

Unraveling the Complex Delithiation Mechanisms of Olivine-Type Cathode Materials, $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$

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ABSTRACT: The delithiation mechanisms occurring within the olivine-type class of cathode materials for Li-ion batteries have received considerable attention owing to the good capacity retention at high rates for LiFePO_4 . A comprehensive mechanistic study of the (de)lithiation reactions that occur when the substituted olivine-type cathode materials $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ ($x = 0, 0.05, 0.125, 0.25, 0.5, 0.75, 0.875, 0.95$ and 1) are electrochemically cycled is reported here, using *in situ* X-ray diffraction (XRD) data, and supporting *ex situ* ^{31}P NMR spectra. On the first charge, two intermediate phases are observed and identified: $\text{Li}_{1-x}(\text{Fe}^{3+})_x(\text{Co}^{2+})_{1-x}\text{PO}_4$ for $0 < x < 1$ (*i.e.* after oxidation of $\text{Fe}^{2+} \Rightarrow \text{Fe}^{3+}$) and $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ for $0 \leq x \leq 0.5$ (*i.e.* the Co-majority materials). For the Fe-rich materials, we study how nonequilibrium, single-phase mechanisms that occur discretely in single particles, as observed for LiFePO_4 at high rates, are affected by Co substitution. In the Co-majority materials, a two-phase mechanism with a coherent interface is observed, as was seen in LiCoPO_4 , and we discuss how it is manifested in the XRD patterns. We then compare the nonequilibrium, single-phase mechanism with the bulk single-phase and the coherent interface two-phase mechanisms. Despite the apparent differences between these mechanisms, we discuss how they are related and interconverted as a function of Fe/Co substitution and the potential implications for the electrochemistry of this system.

1. Introduction

Since the initial publication by Padhi *et al.* in 1997 on LiFePO_4 ,¹ the olivine family has been extensively researched as potential cathode materials for Li-ion batteries. LiFePO_4 's high stability, long cycle life, good reversibility² and safe operating voltage (3.45 V vs. Li^+/Li) have led to its use in commercial batteries. Whilst LiFePO_4 has been widely studied, the mechanism by which it transforms during electrochemical cycling is not trivial. The transformation mechanisms for the substituted, and in principle, higher energy density variants $\text{LiFe}_x\text{M}_{1-x}\text{PO}_4$ ($\text{M} = \text{Mn}, \text{Co}, \text{Ni}$ and $0 \leq x \leq 1$) are even more complex and generally not well understood. Understanding how Li is de-intercalated and re-intercalated upon charging and discharging, respectively, is fundamental to explaining the electrochemical properties of known electrode materials and essential to help develop new electrode materials. Specifically, substitution of Mn, Co, and Ni generally results in poorer electronic performance in terms of rate and capacity, but this is not true of all levels of metal substitution. It is, therefore, important to understand why some compositions show improved performance and others do not.

Here we use time-resolved *in situ* synchrotron X-ray diffraction methods to explore systematically how Co substitution in LiFePO_4 alters the structural transformations that occur on cycling for the entire $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ phase diagram. We start by describing the possible, relevant (de)lithiation mechanisms proposed for $\text{LiFe}_x\text{M}_{1-x}\text{PO}_4$, and how they are, or would be manifested in the X-ray diffraction (XRD) data (Figure 1), to help in the interpretation of the *in situ* XRD data for the $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ series presented in this paper.

Initially, XRD and transmission electron diffraction (TEM) studies carried out on micron-sized LiFePO_4 particles identified a two-phase reaction mechanism (A) (illustrated in Figure 1), in which both end member phases (LiFePO_4 and FePO_4) are present, separated by a coherent interface within a single particle, at intermediate states of charge.^{1,3} This mechanism is observed as the simultaneous disappearance and growth of the XRD reflections of the reactant and product phases, respectively. Although micron-sized particles can be chemically delithiated, their electrochemical performance is poor. LiFePO_4 (space group, *Pnma*) has one-dimensional Li diffusion channels in the *b*-direction,⁴ and its electrochemical performance was found to significantly improve when the particles were nano-sized.⁵ The decrease in particle size also leads to a change in the reaction mechanism since the high energy interface between LiFePO_4 and FePO_4 is no longer stable within a single nanoparticle and only fully lithiated and fully delithiated particles could be detected in *ex situ* XRD studies upon cycling.⁶ These findings were

explained by Delmas *et al.* in their Domino-cascade model⁶ in which the reaction occurs particle-by-particle (**B**) (as shown in Figure 1), resulting in sequential, heterogeneous delithiation of the particles in the electrode. It was proposed that the particles still undergo a two-phase mechanism, but since the interface is energetically unfavorable it propagates very quickly within each particle. It should be noted that due to added strain at the phase boundary that exists during reaction scheme **A**, the full width at half maximum (FWHM) of specific classes of reflections in the diffraction experiment are expected to be larger than if the two phases exist in different particles, such as in scheme **B** (as illustrated in Figure 1). Recent soft X-ray ptychography combined with XAS and TEM measurements have shown that LiFePO_4 and FePO_4 can coexist in particles as small as 100 nm.⁷

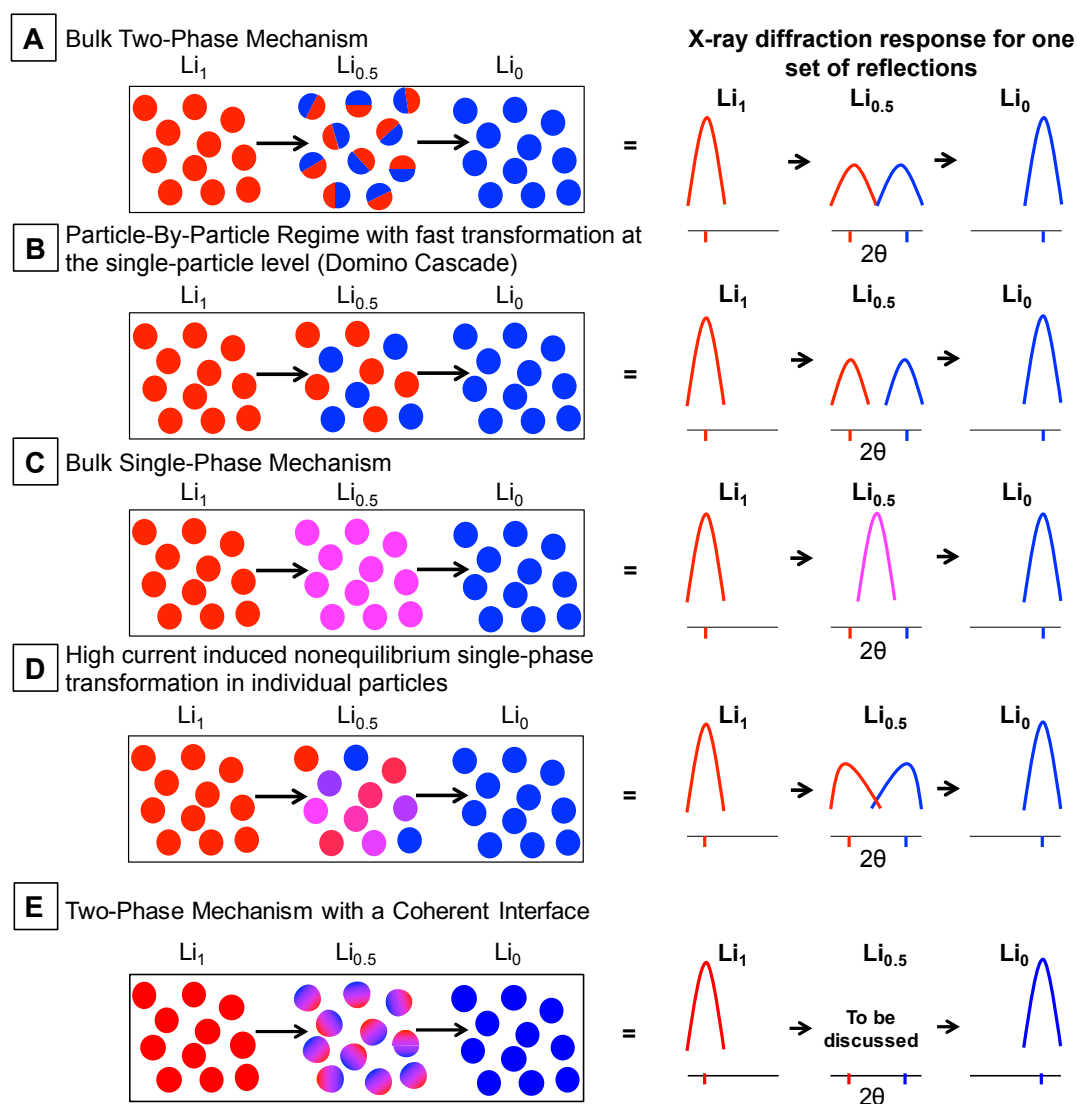


Figure 1. A simplified illustration of five different possible delithiation schemes for the olivine materials and their resulting *in situ* XRD responses for a single reflection (such as the 020 reflection) at the compositions Li_1 , $\text{Li}_{0.5}$ and Li_0 (i.e., LiMPO_4 , $\text{Li}_{0.5}\text{MPO}_4$ and MPO_4): **A** - the bulk two-phase mechanism in which both phases coexist in a single particle, **B** - the particle-by-particle reaction regime, where the particles only exist as either Li_1 or Li_0 , **C** - the bulk single-phase mechanism, **D** - the nonequilibrium single-phase transformation occurring sequentially particle-by-particle and **E** - the two-phase mechanism with a

coherent interface, explored in more detail in this paper.

The good capacity retention at exceptionally high rates for LiFePO₄ nanoparticles⁸ is in apparent contradiction with a two-phase mechanism: two-phase mechanisms typically result in high activation energy barriers for the nucleation and growth of a new phase. Although the Li solubility in Li_δFePO₄ and Li_{1-δ}FePO₄ increases as the particle size decreases, there is still a miscibility gap even for 34 nm particles.⁹ DFT calculations by Malik *et al.* predicted that a single-phase transformation¹⁰ is accessible when an overpotential is applied to nano-sized LiFePO₄. Bazant *et al.* proposed, on the basis of their simulations, that metastable solid-solution phases arise from a kinetic suppression of the phase separation.¹¹ These proposals are supported by our *in situ* XRD studies and those of Zhang *et al.* which captured metastable structures extending across the whole composition Li_yFePO₄ ($0 \leq y \leq 1$)^{12,13} at high cycling rates. The metastable structures were observed as an asymmetric broadening of the Bragg reflections of the end member phases towards each other (Scheme **D**, Figure 1) resulting in the reflections forming one continuous peak. Our simulations of the diffraction data showed that this asymmetric broadening could not be modeled within a simple coherent interface model, Scheme E.^{12,14} In practice it is difficult to determine whether some of the broadening originates from multiple interphases existing within one particle.^{12,15} However, at lower charge rates, since the nano-sized LiFePO₄ particles react very quickly, a few particles at a time, the patterns from the two end member phases will dominate the XRD response and the response is essentially indistinguishable from that seen for Scheme **B** in Figure 1.¹⁶ The nonequilibrium single-phase mechanism (**D**) should be contrasted to that expected for a thermodynamically stable solid solution, where the peaks shift continuously from those of the fully lithiated to the fully delithiated phase (Scheme **C**, Figure 1). If in Scheme **A** (the bulk two-phase reaction), there is some coherency at the interface, there will be a distortion at the interface of the two phases to reduce the strain, leading to the final Scheme, **E**, the coherent interface model. The subtle differences between Scheme **E** and **A**, and how they are manifested in the *in situ* powder XRD patterns of the nanoparticulate olivine materials, will be discussed in detail in the paper.

Here, to explore the delithiation mechanisms occurring within the olivine-class of cathode materials, we study the LiFe_xCo_{1-x}PO₄ series (where $x = 0, 0.05, 0.125, 0.25, 0.5, 0.75, 0.875, 0.95$ and 1). Complex *in situ* XRD patterns are generally observed for nanoparticulate cation substituted-olivine materials on cycling, with both solid solution and two-phase behavior at low cycle rates,^{14,17} suggesting that the mechanism of

(de)lithiation deviates from those of the non-substituted materials. For example, in the Mn-substituted series $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$, an intermediate phase, $\text{Li}_y\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$, was observed in *in situ* XRD patterns, which exhibited a larger Li solubility compared with the end members, $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ and $\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$.¹⁴ A two-phase mechanism was observed between $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ and $\text{Li}_y\text{Fe}_x\text{Mn}_{1-x}\text{PO}_4$ upon charge, however a bulk single-phase transformation (mechanism C) was then seen between the two phases upon discharge. Substitution on the transition metal site in the olivine cathode materials is thought to facilitate the single-phase mechanism,¹⁷⁻¹⁹ helping to improve the rate performance of the cathode materials, as demonstrated in vanadium-substituted LiFePO_4 .²⁰

Very different mechanisms are observed for the Co-containing olivines: Ehrenberg *et al.* observed, by using *in situ* XRD, that the delithiation mechanism of the end member LiCoPO_4 occurs via an intermediate Li_yCoPO_4 , with two distinct reactions occurring: $\text{LiCoPO}_4 \Rightarrow \text{Li}_y\text{CoPO}_4$ and $\text{Li}_y\text{CoPO}_4 \Rightarrow \text{CoPO}_4$.^{21,22} The processes result in significant loss of long-range order.²³ In our previous study using *in situ* XRD and *ex situ* nuclear magnetic resonance spectroscopy we showed that the intermediate phase has the composition $\text{Li}_{2/3}(\text{Co}^{3+})_{1/3}(\text{Co}^{2+})_{2/3}\text{PO}_4$,²⁴ its structure being obtained by a $(a \times 3b \times c)$ supercell expansion of the primitive olivine unit cell. Here we systematically monitor the changes in the *in situ* XRD patterns for high and low substitution levels of both Fe and Co and then analyze how these changes can be understood within the different delithiation reaction schemes (using Figure 1 as a guide). This allows us to develop a systematic understanding of how substitution affects the complex reaction mechanisms in this series.

We first present XRD characterization of the as-synthesized materials in the $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ series (Section 3.1). We then consider Fe-rich $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ ($x \geq 0.875$), and use the whole-powder-pattern fitting as described by Liu *et al.*¹² to study the first 1.5 cycles (Section 3.2). We next study the highly substituted materials, $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ and $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$, and identify the intermediates that are formed upon charging the co-substituted olivines. Relevant NMR spectra are presented to confirm the bulk oxidation changes. Using XRD patterns, refinements and simulations we discuss, in detail, the nature of any coherent interfaces formed during a two-phase reaction and explain how they are manifested in the XRD patterns. We compare the delithiation mechanisms for the transformations between the starting, intermediate and final phases as a function of Co content. We show that the relationships between the different mechanisms are determined by the length of the coherent interface, the ability of the material to tolerate intermediate

Li-compositions, the extent of disorder of Li⁺/vacancies and Fe³⁺/Co²⁺ and the change in volume between the two end member phases. By studying the whole series, trends emerge that were not apparent when single compositions were investigated individually.

2. Experimental Details

2.1 LiFe_xCo_{1-x}PO₄ solid-state synthesis

The carbon-coated series of LiFe_xCo_{1-x}PO₄ ($x = 1, 0.95, 0.875, 0.75, 0.5, 0.25, 0.125, 0.05, 0$) were synthesized via the solid-state method using iron oxalate (Sigma Aldrich, 99.997 %), cobalt oxalate (Sigma Aldrich), lithium carbonate (Sigma Aldrich, 99.997 %), ammonium dihydrogen phosphate (Sigma Aldrich, 99.999 %) and 10 wt. % Ketjen black (AzkoNobel), in a stoichiometric mixture. After high-energy ball milling for 20 minutes, the reaction mixture was pelletized and heated to 600 °C under flowing argon. For $x = 1, 0.95$ and 0.875 , the precursors were heated for 6 hours.²⁵ For $x = 0.75$, they were heated for 6 hours, then cooled and reheated for a further 11 hours. For LiFe_xCo_{1-x}PO₄ ($x = 0.5, 0.25, 0.125, 0.05, 0$), the precursors were heated for 6 hours, cooled and reheated twice for 11 hours, before a final 24 hour heating step. The additional heating and cooling steps were carried out to decrease the amount of impurities present in the final product.

2.2 Film fabrication and battery assembly for the *in situ* XRD studies

The electrode was prepared by grinding 85 wt. % of the carbon coated LiFe_xCo_{1-x}PO₄, 5 wt. % Super P carbon (Alfa Aesar), 5 wt. % carbon black (Vulcan XC-72, Cabot Corporation) and 5 wt. % polytetrafluoroethylene (PTFE) (Sigma Aldrich) in a mortar and pestle. The powder was pressed into a 13-mm-diameter pellet of ~150 μm thickness and weighing ~22 mg. The AMPIX²⁶ cell was assembled in an argon-filled glove box, using Li metal as the counter electrode, a Whatman GF/B borosilicate microfiber filter as the separator, and 1 M LiPF₆ solution in a 1:1 mixture of ethylene carbonate/dimethyl carbonate as the electrolyte (Tomiyama Pure Chemical Industries).

2.3 *In situ* XRD

In situ XRD experiments were performed at the powder diffraction beamline, 11-BM, at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL), using a 12 channel analyzer detector array ($\lambda = 0.413609 \text{ \AA}$, beam size 1.5 x 0.5 mm).²⁷ Data spanning a 0 – 26 ° 2θ range were collected using a step size of 0.002°. To increase experiment throughput, multiple batteries were assembled in a motorized stage and were

translated into the X-ray beam periodically for diffraction measurements. For $x = 0.95$, 0.875, 0.125 and 0.05 each measurement took 10 min 42 s (using a time per step of 0.34 s), scans being obtained every 60 minutes and 25 seconds. For the $x = 1$, 0.75, 0.5, 0.25 and 0 samples, more scans were acquired during parts of the electrochemical cycling where large structural changes had been observed to occur in earlier preliminary measurements of these samples. All these scans took 7 min 40 s (the time per step was 0.23 s). Since the sampling of the electrochemical processes was non-uniform for these batteries, the points where scans have been taken are shown in Figures S1 and S2 in the supporting information and in the main text (for the 1st charge) as indicated in the figure captions. All of the batteries for the *in situ* XRD experiments were galvanostatically cycled at a rate of C/20 using a Maccor Model 4300 cyler. The current was continuously applied whilst the samples were automatically moved in and out of the beam on the sample stage, so that they did not have a chance to “relax”. A rate of C/20 was used for three reasons: (a) the scan time for one XRD pattern took 10 mins 42 sec (for $x = 1$, 0.75, 0.5, 0.25 and 0), which at a rate of C/20, corresponds to change in state of charge of <0.9%, which we thought was small enough to result in minimal peak broadening or other artifacts, (b) since we were studying six cells simultaneously, with scans taking 10 mins 42 sec, if we cycled at C/20, we could collect, on average, ~20 data points on the charge. As these materials are known for having more than one plateau, we felt that it was important to collect as many data points as realistically possible. (c) We wanted all the materials to reach highly charged states (*i.e.* to remove as much Li as possible), and since the Co-containing materials are show poorer electrochemistry than LiFePO₄ at higher rates we therefore chose a moderately slow cycle rate. Rietveld refinements were performed using the Topas Academic software.²⁸ The individual XRD patterns, Rietveld refinements and difference plots for patterns from the *in situ* XRD data of LiFePO₄ during the first charge at 8 %, 57 % and 99 % state of charge are shown in Figure S3 in the SI.

2.4 Whole-powder-pattern fitting of the *in situ* XRD patterns

The same method as that discussed in our earlier paper¹² was used in this study. The background was described by the Chebyshev polynomial. The instrumental broadening was assumed to be negligible and not considered in the refinement; hence the broadening of the diffraction peak is attributed solely to the size and strain effects of the sample.

A Lorentzian peak profile is used to model the size broadening, and the apparent size is assumed to be isotropic with respect to different (hkl) reflections. The dependence of the full width at half maximum (FWHM), β , on θ is given by:

$$\beta = \frac{\lambda}{L \cdot \cos \theta_{hkl}} \quad (1)$$

where λ is the wavelength, and L the refined apparent size parameter. The strain/compositional effect is described by a convolution of a symmetrical and an asymmetrical profile function. A Gaussian profile peak function is chosen to model the symmetrical broadening due to strain, and this strain is also assumed to be isotropic with respect to different (hkl) reflections. The θ dependence of FWHM is given by:

$$\beta = E \tan \theta_{hkl} \quad (2)$$

where E is the refined symmetrical strain parameter. The asymmetrical profile is modeled by an exponential function:

$$f(\theta) = \exp\left(-\frac{2\theta - 2\theta_{hkl}}{\varepsilon_m}\right) \quad (3)$$

where ε_m is the refined parameter and θ is defined in the range $[\theta_{hkl}, +\infty]$ if $\varepsilon_m > 0$ and $[-\infty, \theta_{hkl}]$ if $\varepsilon_m < 0$. Due to the anisotropic change in the lattice parameters from $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ to $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$, where a and b contract and c expands, we have to include an hkl -dependent description of the asymmetrical profile, which is done by including symmetrized spherical harmonics series in ε_m :

$$\varepsilon_m = \sum_{ij} C_{ij} Y_{ij}(\omega, \varphi) \tan \theta_{hkl} \quad (4)$$

where $Y_{ij}(\omega, \varphi)$ are the symmetrized spherical harmonics^{29,30} and C_{ij} are the refined parameters.

The pure strain induced profile for a certain (hkl) reflection is obtained by convoluting the symmetrical Gaussian function and the exponential function defined at the corresponding θ_{hkl} . This convoluted profile corresponds to the variation of the lattice parameters. The population density function (pdf) in 2θ scale for an hkl interplanar spacing of one phase is given by

$$pdf(2\theta)_{hkl} = \frac{1}{E\sqrt{2\pi}} e^{-\frac{(2\theta - 2\theta_{hkl})^2}{2E^2}} \otimes f(\theta) \quad (5)$$

where E is the refined symmetrical strain parameter defined in Eq. (2) and $f(\theta)$ is Eq. (3). The population density of the a , b and c lattice parameters for one phase is given by pdf_{200} ,

pdf_{020} and pdf_{002} , respectively. The total population density (considering both Li-rich and Li-poor phases) is given as

$$pdf(2\theta) = SF_1 \times pdf(2\theta)_{hkl,1} + SF_2 \times pdf(2\theta)_{hkl,2} \quad (6)$$

where SF_1 and SF_2 are the scale factor for the Li-rich and Li-poor phase, respectively. Bragg's law is used to convert the scale from 2θ to d -spacing.

The whole-powder-pattern fitting of the *in situ* diffraction patterns within the 2θ range between 3.5° and 15° was carried out sequentially in the TOPAS structural refinement package.³¹

2.5 Simulations of XRD peak profiles for a coherent interface

A cubic particle with edges parallel to the a , b , c axes of the olivine crystal structure is used for the simulation. Each edge is 100 nm long. The interface is assumed to be perpendicular to the $(h00)$ direction, and the Li concentration and lattice parameter profile along the $(h00)$ direction is assumed to take the following form:

$$a(x) = \frac{a_0 + a_1}{2} + \frac{a_1 - a_0}{2} \tanh\left(\frac{x - x_0}{L}\right) \quad (7)$$

with a_0 and a_1 representing the quantities (Li concentration and lattice parameters) of the two end member phases, respectively, L the width of the interface, x_0 the central position of the interface, and x the coordinate along the $(h00)$ direction. The delithiation process was simulated in discrete steps by varying x_0 from one end of the particle to the other. The value of x_0 was determined in such a way to make sure the global Li concentration is consistent with the state of charge.

X-ray diffraction intensity was simulated following the treatment by Warren.³² For a $(0k0)$ reflection, the diffraction power as a function of diffraction angle 2θ can be expressed as:

$$P(2\theta) = \frac{K}{\sin^2 \theta} \sum_{m'} \sum_m f_{m'} f_m e^{(2\pi i / \lambda)(2 \sin \theta)(R_{m'} - R_m)} \quad (8)$$

where the subscripts m and m' represent the indices of the unit cells, f_m is the structure factor of unit cell m , R_m is the position coordinate of unit cell m , λ is the X-ray wavelength, and K is a factor independent of θ . The summation is performed over all unit cells in the one-dimensional particle. The structure factor f for the (020) reflection is assumed to vary linearly with the Li composition c ³³:

$$f(c) = (1 - c) \cdot f(0) + c \cdot f(1) \quad (9)$$

where $f(0)$ is the structure factor for the (020) reflection of $\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$, and $f(1)$ for that of $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$.

3. Results and Discussion

3.1 Synthesis and Characterization of $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$

The carbon-coated $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ ($x = 0, 0.05, 0.125, 0.25, 0.5, 0.75, 0.875, 0.95$ and 1) materials were synthesized via the solid-state synthesis. Additional heating steps were required for higher Co compositions to decrease the extent of impurities present in the product (including Li_3PO_4 , as shown in Figure S4 the supporting information, SI).²⁵ The average particle size of LiFePO_4 is approximately 120 nm, as determined from scanning electron microscopy (SEM) images of a LiFePO_4 -electrode taken at different magnifications (shown in the SI). The large distribution of particle sizes (from ~ 50 to 350 nm) and spherical-type morphology, are expected for the solid-state synthesis.^{34,35} SEM images of the as-synthesized carbon-coated LiCoPO_4 powder indicate that the particle size is smaller than 50 nm (see Figure S5 in the SI). Therefore, the particles sizes of all the $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ compositions are assumed to be in the nanoparticulate-regime.

3.2 Fe-rich $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ ($x = 1, 0.95$ and 0.875)

3.2.1 First charge

In situ XRD patterns of the Fe-rich substituted olivines (LiFePO_4 , $\text{LiFe}_{0.95}\text{Co}_{0.05}\text{PO}_4$ and $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$) cycled at a rate of C/20 for the first cycle and up to 100 mAh/g of the second charge are presented in Figures 2(a)-(c), respectively. The 2θ range in Figures 2(a)–(c) shows the (020) and (211) reflections of the lithiated and delithiated phases. Only the FePO_4 and the LiFePO_4 reflections are observed when charging LiFePO_4 at this low rate (Figure 2(a)). This is characteristic of a “two-phase reaction” at the electrode level, the delithiated phase being formed at the expense of the fully lithiated phase, with no significant peak shift and broadening (as discussed in the introduction). We cannot determine the exact mechanism of the reaction at the single particle level, *i.e.*, we cannot distinguish whether two phases exist within the same particles or in different particles, at intermediate states of charge, as depicted in schemes **A** and **B** in Figure 1,^{6,10} due to the limited resolution of the experimental setup and the limited fraction of the sample that is expected to be undergoing a transformation (delithiation) at one time at the slow rates used here.

In situ X-ray Diffraction Patterns

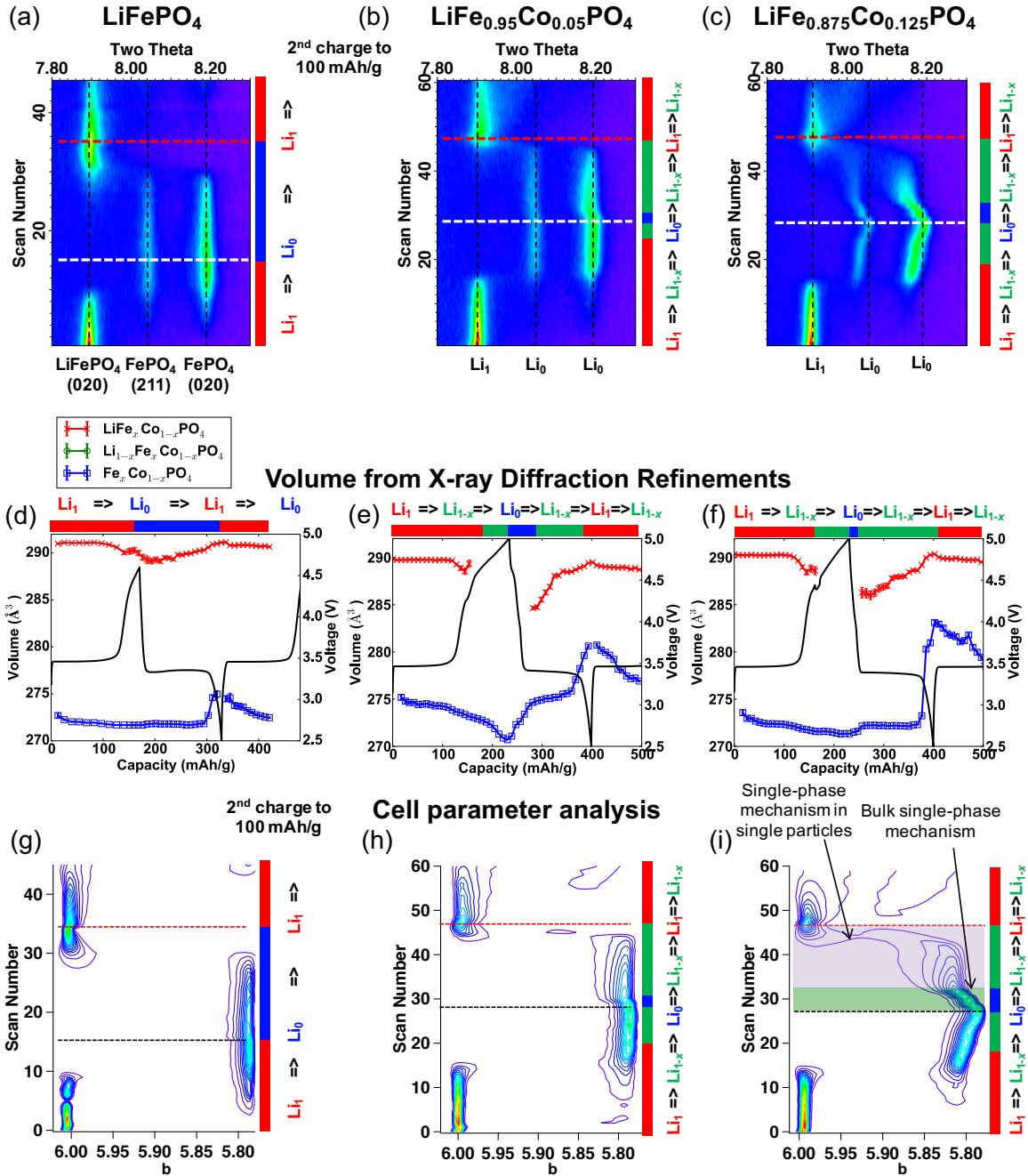


Figure 2. *In situ* XRD data for the first cycle and up to 100 mAh/g of the second charge of the Fe-rich $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ ($x = 1, 0.95$ and 0.875 , (a)–(c), respectively) phases, whilst cycling at a rate corresponding to $C/20$. The x -axis, here and in all of the XRD patterns presented in this paper displays the 2θ region = $7.8 - 8.3^\circ$, ($\lambda = 0.413609 \text{ \AA}$), showing the characteristic (020) and (211) reflections of the end member phases. The y -axis represents the scan number. These scan numbers correspond to the red crosses (and green/blue circles/boxes) marked on the electrochemical data in (d) – (f), for the first charge. The location of the scans in the subsequent discharge and charge are given in the SI. The black dotted vertical lines indicate the positions of the peaks of the fully lithiated and delithiated phases. Unit cell volume changes against capacity (mAh/g) for $x = 1, 0.95$ and 0.875 for the first charge are shown in (d)–(f), respectively. The black line represents the electrochemistry while the red crosses, blue squares and green circles represent the volume of the $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$, $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$, and $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ phases, respectively. (g)–(i) b -lattice parameter variations plotted as population densities as a function of the scan number for $x = 1, 0.95$ and 0.875 , respectively (extracted from refinements using whole-powder-pattern fits). The b -lattice parameters for the lithiated and delithiated phases are ~ 6.0 and 5.8 \AA , respectively. The white, (a)–(c) and black, (g)–(i), dashed horizontal lines indicate the end of the charge while the red dashed lines represent the end of the discharge. The red, green, purple and blue bars alongside the figure show when the Li_1 -, Li_{1-x} -, $\text{Li}_{2/3}$ - and $\text{Li}_0\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ phases, respectively, are being consumed.

In both $\text{LiFe}_{0.95}\text{Co}_{0.05}\text{PO}_4$ and $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$, the evolution of the intensities and positions of the reflections of the end member lithiated phase on charging is similar to that observed for LiFePO_4 . In contrast, the peak positions of the delithiated phases, deviate noticeably from the positions of $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$, shifting towards that of the Li_0 -phase as charging proceeds. The extent of the deviations becomes more significant as the Co content increases.

Rietveld refinements were carried out using the XRD data from the first charge (up to the white dashed horizontal line in Figures 2(a)-(c)) and the changes in the unit cell volumes as a function of capacity are plotted in Figures 2(d)-(f). The theoretical capacity of $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ is between 167 – 170 mAh/g. However, as seen in Figure 2(e) and (f) the charge capacities for the Co-containing materials are noticeably larger than expected due to side reactions (potentially including oxidation of the electrolyte above 4.6 V, the formation of a solid electrolyte interphase at the cathode,^{36,37} metal dissolution,³⁸ and the oxidation of carbon). Nevertheless, the discharge capacities are among the highest recorded for these materials (~160 mAh/g, Table S1 and Figure S6 in the SI), suggesting that the reversibility of the electrochemical reactions is not significantly affected by the side reactions, at least in the first few cycles.

Since the $\text{Fe}^{2+} \Rightarrow \text{Fe}^{3+}$ and the $\text{Co}^{2+} \Rightarrow \text{Co}^{3+}$ redox reactions occur at ~3.5 V and ~4.8 V respectively in the olivine structure, Fe^{2+} is oxidized first upon charging. Therefore, the particles must have a Li content of $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ at the end of the 3.6 V process, because $x\text{Li}$ per formula unit are de-intercalated during the Fe plateau. A continual and gradual shift of the unit cell volume is observed from the $\text{Li}_{1-x}(\text{Fe}^{3+})_x(\text{Co}^{2+})_{1-x}\text{PO}_4$ phase to the fully delithiated $(\text{Fe}^{3+})_x(\text{Co}^{3+})_{1-x}\text{PO}_4$ material on charging at > 3.5 V (Figures 2(e) and (f)), which is indicative of a single-phase transition between the two Li stoichiometries at the bulk (electrode) level, C, for the $\text{Co}^{2+}/\text{Co}^{3+}$ process. Ex-situ ^{31}P NMR spectra of the fully charged material confirm the complete transformation of these phases to $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ (Figure S7).

3.2.2 Subsequent cycles: the discrete nonequilibrium single-phase mechanism, **D**

As seen in Figures 2(a)-(c) the first discharge and second charge appear to have a different *in situ* XRD response as compared with the first charge. The sharp reflections from the pristine structure are not re-formed after the first cycle and instead the reflections are broader and asymmetric (the individual diffraction patterns are plotted in Figure S8 in the SI). Additionally, low intensity, continually shifting peaks are observed

between the $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$, $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ and $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ reflections in the first discharge and second charge, which correspond to compositions with intermediate stoichiometries. The patterns qualitatively resemble those observed by Liu *et al.*¹² during very fast cycling of LiFePO_4 , this phenomenon being attributed to the nonequilibrium single-phase, particle-by-particle delithiation mechanism of LiFePO_4 , **D**.

Following the work of Liu *et al.*,¹² we used whole-powder-pattern fitting to obtain population densities describing the fraction of the sample exhibiting different cell parameters. The population densities of the *b*-lattice parameters for LiFePO_4 , $\text{LiFe}_{0.95}\text{Co}_{0.05}\text{PO}_4$ and $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$ plotted as a function of scan number for the first 1.5 cycles are shown in Figures 2(g)-(i), respectively. Liu *et al.*¹² observed that $\text{Li}_{1-\delta}\text{FePO}_4$ can accommodate a larger deviation in the *a*-, *b*- and *c*-lattice parameters from the end member LiFePO_4 , than $\text{Li}_\delta\text{FePO}_4$ can from FePO_4 (after the first charge). This is supported by phase-field simulations³⁹ and *in situ* XRD experiments,^{25,40} both showing that $\text{Li}_{1-\delta}\text{FePO}_4$ is able to exist in a larger single-phase region than $\text{Li}_\delta\text{FePO}_4$. When 5 % Co is substituted onto the Fe site, the $\text{Li}_{0.05}\text{Fe}_{0.95}\text{Co}_{0.05}\text{PO}_4$ intermediate can tolerate an even larger range of cell parameters, beyond those observed for $\text{LiFe}_{0.95}\text{Co}_{0.05}\text{PO}_4$ and $\text{Fe}_{0.95}\text{Co}_{0.05}\text{PO}_4$. This becomes apparent on discharging. The effect is more pronounced for $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$, which upon discharge, first shows bulk single-phase (solid solution) behavior (**C**) between fully delithiated $\text{Fe}_{0.875}\text{Co}_{0.125}\text{PO}_4$ and the intermediate $\text{Li}_{0.125}\text{Fe}_{0.875}\text{Co}_{0.125}\text{PO}_4$ (*i.e.* a continuous shift of the diffraction peaks, with a narrow distribution in the *b*-lattice parameter); this is then followed by an asymmetric broadening in the diffraction peaks, reflecting a large dispersion of lattice parameters/d-spacings. This asymmetric broadening is a deviation from the conventional two-phase reaction and suggestive of a single-phase, non-equilibrium transformation between $\text{Li}_{0.125}\text{Fe}_{0.875}\text{Co}_{0.125}\text{PO}_4$ and $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$, **D**.

The results in Figure 2 strongly suggest that the nonequilibrium single-phase behavior (**D**), previously observed only at high rates, is present even under the application of a low current. The presence of Co substituted into the LiFePO_4 structure results in more particles reacting at the same time, making it easier to detect the single-phase behavior. However, there is still evidence of nonequilibrium single-phase transition at low cycle rates even for LFP. Interestingly, more particles react simultaneously in the first discharge and second charge, as compared to the first charge. This same phenomenon was also observed at high rates for LiFePO_4 , *i.e.* the asymmetric peak broadening (and hence non-equilibrium limits of solid solution) is more significant in the first discharge and

subsequent cycles than in the first charge.¹² It is not clear what the origin of this phenomenon but it may be related to non-equilibrium Li^+ ion concentrations being present within the electrolyte, particularly when experiments are performed at high rates, simulations being required to explore this hypothesis. The introduction of disorder in the lattice, via the formation of defects (particularly in the case of the Co-materials), or due to the presence of residual Li ions or vacancies in the delithated and lithiated materials, respectively, may also result in an increased entropy of the system and a reduction in the tendency of the system to order, promoting solid solution behavior.

3.3 Highly Co-Substituted phases

3.3.1 $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ and $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$

The electrochemistry and *in situ* XRD patterns for the first charge of the highly substituted olivine material, $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$, are shown in Figures 3 (a) and (b). In agreement with the Fe-rich materials, the intermediate, $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$, is seen at the end of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox plateau. Interestingly, a second intermediate is also observed which, on the basis of our previous study of LiCoPO_4 , in which a $\text{Li}_{2/3}\text{CoPO}_4$ intermediate was identified, has Li stoichiometry $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$.²⁴ Using Vegard's law and assuming a constant variation in the lattice parameters across the series $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ ($0 \leq x \leq 1$) and for $\text{Li}_y\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ ($0 \leq y \leq 1$) we can estimate the expected lattice parameters for $\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ (the resulting approximate position of the (020) reflection is shown with a white ellipse in Figure 3). Surprisingly, the reflections from $\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ are difficult to detect in Figure 3(b) during the first charge, despite a capacity of over 91 % the theoretical capacity (*i.e.* 153 mAh/g of the theoretical 167.75 mAh/g) on both the first and second cycle. The fully delithiated phase is, however, more clearly seen in the second cycle (see Figure S9 in the supporting information, SI) and close inspection of the individual XRD patterns at the end of first charge, as shown in Figure S9 in the SI, does reveal small, weak reflections at the same positions observed for $\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ in the second cycle.

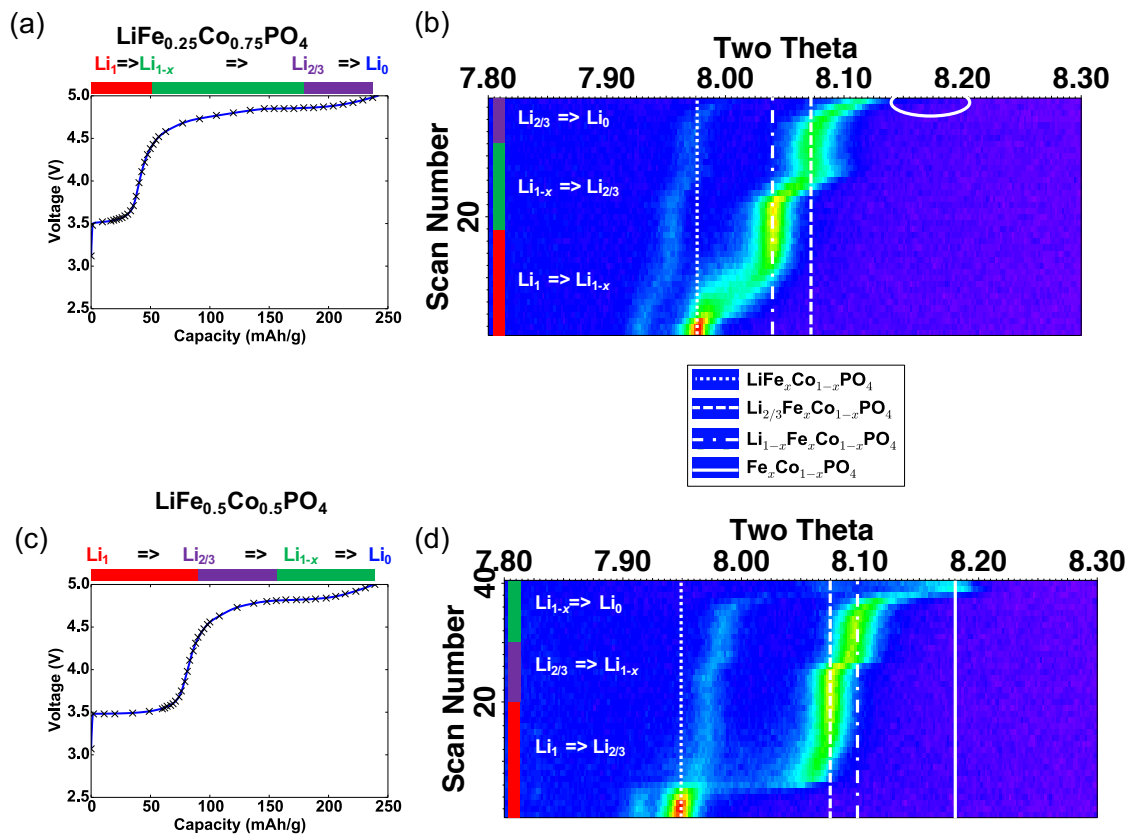


Figure 3. First charge XRD data for (a), (b) $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ and (c), (d) $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ charged at a cycle rate of $C/20$. The electrochemistry collected during the *in situ* XRD experiments is shown by the blue solid line in (a) and (c); the black crosses indicate the times when the XRD patterns were collected, i.e., when the scans were commenced. The *in situ* XRD patterns are shown in (b) and (d) vs. scan number. The red, white, purple and green dashed lines represent the lattice parameters of the $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$, $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$, $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ and $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ phases, respectively. The white dashed ellipse indicates the calculated position of the 020 reflection for the delithiated phase, $\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$, assuming Vegard's law (and using the cell parameters of FePO_4 and CoPO_4). The red, green and purple bars alongside the figure show when the Li_{1-} , Li_{1-x} - and $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ phases, respectively, are being consumed in the reaction.

The *in situ* XRD patterns of the first charge of $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ (Figure 3(d)) contain reflections from two intermediate compositions, in addition to those of the fully lithiated and delithiated materials. Using Vegard's analysis, they are assigned to Li-stoichiometries of, $\text{Li}_{2/3}$ and Li_{1-x} . This is in very good agreement with the first charge of the $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ material where these two phases are formed. Interestingly, both intermediates are formed during the $\text{Fe}^{2+}/\text{Fe}^{3+}$ plateau, $\text{Li}_{2/3}\text{Fe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ forming first, followed by $\text{Li}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}\text{PO}_4$. The $\text{Li}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ phase forms at a charge capacity of 137 mAh/g (which is 81.3% of the theoretical capacity, 168.5 mAh/g), however as discussed, the capacities on the first charge are significantly higher than the theoretical capacities owing to side reactions, SEI formation and/or electrolyte decomposition. Therefore, in order to determine the Li composition of this intermediate we use (a) the unit cell volume, which, by Vegard's Law indicates that the phase has a stoichiometry of $\text{Li}_{0.48}$ and (b) the voltage that the $\text{Li}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ phase forms at, i.e., ~ 4.78 V (*i.e.* after the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox plateau, and before the higher voltage $\text{Co}^{2+}/\text{Co}^{3+}$ plateau).

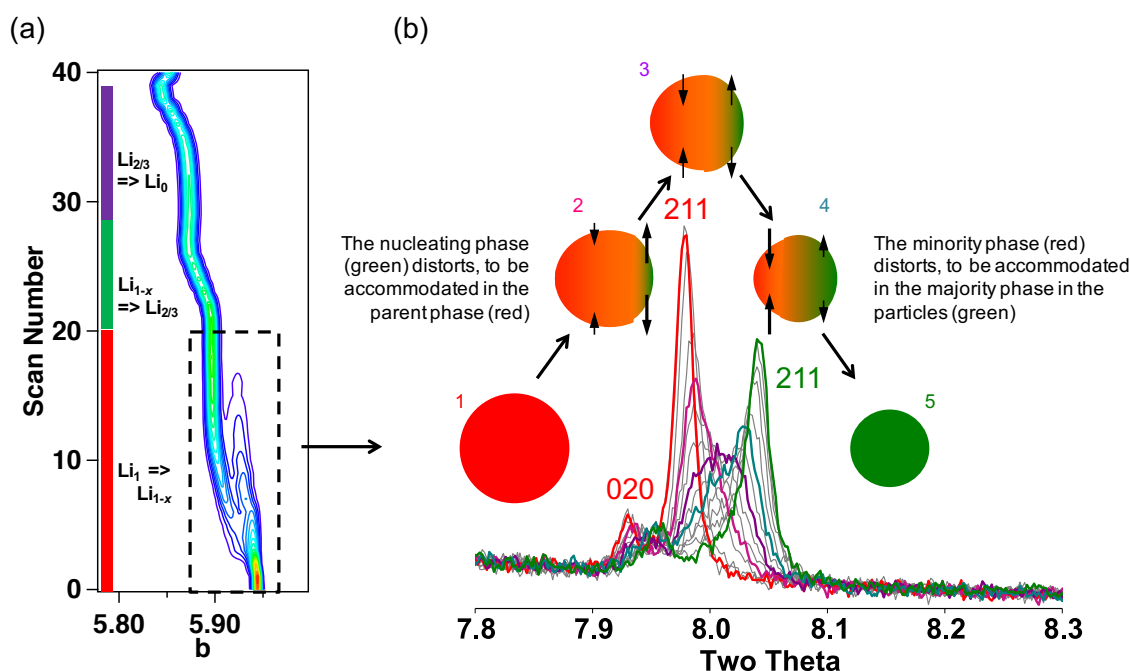


Figure 4. (a) *b*-lattice parameter variations of LiFe_{0.25}Co_{0.75}PO₄ plotted as the population density, as a function of the scan number, extracted from refinements using a whole-powder-pattern fits. (b) The XRD patterns of the phase transition from LiFe_{0.25}Co_{0.75}PO₄ to Li_{0.75}Fe_{0.25}Co_{0.75}PO₄ (*i.e.* scan numbers 0 – 20, the region highlighted by the black dashed line in (a)). The XRD response is characteristic of a coherently nucleating phase (*i.e.*, Li_{0.75}Fe_{0.25}Co_{0.75}PO₄, represented in green) in the parent phase particle (where red represents LiFe_{0.25}Co_{0.75}PO₄). The 5 cartoons at 1 - 5 represent the state of transforming particles at time corresponding to the red, pink, purple, teal and green diffraction patterns (at capacities of 0, 37, 80, 103 and 115 mAh/g, respectively, representing scan numbers 1, 5, 8, 10 and 15, respectively). The red, green and purple bars alongside the figure indicate when the Li_{1-x}, Li_{1-x} and Li_{2/3}Fe_xCo_{1-x}PO₄ phases, respectively, are being consumed in the reaction.

3.3.2 The Coherent Interface

A whole-powder-pattern fit was performed for LiFe_{0.25}Co_{0.75}PO₄ and the population density plot of the *b*-lattice parameter is shown as a function of scan number in Figure 4(a). The first intermediate, Li_{0.75}Fe_{0.25}Co_{0.75}PO₄, is formed via a two-phase reaction from the fully lithiated phase. It can be seen that LiFe_{0.25}Co_{0.75}PO₄ and Li_{0.75}Fe_{0.25}Co_{0.75}PO₄ have significant Li solubility ranges. To study this first phase transition more closely, the individual XRD patterns (in the 2θ range containing the 020 and 211 reflections) for the beginning of charge (LiFe_{0.25}Co_{0.75}PO₄ => Li_{0.75}Fe_{0.25}Co_{0.75}PO₄) are shown in Figure 4(b). When the Li_{0.75}Fe_{0.25}Co_{0.75}PO₄ phase first nucleates in the parent phase (fully lithiated, LiFe_{0.25}Co_{0.75}PO₄, particles), the volume extends towards the volume of LiFe_{0.25}Co_{0.75}PO₄, (which results in a shift in the XRD peak position (Figure 4(b)) suggesting the presence of a coherent interface between the two phases within the same particle (Mechanism E in Figure 1 and Figure 4(b)).¹⁴ The same is observed when LiFe_{0.25}Co_{0.75}PO₄ is the minority phase in the Li_{0.75}Fe_{0.25}Co_{0.75}PO₄ particle.

The distortion to the crystal structure of the minority phase as it nucleates in the

majority phase arises from the structural elasticity in the minority phase allowing it to be accommodated in the majority phase of the particle, whilst reducing the energy at the interface of the two phases. Hence, there is both a change in intensity in the Bragg diffraction peaks (as the nucleating phase grows at the expense of the parent phase) and a shift in the peak positions, owing to the structural distortions. This phenomenon is observed, to a degree, in all the two-phase reactions but is much more pronounced in phase transformations of the highly substituted samples; it was nonetheless clearly visible in the LiCoPO_4 to $\text{Li}_{2/3}\text{CoPO}_4$ reaction.²⁴

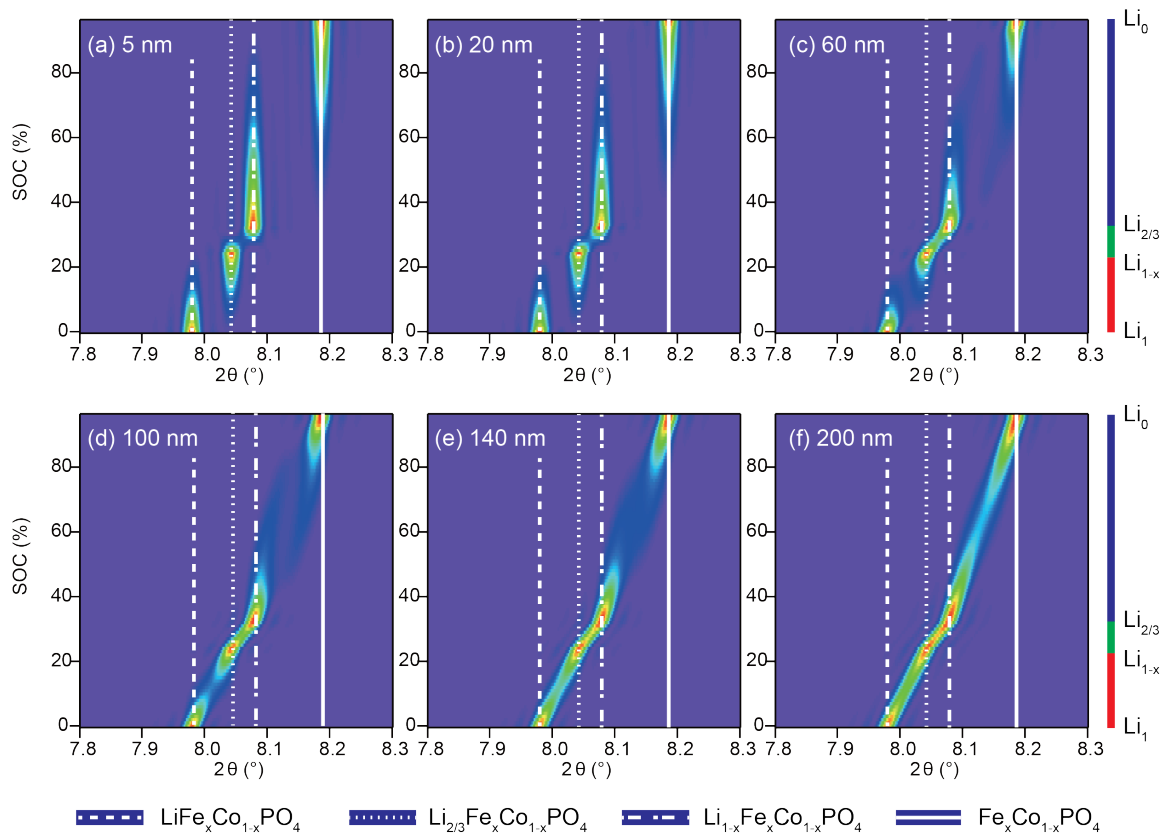


Figure 5. Simulations of the evolution of (020) XRD peak profiles for a two-phase reaction with a coherent interface between; $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ and $\text{Li}_{0.75}\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$, $\text{Li}_{0.75}\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ and $\text{Li}_{2/3}\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ and $\text{Li}_{2/3}\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ and $\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ in 100 nm sized cubic $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ particles assuming the interface is (a) 5 nm, (b) 20 nm, (c) 60 nm, (d) 100 nm, (e) 140 nm and (f) 200 nm in size at different states of charge (SOC). The red, green and purple bars alongside the figure show when the Li_{1-} , Li_{1-x} - and $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ phases, respectively, are being consumed in the reaction.

XRD peak profile simulations were carried out on 100 nm cubic $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ particles. Two-phase reactions between; $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ and $\text{Li}_{0.75}\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$, $\text{Li}_{0.75}\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ and $\text{Li}_{2/3}\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ and $\text{Li}_{2/3}\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ and $\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ were modeled with a coherent interface ranging between 5 and 200 nm in length as described in section 2.5. The length of the interface is defined as the quantity L defined in Eq. (7), which describes a concentration profile along the a -axis of the particle. When the length of the interface approaches or becomes greater than the size of the particle (100

nm), the concentration gradient spans across the entire particle, which does not have two well defined phases and appears more like a single-phase solid solution. (Representative concentration profiles are illustrated in Figure S10) It should be noted that when the coherent interface is 200 nm in size, the peaks continually and gradually shift from the reactants to the products, *i.e.* the response approaches that expected for a bulk single-phase mechanism, Scheme C. The result for the evolution of the (020) XRD peak is shown in Figure 5. There is reasonable agreement between the simulation and the experimental data of the coherent interface: the peaks of the minority phase distorts significantly towards the values of the majority phase (Figure 5(c)). The simulations suggest that the $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4 \Rightarrow \text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ react via the two-phase mechanism with a coherent interface where $60 < L < 100$ nm. In contrast, the reaction of $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ to $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ and $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ to $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ both show a continuous and gradual shift in the XRD peaks, corresponding to the two-phase mechanism with a coherent interface where $L = 200$ nm, *i.e.* the bulk solid-solution mechanism.

Note that we have assumed that the nucleating phase that grows within the majority component has the same composition and thus cell parameters as the bulk phase, the composition varying across the interface. It is also important to emphasize that more than one coherent interface may exist in one particle simultaneously.

3.3.3 Systematic analysis of cell parameter changes

The same analysis as described in Section 3.3.1 for $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ and $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ was carried out for all the $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ phases ($x = 1, 0.95, 0.875, 0.75, 0.125, 0.05$ and 0). The cell parameters for the intermediates and end member phases for all nine ratios were extracted from Rietveld refinements of the XRD patterns (all the raw data is shown in Figure S11 in the SI). Plots of the unit cell volume of the end members and intermediates, extracted from the Rietveld refinements of the XRD patterns are plotted against Fe content (x) (Figure 6). The phases corresponding to $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$, $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$, $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ and $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ are shown by red, green, purple and blue data points. There is a linear increase in the volume of $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ (shown in red), with increasing x . This is in agreement with the literature,^{41,42} and is a result of the homogeneous mixing of the transition metals in the olivine structure (assuming Vegard's Law applies). Similarly, the a and b lattice parameters (shown in Figure S12 in the SI) increase with increasing Fe content, due to the larger ionic radius of Fe^{2+} compared with Co^{2+} (92 and 88.5 pm, respectively, assuming a high-spin ion in an octahedral

environment).⁴³ Interestingly, the *c*-axis decreases with increasing Fe content and although the origin for this behavior is unknown, it is thought to be related to the stiffness of the P-O bonds (effectively rigid PO₄ tetrahedra) and the shared edges between the PO₄ and MO₆ polyhedra,⁴¹ the phosphate ions acting to separate or pillar the chains of edge sharing MO₆ octahedra. The changes in the volume for Fe_xCo_{1-x}PO₄ display the same linear gradient as the lithiated phases (blue dashed line), presumably because the difference in Co and Fe cation sizes is identical for the divalent and trivalent cations. The volume of the Li_{2/3}Fe_xCo_{1-x}PO₄ intermediate (observed for the Co-majority materials, 0 ≤ *x* ≤ 0.5) lies 2/3 of the way between the fully lithiated and delithiated phases (purple dashed line) and the volume of the Li_{1-x}Fe_xCo_{1-x}PO₄ intermediates varies linearly between LiCoPO₄ and FePO₄, with increasing Fe content (green dashed line). This simple analysis using Vegard's rule is in good agreement with the Li-stoichiometries assigned to the intermediates observed during the first charge of LiFe_xCo_{1-x}PO₄ (*x* = 0.95, 0.875, 0.75, 0.5, 0.125 and 0.05). Although no obvious trends for the compositions and cell parameters of the different intermediates emerge when studying each composition individually, when systematically examining the phases as a function of Fe:Co ratio, clear correlations are seen with respect to the Li-composition and cell parameters of the intermediate phases.

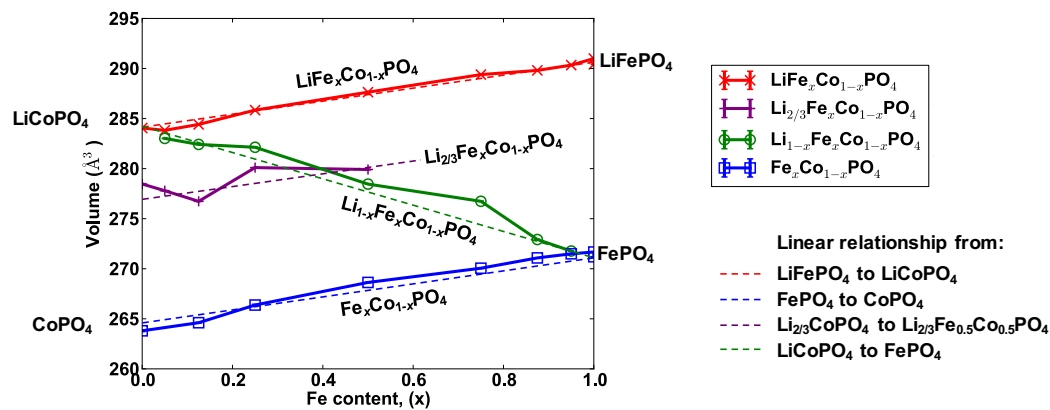


Figure 6. The unit cell volumes of the end member and intermediate phases observed when LiFe_xCo_{1-x}PO₄ is delithiated. The red dashed line represent linear volume changes from LiFePO₄ to LiCoPO₄ calculated using the end member volumes. The same gradient for the lithiated phases (red) was used for the delithiated and Li_{2/3}Fe_xCo_{1-x}PO₄ materials (blue and purple dashed lines, respectively). The blue line was drawn to go through the delithiated unit cell volume data and the purple line is placed 2/3 of the way between the delithiated and lithiated data (i.e., it is not a fit to the data). The green dashed line simply connects the experimental cell volumes of LiCoPO₄ to FePO₄.

The percentage difference in the *a*-, *b*- and *c*-axes, the *ab*-, *ac*- and *bc*-planes and the volume of the two intermediates and the end member structures relative to LiFePO₄ have been calculated and are shown in Figure S13 in the SI. As was observed in the LiFe_xMn_{1-x}PO₄ materials¹⁴ and for LiCoPO₄,²⁴ there is a very small difference (< 2%) in the *bc*-plane between all the structures. Therefore, it strongly suggests that when there is a

coherent interface, it is likely to be in this plane, resulting in the lowest size mismatch and therefore, strain, compared to an interface along the ab and bc -planes. This arises from the contraction of the c -axis upon both increasing Co content and decreasing Li content from LiFePO_4 and the smaller expansion in the b -axis, as compared with the a -axis. We now consider separately how the delithiation mechanisms vary between the starting, intermediate and end member phases, comparing mechanisms as a function of Co content.

3.4 The $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ delithiation mechanisms upon charging

3.4.1 Delithiation mechanisms between the two intermediates $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ and $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$

As shown in Figure 6, when the four substituted olivines $\text{LiFe}_{0.05}\text{Co}_{0.95}\text{PO}_4$, $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$, $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ and $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ are delithiated, two intermediates are observed, $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ and $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$. We now investigate in more detail how the structural transformation between these two intermediate phases occurs, starting with this transformation because it is the simplest mechanism observed in this system. A whole-powder-pattern fit was performed for all four materials during the delithiation between the two intermediates and the population density plots of the b -lattice parameter as a function of scan number are shown in Figure 7 (only the b -lattice parameter changes are shown here for clarity; the a , b and c -lattice parameter changes can be found in Figures S14, S15 and S16 in the SI). The decrease in the intensity of the lattice parameter population densities for $\text{LiFe}_{0.05}\text{Co}_{0.95}\text{PO}_4$ is attributed to the loss of long-range order, similar to that observed upon charging LiCoPO_4 . For the three higher Fe-content materials continuous intensity is observed connecting the lattice parameters of the $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ and $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ phases, providing evidence for a bulk single-phase transformation, **C**. This is noticeably different from the response in the lattice parameters observed for both the discrete nonequilibrium single-phase mechanism, **D**, and the two-phase mechanism exhibiting a large coherent interface (shown in Figure 4(b) and denoted from here onwards as Scheme **E**).

The single-phase mechanism between the intermediates appears to be preferred due to the disorder of the transition metals on the Fe/Co sublattice. The homogeneous mixing of Fe^{2+} and Co^{2+} on the transition metal sublattice in the starting materials,⁴² results in a random distribution of Fe^{3+} and Co^{2+} in the intermediate $\text{Li}_{1-x}(\text{Fe}^{3+})_x(\text{Co}^{2+})_{1-x}\text{PO}_4$. Unless there is an energy gain for Li^+ /vacancy ordering, this also results in a random distribution of Li^+ ions in the particles, Li^+ preferentially occupying sites close to Co^{2+} (or more

generally M^{2+}) due to reduced Li^+ -transition metal cation repulsive coulombic interactions arising from the lower charge of Co^{2+} vs. Fe^{3+} . The existence of a distribution of Li^+ /vacancies and $\text{Fe}^{3+}/\text{Co}^{2+}$ in the intermediate $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$, helps favor the bulk single-phase mechanism for the $\text{Co}^{2+}/\text{Co}^{3+}$ process for $\text{LiFe}_{0.05}\text{Co}_{0.95}\text{PO}_4$, $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$ and $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$. As discussed in Section 3.3.1, the $\text{Li}_{2/3}$ -intermediate is also formed on the $\text{Fe}^{2+}/\text{Fe}^{3+}$ oxidation plateau for $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$, which means that this single-phase mechanism also occurs between the intermediates during Fe^{2+} oxidation. Therefore, it is likely that the single-phase mechanism between the intermediates is also preferred due to the small change in volume between $\text{Li}_{2/3}\text{Fe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ and $\text{Li}_{1-x}\text{Fe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ (see inset in Figure 7).

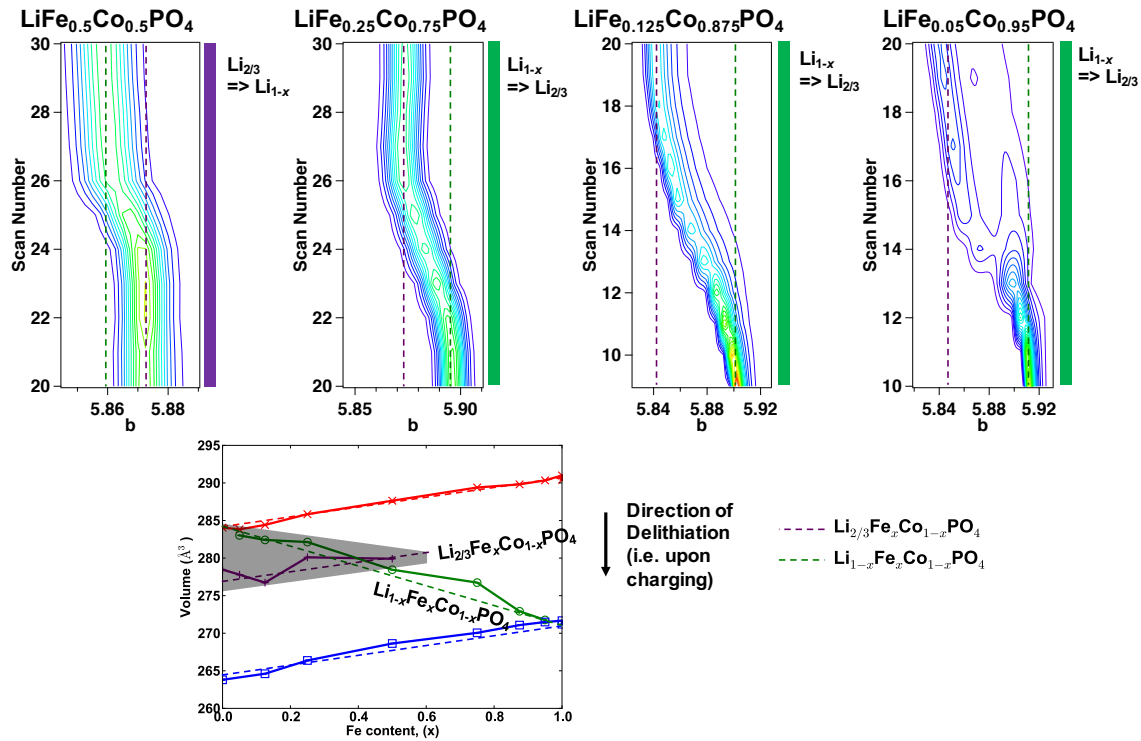


Figure 7. b -lattice parameter variations plotted as population densities relative to the scan number for $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$, $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$, $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$ and $\text{LiFe}_{0.05}\text{Co}_{0.95}\text{PO}_4$. These were extracted from refinements using whole-powder-pattern fits. The bottom figure shows the volume changes between the intermediate phases, the grey shaded area indicating the phases being investigated in this section and whose cell parameters are shown in this Figure. The green and purple bars alongside the figure indicate when the Li_{1-x} - and $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ phases, respectively, are being consumed in the reaction.

3.4.2 Delithiation mechanisms to form the fully delithiated phase, $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$

We now examine the mechanisms that occur to form $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ at the end of the first charge. A whole-powder-pattern fit was performed for $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$, $\text{LiFe}_{0.75}\text{Co}_{0.25}\text{PO}_4$, $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ and $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$ and the population density plots of the b -lattice parameter as a function of scan number are shown in Figure 8, in the region of the charge profile when the fully delithiated phase forms. For the Fe rich

samples, this represents the transformation from $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ to $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$, while for the higher Co-content sample ($\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$) this corresponds to a transition from the $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ phase. Three samples were not included in this analysis because the fully delithiated phase was not clearly observed on the first charge ($\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$; Section 3.3.1), no XRD patterns were obtained for the full charge (for $\text{LiFe}_{0.05}\text{Co}_{0.95}\text{PO}_4$) due to time limitations at the synchrotron, and for LiCoPO_4 the significant loss of long range order results in reduced intensity of the Bragg reflections making the data difficult to interpret using this method of analysis.

When $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$ is fully delithiated, there is a continuous and gradual shift in the lattice parameters from the $\text{Li}_{0.125}\text{Fe}_{0.875}\text{Co}_{0.125}\text{PO}_4$ phase to $\text{Fe}_{0.875}\text{Co}_{0.125}\text{PO}_4$ indicating that the bulk single-phase mechanism, Scheme C, is observed. As discussed in Section 3.4.1, the single-phase mechanism is preferred due to (i) the disorder of Li^+ /vacancies and $\text{Fe}^{3+}/\text{Co}^{2+}$ in $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$, which helps favor the single-phase mechanism during the oxidation of Co^{2+} , and (ii) the small change in volume. For both $\text{LiFe}_{0.75}\text{Co}_{0.25}\text{PO}_4$ and $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$, single-phase behavior is also observed on delithiating $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$, however, fewer particles appear to be reacting at once compared with $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$ (*i.e.* the number of particles decreases for decreasing Fe-content from $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$ to $\text{LiFe}_{0.75}\text{Co}_{0.25}\text{PO}_4$ to $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$). A continuous shift in the lattice parameters can be seen from $\text{Li}_{1-x}\text{Fe}_{0.75}\text{Co}_{0.25}\text{PO}_4$ to $\text{Fe}_{0.75}\text{Co}_{0.25}\text{PO}_4$, whereas for the $\text{Li}_{0.5}\text{Fe}_{0.5}\text{Co}_{0.5}\text{PO}_4 \Rightarrow \text{Fe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ reaction significant asymmetric deviations of the end member phases towards each other are observed. This implies that the single-phase mechanism is, to a degree, occurring discretely between particles, D, rather than simultaneously (*i.e.* at the bulk level, C). This change from particles reacting discretely compared with simultaneously is even more pronounced during the reaction of $\text{Li}_{2/3}\text{Fe}_{0.125}\text{Co}_{0.875}\text{PO}_4$ to form $\text{Fe}_{0.125}\text{Co}_{0.875}\text{PO}_4$.

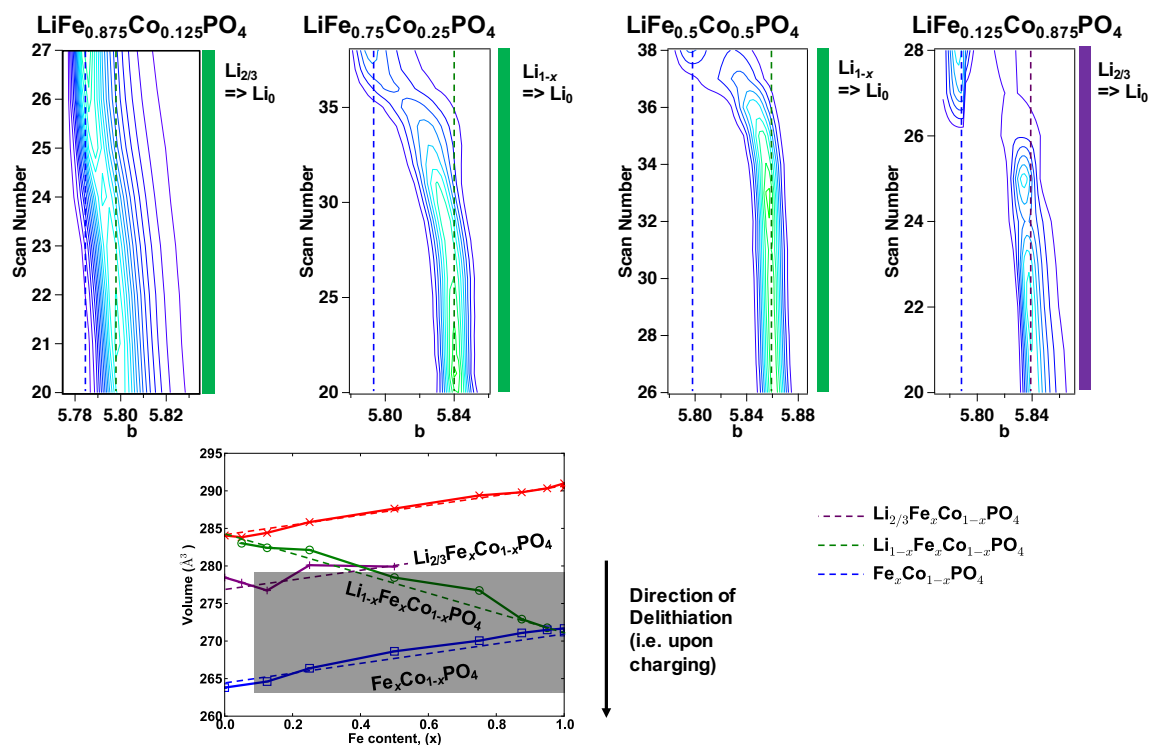


Figure 8. b -lattice parameter variations plotted as population densities relative to the scan number for $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$, $\text{LiFe}_{0.75}\text{Co}_{0.25}\text{PO}_4$, $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ and $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$. These were extracted from refinements using whole-powder-pattern fits. The bottom figure shows the volume changes as a function of Fe content, the grey shading indicating the phase changes being investigated in this figure. The green and purple bars alongside the figure shows when the Li_{1-x} - and $\text{Li}_{2/3}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ phases, respectively, are being consumed in the reaction.

To summarize, during the oxidation of Co^{2+} to Co^{3+} , a single-phase (solid-solution) mechanism occurs within individual particles to form fully delithiated $\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$. At low levels of Fe-substitution (*i.e.* $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$), the reaction occurs discretely, particle-by-particle. As the level of Fe-substitution increases, more particles react simultaneously resulting in increasingly more bulk single-phase like behavior. At high Fe-contents, *i.e.* $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$ essentially ideal single-phase behavior is observed.

3.4.3 Delithiation mechanisms occurring during the reaction of fully lithiated $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$

Finally, we examine the first delithiation reaction that occurs upon charging $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ for $x = 1, 0.95, 0.875, 0.75, 0.5, 0.25, 0.125$ and 0.05 . A whole-powder-pattern fit was performed for all eight of the materials and the population density plots of the b -lattice parameter as a function of scan number are shown in Figure 9 for the initial delithiation of the pristine $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ phase. LiCoPO_4 is not included here since we focus here on the mechanism that occurs on the $\text{Fe}^{2+}/\text{Fe}^{3+}$ oxidation plateau.

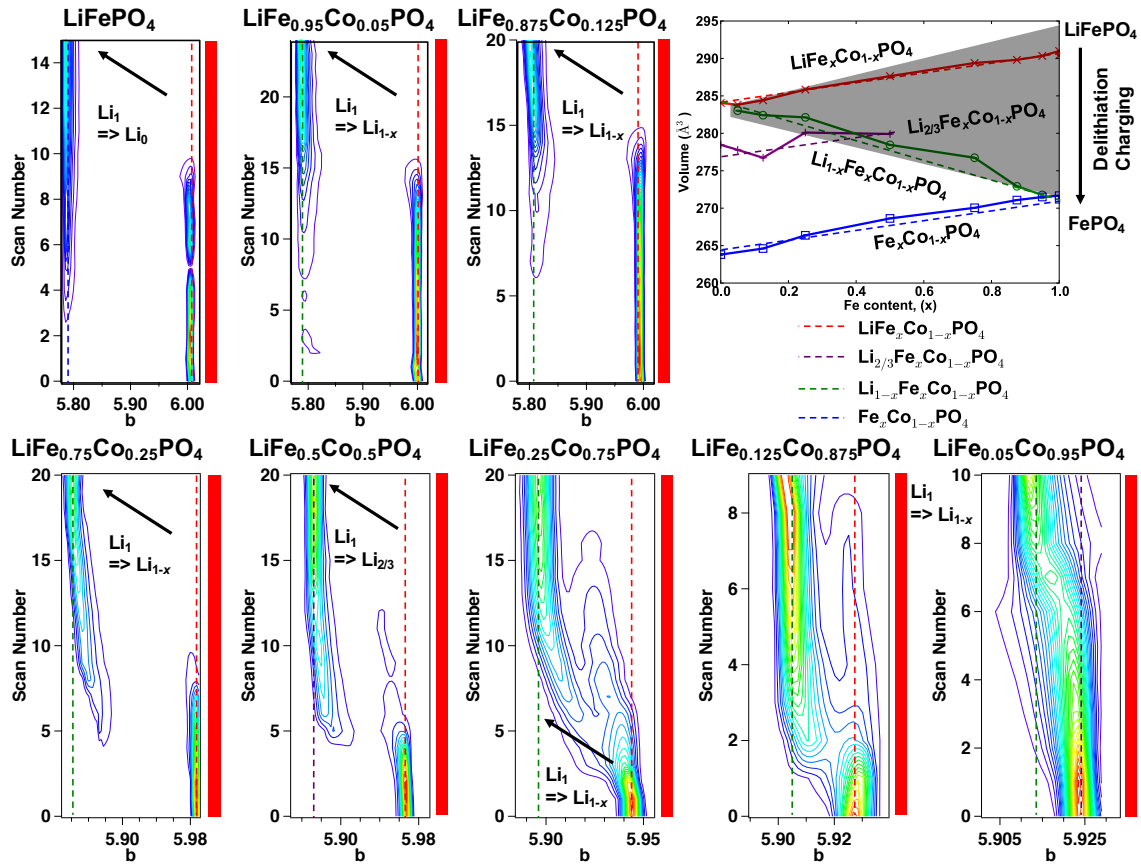


Figure 9. Lattice parameter variations plotted as population densities relative to the scan number for $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$, where $x = 1, 0.95, 0.875, 0.75, 0.5, 0.25, 0.125$ and 0.05 . These were extracted from refinements using whole-powder-pattern fits. The top right hand side inset shows the volume changes, the grey shaded area highlighting those that occur when the fully lithiated phase is delithiated. The red bars alongside the figure represent that it is the $\text{Li}_1\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ phase that is being consumed, as the material is delithiated.

As discussed in Section 3.2, the delithiation of the Fe-rich materials (LiFePO_4 , $\text{LiFe}_{0.95}\text{Co}_{0.05}\text{PO}_4$ and $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$) appears to occur via a simple “two-phase” reaction (as only the two end member phases are observed, as depicted in Mechanism **B**). However, further analysis of the first discharge and second charge reveals that the transformation between the two phases (LiFePO_4 and FePO_4 , and $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ and $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ for $x = 0.95$ and 0.875) occurs via the nonequilibrium single-phase mechanism, **D**. Since very few particles react at once, the two end member phases dominate the response. As the Co-substitution levels increases (from 0 to 0.05 to 0.125), more particles react at once and the asymmetric deviations from the end member phases towards each other are more discernible, even in the 1st charge (Figure 9 for $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$).

The delithiation mechanisms of $\text{LiFe}_{0.75}\text{Co}_{0.25}\text{PO}_4$ and $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ at the onset of charge involve a bulk shift of the lattice parameters from those of the end members, $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ and $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$, as well as an asymmetric broadening in the parameters towards each other. In Section 3.3, we ascribed the behavior seen for the

delithiation of $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ to form $\text{Li}_{0.75}\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ to that of a two-phase reaction occurring in the presence of a coherent interface. Therefore the behavior of $\text{LiFe}_{0.75}\text{Co}_{0.25}\text{PO}_4$ and $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$ is likely to be intermediate to that of the Fe-rich materials and $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$. We will discuss how these mechanisms are related in more detail in Section 3.5.

$\text{LiFe}_{0.05}\text{Co}_{0.95}\text{PO}_4$ reacts via a bulk single-phase mechanism (C) to form the $\text{Li}_{0.95}\text{Fe}_{0.05}\text{Co}_{0.95}\text{PO}_4$ intermediate, as shown by continuous shift in lattice parameters, whereas $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$ has more “two-phase”-like behavior, as shown by the coexistence of the $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$ and $\text{Li}_{0.875}\text{Fe}_{0.125}\text{Co}_{0.875}\text{PO}_4$ lattice parameters, with some shift in the parameters towards each other. As the Fe-content decreases two phenomena occur: the difference in the cell parameters between $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ and $\text{Li}_{1-x}\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$ decreases and the substitution levels (*i.e.* the disruption in the lattice) decrease. The former will favor the single-phase mechanism (as observed for $\text{LiFe}_{0.05}\text{Co}_{0.95}\text{PO}_4$) and the latter will result in shorter coherent interface (as the lattice has fewer dopant Fe-particles leading to reduced structural elasticity) in the two-phase reaction, as seen for $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$. These two competing phenomena must cause the apparent “break” in trend for $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$.

3.5 Discussion of how the mechanisms are related and inter-convert

As demonstrated in Section 3.4, there is not a sharp cut-off between the various different mechanisms as the Co content increases. In Figure 10 we summarize how the mechanisms are interconnected. From previous studies^{3,6} on partially charged samples of LiFePO_4 , we know that as we increase the particle size, the two end member phases (*i.e.* FePO_4 and LiFePO_4) are able to coexist within a particle, rather than existing in separate particles (the transition from Scheme B to A in Figure 10).

We saw in Section 3.2 that at slow cycle rates nano-particulate LiFePO_4 delithiates via the single-phase mechanism with few particles reacting at once (Scheme B). As the Co-content increases from LiFePO_4 to $\text{LiFe}_{0.95}\text{Co}_{0.05}\text{PO}_4$ and $\text{LiFe}_{0.875}\text{Co}_{0.125}\text{PO}_4$, more particles react simultaneously during delithiation of the fully lithiated phase on the plateau of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ oxidation reaction, as demonstrated by the pathway from Scheme B to D in Figure 10. The studies by Liu *et al.* showed that as the current applied to the system increases, the same trend is observed, Scheme B to D.¹² A more pronounced effect (*i.e.* even more particles react simultaneously) is seen when forming the fully delithiated phase during the $\text{Co}^{2+}/\text{Co}^{3+}$ oxidation reaction for increasing Fe-content, for $x = 0.125$,

0.5, 0.75 and 0.875 (Scheme **D** to **C**), eventually leading to the bulk single-phase mechanism (**C**) for the transformation between $\text{Li}_{0.125}\text{Fe}_{0.875}\text{Co}_{0.125}\text{PO}_4$ and $\text{Fe}_{0.875}\text{Co}_{0.125}\text{PO}_4$.

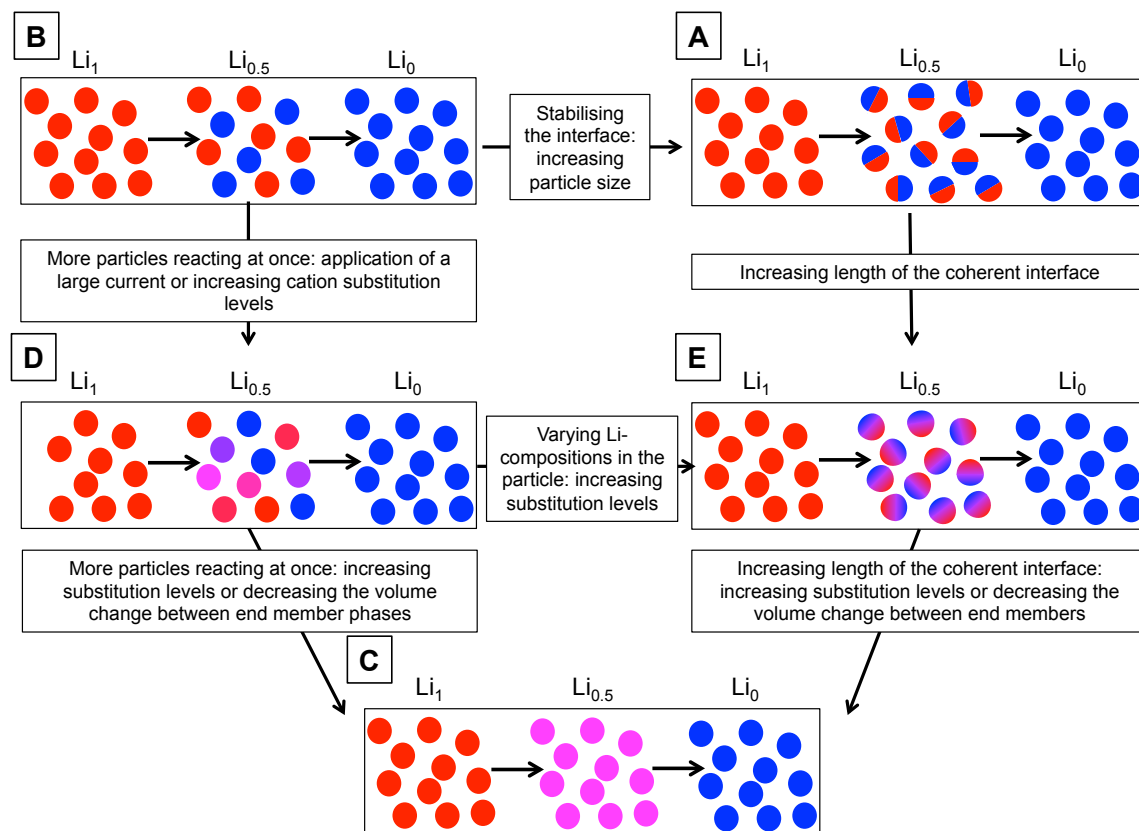


Figure 10. A schematic showing how the apparently different delithiation mechanisms are interconnected. The lettering A – E corresponds to that introduced in Figure 1.

Using Figure 10, we are now able to better understand the trend in the mechanisms observed in Figure 9. We know that increasing the Co-content in the substituted olivines increases the number of particles that react simultaneously during the plateau of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ oxidation reaction, Scheme **B** \Rightarrow **D**, and we know that a two-phase mechanism containing a coherent interface was observed when $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ was delithiated to form $\text{Li}_{0.75}\text{Fe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ (Scheme **E**). Therefore between $\text{LiFe}_{0.75}\text{Co}_{0.25}\text{PO}_4$, $\text{LiFe}_{0.5}\text{Co}_{0.5}\text{PO}_4$, the mechanism is transitioning from **D** to **E**; both more particles are reacting at once and the intermediate lithium compositions are now able to coexist within a particle, rather than between particles. As we further increase in Co-content from $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$ to $\text{LiFe}_{0.05}\text{Co}_{0.95}\text{PO}_4$, we move from scheme **E** to **C**; the length of the coherent interface increases to the size of the particles (as demonstrated in our simulations in Figure 5). As explained in Section 3.4.3, the apparent “anomaly” in the mechanisms for $\text{LiFe}_{0.125}\text{Co}_{0.875}\text{PO}_4$ arises from opposing effects arising from the decrease in the change in volume during the reaction and the reduced coherency at the

interface (owing to the decreasing amount of disorder resulting from reduced Co-content). Therefore, even though it is possible to correlate the trends in the behavior in the mechanisms with changing substitution levels, because of the complicated interplay between lattice disruption and change in volume it is still not trivial to predict what mechanism will occur when. Nonetheless, by studying the whole series, considerable insight into the general trends and dominant factors in controlling the mechanism do emerge from this study.

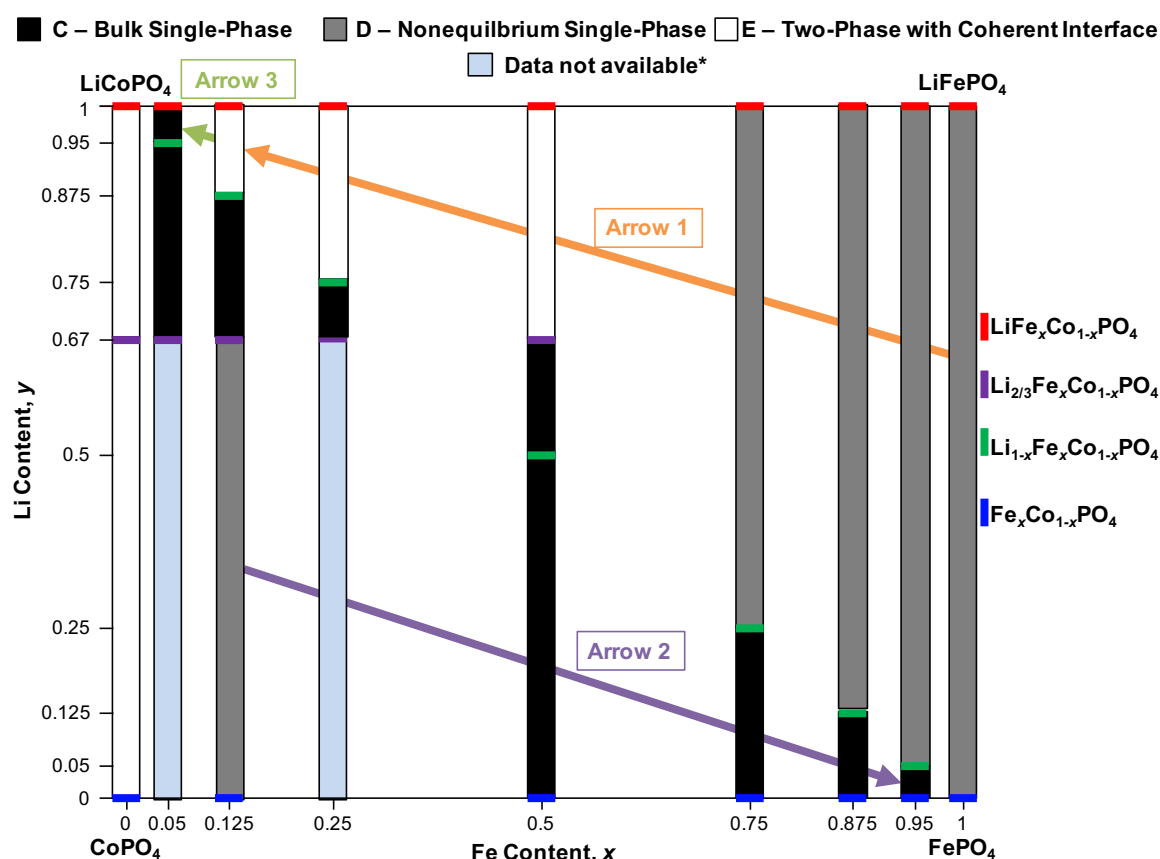


Figure 11. A pseudo-phase diagram of $\text{Li}_y\text{Fe}_x\text{Co}_{1-x}\text{PO}_4$, showing the evolution of the phases and the mechanisms by which they delithiate for decreasing Li content and varying Fe content ($0 \leq x, y \leq 1$). Red, green, purple and blue represent the Li_1 , Li_{1-x} , $\text{Li}_{2/3}$ and $\text{Li}_0\text{-Fe}_x\text{Co}_{1-x}\text{PO}_4$ phases, respectively and the black, grey and white bars represent (C) the bulk single-phase mechanism, (D) the nonequilibrium single-phase mechanism occurring particle-by-particle and (E) the two-phase mechanism with a coherent interface, respectively. Arrow 1 shows varying Li-compositions existing *within* rather than *between* the particles; Scheme D to Scheme E. The direction of arrow 1 shows the change of the mechanism from the single-phase transition occurring discretely between particles to the two-phase mechanism with significant coherency at the interface. The direction of arrow 2 indicates an increase in the number of particles reacting simultaneously; Scheme D to Scheme C. Arrow 3 shows an increasing length of the coherent interface; i.e., a transition from Scheme E to D. * The end of charge for $\text{LiFe}_{0.05}\text{Co}_{0.95}\text{PO}_4$ was not collected owing to limitations at the beamline and the fully delithiated phase was not observed on the first charge for $\text{LiFe}_{0.25}\text{Co}_{0.75}\text{PO}_4$.

4. Conclusions

A comprehensive mechanistic study on the delithiation of the co-substituted $\text{LiFe}_x\text{Co}_{1-x}$.

$x\text{PO}_4$ materials was performed by using *in situ* XRD. Correlations between the seemingly different mechanisms have been discussed within the co-substituted olivines (as summarized in Figure 11), the $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ series, $0 \leq x \leq 0.95$. They are distinguished by the length of the coherent interface and whether the intermediate Li-compositions (*i.e.* those between the fully lithiated, fully delithiated and intermediate values) coexist within or between the particles. Increasing the Co-substitution levels increases the number of observable particles reacting via the single-phase mechanism during the plateau of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ oxidation reaction and vice versa (*i.e.* Fe-substitution increases the observable number of reacting particles via the single-phase mechanism during the $\text{Co}^{2+}/\text{Co}^{3+}$ oxidation reaction). From previous studies,¹² we know that this is also the case when a larger current is applied. Increasing the substitution levels also allows intermediary Li-compositions to exist within the particle, rather than between particles (*i.e.* the coherent interface). It was also observed that the difference in the volume between the two species in each transformation is important and when there is a small difference in volume the single-phase reaction is likely to occur.

This study helps to establish how the solid solution mechanisms are related to the two-phase mechanism, how the mechanisms are affected by the varying length of the coherent interfaces, and how the different mechanism can be distinguished using *in situ* XRD. It is key to understand how the battery electrode materials lithiate and delithiate in order to optimize current materials and provide a foundation for what characteristics future cathode materials should have (*i.e.* dopant and substituted materials). Critically, the formation of interfaces vs. solid solutions during structural transformations can have implications for the fracturing of particles over multiple cycles: no energetically unfavorable interfaces are formed for a solid solution leading to improved capacity retention. Furthermore, solid solution mechanisms should, in general, lead to higher rate materials and improved performance.

Associated Content

Supporting Information

Supporting Information: the electrochemistry recorded during the *in situ* XRD experiments and the points in the electrochemistry that the diffraction patterns were collected; three individual *in situ* XRD patterns, Rietveld refinements and difference plots of LiFePO_4 at different states of charge; XRD patterns of $\text{LiFe}_x\text{Co}_{1-x}\text{PO}_4$ (where $0 \leq x \leq 1$); SEM image of a LiFePO_4 -composite electrode and particle size analysis and SEM

images of as synthesised-LiCoPO₄; the discharge capacities obtained during the *in situ* XRD studies; the electrochemical data collected during the *in situ* XRD experiments; *ex situ* ³¹P NMR spectra at the end of the first charge for LiFe_xCo_{1-x}PO₄ (where 0 ≤ x ≤ 1); individual XRD patterns at different states of charge for the Fe rich materials, x = 1, 0.95 and 0.875; evidence for the formation of the fully delithiated Fe_{0.25}Co_{0.75}PO₄ phase at the end of the second charge; concentration profile along the *a*-axis of the 100 nm particle used in the simulation; the XRD patterns for the first charge; the *a*, *b* and *c* unit cell parameters for LiFe_xCo_{1-x}PO₄, Fe_xCo_{1-x}PO₄, Li_{1-x}Fe_xCo_{1-x}PO₄ and Li_{2/3}Fe_xCo_{1-x}PO₄ (where 0 ≤ x ≤ 1) as a function of Fe content; the lattice parameters of the percentage change in the lattice parameters from LiFePO₄ for LiFe_xCo_{1-x}PO₄, Fe_xCo_{1-x}PO₄, Li_{1-x}Fe_xCo_{1-x}PO₄ and Li_{2/3}Fe_xCo_{1-x}PO₄ (where 0 ≤ x ≤ 1) and the *a*-, *b*- and *c*-lattice parameter variations plotted as populations densities relative to scan number for all the reactions discussed in this paper.

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