Phase boundary propagation in large $LiFePO_4$ single crystals on delithiation

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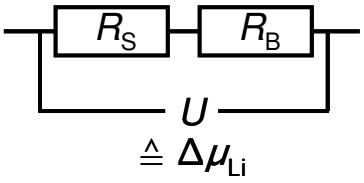
Supporting Information

Appendix

We assume steady state growth and can hence ignore capacitive current elements in the below equivalent circuit.



S: surface, B: bulk

$$j \propto \frac{1}{R_S + R_B}\Delta\mu_{Li}$$

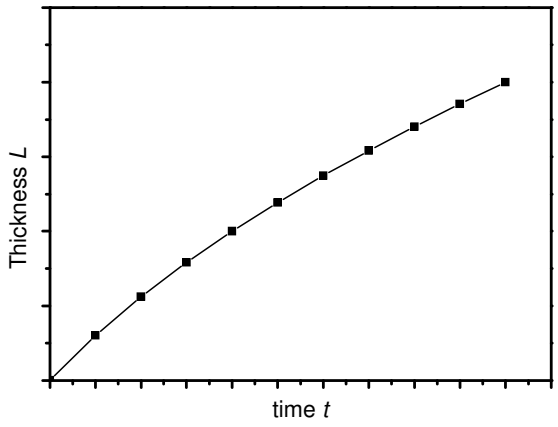
$$R_S = \frac{1}{s};\ R_B = \frac{L}{\sigma^{\delta}}$$

$$\frac{dL}{dt} = \left(\frac{1}{s} + \frac{L}{\sigma^{\delta}}\right)^{-1}\Delta\mu_{Li}$$

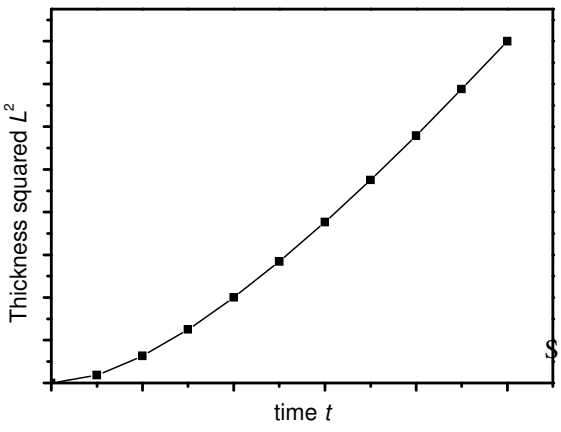
L: thickness of growth layer, s: reaction constant of surface (or interfacial) reaction, $\bullet^{\delta}$: ambipolar conductivity of Li

$$L = -\frac{\sigma^{\delta}}{s} + \sqrt{\frac{\sigma^{\delta 2}}{s^2} + 2\sigma^{\delta}\Delta\mu_{Li}t}$$

L vs. t representation



L^2 *vs. t* representation



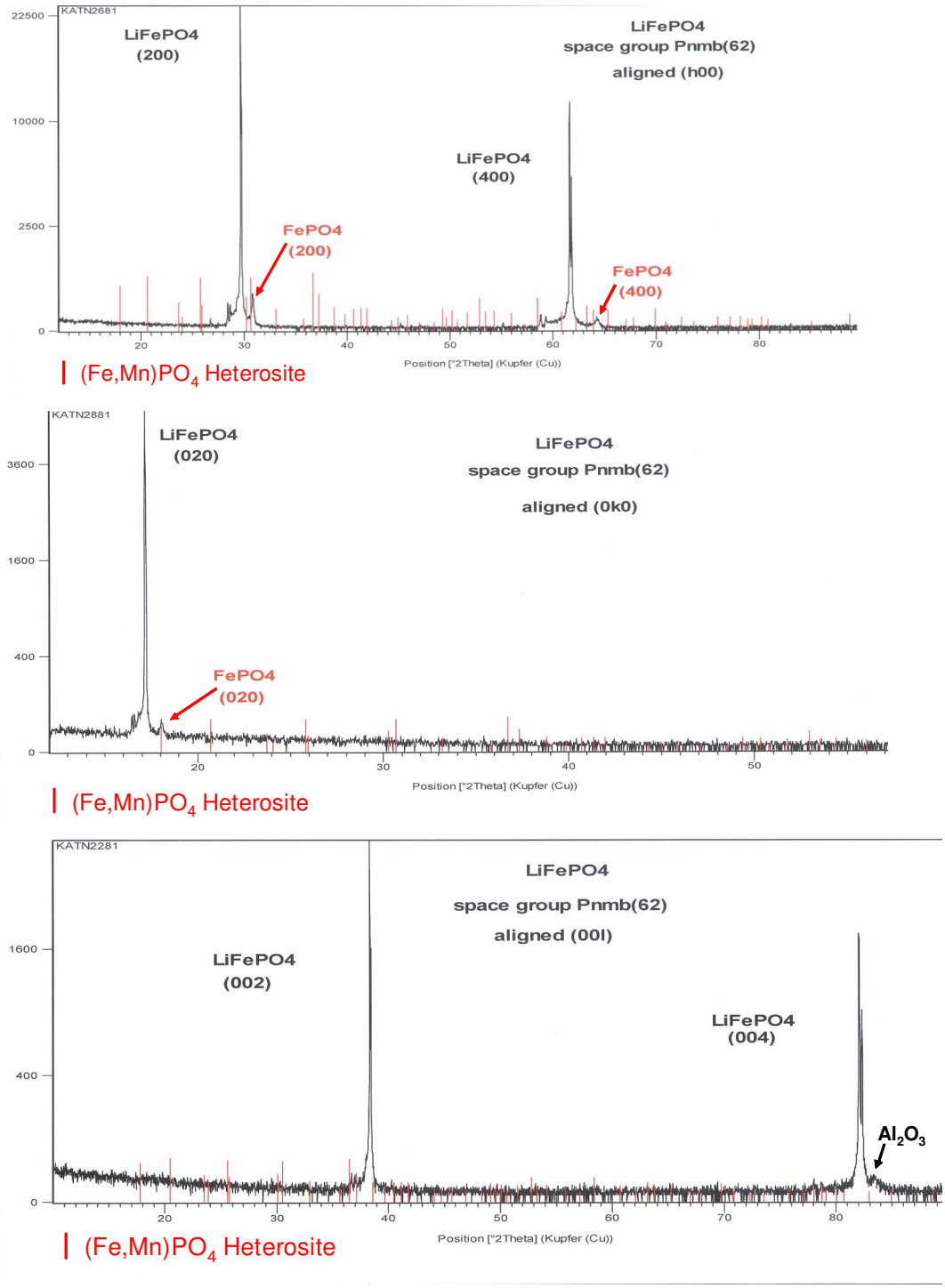


Figure S1. Powder XRD pattern of the partially delithiated $LiFePO_4$ single crystal. In addition to the a) [h00], b) [0k0], and c) [00l] peaks of $LiFePO_4$ the corresponding diffraction peaks for $FePO_4$ can be seen demonstrating epitaxial growth of $FePO_4$. c) Due to the increased *c*-parameter in $FePO_4$ compared to $LiFePO_4$ and the corresponding peak shift to lower 2Θ values the [002] peak of $FePO_4$ is not visible.

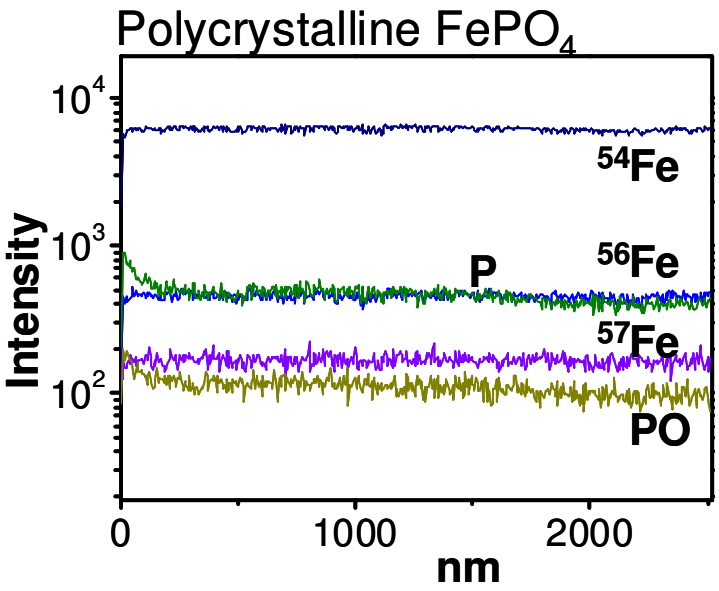


Figure S2. SIMS analysis of polycrystalline $FePO_4$.

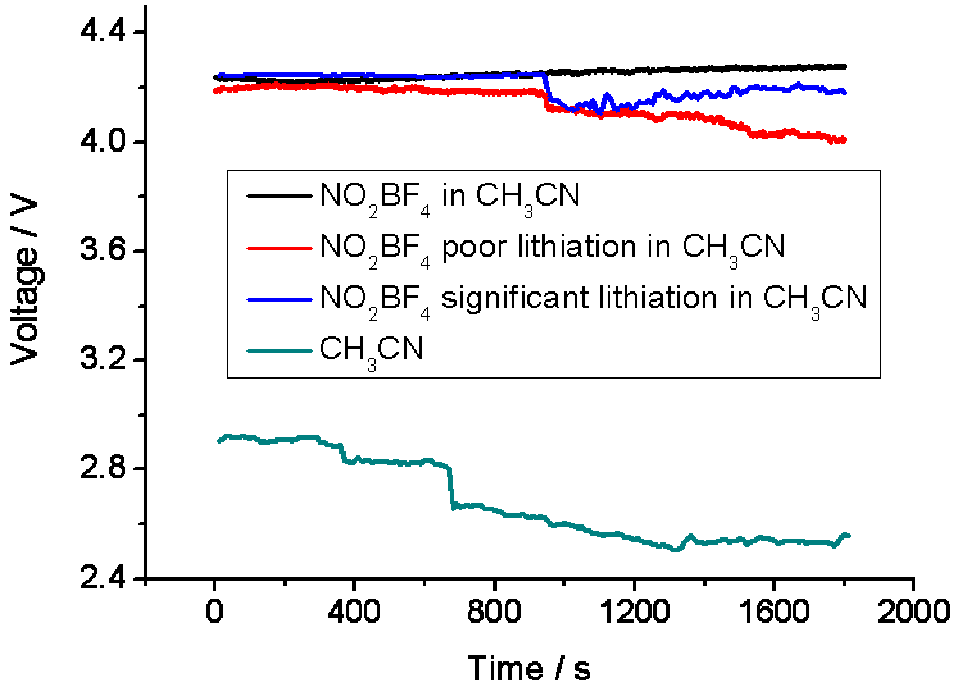


Figure S3. The measurement of redox potential of NO_2BF_4 dissolved in acetonitrile (CH_3CN) (cell: $NO_2BF_{4\,(CH3CN)}$ / lithium ion conducting glass ceramic / Li foil). The redox potential of NO_2BF_4 is sound to be 4.2 V (black curve). Contacting NO_2BF_4 with $LiFePO_4$ and then removing it leads only to a small decrease of the potential (red curve), quite independent of the degree of lithiation (blue curve). (Note that at least NO_2 leaves the system).

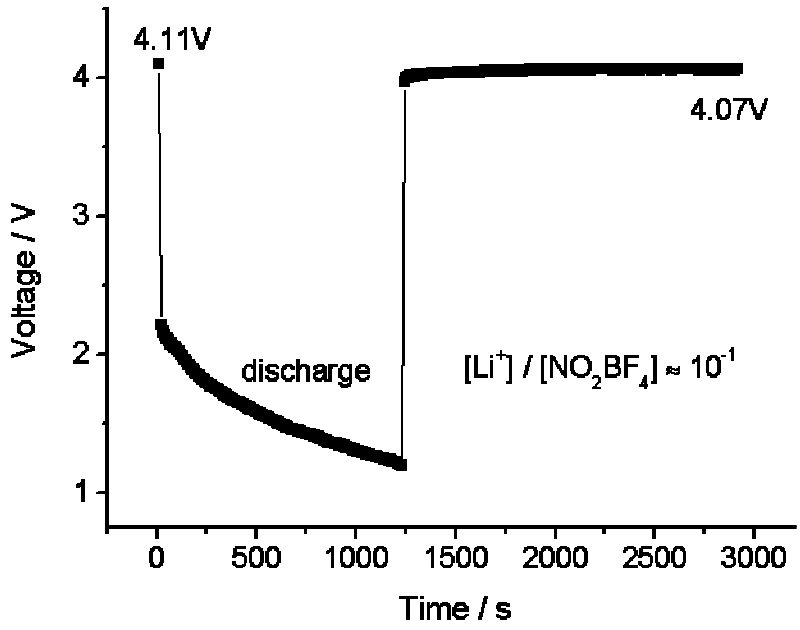


Figure S4. The redox potential of NO_2BF_4 dissolved in acetonitrile (CH_3CN) before and after the electrochemical incorporation of Li into the NO_2BF_4 (cell: $NO_2BF_{4\,(CH3CN)}$ / lithium ion conducting glass ceramic / Li foil). Before the discharging, the OCV is around 4.11 V, and after the discharging, the voltage goes back to 4.07 V. The mole ratio of Li^+ to NO_2BF_4 was around 0.1.