

LiFePO₄: From single crystals to nanostructures

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Batteries based on the light, small and very electropositive element lithium are undoubtedly significant devices for our technology-based society. Among the materials of interest, FePO₄ is one of the most important materials in this context. On discharging it transforms to LiFePO₄ which can be reversibly delithiated on charging. Unlike electronic devices not only electronic carriers are relevant, but also ionic carriers as to enable mass transport and electrochemical reaction. In spite of the importance, examples of systematically studying the charge carrier chemistry in battery-relevant materials are extremely rare. In our work that essentially started with the growth of large LiFePO₄ single crystals we were able to perform such studies on both LiFePO₄, and more recently FePO₄ [1]. As we found, the former intrinsically conducts electrons by a hole- and lithium ions by a vacancy-mechanism whereas excess electrons and lithium interstitials are predominant in FePO₄. These thorough defect-chemical studies based on pure, Al-, Si- and Na-doped materials enabled a quantitative interpretation of the ionic and electronic conductivities as well as of chemical Li-diffusion coefficients as a function of lithium activity (cell voltage), temperature and acceptor or donor doping content. Figure 1 gives the dopant-dependence of both LiFePO₄ and FePO₄ that is in full accordance with our experimental results.

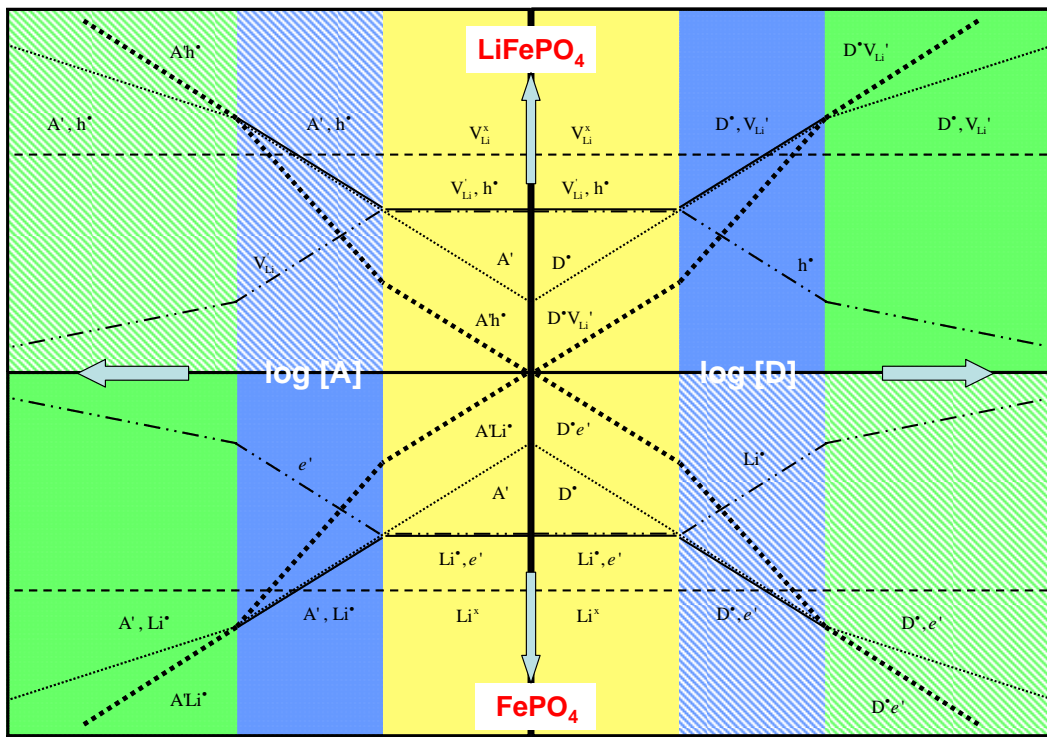


Figure 1: Dependence of defect concentrations in LiFePO₄ and FePO₄ on acceptor (A) and donor (D) content. Please note the symmetry that is highlighted by the colors. The symmetry is immediate consequence of the fact that the charge carriers in LiFePO₄ are Li-vacancies and electron holes while in FePO₄ they are Li-interstitials and excess electrons.

Figure 2 displays a snapshot of our recording the interface motion when LiFePO₄ transforms into FePO₄ on chemical delithiation. The growth turns out to be diffusion-controlled but the FePO₄ formed being highly porous and penetrated by cracks owing to the large volume changes [2].

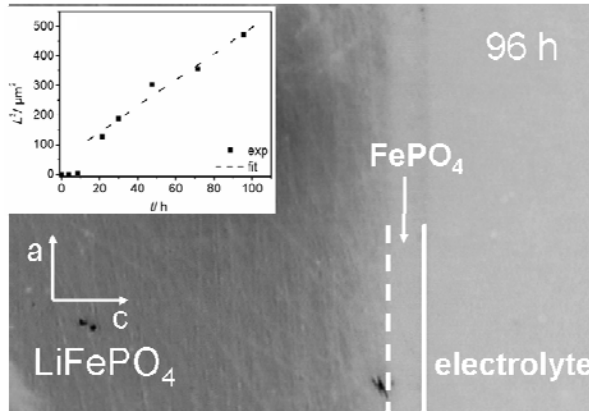


Figure 2: Formation of a transparent FePO_4 layer at the surface of a LiFePO_4 single crystal induced by chemical delithiation and observed by optical microscopy (negatives of the pictures are shown for better contrast). Solid line marks the solid/solution interface, dashed line the $\text{LiFePO}_4/\text{FePO}_4$ interface. The interface motion could be clearly followed as a function of time. (Inset: Square of thickness L^2 of the FePO_4 layer as a function of time t). The kinetics is controlled by diffusion through a porous FePO_4 structure. From Ref. [2].

Besides faster transport kinetics, the avoidance of such mechanical complications is a great advantage of nano-structured electrodes. In order to study effects of size on voltage and phase transformation we prepared nano-crystalline and amorphous nano-crystals as well as nano-wires [3].

As in previous studies of us we can attribute the significant e.m.f. variation for the amorphous material to the loss of long-range order or alternatively to capillary effects of crystallites with vanishing size. The e.m.f. variations of crystals in the range of 10-100nm are due to variations in surface chemistry (surface tension) rather than size.

A further interesting feature of nano-crystals or amorphous particles is the varied equilibrium storage behavior. There are various examples and explanations in the literature of substantial variations in miscibility gap up to the observation of complete miscibility. A recent observation of us made the picture even more colorful [4], it showed that at least parts of the nano-tubes showed a staging behavior; for a material which under macroscopic condition would be in the middle of the miscibility gap, we observed by high resolution TEM (Fig. 3) absence of de-mixing and occupation of every other row similar as in graphite. Obviously the formation of interfaces is — relative to the bulk contribution — so costly in these wires that it is avoided.

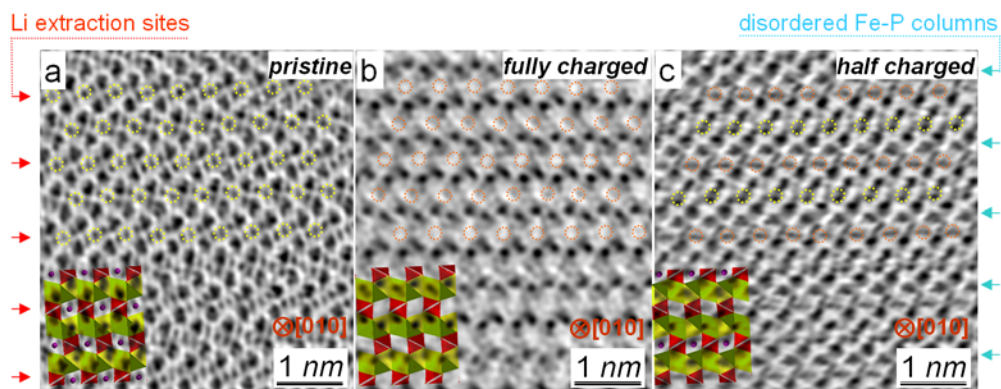


Figure 3: High resolution aberration corrected TEM results for LiFePO_4 nanotubes showing Li ions of partially delithiated LiFePO_4 at every other row. (a) Pristine material with the atomic structure of LiFePO_4 shown at inset; (b) fully charged state with the atomic structure of FePO_4 given for comparison; and (c) half charged state showing the Li staging. Note that Li sites are marked by yellow circles; and the delithiated sites are marked by the orange circles. From Ref. [4].

The fact that the latter phenomenon can be conceived equally well as ordering of point defects, forming precursors of interfaces or as internal heterostructures shines light on the exciting intermediate thermodynamic situation of such systems in which the difference between phases and components is blurred and hence the difference between compositional and morphological complexity.

References:

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