

## Supporting Information

### **Ionothermal Synthesis of Polyanionic Electrode Material $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$ Through Topotactic Reaction**

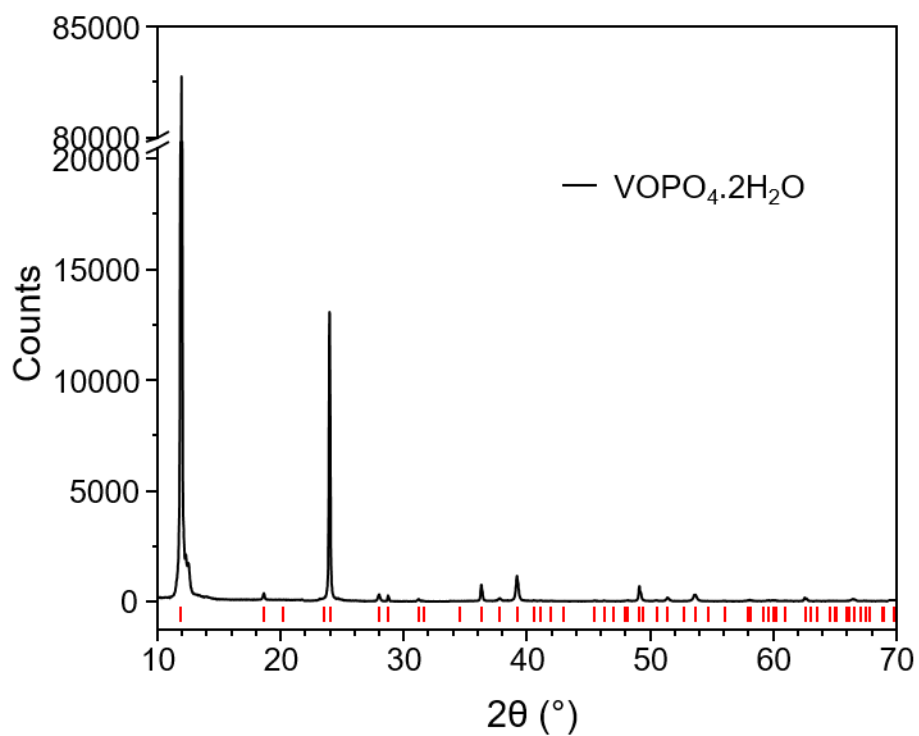
Jacob Olchowka <sup>a,c,d,\*</sup>, Long H.B. Nguyen <sup>a,b,c</sup>, Emmanuel Petit <sup>a,c</sup>, Paula Sanz Camacho <sup>a</sup>, Christian Masquelier <sup>b,c,d</sup>, Dany Carlier <sup>a,c,d</sup>, Laurence Croguennec <sup>a,c,d</sup>

<sup>a</sup> CNRS, Univ. Bordeaux, Bordeaux INP, ICMCB UMR 5026, F-33600, Pessac, France.

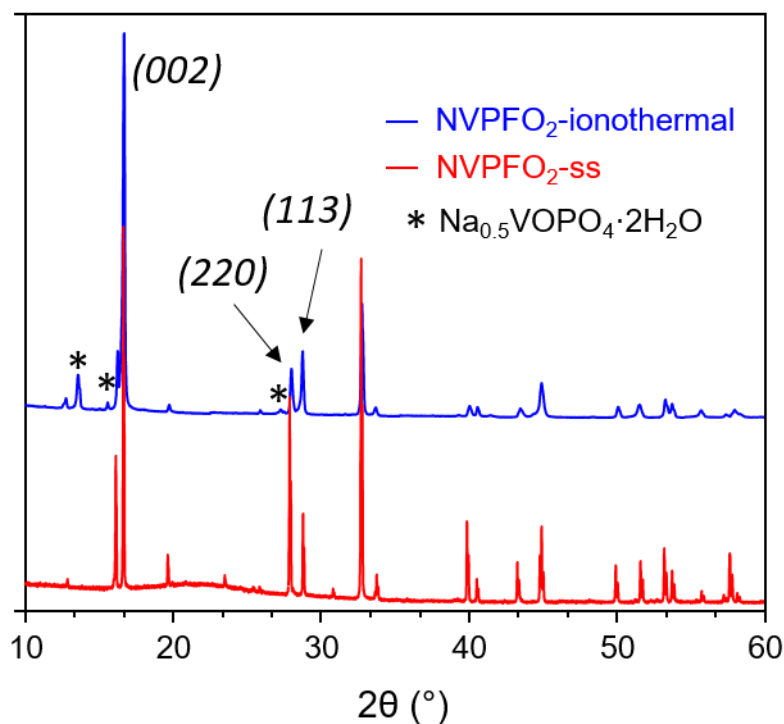
<sup>b</sup> Laboratoire de Réactivité et de Chimie des Solides, CNRS-UMR# 7314, Université de Picardie Jules Verne, F-80039 Amiens Cedex 1, France.

<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, Amiens, F-80039 Cedex 1, France.

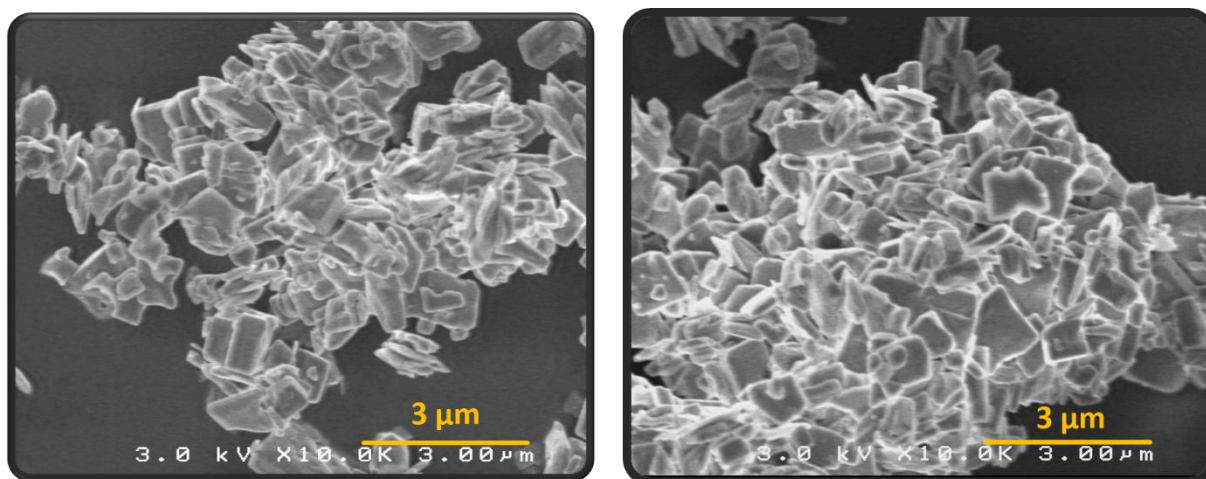


**Figure S1.** XRD pattern of the synthesized precursor  $\alpha$ -VOPO<sub>4</sub>·2H<sub>2</sub>O. All the reflections fit well to the theoretical pattern (ICSD: 01-084-0111) marked with red sticks. The shoulder observed for the diffraction peak at 12°, which corresponds to (001) reflection, most probably comes from stacking faults.

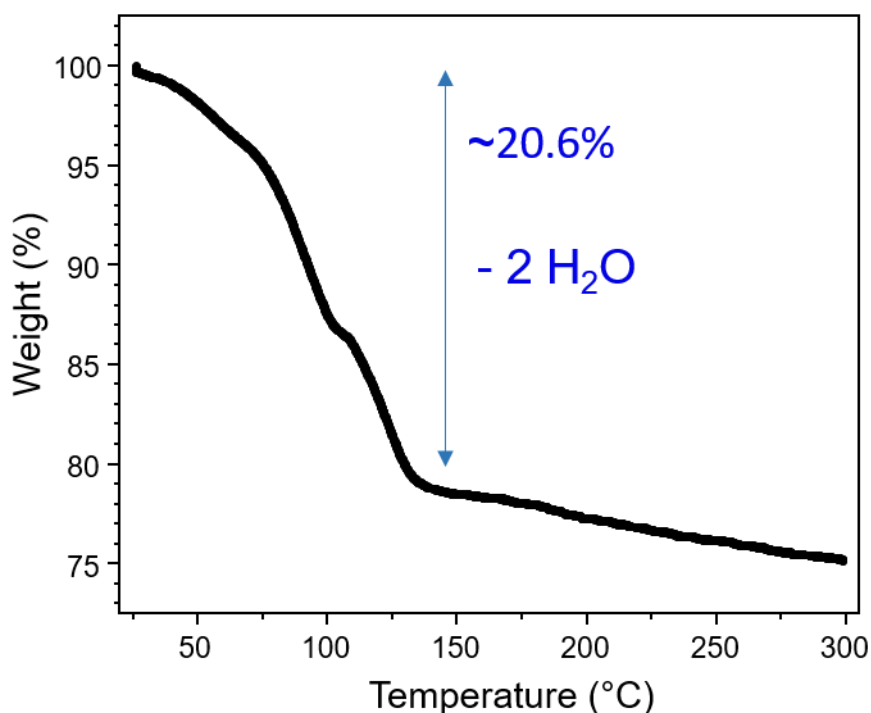


**Figure S2.** Comparison between XRD pattern of samples obtained by solid-state synthesis (red) and ionothermal approach (blue). Reflections attributed to Na<sub>0.5</sub>VOPO<sub>4</sub>·2H<sub>2</sub>O impurities are marked with asterisks. For sample obtained by ionothermal synthesis, (002) reflection is intense and (220) has a lower intensity compared to (113) one due to platelet-like morphology. The rotating capillary measurement did not allow to minimize enough this preferential orientation to perform a Rietveld refinement of quality.

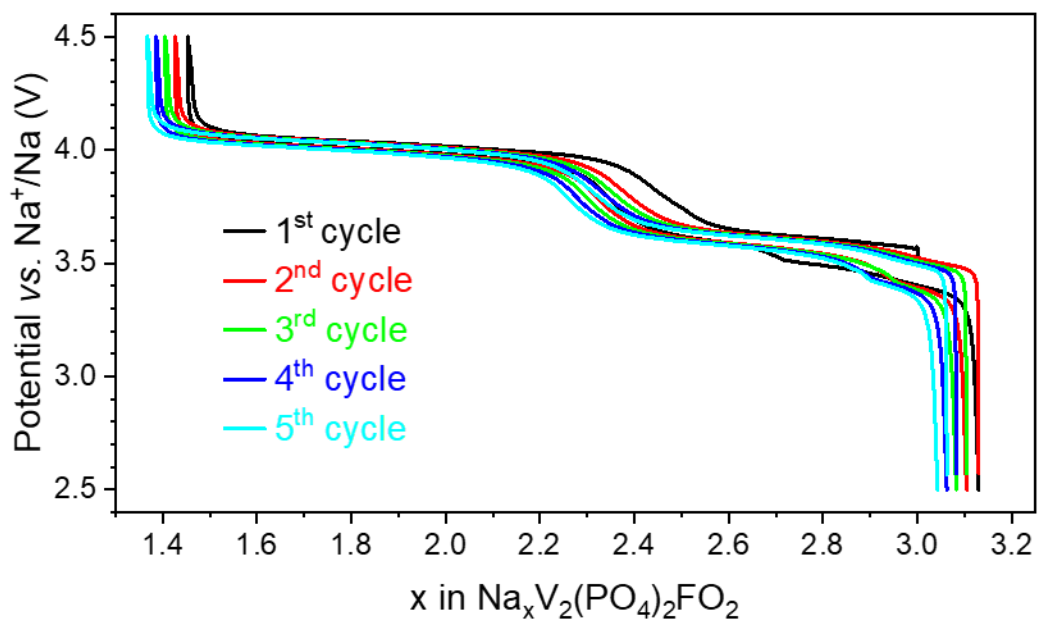
The impurity was indexed from the ICSD database 01-081-1929.



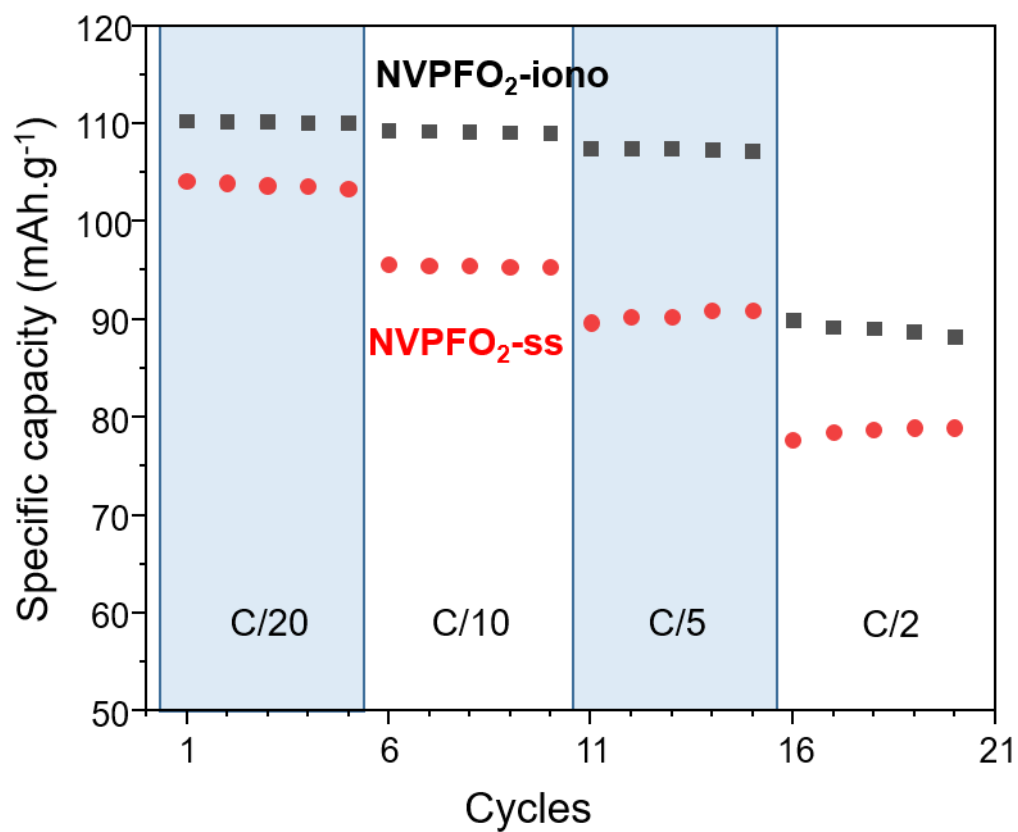
**Figure S3.** SEM images of  $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{FO}_2$  synthesized by solid-state method. The particles are polydispersed (from several hundred of nanometers to micrometer range) and have no particular shape.



**Figure S4.** Thermogravimetric analysis of  $\alpha\text{-VOPO}_4\cdot 2\text{H}_2\text{O}$  under air. At 140 °C, a weight loss of around 20.6% is observed and is attributed to the loss of 2 water molecules. The dehydration process is characterized by two steps: The first one below 100 °C most probably corresponds to the departure of free water molecules localized into the interlayer space and the second one between 100 and 140 °C to the water molecules involved in the vanadium coordination spheres.



**Figure S5.** Galvanostatic charge/discharge curves of NVPFO<sub>2</sub>-iono performed in a half-cell versus Na metal at C/20. After the first cycle, the profile of the curve remains unchanged and perfectly reversible.



**Figure S6.** Comparison between the specific capacities of NVPFO<sub>2</sub>-iono (in black) and NVPFO<sub>2</sub>-ss (in red) obtained at different current densities.

**Table S1.** Comparison of specific capacities obtained in half Na cells at different cycling rates for NVPFO<sub>2</sub>-iono (this work) and for a series of Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(F,O)<sub>3</sub> compositions reported in literature.

Material	Capacity	Cycling rate	Reference in the manuscript
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> F <sub>3</sub>	93.5 mAh.g <sup>-1</sup>	C/10	20
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> F <sub>3</sub>	~80 mAh.g <sup>-1</sup>	C/10	21
c- Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> F <sub>3</sub> -SPS	~100 mAh.g <sup>-1</sup>	C/10	21
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> FO <sub>2</sub>	~95 mAh.g <sup>-1</sup>	C/10	51
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> F <sub>2.2</sub> O <sub>0.8</sub>	~80 mAh.g <sup>-1</sup>	C/10	51
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> FO <sub>2</sub>	~100 mAh.g <sup>-1</sup>	C/10	52
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> FO <sub>2</sub>	~95 mAh.g <sup>-1</sup>	C/20	53
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> FO <sub>2</sub>	~35 mAh.g <sup>-1</sup>	C/2	54
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> FO <sub>2</sub> /rGO (solvothetmal)	~100 mAh.g <sup>-1</sup>	C/2	54
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> FO <sub>2</sub>	~100 mAh.g <sup>-1</sup>	C/20	55
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> FO <sub>2</sub> /rGO	~120 mAh.g <sup>-1</sup>	C/20	55
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> F <sub>3</sub>	~88 mAh.g <sup>-1</sup>	C/2	56
Na <sub>3</sub> V <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> F <sub>3</sub> -SWCNT	~117 mAh.g <sup>-1</sup>	C/2	56
<b>Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>FO<sub>2</sub>-iono</b>	<b>~110 mAh.g<sup>-1</sup></b>	<b>C/10</b>	<b>(this work)</b>