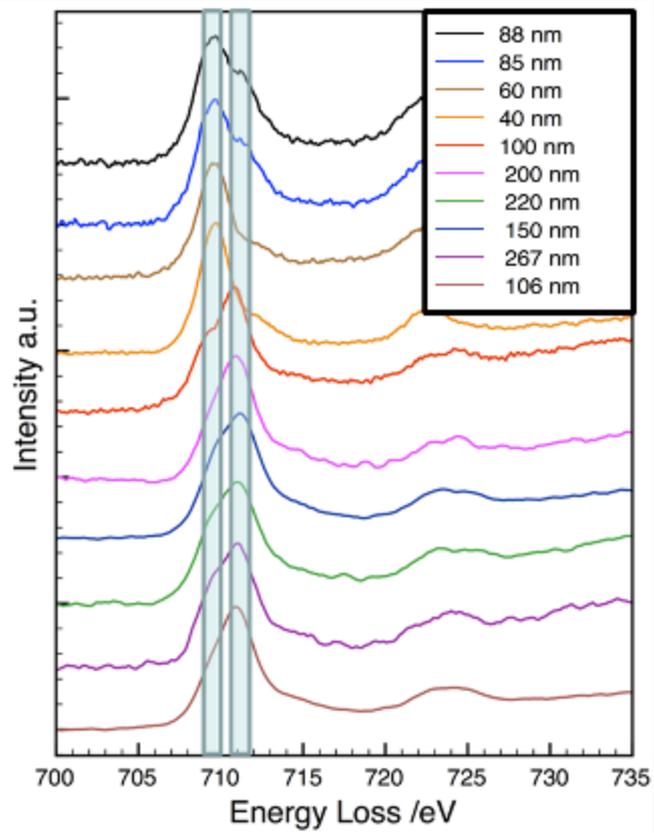


Figure 1. Fe L_{3,2} EELS, note the shift of the L₃ edge position from top to bottom as function of the sample thickness (charged state 1st cycle)