Local atomic and electronic structure in the LiVPO₄(F,O) tavorite-type materials from solid-state NMR combined with DFT calculations

Tahya Bamine, Edouard Boivin, Christian Masquelier, Laurence Croguennec, Elodie Salager, Dany Carlier

To cite this version:
Tahya Bamine, Edouard Boivin, Christian Masquelier, Laurence Croguennec, Elodie Salager, et al.. Local atomic and electronic structure in the LiVPO₄(F,O) tavorite-type materials from solid-state NMR combined with DFT calculations. Magnetic Resonance in Chemistry, Wiley, 2020, Solid-State NMR, 58 (11), pp.1109-1117. 10.1002/mrc.5059 . hal-02945311

HAL Id: hal-02945311
https://hal.archives-ouvertes.fr/hal-02945311
Submitted on 7 Oct 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Local atomic and electronic structure in the LiVPO$_4$(F,O) Tavorite-type materials from Solid State NMR combined with DFT calculations

Tahya Bamine$^{a,b}$, Edouard Boivin$^{a,b,d}$, Christian Masquelier$^{b,c,d}$, Laurence Croguennec$^{a,b,c}$, Elodie Salager$^{b,e}$, and Dany Carlier$^{a,b,c,*}$

$^a$ CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB UMR 5026, F-33600 Pessac, France
$^b$ RS2E, Réseau Français sur le Stockage Electrochimique de l’Energie, FR CNRS 3459, F-80039 Amiens Cedex 1, France
$^c$ ALISTORE-ERI, FR3104, 80039 Amiens cedex, France
$^d$ Laboratoire de Réactivité et de Chimie des Solides, UMR CNRS 7314, Université de Picardie Jules Verne, F-80039 Amiens Cedex 1, France
$^e$ CNRS, CEMHTI UPR 3079, Université d’Orléans, Orléans, France

Abstract

$^7$Li, $^{31}$P and $^{19}$F solid state NMR spectroscopy was used to investigate the local arrangement of Oxygen and Fluorine in LiVPO$_4$F$_{1-y}$O$_y$ materials, interesting as positive electrode materials for Li-ion batteries. From the evolution of the 1D spectra versus y, 2D $^7$Li RFDR experiments combined and a tentative signal assignment based on DFT calculations, it appears that F and O are not randomly dispersed on the bridging X position between two X-VO$_4$X$_2$ octahedra (X = O or F), but tend to segregate at a local scale. Using DFT calculations, we analyzed the impact of the different local environments on the local electronic structure. Depending on the nature of the VO$_4$X$_2$ environments, vanadium ions are either in the +III or in the +IV oxidation state and can exhibit different distributions of their unpaired electron(s) on the d orbitals. Based on those different local electronic structures and on the computed Fermi contact shifts, we discuss the impact on the spin transfer mechanism on adjacent nuclei and propose tentative signal assignments. The O/F clustering tendency is discussed in relation with the formation of short V$^{IV}$=O vanadyl bonds with a very specific electronic structure and possible cooperative effect along the chain.

Keywords

NMR, $^7$Li, $^{31}$P, $^{19}$F, DFT, solid-state, paramagnetic, RFDR, Fermi contact shift, Li-ion battery, electrode material.
Introduction

Among the wide varieties of LiMXO$_4$Y tavorite-type compositions with M = V, Fe, Mn or Ti, and X = P or S [1], vanadium-based LiVPO$_4$F and LiVPO$_4$O (Figure 1) appear to be the most attractive ones as positive-electrode materials for lithium-ion batteries. Indeed, they exhibit high working voltages (i.e., 4.26 and 3.95 V vs Li$^+$/Li, respectively) and thus high theoretical energy densities with the exchange of one electron per vanadium [2]. Nevertheless, among the numerous studies reporting on apparently pure LiVPO$_4$F, discrepancies in the average crystal structure and electrochemical properties are observed [2-5]. Using 2D $^7$Li MAS NMR we evidenced the presence of defects in LiVPO$_4$F [6] whose amounts may vary according to the synthesis conditions. Following this work, we identified the nature of the defects using $^7$Li MAS NMR combined with DFT calculations [7]: F$^-$ ions are substituted locally by O$^{2-}$, thus forming V$^{4+}$ ions involved in a vanadyl bond with a very specific electronic structure that modifies the Fermi contact shifts observed for adjacent Li$^+$ ions. Recently, Kang and co-workers reported a LiVPO$_4$F$_{0.75}$O$_{0.25}$ phase, whose average structure is similar to that of LiVPO$_4$F (despite the large O$^{2-}$/F$^-$ substitution ratio) showing the possibility of extended substitution of fluorine by oxygen [5]. In a recent study, we synthesized several LiVPO$_4$F$_{1-y}$O$_y$ phases with control of the substitution ratio of oxygen for fluorine in order to study the influence of vanadyl-type defects on the average structure as well as on the local environment around vanadium [8]. The concentration of vanadyl-type defects was shown to have a strong influence on the electrochemical behavior in terms of redox processes involved, energy density, cyclability and rate capability [8, 9]. A better understanding of the local structural arrangement is of prime importance for further material optimization.

The LiVPO$_4$F and LiVPO$_4$O structures are not described in the same model, due to the presence of vanadyl bonds (i.e. short V$^{IV}$=O bonds) along the chains in LiVPO$_4$O that requires a unit cell twice larger than the one used for LiVPO$_4$F (Figure 1). As described in Ref. [8] all the intermediate compositions LiVPO$_4$F$_{1-y}$O$_y$ (y < 0.9) can be described considering a LiVPO$_4$F-type model. No superstructure peaks were observed suggesting thus a disordered sequence of V$^{III}$ and V$^{IV}$ (involved in vanadyl V$^{IV}$=O bond) along the chains. Nevertheless, the presence of microstrains and the deviation from the Vegard’s law for the cell parameters have suggested a possible clustering along the chains, without long-range ordering.
Figure 1: a) Structure of LiVPO₄F along the [001] (left) and the [100] (right) directions: VO₄F₂ octahedra in blue, PO₄ tetrahedra in red and lithium in purple. b) V-F and V-O distances along the chains of vanadium octahedra in LiVPO₄F and in LiVPO₄O.

As diffraction gives access only to an average long-range description, no in-depth information on the V–F bonds facing the vanadyl-type bonds (in F– (V⁴⁺O)) and on the V–O bonds facing the V–F ones (in O– (V³⁻ F)) can be obtained from this technique. From IR and XAS studies, we evidenced that vanadyl bonds were locally formed in agreement with the predictions of DFT calculations [7]. However, those characterization techniques did not allow to investigate the possibility of clustering which might be expected if one considers cooperative effect due to the alternation of short and long bonds along the chains. Using Magic Angle
Spinning (MAS) NMR techniques combined with DFT calculations we investigate, in this paper, the local atomic and electronic structure in those materials.

**Experimental part**

The mixed valence (i.e. $V^{III}/V^{IV}$) LiVPO$_4$F$_{1-x}$O$_x$ phases were obtained through one-step solid-state syntheses as described in Ref. [8] from V$_2$O$_5$, LiF and H$_3$PO$_4$ precursors. Three mixed valence compositions were prepared: LiVPO$_4$F$_{0.65}$O$_{0.35}$, LiVPO$_4$F$_{0.45}$O$_{0.55}$ and LiVPO$_4$F$_{0.25}$O$_{0.75}$. In order to confirm the fluorine content obtained which is, assuming the LiVPO$_4$F$_{1-x}$O$_x$ composition, related to the average oxidation state of vanadium, the magnetization of all materials were measured as a function of temperature in the paramagnetic domain. Quasi-stoichiometric LiVPO$_4$F was synthesized through a two-step carbothermal reduction as described previously [2] from V$_2$O$_5$ reduced by a small excess of C$_{5P}$ carbon in the presence of NH$_4$H$_2$PO$_4$ and addition of LiF. LiVPO$_4$O was synthesized by a solid-state reaction as described in Ref. [8] from V$_2$O$_5$, Li$_3$PO$_4$ and NH$_4$H$_2$PO$_4$ precursors.

$^7$Li MAS NMR spectra were recorded on a Bruker Avance III spectrometer with a 7 T magnet (116 MHz resonance frequency for $^7$Li). A standard Bruker 2.5 mm MAS probe at a 30 kHz spinning frequency was used. A Hahn echo sequence synchronized with one rotor period was used with a 90° pulse of 1.2 µs and a recycling delay of 2s. 1M LiCl aqueous solution was used as 0 ppm external reference. $^{31}$P ss-NMR spectra were acquired on a Bruker Avance III spectrometer with a 2.35 T magnetic field at a resonance frequency of 40.6 MHz by using a standard Bruker 2.5 mm magic-angle spinning (MAS) probe with a 30 kHz spinning frequency. A Hahn echo sequence synchronized with one rotor period was applied with a 90° pulse of 1.1 µs and a recycle delay of 1 s. H$_3$PO$_4$ 85% (Sigma-Aldrich) was used as external reference for 0 ppm chemical shift. $^{19}$F ss-NMR spectra were acquired on a Bruker Avance III spectrometer with a 2.35T magnetic field at a resonance frequency of 94.3 MHz by using a standard Bruker 2.5 mm magic-angle spinning (MAS) probe with a 30 kHz spinning frequency. A Hahn echo sequence synchronized with one rotor period was applied with a 90° pulse 1.0 µs and a recycle delay of 1 s. A CFCl$_3$ (1M) solution was used as external reference for 0 ppm chemical shift.
Extra $^7$Li NMR experiments were performed at the French national platform IR-RMN-THC FR3050 CNRS (Orléans, France), on a Bruker Avance III spectrometer with a 17.6 T magnet (291.5 MHz resonance frequency for $^7$Li) and a wide-bore Bruker 1.3 mm MAS probe with a spinning rate of 64 kHz. The chemical shifts were referenced to an aqueous 1 mol.L$^{-1}$ LiCl solution. Two-dimensional $^7$Li-$^7$Li EXSY and fp-RFDR correlation spectra were recorded with a repetition time of 50 ms (sufficient for relaxation of the signals of interest—peaks 2 and 4 are saturated) and a RF power of 98.3 W (208 kHz). The other conditions were similar to those used for the study published earlier [6]. All spectra were processed with an exponential filter (line broadening 200 Hz) using the Topspin software. The spectra were then imported in Matlab (The MathWorks Inc) using a home-made script for plotting the figures with controlled contours and color-code.

Fermi contact shift that are mainly responsible for the shifts observed for paramagnetic materials can be expressed as:

$$
\delta_{iso}^i(T) = \frac{1}{3SN_A} \rho^i(0) \chi_M(T) \quad \text{eq. (1)}
$$

where S is the spin quantum number of the paramagnetic ion, $\rho^i(0)$ is the electronic spin density on the $i$ nucleus and $\chi_M$ the experimental molar magnetic susceptibility (at the temperature of the NMR measurement, here 320 K while spinning at 30 kHz). First principles calculations were used to compute the electronic spin density at the probe nucleus within the Density Functional Theory (DFT) framework. The standard PAW-PBE potentials as implemented in the Vienna ab initio Simulation Package (VASP) code [10] were used for O, P, and V whereas the “sv” PAW-PBE potential that treats the 1s shell as valence states was chosen for Li [10]. All calculations were spin polarized type with a ferromagnetic type ordering which is considered appropriate for the Fermi contact shift, as described in reference [11]. A plane wave energy cut-off of 600 eV and a k-mesh dense enough to reach convergence were used. Generalized Gradient Approximation + U (U = 4.0 eV) approach, where Hubbard type interaction is added to localize 3d electrons, was used. In our previous study on LiVPO$_4$F, several values were used for the U term: as 4 eV led to good agreement between calculated and experimental shifts it has been chosen in the present study (ref [7]). Further details concerning the Fermi contact shifts calculations using this method can be found in ref [7, 12-13]. To model the substituted phases, several O/F arrangements based on a 128-atom supercell (2a x 2b x 2c) were used for LiVPO$_4$F$_{0.25}$O$_{0.75}$, LiVPO$_4$F$_{0.5}$O$_{0.5}$ or LiVPO$_4$F$_{0.75}$O$_{0.25}$ compositions. The structure of the supercell was relaxed using GGA+U, and the different local electronic
structures were analyzed. 3D calculated spin density maps were plotted using the VESTA software (Visualization for Electronic and Structural Analysis) [14].

**Results and discussion**

**Figure 2a** shows the $^7$Li MAS NMR spectra recorded for five LiVPO$_4$F$_{1-y}$O$_y$ samples with $y = 0, 0.35, 0.55, 0.75$ and $1$. A rather sharp signal (#4) centered at 115 ppm is observed for LiVPO$_4$F, in agreement with previous publications [15-16] and is attributed to the unique Lithium site identified by diffraction [2].
Figure 2: a) $^7$Li MAS NMR spectra of the series of five LiVPO$_4$F$_{1-y}$O$_y$ compositions. The global intensity of the signals obtained for the two end members phases, LiVPO$_4$F and LiVPO$_4$O, has been divided by 10. In inset, a schematic illustration of the lithium environment vs. V$_a$ and V$_b$ octahedra (V octahedra sharing an edge with Li polyhedra are only depicted); V$_a$ and V$_b$ do not belong to the same chain; positions in red = O, positions in red/black = O or F (bridging position). The z-axis indicates the direction of the vanadyl bonds, when present. The different signals observed are labelled 1 to 6 to facilitate the discussion in the text. b) Tentative decomposition of the 1D $^7$Li MAS NMR spectra of LiVPO$_4$F$_{0.45}$O$_{0.55}$ phase using 6 contributions with a pseudo voigt lineshape in addition to the LiF contribution around 0 ppm. Note that especially in the grey regions with strong overlap, more contributions could have been considered.
The spectrum for the LiVPO₄F sample also exhibits a weak signal at -1 ppm assigned to the presence of residual LiF and other additional signals at 4 ppm (peak #1), 84 ppm (peak #3) and 186 ppm (peak #6) which have been assigned, based on DFT calculations, to vanadyl-type defects [7]. The examination of the NMR spectrum of LiVPO₄O shows a single sharp peak at 79 ppm (peak #2). In LiVPO₄O, as there are two crystallographic sites for Lithium [17], two ⁷Li MAS NMR signals would have been expected. In our conditions, we, however observe only one signal, probably due to the high structural similarity between both sites and/or to fast lithium mobility between them. Note that a Fermi contact shift calculation indeed predicts two very similar shifts for the two Li sites (for more details see Figure S1 in supplementary information).

For all the Tavorite-type phases discussed here, the lithium-coordination polyhedra share two edges and two separate corners with four VO₄X₂ octahedra, with X being an O or F anion. The e₈ orbitals of vanadium being empty (i.e. t₂₈² for V⁴⁺ and t₂₈¹ for V⁴⁺), the main spin transfer from vanadium to lithium leading to the Fermi contact shift occurs from the t₂₈ orbitals pointing towards common edges between the LiO₄X and VO₄X₂ polyhedra (i.e. an O-O edge and an O-X edge, X = bridging anion, O or F). This simplified lithium environment is depicted in the inset of Figure 2a. The two vanadium sites sharing an edge with the Li polyhedra are labeled Vₐ and Vₐ depending on the nature of the common edge (O-O for Vₐ and O-X (X = O or F) for Vₐ) and don’t necessarily correspond to the V(1) and V(2) crystallographic sites. Note that Vₐ and Vₐ do not belong to the same chain.

For LiV⁴⁺PO₄F, the two d electrons are homogeneously distributed in the three t₂₈ orbitals. The spin transfer is strong due to the local electronic structure and to the contribution of both vanadium octahedra sharing an edge with the lithium polyhedra [7]. In the case of LiV⁴⁺PO₄O, the presence of vanadyl bonds along the z direction, indicated in the inset of Figure 2, induces a lift of degeneracy of the t₂₈ orbitals: the d₁ and one of the dₓz/dᵧz orbitals are involved in the strong covalent V⁴⁺=O vanadyl bond, while the dₓy orbital is stabilized and is the one carrying the unpaired electron [7;12] (as described in Figure S2 in supplementary information). Therefore, in LiVPO₄O a spin transfer mechanism from V⁴⁺ to Li can occur only from the dₓy orbital through the O-O edge shared with Vₐ (see Figure 2a). The orientation of the Vₐ site and...
its electronic configuration do not allow the possibility of such spin transfer as discussed in Ref [7]. 

The mixed valence V\textsuperscript{III}/V\textsuperscript{IV} LiVPO\textsubscript{4}F\textsubscript{1-y}O\textsubscript{y} samples exhibit \textsuperscript{7}Li NMR spectra with very broad contributions located in the neighboring of the signals observed for LiVPO\textsubscript{4}F (isotropic peak and defects contributions) and LiVPO\textsubscript{4}O. Actually at least six components can be distinguished, in addition to a quasi-non-shifted peak at -1 ppm (denoted as LiF in Figure 2), as can be seen on the tentative decomposition of the spectra (Figure 2b and Figure S3 for the other spectra). The presence of residual LiF was also confirmed \textsuperscript{19}F NMR spectra, as discussed below. Note that the \textsuperscript{7}Li spectrum obtained for the LiVPO\textsubscript{4}F\textsubscript{0.25}O\textsubscript{0.75} sample is really similar to the spectrum recently reported by Parapari et al. for a sample prepared from LiVPO\textsubscript{4}O and LiF heated at 800°C for 1h [18]. By analogy with the end-member phases, two contributions can be assigned: the signal around 120 ppm (#4) assigned to Li in interaction with two F-V\textsuperscript{III}-O\textsubscript{4}-F octahedra (LiVPO\textsubscript{4}F-like environment) and the signal around 75 ppm (#2) assigned to Li in interaction with two O-V\textsuperscript{IV}-O\textsubscript{4} octahedra (LiV\textsuperscript{IV}PO\textsubscript{4}O-type contribution).

In order to assign the remaining signals observed around 10 ppm (#1), 85 ppm (#3), 150 ppm (#5) and 195 ppm (#6), DFT calculations were performed with structural models taking into account several F/O and V\textsuperscript{III}/V\textsuperscript{IV} spatial distributions for the LiVPO\textsubscript{4}F\textsubscript{0.75}O\textsubscript{0.25}, LiVPO\textsubscript{4}F\textsubscript{0.5}O\textsubscript{0.5} and LiVPO\textsubscript{4}F\textsubscript{0.25}O\textsubscript{0.75} compositions. Indeed, using large supercells, we were able to distribute F and O differently on the X positions of VO\textsubscript{4}X\textsubscript{2} octahedra so that very homogeneous cells as well as “clustered” ones were considered. From the corresponding Fermi contact shift calculations for the \textsuperscript{7}Li atoms, a complete assignment of the signals is not trivial since several Li environments with V\textsuperscript{III}/V\textsuperscript{IV} either in V\textsubscript{a} or V\textsubscript{b} sites lead to rather similar shifts. To that end, in Figure S4, we summarize the different oxidation states and electronic structures that were found theoretically depending on the V local environments vs. O/F. We also indicate the expected spin transfer (ST) on an adjacent Li, stronger or weaker compared to the one expected from V\textsuperscript{III} in LiVPO\textsubscript{4}F. As intuitively expected, we do not observe the formation of a V\textsuperscript{3+} ion in a O-VO\textsubscript{4}-O (VO\textsubscript{6}) octahedron nor the formation of a V\textsuperscript{4+} ion in a F-VO\textsubscript{4}-F one (VO\textsubscript{4}F\textsubscript{2}). For the VO\textsubscript{6} environment, whatever the nature of the adjacent VO\textsubscript{4}X\textsubscript{2} octahedra, the formation of a short V=O bond is observed after structural optimization along the local z direction and the V\textsuperscript{4+} ions exhibit the same electronic structure as in LiVPO\textsubscript{4}O: d\textsubscript{xy,1}. If V\textsuperscript{IV} is in a V\textsubscript{b} position, no spin transfer toward the adjacent Li is expected whereas if it is in V\textsubscript{a} a strong spin transfer is expected (Figure 3). For the VO\textsubscript{4}F\textsubscript{2} environment, depending on the nature
of the adjacent VO₄X₂ octahedra, the electronic structure of the V³⁺ differs: either the three t₂g orbitals are partially occupied as in LiVPO₄F, or only the dₓz and dᵧz orbitals are carrying the spins. In both cases, a spin transfer similar to the one observed in LiVPO₄F is expected toward the Li site sharing an edge [7]. For the O-VO₄-F environment, the vanadium ions can be +III or +IV depending on the nature of the adjacent VO₄X₂ octahedra, with various predicted spin transfer magnitudes depending on the nature of the V sites, Vₐ and Vₐ, and on their electronic spin structures (Figure S4).

As Li polyhedra is sharing an edge with one VₐO₄X₂ polyhedron and another with one VₐO₄X₂ site as represented in Figure 2a, two types of spin transfer may occur. Based on the Fermi contact shifts calculations we propose in Table I the tentative assignments of the ⁷Li signals for the various LiVPO₄F₁₋₂O₃ phases.

**Figure 3:** Calculated 3D spin density map around Li in LiVPO₄O showing the local electronic structure of the two V⁴⁺ ions in VO₆ octahedra sharing an edge with the LiO₅ polyhedra. A V⁴⁺ ion located in a Vₐ site can transfer spin density on Li as the dₓz orbital carrying the unpaired electron is properly oriented, but no spin transfer is expected from a V⁴⁺ ion in a Vₐ site.
Table I: Tentative assignment of the $^7$Li MAS NMR signals to the different Li environments versus $V^{III}$ and $V^{IV}$ in Va and Vb sites, based on Fermi contact shifts calculated for the models taking into account the different distribution of O and F in the X (bridging) position. For more clarity the different $VO_xX_2$ octahedra are denoted by $X-V^{III}-X$ or $X-V^{IV}-X$ with $X = O$ or F.

<table>
<thead>
<tr>
<th>Signal label</th>
<th>Proposed corresponding Li Environment</th>
<th>Calculated Fermi contact shifts range (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Va</td>
<td>Vb</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>F-V$^{IV}$-O</td>
<td>O-V$^{IV}$-O</td>
</tr>
<tr>
<td>2</td>
<td>O-V$^{IV}$-O</td>
<td>O-V$^{IV}$-O</td>
</tr>
<tr>
<td>3</td>
<td>O-V$^{IV}$-O or F-V$^{IV}$-O</td>
<td>F-V$^{IV}$-O</td>
</tr>
<tr>
<td>4</td>
<td>F-V$^{III}$-F</td>
<td>F-V$^{III}$-F</td>
</tr>
<tr>
<td>5</td>
<td>F-V$^{III}$-F or F-V$^{III}$-O</td>
<td>F-V$^{III}$-F or F-V$^{III}$-O</td>
</tr>
<tr>
<td>6</td>
<td>O-V$^{IV}$-O</td>
<td>F-V$^{III}$-F</td>
</tr>
</tbody>
</table>

As the $^7$Li signals from environments near $V^{4+}$ or $V^{3+}$ are overlapping, it was not possible to discuss further the local arrangement in the LiVPO$_x$F$_{1-y}$O$_y$ series, based on the evolution of the signals intensity versus y, that would have T2 measurements for the different Li sites in our Hahn echo conditions. We therefore used 2D $^7$Li NMR experiments to investigate the possibility of a partial clustering of $V^{4+}$-rich and $V^{3+}$-rich domains in similar conditions to those reported by Messinger et al. in ref [6] for the detection of vanadyl type defects in LiVPO$_4$F. Finite pulse radiofrequency driven recoupling (fp-RFDR) [19,20] is implemented during the mixing time of a two-dimensional $^7$Li-$^7$Li experiment to reintroduce the homonuclear dipolar couplings otherwise averaged out by MAS. Such dipolar couplings can usually be reintroduced for distances less than 1 nm, and are therefore a marker of spatial proximity at the nanometer scale.
Figure 4: $^7$Li-$^7$Li fp-RFDR correlation spectra with a mixing time of 5 ms for a) LiVPO$_4$F$_{0.25}$O$_{0.75}$, b) LiVPO$_4$F$_{0.45}$O$_{0.55}$ and c) LiVPO$_4$F$_{0.65}$O$_{0.35}$. The $^7$Li spectrum of the corresponding phase after the RFDR mixing (no $t_1$ evolution) is displayed on top of each 2D correlation plot.
Figure 4 shows the $^7$Li-$^7$Li fp-RFDR correlation spectra for the three intermediate compositions, namely LiVPO$_4$F$_{0.25}$O$_{0.75}$, LiVPO$_4$F$_{0.45}$O$_{0.55}$ and LiVPO$_4$F$_{0.65}$O$_{0.35}$. Cross-peaks are observed between the components previously labelled 1, 3, 4 and 6 for all compositions, although much fainter in LiVPO$_4$F$_{0.25}$O$_{0.75}$. These cross-peaks are absent in EXSY experiments run in the same conditions (see Figures S5, S6, S7) and are therefore assigned to proximity in space rather than to chemical exchange or mobility of the Li ions. The Li environments leading to signals #1, #3 and #6, arise from the defects in close proximity with the Li environment LiVPO$_4$F-type (signal #4) as demonstrated in our previous work [6]. Interestingly, this clustering of the defects with the LiVPO$_4$F-type environment is still observed (although less easily) in the F-poor composition. We tested a range of mixing times (from 1 ms to 10 ms, see Figures S6, S7, S8) to probe shorter and longer distances and did not detect any cross-peaks for Li environments leading to signal #5 and to signal #2 (LiVPO$_4$O-type). We therefore conclude that they are isolated for the three compositions probed in this work.

Figure 5: $^{31}$P MAS NMR spectra of the series of five LiVPO$_4$F$_{1-y}$O$_y$ compositions. The global intensity of the signal obtained for the end members phases, LiVPO$_4$F and LiVPO$_4$O, have been divided by 10. In inset, a schematic illustration of the Phosphorous environment vs. V octahedra; positions in red = O, positions in red/black = O or F (bridging position). The different signals observed are labelled 1 to 6 to facilitate the discussion in the text. $\$ = signal assigned to a diamagnetic impurity.
Figure 5 shows the $^{31}$P MAS NMR spectra recorded for the series of LiVPO$_4$F$_{1-y}$O$_y$ compositions. In Tavorite-type structures, the PO$_4$ tetrahedra are connected to four different transition metal octahedra via the oxygen belonging to the VO$_4$ plane of these octahedra. As also discussed by Castets et al. for the LiMP0$_4$OH tavorite series, in our case (i.e. $t_2g^2e_g^0$ or $t_2g^1e_g^0$) the spin transfer to the 2s (or the sp$^3$ hybrid) orbital of Phosphorus occurs from the $t_2g$ orbitals (via $\pi$ overlap with a p orbital of oxygen) [21]. In LiVPO$_4$F, two $^{31}$P MAS NMR signals are observed: one located at 3871 ppm (#5 in Figure 5) and a second one, weaker and unresolved due to the overlap with a spinning side band, located at larger shifts (#6). That latter isn’t expected regarding the unique phosphorous site in the structure and could correspond to the defects’ contribution (better seen by $^7$Li NMR). The two signals at 1613 ppm and 1441 ppm (#1 and #2) observed for LiVPO$_4$O confirm the existence of two crystallographic sites in this phase. Based on the DFT Fermi contact shift calculations we can assign the most shifted signal to P(1) and the less shifted one to P(2) (Figure S1) (P(1) and P(2) designation being similar to ref [2]). The $^{31}$P NMR spectra of the other LiVPO$_4$(O,F) phases with V$^{3+}$ and V$^{4+}$ are overall very broad due to the large amount of possible P environments versus V$^{3+}$/V$^{4+}$ with different electronic structures as summarized in Figure S4. Nevertheless, we can assign signals #1/#2 and #5 to P environments close to those observed in LiVPO$_4$O and LiVPO$_4$F respectively. The signals #3, #4 and #6 can be assigned then to P surrounded by both V$^{3+}$ and V$^{4+}$ ions in different VO$_4$X$_2$ sites, therefore with various electronic structures as depicted in Figure S4. A further analysis of the $^{31}$P spectra is delicate considering the overall broadening of the signals that strongly overlap.

Contrarily to $^7$Li and $^{31}$P NMR, $^{19}$F nuclei are surrounded by two vanadium ions of the same chain (Figure 1), that are obviously in F-VO$_4$-X octahedra. Therefore, $^{19}$F NMR may be the most relevant probe to investigate the possibility of V$^{3+}$ or V$^{4+}$ clusters formation within a chain that would result from a cooperative effect of the vanadyl bond formation with alternation of long and short V-O distances along the chain. Consequently, the four $^{19}$F MAS NMR spectra of the LiVPO$_4$F$_{1-y}$O$_y$ series are compared in Figure 6.
Figure 6: $^{19}\text{F}}$ MAS NMR spectra of the series of four LiVPO$_4$F$_{1-y}$O$_y$ compositions with the isotropic peak highlighted by # and the spinning side bands by *. The additional signals assigned to LiF and to the probe contribution are marked as \(\nabla\) and \(|\) respectively. In inset, a schematic illustration of the Fluorine environment vs. V octahedra; positions in red = O, positions in red/black = O or F (bridging position).

These spectra exhibit a strong parasitic contribution from the probe (which contains Teflon) around -150 ppm and from an LiF impurity at -208 ppm. The isotropic peak is located at -1500 ppm for LiVPO$_4$F and all other contributions regularly separated are assigned to spinning side bands [7]. Surprisingly, no other peak which could be assigned to a Fluorine nucleus in interaction with V$^{4+}$ cations can be detected for mixed valence samples. We expected a weak spin transfer from V$^{4+}$ to F since the electronic spin located in the $d_{xy}$ orbital is not pointing toward F. For the LiVPO$_4$F$_{1-y}$O$_y$ series only a slight shift (around 10 ppm) and a slight broadening of the $^{19}\text{F}}$ signal is detected. The global intensity of this signal decreases gradually with the substitution of F by O. Nevertheless, due to the presence of the probe signal that may overlap with spinning side bands, the precise integration of the NMR signal cannot be performed. This study, however, shows that a negligible number of F-V$^{4+}$-O environments exist along the chain that corroborates the clustering tendency of O in the vanadium chain, with the formation of O-rich (therefore V$^{4+}$-rich) domains and F-rich (therefore V$^{3+}$) ones.
Conclusion

Multinuclear solid-state NMR was used to investigate the local arrangement of oxygen and fluorine in the bridging X position of the vanadium VO$_4$X$_2$ octahedra along the chains in the LiVPO$_4$F$_{1-y}$O$_y$ series. The evolution of the $^7$Li, $^{31}$P and $^{19}$F 1D spectra and the 2D $^7$Li fp-RFDR experiments performed along the series indicates that F and O are not randomly dispersed on the X position in the LiVPO$_4$F$_{1-y}$O$_y$ materials, but tend to segregate at a local scale. This can be induced by the formation of short V$^{IV}$=O bonds that would be more stable if a cooperative effect was possible with alternating long V$^{IV}$-O and short V$^{IV}$=O bonds. This would result in O-V$^{IV}$O$_4$-O-rich domains and F-V$^{III}$O$_4$-F-rich ones along the chains. Using DFT calculations on model compounds, we analyzed the impact of the different local environments on the local electronic structure. Depending on the nature of the VO$_4$X$_2$ environments, vanadium ions are in the +III or +IV oxidation states and can exhibit different repartitions of their unpaired electron(s) on the d orbitals. Based on that range of local electronic structures and computed Fermi contact shifts, we could then discuss the impact of the spin transfer mechanism on adjacent nuclei and propose tentative signal assignments.

The O/F clustering tendency observed here is in good agreement with the observation of microstrains and deviations from the Vegard’s law for the solid solution LiVPO$_4$F$_{1-y}$O$_y$ reported in our previous study. The present study is a first step to better understand the complex redox behavior observed for the LiVPO$_4$F$_{1-y}$O$_y$ materials in Li cells with the activation of the V$^{IV}$=O/V$^V$=O redox couple during the first step of the charge, and then upon further Li$^+$ extraction the activation of the V$^{3+}$/V$^{4+}$ redox couple in fluorine-rich environments [9], that may result from the complex electronic structure and clustering tendency observed.

Acknowledgments

The authors acknowledge FEDER, the Région Hauts-de-France and the RS2E Network for the funding of EB’s PhD thesis, as well as the financial support of Région Nouvelle Aquitaine and of the French National Research Agency (STORE-EX Labex Project ANR-10-LABX-76-01 and HIPOLITE Progelec project ANR-12-PRGE-0005-02). Financial support from the IR-RMN-THC Fr3050 CNRS for conducting the research is also gratefully acknowledged, as well as the Mésocentre de Calcul Intensif Aquitain (MCIA) and the modelling centre (ISM) for computing facilities. P. Aurel (ISM) is acknowledged for technical assistance.
References:


