Solid solutions of LiFe$_{1-y}$M$_y$PO$_4$ (M = Co, Ni) within the whole substitution range (0 ≤ y ≤ 1) are systematically investigated as safe high-voltage positive electrode materials for Li-ion battery. Especially the similarities and differences between the Co- and Ni-substitution schemes are highlighted. With increasing substitution level y, the orthorhombic unit cell shrinks and the Li$^{+}$-ion diffusion channel area decreases, more rapidly for the smaller-sized Ni substituent. While the Co$^{2+}$/Co$^{3+}$ redox couple shows reversible electrochemical activity, only an initial, partial delithiation is achieved for the Ni$^{2+}$/Ni$^{3+}$ couple at all y. However, both substitution schemes similarly affect the Fe$^{2+}$/Fe$^{3+}$ redox couple by increasing its potential and enhancing the kinetics. Particularly, a mutual influence of Fe and Co/Ni on the delithiation/lithiation characteristics is proposed: ex situ XRD analysis shows signs of a phase-composition change in the Fe$^{2+}$/Fe$^{3+}$ region for higher y, and correspondingly, a changed Co$^{2+}$/Co$^{3+}$ redox mechanism for lower y is indicated by cyclic voltammetry. We suggest that this behavior is related to a substitution-induced decrease in the volume change between the lithiated and delithiated phases. For the Co-substitution scheme, a composition around y ≈ 0.5 seems optimal for combining a high energy density and a kinetically beneficial, diffusional single-phase delithiation/lithiation mechanism.

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of 86 mAh g$^{-1}$ at C/10 rate. Also Wolfenstine et al.$^{39}$ reported electrochemical activity for their LiNiPO$_4$/C sample (oxidation at 5.3 V and reduction at 5.1 V vs. Li/Li$^+$).

The lack of electrochemical activity in LiNiPO$_4$ can originate from the very poor electrical conductivity (lower than for LiFePO$_4$ and LiCoPO$_4$),$^{39,44}$ small lattice volume and slow Li$^{+}$-ion diffusion.$^{45}$ Large particle size due to synthesis conditions,$^{41}$ and the stability of the Ni$^{2+}$/Ni$^{3+}$ couple, requiring high potentials. Additionally, no stable phase for the fully-delithiated form NiPO$_4$ is known and crystal lattice destruction upon delithiation is possible.$^{39,41,45}$ Increased amounts of Li-M site exchange (antisite defect) have been speculated, as Li$^+$ and Ni$^{2+}$ are more similar in size than for example Li$^+$ and Fe$^{3+}$ or Co$^{2+}$.$^{44}$ As a result, the Li$^+$ diffusion channels would be blocked by the immobile Ni$^{2+}$.

Although the theoretical energy densities of LiCoPO$_4$ and LiNiPO$_4$ materials are very high, the experimentally achieved, practical values are worse than those measured for LiFePO$_4$ due to low specific discharge capacities/lack of electrochemical activity and high polarization. To improve the electrochemical performance, an interesting alternative would be to use mixed LiFe$_{1-y}$M$_y$PO$_4$ (M = Co, Ni) systems at higher substitution levels ($y = 0.2 – 0.8$), where the $M^2+/M^3+$ redox couple reacts at its own plateau increasing the average electrode potential and thus the obtainable cell voltage and energy density. At the same time, adequate electronic and ionic conductivity and structural stability can be maintained with the Fe in the structure. In literature, many studies have focused only on low substitution levels ($y = 0 – 0.1$) of Co or Ni,$^{31,36,41}$ having the purpose of improving the material properties of LiFePO$_4$, e.g., the electronic or ionic conductivity. However, the electrochemical performance at higher substitution levels $y$ is less studied for LiFe$_{1-y}$Co$_y$PO$_4$,$^{39,40,43,42,53}$ and especially for LiFe$_{1-y}$Ni$_y$PO$_4$,$^{41,54,55}$ materials, and furthermore, systematic studies comparing their characteristics inside a wide compositional range ($0 \leq y \leq 1$) are scarce.$^{42}$

In this study, the electrochemical performance and related delithiation/ lithiation characteristics of LiFe$_{1-y}$M$_y$PO$_4$/C ($M = Co, Ni$) solid-solutions are systematically evaluated and compared in the whole substitution range, $0 \leq y \leq 1$. Although the Co$^{2+}$/Co$^{3+}$ and Ni$^{2+}$/Ni$^{3+}$ redox couples are demonstrated to differ in their electrochemical behavior, with Ni$^{2+}$/Ni$^{3+}$ significantly more difficult to activate in a reversible manner, a similar influence on the Fe$^{2+}$/Fe$^{3+}$ redox couple characteristics is revealed. Both substitution schemes enhance the Fe$^{2+}$/Fe$^{3+}$ couple kinetics, increase its redox potential, and at higher substitution levels introduce signs of changed phase-composition during the Fe$^{2+}$/Fe$^{3+}$ region delithiation/lithiation. Correspondingly, higher Fe contents are found to change the Co$^{2+}$/Co$^{3+}$ couple delithiation mechanism. Especially, to our knowledge the changed Fe$^{2+}$/Fe$^{3+}$ redox region phase-composition at higher Ni contents is indicated for the first time.

Experimental

Series of LiFe$_{1-y}$Co$_y$PO$_4$/C and LiFe$_{1-y}$Ni$_y$PO$_4$/C samples were prepared through solid state reaction synthesis from stoichiometric amounts of Li$_2$CO$_3$ (Sigma-Aldrich, approx. 99%), Fe(C$_7$O$_4$)$_2$·2H$_2$O (Alfa Aesar, 99%), Co(C$_6$O$_4$)$_2$·2H$_2$O (Alfa Aesar, 99.995%) or Ni(C$_6$O$_4$)$_2$·2H$_2$O (Alfa Aesar), and NH$_4$H$_2$PO$_4$ (J. T. Baker, 98.4%). The starting materials were first heat treated at 350°C for 6 h in an argon gas flow, after which 5 wt-% of sucrose (Merck) was added to obtain carbon-coated particles. The second heat-treatment step was performed at 680°C for 8 h in an argon gas flow. More detailed information on the synthesis procedure has been presented elsewhere.$^{56}$

To characterize the active material powders, X-ray diffraction (XRD) patterns were recorded in air at room-temperature using a Panalytical X’Pert Pro MPD Alpha-1 diffractometer with Cu Ka1 radiation (V = 40 kV, I = 40 mA) in a 20 range of 5 – 120° with 0.013° step size. Lattice parameters and Li and (Fe, M) site occupancies were refined with the Rietveld refinement program Fullprof$^{57}$ from the XRD data. Mössbauer spectra were recorded by a Mössbauer Spectroscopy System (FGX-222ST, Topologic Systems Inc.) with a Cyclotron$^{57}$ Co-Rh radiation source (experimental details presented elsewhere)$^{58}$ The specific surface areas of the active material powders were measured by the Brunauer-Emmett-Teller (BET) method with N$_2$ absorption (Autosorb-1, Quantachrome Instruments), and the morphology was probed with scanning electron microscopy (SEM, JSM-7500F) using 5 kV acceleration voltage. The amount of carbon coating was estimated by thermogravimetry (TG) measurements (Pyris 1 TGA, PerkinElmer).

The composite electrodes were prepared by mixing in ball mill 80 wt-% of the carbon coated active material powder, 10 wt-% conductive carbon black (SuperC65, Timcal), and 10 wt-% polyvinylidene fluoride (Solef 5130, Solvay) dissolved in n-methyl-2-pyrrolidone (Life Science, Basf). The obtained slurry was coated on aluminum foil using doctor blade technique. Electrode samples of 14 mm diameter were calendered at 6 t pressure, dried in vacuum at 110°C for 24 h, and then transferred under vacuum to argon-filled glove box, where the test cells were assembled. Standard coin cells (Hohsen) were used for testing with metallic lithium (Sigma-Aldrich, thickness 0.38 mm, 99.9% trace metals basis) as the counter electrode and a circular piece of 260 μm thick glass fiber filter (GF/A, Whatman) as the separator. The electrolyte was 1 M LiPF$_6$ dissolved in a 1:1 mixture of ethylene carbonate and dimethyl carbonate (LP 30, Merck). The cells were left to stabilize for 24 h before testing.

The electrochemical activity and performance were tested by cyclic voltammetry and galvanostatic charge-discharge cycling tests. All potentials are presented here versus the lithium counter electrode (vs. Li/Li$^+$). Cyclic voltammetry measurements were performed using an Autolab potentiostat (PGSTAT302N) and Nova software (version 1.7, Eco Chemie). The voltammograms were recorded at 0.05 mV s$^{-1}$ scan rate inside a potential window of 2.7 – 5.2 V. Electrochemical cycling tests were performed with a Nawere battery cyclingulator. In rate capability measurements, discharge current was varied from 0.1 C to 4 C, while the charge current was kept constant at 0.2 C for 0.5 C and higher discharge currents. Charging was done at a constant current rate until the cutoff voltage was reached, followed by a constant voltage charge at the cutoff voltage until the current reduced to 0.03 C. The discharge was performed at constant current until the cutoff voltage was reached. For charging, cutoff voltages of 4.1 and 4.9 V were used. In addition, 4.99 V was tested. The discharge cutoff voltage was 2.7 V for all tests. The current values were based on the active material mass and a theoretical capacity of 170 mAh g$^{-1}$ for all the material compositions.

For the ex situ analysis, the coin cells were cycled with 0.03 C constant current for one cycle (with charge and discharge cutoff voltages of 4.99 V and 2.7 V, respectively), and then charged (delithiated) to approximately half-way of the Fe$^{2+}$/Fe$^{3+}$ redox couple region (based on the preceding Fe$^{2+}$/Fe$^{3+}$ discharge plate), which was disassembled in glove box under argon and the electrodes were rinsed three times with anhydrous dimethyl carbonate (Sigma-Aldrich, > 99%). The electrode samples were investigated by XRD and$^{57}$ Mössbauer spectroscopy; details of these experiments were described earlier.$^{56}$ For the Mössbauer measurements, the samples were sealed inside polymer-coated aluminum pouch in the argon atmosphere.

Results and Discussion

Structure and morphology.—The two sample series, LiFe$_{1-y}$Co$_y$PO$_4$/C and LiFe$_{1-y}$Ni$_y$PO$_4$/C, show solid solubility for the entire substitution range, from $y = 0$ to 1. Representative XRD patterns and the lattice-parameter variations with $y$ are displayed in Fig. 1 (data of complete series is presented elsewhere$^{59}$). In addition, the product a $= c$ is plotted with $y$ in Fig. 1, to estimate the cross-sectional area of the 1D Li$^+$-ion diffusion channels along the b direction.$^{59}$ For the higher Co and Ni contents, traces of impurity phases are observed, as shown in Fig. 1 for the $y = 0$ compositions. This is due to carbothermal reduction of the phosphate phase when heated in argon atmosphere with carbon containing precursors or carbon additive, resulting in production of secondary
These phosphide phases are highly electrically conductive, and thus increase the conductivity of the sample. Small phosphide contents are found to even improve the discharge capacity, but higher amounts lead to performance deterioration, as the phosphides are electrochemically inactive and may prevent Li$^+$-ion transfer at the particle surface. For our Co-substituted samples, few impurity peaks arising from Co$_2$P and Li$_4$O$_7$P$_2$ are observed for the $y = 0.8$ and 1 compositions (total amount < 5%). For the Ni substitution, a trace of impurities (Ni$_3$P) is seen for $y = 0.6$. At $y = 0.8$, a yet tiny amount (< 3%) of impurity peaks is present, but for $y = 1$, considerable amounts (< 14%) of secondary phases are observed, identified mainly as Ni$_3$P and Li$_4$O$_7$P$_2$. According to our systematic $^{57}$Fe Mössbauer spectroscopy study reported elsewhere, a small amount of amorphous Fe-containing impurities is present in $y \leq 0.8$ samples for both Co and Ni.

As shown in Fig. 1, the lattice-parameter variation is essentially linear with $y$ for both the Co- and Ni-substitution schemes. The $a$ and $b$ parameters decrease with increasing $y$ more strongly for the smaller-sized Ni substituent. For the Co substitution the lattice contraction is anisotropic, as the $c$ parameter rather slightly increases. On the contrary, a minor decrease in $c$ with $y$ is seen for the Ni-substituted samples. With increasing $y$, the Li$^+$-ion diffusion channel area ($a \times c$) decreases for both the Co and Ni substitutions, but the contraction is more significant for LiFe$_{1-y}$Co$_y$PO$_4$.

Morphology of the LiFe$_{1-y}$M$_y$PO$_4$ samples was probed with SEM and BET analyses. Representative SEM images are shown in Fig. 2, and the measured specific BET surface areas in Fig. 3. The active material particles in Fig. 2 are mostly ellipsoid-shaped and have a wide particle size distribution in the submicron range (approx. 500 – 50 nm). For the Ni substitution, slightly more agglomeration with increasing $y$ is observed, and the particle size distribution is broader with more small particles. However, all samples have their particle sizes in the same order of magnitude. Furthermore, the BET areas do not show significant differences with varying $y$ and the choice of the substituent (Fig. 3). For LiFe$_{1-y}$Co$_y$PO$_4$ samples, the BET areas decrease to some extent with increasing Co content. On the contrary, the surface areas of LiFe$_{1-y}$Ni$_y$PO$_4$ samples slightly increase with increasing Ni content, possibly due to the observed impurity phases ($y = 0.8$ and 1), as impurities have been reported to restrict the particle growth. This could explain the different particle size distribution and increased agglomeration, too. From TG analysis, the amount of actual carbon coating was estimated to be 1–2 wt-%.

**Cyclic voltammetry.**—Cyclic voltammograms at 0.05 mV s$^{-1}$ rate are presented in Fig. 4 for LiFe$_{1-y}$Co$_y$PO$_4$ and in Fig. 5 for LiFe$_{1-y}$Ni$_y$PO$_4$ electrodes. For $y = 0$, a minor anodic current is observed at > 4.7 V potentials, related to parasitic reactions, i.e. here...
electrolyte oxidation, as no electrochemical reactions of the Fe$^{2+}$/Fe$^{3+}$ redox couple take place at $>$ 4 V potentials. The parasitic reaction is apparently more pronounced in the first scan. However, it is possible that the Co- and Ni-substituted samples at higher substitution levels $y$ enhance the electrolyte decomposition.

As presented in Fig. 4, the Co$^{2+}$/Co$^{3+}$ redox couple can be reversibly delithiated and lithiated at all substitution levels. For $y = 1$ (LiCoPO$_4$), two oxidation peaks are clearly resolved at 4.83 and 4.93 V, consistent with literature,$^{9,33,36}$ and showing the existence of two two-phase reactions, LiCoPO$_4$↔Li$_x$CoPO$_4$ and Li$_y$CoPO$_4$↔CoPO$_4$. The ratio of peak areas is approximately 1:2, in accordance with an intermediate composition close to $x = 2/3$. Also for $y = 0.8$, two oxidation peaks (approx. at 4.78 and 4.89 V) are observed, yet the one at lower potentials is very flat. Interestingly, for $y = 0.6$, the oxidation peak shows a small shoulder at the low potential side; for $y \leq 0.4$, only one peak is seen. During lithiation, one clearly resolved reduction peak is detected for all substitution levels. The replacement of two Co$^{2+}$/Co$^{3+}$ oxidation peaks by a single peak for $y < 0.6$ indicates that an increasing Fe content (decreasing Co content $y$) in LiFe$_{1-y}$Co$_y$PO$_4$ changes the Co$^{2+}$/Co$^{3+}$ redox couple delithiation mechanism compared to that in LiCoPO$_4$. This confirms the results of Kosova et al.$^{38}$ for LiFe$_{1-y}$Co$_y$PO$_4$ materials, where $dQ/dU$ measurements showed two oxidation peaks at the Co$^{2+}$/Co$^{3+}$ redox region for $y \geq 0.9$, but only one peak for $y \leq 0.5$. For $y = 0.75$, a shoulder on the low-voltage side of the oxidation peak was seen. Bramnik et al.$^{60}$ reported corresponding data for LiFe$_{0.5}$Co$_{0.5}$PO$_4$, where one oxidation peak with a shoulder at the lower potential side was detected at the Co$^{2+}$/Co$^{3+}$ redox region. Changes in the delithiation/lithiation mechanisms will be discussed in more detail later in the text.

In Fig. 5 it is seen that the Ni$^{2+}$/Ni$^{3+}$ redox couple does not show reversible electrochemical activity within the 2.7 – 5.2 V potential range. Only during the first delithiation, part of the lithium can be extracted. The corresponding oxidation reaction is seen as a broad peak at approx. 4.5 – 4.9 V. However, in the subsequent cathodic scan, no peak corresponding to the reduction of Ni$^{3+}$ and lithium insertion into the structure at $>$ 4 V potentials is observed, and only the Fe$^{2+}$/Fe$^{3+}$ couple can be reversibly lithiated. In general, the lithium insertion has been more difficult to achieve than the lithium extraction (delithiation).$^{39,41}$ Compared to the theoretical redox potential of LiNiPO$_4$ (5.1 V or above), the Ni$^{2+}$/Ni$^{3+}$ oxidation reaction peak in Fig. 5a appears at lower potentials than expected. For LiFe$_{0.5}$Ni$_{0.5}$PO$_4$/C, oxidation at 5.2 V has been reported.$^{41}$ The electrical conductivity seems to play a crucial role,$^{28,39}$ only chemical delithiation was achieved for LiFe$_{0.5}$Ni$_{0.5}$PO$_4$ without carbon-coating.$^{54}$

In Fig. 6, the effects of the Co and Ni substituents on the average potential (midpoint of the oxidation and reduction peaks) and redox peak separation are presented. Additionally, the redox peak areas (corresponding to the amount of oxidized/reduced material in mAh g$^{-1}$) are compared to the theoretical values. For the Fe$^{2+}$/Fe$^{3+}$ and Co$^{2+}$/Co$^{3+}$ redox couples, data are taken from the second delithiation/lithiation cycle, but the peak areas for the Ni$^{2+}$/Ni$^{3+}$ oxidation are calculated from the first cycle, as no electrochemical activity was observed thereafter. The actual values are in reality smaller due to overlapping parasitic electrolyte oxidation reactions, which were observed especially during the first scan at high potentials. For LiFe$_{0.5}$Co$_{0.5}$PO$_4$ at $y = 0.8$ and 1, an average value of the two oxidation peaks was taken to calculate the average potential and peak separation.

From Fig. 6a, the average potential of the Fe$^{2+}$/Fe$^{3+}$ redox couple increases with increasing content of the substituent for both Co and Ni substitution. For the Co$^{2+}$/Co$^{3+}$ couple, a similar effect is observed; the average potential decreases with increasing amount of Fe (decreasing $y$), when $y \leq 0.6$. At $y = 0.8$ and 1, the average potential is lower, but the splitting of the oxidation response into two peaks interferes with defining the average potential. Based on Fig. 5, the Ni$^{2+}$/Ni$^{3+}$ oxidation peak is observed roughly at the same potential for all Ni contents $y$ (varying Fe content), which differs from the behavior observed for LiFe$_{1-y}$Co$_y$PO$_4$.

The shift of redox potentials (Fig. 6a) is related to the co-existence of two different transition metal species in the structure at the same lattice site. Muraligandh et al.$^{52}$ explained that the shift of redox energies, resulting in the shift redox potentials, is due to changes in the $M$–O bond covalence, determined by either changes in the electronegativity or in the $M$–O bond length. For the LiFe$_{1-y}$Co$_y$PO$_4$ series, substituting Fe by the less electropositive Co decreases the Fe–O bond covalence, thus lowering the Fe$^{2+}$/Fe$^{3+}$ redox couple energy and increasing the

![Figure 4](https://example.com/figure4.png)  
Figure 4. Cyclic voltammograms for LiFe$_{1-y}$Co$_y$PO$_4$ electrodes at 0.05 mV s$^{-1}$ scan rate (2nd delithiation/lithiation cycle) (a) full measurement range; (b) 4.5 – 5.2 V vs. Li/Li$^+$.

![Figure 5](https://example.com/figure5.png)  
Figure 5. Cyclic voltammograms for LiFe$_{1-y}$Ni$_y$PO$_4$ electrodes at 0.05 mV s$^{-1}$ scan rate. (a) 1st; (b) 2nd delithiation/lithiation cycle.
On the contrary, the Co2+ with the Co substitution. Fe–O bond covalence, thus increasing the Fe2+ less electropositive than Co, it may have a corresponding effect on the dox couple energy and lowered redox potential. As Ni is even slightly leading to a decreased redox potential.1,52

For the LiFe1- substitutions on the Fe2+/Ni3+ couple is electrochemically active as the Fe2+/Ni3+ redox couples; on oxidation/reduction peak areas of the (c) Co2+/Co3+ and Ni2+/Ni3+, and (d) Fe2+/Fe3 redox couples. Theoretical values for peak areas are shown for comparison.

The peak separation values in Fig. 6b indicate that substitution enhances the Fe2+/Fe3+ redox couple kinetics compared to y = 0. Due to substitution, mixed valence states at the FeM site are introduced. On the contrary, the Co2+/Co3+ couple kinetics deteriorate with increasing Co content. According to Fig. 6c, only a small part of the Ni2+/Ni3+ redox couple can be utilized even in the first delithiation scan. Surprisingly, at higher y, the amount of active Ni increases with decreasing Fe content, although degradation of the conductivity properties is expected. The enhanced activity could be explained by the increased amount of impurities, resulting in the higher electrical conductivity, and by a slightly higher BET area, too. On the contrary, a relatively higher amount of the Co2+/Co3+ couple is electrochemically active (oxidized/reduced) at the higher Fe contents. The deteriorating electrochemical performance of the Co2+/Co3+ couple at higher y is possibly due to insufficient electrical conductivity, decreased lattice volume and Li+–ion diffusion channel area, and other kinetic limitations related to the Co2+/Co3+ couple and its high redox potential. For the Fe2+/Fe3+ couple (Fig. 6d), slightly higher peak areas are shown with the Co substitution.

Rommel et al.45 pointed out that much of the electrochemical activity reported for Ni2+/Ni3+ in LiNiPO4 materials could actually arise from electrolyte decomposition reactions at high potentials, explaining the observed irreversibility. However, we believe that the broad oxidation peak observed at 4.5 – 4.9 V (Fig. 5) is mainly related to the electrochemical activity of the Ni2+/Ni3+ redox couple as the peak area increases with increasing Ni content, and the peak is terminated at approx. 4.9 V, whereas the electrolyte oxidation would be enhanced with increasing potential. Moreover, for y = 0, no peak is observed above 4 V. Additionally in our study, the Ni-substituted samples showed BET surface areas and particle sizes comparable to those of the Co-substituted samples, and thus a too large particle size cannot account for the lack of electrochemical activity. At y = 0.2, for example, the amount of Fe in the structure is high, and it should thus give a reasonable electrical conductivity, too. Contraction of the unit cell volume and Li+ diffusion channels were observed for Ni substitution, but again, for low substitution levels these are comparable to higher Co contents. The concentration of Li-(Fe,Ni) antisite defects was estimated to be negligible or very small (< 2% for all y in LiFe1-xMnxPO4) based on Rietveld refinement of the XRD data. Thus the Li-Ni site exchange cannot explain the lack of Ni2+/Ni3+ redox activity. In conclusion, the Ni2+/Ni3+ redox couple appears to be intrinsically much more difficult to activate than the Co2+/Co3+ redox couple.

**Partially delithiated electrodes.**— The effects of Co and Ni substitutions on the Fe2+/Fe3+ redox couple delithiation/lithiation reaction were studied by ex situ XRD analysis of partially delithiated electrodes for y = 0, 0.2, and 0.6 compositions; XRD patterns collected at approx. halfway of the Fe2+/Fe3+ redox couple region are shown in Fig. 7. In addition, 57Fe Mössbauer spectra for the Fe2+ and Fe3+ components in the corresponding partially delithiated electrode samples, investigated in detail elsewhere, are presented.56

In Fig. 7, two sets of diffraction peaks are observed for y = 0 and 0.2 (both Co and Ni), implying the existence of two separate phases. For y = 0, the compositions of the two phases upon delithiation/lithiation are known to be LiFePO4 and FePO4, and the corresponding peak positions and hkl indexes are marked in Fig. 7. For y = 0.2, the two-phase structure is preserved, but the peaks are shifted compared to y = 0, implying a change in the lattice parameters. According to Rietveld refinement, the difference in the unit cell volumes of the two phases becomes smaller with incorporation of Co or Ni (from y = 0 to y = 0.2), due to a decreased volume of the lithiated (lithium-rich) and increased volume of the delithiated (lithium-poor) phases. The relative diffraction intensities in the Ni-substituted y = 0.2 sample indicate a smaller amount of the phase with the higher lithiation degree. However, somewhat different delithiation states can have affected the intensities, and additionally, the phase compositions for y = 0.2 might not equal to x = 1/y = 0 for the delithiated/delithiated phases.

For the y = 0.6 samples, only one set of reflections is observed, suggesting the material is in a single phase. A slight shift in the peak
positions is seen, but otherwise the two substitution schemes, Co and Ni, do not show any difference. The diffraction patterns of $y = 0.6$ samples are similar to the results of Kosova et al., who performed in situ diffraction measurements on a LiFe$_{0.5}$Co$_{0.5}$PO$_4$ material ($y = 0.5$). They discovered only one set of reflections for every delithiation state (1.00 > $x$ > 0.04), and a single-phase solid-solution mechanism was concluded to prevail at both Fe$^{2+}$/Fe$^{3+}$ and Co$^{2+}$/Co$^{3+}$ redox regions.

According to the Mössbauer spectra in Fig. 7, for the Fe$^{2+}$/Fe$^{3+}$ couple approx. half-delithiated, the Fe$^{3+}$ component shows a significantly decreasing quadrupole splitting (QS) value (decreasing doublet width) with increasing $y$ for both Co- and Ni-substitution schemes, whereas QS for the Fe$^{2+}$ component remains constant. This implies an increasing electrical environment symmetry for the Fe$^{3+}$ with $y$, which was attributed to an increased Li$^+$ occupancy around Fe$^{3+}$ due to presence of CoNi in the same phase.

We suggest here that the disappearance of the second phase peaks in Fig. 7 indicates a change in the Fe$^{2+}$/Fe$^{3+}$ redox couple reaction mechanism, that is, a transition from the two-phase reaction in $y = 0$ and $y = 0.2$ to a single-phase solid-solution mechanism in $y = 0.6$ for both Li$_x$Fe$_{1-y}$Co$_y$PO$_4$ and Li$_x$Fe$_{1-y}$Ni$_y$PO$_4$ at the approx. halfway of the Fe$^{2+}$/Fe$^{3+}$ region. However, domains with two-phase compositions can again exist at higher/lower degrees of delithiation than the probed single state at the Fe$^{2+}$/Fe$^{3+}$ region. In situ experiments are needed for ideal measurement conditions and investigating the entire continuous range of $x$ (1 ≤ $x$ ≤ 0). Additionally, more samples with different substitution levels $y$ should be probed for obtaining a more detailed insight.

In addition to the Fe$^{2+}$/Fe$^{3+}$ redox couple delithiation mechanism, changes in the Co$^{2+}$/Co$^{3+}$ oxidation peak in cyclic voltammetry measurements were discussed earlier. According to Kosova et al., the peak related to the formation of the partly lithiated Co$^{2+}$/Co$^{3+}$ couple intermediate phase disappears at higher Fe contents ($y ≤ 0.5$ in LiFe$_{1-y}$Co$_y$PO$_4$), and a single-phase diffusion mechanism replaces the two-phase processes observed in LiFePO$_4$ and LiCoPO$_4$. They also claimed that this would apply to all compositions $y ≤ 0.5$ at all delithiation states. From the XRD patterns at $y = 0.2$, at least the approx. half-way of the Fe$^{2+}$/Fe$^{3+}$ redox region shows signs of a two-phase mechanism. Moreover, for Mn substituted LiFe$_{1-y}$Mn$_y$PO$_4$ materials, a single-phase Fe$^{2+}$/Fe$^{3+}$ reaction mechanism has been observed only for certain $y$ and specific states of delithiation/lithiation.62,63 On the other hand, Bramnik et al. assigned the shoulder observed before the actual oxidation peak in LiFe$_{0.5}$Co$_{0.5}$PO$_4$ to the change of the Fe$^{2+}$/Fe$^{3+}$ redox reaction to the Co$^{2+}$/Co$^{3+}$ reaction. Based on an in situ diffraction study, the delithiation process was suggested to proceed via two subsequent two-phase regions (Fe$^{2+}$/Fe$^{3+}$ and Co$^{2+}$/Co$^{3+}$), separated by a solid-solution domain (0.7 < $x$ < 0.25) at the Fe$^{2+}$/Fe$^{3+}$ to Co$^{2+}$/Co$^{3+}$ transition region. For lithiation, the domain was observed to be narrower ($Δx = 0.3$). The measurements presented in our study do not contradict the results of Bramnik et al.60

To discuss the effect of substitution, literature data concerning the unit cell volumes of different Li$_x$Fe$_{1-y}$M$_y$PO$_4$ ($M = \text{Co, Ni}$) compositions at varying lithiation states $x$ are collected in Fig. 8. In addition, the corresponding decrease in the unit cell volume from the lithiated to the delithiated composition is plotted. Computational values for the delithiated NiPO$_4$ phase show a large variation depending on the method (GGA or GGA+U), however, the value from GGA calculation is closer to the experimental value based on Li$_{0.09}$NiPO$_4$ composition. According to Fig. 8, the volume change between lithiated ($x = 1$) and delithiated ($x = 0$) phases is larger for the end member compositions ($y = 0$ or 1) than for the mixed compositions. For $y = 0$ or 1, the volume change is close to 7% (except for the GGA+U calculation value for LiNiPO$_4$). Otherwise no obvious difference between LiFePO$_4$, LiCoPO$_4$ or LiNiPO$_4$ is observed, although for LiCoPO$_4$, the volume change between the different co-existing phases is significantly smaller for a delithiation/lithiation process via the intermediate phase.21,22 For LiNiPO$_4$, the volume change upon delithiation corresponds to LiFePO$_4$, and consistently indications of a similar two-phase mechanism have been suggested.64 The volume change in mixed compositions is clearly smaller, 2–5%, and the influence of substitution appears especially as an increasing volume of the delithiated ($x = 0$) phase.
existence of solid-solution domains in LiFe1-xMxPO4 (M = Co, Ni) materials at varying lithiation states. Decrease in the unit cell volume between the lithiated/delithiated compositions with varying y. Data for LiNiPO4 (Ramana et al.64) is between x = 1 and x = 0.09 and for LiFe0.5Co0.5PO4 (Kosova et al.33) between x = 1 and x = 0.04.

suggested, too. We anticipate that the appearance of single-phase solid-solution domains at higher substitution levels is related to the diminished volume difference between the lithiated/delithiated phases due to the Co or Ni substitution.

Kosova et al.33 related origins of the changed reaction mechanisms and the Co2+/Co3+ intermediate phase disappearance in LiFe1-xMxPO4 for y ≤ 0.5 to changes in the electronic structure and mutual influence of Fe and Co on the miscibility gap of the end and intermediate phases. Furthermore, for LiFe1-xCoPO4 materials, a slightly shorter M–O distance has been reported for y = 0.75 – 0.8. Nyten et al.66 suggested that Co substitution at y < 0.75 levels does not lead to structure distortion, but a less stable structure would be found for y > 0.75. This could be related to the changed Co2+/Co3+ redox mechanism, observed for y < 0.6 in our study and by Kosova et al.33

On the other hand, in the computational study of Malik et al.,67 the existence of solid-solution domains in LiFe1-xMnPO4 materials was speculated to originate from the random distribution of Mn3+, which leads to a mutual disturbance of the attractive Mn3+-Li2+ and repulsive Fe3+-Li2+ interactions. Similar schemes were suggested to be applicable to other mixed metal phosphates, too. The substitution-induced increase in the electrical environment symmetry of the Fe3+ component in partially delithiated samples (Fig. 7) implies a possibly diminished octahedral distortion of the Fe3+O6 octahedra. This could affect the reduced volume change observed between lithiated/delithiated phases for the substituted samples, where especially the unit cell volume of the Fe3+-containing delithiated phase increases with substitution (Fig. 8).

Galvanostatic cycling tests.—Electrochemical performance was tested by galvanostatic cycling inside different voltage ranges and at different current rates. The discharge curves for LiFe1-xCoPO4 and LiFe1-xNiPO4 are presented in Fig. 9 at different charge cutoff voltages. The rate capability results for LiFe1-xCoPO4 are shown in Fig. 10, where specific discharge capacities, average discharge voltages, and specific discharge energies at different C-rates are presented.

In Fig. 9, substitution-induced shifts in the redox potentials (corresponding to Fig. 6a) are observed. In Fig. 9a, due to the restricted charge cutoff voltage (4.1 V), only the Fe2+/Fe3+ redox couple participates in the charge/discharge process. However, an increment of up to 50 mV is demonstrated in the Fe2+/Fe3+ redox couple potential due to the substitution. In Fig. 9b, higher Fe contents lower the Co2+/Co3+ couple potential; for y = 0.8 and 1 lower potentials are seen possibly due to increased polarization.

When comparing the Co- and Ni-substitution schemes at the same substitution levels y, it is observed that with the Ni-substituted samples, lower discharge capacities are achieved. This may be due to the lower intrinsic conductivity and smaller size of Li2+–ion diffusion channels. The amount of Li–Fe Nina site exchange was estimated to be very small in the Ni-substituted samples, and it is thus not predicted to significantly hinder the Li2+–ion diffusion. The higher substitution levels (y = 0.6 and 0.8) show a more sloping Fe2+/Fe3+ redox plateau, which may be related to a single-phase solid-solution mechanism,66 as two-phase reactions produce very flat charge/discharge profiles. However, polarization effects can affect the potential profile shapes, too.

In Fig. 10a, the discharge capacity of LiFe1-xCoPO4 electrodes inevitably drops with increasing y. Due to its poor kinetics, the Co2+/Co3+ couple delithiation may be incomplete at the end of charge with 4.9 V cutoff voltage, resulting in lower discharge capacities. When the charge cutoff voltage of 4.99 V was tested (results not shown here), higher initial capacities were achieved (90 mAh g⁻¹ for y = 1), due to the better utilization of the Co2+/Co3+ couple. However, the capacity fade was faster.

As shown in Fig. 10b, significantly higher average voltages are achieved when the Co2+/Co3+ couple is incorporated (y > 0). However, for y = 1 the discharge voltage degradation is fast, and also

![Figure 8](a) Literature values for unit cell volumes of different LiFe1-xMxPO4 (M = Co, Ni) materials at varying lithiation states. (b) Decrease in the unit cell volume between the lithiated/delithiated compositions with varying y. Data for LiNiPO4 (Ramana et al.64) is between x = 1 and x = 0.09 and for LiFe0.5Co0.5PO4 (Kosova et al.33) between x = 1 and x = 0.04.

![Figure 9](a) Galvanostatic discharge curves at 0.1 C rate for (a) LiFe1-xCoPO4 and LiFe1-xNiPO4 electrodes (4.1 V vs. Li/Li⁺ charge cutoff voltage); (b) LiFe1-xCoPO4 electrodes (4.9 V vs. Li/Li⁺ charge cutoff voltage).
y = 0.8 shows a considerable voltage fade and poor performance at higher C-rates. Again it is concluded that the presence of Fe is crucial for the electrochemical performance. However, when the discharge energies in Fig. 10c are compared, y = 0.2, 0.4, and 0.6 can compete with the discharge energy of y = 0, especially at lower C-rates.

Conclusions

Olivine-structured LiFe1−yMPO4/C (M = Co, Ni) solid-solutions were systematically investigated and compared for their electrochemical performance and delithiation/lithiation characteristics. Activation of the Ni2+/Ni3+ redox couple was intrinsically more difficult in comparison to the Co2+/Co3+ couple: for all y, only the first delithiation showed irreversible, partial oxidation of Ni2+/Ni3+. Possibly the poor electrical conductivity is not enhanced enough even for the higher Fe contents, and the more strongly decreased unit cell volume and Li1−-ion diffusion channel area may affect the activity in comparison to the Co substitution. At higher y, the impurity phases (especially the electrically conductive Ni1P) presumably enhance the activity. The unchanged Fe2+/Fe3+ redox couple activity and the ex situ XRD measurements of the LiFe1−yNiPO4 electrodes did not suggest any significant, irreversible structure changes during the initial delithiation. For the Co2+/Co3+ couple, reversible delithiation/lithiation was observed at all y, but a sufficient amount of Fe was crucial for the Co2+/Co3+ redox region performance. In rate capability testing, the LiFe1−yCoPO4 electrodes at 0.2 < y ≤ 0.6 showed comparable energy densities with the y = 0 compound.

The effect of the Ni substituent, although itself inactive, on the Fe2+/Fe3+ couple redox potential and kinetics was found similar to the Co substituent. Additionally, signs of changed phase-composition at the partially delithiated Fe2+/Fe3+ region were observed for higher substitution levels (y = 0.6) for both the Co- and Ni-substitution schemes. Furthermore, for y < 0.6, a changed delithiation mechanism of the Co3+/Co2+ couple in LiFe1−yCoPO4 was indicated, in comparison to Co2+/Co3+ in LiCoPO4 material. In terms of achieving high energy densities and kinetically beneficial single-phase domains (appearing at both Fe2+/Fe3+ and Co2+/Co3+ redox regions), compositions around y ≈ 0.5 seem to be optimal for the LiFe1−yCoPO4 system.

The mutual influence of Fe and Co/Ni in the mixed LiFe1−yMPO4 (M = Co, Ni) compositions may lead to a decreased volume change between the lithiated/delithiated phases. Furthermore, signs of a diminished octahedral distortion of the Fe3+/Fe2+ octahedra with increasing y were found in a 4Fe Mössbauer study. The reduced volume change is suggested to be related to a decreased miscibility gap in comparison to the y = 0 or 1 end members, which is observed as appearance of single-phase solid-solution domains. The substitution level y (approaching y = 1) at which the volume difference between the lithiated/delithiated phases again begins to increase is an interesting question.

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