Supporting Information

High-energy nanostructured $Na_3V_2(PO_4)_2O_{1.6}F_{1.4}$ cathode for sodium-ion batteries and a new insight into its redox chemistry

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Experimental section

Synthesis

All the reagents and solvents were purchased from commercial suppliers and used without further purification. Vanadyl (IV) acetylacetonate (VO(C₅H₇O₂)₂) and vanadium (III) acetylacetonate (V(C₅H₇O₂)₃) were used as vanadium resources, while H₃PO₄ (85%) and NaF were used as phosphorus and fluorine resources in the synthesis of Na₃V₂(PO₄)₂F_{3-2y}O_{2y} ($0 \le y \le 1$). In order to obtain Na₃V₂(PO₄)₂F_{3-2y}O_{2y} ($0 \le y \le 1$) compounds with different valence state of vanadium and fluorine content, different molar ratio of VO(C₅H₇O₂)₂ and V(C₅H₇O₂)₃ was used as precursors rather than altering the amount of fluorine sources. The slight excess of H₃PO₄ and NaF (V: P: F=1: 1.5: 1.7) was employed instead of the stoichiometry in order to guarantee that vanadium precursors can react completely. The overall reaction can be written as follows:

$$\begin{split} \mathsf{yVO}(\mathsf{C}_{5}\mathsf{H}_{7}\mathsf{O}_{2})_{2} + (1-\mathsf{y})\mathsf{V}(\mathsf{C}_{5}\mathsf{H}_{7}\mathsf{O}_{2})_{3} + \mathsf{H}_{3}\mathsf{PO}_{4} + 1.5\mathsf{NaF} & \rightarrow 0.5\mathsf{Na}_{3}\mathsf{V}_{2}(\mathsf{PO}_{4})_{2}\mathsf{F}_{3-2\mathsf{y}}\mathsf{O}_{2\mathsf{y}} \\ & + (3-\mathsf{y})\mathsf{C}_{5}\mathsf{H}_{8}\mathsf{O}_{2} + \mathsf{yHF} \end{split}$$

Furthermore, the syntheses were carried out by a microwave-assisted solvothermal reaction at 120 $^{\circ}$ C for 3 h using a microwave-hydrothermal parallel synthesizer (XH-8000, Beijing Xiang Hu Sci&Tech Development Co., LTD). Different kinds of reaction solvents were applied for the solvothermal reaction to investigate the effect of solvents on the electrochemical performance, and the optimized one is a mixed solvent of deionized water and ethanol with a ratio of 20:20 (mL). The representative compounds Na₃V₂(PO₄)₂F_{3-2y}O_{2y} (y = 1.0, 0.8, 0.6) were synthesized through a similar process and discussed in detail in the main article.

In the typical synthesis of $Na_3V_2(PO_4)_2O_2F$, 1.061 g (4 mmol) $VO(C_5H_7O_2)_2$ was dissolved into 20 mL deionized water and 20 mL ethanol. And then 415 uL H_3PO_4 (85%, 6 mmol) was added to this solution, followed by addition of 0.28 g (6.8 mmol) NaF under magnetic stirring. Subsequently, the solution was ultrasound-treated for 15 min and then transferred into a 100 mL Teflon-lined high pressure autoclave. Afterwards, the autoclave was capped tightly and placed in the microwave synthesizer with magnetic stirring, and the heating up time and heating preservation time were set to be 20 min and 3 h, respectively. After cooling down to room temperature, the resultant light blue precipitates were harvested by pumping filtration and thoroughly rinsed with deionized water and ethanol for 3-6 times, followed by vacuum desiccation at 80 °C for 12 h. Finally, 0.799 g powder was obtained with a yield of 96.8%. Other two compounds with an average vanadium valence state of 3.8 (y = 0.8) and 3.6 (y = 0.6) were also fabricated following the same procedure, just taking different molar ratio of VO($C_5H_7O_2$)₂ and V($C_5H_7O_2$)₃ as precursors according to the overall reaction equation. These products were obtained with yields of 96.8% (y = 1.0), 95.8% (y = 0.8), 96.2% (y = 0.6), respectively.

Materials characterization

X-ray diffraction (XRD) patterns were conducted on a Rigaku Ultima IV X-ray Diffractometer with Cu-K α radiation (V = 35 kV, I = 25 mA, λ =1.5418 Å) in the 2 θ range 10°-80°. The room-temperature XRD patterns were refined with the space group of *I4/mmm* using the Rietveld method and FullProf software. Flourier transform infrared spectroscopy (FTIR) spectra were performed with a Nexus670 infrared spectrometer (Nicolet) in the wavenumber range of 4000–400 cm⁻¹ in transmission mode. Scanning electron microscopy (SEM) micrographs were taken by a Quanta 400 FEG field emission scanning electron microscope operated at 20 kV. Transmission electron microscopy (TEM) images were taken on a JEOL JEM-2100F electron microscope operated at 200 kV. X-ray photoelectron

spectroscopy (XPS) analyses were conducted on an ESCALAB 250Xi X-ray photoelectron spectrometer operating at 150 W, with Al–K α radiation (hv = 1486.6 eV).

NMR/EPR Tests

²³Na/³¹P Solid-state Nuclear Magnetic Resonance (SSNMR) experiments were performed on a widebore 14.1 T Bruker AVANCE III spectrometer, operating at Larmor frequencies of 158.75 MHz and 242.94 MHz for ²³Na and ³¹P, respectively. Triple-resonance 2.5-mm MAS probe was used for all experiments. The ²³Na MAS spectra were acquired using a Hahn-echo pulse sequence (90° pulse-τ-180° pulse-τ-acq), with 90° pulse length of 2.0 µs, and a recycle interval of 100 ms. The ³¹P spectra were acquired with the same pulse sequence, together with the MATPASS method, using 90° pulse of 1.5 µs. Chemical shifts were calibrated with respect to NaCl (7.21 ppm for ²³Na) and NH₄H₂PO₄ (0.81 ppm for ³¹P).

¹⁹F SSNMR experiments were performed on a 14.1 T Agilent DD2 spectrometer equipped, operating at Larmor frequency of 564.69 MHz for ¹⁹F. Commercial Agilent quadrupole-resonance 3.2-mm T3 MAS probe and 3.2 mm ZrO₂ rotors were used for all experiments. The ¹⁹F MAS spectra were acquired using a one pulse sequence, with 90° pulse length of 2.5 μs (61 dB), and a recycle interval of 200 ms. All the ¹⁹F chemical shifts were referenced to 1 M CCl₃F (aq) (0 ppm).

Continuous-wave (CW) X-band EPR spectrum was performed at 2 K with a Bruker EMX plus 10/12 spectrometer, microwave power (0.1 mW), modulation amplitude (2 G), modulation frequency (100 kHz), sweep time (96 s), conversion time (16 ms) and time constant (163.84 ms) were reasonably set. The EPR signals were normalized by mass with the same series.

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Electrochemical testing

The electrochemical properties were evaluated using CR2032 coin cells with sodium disks as the counter/reference electrode. The working electrodes were made by casting a slurry of 70 wt % active materials, 20 wt % acetylene black, and 10 wt % carboxymethyl cellulose (CMC) binder in deionized water on an aluminium foil and dried at 110 °C for 3 hours in vacuum. The loading density of active materials on each piece of working electrode (14 mm) is about 2.0-2.5 mg/cm². The electrolyte was made with 1 mol L⁻¹ NaPF₆ dissolved in ethylene carbonate (EC) and propylene carbonate (PC) (1:1 in v/v) containing 5 vol % fluoroethylene carbonate (FEC) additive, and 60 µL electrolyte is used for each cell. Whatman glassy fiber (GF-D) was employed as the separator. All the cells were assembled in an Ar-filled glovebox with oxygen and water less than 0.1 ppm and were tested at 25 $^{\circ}$ C. The galvanostatic charge and discharge tests were performed on a LAND 2001A battery test system in the voltage range of 2.0-4.8 V vs. Na⁺/Na for half cells. All the specific capacities were calculated based on the total mass of $Na_3V_2(PO_4)_2F_{3-2y}O_{2y}$ (y = 1, 0.8, 0.6). Cyclic voltammetry (CV) testing was carried out on a CHI660e electrochemical workstation at the varied scan rates from 0.1 to 1 mV s⁻¹. Electrochemical impedance spectra (EIS) were also conducted on a CHI 660a electrochemical workstation with the frequency range of 0.01 Hz to 100 KHz. The charged and discharged samples at given states-of-charge (SOC) were collected by disassembling the electrochemical cells inside an Ar-filled glovebox and then washed several times with PC. The wet electrodes were dried overnight at room temperature in Ar-filled glovebox before being packed into the rotors for the SSNMR experiments or the paramagnetic quartz tubes for EPR tests.



Fig. S1 (a) XRD patterns and yields of the as-synthesized NVOPF samples at different solvothermal reaction solvents for 3 h and (b) the corresponding cycling performances of these products at a current rate of 1C in the potential window of 2.0-4.3 V *vs.* Na⁺/Na. It is obvious that a mixed solvent of deionized water and ethanol with a ratio of 20:20 (mL) is the optimized choice considering on both the yield and Na storage performance.



Fig. S2 SEM micrographs of the as-synthesized (a) NVOPF and (b) NV_{3.6}OPF.



Fig. S3 (a, b, c) XPS survey spectra of NVOPF, $NV_{3.8}OPF$, and $NV_{3.6}OPF$, respectively.

a	Na	V	Ρ	ο	F
b	Na	v	Ρ	0	F
C	Na	v	P	0	Р. С.

Fig. S4 (a, b, c) EDX elemental mapping images of NVOPF, NV $_{3.8}$ OPF and NV $_{3.6}$ OPF, respectively.



Fig. S5 (a) ³¹P MAS NMR spectra obtained by using a Hahn-echo pulse sequence (90°- τ -180°- τ -acq) of the NVOPF (v_R = 23 KHz), NV_{3.8}OPF (v_R = 25 KHz), and NV_{3.6}OPF (v_R = 25 KHz), respectively. (b) Isotropic ³¹P MAS NMR spectra of NVOPF, NV_{3.8}OPF, and NV_{3.6}OPF obtained by extracting center row slice from the 2D MATPASS spectra.

Solid-state NMR characterization of paramagnetic solids is often very difficult because the strong hyperfine couplings between unpaired electron and nuclear spin give rise to large paramagnetic shifts and shorten the lifetime of nuclear magnetization. This problem can be partially solved by applying fast MAS to reduce the overlap between the main peaks from spinning sidebands. However, when the spinning speed is limited or the hyperfine coupling is too large, the isotropic peaks are often overlapped with nearby spinning sidebands. This problem is encountered in our work where the introduction of V³⁺ ions leads to larger hyperfine coupling. As show in **Fig. S5a**, the overlapping becomes more apparent with increasing content of V³⁺.

To aid the spectra assignment, we then applied projection-MATPASS method (MAT: magic-angle turning, PASS: phase-adjusted sideband separation) which allows the resolving of isotropic and anisotropic interactions in a simple 2D experiment, as displayed in **Fig. S5b**.¹⁻ ³ This method has been successfully applied in the recording of high-resolution SSNMR spectra of lithium battery materials.



Fig. S6 ¹⁹F MAS SSNMR spectra of the obtained NVOPF, NV_{3.8}OPF, and NV_{3.6}OPF, respectively.



Fig. S7 Fully displayed continuous-wave X-band EPR spectra of (a) NV_{3.8}OPF and (b) NV_{3.6}OPF recorded under 2 K.



Fig. S8 Galvanostatic charge/discharge voltage profiles of the (a) NVOPF, (b) $NV_{3.8}OPF$, and (c)

 $\mathsf{NV}_{3.6}\mathsf{OPF}$ electrodes under various current rates.



Fig. S9 (a, b, c) CV profiles at various scan rates from 0.2 to 1.0 mV s⁻¹ of the NVOPF, NV_{3.8}OPF and NV_{3.6}OPF electrodes. (d, e, f) The corresponding linear fittings for the relationship between i_p and $v^{1/2}$ from CV profiles.

The Na⁺ apparent diffusion coefficient ($D_{app,Na}$) can be calculated according to the following Randles-Sevcik equation S1:^{4, 5}

$$I_p = 2.69 \times 10^5 n^{3/2} A D_{app, Na}{}^{1/2} C_0 v^{1/2}$$
(S1)

where I_p (A) is the peak current, *n* is the charge transfer number per molecule formula during the redox reaction (*n* = 2 for the present NVOPF, NV_{3.8}OPF, and NV_{3.6}OPF), *A* (cm²) is the surface area of the electrode, C_0 is the concentration of inserted Na⁺ in the electrode (7.7 × 10⁻³ mol cm⁻³),⁶ v (V s⁻¹) is the scan rate, and $D_{app,Na}$ (cm² s⁻¹) is the Na⁺ diffusion coefficient.

Fig. S9d, e, f present the linear fitting profiles between i_p and $v^{1/2}$. The excellent fitting results imply that the Na-intercalation/extraction reactions of NVOPF, NV_{3.8}OPF and NV_{3.6}OPF are diffusion-controlled processes. Hence, the apparent Na⁺ diffusion coefficients ($D_{app,Na}$) were calculated according to the Randles-Sevcik equation, as summarized in **Table S1**. The $D_{app,Na}$ values of the NV_{3.8}OPF electrode for peaks A1, C1, A2, and C2 are 4.84×10^{-11} , 1.04×10^{-11} , 1.86×10^{-11} , and 1.81×10^{-11} cm² s⁻¹, respectively, which are much larger than those of NVOPF except for peak C1, indicating that both Na⁺ extraction/intercalation processes are kinetically more rapid with higher ionic conductivity. Further substitution with V³⁺O₄F₂ shows no further improvement in $D_{app,Na}$ values, which matches well with the EIS results (Fig. 3d). In general, the V³⁺O₄F₂ local environment in NV_{3.8}OPF would improve the intrinsic conductivity (V³⁺ contains two unpaired electrons, whereas V⁴⁺ contains only one) and make the structure less rigid to assist Na⁺ diffusion. It has also been reported that the intermediate phase Na₂V₂(PO₄)₂O_{1.6}F_{1.4} (space group: *I4/mmm*) shows dramatically increased electrical conductivity (by 5 orders of magnitude) in contrast to the pristine state, which contributes to the excellent rate capability. Besides, too much F anions in NV_{3.6}OPF can provide exceptionally strong inductive effects, which would in turn impede Na⁺ diffusion and enhance electrochemical polarization. Hence, it is not surprising that $NV_{3.8}OPF$ with a moderate amount of $V^{3+}O_4F_2$ local environment exhibits the best Nastorage performance among all the studied materials.

	NVOPF	NV _{3.8} OPF	NV _{3.6} OPF
A1	2.37 × 10 ⁻¹¹	4.84 × 10 ⁻¹¹	3.98 × 10 ⁻¹¹
C1	1.43 × 10 ⁻¹¹	1.04 × 10 ⁻¹¹	7.03 × 10 ⁻¹²
A2	1.40×10^{-11}	1.86 × 10 ⁻¹¹	9.58 × 10 ⁻¹²
C2	1.47 × 10 ⁻¹¹	1.81 × 10 ⁻¹¹	1.25 × 10 ⁻¹¹

Table S1. The calculated $D_{app,Na}$ (cm² s⁻¹) for the NVOPF, NV_{3.8}OPF, and NV_{3.6}OPF electrodes.



Fig. S10 Cyclic performance of the $NV_{3.6}OPF$ electrode under 5C.



Fig. S11 ex-situ TEM image of the $NV_{3.8}OPF$ electrode after cycling at 2C for 300 cycles.



Fig. S12 Rescaled continuous-wave X-band EPR spectra of pristine and full-charged $NV_{3.8}OPF$ electrodes.

Supplementary references

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