Synthesis and electrochemical performance of Li$_{2}$Co$_{1-x}$M$_{x}$PO$_{4}$F (M = Fe, Mn) cathode materials

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Abstract
In the search for high-energy materials, novel 3D-fluorophosphates, Li$_2$Co$_{1-x}$Fe$_x$PO$_4$F and Li$_2$Co$_{1-x}$Mn$_x$PO$_4$F, have been synthesized. X-ray diffraction and scanning electron microscopy have been applied to analyze the structural and morphological features of the prepared materials. Both systems, Li$_2$Co$_{1-x}$Fe$_x$PO$_4$F and Li$_2$Co$_{1-x}$Mn$_x$PO$_4$F, exhibited narrow ranges of solid solutions: $x \leq 0.3$ and $x \leq 0.1$, respectively. The Li$_2$Co$_{0.9}$Mn$_{0.1}$PO$_4$F material demonstrated a reversible electrochemical performance with an initial discharge capacity of 75 mA·h·g$^{-1}$ (current rate of C/5) upon cycling between 2.5 and 5.5 V in 1 M LiBF$_4$/TMS electrolyte. Galvanostatic measurements along with cyclic voltammetry supported a single-phase de/intercalation mechanism in the Li$_2$Co$_{0.9}$Mn$_{0.1}$PO$_4$F material.

Introduction
In recent years the range of application of Li-ion batteries has been expanded from small-sized portable electronics to large-scale electric vehicles and stationary energy storage systems. Large-scale energy applications require batteries that are economically efficient, highly safe and that provide a high energy and power density. Today most of the cells in use have almost reached their intrinsic limits, and no significant improvements are expected. Therefore, current research in this field is directed towards the development of new high-performance materials. The specific energy of Li-ion batteries can be enhanced by applying cathode materials that operate at high voltages, and/or by increasing the specific capacity with materials that could cycle more than one Li atom per active transition metal atom. In this respect, fluorophosphates of the general formula A$_2$MPO$_4$F seem to be very attractive since they are expected to exhibit a high operating potential because of the increased ionicity of the M–F bond. Furthermore, A$_2$MPO$_4$F cathode materials may reach capacity values larger than 200 mA·h·g$^{-1}$, if more than
the operating voltage of these compounds to values that are
sustained by conventional electrolytes. This might be achieved through a complete or a partial substitution of Co\(^{2+}\) by Fe\(^{2+}\) or Mn\(^{2+}\) with lower values of the of M\(^{2+}/M^{3+}\) redox potential. Here, we report on the synthesis and the investigation of Li\(_2\)Co\(_{1-x}\)M\(_{x}\)PO\(_4\)F (M = Fe, Mn) fluorophosphates, which have not been yet identified. Furthermore, different high-voltage electrolytes systems were tested and utilized to evaluate the electrochemical performance of the new synthesized compounds.

Results and Discussion

Testing of electrolytes

An electrochemical window that extends above 5.5 V (vs Li/Li\(^{+}\)) has been reported for several electrolytes systems based on sulfone or dinitrile solvents [10-14]. For instance, tetramethylene sulfone (TMS) in the presence of an imide salt (LiTFSI) demonstrated a resistance to electrochemical oxidation up to 6 V vs Li/Li\(^{+}\) [11], while 1 M LiBF\(_4\)/(EC)/DMC/sebacitrile was used to examine the high-voltage performance of the fluorophosphate Li\(_2\)NiPO\(_4\)F [10]. We chose 1 M LiBF\(_4\)/TMS to investigate the electrochemical activity of the fluorophosphate materials. LiBF\(_4\) salt was chosen instead of LiTFSI, because the last one corrodes the aluminum current collector at high potentials.

Preliminarily, the stability of both electrolytes was investigated by cyclic voltammetry to further establish their compatibility with high-voltage cathode materials. Two types of working electrodes were used to evaluate the electrochemical window of the electrolytes: 1) Al-foil (since it is used as a current collector for the positive electrode); 2) an “idle electrode”, which consisted of Al\(_2\)O\(_3\)/C/PVdF in a ratio of 80/10/10, in order to imitate the effect of the carbon- and binding electrode components at high potentials. Because the loading mass and the effective surface area of the active material on the electrodes that were used for electrolyte testing were similar in all experiments, the obtained current values were compared without normalization.

Both electrolytes exhibited an electrochemical stability up to 5.5 V (vs Li/Li\(^{+}\)) with aluminum as the working electrode (Figure 2a). For the first cycle the current detected at the highest potential did not exceed 0.4 μA, and it decreased (to 0.001 μA) upon subsequent cycling. It is clearly seen that the effect of the oxidation processes occurred at the Al electrode is negligible for both electrolytes when compared to a scanning with the idle electrode (Figure 2b). In the anodic sweep the commercial electrolyte showed a small increase in oxidation current at 4.8 V followed by drastic growth (up to 40 μA) around 5.2 V, while for the TMS electrolyte irreversible oxidation current peaks of 5 μA were detected. These results confirmed the reasonable
stability of 1 M LiBF₄/TMS electrolyte up to 5.5 V, which agrees with data reported previously [12,13].

Investigation of Li₂(Co,M)PO₄F (M = Mn, Fe)

Applied synthesis approaches were directed not only towards the investigation of Li₂Co₁₋ₓMₓPO₄F solid solutions, but also to the preparation of the corresponding electrode materials. Because of poor electronic and ionic conductivity that is inherent to polyanionic compounds, a carbon coating (for improving the electronic surface conductivity) and a downsizing of the particles (in order to shorten the Li-ion transfer paths) were applied to enhance the electrochemical performance of the investigated materials. In order to reduce the particle size and to prevent grain coalescence the lowest temperatures usable for the formation of the pure olivine precursors and the fluorophosphates were always chosen.

The Li₂CoPO₄F/C composite for electrochemical measurements was synthesized according to a procedure that was optimized previously [4]. A mixture of LiCoPO₄/C with 1.05 equiv of LiF was annealed at 670 °C for 1 h under Ar-flow and subsequently quenched to room temperature. The XRD pattern confirmed the formation of Li₂CoPO₄F, though a small amount of WC (about 1%, from the ball-milling media) was also detected (Figure 3). The refined unit cell parameters of Li₂CoPO₄F/C (a = 10.444(3) Å, b = 6.374(2) Å, c = 10.868(3) Å, V = 723.6(5) Å³) were in agreement with previously reported data [1,4]. The residual carbon in Li₂CoPO₄F/C was found to be 1.7%. According to the SEM images the synthesized material consisted of almost uniform particles with an average size of 0.7–0.9 μm (Figure 4).

Figure 2: Cyclovoltammetry curves (first cycle) of 1 M LiPF₆ in EC/DMC (black) and 1 M LiBF₄ in TMS (red) at scan rate of 0.1 mV·s⁻¹. (a) Aluminum electrode, (b) idle electrode consisting of Al₂O₃/C/PVdF in an 80/10/10 ratio.

Figure 3: Powder XRD patterns of Li₂CoPO₄F/C (a) and Li₂Co₀.₉Mn₀.₁PO₄F (b). A theoretical pattern of Li₂CoPO₄F calculated by using PDF 56-149 is shown on the bottom. Reflections corresponding to WC are marked by an asterisk.

Figure 4: SEM images of fluorophosphate materials a) Li₂CoPO₄F/C, b) Li₂Co₀.₉Mn₀.₁PO₄F/C, c) Li₂Co₀.₉Fe₀.₃PO₄F.
In order to investigate the Li$_3$Co$_{1−x}$Mn$_x$PO$_4$F solid solutions a combination of freeze-drying and solid-state techniques was applied. A mixture of LiCo$_{0.5}$Mn$_{0.5}$PO$_4$ obtained from cryogranulate was annealed with 1.05 equiv of LiF in the temperature range of 650–700 °C for 1–2 h. Annealing at 680 °C for 1 h was found to be optimum for the preparation of the Li$_2$Co$_{0.9}$Mn$_0.1$PO$_4$F phase. The XRD pattern of this sample (Figure 3) was indexed as an orthorhombic unit cell with parameters $a = 10.465(2)$ Å, $b = 6.3998(9)$ Å, $c = 10.898(2)$ Å and $V = 729.9(2)$ Å$^3$. No peaks of the olivine phase were observed, though a small amount of WC (about 1%, from the ball-milling media) was detected in the XRD pattern. Further attempts to increase the Mn content in Li$_2$Co$_{1−x}$Mn$_x$PO$_4$F ($x = 0.2, 0.3$) by varying the annealing temperature and the heating duration ended up with multiphase samples that contained impurities of olivine and Li$_3$PO$_4$. Moreover, the unit cell parameters of the formed fluorophosphates were found to be close to those of Li$_2$Co$_{0.9}$Mn$_0.1$PO$_4$F. These results clearly indicated that Li$_2$Co$_{1−x}$Mn$_x$PO$_4$F exhibited a very limited range for the solid solution ($x \leq 0.10$). For electrochemical testing Li$_2$Co$_{0.9}$Mn$_0.1$PO$_4$/C was synthesized by adding carbon black (5 wt %) to the olivine precursor at an intermediate step of preparation. The XRD pattern of the obtained sample confirmed the formation of pure fluorophosphate with cell parameters similar to those given above. EDX analysis of the prepared material found the Co/Mn ratio to be 0.89(1)/0.11(1), which agreed with the expected values from the chemical formula. The morphology of this sample was investigated by SEM and showed particles of submicron size (Figure 4). The residual carbon in the prepared composite was determined to be as 3.1% by TG analysis. This value was taken into account during the preparation of the electrode.

The synthesis of the iron-substituted fluorophosphates, Li$_2$Co$_{1−x}$Fe$_x$PO$_4$F, was performed by a two-step solid-state process. The optimization of the preparation conditions was done for the composition of $x = 0.3$. Figure 5a represents XRD patterns of the samples obtained by annealing mixtures of LiCo$_{0.7}$Fe$_{0.3}$PO$_4$ and LiF (with 10 wt % excess) at different temperatures. According to the XRD data, the fluorophosphate phase started to form above 700 °C, and further enhancement of the annealing temperature resulted in a decrease of the olivine impurities and in an increase of the fluorophosphate constituent. The formation of the almost pure Li$_2$Co$_{0.7}$Fe$_{0.3}$PO$_4$F was observed upon heating at 740–750 °C. Above these temperatures (>760 °C) samples melted and were heavily contaminated by cobalt oxide. Thus, the annealing at 750 °C for 1 h in Ar was found to be optimum to yield Li$_2$Co$_{0.7}$Fe$_{0.3}$PO$_4$F. A tuning of the annealing temperature allowed us to synthesize pure fluorophosphates with different levels of substitution, Li$_2$Co$_{1−x}$Fe$_x$PO$_4$F ($x = 0.1–0.3$) (Figure 5b). The XRD patterns of obtained samples were indexed on the base of an orthorhombic structure with a $Pnma$ space group and the unit cell parameters that are listed in Table 1. Careful inspection of the XRD data revealed negligible amounts of Li$_2$PO$_4$ and Co admixtures. It is evident from the obtained results that the synthesis of Fe-substituted compounds requires increased annealing temperatures that depend on the Fe-content in Li$_2$Co$_{1−x}$Fe$_x$PO$_4$F. For a higher Fe-substitution higher annealing temperatures are needed. The solid-state synthesis at elevated temperatures resulted in large micrometer-sized particles (2–4 μm) as observed by SEM (Figure 4). It should be noted that the presence of LiF, which is used as the reagent, promoted the coalescence of small particles and induced crystalline growth because of fluxing at elevated temperatures. In spite of varying the preparation conditions all attempts to increase the substitution level of Fe in Li$_2$Co$_{1−x}$Fe$_x$PO$_4$F ($x = 0.4, 0.5$) led to multi-phase samples, with the fluorophosphate phases having cell parameters close to those of Li$_2$Co$_{0.7}$Fe$_{0.3}$PO$_4$F. Thus, it was concluded that the solid-solution range of Li$_2$Co$_{1−x}$Fe$_x$PO$_4$F was limited to $x \leq 0.3$. Efforts to prepare a Li$_2$Co$_{0.7}$Fe$_{0.3}$PO$_4$F/C composite by adding carbon black or glucose to the initial mixtures of reagents resulted in

![Figure 5: a) XRD patterns of a mixture of LiCo$_{0.7}$Fe$_{0.3}$PO$_4$ and LiF, annealed at different temperatures, starting from 670 °C. XRD peaks that correspond to impurities are marked. b) XRD patterns of Li$_2$Co$_{1−x}$Fe$_x$PO$_4$F ($x = 0.1, 0.2, 0.3$), synthesized at the denoted temperatures.](image)
Table 1: Unit cell parameters of fluorophosphates Li$_2$Co$_{1-x}$M$_x$PO$_4$F (M = Mn, Fe).

| $x$ (M) | a, Å   | b, Å     | c, Å     | V, Å$^3$  |
|--------|--------|----------|----------|-----------|
| 0      | 10.439(2) | 6.3731(12) | 10.864(2) | 722.8(2)  |
| 0.1 (Mn) | 10.465(2) | 6.3998(9)  | 10.898(2) | 729.9(2)  |
| 0.1 (Fe)  | 10.440(2) | 6.3862(13) | 10.867(3) | 724.5(4)  |
| 0.2 (Fe)  | 10.442(2) | 6.4103(14) | 10.884(2) | 728.6(3)  |
| 0.3 (Fe)  | 10.453(1)  | 6.4096(8)  | 10.888(12)| 729.5(2)  |

According to the obtained results Li$_2$Co$_{1-x}$Fe$_x$PO$_4$F and Li$_2$Co$_{1-x}$Mn$_x$PO$_4$F systems exhibit limited ranges of solid solution. This finding might be explained by differences in the sizes of transition metal ions: Apparently, the structure framework becomes unstable upon higher substitution of Co$^{2+}$ (0.735 Å) by larger Fe$^{2+}$ (0.780 Å) and Mn$^{2+}$ (0.820 Å) [15]. Indeed, while Li$_2$MPO$_4$F (M = Co, Ni) can be obtained by direct synthesis, the preparation of 3D-Li$_2$FePO$_4$F requires the electrochemical ion-exchange of the Na-counterpart, and the corresponding Mn-based fluorophosphate has not been yet identified [16]. It is reasonable, that a substitution of Co$^{2+}$ by Mn$^{2+}$, which has the largest ionic radius, only takes place in a smaller range ($x \leq 0.10$) than in the case of Fe$^{2+}$ ($x \leq 0.30$). In both cases the substitution results in considerable expansion of the unit cell (ca. 7 Å$^3$) for the highest level of substitution (Table 1).

Electrochemical performance of Li$_2$(Co,M)PO$_4$F (M = Mn, Fe)

According to galvanostatic measurements performed at a rate of C/5 (Figure 6) Li$_2$CoPO$_4$F starts to discharge at approx. 5 V, which agrees well with previous results. The Li/Li$_2$CoPO$_4$F cells delivered initial discharge capacities of ca. 90 and 85 mA·h·g$^{-1}$ with the commercial and the sulfone-based electrolyte, respectively, and these values corresponded to a reversible de/intercalation of about 0.65 Li. During the initial cycles the charge capacity values were remarkably higher than the corresponding discharge capacities. This discrepancy in the capacities may result from a decomposition of the electrolyte on the conductive carbon and on the fluorophosphate material at high potentials. For the TMS electrolyte this discrepancy disappeared upon subsequent cycling. During the 10th cycle the corresponding values became almost equal, with a coulombic efficiency of 98% (Figure 6). Moreover, there is less capacity fading when using the TMS electrolyte. During the 10th cycle the discharge capacity decreased to about 83% of the initial value in contrast to a decrease to about 45% found with the commercial electrolyte. The obtained results indicated a rather stable electrochemical performance of the Li$_2$CoPO$_4$F material at high voltages in the 1 M LiBF$_4$/TMS electrolyte.
decrease of the irreversible capacity, which leads to the high
columbic efficiency, implies that this electrolyte forms a stable
solid-electrolyte interface on the electrode surface, but this
suggestion should be further investigated and confirmed.

A preliminary investigation of the electrochemical behavior of
Li₂Co₀.₇Fe₀.₃PO₄F was carried out with electrodes prepared
from the well crystallized sample. Potentiodynamic measure-
ments in both electrolytes resulted in broad peaks on the anodic
and cathodic branches with the discharge capacity values being
lower than 10 mA·h·g⁻¹. Because of the poor electrochemical
activity, which is ascribed to the non-optimized morphology of
the electrode material (particle size of 2–4 μm), any compar-
isons of Li₂Co₀.₇Fe₀.₃PO₄F with the unsubstituted material
were unreasonable.

Figure 7 shows the cyclovoltammetry (CV) curves of the Li/
Li₂Co₀.₉Mn₀.₁PO₄F cells cycled in both electrolytes. For the
TMS electrolyte two oxidative peaks (at 4.9 V and 5.2 V) and a
broad reductive peak (at 4.8 V) were observed in the first
anodic and cathodic scans, respectively. During the second
cycle the two oxidative peaks merged, and the broad peaks on
the anodic (∼5.1 V) and cathodic (4.8 V) branches showed
charge and discharge capacities of 135 and 70 mA·h·g⁻¹, res-
pectively. The CV curves that were recorded in the commercial
electrolyte were quite similar. The presence of two oxidative
peaks in the first anodic scan (Figure 7) hints at the occurrence
of at least two redox processes. We related them to the struc-
ture transformation upon deintercalation of Li, followed by a
further removal of Li from the transformed structure. This irre-
versible structure transformation, which occurs upon first
charging, was investigated by ex-situ XRD studies and
described in detail in our previous paper. This transformation
resulted in an expansion of the framework and a probable redis-
tribution of Li ions within the framework [4]. Similar features
were observed in CV curves of Li₂CoPO₄F by D. Wang et al.
[5] and S. Amaresh et al. [8]. This indicates the intrinsic nature
of this transformation.

Galvanostatic measurements on Li₂Co₀.₉Mn₀.₁PO₄F (Figure 8)
revealed the highest discharge capacities of 75 and 85 mA·h·g⁻¹
in TMS and the commercial electrolytes, respectively. As in the

Figure 7: Cyclovoltammetry curves of the Li₂Co₀.₉Mn₀.₁PO₄F elec-
trodes in the commercial (a) and the sulfone-based (b) electrolytes
recorded at 0.1 mV s⁻¹.

Figure 8: Charge-discharge curves of Li₂Co₀.₉Mn₀.₁PO₄F in the
commercial (a) and the sulfone-based (b) electrolytes measured at
C/5.
case of Li$_2$CoPO$_4$F, the capacity fading of the Mn-substituted fluorophosphate was slower in the TMS electrolyte. Sloping charge–discharge profiles and broad CV peaks suggest a single-phase (solid-solution) reaction mechanism, similar to Li$_2$CoPO$_4$F [4,8]. There is no visible change in the operating potential of Li$_2$Co$_{0.9}$Mn$_{0.1}$PO$_4$F. Therefore it was difficult to draw a decisive conclusion on the effect of Mn-substitution on the electrochemical activity of the Li$_2$CoPO$_4$F system. A further optimization in synthesis and formulation of the cathode material (particle investigation and carbon coating) of Mn- and Fe-substituted fluorophosphates will improve their electrochemical performance and, thereby, answer the question about a possible fine tuning of the operating voltage of this fluorophosphate family through substitutions on the transition metal site.

**Conclusion**

New fluorophosphates, Li$_2$Co$_{1-x}$Mn$_x$PO$_4$F and Li$_2$Co$_{1-x}$Fe$_x$PO$_4$F, were successfully synthesized and investigated. Both systems exhibited narrow ranges of solid solution that agreed well with the ionic sizes of the transition metals. Good cycling and capacity behavior was attained with the 1 M LiBF$_4$/TMS electrolyte. Galvanostatic measurements revealed a reversible electrochemical activity with discharge capacities as high as 90 and 75 mA·h·g$^{-1}$ for Li$_2$CoPO$_4$F and Li$_2$Co$_{0.9}$Mn$_{0.1}$PO$_4$F respectively. A further investigation that includes the optimization of the electrode materials and the development of a high-voltage electrolyte is required to evaluate all potentials of this Li$_2$Co$_{1-x}$M$_x$PO$_4$F (M = Mn, Fe) fluorophosphate family.

**Experimental**

The fluorophosphates, Li$_2$CoPO$_4$F and Li$_2$Co$_{1-x}$M$_x$PO$_4$F (M = Mn, Fe) were synthesized in a two-steps process. In the first step LiCo$_1$–M$_x$PO$_4$ olivine precursors were prepared through freeze-drying or ceramic techniques, depending on the transition metal. Thus, LiCo$_1$–M$_x$PO$_4$F (M = Mn, Fe) fluorophosphate family. The electrochemical evaluation was performed in two-electrode configuration cells with Li-metal foil acting both as the reference and counter electrodes, borosilicate glass was used as the electrolyte. The electrochemical evaluation was performed in two-electrode configuration cells with Li-metal foil acting both as the reference and counter electrodes, borosilicate glass was used as the electrolyte.
a separator. The positive electrodes were prepared by thoroughly mixing the active material (80 wt %) with carbon Timcal Super C (10 wt %) and PVdF (10 wt %) dissolved in a minimal amount of N-methyl-pyrrolidone. This cathode slurry was cast on an Al-foil collector by using the doctor-blade technique with a typical loading of 1 mg cm\(^{-2}\). The prepared electrodes were dried, rolled and then dried again at 100 °C under vacuum for several hours. The electrochemical evaluation was carried out by using the following electrolytes: 1) 1 M LiPF\(_6\) solution in ethylene carbonate (EC) and dimethylcarbonate (DMC) with a volume ratio of 1:1 (commercial electrolyte, Merck); 2) 1 M solution of LiBF\(_4\) in tetramethylene sulfone (TMS). The latter electrolyte was prepared by dissolving an appropriate amount of LiBF\(_4\) (99.99%, Aldrich) in TMS that was purified up to 99.8% before. The electrochemical cells were assembled in an Ar-filled glove box. All tested cells were left to relax before the measurements (10–20 h). A potentiostat/galvanostat Biologic VMP-3 was used for data collecting. The cyclic voltammetry scanning was performed in the voltage range of 2.5–5.5 V at a rate of C/5 (the current required to deintercalate one Li ion from \(\text{LiPF}_6\) in 5 hours).

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