

Oxides & Co. - Old New Materials to Store Lithium

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Lithium-ion batteries (LIBs) are now considered to be the most available power sources for portable devices. The next generation of high-end rechargeable batteries will still rely on lithium-ion host materials. Later, post-lithium-ion systems, at first Li/S, are expected to enter the market. But oxides and, more generally, inorganic solid materials reacting reversibly with lithium, will remain the backbone of the future battery systems. Clearly, independently of the technology, understanding the fundamental properties of battery materials and the interactions of these materials with their environment will be the key to further improvements in energy density, safety, and life time of batteries.

In the presentation, focus will be on some interesting effects related to lithium insertion and deinsertion, recently identified in industrially used metal oxide electrodes like NCA, $\text{Li}(\text{Ni},\text{Co},\text{Al})\text{O}_2$ and LFP, LiFePO_4 . The data on NCA suggest an unknown irreversible activation of the material in the first electrochemical cycle which seems to be a combination of an irreversible two-phase transition and a reversible solid solution reaction mechanism. For LFP we found an obvious “memory effect” in the charging curve after a shallow depth of charge and discharge. In contrast to Ni-Cd and Ni-MH batteries, the memory effect of LFP appears already after only one partial cycle. The understanding of the memory effect is highly essential for the exact estimation of the SOC and the effective use of LIBs based on LFP. Additionally, this notable behavior gives us a strong hint to make the real charge/discharge reaction mechanism and kinetics of LiFePO_4 clear. Moreover, LiFePO_4 is described to be a phase separating material when cycled under low current density conditions. But *in situ* synchrotron X-ray diffraction under ultra-high rate alternating current and medium rate direct current density excitation revealed a continuous but current-dependent solid-solution regime of LiFePO_4 and FePO_4 .

In another example, the reaction with lithium of metal titanium oxyphosphates, also called metal titanil phosphates, $\text{M}_{0.5}\text{TiOPO}_4$ with $\text{M} = \text{Ni}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+},$ and Mg^{2+} , will be discussed. These oxyphosphates are a family of isostructural materials exhibiting an unexpectedly high specific charge; they react with over four lithium ions per formula unit upon lithiation. This is more than the 2 lithium ions expected based on the oxidation state of the two metals in the original structure and also more than the 1.5 lithium ions expected based on the vacant octahedral sites in the unit cell. The reaction mechanism upon lithiation and delithiation was therefore investigated using a combination of XAS, ^{31}P -NMR, XRD, EDX, and electrochemical techniques. Surprisingly, the oxyphosphate materials react, through several steps, via a combination of insertion and conversion processes, the reaction mechanism being dependent on the (transition) metal in the structure. For example, during lithiation of $\text{Cu}_{0.5}\text{TiOPO}_4$, first the copper is extruded irreversibly by forming LiTiOPO_4 . Afterwards, Ti^{4+} is reduced reversibly in an insertion reaction followed by a conversion reaction. The conversion reaction leads to an amorphization of the sample while titanium is reduced to oxidation states below 2+.