

A combined solid-state nuclear magnetic resonance and in situ X-ray diffraction study of the lithium deintercalation mechanism for $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ ($0 \leq x \leq 1$)

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Olivine-type LiFePO_4 (LFP) is a promising cathode material for lithium ion batteries, owing to its high stability, long cycle life, fast charge rates in nano-LFP, high reversible theoretical capacity (170 mAh/g, compared to 140 mAh/g in LiCoO_2)² and safe operating voltage (3.4 V vs. Li^+/Li). However, the low operating voltage is also its disadvantage, as the energy density is low (580 Wh/kg).

Substitution of Fe with transition metals that have higher redox potentials (e.g. Mn, Co and Ni), results in cathode materials with a higher theoretical energy density. In LiCoPO_4 (LCP), the redox reaction occurs at 4.8 V (compared with 3.4 V in LFP).³ However, it has more sluggish kinetics compared with LFP, making it harder to delithiate. In the binary system, $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ ($0 \leq x \leq 1$), the high energy density is coupled with the ease of delithiation originating from the two end members.

In order to understand the affect of substitution on the transition metal site, the Li (de)intercalation reaction is studied during (dis)charge, respectively. In situ X-ray diffraction (XRD) is a very powerful technique, which allows us to monitor the long-range Bragg diffraction peaks, whilst the battery is cycled. Solid-state nuclear magnetic resonance (NMR) is an ideal complementary technique, probing the short-range coordination of the nucleus under observation. By studying the mechanism of $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ ($x = 1, 0.95, 0.875, 0.75, 0.5, 0.25, 0.125, 0.05$ and 0) a thorough understanding of the affect of substituting the transition metal onto the Fe site of the olivine material at different ratios is obtained.

LFP has been extensively studied and the in situ XRD data (Fig. 1) agrees with previous literature⁴, showing the peaks corresponding to the FePO_4 (FP) phase growing at the expense of the LFP peaks. This is generally thought to be indicative of a two-phase mechanism. Note that other mechanisms such as the Domino Cascade model⁵ and the solid solution mechanism⁶ will also give similar XRD characteristics. Both the NMR spectra and the XRD patterns for LCP (Fig. 2) demonstrate that the delithiation occurs via an intermediate phase, Li_xCoPO_4 . Ehrenberg et al., report this to be $\text{Li}_{0.7}\text{CoPO}_4$.⁷ The in situ XRD also shows a loss of long-range order as the material is cycled, as indicated by the broadening and decrease in Bragg diffraction peaks.

Fig. 3 shows the in situ XRD patterns for $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ and $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$, for 1.5 cycles. In the former, there is clear evidence for a solid solution

mechanism upon discharging, shown by the continual and gradual shift of the XRD peaks. At higher Co ratios, there is now evidence of the solid solution upon charging and the presence of two intermediate phases. A solid solution pathway has a lower activation barrier than a two-phase mechanism and therefore it has high rate implications.

The results demonstrate clear differences in the reaction pathways and phase stability as a function of Co substitution and have implications for electrochemical performance.

References:

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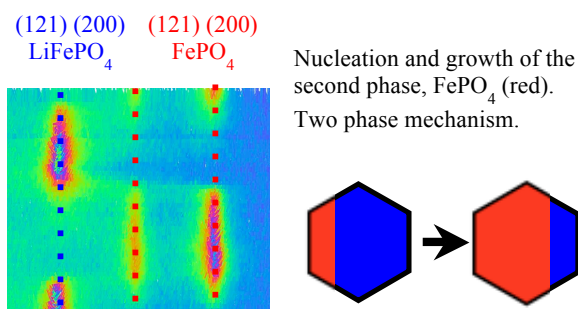


Fig. 1: In situ XRD patterns (showing the (121) and (200) reflections) of LFP (a) for 2 cycles. This is, generally, indicative of a two-phase mechanism (b).

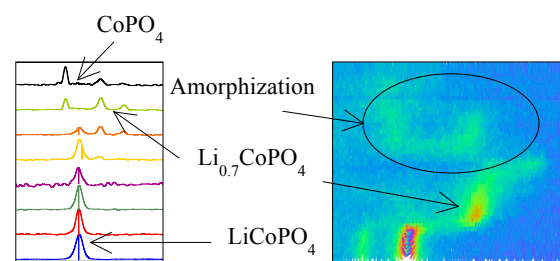


Fig. 2: Ex situ NMR (2a) and in situ XRD (2b) of LCP. In both techniques an intermediate is observed. There is also loss of long-range order, shown in the XRD patterns.

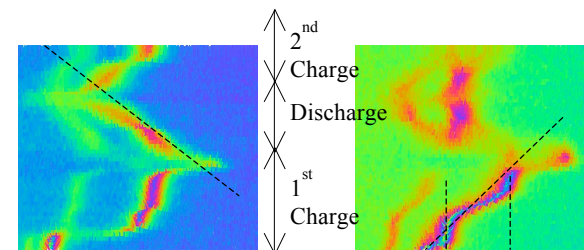


Fig. 3: In situ XRD patterns (concentrating on the (121) and (200) reflections) of $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ (3a) and $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$ (3b) for 1.5 cycles. The continual and gradual shift of the peaks is indicative of a solid solution mechanism.