



	Experiment title: Direct observation of the phase transformation mechanism in single grains during (dis)charge in LiFePO ₄ electrodes	Experiment number: MA-1595
Beamline: ID11	Date of experiment: from: 21 feb 2013 to: 26 feb 2013	Date of report: 21 August 2014
Shifts: 15	Local contact(s): J.P. Wright	<i>Received at ESRF:</i>
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Report:

Applications such as (hybrid) electric vehicles require rechargeable batteries with a high energy and power density. Most commercialized Li-ion electrode materials, form solid solutions upon (dis)charge of Li, which is held responsible for the good Li-ion kinetics necessary for high power densities of Li-ion batteries. Instead, LiFePO₄ stores Li through a two-phase transformation between FePO₄ (FP) and LiFePO₄ (LFP) introducing additional kinetic barriers due to nucleation. Despite of these additional barriers unusual fast kinetics has been observed raising a fundamental debate on the phase transition mechanism in this type of Li-ion storage materials. The experiment aimed to directly observe of the phase transition mechanism by in-situ observation of the diffraction of individual electrode particles for nano-sized particle under variable (dis)charge conditions.

To determine the phase transition mechanism dependence on the (dis)charge rate, we performed an in situ synchrotron diffraction study with (dis)charge rates ranging from a very low rate of C/5 up to ultrahigh rates of 60C, where C/n denotes the rate at which a full charge or discharge takes n hours. The in situ XRD measurements were performed using a monochromatic X-ray beam with an energy of $E = 40$ keV, a beam size of 50 μm and a FReLoN2k CCD detector. During exposure the sample was continuously rotated around the axis perpendicular to the X-ray beam over an angular range of 1° with an exposure time of 10 s (C/5, 5C), 5 s (10C) and 1 s (60C). Additional scans with a beam size of about 1 micron were performed to monitor the transformation of individual FP/LFP particles during charging and discharging.

In Fig. 1 the rate-dependent charge and subsequent discharge voltage profiles demonstrate the anticipated decreasing capacities and growing overpotentials upon increasing rates. The in situ diffraction shows a marked difference in the evolution of the {200} reflection between C/5 and 60C charging. At C/5 the {200} reflection of the Li-rich phase gradually diminishes as the {200} reflection of the Li-poor phase grows, consistent with the established first-order phase transition that occurs upon delithiating LFP. During this phase transition the initial LFP phase is converted into the FP phase both having the orthorhombic $Pnma$ space group. This is associated with a reduction in the a -lattice parameter, which is responsible for the shift of the {200} reflection toward higher diffraction angles. A surprising observation during 60C charging is the gradual shift of the {200} from the Li-rich phase position toward the Li-poor position showing considerable intensity between the two reflections, which is absent at C/5 charging. This gradual change in transformation behaviour is also reflected in the series of patterns shown in Fig. 2. It is found that at high rates the solubility limits in both phases increase dramatically, causing a fraction of the electrode to bypass the first-order phase transition [1]. The analysis of the transformation behaviour of individual FP/LFP particles during charging and discharging is currently in progress.

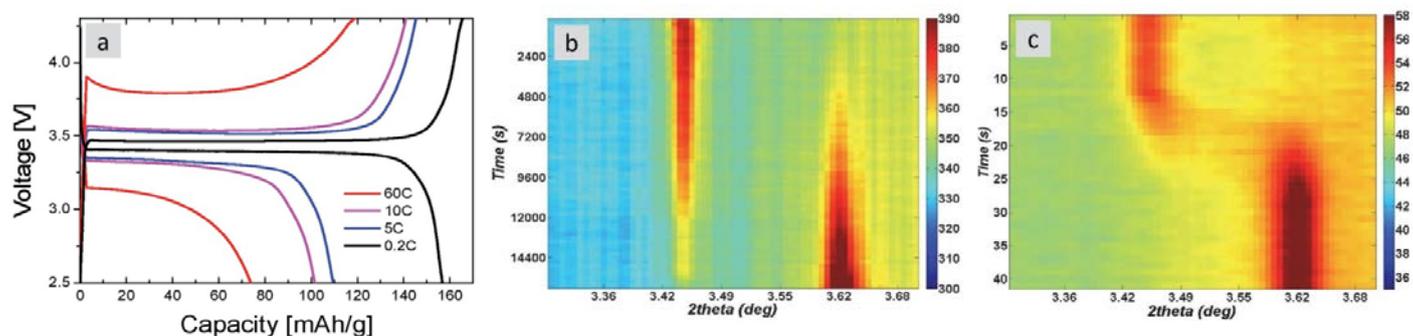


Fig. 1: (a) Rate dependent electrochemistry of the in-situ LiFePO₄ electrodes showing one charge and subsequent discharge after slow initial cycling. C/n denotes the rate at which a full charge or discharge takes n hours. (b) Time evolution of the {200} reflection during C/5 charging. (c) Time evolution of the {200} reflection during 60C charging.

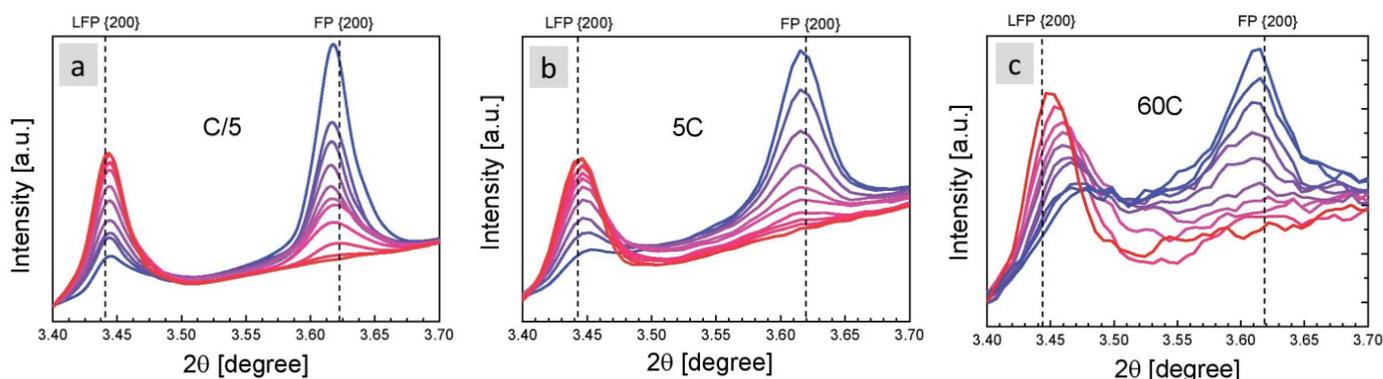


Fig. 2: Evolution of the {200} reflection during C/5, 5C and 60C charging. The vertical lines indicate the equilibrium {200} position reflecting the equilibrium unit cell parameters a in both the Li-rich (LFP) and Li-poor (FP) phases.

Reference:

[1] X. Zhang, M. van Hulzen, D.P. Singh, A. Brownrigg, J.P. Wright, N.H. van Dijk, M. Wagemaker, Nano Letters 14 (2014) 2279-2285.