Structure and Electrochemistry of Two-Electron Redox Couples in Lithium Metal Fluorophosphates Based on the Tavorite Structure

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ABSTRACT: An electrochemical and structural study of the two-electron redox couple comprising the tavorite-type series of fluorophosphates Li$_{1+x}$VPO$_4$F ($x = 0, 1$) shows that both intercalation of LiVPO$_4$F with Li (to give Li$_2$VPO$_4$F) and deintercalation (to give VPO$_4$F) proceed by a two-phase mechanism. Structural models for each of the three phases were determined by Rietveld refinements of combined neutron and X-ray diffraction data of the isolated pure phase materials. LiVPO$_4$F crystallizes in the triclinic space group $P$
 and is isostructural to many known fluorophosphates whereas both Li$_1$VPO$_4$F and VPO$_4$F crystallize in the monoclinic space group $C2/c$, although they have very closely related structures to the parent. Solid-state $^{6,7}$Li NMR studies of Li$_1$VPO$_4$F reveal the two lithium sites are clearly distinguishable, with more than 100 ppm separation between the resonances. 2D exchange NMR is used to demonstrate the time scale of ion dynamics between the two sites.

KEYWORDS: Li-ion battery, Li-ion two-electron redox couple, lithium metal fluorophosphate, tavorite, cathode, solid-state Li NMR, 2D NMR

INTRODUCTION

Lithium transition metal phosphate and fluorophosphates are important positive electrode materials for safe, low-cost lithium-ion cells. The most prominent compounds of this group studied to date have been the olivine phosphates, namely LiFePO$_4$ and LiMnPO$_4$. Because of structural nuances, the olivine LiFePO$_4$ has a higher voltage (3.5 V) than most other iron phosphates, which allows the fabrication of Li-ion cells with high energy densities. The major limitations of LiFePO$_4$, namely poor electrical conductivity and one-dimensional Li-ion diffusion, have been partially overcome by decreasing the crystallite size to the nanoscale and coating conductive additives onto the surface. However, these approaches add to the complexity of the material’s manufacture.

This has prompted us to explore the next generation of cathode materials that might exhibit more attractive features with fewer inherent limitations. In the search for structural frameworks that overcome the 1D ion conductivity challenge of olivine, a variety of fluorophosphates have been revealed as attractive compounds. Na$_2$FePO$_4$F has been shown to exhibit solid-solution behavior when cycled in a lithium cell and has an average potential of 3.3 V vs Li/Li$.^{9}$ The compound also exhibits good ionic conductivity and one-dimensional Li-ion diffusion, and coating conductive additives onto the surface. However, these approaches add to the complexity of the material’s manufacture.

Another important class of fluorophosphates materials comprises compounds based on the tavorite (LiFePO$_4$OH) structure. There are several known compounds of this structure type including LiAlPO$_4$OH, LiAlPO$_4$F, LiMnPO$_4$OH, LiGaPO$_4$OH, and fluorosulphates such as LiMgSO$_4$F and LiFeSO$_4$F. The spacious structure contains Li tunnels in multiple directions which allows for good Li-ion transport in these materials. Up to this point, two fluorophosphates from this family have been explored as potential Li-ion battery cathodes: LiFePO$_4$F and LiVPO$_4$F. LiVPO$_4$F is a promising positive electrode material with a potential of 2.8 V and its synthesis by solid-state and ionothermal methods have been reported previously. Li$_1$VPO$_4$F was first reported in 2003 as a 4.1 V positive electrode material with a theoretical capacity of 155 mAh g$^{-1}$, corresponding to the extraction of one Li.$^{29}$ Interestingly, it was later shown that Li$_1$VPO$_4$F could also intercalate Li at a potential of about 1.8 V.$^{29}$ Since Li$_2$VPO$_4$F was shown to function as both a positive and negative electrode, this led to the report of a Li$_1$VPO$_4$F/LiVPO$_4$F symmetric cell with one electrode working on the $V^{2+}$ → $V^{4+}$ redox couple and the other working on the $V^{3+}$ → $V^{2+}$ redox couple.$^{29}$

Although structural data exist on the parent Li$_2$VPO$_4$F, no such data exist on the electrode materials upon discharge or charge. Here we report the structure of the reduced tavorite phase Li$_1$VPO$_4$F determined by a combined refinement of X-ray and neutron diffraction, as well as the structure of the fully oxidized VPO$_4$F. X-ray diffraction and electrochemical studies were used to confirm the mechanism of lithium (de)-intercalation for each compound.$^{6,7}$Li solid-state NMR was also used to probe the Li positions and occupancies in both
LiVPO₄F and the reduced phase Li₂VPO₄F. Our findings reveal the important structural features that underlie the high degree of reversibility in this two electron electrochemical couple.

■ EXPERIMENTAL SECTION

Synthetic Methods. LiVPO₄F. Our synthesis was similar to the method reported by Barker et al.²⁸ V₂O₅ (Aldrich, 99%+) and H₂PO₄ (BDH, 99%) were mixed in a 0.5:1:1.5 molar ratio and fired at 750 °C under a flowing Ar atmosphere to produce VPO₄/C. Stoichiometric amounts of VPO₄/C and LiF were ground in zirconia milling media and subsequently fired at 600 °C for 1 h under an Ar atmosphere.

Li₂VPO₄F. LiVPO₄F was stirred with a stoichiometric amount of LiAlH₄ in tetrahydrofuran in an argon-filled glovebox for 44 h. The product was washed with tetrahydrofuran and stored under argon. Li₂VPO₄F. Stoichiometric amounts of LiVPO₄F and NOBF₄ were stirred in acetone in a glovebox for 16 h. The product was filtered, rinsed with acetone and dried under ambient conditions.

Elemental Analysis. Inductively coupled plasma mass spectroscopy (ICP-MS), as per EPA 3050, was also used to determine the relative quantities of Li, V, and P.

Electrochemistry. The LiVPO₄F/C composite, carbon (Super S) and poly(vinylidene fluoride), PVDF, were mixed in a 87:3:10 mass ratio. N-methyl pyrrolidone was added to this mixture and the resultant slurry was cast on C-coated Al foil and dried for 24 h under vacuum. Circular discs cut from this foil were cycled in coin cells vs. metallic Li with 1 M LiPF₆ in ethylene carbonate and dimethyl carbonate in a 1:1 volume ratio as the electrolyte. The cells underwent galvanic cycling on a Biologic VMP3 instrument at a rate of C/10 (1 Li in 1 h).

Solid-State NMR. ⁷Li and ¹⁹F MAS NMR experiments were performed at Larmor frequencies of 116.6 and 44.1 MHz, respectively, on a Bruker AV300 spectrometer. A custom built probe supporting 1.8 mm rotors was used with MAS frequencies ranging from 25 kHz to 40 kHz. By adjusting spinning speeds from 25 kHz to 40 kHz, a temperature range of 303 to 330 K was available. Both ⁷Li and ¹⁹F 1D spectra were acquired using 90° pulse lengths ranging from 2.0 to 2.5 μs and recycle delay of 100 ms. Spin–lattice relaxation times (T₁) were determined using the standard inversion recovery sequence included in the Bruker software package. Two-dimensional exchange (EXSY) spectra were acquired using mixing times ranging from 2 to 17 ms. The number of slices in the indirect dimension was 2048. Phase-sensitive detection in t₁ was achieved through the use of States-TPPPI.²⁷

⁷Li(P²F) REDOR studies were carried out on a Bruker AV500 spectrometer with ⁷Li and ³¹P Larmor frequencies of 76.3 and 469.5 MHz, respectively. The same 1.8 mm probe as described above was used for these experiments with the ¹H channel modified to allow for ³¹P dephasing. A ³¹P π pulse length of 4.40 μs was used. All spectra were referenced to 1 M ⁶LiCl (aq) (0 ppm), and CFCl₃ for ¹⁹F experiments. Temperatures were calibrated using Sm₂S₃O₇ as described elsewhere.³⁸

■ RESULTS AND DISCUSSION

Structure. Carbon-coated LiVPO₄F was successfully prepared by a solid-state route similar to a previous report.²⁶ A high-resolution X-ray diffraction pattern obtained at a synchrotron source along with its Rietveld refinement is shown in Figure 1 and the results are listed in Table 1. LiVPO₄F adopts theavorite structure and is isostructural with several known hydroxyphosphates such as LiFePO₄OH³⁷ and fluorophosphates including LiAIPO₄F, which crystallize in the trigonal space group P1. Figure 2 depicts the crystal structure derived from the refinement. [V²⁺F₆O₁₆] octahedra form corner-sharing chains in the (010) direction, where alternate octahedra are tilted. The F ligands act as the bridging ligands. These chains are connected by corner-sharing phosphate tetrahedra to make a spacious 3D framework: wide tunnels (>3 Å in diameter) are present along all of the (100), (010), and (001)
directions. The refined unit cell volume of 174.31 Å³ is very similar to that reported by Barker and co-workers of 174.35 Å³, even though the choice of the two triclinic cells differed, as evidenced by the difference in angles between the two reported cells.

It is widely known that lithium fluorophosphates with the tavorite structure favor a low-symmetry octahedral lithium site with a large anisotropic thermal parameter, which is usually refined as a split lithium position, such as in LiAlPO₄F. This is also true for LiVPO₄F (see Table 2). Refinements using a single Li site (isotropic thermal parameter) provided much higher Rwp values than using a split site to describe the lithium coordination. The distribution of lithium over these sites varies based on the method of preparation and the nature of the anion (OH vs F) as these factors influence the geometry of the site itself. The lithium co-ordination in LiVPO₄F is shown in Figure 2 and bond distances are summarized in Table 2. In LiVPO₄F, the centers of the two Li sites Li₁ and Li₂ are approximately 0.79 Å apart. The Li₁ site has one Li–F bond and two Li–O bonds that are 1.92–2.12 Å in length, all of which are consistent for bond distances with Li in a 4-coordinate environment. Two additional oxygen ligands are 2.29 and 2.43 Å from the Li₁ site, thus the Li₁ environment may be described as 5-coordinate geometry. The last oxygen ligand is greater than 3 Å from Li₁. In contrast, the Li₂ site may be described as having [5 + 1] geometry. Li₂ has one close F ligand and 4 oxygen ligands at distances varying between 1.98 and 2.32 Å. A fifth oxygen ligand (O₃) is 2.88 Å from Li₂. With the difference in coordination and bond lengths, it is not surprising that the two Li sites are not equally

Table 1. Lattice Constants and Atomic Parameters of LiVPO₄F Refined from Powder XRD Data

<table>
<thead>
<tr>
<th>atom</th>
<th>Wychoff</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Occ</th>
<th>Uiso</th>
</tr>
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<tr>
<td>Li (1)</td>
<td>2i</td>
<td>0.389(2)</td>
<td>0.334(1)</td>
<td>0.659(2)</td>
<td>0.18(1)</td>
<td>0.015</td>
</tr>
<tr>
<td>Li (2)</td>
<td>2i</td>
<td>0.373(2)</td>
<td>0.236(1)</td>
<td>0.517(2)</td>
<td>0.82(1)</td>
<td>0.015</td>
</tr>
<tr>
<td>V (1)</td>
<td>1a</td>
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<td>0</td>
<td>0</td>
<td>1.0</td>
<td>0.0043(3)</td>
</tr>
<tr>
<td>V (2)</td>
<td>1b</td>
<td>0</td>
<td>1/2</td>
<td>1/2</td>
<td>1.0</td>
<td>0.0059(3)</td>
</tr>
<tr>
<td>P (1)</td>
<td>2i</td>
<td>−0.6476(2)</td>
<td>−0.2515(2)</td>
<td>0.0719(2)</td>
<td>1.0</td>
<td>0.0070(3)</td>
</tr>
<tr>
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<td>0.1701(4)</td>
<td>1.0</td>
<td>0.015(2)</td>
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<td>0.016(2)</td>
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<td>−0.4100(3)</td>
<td>0.2163(4)</td>
<td>1.0</td>
<td>0.013(2)</td>
</tr>
<tr>
<td>O (4)</td>
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<td>−0.3597(3)</td>
<td>−0.2503(4)</td>
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<td>0.014(2)</td>
</tr>
<tr>
<td>F (1)</td>
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<td>0.0875(3)</td>
<td>0.2450(2)</td>
<td>0.3585(3)</td>
<td>1.0</td>
<td>0.015(2)</td>
</tr>
</tbody>
</table>

Agreement factors: $R_{wp} = 10.30\%$, $R_p = 7.88\%$, $R_F^2 = 3.45\%$. 

Figure 1. Synchrotron X-ray diffraction pattern ($\lambda = 0.4122$ Å) and Rietveld refinement of LiVPO₄F synthesized by a solid-state method. The experimental points are black, the fit is shown in red, the calculated reflections are shown in blue and the difference map is shown in gray. The lattice parameters and atomic positions are listed in Table 1.

Figure 2. Pictorial representation of the structures of LiVPO₄F with a close-up view of the split lithium position. The vanadium octahedra are shown in blue, phosphate tetrahedra are shown in yellow, and the Li atoms are shown in white.
occupied. In our refinement, the occupancy of the Li1 and Li2 sites was found to be 18 and 82% respectively as corroborated by NMR measurements (vide infra). The higher thermodynamic stability that results from the larger number of ligands in the Li2 site renders it the slightly preferred Li environment. This is not the case in LiFePO4(OH),17 where the relative occupancy of the Li1 and Li2 sites in that structure is reported to be 1:1.

Electrochemistry. Figure 3 depicts the full electrochemical curve of LiVPO4F, starting with discharge (red arrow). At a rate of C/10, 0.85 Li may be intercalated into the material at a potential of 1.8 V (vs. Li/Li+). The observed flat plateau of the electrochemical profile in this region implies the reduction of LiVPO4F to Li2VPO4F proceeds via a two-phase process. This is in contrast to the case of reduction of LiFePO4F24 and LiFePO4(OH)40 where approximately half of the electrochemical curve exhibited sloping behavior. Charging the cell back to LiVPO4F shows the same two-phase behavior. As the reoxidation of V2+ to V3+ nears completion, we observe a rise in the voltage up to 4.25 V which occurs between Li1.25VPO4F and LiVPO4F, unlike the more gradual voltage rise to 4.25 V between Li1.25VPO4F and Li0.87VPO4F observed in Barker’s study.29 The oxidation process continues (from V3+ to V4+) on two new plateaus (4.25 V vs Li/Li+ for Li1−xVPO4F, 0 < x < 0.35 and 4.3 V vs Li/Li+ for Li1−xVPO4F, 0.35 < x < 1.0) until complete oxidation is achieved. Reintercalation of the VPO4F occurs at 4.20 V vs Li/Li+ and once 1.0 Li has been intercalated, the potential drops sharply to 1.8 V where intercalation to Li3VPO4F continues. The hysteresis must arise from kinetic effects, where insertion of the second lithium is more difficult than its deinsertion owing to volume expansion.

We prepared various compositions of Li1−xVPO4F (0 ≤ x ≤ 1) by chemical oxidation (with NOBF4) and Li1+xVPO4F (0 ≤ x ≤ 1) by chemical reduction (with LiAlH4) of LiVPO4F to verify the two-phase nature of each vanadium redox step observed in the electrochemistry. Indeed, X-ray diffraction also shows this to be the case. Figure 4 depicts the evolution of Li1−xVPO4F from x = 0 to x = 1 formed upon chemical reduction of LiVPO4F with LiAlH4. Two-phase behavior was observed as the quantity of LiVPO4F decreases and the quantity of Li3VPO4F increases with increasing x.

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Table 2. Summary of Bond Distances for Li Environment in LiVPO4F and Li3VPO4F

<table>
<thead>
<tr>
<th>atom</th>
<th>ligand</th>
<th>LiVPO4F distance (Å)</th>
<th>Li3VPO4F distance (Å)</th>
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<td>Li1</td>
<td>F1</td>
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<td>2.062</td>
</tr>
<tr>
<td></td>
<td>O2e</td>
<td>2.071</td>
<td>2.071</td>
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<tr>
<td></td>
<td>O2b</td>
<td>2.135</td>
<td>2.135</td>
</tr>
<tr>
<td></td>
<td>O1b</td>
<td>2.183</td>
<td>2.183</td>
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<tr>
<td></td>
<td>O1a</td>
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</tr>
<tr>
<td></td>
<td>O1c</td>
<td>2.479</td>
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</tr>
<tr>
<td></td>
<td>F1c</td>
<td>1.824</td>
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<td>O2d</td>
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<td></td>
<td>O1b</td>
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<td></td>
<td>O1d</td>
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Figure 3. Electrochemical curve of LiVPO4F/C composite cycled vs Li/Li+ starting in discharge (as shown by the red arrow). The active material loading was 5 mg/cm2 and the cell was cycled at a rate of C/10.

Figure 4. X-ray powder diffraction patterns of Li1+xVPO4F, synthesized by the chemical reduction of LiVPO4F with LiAlH4. Two-phase behavior was observed as the quantity of LiVPO4F decreases and the quantity of Li3VPO4F increases with increasing x.
LiVPO$_4$F until almost complete intercalation of one equivalent of Li, where the reduced phase is the only vanadium fluorophosphate phase present. This phase has the stoichiometry Li$_2$VPO$_4$F, which was verified by elemental analysis that confirmed a Li:V:P ratio of very close to 2:1:1.

Li$_2$VPO$_4$F was prepared ex-situ by stirring LiVPO$_4$F with the chemical reducing agent LiAlH$_4$ in an inert atmosphere. Its X-ray diffraction and neutron diffraction patterns are shown in panels a and b in Figure 5, respectively, along with the combined Rietveld refinement. The fits and resultant lattice parameters/atomic positions are listed in Table 3. A comparison of the structures of LiVPO$_4$F and Li$_2$VPO$_4$F (Figure 6) makes it clear that although Li$_2$VPO$_4$F (C$_2$/c) crystallizes in a different space group than LiVPO$_4$F (P$_1$), Li$_2$VPO$_4$F is closely related to the parent phase. The exact same structural motif is present in Li$_2$VPO$_4$F, namely one-dimensional chains of VO$_4$F$_2$ octahedra which propagate (in the C$_2$/c cell) along the c-axis and that are connected by phosphate tetrahedra to form a fully corner-shared framework. Li ions partially occupy two general sites: Li1 ions reside in octahedral sites along the edges of the (110) tunnels (see Figure 6). These

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**Table 3. Lattice Constants and Atomic Parameters for Li$_2$VPO$_4$F Refined from Combined X-ray and Neutron Diffraction Powder Data**

<table>
<thead>
<tr>
<th>atom</th>
<th>Wychoff</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Occ.</th>
<th>U$_{iso}$</th>
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<tr>
<td>V(1)</td>
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<tr>
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<tr>
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<td>8f</td>
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<td>0.2177(1)</td>
<td>0.4394(2)</td>
<td>0.5</td>
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"X-ray diffraction agreement factors: \( R_{wp} = 11.08\% \), \( R_p = 8.40\% \), \( R_F^2 = 6.79\% \). Neutron diffraction agreement factors: \( R_{wp} = 4.28\% \), \( R_p = 7.93\% \), \( R_F^2 = 4.92\% \). Combined statistics: \( R_{wp} = 9.24\% \), \( R_p = 8.40\% \)."

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![Figure 5](image-url)  
(a) X-ray diffraction pattern and (b) neutron diffraction pattern and Rietveld refinement of Li$_2$VPO$_4$F synthesized by chemical reduction of LiVPO$_4$F with LiAlH$_4$. For each pattern, the experimental points are black, the fit is shown in red, the calculated reflections of Li$_2$VPO$_4$F are shown in blue, calculated reflections of Al are shown in green and the difference map is shown in gray. The lattice parameters and atomic positions are listed in Table 3.

![Figure 6](image-url)  
Pictorial representation of the structures of VPO$_4$F, LiVPO$_4$F, and Li$_2$VPO$_4$F depicting the chains of corner-shared vanadium octahedra and phosphate tetrahedra common to each structure. The vanadium octahedra are shown in blue, phosphate tetrahedra are shown in yellow, and the Li atoms are shown in white.
sites are nested between pairs of V octahedra and the Li1 site shares edges with both vanadium sites. This site is quite similar in location to the original split Li position in LiVPO₄F. Although the change in symmetry of the lattice in lithiation makes this difficult to determine from the fractional coordinates, visual comparison of the frameworks shows it clearly (Figure 6). The Li ions which reside in the Li2 sites are located at the center of the (110) tunnels and also sit between pairs of vanadium octahedra. The Li2 ions are face-shared with both vanadium octahedra of the pair, and correspond to the lithium that is inserted on reduction (ie, the new site). The structure of Li₂VPO₄F differs considerably from other Li₂MPO₄F compounds such as Li₂FePO₄F and Li₂NiPO₄F, both of which crystallize in orthorhombic space groups, Pbcn and Pnma, respectively.

The volume change for the transition from LiVPO₄F to Li₂VPO₄F (7.4%) is fairly typical for phosphates, and the lattice mismatch between the two phases is one of the main reasons the electrochemical potential is flat in this region.

Figure 7. X-ray powder diffraction patterns of Li₁₋ₓVPO₄F, synthesized by the chemical oxidation of LiVPO₄F with NOBF₄ under an argon atmosphere. On partial oxidation of LiVPO₄F to LiₓVPO₄F, a mixture of LiVPO₄F and a new phase is apparent in the diffraction pattern. Complete oxidation shows only the presence of this new phase, namely VPO₄F. An X-ray diffraction pattern and subsequent Rietveld refinement on the pure VPO₄F powder sample is shown in Figure 8 and the refinement results are summarized in Table 4. The structure (Figure 6) is also strongly related to LiVPO₄F, and is also isostructural with FeSO₄F which crystallizes in the same C2/c lattice. VPO₄F consists of corner-shared chains of VO₄F₂ octahedra interconnected by phosphate groups via corner-sharing where the tunnels are obviously free of lithium ions. The volume change for the transition from LiVPO₄F ↔ VPO₄F is 8.5%, roughly 2% greater than the volume difference for LiFePO₄ ↔ FePO₄, which is one of the reasons two-phase behavior is observed in this region of the electrochemical curve. This is substantially larger than in LiFePO₄ ↔ FePO₄ olivine, for example (6.7%), and yet the two phase electrochemical transition takes place with very low polarization suggestive of high Li-ion mobility and relatively rapid kinetics.

Solid-State NMR. The “split” crystallographic site for lithium in LiVPO₄F was observed as a broad line in the ⁷Li

Table 4. Lattice Constants and Atomic Parameters of VPO₄F Refined from Powder XRD Data

<table>
<thead>
<tr>
<th>atom</th>
<th>Wychoff</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Occ.</th>
<th>U_aniso</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>4d</td>
<td>0.25</td>
<td>−0.25</td>
<td>0</td>
<td>1.0</td>
<td>0.015(1)</td>
</tr>
<tr>
<td>P</td>
<td>4e</td>
<td>0.5</td>
<td>0.1245(3)</td>
<td>0.25</td>
<td>1.0</td>
<td>0.012(1)</td>
</tr>
<tr>
<td>F</td>
<td>4e</td>
<td>0</td>
<td>−0.1684(4)</td>
<td>−0.25</td>
<td>1.0</td>
<td>0.014(1)</td>
</tr>
<tr>
<td>O (1)</td>
<td>8f</td>
<td>0.3309(3)</td>
<td>0.0037(4)</td>
<td>0.0749(4)</td>
<td>1.0</td>
<td>0.012(1)</td>
</tr>
<tr>
<td>O (2)</td>
<td>8f</td>
<td>0.3951(3)</td>
<td>0.2479(4)</td>
<td>0.3456(2)</td>
<td>1.0</td>
<td>0.014(1)</td>
</tr>
</tbody>
</table>

Agreement factors: R_wp = 8.88%, R_p = 6.80%, R_F² = 4.76%.

Figure 8. X-ray diffraction pattern and Rietveld refinement of VPO₄F synthesized by chemical oxidation of LiVPO₄F. The experimental points are black, the fit is shown in red, the calculated reflections are shown in blue, and the difference map is shown in gray. The lattice parameters and atomic positions are listed in Table 4.
MAS NMR spectrum collected at 330 K (MAS = 40 kHz), with a paramagnetic shift centered at an average of 112 ppm (Figure 9). This broad line could be deconvoluted into two

resonances separated by 3 ppm with a ratio very similar to the Rietveld refinement of the split site using a “blind fit”, although other constrained fits also provided a reasonable fit. The chemical shift range for $^6$Li and $^7$Li is normally on the order of ±10 ppm. The high value for the observed shift is attributed to the geometry dependent hyperfine coupling of the Li-nuclei with the unpaired electron density sitting on the V$^{III}$ transition metal center. The relatively short spin−lattice relaxation time ($T_1$) of this resonance (6.5 ± 0.2 ms) also reflects the paramagnetic nature of the Li-resonance. The high frequency shift of 112 ppm is consistent with that reported for other lithium vanadium(III) phosphates.

Upon 50% lithiation of LiVPO$_4$F to form Li$_{1.5}$VPO$_4$F, two new resonances emerge. The first is centered at 46 ppm and the second at −47 ppm, measured under 40kHz MAS (at 330 K). These sites are herein referred to as sites A and B, respectively. The peak belonging to the parent LiVPO$_4$F phase remains but broadens slightly. A resonance centered at 0 ppm is also observed and is attributed to a diamagnetic Li impurity as it has a considerably longer $T_1$ relaxation time (>60 s). After lithiation to Li$_2$VPO$_4$F, a slight amount of the parent LiVPO$_4$F remains but resonances belonging to the A and B sites now dominate the spectrum. Integration of these sites over the entire sideband manifold yields a ratio of 1:1 for the A:B sites, which clearly correlate to the A and B resonances, we analyzed the geometry dependent hyperfine coupling between the unpaired electron spin density and the Li atoms. There are two mechanisms for electron spin density transfer which are found to be most effective when the Li−O−V (or Li−F−V) orbitals overlap at angles close to 90 or 180°. Because Li$_2$VPO$_4$F has orbital overlap angles closer to 90°, the 180° interactions are ignored. For the mechanisms involving 90° orbital overlap, unpaired electron spin density sitting in the t$_{2g}$ orbital of V in an
octahedral environment is able to delocalize onto the Li $s$ orbital leading to an increase in the paramagnetic shift. Comparison of the local Li environments of Li1 and Li2 in reference to the V centers clearly shows that Li1 has a larger number of Li−O−V angles closer to 90° than does Li2 (Figure 10). A greater amount of electron density spin density is therefore localized on the Li nucleus meaning a higher paramagnetic shift is observed. As well, Li1 resides in the analogous structural position to the split Li site in the parent material, LiVPO$_4$F, and is changed by roughly 70 ppm, as expected for the change in oxidation state at the vanadium center (vida supra). Therefore, resonance A is assigned to Li1. Conversely, Li2 has much poorer Li−O−V and Li−F−V overlap and gives rise to the lower frequency resonance labeled B. It is interesting to note that, while the two sites can be distinguished from each other and assigned based on these arguments, there is not an obvious justification for the significantly negative chemical shift observed for Li2. Related studies of the transition metal olivines have shown similarly negative chemical shifts for the Ni and Co phases, which were correlated with the number of unpaired electrons, and which orbital they occupy. Another factor may be that Li2 is face-shared between two vanadium sites (Figure 10), whereas Li1 is edge-shared between two vanadium sites, but as both sites have 4 Li−O−V interactions close to 90 degrees the impact of this is not clear.

Figure 11. $^6$Li($^{19}$F) REDOR buildup curves for resonances A (triangles) and B (circles). MAS = 35 kHz.

Figure 12. Deconvolution of sideband manifold for $^7$Li MAS spectrum of Li$_{1.5}$VPO$_4$F. Experimental spectrum shown on left. Sideband manifold belonging to each of the crystallographic Li sites (as modeled in DMfit) on right. From top to bottom on right-hand side — modeled manifold for parent LiVPO$_4$F, A site, and B site. Asterisks denote spinning sidebands.
When comparing the Li1 and Li2 sites, the larger anisotropy of $^6\text{Li}^{19}\text{F}$ REDOR reintroduces $^6\text{Li}$ to the single F environment using $^6\text{Li}$ REDOR measurements. $^6\text{Li}^{19}\text{F}$ REDOR reintroduces $^6\text{Li}^{19}\text{F}$ dipolar couplings that are averaged through MAS. The observed nucleus ($^6\text{Li}$) is measured using a spin–echo sequence with ($S$) and without ($S_0$) the application of a series of $\pi$ pulses on the dephased nucleus ($^{19}\text{F}$). The normalized difference in $^6\text{Li}$ signal intensity ($i_{\text{XX}}$) is then plotted as a function of the dipolar evolution time ($N\tau_R =$ number of rotor periods times the rotor period). Stronger REDOR buildup curves arise from stronger dipolar couplings ($D_{ij}$) which are inversely dependent on the internuclear distance between the two spins ($i$ and $j$) (eq 1),

$$D_{ij} = \frac{\hbar}{4\pi} \frac{1}{r_{ij}^3} \gamma_i \gamma_j$$

where $\gamma_i$ and $\gamma_j$ are the gyromagnetic ratios of the two spins. Figure 11 shows the $^6\text{Li}^{19}\text{F}$ REDOR curves observed for resonances A and B. The stronger REDOR buildup for the B resonance ($^6\text{Li}$) is consistent with this site having one short Li–F internuclear distance of 1.82 Å, and a second Li–F contact at 2.49 Å (see Table 7). The single Li1–F distance of 2.06 Å gives rise to the weaker REDOR buildup curve for resonance A ($^6\text{Li}$).

Separation of the sideband manifolds belonging to the different Li sites allows for a more detailed analysis of the Li– environments within this system. A $^6\text{Li}$ MAS spectrum showing the full sideband manifold of $^6\text{Li}^{19}\text{PO}_{4}$F is shown in Figure 12. Using the DMFit program, the sideband manifolds of each Li site were modeled. This allowed for determination of the chemical shift anisotropy ($\Delta_{\text{CSA}}$), axial symmetry ($\eta$), and span ($\Omega$) of each site (Table 8). The substantial increase in the span of the sideband manifolds of A and B ($\Omega = 2400$ and 2700 ppm, respectively) as compared to the parent LiVPO$_4$F ($\Omega = 1350$ ppm) is consistent with the increase in electron spin density sitting on the transition metal center. This increase leads to stronger electron-Li dipolar coupling interaction which largely governs the span of CSA in paramagnetic systems.

When comparing the Li1 and Li2 sites, the larger anisotropy of the Li2 site vs the Li1 site ($\Delta_{\text{CSA}} = 1205$ ppm vs 705 ppm) is expected as Li1 is a six coordinate site (LiO$_5$F), whereas the Li2 sits in a much more asymmetric environment composed of a five coordinate LiO$_3$F$_2$ polyhedra with an additional long Li–O bond (see Figure 10 and Table 7).

We explored exchange of the Li$^+$ between these two sites using 2D EXSY experiments. In these studies, each spin is frequency labeled during the evolution period, $t_1$. The exchange processes are allowed to take place during a mixing period of set length, $\tau_{\text{mix}}$, which is limited by the $T_2$ times of the nuclei. Cross peaks appear at off-diagonal sites corresponding to the sites involved in the exchange process. Samples partially enriched with $^4\text{Li}$ (which has an inherently longer $T_1$, see Tables 5 and 6) were used for the exchange experiments in order to probe mixing times long enough for exchange processes to occur. Spin–lattice relaxation times of both spins were determined at room temperature for $^4\text{Li}$ using a nonselective inversion recovery experiment, and found to be $22.7 \pm 0.5$ and $16.3 \pm 0.5$ ms for sites A and B, respectively (Table 6). Figure 13a shows $^4\text{Li}$ 2D EXSY spectra acquired at 303 K (Figure 13b). The mixing time in these experiments was extended to 15 ms, which provided sufficient time for the exchange process to take place. Evaluation of the activation energy of this exchange process could not be determined using the 2D version of the exchange spectroscopy, because the relatively slow correlation time does not fall within the limits of spin–lattice relaxation times of both spins. To overcome this limitation, the 1D version of the EXSY experiment, together with chemical exchange calculations which include both relaxation and ion dynamics contributions to the exchange matrix have been utilized. Using this methodology, the activation energy for ion exchange between sites A and B was determined to be 0.45 eV.
as will be reported in a subsequent publication. We note that similar low activation energies for Li ion hops of 0.4 eV in the fluorosulphate tavorite, LiFeSO₄F, have been calculated using atomistic modeling methods.49

CONCLUSIONS

We determined the structural relationship between the three members of the two-electron redox couple that spans the tavorite-type series of fluorophosphates Li₁₋ₓVPO₄F (x = 0,1) using a combination of X-ray and neutron diffraction, and report for the first time the isolation and structure of the two extreme end members, VPO₄F and Li₂VPO₄F. The three materials have closely related structures that result in two-phase transitions either on oxidation or reduction of 1e⁻ (and Li⁺) from LiVPO₄F. A slight change in symmetry accompanies this process, and the parent structure converts from P̅1 to C2/c in both cases owing to a small "twist" in the framework. Overall, the two electron redox couple spans a substantial volume change of 15.9%, which might be expected to give large electrochemical polarization because of the difficulty of phase boundary transport. However, the polarization at intermediate rates is very low, which is likely due to facile ion transport in the tavorite-type lattice. Solid-state⁶Li NMR studies of Li₂VPO₄F allow us to distinguish the two lithium sites that exchange at slightly above room temperature (330 K), with a low activation energy in accord with our previous modeling studies.

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REFERENCES


Figure 13. ⁶Li 2D EXSY spectrum over a variable temperature range shows evidence of thermally activated chemical exchange in the Li₂VPO₄F phase. (a) T = 303 K (MAS = 25 kHz) and (b) T = 330 K (MAS = 40 kHz). For both experiments, τmix = 15 ms.
(23) Tripathi, R.; Ramesh, T. N.; Ellis, B. L.; Nazar, L. F Angew. Chem. 2010, 49 (46), 8738.