Supporting Information

Rate induced solubility and suppression of the first-order phase transition in olivine LiFePO_4

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Figure S1. Diffraction pattern at approximately 5% state of charge during 10C charging displaying a weak intermediate reflection with the a -lattice parameter equal to 10.03 Å representing a meta stable composition between the FP and LFP phase.

Figure S2. (a-d) Evolution of the $\{211\}$ and $\{020\}$ reflections during C/5, 5C, 10C and 60C charging. The vertical lines indicate the equilibrium $\{211\}$ and $\{020\}$ position reflecting the equilibrium unit cell parameters in both the Li-rich (LFP) and Li-poor (FP) phases.

Methods

Sample preparation. The starting material was carbon coated LiFePO_4 from Phostech with an average particle size of 140 nm. Regular LiFePO_4 cathodes were prepared through mixing a slurry of LiFePO_4 , Carbon Black (Super P), PVDF, (polyvinylidene fluoride, Solvay) in NMP (N-methylpyrrolidone, with a mass ratio of the active material (LiFePO_4), carbon black (SuperP) and binder (PVDF) of 80:10:10. In addition carbonate template electrodes were prepared to reach high capacities at high rates as reported recently³⁶. For the electrodes, 40 wt% NaHCO_3 (Aldrich) is added to the electrode slurry mixing, a large part which is lost by dissolution in the solvent. The final slurry was casted on carbon coated Aluminium current collectors by doctor blading. The coatings were dried on a heater plate under air at approximately 155 °C overnight followed by drying under vacuum at around 60 °C for more than 24 hours. The resulting coatings were pressed using a roller hand press to enhance the electronic contact. After mechanical compaction the NaHCO_3 templated electrodes were washed in demineralized water that reacts with the NaHCO_3 to form NaOH and gaseous CO_2 , resulting in a an electrode where the interconnectivity of the porosity in the electrodes is improved as demonstrated previously³⁶. Finally, the electrodes are dried for at least 3 hours under vacuum at 100 °C. The results are reported on electrodes with loading density between 2 and 4 mg/cm^2 and with a thickness of approximately 10-20 μm .

Battery preparing and testing. The electrode were assembled in 'coffee-bag' type cells built following the plastic Li-ion cell procedure. All the samples were assembled under argon atmosphere (<0.1 ppm $\text{O}_2/\text{H}_2\text{O}$). The electrodes were separated by glass microfiber filters (Whatman) with a few droplets of 1 mol/liter LiPF_6 (EC:DMC 1:1, Novolyte) electrolyte. All the electrochemical tests were performed galvanostatically within a voltage window of 4.3 and 2.5 V vs Li/Li^+ using an Autolab PGSTAT302N potentiostat/galvanostat.

In situ synchrotron X-ray diffraction. The in situ XRD measurements were performed at the ID11 beam line of the ESRF (France), using a monochromatic X-ray beam with $\lambda = 0.30996 \text{ \AA}$ ($E=40 \text{ keV}$), 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). The sloping background in the diffraction patterns is due to small angle and incoherent scattering of the plastic of the pouch cells and the electrolyte and separator.