

A computational investigation on fluorinated-polyanionic compounds as positive electrode for lithium batteries

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Abstract

First principles calculations have been used to investigate the effect of fluorine substitution on the electrochemical properties of $\text{Li}_2\text{VOSiO}_4$ and LiFePO_4 . Several models of hypothetical LiVSiO_4F and $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$ within the structure of the corresponding parent compounds have been analyzed. The computational results indicate that the lithium insertion voltage is largely controlled by the crystallographic site that fluorine ions occupy in the structure. In some models of LiVSiO_4F and $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$ lithium deinsertion causes a too large M–F distance (indicative of M–F bond breaking), being the predicted lithium insertion voltage about 0.3 V lower than that of the parent compound. In the energetically most stable model of hypothetical- LiVSiO_4F the V–F bond is retained, and a voltage increasing of 0.5 V is predicted with respect to that of the parent compound. For hypothetical $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$ models consisting on FeO_6 and FeO_4F_2 octahedra the lithium deinsertion produces solely the oxidation of Fe^{2+} surrounded by oxygen ions, which is accompanied by a voltage decreasing. These findings are supported by the computational results on the known intercalation compound LiVPO_4F .

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1. Introduction

The chemistry of fluorine containing compounds is getting increasing relevance in the field of lithium battery materials [1–5], touching also on polyoxianionic positive electrode materials. Barker et al. reported the electrochemical properties of the fluorophosphates LiMPO_4F , where M refers to a transition metal ion [6]. Interestingly, the $\text{V}^{3+}/\text{V}^{4+}$ redox couple in LiVPO_4F operates at 4.01 V which is 0.3 V above that of the same redox couple in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ [7]. In this connection, Yin et al. [8] reported a similar operating voltage of the $\text{V}^{3+}/\text{V}^{4+}$ couple (4.15 V) in $\text{Li}_5\text{V}(\text{PO}_4)_2\text{F}_2$ whereas the $\text{V}^{4+}/\text{V}^{5+}$ couple operates at 4.65 V. Sorensen et al. [9] reported the new material $\text{Ag}_4\text{V}_2\text{O}_6\text{F}_2$ that intercalates Li at 3.5 V as compared to 3.25 V for its counterpart AgV_3O_8 . These voltage differences can be ascribed to the presence of fluorine in the structure, suggesting the idea that fluorophosphates should have a voltage higher than related phosphates. This is, in principle, what one could expect

when an oxygen ion is replaced by a fluorine one: the more ionic M–F bond stabilizes the energy of the antibonding M-d orbitals of the transition metal ion, consequently increasing the voltage at what lithium insertion takes place.

The effect that fluorine substitution might have on the electrochemical properties of polyanionic compounds has not been fully investigated to date. With this aim, we have performed a computational investigation on fluorine substitution in two polyoxianionic compounds: the silicate Li_2VSiO_5 , which has been recently reported to be electrochemically active at 3.6 V versus lithium metal [10], and olivine- LiFePO_4 , well-known to reversibly intercalate lithium ions at 3.5 V [11]. In addition, the above-mentioned LiVPO_4F material was also studied. In computational studies the structure and composition enter as independent variables; in contrast to experiments where changing the composition often also leads to structural changes. Therefore, a computational investigation will allow working at a fix composition of the *hypothetical* compounds LiVSiO_4F and olivine- $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$ while having a full control over the structure, making possible to check several models with fluorine ions located in different sites over the structure. Along these lines we will show that the effect of the fluorine ions on the lithium

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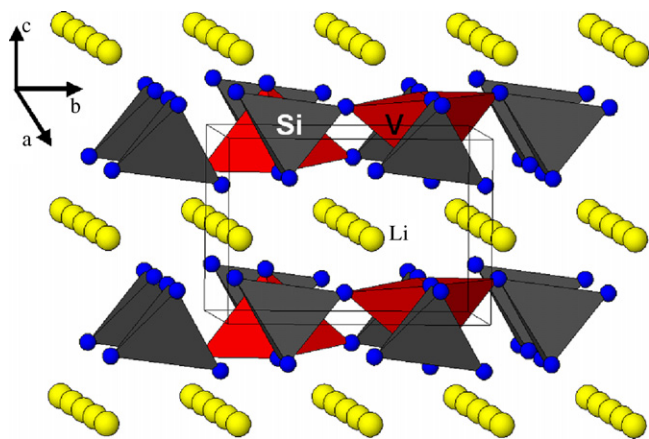


Fig. 1. Schematic representation of the Li_2VSiO_5 structure.

insertion voltage, and in a greater extent over the general electrochemical behavior, depends on the crystallographic site they occupy in the polyanionic structure.

2. Structures

2.1. Li_2VSiO_5 and LiVSiO_4F

The structure of Li_2VSiO_5 [12] can be viewed as stacking along the c direction of $[\text{VOSiO}_4]_\infty$ layers linked together by lithium ions located in distorted LiO_6 octahedra. The Si^{4+} ions are located in regular tetrahedral (Td) sites, whereas V^{4+} ions occupy square pyramidal (SP) sites, presenting four equivalent V–O distances in the basal plane and a shorter one corresponding to the apical oxygen which is the typical vanadyl bond. The $[\text{VOSiO}_4]_\infty$ sheets are built up from SiO_4 –Td and VO_5 –SP sharing corners to form infinite chains running along the $[1\ 0\ 0]$ and $[0\ 1\ 0]$ directions (Fig. 1).

Aiming to investigate the influence of fluorine substitution over the $\text{V}^{4+}/\text{V}^{5+}$ redox couple, the composition of the fluorinated compound was set up to be LiVSiO_4F . The hypothetical structure of LiVSiO_4F has been derived from that of the parent silicate Li_2VSiO_5 removing along $[0\ 1\ 0]$ one every two rows of lithium ions running along the $[1\ 0\ 0]$ direction (for details about this ordered structure see [13]). It is evident that: (a) the substituted F ion could adopt different positions in the coordination sphere of a vanadium atom, mainly in the base of the square pyramid or its apical vertex; and (b) for a given position (axial/apical) several F orderings/configurations are possible. Whenever F ions sit in the base of the SP occupied by vanadium, the environment around Si atoms will also be substantially modified. The LiVSiO_4F ordered structures chosen for the present study will be denoted as structures I, II, III and IV. In structure I (Fig. 2) the F ions replace the vanadyl oxygen. Thus the structure is built up from VO_4F and SiO_4 polyhedra. In the remainder structures (II, III and IV) F ions are placed in the base of the V^{4+} square pyramid, positions that are shared with the SiO_4 tetrahedra. In structures II and III the F ions substitute one oxygen atom of every VO_5 –SP basal plane along $[0\ 1\ 0]$ and $[1\ 0\ 0]$ directions, respectively; in both cases VO_3FO and SiO_3F polyhedra exist

(Fig. 3). Structure IV corresponds to a configuration with two distinct types of vanadium atoms: V(1) located at $\text{VO}_2\text{F}_2\text{O}$ –SP (double substituted VO_5 square-pyramids) and V(2) in a non-substituted VO_5 –SP; accordingly SiO_2F_2 and SiO_4 polyhedra appear (Fig. 4). From all these structures lithium ions can be fully removed leading to the corresponding VSiO_4F phases, whose optimized structures are shown in Figs. 2–4.

2.2. Olivine- LiFePO_4 and $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$

The olivine structure is usually described in terms of a hexagonal close-packing of oxygen with Li and Fe ions located in half of the octahedral sites and P in one eighth of the tetrahedral positions. The FeO_6 octahedra share four corners in the cb -plane being cross-linked along the a -axis by the PO_4 groups, whereas Li ions are located in rows, running along a , of edge-shared LiO_6 octahedra which appear in between two consecutive $[\text{FeO}_6]_\infty$ layers lying on the cb -plane, above described. Fig. 5 shows a schematic representation of the two hypothetical structures chosen for olivine-like $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$ among the numerous possible configurations. In the first model the fluorine ions were placed in anionic sites in such a way to solely obtain FeO_5F octahedra (structure O-I); besides PO_3F and PO_4 groups exist (Fig. 5a). In the second model (O-II) both FeO_4F_2 and FeO_6 octahedra are present, the two F ions being in “cis” configuration; as in the previous structure PO_3F and PO_4 tetrahedra appear (Fig. 5b).

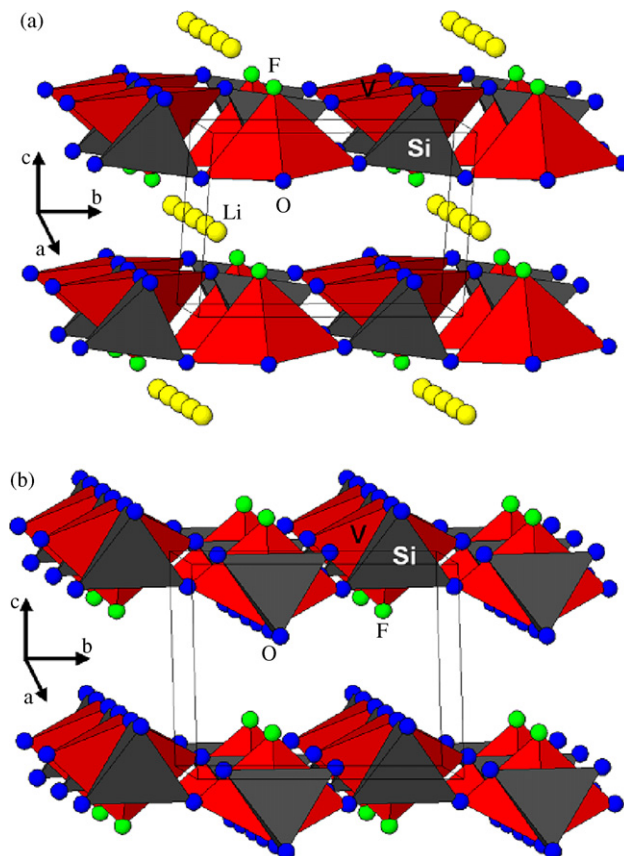


Fig. 2. Schematic representation of the optimized structure of LiVSiO_4F (a) model I and its delithiated derivative (b).

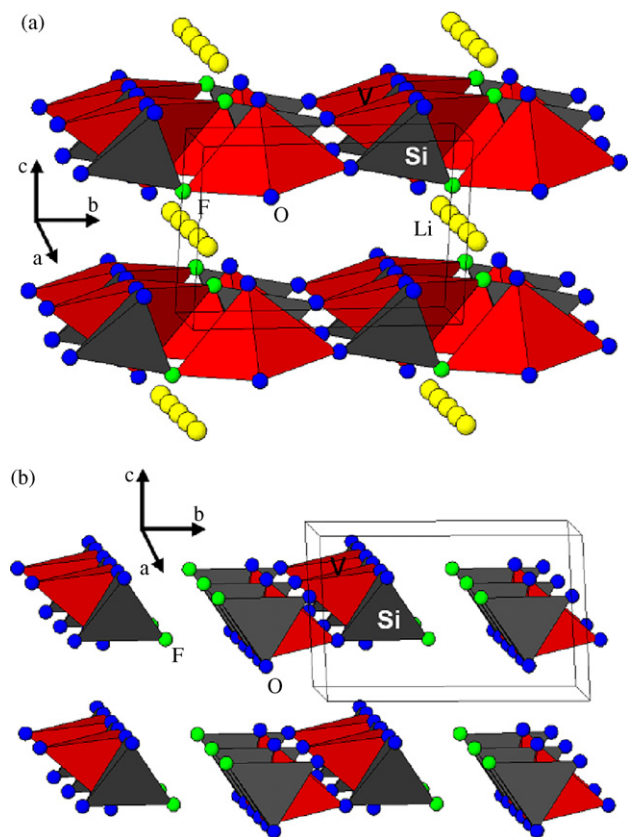


Fig. 3. Schematic representation of the optimized structure of LiVSiO_4F (a) model II and its delithiated derivative (b). Model III is the equivalent but with F ions along $[010]$ direction (see text).

2.3. LiVPO_4F

This structure comprises a three-dimensional network built up from PO_4 tetrahedra and VO_4F_2 octahedra: the F ions are located in anionic positions not belonging to the phosphate groups [7] (Fig. 6). The lithium deinsertion process from LiVPO_4F is currently under investigation [7], and apparently VPO_4F retains the structure of the parent compound.

3. Methodology

The total energies of all the compounds under investigations were calculated using the Projector Augmented Wave (PAW) [14,15] method as implemented in the Vienna *ab initio* Simulation Package (VASP) [15]. The exchange and correlation energies have been approximated in the Generalised Gradient Approximation with the Hubbard parameter correction (GGA + U). Computational details for the $\text{Li}_2\text{VSiO}_5(\text{F})$ and $\text{LiFePO}_4(\text{F})$ systems are provided in references [13] and [16], respectively. For LiVPO_4F a U correction term of 3 eV was used. The energy cut-off for the plane wave basis set was kept fix at a constant value of 500 eV and the reciprocal space sampling done with k -point grids of $4 \times 4 \times 4$. Full relaxation was allowed and the final energies of the optimized geometries were recalculated so as to correct for changes in basis during relaxation. All calculations are spin polarized.

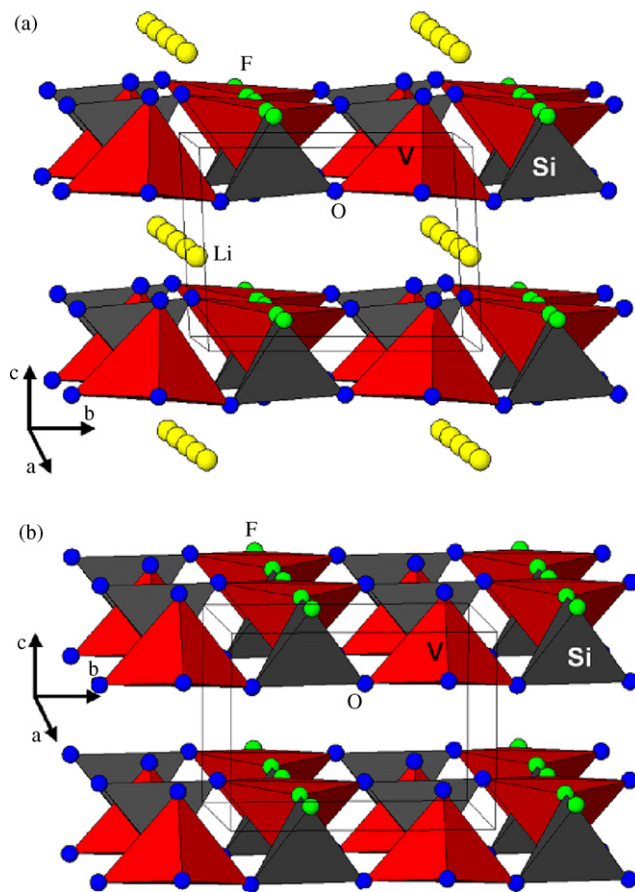


Fig. 4. Schematic representation of the optimized structure of LiVSiO_4F (a) model IV and its delithiated derivative (b).

4. Results and discussion

4.1. $\text{Li}_2\text{VOSiO}_4$ and LiVSiO_4F

Table 1 summarizes the calculated stabilization energy of LiVSiO_4F and VSiO_4F for the structures I–IV, taking as the zero of energy that of the most stable structure. Noticeably, LiVSiO_4F is more stable in structure I, with the F ions in the apical vertex of the VO_4F vanadium square pyramids. However, it is worth pointing out that this apical fluorine is *not bonded to vanadium by a double bond* (similar to the V–O vanadyl bond) since fluorine is unable to form double bonds. As it will be discussed below, this is obvious from the V–F distance. Placing F ions in the basal plane of the SP– VO_4F leads to an energy increase

Table 1
Energy differences (eV/formula unit) and calculated lithium insertion voltage for $\text{Li}_x\text{VSiO}_4\text{F}$ ($x=0, 1$) structures

| $\text{Li}_x\text{VSiO}_4\text{F}$ Structure | Energy difference (eV/formula unit) | | Calculated Redox vs. Li (V) potential $\text{V}^{5+}/\text{V}^{4+}$ |
|---|--|-------|--|
| | $x=1$ | $x=0$ | |
| I | 0 | 0.78 | 4.13 |
| II | 0.17 | 0 | 3.27 |
| III | 0.14 | 0.002 | 3.23 |
| IV | 0.47 | 0.95 | 3.78 |

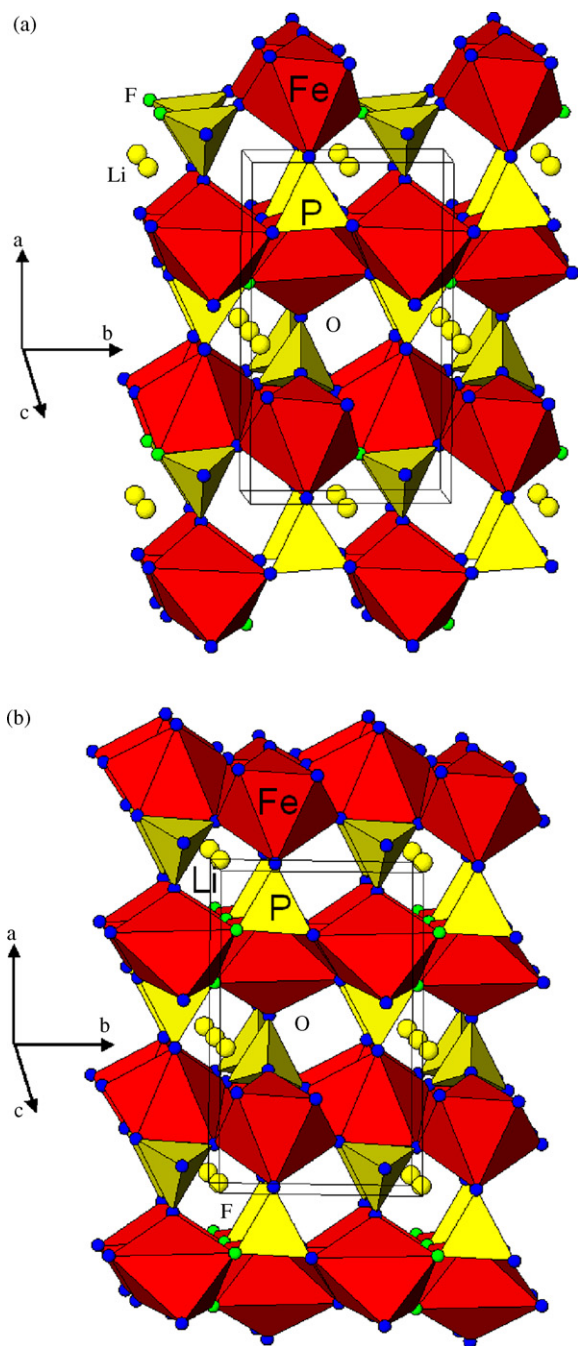


Fig. 5. Schematic representation of the optimized structure of $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$ (a) model O-I and (b) model O-II.

of 0.17 eV and 0.14 in structures II and III, respectively. The calculated destabilization of structure IV with respect to structure I is 0.5 eV. Regarding the relative stability of the delithiated VSiO_4F phases, structure II is now the most stable, having an energy 0.78 eV below that of structure I. The energy difference between the delithiated structures II and III is negligible, stressing the slight influence of the relative orientation of the Li chain on the structure stability. Structure IV displays a large energetic destabilization, close to 1 eV, with respect to that of structure II.

As observed in Table 1, the huge energy differences arising from the distinct F locations in the Li_xVSiO_5 structures induce

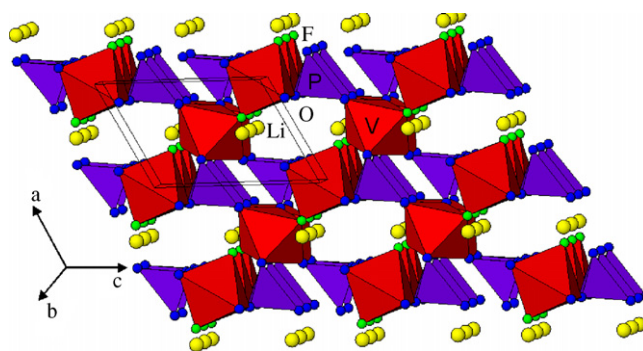


Fig. 6. Schematic representation of the LiVPO_4F structure.

largely spread values for the predicted lithium intercalation voltages. The calculated voltages range from 3.27 V in structure II to 4.13 V in structure I, being the experimental voltage of the parent silicate Li_2VSiO_5 3.6 V [10] (the calculated voltage for Li_2VSiO_5 is 3.57 V [13]). This suggests that the effect of fluorine substitution is to shift the redox energy of the $\text{V}^{5+}/\text{V}^{4+}$ couple by ± 0.4 V. The voltage increase predicted for structures I (0.56 V) and IV (0.21 V) is comparable to that reported for the $\text{V}^{3+}/\text{V}^{4+}$ couple (0.3 V) when going from $\text{Li}_3\text{V}_2(\text{PO}_4)$ to LiVPO_4F . On the contrary, the decrease of the predicted voltages for structures II and III (0.3 V) contradicts the idea of promoting the ionic character of the V–X bond through the fluorine substitution.

Table 2 collects the calculated lattice parameters of the parent compound together with the studied fluorinated- structures. The volume of structures I–IV is larger than that of the parent silicate. At first view, the increment of the lattice parameters due to fluorine substitution is surprising, since F^- ions are smaller than O^{2-} ions ($r^{\text{VI}}(\text{F}^-) = 1.33 \text{ \AA}$, $r^{\text{VI}}(\text{O}^{2-}) = 1.40 \text{ \AA}$). However, a lattice expansion has also been observed in $\text{LiMn}_2\text{O}_{4-x}\text{F}_x$ spinels in comparison to the parent oxide-spinel. A moderate expansion of the c -axis (4%) and volume (2%) are observed when lithium ions are removed from the structure I. Removing lithium ions from structures II and III causes an important distortion of the ab -plane, as can be seen in Fig. 3, and a volume variation of 9%.

Table 3 summarizes some selected interatomic distances in $\text{Li}_x\text{VSiO}_4\text{F}$ ($x=0.1$) structures compared to that of the parent silicate. All the distances obtained are similar to those found in analogous oxides or oxifluorides of tetra or pentavalent vanadium. As stated above, fluorine is unable to form double bonds, thus the V–F distance involving the apical fluorine ion of the $\text{SP-VO}_4\text{F}$ in structure I (both lithiated and deinserted) is similar to those found in other compounds with simply-bonded V–F contacts. As a consequence, the V–O distances in the basal plane are shortened (reinforcement of the V–O bonds) with respect to those in the parent compound, Li_2VSiO_5 , since the “bond capacity” (electron density) of central V atoms remains unchanged. When lithium is removed from model I the structure is essentially retained though the square pyramids become distorted and the V–O and V–F distances are shortened due to the smaller size of V^{5+} (Fig. 3). The SiO_4 tetrahedra are retained in both of the structure I fluorinated compounds (either lithium-inserted or deinserted), thus only slight variations are observed in the Si–O distances with respect to that of the parent silicate.

Table 2
Calculated lattice parameters for $\text{Li}_x\text{VSiO}_4\text{F}$ ($x=0,1$) structures and Li_xSiVO_5

| Structure | x | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) | V (Å ³) |
|------------------------------------|-----|---------|---------|---------|--------------|-------------|--------------|-----------------------|
| $\text{Li}_x\text{VSiO}_4\text{F}$ | 0 | 6.006 | 6.291 | 5.095 | 91.8 | 90 | 90 | 192.453 |
| Structure I | 1 | 6.266 | 6.580 | 4.595 | 85.6 | 90 | 90 | 188.909 |
| $\text{Li}_x\text{VSiO}_4\text{F}$ | 0 | 5.950 | 7.590 | 4.732 | 93 | 89 | 90 | 213.48 |
| Structure II | 1 | 6.351 | 6.751 | 4.598 | 85.7 | 90 | 90 | 196.624 |
| $\text{Li}_x\text{VSiO}_4\text{F}$ | 0 | 7.638 | 5.951 | 4.623 | 90.1 | 93 | 90 | 209.886 |
| Structure III | 1 | 6.628 | 6.437 | 4.604 | 88.2 | 89.5 | 90 | 196.37 |
| $\text{Li}_x\text{VSiO}_4\text{F}$ | 0 | 6.506 | 6.311 | 4.687 | 90.1 | 90 | 90 | 192.44 |
| Structure IV | 1 | 6.542 | 6.430 | 4.763 | 87 | 90 | 90 | 200.078 |
| | 1 | 6.256 | 6.256 | 4.643 | 86.7 | 90 | 90 | 184.50 |
| | | (6.206) | (6.206) | (4.449) | (90) | (90) | (90) | (171.35) |
| Li_xSiVO_5 | 2 | 6.409 | 6.409 | 4.487 | 90 | 90 | 90 | 184.31 |
| | | (6.368) | (6.368) | (4.571) | (90) | (90) | (90) | (185.36) |

Experimental data are given in parentheses.

In structures II and III, consisting of VOFO_3 and SiO_3F polyhedra (Fig. 3), the V–F distances are somewhat longer than reported values in the literature for V–F bonds; thus it is quite doubtful whether these V–F contacts can be considered as effective bonds. Moreover, these distances become as long as 3.19 Å in delithiated-compounds. Worth to note, the Si–F distances suffer an important shortening upon lithium extraction in both the II and II models. In these structural models the fluorine ions are shared by V and Si, giving sequences V–F–Si. As the F–Si bond gets shorter, the V–F distance becomes larger to the extend

that the V and F ions cannot be considered bonded anymore. Finally, both models II and III yield the same delithiated structure (Fig. 3): the environment of V ions is far from a SP, oxygen atoms are displaced so as to form a distorted tetrahedron around the central V atom. The stabilization gained by the V^{5+} ion in a tetrahedral environment also favors the breaking of the V–F bonds. The lack of V–F bonds in structures II and III explains why their calculated lithium insertion voltages are lower than that of the silicate (Table 1); to raise up the voltage of the parent silicate it would be necessary to increase the ionic character of

Table 3
Selected bond lengths (in Å) for the optimized structures of Li_xVSiO_5 and $\text{Li}_x\text{VSiO}_4\text{F}$ ($x=1, 0$)

| $x=2$ | $x=1$ | | | |
|----------------------------|--|---|--|---|
| Li_xVSiO_5 | $\text{Li}_x\text{VSiO}_4\text{F}$ Structure I | $\text{Li}_x\text{VSiO}_4\text{F}$ Structure II | $\text{Li}_x\text{VSiO}_4\text{F}$ Structure III | $\text{Li}_x\text{VSiO}_4\text{F}$ Structure IV |
| V^{4+} | | | | |
| 1.6712 | 1.8364 | 1.6593 | 1.6579 | 1.6644 |
| 1.9885×4 | 1.8378 | 1.8831 | 1.8879 | 1.9307 |
| | 1.8624 | 1.9565×2 | 1.9214 | 1.9844×2 |
| | 1.8874 (F) | 2.4010 (F) | 2.0446 | 2.0443 |
| | 2.1054 | | 2.2427 (F) | 2.0850 (F) $\times 2$ |
| Si–O | | | | |
| 1.6475×4 | 1.6169 | 1.5949 | 1.5999 | 1.6351×2 |
| | 1.6277 | 1.6223×2 | 1.6220 | 1.6587 |
| | 1.6645 | 1.7350 (F) | 1.6305 | 1.6939 |
| | 1.6649 | | 1.6994 (F) | 1.6761 (F) $\times 2$ |
| $x=1$ | $x=0$ | | | |
| Li_xVSiO_5 | $\text{Li}_x\text{VSiO}_4\text{F}$ Structure I | $\text{Li}_x\text{VSiO}_4\text{F}$ Structure II | $\text{Li}_x\text{VSiO}_4\text{F}$ Structure III | $\text{Li}_x\text{VSiO}_4\text{F}$ Structure IV |
| $\text{V}^{5+}\text{–O}$ | | | | |
| 1.6461 | 1.7864 (F) | 1.6226 | 1.6211 | 1.6256 |
| 1.7994 | 1.8098×2 | 1.7822 | 1.7840 | 1.8935 |
| 1.8798×2 | 1.8294×2 | 1.8114×2 | 1.8113 | 1.8936×2 |
| 2.0475 | | 3.19 (F) | 1.8126 | 1.8979 |
| | | | 3.7564 (F) | 2.0449(F) $\times 2$ |
| Si–O | | | | |
| 1.6408 | 1.6331 | 1.5993 | 1.5973 (F) | 1.6232×2 |
| 1.6445 | 1.6358 | 1.6409×2 | 1.6396 | 1.6929 |
| 1.6490×2 | 1.6575 | 1.6533 (F) | 1.6413 | 1.6973 |
| | 1.6576 | | 1.6543 | 1.6717(F) $\times 2$ |

Table 4
Calculated lattice parameters for $\text{Li}_x\text{FePO}_{3.5}\text{F}_{0.5}$ ($x=0.5, 1$) and LiFePO_4

| Compound | a (Å) | b (Å) | c (Å) | Volume (Å ³) |
|---|---------------------|-------------------|-------------------|--------------------------|
| OI– $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$ | 10.493 | 6.196 | 4.839 | 314.19 |
| OI– $\text{FePO}_{3.5}\text{F}_{0.5}$ | 9.888 | 6.540 | 5.055 | 325.09 |
| OII– $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$ | 10.341 | 6.287 | 4.883 | 317.52 |
| OII– $\text{FePO}_{3.5}\text{F}_{0.5}$ | 10.162 | 6.277 | 4.958 | 316.27 |
| Olivine– LiFePO_4 | 10.4027 (10.337) | 6.0773 (6.011) | 4.7512 (4.695) | 300.37 (291.1) |
| Olivine– FePO_4 | 9.9734 (9.821) | 5.9213 (5.792) | 4.8690 (4.788) | 287.54 (272.3) |

Experimental data are given in parentheses.

the V–O bond introducing fluorine ligands in the coordination sphere of the vanadium atoms.

Structure IV also contains F ions in the basal plane of the V–SP, but in this case two types of vanadium exist: V(1) atoms have two fluorine in their coordination sphere whereas V(2) ions are coordinated to five oxygen atoms (Fig. 4). Having two opposite fluorine atoms in the V environment seems to prevent the strong deformation of the V–SP: the V–F bond is retained, therefore raising up the intercalation voltage.

Among the calculated LiVSiO_4F structures, structure I results to be the most stable, with a moderate structural stress with cycling. Based on these calculations and encouraged by the predicted redox potential of LiVSiO_4F when crystallizing in type-I structure (4.16 V), we have faced the synthesis of this material. Although the first experimental trials have so far been unsuccessful, resulting in a phase mixture rather than in single-phase $\text{LiVOSiO}_4\text{F}$ samples, we have embarked in a survey of various experimental parameters (nature of the F-precursors, annealing temperatures and atmospheres) so as to corner the phase diagram within Li–V–Si–O–F system.

4.2. Olivine– LiFePO_4 and $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$

Two hypothetical structures were analyzed: one with equivalent iron in FeO_5F octahedra (Fig. 5a) and another with two kinds of iron ions located in FeO_4F_2 and FeO_6 octahedra, (Fig. 5b). The structure consisting on FeO_5F octahedra is more stable, with energy differences of 30 and 70 meV for lithiated and delithiated compounds, respectively. Calculated voltages are 3.18 V for structure O-I and 3.26 V for structure O-II, to be compared with the calculated voltage of LiFePO_4 , 3.51 V [16]. Table 4 summarizes the calculated lattice parameters for these structures. Upon lithium insertion structure O-I suffers an expansion of 3.5% accompanied by important lattice distortion, whereas structure O-II remains virtually unchanged (volume contraction of 0.4%).

Complete lithium deinsertion from $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$ will lead to $\text{FePO}_{3.5}\text{F}_{0.5}$ with Fe ions in a formal oxidation state of 2.5, or more likely a mixture of Fe^{2+} and Fe^{3+} ions. The oxidation state of Fe ions in $\text{FePO}_{3.5}\text{F}_{0.5}$ compounds have been obtained by integrating the net electron spin density over a 2 Å-radius sphere around each iron ion. Results are given in Table 5 together with the interatomic distances. The structure O-I, comprising FeO_5F

octahedra, shows Fe^{3+} –F distances of about 2.9 Å, suggesting the rupture of the Fe–F bond under lithium deinsertion. As discussed in the LiVVOFO_3 system, whenever the M–F distances get too large, (indicative of M–F bond breaking), and the lithium insertion voltage of the fluorine-substituted compound is below that of the parent compound. This situation is prompt to occur in those cases where the TM polyhedra containing a unique F ion are highly asymmetric. Accordingly, the calculated voltage of the O-I structure is lower than that of the parent LiFePO_4 in 0.32 V, i.e. the same voltage difference encountered in the $\text{LiVSiO}_4(\text{F})$ system.

The voltage shift from 3.5 V in LiFePO_4 to 3.26 V in structure O-II is also rooted on the non-existence of Fe^{3+} –F bonds. As shown in Table 5 lithium removal from O-II leads to $\text{FePO}_{3.5}\text{F}_{0.5}$ with no $\text{Fe}^{3+}\text{O}_5\text{F}$ octahedra, but only Fe^{3+}O_6 octahedra. Since the Fe^{2+} ions bonded to fluorine are not oxidized, the voltage increasing associated to a more ionic Fe–F bond with respect to the Fe–O bond cannot be observed. Two structural models more consisting on FeO_4F_2 and FeO_6 octahedra were investigated. In all cases the Fe ion which get oxidized is the one no coordinated to fluorine ions, and consequently, fluorine substitution does not raise the lithium deinsertion voltage of the parent LiFePO_4 .

4.3. LiVPO_4F

The calculated lithium deinsertion voltage from LiVPO_4F is 3.94 V in good agreement with the experimental one (4.01 V [7]). The calculated volume ($V=179.38 \text{ Å}^3$) differs in 3% with the experimental ($V=174.21 \text{ Å}^3$), i.e. within the usual GGA + U volume overestimation of about 5%. Under fully lithium removal a moderate volume expansion (4%) is predicted, in agreement with the good electrochemical performance observed for LiVPO_4F , a material displaying a long term cyclability with low capacity fading and constant voltage [7,17].

Regarding the V–F distances, in LiVPO_4F the calculated average distance is 2.00 Å (experimental is 1.80 Å), consistently with a V^{3+} –F bond. In the delithiated compound the average V^{4+} –F distance is 1.97 Å (there are no experimental data available). Clearly, in both lithiated and delithiated compounds the

Table 5
Selected bond lengths (in Å) for the optimized structures of $\text{Li}_x\text{FePO}_{3.5}\text{F}_{0.5}$ ($x=0, 0.5$)

| Compound | Structure O-I | | Structure O-II | |
|--------------------------|------------------|------------------|------------------|------------------|
| Lithiated ($x=0.5$) | 2.0570 | 2.0658 | 1.9723 | 2.0928 |
| | 2.0570 | 2.1121 | 2.0618 | 2.1202 |
| | 2.1252 | 2.1160 | 2.0896 | 2.1351 |
| | 2.1434 | 2.1990 | 2.1045 | 2.2191 |
| | 2.2430 | 2.2424 | 2.3649 (F) | 2.2289 |
| | 2.5901 (F) | 2.3371 (F) | 2.5120 (F) | 2.4216 |
| Delithiated ($x=0$) | Fe^{2+} | Fe^{3+} | Fe^{2+} | Fe^{3+} |
| | 1.9649 | 1.8993 | 1.9697 | 1.8871 |
| | 1.9739 | 1.9154 | 2.0123 | 1.9202 |
| | 2.2066 | 2.0216 | 2.0842 | 2.1245 |
| | 2.2728 | 2.0258 | 2.0922 | 2.1460 |
| | 2.2797 | 2.1158 | 2.3935 (F) | 2.2245 |
| | 2.6623 (F) | 2.8970 (F) | 2.6833 (F) | 2.2241 |

V–F bond is retained. This, together with the presented results in $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$ and LiVSiO_4F supports the idea that the voltage increase in fluorinated compounds is sustained by the presence of M–F bonds.

5. Conclusions

The computational result evidence that in substituted fluorinated–polyanionic compounds the lithium insertion voltage, and in a greater extend the general electrochemical behavior, depends on the particular crystallographic site that F ions occupy in the structure. We found that within a given composition ($\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}/\text{LiVSiO}_4\text{F}$), a lithium insertion *voltage higher* than that of the parent compound is necessarily rooted on the *existence of stable $\text{M}^{n+1}\text{–F}/\text{M}^{n+}\text{–F}$ bonds*. This situation was not found in any of the explored $\text{Li}_{0.5}\text{FePO}_{3.5}\text{F}_{0.5}$ models, while for LiVSiO_4F a voltage increasing of about 0.5 V is predicted. In both compounds the *rupture* of the M–F bonds upon lithium deinsertion leads to a lithium insertion voltage 0.3 V *below* that of the parent compound. The present study shed on key thoughts to balance the advisability of attempting a fluorine substitution in a particular polyoxianionic compound.

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