

## Supplementary information

# Crystal structure and lithium diffusion pathways of a potential positive electrode material for Lithium-ion batteries: $\text{Li}_2\text{V}^{\text{III}}(\text{H}_{0.5}\text{PO}_4)_2$

Edouard Boivin <sup>a,b,c</sup>, Christian Masquelier <sup>a,c,d</sup>, Laurence Croguennec <sup>b,c,d</sup>,  
and Jean-Noël Chotard <sup>a,c,d</sup>

<sup>a</sup> *Laboratoire de Réactivité et de Chimie des Solides, CNRS-UMR#7314,  
Université de Picardie Jules Verne, F-80039 Amiens Cedex 1, France.*

<sup>b</sup> *CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB UPR 9048, F-33600 Pessac, France.* <sup>c</sup> *RS2E, Réseau  
Français sur le Stockage Electrochimique de l'Energie, FR CNRS 3459,  
F-80039 Amiens Cedex 1, France.*

<sup>d</sup> *ALISTORE-ERI European Research Institute, FR CNRS 3104, F-80039 Amiens Cedex 1, France.*

**Table S1:** Data collection and refinement details

| <b>Data collection</b>   |                                      |
|--|--------------------------------------|
| Diffractometer   | Bruker D8 Venture                    |
| Radiation type   | Mo K $\alpha$ ( $\lambda=0.71073$ Å) |
| Temperature (K)  | 293                                  |
| Crystal size (mm)  | 0.14 $\times$ 0.09 $\times$ 0.07     |
| Absorption correction  | Numerical (SADABS; Bruker, 2013)     |
| $\mu$ (mm <sup>-1</sup> )  | 2.35                                 |
| Data collection  | APEX3 (BRUKER)                       |
| No. of measured,<br>independent and<br>observed [ $I > 2\sigma(I)$ ] reflections | 65122,<br>3250,<br>2702              |
| $(\sin \theta/\lambda)_{\max}$ (Å <sup>-1</sup> )                                | 1.116                                |
| <b>Refinement</b>  |                                      |
| <i>Cell refinement software</i>  | SAINT (BRUKER)                       |
| $R_{\text{int}}$   | 0.059                                |
| <i>Data reduction software</i>   | SAINT (BRUKER)                       |
| <i>Structure solving software</i>  | SHELXS97                             |
| <i>Structure solving method</i>  | Direct method                        |
| <i>Structure refinement software</i>   | SHELXL (Sheldrick, 2014)             |
| $R[F^2 > 2\sigma(F^2)]$  | 0.029                                |
| $wR(F^2)$  | 0.067                                |
| $S$  | 1.10                                 |
| No. of reflections   | 3250                                 |
| No. of parameters  | 62                                   |
| H-atom treatment   | No H-atom parameter refined          |
| $\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å <sup>-3</sup> )                      | 1.04, -0.73                          |
| Molecular graphic  | VESTA                                |
| Formatting CIF file  | CHECKCIF                             |

**Table S2:** Anisotropic displacement parameters ( $\text{\AA}^2$ )

|              | <b>U11</b> | <b>U22</b> | <b>U33</b> | <b>U12</b>  | <b>U13</b> | <b>U23</b>  |
|--------------|------------|------------|------------|-------------|------------|-------------|
| <b>V(1)</b>  | 0.00441(5) | 0.00463(5) | 0.00461(5) | 0.00026(4)  | 0.00148(4) | -0.00039(4) |
| <b>P(1)</b>  | 0.00400(6) | 0.00539(6) | 0.00505(6) | -0.00069(4) | 0.00164(4) | -0.00055(4) |
| <b>O(1)</b>  | 0.0043(2)  | 0.0072(2)  | 0.0099(2)  | -0.0016(1)  | 0.0006(1)  | 0.0001(1)   |
| <b>O(2)</b>  | 0.0095(2)  | 0.0073(2)  | 0.0095(2)  | -0.0021(1)  | 0.0023(2)  | -0.0035(1)  |
| <b>O(3)</b>  | 0.0082(2)  | 0.0102(2)  | 0.0091(2)  | -0.0018(2)  | 0.0050(2)  | 0.0011(2)   |
| <b>O(4)</b>  | 0.0085(2)  | 0.0150(2)  | 0.0067(1)  | 0.0033(1)   | 0.0024(1)  | -0.0020(2)  |
| <b>Li(1)</b> | 0.0138(7)  | 0.0139(7)  | 0.0145(7)  | -0.0032(6)  | 0.0030(6)  | 0.0019(6)   |

**Table S3:** Bond lengths (below the diagonal) and angles (above the diagonal) in coordination polyhedra of  $V^{3+}$ ,  $Li^+$  and  $P^{5+}$  in  $Li_2V^{III}(H_{0.5}PO_4)_2$ . The polyhedral distortion is calculated as  $\Delta = \frac{1}{N} \sum_{i=0}^N \frac{(d_i - \langle d \rangle)^2}{\langle d \rangle^2}$  with N the number of bond distances considered,  $d_i$  the distance between the atom i and the central atom of the polyhedron and  $\langle d \rangle$  the average of the distances considered.

| <b>VO<sub>6</sub></b>                             |                 |                 |                 |                 |                 |                 |
|---|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|   | <b>O(1)</b>     | <b>O(1')</b>    | <b>O(2)</b>     | <b>O(2')</b>    | <b>O(3)</b>     | <b>O(3')</b>    |
| <b>O(1)</b>                                       | <b>2.018(2)</b> | 180             | 88.9(2)         | 91.1(2)         | 93.4(2)         | 86.6(2)         |
| <b>O(1')</b>                                      | 4.037(2)        | <b>2.018(2)</b> | 91.1(2)         | 88.9(2)         | 86.6(2)         | 93.4(2)         |
| <b>O(2)</b>                                       | 2.835(2)        | 2.891(2)        | <b>2.031(2)</b> | 180             | 84.0(2)         | 96.0(2)         |
| <b>O(2')</b>                                      | 2.891(2)        | 2.835(2)        | 4.062(2)        | <b>2.031(2)</b> | 96.0(2)         | 84.0(2)         |
| <b>O(3)</b>                                       | 2.905(3)        | 2.738(3)        | 2.679(3)        | 2.977(2)        | <b>1.974(2)</b> | 180             |
| <b>O(3')</b>                                      | 2.738(3)        | 2.905(3)        | 2.977(2)        | 2.679(3)        | 3.948(2)        | <b>1.974(2)</b> |
| $\Delta = 1.11 \times 10^{-4}$                    |                 |                 |                 |                 |                 |                 |
| <b>HPO<sub>4</sub></b>                            |                 |                 |                 |                 |                 |                 |
|   | <b>O(1)</b>     | <b>O(2)</b>     | <b>O(3)</b>     | <b>O(4)</b>     | <b>H(1)</b>     | <b>H(1')</b>    |
| <b>O(1)</b>                                       | <b>1.533(2)</b> | 111.5(2)        | 109.8(2)        | 111.6(2)        | 93.1(2)         | 84.7(2)         |
| <b>O(2)</b>                                       | 2.503(3)        | <b>1.523(2)</b> | 110.1(2)        | 108.0(3)        | 109.7(3)        | 121.1(3)        |
| <b>O(3)</b>                                       | 2.505(3)        | 2.503(3)        | <b>1.530(2)</b> | 105.7(2)        | 124.1(3)        | 116.6(2)        |
| <b>O(4)</b>                                       | 2.547(2)        | 2.483(2)        | 2.451(2)        | <b>1.546(2)</b> | <b>128.9(4)</b> | 124.4(3)        |
| <b>H(1)</b>                                       | 2.856(2)        | 3.133(2)        | 3.423(2)        | <b>1.018(2)</b> | 2.329(1)        | 14.8(1)         |
| <b>H(1')</b>                                      | 2.971(2)        | 3.720(2)        | 3.639(2)        | <b>1.466(2)</b> | 0.58            | 2.692(1)        |
| $\Delta = 2.96 \times 10^{-5}$ (PO <sub>4</sub> ) |                 |                 |                 |                 |                 |                 |
| <b>LiO<sub>4</sub></b>                            |                 |                 |                 |                 |                 |                 |
|   | <b>O(1)</b>     | <b>O(2)</b>     | <b>O(3)</b>     | <b>O(4)</b>     |                 |                 |
| <b>O(1)</b>                                       | <b>1.952(6)</b> | 113.3(4)        | 119.1(4)        | 125.1(5)        |                 |                 |
| <b>O(2)</b>                                       | 3.344(2)        | <b>2.052(4)</b> | 83.3(3)         | 91.0(3)         |                 |                 |
| <b>O(3)</b>                                       | 3.390(3)        | 2.679(3)        | <b>1.978(6)</b> | 111.9(4)        |                 |                 |
| <b>O(4)</b>                                       | 3.478(2)        | 2.869(3)        | 3.272(2)        | <b>1.968(5)</b> |                 |                 |
| $\Delta = 3.69 \times 10^{-4}$                    |                 |                 |                 |                 |                 |                 |

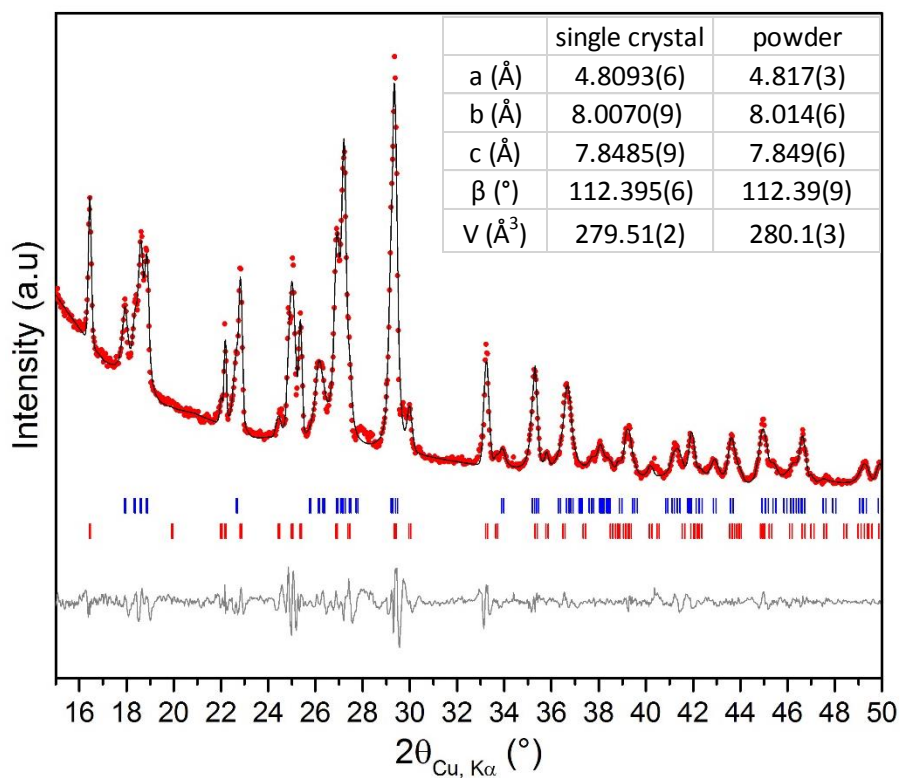


Figure S1: Rietveld refinement of structure from X-ray powder diffraction. The theoretical Bragg contributions for  $\text{Li}_2\text{V}^{\text{III}}(\text{H}_{0.5}\text{PO}_4)_2$  are depicted as red markers and those of  $\text{LiVPO}_4\text{OH}$  as blue ones.

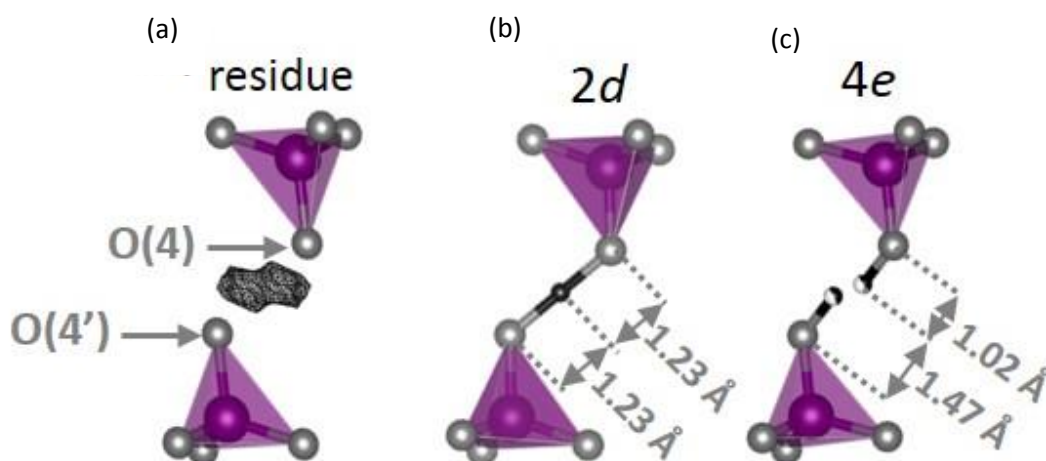


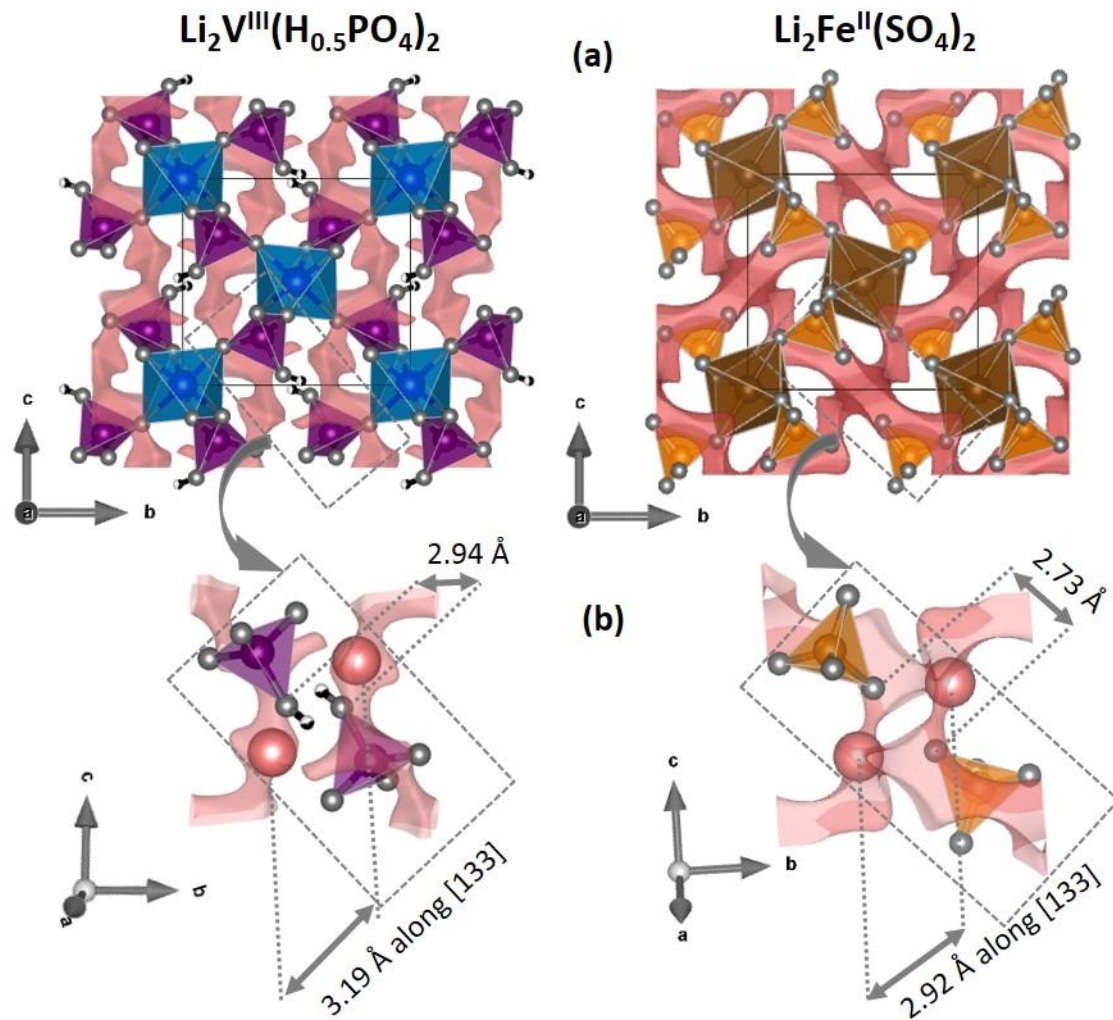
Figure S2: The residual electronic density located between two “free” oxygens (a) and the two models proposed for hydrogen position are illustrated in (b) and (c)

The distribution of residual electronic density between the O(4) and O(4') is peanut-shaped (Fig S2a). Two models can therefore be proposed:

i) H atoms are located on a fully occupied  $2d$  ( $\frac{1}{2}, \frac{1}{2}, 0$ ) Wyckoff site (on the inversion center of the peanut-shape residual electronic density) leading to two symmetrically equivalent O-H distances ( $d_{O(4)-H(1)} = d_{O(4')-H(1)} = 1.227(2)$  Å and a O(4)-H-O(4') angle of  $180^\circ$ ) (Fig S2b),

ii) H atoms are located on a  $4e$  position half occupied site generating two different O-H distances ( $d_{O(4)-H(1)} = 1.018(2)$  Å and  $d_{O(4)-H(1')} = 1.466(2)$  Å and an O(4)-H-O(4') angle of  $153.4(3)^\circ$ ) (Fig S2c). If the hydrogen atom occupies a  $2d$  Wyckoff position a three-centers four-electrons bond has to be considered and in the case of  $4e$  position a more common hydroxyl group involved in a hydrogen bond would be formed.

As it's very difficult to precisely localize H atoms in inorganic materials we weren't able to refine the fractional coordinates of this hydrogen, subsequently at the center of each lobes of the peanut-shaped residual electronic density (i.e. 0.45, 0.51, 0.01). This position is very close to the one found by Jin-Xiao Mi *et al.*<sup>1</sup> for the iron phase (i.e. 0.45, 0.52, 0.02). Based on this result, and even if the non-peculiar position of hydrogen can't be precisely determined, the split model was chosen.



**Figure S3:** In (a) Projection along [100] of Lithium paths obtained from Bond Valence Energy Landscape (BVEL) with an energy of 1.6 eV above minimum for  $\text{Li}_2\text{Fe}(\text{SO}_4)_2$  (right) and  $\text{Li}_2\text{V}^{\text{III}}(\text{H}_{0.5}\text{PO}_4)_2$  (left) and in (b) enlargement of the path corresponding to the shorter Li-Li distance (along [133]) showing that a hopping between two Li sites is possible in  $\text{Li}_2\text{Fe}(\text{SO}_4)_2$  whereas it isn't allowed in  $\text{Li}_2\text{V}^{\text{III}}(\text{H}_{0.5}\text{PO}_4)_2$ .

#### References:

1. Mi, J.-X. et al. Synthesis, Magnetism, and Crystal Structure of  $\text{Li}_2\text{Fe}[(\text{PO}_4)(\text{HPO}_4)]$  and its Hydrogen Position Refinement. *Zeitschrift für Anorg. und Allg. Chemie* 2004, 630, 1632–1636.