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Effect of Fe<sup>2+</sup> substitution on the structure and electrochemistry of LiCoPO<sub>4</sub> prepared by mechanochemically assisted carbothermal reduction<sup>†</sup>

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 $LiCo_{1-v}Fe_vPO_4$  solid solutions ( $0 \le y \le 1$ ) were prepared by the mechanochemically assisted carbothermal reduction of Co<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>. Mechanical activation was performed using a high-energy planetary mill AGO-2. The samples were characterized in detail by X-ray powder diffraction (XRD) using a Rietveld refinement, Fourier transform infrared spectroscopy (FTIR), Mössbauer spectroscopy, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), galvanostatic cycling, and galvanostatic intermittent titration technique (GITT). According to XRD, all the samples are single-phase solid solutions, crystallized in an orthorhombic structure (S.G. Pnma). The cell volume of  $LiCo_{1-\nu}Fe_{\nu}PO_4$  linearly increases vs. the Fe content. All the Fe ions are in the 2+ oxidation state and are octahedrally coordinated. The  $LiCo_{1-v}Fe_vPO_4$  solid solutions show improved electrochemical performance, compared with LiCoPO<sub>4</sub>. Based on the data from XRD and GITT, the improvement is attributed to the enhanced Li<sup>+</sup> diffusion, due to the enlargement of the 1D diffusion channels in the polyanion structure of LiCoPO<sub>4</sub> and the reduced cell volume change in the material during the Li extraction/insertion process. Moreover, a systematic decrease in the average potential of the  $Co^{2+}/Co^{3+}$  redox pair is observed with the increased Fe content, leading to the reaction termination in the electrochemical window of conventionally available electrolytes. In situ synchrotron diffraction shows that upon charging LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub>, the twophase mechanism of Li (de)intercalation at the Fe<sup>2+</sup>/Fe<sup>3+</sup> and Co<sup>2+</sup>/Co<sup>3+</sup> redox stages changes to a solid solution-like mechanism, contrary to the pristine LiFePO<sub>4</sub> and LiCoPO<sub>4</sub> materials.

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## Introduction

Currently, there is intense research activity aimed at alternative electrode materials for the next generation of rechargeable lithium-ion batteries, particularly for their use in electric and hybrid electric vehicles.<sup>1</sup> In the family of lithium metal phosphates LiMPO<sub>4</sub>, where M = Fe, Mn, Co, or Ni, the voltage of the redox pair varies for different transition metals from 3.4 V for Fe to 4.1 V for Mn, 4.8 V for Co, and 5.1 V *vs.* Li/Li<sup>+</sup> for Ni.<sup>2-6</sup> Although LiMnPO<sub>4</sub> has a favorable position of the redox pair, it shows rather low capacity and rate capability, due to the large lattice distortions upon cycling induced by the Jahn–Teller effect, arising from  $Mn^{3+}$ , and low electronic conductivity. A very high potential for LiNiPO<sub>4</sub> makes it not appropriate for use with conventionally available non-aqueous electrolytes with a voltage

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stability window in the range of 3.5–4.8 V vs. Li/Li<sup>+</sup>. The specific energy of LiMPO<sub>4</sub> increases from 578 W h kg<sup>-1</sup> for LiFePO<sub>4</sub> to 802 W h kg<sup>-1</sup> for LiCoPO<sub>4</sub>. Thus, LiCoPO<sub>4</sub> is a strong candidate as a high-voltage cathode material. However, LiCoPO<sub>4</sub> has even lower electric conductivity ( $\sigma \sim 10^{-15}$  S cm<sup>-1</sup>) than LiFePO<sub>4</sub> ( $\sigma \sim 10^{-9}$  S cm<sup>-1</sup>), and its operating voltage is at the boundary of the electrolyte stability window, which causes the decomposition of the electrolyte and its interaction with the cathode material. As a result, a fast degradation of the cathode material and capacity fading of the cell occur upon cycling.

Pure LiCoPO<sub>4</sub> exhibits poor electrochemical properties.<sup>7</sup> It has been shown that nanosizing, doping and coating it by conducting carbon allows one to improve its conductivity and cycling performance.<sup>8</sup> Carbon controls the particle size of LiCoPO<sub>4</sub> and inhibits particle growth under synthesis. Metal doping improves the interior conductivity and cycling performance, and enhances the charge–discharge capacity of LiCoPO<sub>4</sub>. Recently, mixed transition-metal systems have attracted considerable interest. It has been predicted theoretically<sup>9</sup> and supported experimentally<sup>10-12</sup> that a partial substitution of Co<sup>2+</sup> for Fe<sup>2+</sup> in LiCoPO<sub>4</sub> shifts the Co<sup>2+</sup>/Co<sup>3+</sup> redox pair

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to lower voltages slightly, thus improving the electrochemical performance of the phosphate cathodes in the existing electrolytes.

The structure and electrochemical properties of the  $LiCo_{1-\nu}Fe_{\nu}PO_{4}$  solid solutions have already been described in literature.12-19 Although most of the researchers observed the linear relationship of the lattice parameters with the increased Fe content, the authors of ref. 13 and 14 noticed some deviation from the linearity for Co-rich compositions, implying somewhat stronger M - O(M = Co, Fe) bonding and thus better electrochemistry for LiCo<sub>0.75</sub>Fe<sub>0.25</sub>PO<sub>4</sub>. To improve the electrochemical performance of  $LiCo_{1-\nu}Fe_{\nu}PO_4$ , some researchers have suggested using nonstoichiometric compositions. For example, it was noticed that Li-rich  $\operatorname{Li}_{1+x}[\operatorname{Co}_{1-y}\operatorname{Fe}_{y}]_{1-x}\operatorname{PO}_{4}(0 \le x \le 0.2; 0 \le$  $v \leq 0.2$ ) compositions showed improved electrochemical performance, which was attributed to the increase in the conducting properties.<sup>17</sup> On the other hand, according to ref. 18 the presence of Fe<sup>3+</sup> on the Li and Co sites appeared to stabilize the structure of Li<sub>0.92</sub>Co<sub>0.8</sub>Fe<sub>0.12</sub><sup>2+</sup>Fe<sub>0.08</sub><sup>3+</sup>PO<sub>4</sub>. Thus, the relationship between the structure and electrochemical behavior of  $LiCo_{1-\nu}Fe_{\nu}PO_{4}$  solid solutions is still under investigation.

The structure and electrochemical behavior of the electrode materials, especially of those with fine particles, depend strongly on the preparation method. Highly dispersed LiCoPO<sub>4</sub>based cathode materials are usually obtained by solution methods (sol-gel,<sup>19,20</sup> hydrothermal,<sup>21</sup> solvothermal,<sup>22</sup> ionothermal,23 rheological,24 etc.). However, these methods lead to the formation of waste products which require additional treatment. When the conventional solid state synthesis is used, the phase composition of the final product depends strongly on the synthesis conditions (temperature, gas atmosphere, etc.), which often leads to the formation of some impurity phases, such as metal pyrophosphates and Co<sub>2</sub>P. Muraliganth et al.<sup>12</sup> used a preliminary high-energy mechanical milling of the reagent mixture of lithium carbonate, diammonium hydrogen phosphate, and divalent oxalate dehydrates of M (M = Fe, Mn, Co, and Mg) in a FRITSCH mill and succeeded in the preparation of carbon-coated olivine  $LiM_{1-\nu}M_{\nu}PO_4$  (M = Fe, Mn, Co, and Mg) solid solution nanoparticles with good electrochemical properties; however, the process of mechanical milling was too long (10 h at a speed of 500 rpm), while the amount of carbon in the cathode mass was too high (40 wt%). On the other hand, Han et al.<sup>16</sup> synthesized LiCo<sub>1-v</sub>Fe<sub>v</sub>PO<sub>4</sub>/C by using a vibratorytype mill followed by microwave heating for 2-4 min to obtain final products. However, the amounts of the Fe dopant (y) in their work were only 0.05 and 0.1. The development of environmentally friendly and energy-efficient methods is highlighted. In our previous investigations, it has been shown that the preliminary short-term solid state mechanical activation (MA) of the reagent mixture in high-energy mills allows one to obtain a highly-reactive precursor, due to the fine grinding and mixing of reagents at the atomic level.25 This noticeably decreases the temperature and the duration of the subsequent thermal treatment and results in obtaining fine and homogeneous final products.

The aim of the present work was to study the effect of  $Fe^{2+}$  substitution for  $Co^{2+}$  on the crystal and local structure, as well

as on the electrochemistry of  $\text{LiCo}_{1-y}\text{Fe}_{y}\text{PO}_{4}$  ( $0 \le y \le 1$ ) prepared by mechanochemically assisted carbothermal reduction using  $\text{Co}_{3}\text{O}_{4}$  and  $\text{Fe}_{2}\text{O}_{3}$ . The obtained results lead to a better understanding of the factors that influence the electrochemical performance of mixed transition-metal systems.

### Experimental

### Material synthesis

The synthesis process of  $\text{LiCo}_{1-y}\text{Fe}_{y}\text{PO}_{4}$  ( $0 \le y \le 1$ ) is described elsewhere.<sup>26</sup> MA of the stoichiometric reagent mixtures of  $\text{Li}_2\text{CO}_3$ ,  $\text{Co}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  ( $\alpha$ -modification), and  $(\text{NH}_4)_2\text{HPO}_4$  (qualification "pure for analysis") with carbon "P 277" (from the Institute of Problems of Hydrocarbons Processing SB RAS, Omsk, Russia) as the reducing (in the amount necessary to reduce  $\text{Co}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ ) and covering agent (additional 5 wt%) was performed using a high-energy AGO-2 planetary mill (Novic, Novosibirsk, Russia) in an Ar atmosphere for 5 min. The activated mixtures were subsequently annealed at 750 °C for 1 h under an Ar flow.

### Material characterization

X-ray powder diffraction (XRD) analysis was performed using a Bruker D8 Advance diffractometer, Cu K $\alpha$  irradiation ( $\lambda$  = 1.54181 Å). XRD patterns were collected over the range of  $10-70^{\circ}$ with a step of  $0.02^{\circ}$  s<sup>-1</sup> and an uptake time of 0.3–0.5 s. Structural refinement of the XRD data was carried out by the Rietveld method using the GSAS software package. Fourier transformed infrared spectra (FTIR) were measured with a Bomem FTIR spectrometer in the 4000-400 cm<sup>-1</sup> range using pellets with CsI. Mössbauer spectra were recorded using a NZ-640 spectroscope, Hungary, with a  $Co^{57}$   $\gamma$ -ray source at room temperature. The particle size and morphology were investigated by SEM electron microscopy using a Hitachi TM-1000 scanning electron microscope. The chemical composition of the samples was analyzed by means of energy-dispersive X-ray spectroscopy (EDX) using a UltraDry EDS detector. The carbon content in the final products was determined by elemental analysis using a CNHS EURO EA 3000 analyzer.

#### **Electrochemical characterization**

For the electrochemical testing, the composite cathodes were fabricated by mixing 80 wt% active material (carbon coated) with 15 wt% Super P conductive carbon (Timcal Ltd.) and 5 wt% PVDF/NMP binder. The mixed slurry was then pasted on the aluminum foil to obtain working electrodes. The loading density of the prepared samples was 2–3 mg cm<sup>-2</sup>, and an electrode diameter of 10 mm was used throughout. The working electrodes were dried at 120 °C before cell assembly. Swagelok-type cells were assembled in an argon-filled glovebox with Li as the anode; 1 M LiPF<sub>6</sub> (Sigma Aldrich, 99.99%) solution in a mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) (Alfa Aesar, 99%) 1 : 1 by weight as the electrolyte; and a glass fiber filter (Whatman, Grade GF/C) as the separator. Cycling was performed using a galvanostatic mode at C/10 charge/discharge rates in the range of 3.0–5.0 V vs. Li/Li<sup>+</sup> at

room temperature. The GITT measurements were carried out at a C/20 rate ( $I_0 = 8.4 \text{ mA g}^{-1}$ ) by applying a galvanostatic step of 20 min and a relaxation time of 40 min.

### In situ synchrotron diffraction

Phase transitions upon cycling were studied by *in situ* synchrotron diffraction at the High-Resolution Powder Diffraction (HRPD) beamline P02.1 of the PETRA III electron storage ring at DESY (Hamburg, Germany) ( $\lambda = 0.20727$  Å). Diffraction patterns were recorded each 2 min by a PerkinElmer XRD 1621 detector under galvanostatic cycling of the samples at a C/10 rate at room temperature, using polyamide cell described elsewhere.<sup>27</sup>

### Results and discussion

### Crystal structure and morphology

Fig. 1 shows the XRD patterns of  $LiCo_{1-y}Fe_yPO_4$  ( $0 \le y \le 1$ ) prepared by mechanochemically assisted solid state synthesis. According to the XRD, all the samples are single-phase solid solutions; their XRD patterns did not show any peaks corresponding to impurity phases, such as Co<sub>2</sub>P or metal pyrophosphates, which are usually formed upon heating LiCoPO<sub>4</sub> at T > 700 °C for long periods of time in a reducing gas atmosphere owing to its decomposition.18,21 The observed XRD patterns are consistent with the PDF card no. 78-5576, and the corresponding Bragg reflections are indexed according to an orthorhombic structure with the Pnma space group. The framework structure of the LiCo<sub>1-v</sub>Fe<sub>v</sub>PO<sub>4</sub> solid solutions consists of PO<sub>4</sub> tetrahedra with  $M^{2+}$  ions (M = Co, Fe) in the corner-sharing octahedral positions and Li<sup>+</sup> ions in the edge-sharing octahedral positions. The latter run parallel to the *b* axis. One-dimensional pathways for Li<sup>+</sup> diffusion are realized along the [010] channels.<sup>2</sup>



**Fig. 1** X-ray diffraction patterns of the  $\text{LiCo}_{1-y}\text{Fe}_y\text{PO}_4$  ( $0 \le y \le 1$ ) samples. The row of short vertical lines marks the theoretical positions and intensity of the pure LiCoPO<sub>4</sub> reflections (PDF card no. 78-5576). The diffraction peaks of LiCo<sub>1-y</sub>Fe<sub>y</sub>PO<sub>4</sub> are indexed.

The Rietveld refined XRD patterns of the LiCoPO4 and LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub> samples are shown in the ESI, Fig. S1<sup>+</sup> as an example. Fig. 2a presents the Rietveld refined lattice parameters for  $LiCo_{1-y}Fe_{y}PO_{4}$  ( $0 \le y \le 1$ ) and Table S1 in the ESI<sup>†</sup> contains the atomic positions for all the solid solutions. One can see that the lattice parameters of the solid solutions vary linearly vs. Fe content, thus obeying Vegard's law. The a and b parameters increase with the increase in the substituted amount of Fe, due to the larger radius of Fe<sup> $^{2+}$ </sup> ions (0.78 Å) compared to that of Co<sup> $^{2+}$ </sup> ions (0.75 Å), while the *c* parameter decreases (a small deviation of linearity is observed only for the sample with y = 0.05). The anisotropic change of cell parameters results in an increase in the cell volume with Fe substitution. Note, that the observed cell parameters are slightly lower than those in the literature.<sup>14</sup> The enlargement of the  $a \times c$  value evidences an increase in the cross-sectional area of the 1D channels along the b direction in the olivine structure, which correlates with the literature data.12-14



**Fig. 2** Variation of lattice parameters *a*, *b*, *c*, cell volume *V* (a), and average M - O distances (b) for the LiCo<sub>1-y</sub>Fe<sub>y</sub>PO<sub>4</sub> samples. The value  $a \times c$  is proportional to the cross-section area of the diffusion channels along *b* direction. Data<sup>14</sup> are denoted by asterisks.

Unfortunately, close similarity of the X-ray atomic structure factors for Co<sup>2+</sup> and Fe<sup>2+</sup> ions does not allow one to distinguish between Co and Fe in the LiCo<sub>1-v</sub>Fe<sub>v</sub>PO<sub>4</sub> structure on the basis of the XRD data. According to the neutron powder diffraction study of  $\text{LiCo}_{1-y}\text{Fe}_{y}\text{PO}_{4}$  (0.25  $\leq y \leq 1$ ) performed by Nyten et al.,<sup>14</sup> Co<sup>2+</sup> and Fe<sup>2+</sup> ions are randomly distributed in the octahedral 4c sites without distortion of the olivine structure. Fig. 2b shows that the calculated average M - Odistance gradually increases from 2.13 Å to 2.16 Å with the increase in the Fe content. According to ref. 13 and 14, the shortest mean distance M - O (M = Co, Fe) among the  $LiCo_{1-\nu}Fe_{\nu}PO_4$  (0.25  $\leq y \leq 1$ ) compositions was observed for  $LiCo_{0.75}Fe_{0.25}PO_4$  (2.115 Å), implying a somewhat stronger M - O bonding for y = 0.75. This was supported by the XPS results, where the highest O1s binding energy (suggesting shorter Fe/Co-O distance) was observed for the similar composition LiCo<sub>0.8</sub>Fe<sub>0.2</sub>PO<sub>4</sub>.<sup>13</sup>

According to the elemental microanalysis, the amount of carbon after annealing was about 6.50%  $\pm$  0.05% for all compositions.

The morphological characterization of the synthesized samples was carried out by SEM. Fig. 3a presents the SEM images of the  $LiCo_{0.5}Fe_{0.5}PO_4$  sample as an example. All the samples show no dramatic variations in morphology (ESI, Fig. S2†). One can see that the submicron-sized (~200 nm) primary particles with nearly spherical shapes are agglomerated into loose, irregularly shaped secondary particles. The chemical composition of the prepared samples was confirmed by the EDX spectroscopy (Fig. 3b). As can be seen from the elemental maps, Co and Fe ions are homogeneously distributed in the  $LiCo_{1-v}Fe_vPO_4$  samples (Fig. 3c).



Fig. 4 FTIR spectra of the  $LiCo_{1-y}Fe_yPO_4$  ( $0 \le y \le 1$ ) samples.

#### Local structure

The local structure of the LiCo<sub>1-y</sub>Fe<sub>y</sub>PO<sub>4</sub> solid solutions was investigated by FTIR and Mössbauer spectroscopy. The vibration modes of LiFePO<sub>4</sub> and the positions of the corresponding bands have already been discussed in ref. 28 and 29. The FTIR spectra of the prepared LiCo<sub>1-y</sub>Fe<sub>y</sub>PO<sub>4</sub> solid solutions represent the intramolecular vibrations of the PO<sub>4</sub> group ( $T_d$  point group): the symmetric  $v_1$  and asymmetric  $v_3$  stretching modes are in the 900–1150 cm<sup>-1</sup> range and the asymmetric  $v_4$  and symmetric  $v_2$ 



Fig. 3 SEM image (a), EDX pattern (b), and element map (c) of the  $LiCo_{0.5}Fe_{0.5}PO_4$  sample.



Fig. 5  ${}^{57}$ Fe Mössbauer spectra of the LiCo<sub>1-y</sub>Fe<sub>y</sub>PO<sub>4</sub> (0.05 < y  $\leq$  0.9) samples.

Table 1 The width, QS, IS and Fe<sup>2+</sup> content for the as-prepared  $LiCo_{1-v}Fe_vPO_4$  samples from Mössbauer spectroscopy data

No.	y in LiCo <sub>1–y</sub> Fe <sub>y</sub> PO <sub>4</sub>	Width, mm s <sup>-1</sup>	QS, mm s <sup>-1</sup>	IS, mm s <sup>-1</sup>	Fe <sup>2+</sup> content, %
1	0.05	0.26	2.95	1.22	100
2	0.10	0.25	2.96	1.22	100
3	0.25	0.27	2.97	1.23	100
4	0.50	0.33	2.91	1.22	100
5	0.75	0.31	2.94	1.22	100
6	0.90	0.31	2.94	1.23	100
7	1.00	0.36	2.95	1.22	100

bending vibrations are in the 500–650 cm<sup>-1</sup> range (Fig. 4). In general, the infrared spectra of LiFePO<sub>4</sub> and LiCoPO<sub>4</sub> are very similar; however, all the bands gradually shift to lower values when the Fe content increases. It is well known that the phosphate vibrations do not only consist of P and O motion; therefore, the observed shift may be explained by an increase in Co–O covalence in the solid solutions when Co is replaced by the more electropositive Fe due to the inductive effect.

The Mössbauer experimental spectra of all the  $\text{LiCo}_{1-y}\text{Fe}_{y}\text{PO}_{4}$  samples are well fitted by a single symmetric doublet (Fig. 5). No additional lines are observed. Table 1 represents the values of the isomeric shift (IS), the quadrupole splitting (QS), and the line width of the prepared samples. They do not change noticeably for all the compositions. Thus, it can be concluded that the doublet originates from 100% of the octahedral  $\text{Fe}^{2+}$  ions in the olivine structure; no impurity Fe phases were detected, confirming the conclusion of the XRD analysis on the phase purity of the samples prepared.

#### Li extraction/insertion behavior

The charge–discharge profiles of the second cycle for the prepared  $\text{LiCo}_{1-y}\text{Fe}_{y}\text{PO}_{4}$  samples in the 3.0–5.0 V range at the C/ 10 rate are shown in Fig. 6. Two redox plateaus,  $\text{Fe}^{2+}/\text{Fe}^{3+}$  at 3.4 V and  $\text{Co}^{2+}/\text{Co}^{3+}$  at 4.7 V, are well distinguishable and their contribution relates to the initial Fe/Co composition ratio. Fig. 7 represents the theoretical and experimental total discharge



Fig. 6 Charge–discharge profiles of the  $LiCo_{1-y}Fe_yPO_4$  samples in the 3.0–5.0 V range.

capacity of  $\text{LiCo}_{1-y}\text{Fe}_{y}\text{PO}_{4}$  vs. Fe content (y) and the separate discharge capacities at the 3.4 V and 4.7 V plateaus, corresponding to the two redox pairs of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  and  $\text{Co}^{2+}/\text{Co}^{3+}$ , respectively. It is clear that the change in the total experimental capacity is not linear. Most of the activity loss appears in the  $\text{Co}^{2+}/\text{Co}^{3+}$  range, especially at a high Co content. A similar predominant activity loss in the  $\text{Mn}^{2+}/\text{Mn}^{3+}$  redox couple was also observed for the  $\text{LiFe}_{1-y}\text{Mn}_{y}\text{PO}_{4}$  solid solutions with an



Fig. 7 Discharge capacity at 3.4 V (a) and at 4.7 V (b) plateaus, and the total one (c) vs. Fe content compared to the theoretical capacity in the 3.0-5.0 V range.

increased Mn content.<sup>26</sup> The cyclic performance of the  $LiCo_{1-y}Fe_yPO_4$  samples in the 3.0–5.0 V range is shown in Fig. 8 and demonstrates a significant improvement in the reversible capacity with the increase in Fe content. An increase in the capacity of the  $LiCo_{1-y}Fe_yPO_4$  solid solutions in respect to  $LiCoPO_4$  may be explained by the enlargement of the 1D channels in the olivine structure that follows from the XRD data and from an increase in the Co–O covalence may be concluded from the FTIR measurements (see above).

Based on the experimentally obtained data on capacity and average potential, we calculated the energy densities for the  $\text{LiCo}_{1-y}\text{Fe}_{y}\text{PO}_{4}$  solid solutions under study as a function of Fe content. A comparison of the theoretical and practical energy densities of the samples is shown in the ESI, Fig. S3.† It is seen that the experimental energy density of the as-prepared undoped LiCoPO<sub>4</sub> is only 376 W h g<sup>-1</sup>, *i.e.*, 46% of the theoretical value, while the experimental energy density of LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub> increases up to 484 W h g<sup>-1</sup>, *i.e.*, 70% of the theoretical value.

It should be noted that the opinions on the nature of the lithiation/delithiation mechanism and the structure evolution of LiCoPO<sub>4</sub> are inconsistent in the literature. A cyclic voltammetry study performed by Amine et al.7 has revealed only one oxidation and one reduction peak, which is characteristic for a reversible one-step electrochemical process. In contrast, Bramnik et al.<sup>30</sup> have observed a two-step character of electrochemical oxidation/reduction, which displayed by two plateaus during galvanostatic charge/discharge. The plateaus become more pronounced in the second and subsequent cycles. A two-phase mechanism of Li extraction/insertion from/in LiCoPO4 was confirmed by in situ synchrotron diffraction.30 The additional redox peaks at 4.7-4.8 V were attributed to the formation of the Li<sub>0.7</sub>CoPO<sub>4</sub> intermediate phase. The difference in the cell volume between the pristine and delithiated phases was reported to be about 7%, similar to LiFePO<sub>4</sub>. The authors of ref. 31 found that different delithiation mechanisms in LiCoPO<sub>4</sub> are observed for the samples obtained at different temperatures: lithium deinsertion from LT-LiCoPO4 does not lead to the formation of the intermediate phase in contrast to HT-LiCoPO<sub>4</sub>.

In our opinion, the varied character of the voltage-composition curves for LiCoPO<sub>4</sub> (one-step *vs.* two-step behavior) depends not only on the particle size but also is a result of the morphology of the samples and the presence of dopants. The influence of Fe substitution on the mechanism of Li (de)intercalation from/in  $\text{LiCo}_{1-\nu}\text{Fe}_{\nu}\text{PO}_4$  has not yet been studied.

The dQ/dU = f(U) plots for the prepared  $\text{LiCo}_{1-y}\text{Fe}_{y}\text{PO}_{4}$  solid solutions are presented in Fig. 9. One can see that the intermediate  $\text{Co}^{2+}/\text{Co}^{3+}$  oxidation peak, corresponding to the formation of the intermediate phase, disappears for the samples with  $y \ge 0.5$ , while the additional reduction peak is absent for all substituted samples.

In situ X-ray diffraction studies using synchrotron radiation were performed to establish the Li intercalation/deintercalation mechanism during charging of the prepared LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub>. Fig. 10 shows the selected XRD patterns of LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub> upon the first charge. One can see the presence of one set of reflections in the whole voltage range, indicating that the two-phase mechanism characteristic for the undoped LiCoPO<sub>4</sub> is replaced by a solid solution-like mechanism. A shift of the reflections to larger angles is observed, due to the gradual oxidation of Fe<sup>2+</sup> and Co<sup>2+</sup> ions to Fe<sup>3+</sup> and Co<sup>3+</sup>, without the formation of new phases. The intermediate region, where transition from one redox couple to another occurs, is characterized by a more significant shift of the reflections. The replacement of the two two-phase mechanism of Li deintercalation in Co-rich LiCo<sub>1-v</sub>Fe<sub>v</sub>PO<sub>4</sub> solid solutions by a single-phase diffusion mechanism in the compositions with  $y \ge 0.5$  within the whole





5

: 0 00

y = 0.75

y = 0.90

Cycle number

10

15

= 0.05

v = 0.1

y = 0.25

Fig. 9 ~dQ/dU vs. voltage plots for the  $LiCo_{1-y}Fe_yPO_4$  samples in the 3.0–5.0 V range.

Discharge capacity (mA h  $g^{-1}$ 

150

120

90

60

30

0



Fig. 10 Selected XRD patterns of Li<sub>x</sub>Co<sub>0.5</sub>PO<sub>4</sub> upon charge obtained by *in situ* synchrotron diffraction.

voltage range (in both the Fe<sup>2+</sup>/Fe<sup>3+</sup> and Co<sup>2+</sup>/Co<sup>3+</sup> regions) is reported for the first time. This is undoubtedly related to the changes in the electronic structure of these materials, and the mutual influence of Fe and Co ions on the miscibility gap of the initial, intermediate, and final phases, *etc.* It should be noted that a single-phase mechanism was observed in a wide intermediate region in the previous publications on the mixed olivine  $\text{LiFe}_{1-y}\text{Mn}_y\text{PO}_4$  phosphates, and its width increased with the reduction in the particle size.<sup>32,27</sup> However, this question needs further theoretical and experimental study.

Fig. 11 shows the variation of the calculated cell parameters upon Li deintercalation ( $x_{Li}$ ) in comparison with the data for LiCoPO<sub>4</sub>, Li<sub>0.7</sub>CoPO<sub>4</sub> and CoPO<sub>4</sub> obtained in ref. 30. As seen from the figure, this variation is less pronounced for the LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub> solid solution than for the undoped LiCoPO<sub>4</sub>.

 $\Delta V$  changes from 7.0% for LiCoPO<sub>4</sub> to 3.7% for LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub>. This correlates with the first-principles calculations of the crystal and electronic structure of the doped LiCoPO<sub>4</sub>,<sup>33</sup> showing that both the Li site and metal site doping may reduce the volume change of the material during the Li extraction/ insertion process. According to a DFT study performed by Osnis *et al.*,<sup>9</sup> the changes in the cell volumes as a function of transition metal composition in mixed transition metal olivine phosphates may largely be ascribed to the changes in the atomic volumes of oxygen atoms, which modulate the electron charge distribution. Thus, an appropriate metal site doping of LiCoPO<sub>4</sub> can enhance its structural stability during the Li extraction/ reinsertion process, and hence a good reversibility and long cycle lifetime of the cathode can be expected.

Fig. 12a shows a shift of the midpoint of the cathodic and anodic peaks for each of the Fe<sup>2+</sup>/Fe<sup>3+</sup> and Co<sup>2+</sup>/Co<sup>3+</sup> redox couples on the galvanostatic charge/discharge curves. It is seen that the  $Co^{2+}/Co^{3+}$  average redox potential decreases constantly with the increase in the Fe content, until the shift finally approaches  $\sim 0.13$  V: from 4.79 V for LiCoPO<sub>4</sub> to 4.76 for the sample with y = 0.5, and to 4.66 V for the sample with y = 0.9. The  $Fe^{2+}/Fe^{3+}$  average potential changes from 3.48 V for the sample with y = 0.25 to 3.43 for the sample with y = 0.9, *i.e.*, it increases vs. the Co content. It is well known that the redox energies of M ions in the polyanion-containing cathodes are influenced by the inductive effect introduced by the counter cations. In the case of the  $LiCo_{1-\nu}Fe_{\nu}PO_4$  solid solutions, the polyanion  $PO_4$  is fixed, and the shifts in the redox potential can be associated with the change in the electronic state of the M<sup>2+</sup> cation. Muraliganth et al.12 explained the shifts in the redox potentials in the doped LiMPO<sub>4</sub> by considering the changes in the covalence of the M - O bonds caused by the changes in the



Fig. 11 Variation of cell parameters upon Li deintercalation for  $LiCo_{0.5}Fe_{0.5}PO_4$  (this work) and for  $LiCoPO_4$  from ref. 30 (denoted by asterisks).



Fig. 12 Average redox potential vs. Li/Li<sup>+</sup> (a) and the magnitude of peak separation of the  $Co^{2+}/Co^{3+}$  and  $Fe^{2+}/Fe^{3+}$  redox pairs (b) for the  $LiCo_{1-\nu}Fe_{\nu}PO_{4}$  samples.

electronegativity of M or the M – O bond length. Thus, the substitution of the more electropositive  $Fe^{2+}$  for  $Co^{2+}$  increases the Co–O covalence, due to the inductive effect, and thereby raises the  $Fe^{2+}/Fe^{3+}$  redox energy and decreases the voltage of the  $Co^{2+}/Co^{3+}$  pair. A similar systematic shift of the  $Fe^{2+}/Fe^{3+}$  redox potential has been observed earlier for the  $LiFe_{1-y}Mn_yPO_4$  solid solutions and is explained on the basis of a super-exchange interaction between the Fe–O–Mn ions and by the possible increase in the average metal-oxide bond length and the ionicity of each transition metal.<sup>10</sup> This leads to a lower Fe 3d–O 2p antibonding state and to a higher redox potential.<sup>11</sup> Such an explanation is in agreement with the FTIR data obtained in this work (see Fig. 4).

Besides the shift of the  $Fe^{2+}/Fe^{3+}$  and  $Co^{2+}/Co^{3+}$  redox peaks, the change in the peak separation as a function of Fe content is also observed (Fig. 12b). The magnitude of the peak separation of the  $Co^{2+}/Co^{3+}$  and  $Fe^{2+}/Fe^{3+}$  redox pairs becomes smaller with an increase in Fe doping, pointing to the enhanced electric conductivity of the  $LiCo_{1-y}Fe_yPO_4$  solid solutions. These results are in accord with EIS data of ref. 21, where a significant decrease in interphase resistance and an increase in electrical conductivity were observed in the Fe-doped  $LiCoPO_4$  with the increase in Fe content.

### Galvanostatic intermittent titration technique (GITT)

The galvanostatic intermittent titration technique (GITT) is extensively used to calculate the coefficient of chemical diffusion. The classical application of this technique is related to the systems with topotactic solid-state intercalation reactions that lead to the formation of solid-solution phases. In the case of two-phase systems (such as LiCoPO<sub>4</sub> and LiFePO<sub>4</sub>), the coefficient of chemical diffusion obtained from GITT may be considered as an effective value. However, the in situ synchrotron diffraction study of LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub> upon delithiation performed in this work (Fig. 10 and 11) reveals that the process is characterized by a solid solution-like behavior. This allows us to use the GITT measurements to obtain the equilibrium redox potentials and to evaluate the lithium diffusion coefficient at different stages of Li intercalation-deintercalation in LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub>.

Fig. 13 shows the charge/discharge curves of the  $LiCo_{0.5}Fe_{0.5}PO_4$  sample obtained by GITT during the first cycle in the 3.0–5.0 V range, illustrating the voltage dependence on the Li content under load and rest. The cell was charged and discharged at a constant current C/20 ( $I_0 = 8.4 \text{ mA g}^{-1}$ ) for an interval of 20 min, followed by an open-circuit stand for 40 min to allow the cell voltage to relax to its steady-state value ( $E_s$ ). As can be seen, the Fe<sup>2+</sup>/Fe<sup>3+</sup> and Co<sup>2+</sup>/Co<sup>3+</sup> redox pairs in LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub> exhibit rather flat OCV profiles and short relaxation spikes, revealing fast reaction kinetics with a small polarization and fast equilibration. The additional plateau, a characteristic of the formation of the intermediate phase in the Co<sup>2+</sup>/Co<sup>3+</sup> range, is absent, which correlates with the data presented in Fig. 9.

The diffusion coefficient of lithium ions was calculated using eqn (1), developed by Weppner *et al.*:<sup>34</sup>



Fig. 13 OCV curve for LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub> from GITT measurement.

$$D_{\mathrm{Li}^{+}} = \frac{4}{\pi} \left( \frac{V_{\mathrm{M}}}{\mathrm{SF}} \right)^{2} \left( I_{0} \frac{\delta E_{\mathrm{s}} / \delta x}{\delta E / \delta t_{2}^{2}} \right), \text{ at } t \ll \tau$$
(1)

where  $V_{\rm M}$  is the molar volume of mixed metal phosphate (42.87 cm<sup>3</sup> mol<sup>-1</sup>), *S* is the surface area of the electrode (32 000 cm<sup>2</sup> g<sup>-1</sup>), *F* is Faraday's constant (96 485 C mol<sup>-1</sup>),  $I_0$  is the current pulse (0.084 A g<sup>-1</sup>),  $\delta E_s/\delta x$  is a slope of equilibrium open circuit voltage *vs*. Li content *x* which can be obtained from the differential of the OCP curve, shown in Fig. 13, and  $\delta E/\delta t^{1/2}$  is a slope of the voltage change *vs*. the square root of time.

Fig. 14a presents the GITT curves for LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub> during the first cycle as a function of time in the 3.0–5.0 V range. The applied current pulse and the resulting potential profile of LiFe<sub>0.5</sub>Co<sub>0.5</sub>PO<sub>4</sub> for a single titration at the first charge are shown in Fig. 14b. Various parameters,  $\Delta E_{\tau}$ ,  $\Delta E_{s}$ , *etc.* are labeled schematically. Fig. 14c shows a rather good linear relationship of *E vs.*  $\tau^{1/2}$ , which indicates that eqn (1) is suitable for the calculation of  $D_{\text{Li}^+}$ . The calculated values of  $D_{\text{Li}^+}$  during the charge/discharge processes are within the range from 10<sup>-13</sup> to 10<sup>-16</sup> cm<sup>2</sup> s<sup>-1</sup> as plotted in Fig. 14d. The relatively high  $D_{\text{Li}^+}$  in the LiFe<sub>0.5</sub>Co<sub>0.5</sub>PO<sub>4</sub> electrode indicates good kinetic characteristics, especially for the intermediate range, thus providing



**Fig. 14** GITT curves of LiFe<sub>0.5</sub>Co<sub>0.5</sub>PO<sub>4</sub> as a function of time in the 3.0–5.0 V range (a); *U vs. t* profile for a single GITT titration (b); plot of voltage *U vs.*  $t^{1/2}$  (c); Li<sup>+</sup> diffusion coefficient  $D_{\text{Li}^+}$  calculated from the GITT data as a function of cell voltage during charge and discharge processes (d).

evidence for the enhanced Li<sup>+</sup> diffusion in the solid solution as compared with pure LiCoPO<sub>4</sub> ( $D_{\text{Li}^+} \sim 10^{-15}$  to  $10^{-18}$  cm<sup>2</sup> s<sup>-1</sup>).

# Conclusion

Single-phase olivine  $LiCo_{1-y}Fe_{y}PO_{4}$  ( $0 \le y \le 1$ ) solid solutions with fine particles have been successfully prepared by the modern environmentally friendly and energy-efficient mechanochemically assisted carbothermal reduction. It has been shown that, due to the shift of the  $Co^{2+}/Co^{3+}$  redox potential to a lower voltage, more capacity can be utilized from the  $Co^{2+}/Co^{3+}$  redox pair in the LiCo<sub>1-v</sub>Fe<sub>v</sub>PO<sub>4</sub> solid solutions upon cycling in the 3.0–5.0 V range than in pure LiCoPO<sub>4</sub>. The improvement of the electrochemical behavior of the  $LiCo_{1-\nu}Fe_{\nu}PO_4$  solid solutions is attributed to the enhanced Li<sup>+</sup> diffusion, due to the enlargement of the 1D diffusion channels in the polyanion structure of LiCoPO<sub>4</sub> and the reduced cell volume change in the material during the Li extraction/insertion process. For the first time, the occurrence of a single-phase diffusion mechanism in the LiCo<sub>0.5</sub>Fe<sub>0.5</sub>PO<sub>4</sub> composition upon charging within the whole voltage range (in both the Fe<sup>2+</sup>/Fe<sup>3+</sup> and Co<sup>2+</sup>/Co<sup>3+</sup> regions) has been established instead of the two-phase mechanism characteristic for the pristine LiCoPO<sub>4</sub> and LiFePO<sub>4</sub> materials.

Thus, a synthesis of mixed transition-metal systems is suggested to be a practical approach to tune the voltage of Li ion battery materials, such as  $LiCoPO_4$ , to lower values in order to avoid the decomposition of the electrolytes commercially used nowadays and to enhance their cyclability due to the enhanced  $Li^+$  diffusion.

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