

Electronic Supporting Information (ESI) for

A phase-transfer assisted solvo-thermal strategy for low-temperature synthesis of $\text{Na}_3(\text{VO}_{1-x}\text{PO}_4)_2\text{F}_{1+2x}$ cathodes for sodium-ion batteries

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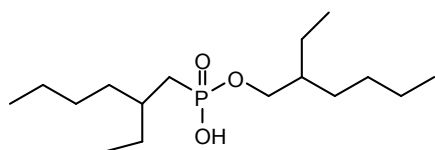
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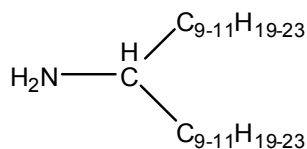
Material and methods

Chemicals

Vanadium (III) acetylacetonate (Sigma-Aldrich, 97%) and vanadium (IV) -oxy acetylacetonate (Sigma-Aldrich, 97%) were used as vanadium resources for the synthesis of $\text{Na}_3(\text{VO}_{1-x}\text{PO}_4)_2\text{F}_{1+2x}$ ($x = 0, 0.5$ and 1), respectively. PC-88A (2-ethylhexyl phosphonic acid mono 2-ethylhexyl ester, purity > 95%) and N1923 (secondary carbon primary amine, purity > 99%) were kindly supplied by Shanghai Rare-earth Chemical Co., Ltd., which were used to prepare acid-base-coupled extractant PN and used as received without further purification. Their chemical structures are shown as follows:



PC-88A



N1923

All other reagents employed in this work, such as H_3PO_4 (83%, 14.4968 mol/L) and NaF (>98%), were purchased from Beijing Chemical Reagent Co. with analytical grade.

Preparation of PN and PN- H_3PO_4

In this work, the acid-base-coupled extractant PN was used to transfer phosphoric acid into an organic phase (hereafter abbreviated as PN-H₃PO₄). PN was prepared through the reaction of equal moles of the commercial extractants PC-88A and N1923 as described in our previous work.²² The reaction flask is hot with the generation of heat once PC-88A and N1923 were mixed, indicating that it is not a physical blending but an acid-base neutralization reaction.

PN-H₃PO₄ was prepared as follows. First, PN was diluted by heptane to be 16% PN-heptane (wt/v). Secondly, 250 ml 16% PN-heptane was used to mix with 20 ml 83% phosphoric acid (commercially available) for 30min and then left to stand. Finally, a homogeneous solution was obtained and then used as phosphorus resources, where the concentration of H₃PO₄ was calculated as 1.06 mol/L.

Preparation of micro-crystals Na₃(VPO₄)₂F₃, Na₃(VO_{0.5}PO₄)₂F₂ and Na₃(VOPO₄)₂F

In a typical synthesis of porous Na₃(VPO₄)₂F₃, 179.5 mg (0.5 mmol) [CH₃COCHCOCH₃]₃V was dissolved in 1.5 ml ethanol and 0.5 ml acetone, which was thoroughly mixed with 1.5 ml of PN-H₃PO₄ to attain a solution A according to a V/PO₄ molar ratio of 1:3. In order to guarantee that the vanadium precursor reacts completely, the excess of PO₄ was adopted instead of the stoichiometry. Then 35 mg NaF powder was added into the solution A according to the ratio of V: P: F = 1:3:1.67. The obtained mixture was ultrasound-treated for 10 min. Finally, the mixture was transferred into a teflon cup of 45 ml inner volume, placed in a steel autoclave, and carefully sealed. The autoclave was heated in a furnace at 80-140 °C for 10 h. Then the system was allowed

to cool to room temperature. The resulting suspensions were centrifuged, and the obtained light blue precipitates were thoroughly washed with ethanol and deionized water to remove possible ionic or organic remnants, subsequently dried in air at 60 °C for 5 h. Finally, 89.7 mg powder was obtained with a yield of 85.9%. Furthermore, the extractant PN can be easily recycled from the mother liquid (supported by IR data) after the recovery of ethanol and acetone by a rotary evaporation, then washing by hydrochloric acid and water in turns for several times. The reaction can also be readily scaled up to meet the demand for the preparation of a larger amount of products. Furthermore, $\text{Na}_3(\text{VO}_{0.5}\text{PO}_4)_2\text{F}_2$ and $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ were prepared by the same procedure taking the mixture of 89.8 mg (0.25 mmol) $[\text{CH}_3\text{COCHCOCH}_3]_3\text{V}$ and 68.4 mg (0.25 mmol) $[\text{CH}_3\text{COCHCOCH}_3]_2[\text{VO}]$, 136.7 mg (0.5 mmol) $[\text{CH}_3\text{COCHCOCH}_3]_2[\text{VO}]$ as starting materials, respectively. Finally, the products were obtained with a yield of 86.4% and 84.8%, respectively.

Materials characterizations and electrochemical properties

The structures of the materials were characterized with an X'Pert Pro MPD X-ray diffractometer (Philips, The Netherlands) using Cu K α radiation (1.5405 Å). The morphologies of the materials were observed with a scanning electron microscope (Hitachi S-4800) and a transmission electron microscope (JEM-2100F). Fourier transform infrared spectroscopy (FTIR) measurements were performed on a Bruker Tensor 27 Spectrometer using KBr pellets (32 scans at a resolution of 4 cm⁻¹) in transmission mode. The Brunauer-Emmett-Teller (BET) surface area was deduced from an isotherm analysis.

For electrochemical measurements, the working electrode was prepared by mixing the active materials (70 wt.%), acetylene black (25 wt.%) and polytetrafluoroethylene (PTFE) (5 wt.%)

binder together and then pressing into a tape. The working electrodes were dried at 110 °C under vacuum for 10 h. The used electrolyte is 1 M NaClO₄ in EC: DEC (ethylene carbonate/diethyl carbonate, 5:5 in volume) containing 2 wt.% fluoroethylene carbonate (FEC) as a functional additive. The coin-type (CR2032) cells were assembled with pure sodium foil as the counter electrode, and a glass fiber as the separator in an argon-filled glove box. The charge and discharge measurements were carried out on a Land BT2000 battery test system (Wuhan, China) in the voltage range of 2.5–4.3 V at room temperature.

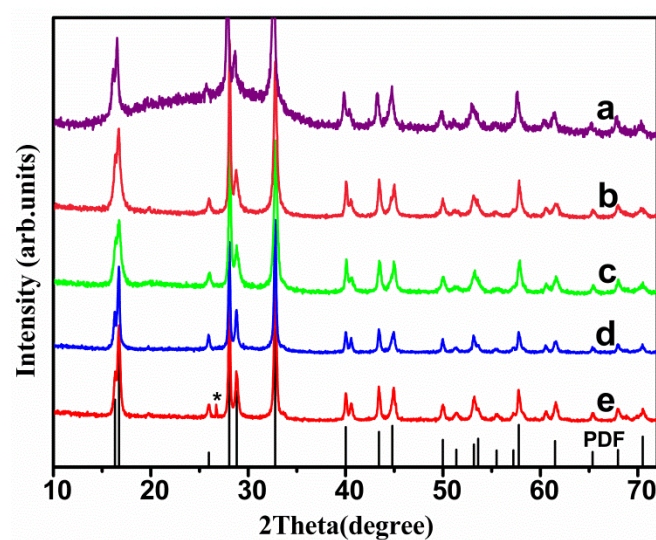


Figure S1. XRD patterns of as-synthesized Na₃(VPO₄)₂F₃ samples at 120 °C for 10 h at different molar ratio of V:P:F. (a) 1:1.2:1.67; (b) 1:3:1.67; (c) 1:4:1.67; (d) 1:5:1.67; (e) 1:6:1.67.

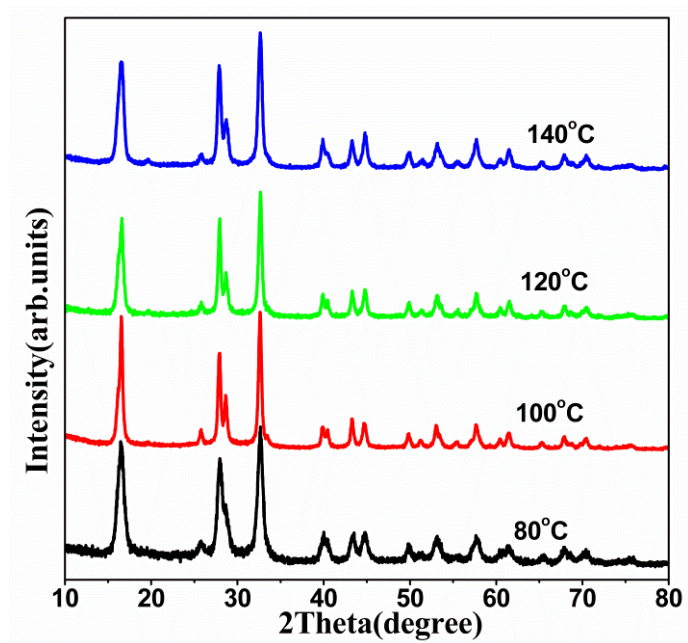


Figure S2 XRD patterns of as-synthesized $\text{Na}_3(\text{VPO}_4)_2\text{F}_3$ samples at a molar ratio of V:P:F = 1:3:1.67 at different temperatures (80 -140 °C) for 10 h.

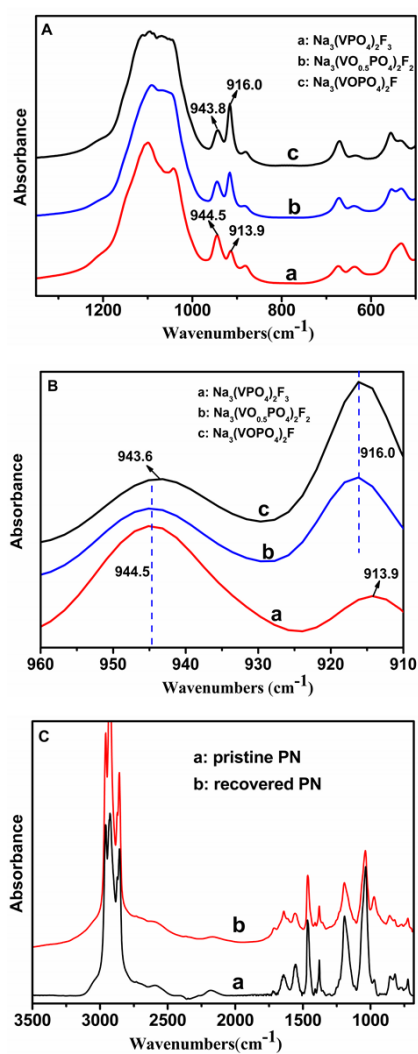
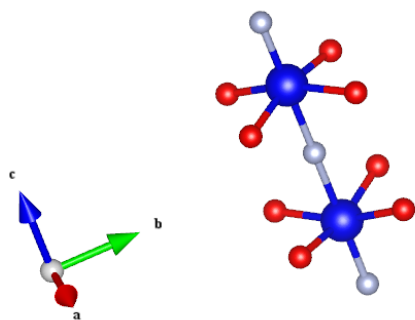
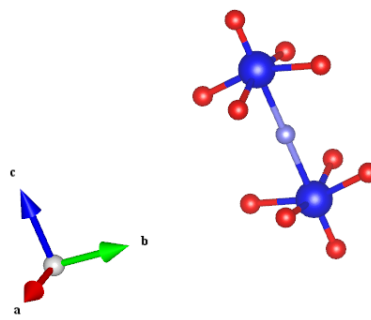


Figure S3 FTIR spectra. (A) Na₃(VPO₄)₂F₃ (a), Na₃(VO_{0.5}PO₄)₂F₂ (b) and Na₃(VOPO₄)₂F (c); (B) The enlarged range of 960 - 910 cm⁻¹ in A. (C) the recovered PN and pristine PN.

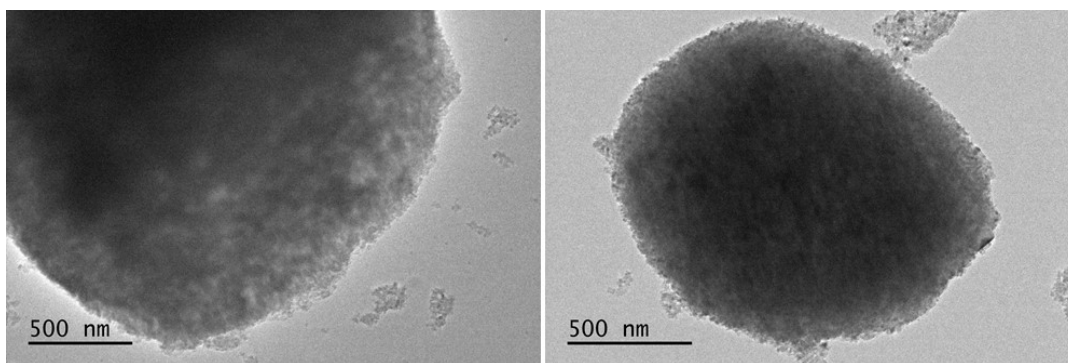


(A) $V_2O_8F_3$ (V^{3+})



(B) $V_2O_{10}F$ (V^{4+})

Figure S4 Crystal geometries of $V_2O_8F_3$ (V^{3+}) (A) and $V_2O_{10}F$ (V^{4+}) (B), red ball: oxygen; blue ball: vanadium; grey ball: fluorine



(A)

(B)

Figure S5 Typical TEM images for porous $\text{Na}_3(\text{VPO}_4)_2\text{F}_3$ (A) and $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ (B) samples.

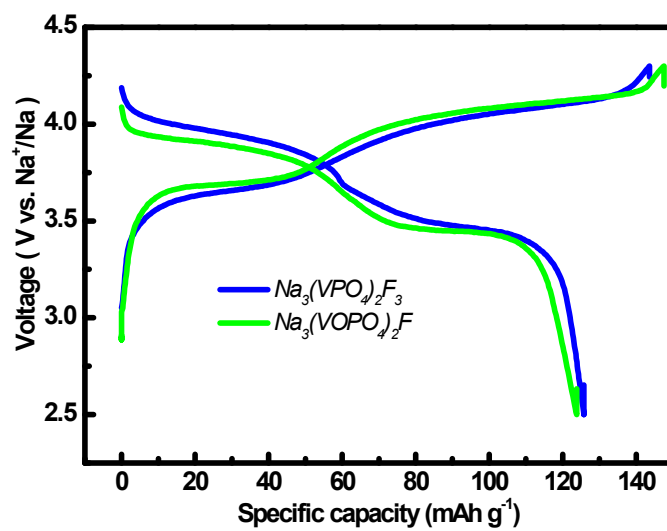


Figure S6 Comparison of the first charge and discharge curves of $\text{Na}_3(\text{VPO}_4)_2\text{F}_3$ and $\text{Na}_3(\text{VOPO}_4)_2\text{F}$ electrodes.

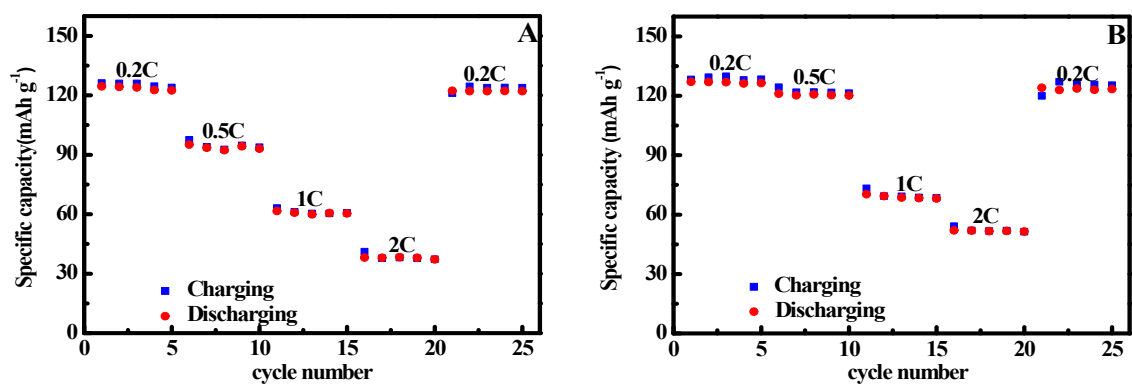


Figure S7 Comparison of the rate performance of Na₃(VPO₄)₂F₃ (A) and Na₃(VOPO₄)₂F (B) electrodes.