Electronic Supporting Information

Dual anionic substitution engineering advanced NASICON phosphate cathode in sodium-ion batteries

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Experimental section

Sample preparation:

VPO_4 & $VOPO_4$ sample preparation:

According to the corresponding stoichiometric ratio, the V_2O_5 (Sigma-Aldrich, 99%), $H_2C_2O_4{\cdot}2H_2O$ (Sigma-Aldrich, 99%) (molar ratio = 1:3) and $NH_4H_2PO_4$ (Sigma-Aldrich, 99%) were stirred in deionized water at 70 °C for 3 h by the liquid phase method. The solution was dried at 120 °C for 12 h to obtain a solid powder. And then sintered in an argon or air atmosphere at 750 °C for 8 h to obtain the VPO_4 or $VOPO_4$ sample, respectively.

$Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x}$ ($0 \leq x \leq 1$) sample preparation:

Mix VPO_4, $VOPO_4$, Na_2CO_3 (Sigma-Aldrich, 99%) and NaF (Sigma-Aldrich, 99%) in a stoichiometric ratio as precursors and subject them to wet ball milling. By controlling

the ratio of VPO_4 and $VOPO_4$, the precursor in the different F/O ratio further changes. Specifically, the reaction was carried out according to formula (1)[1]:

$$(1-x)VOPO_4 + xVPO_4 + \left(\frac{1}{2}+x\right)NaF + \left(\frac{1-x}{2}\right)Na_2CO_3 \rightarrow \frac{1}{2}Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x} + gas \quad (1)$$

The mixed precursors in absolute ethanol were performed by planetary ball-milling at a speed of 500 rpm for 20 h. The resulting slurry was dried at 80 °C for 12 h, and then sintered at 750 °C for 1.5 h in Ar atmosphere. In the end, powder samples of $Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x}$ ($0 \leq x \leq 1$) with different x values are obtained. The F/O ratio is determined by the molar ratio of VPO_4 and $VOPO_4$. According to Formula 1, the vanadium in $Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x}$ with specific valence state could been obtained by adjusting the ratio of VPO_4 and $VOPO_4$.

Materials characterization:

The X-ray diffractometer (D8 Bruker) is used to collect X-ray diffraction (XRD) of samples, which uses Cu K_α radiation (λ = 1.5406 Å) in the scanning range (2θ) of 5-80° to collect materials‘ composition information. The morphology of the samples was investigated by Hitachi SU8000 scanning electron microscopy (SEM) operating at 10 kV. The images of transmission electron microscopy (TEM) were collected on the JEOL-2100F. The Fourier transform infrared (FTIR) spectrum was made to analyze the chemical bond on Nicolet 6700. The X-ray photoelectron spectroscopy (XPS) was performed on the corresponding spectrophotometer (ESCALABMKLL).

Electrochemical measurement:

A specific proportional slurry of active material, carbon black, and sodium carboxymethylcellulose (CMC, Sigma-Aldrich) was mixed at a mass ratio of 7:2:1,

dispersed in deionized water and casted on aluminum foils. The loading density of active material on the working electrodes was about 1.0-1.5 mg cm^{-2}. After drying in vacuum at 60 °C for 12 h, the electrodes transferred to the argon-filled atmosphere glovebox for assembling the coin cells (CR2032). Na metal (Sigma-Aldrich) and glass microfiber filter (Whatman) were employed as counter electrode and separator, respectively. The electrolyte composition was 1 M $NaClO_4$ with the solvent propylene carbonate (PC) and the additive 5 vol % fluoroethylene carbonate (FEC). The battery testing system (Neware CT-4000) was used to test galvanostatic charge/discharge (GCD) in the voltage window of 2.0 V-4.3 V *vs*. Na^+/Na at room temperature. CHI600E electrochemical workstation was carried on testing cyclic voltammetry (CV) at different scanning rates in 2.0 V-4.3 V *vs*. Na^+/Na.

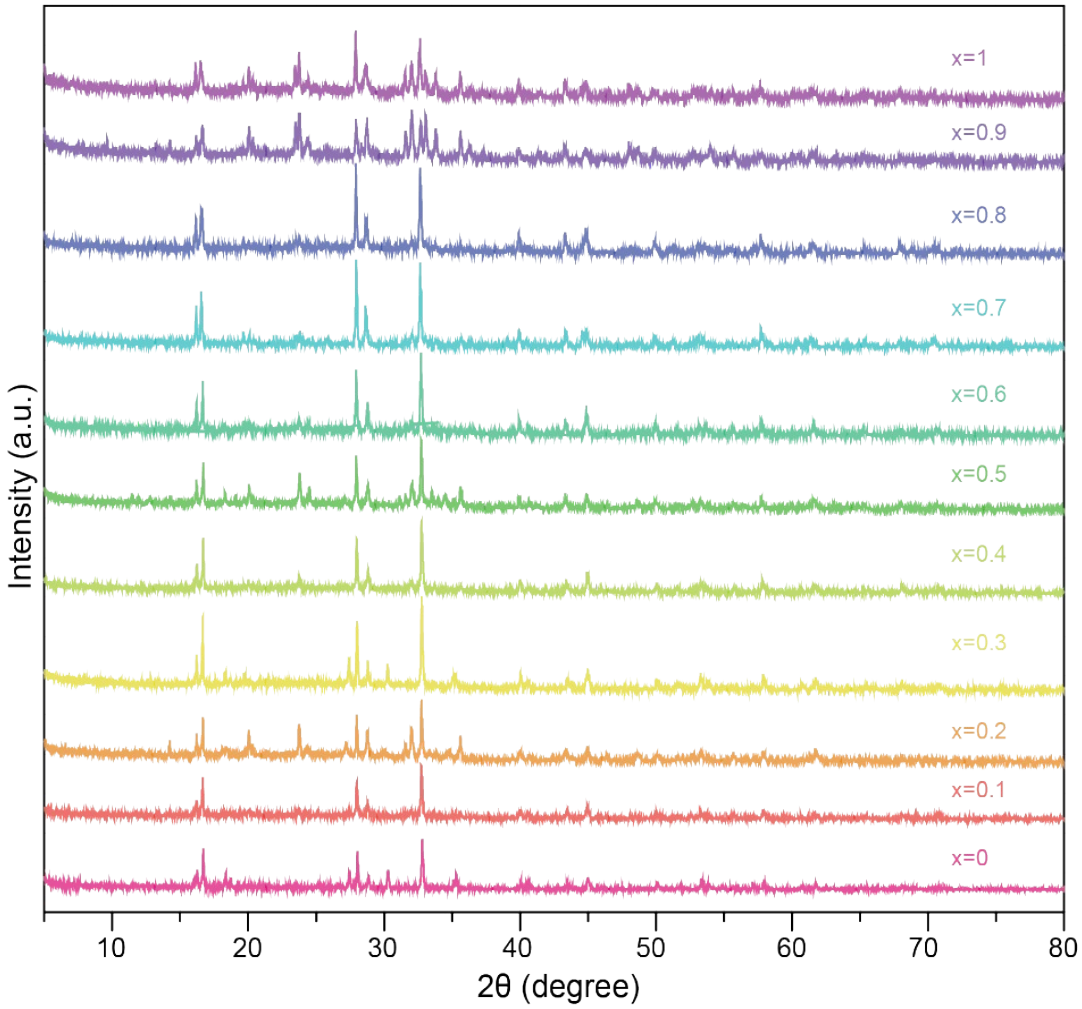

Figure S1 XRD patterns of the as-synthesized $Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x}$ ($0 \leq x \leq 1$).

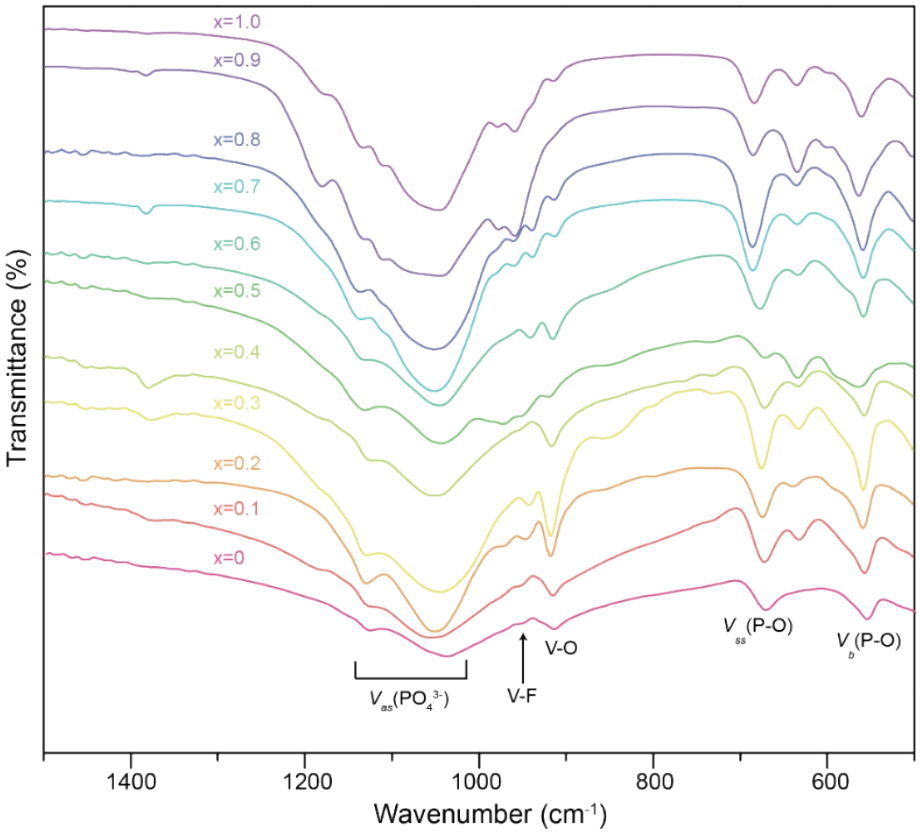

Figure S2 FTIR spectra of the as-synthesized $Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x}$ ($0 \leq x \leq 1$).

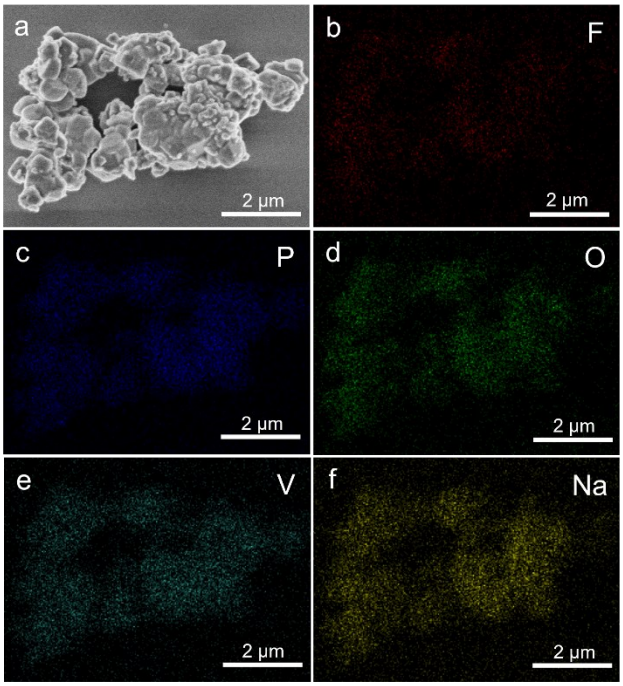

Figure S3 SEM image and corresponding EDS mapping of the as-synthesized $Na_3V_2(PO_4)_2O_{0.6}F_{2.4}$.

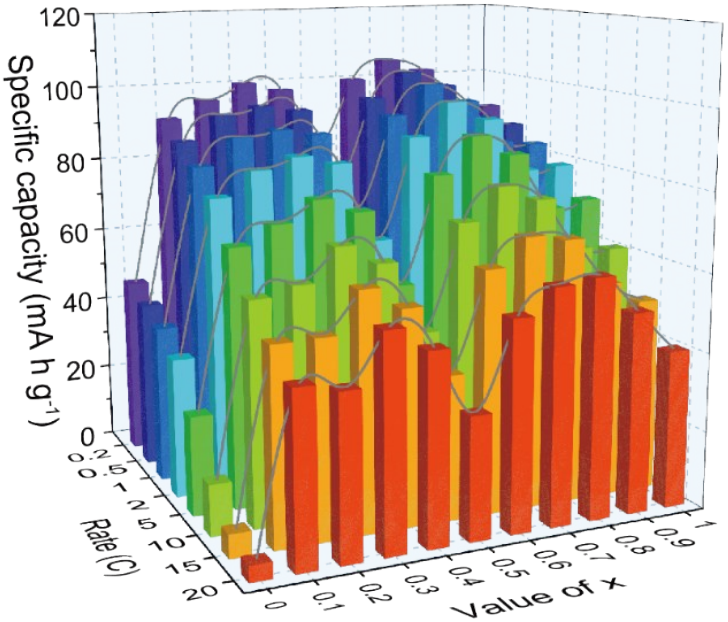

Figure S4 The rate performance of the $Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x}$ ($0 \leq x \leq 1$) from 0.2 C to 20 C.

Table S1 The ICE of $Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x}$ materials.

x in $Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x}$	ICE
0	96.18%
0.3	84.93%
0.5	81.58%
0.7	89.38%
1	88.12%

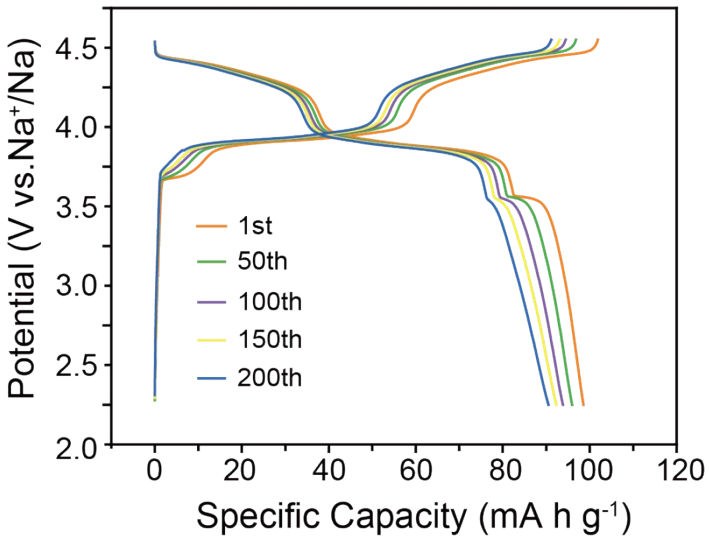

Figure S5 The GCD curves of $Na_3V_2(PO_4)_2O_{0.6}F_{2.4}$ during different cycles at 0.5 C.

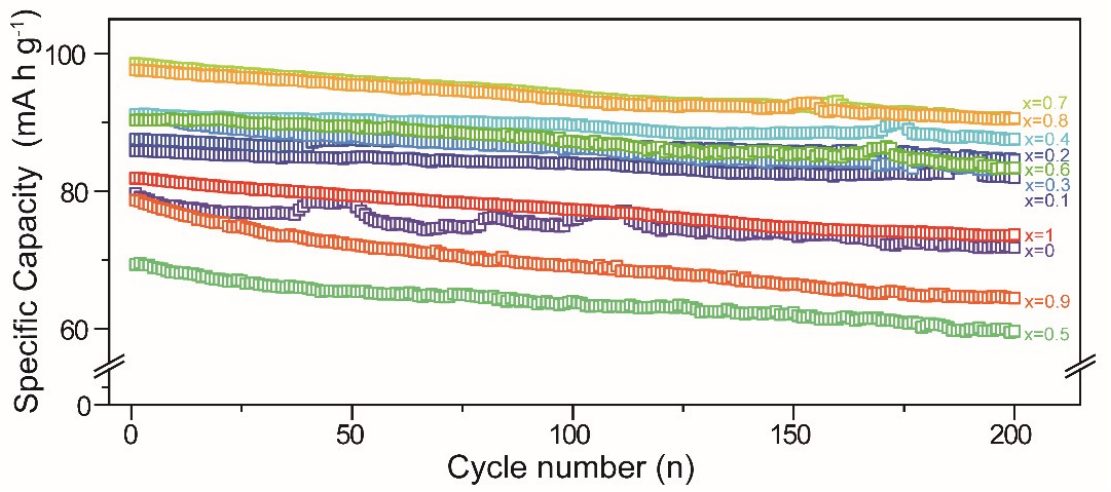

Figure S6 The cycle performance of the $Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x}$ ($0 \leq x \leq 1$) at 0.5 C.

Calculation process $D_{app,Na}$ through CV tests:

The $D_{app,Na}$ was calculated from the following Randles-Sevcikequation (2)[2]:

$$i_p = 2.69 \times 10^5 n^{\frac{3}{2}} A D_{app,Na}^{\frac{1}{2}} C_0 v^{\frac{1}{2}} \quad (2)$$

where i_p is the peak current density, n is the electron-transfer number per molecule formula during the redox reaction, A is the surface area of the electrode, C_0 is the concentration of Na^+ in the electrode, and v is the scan rate.

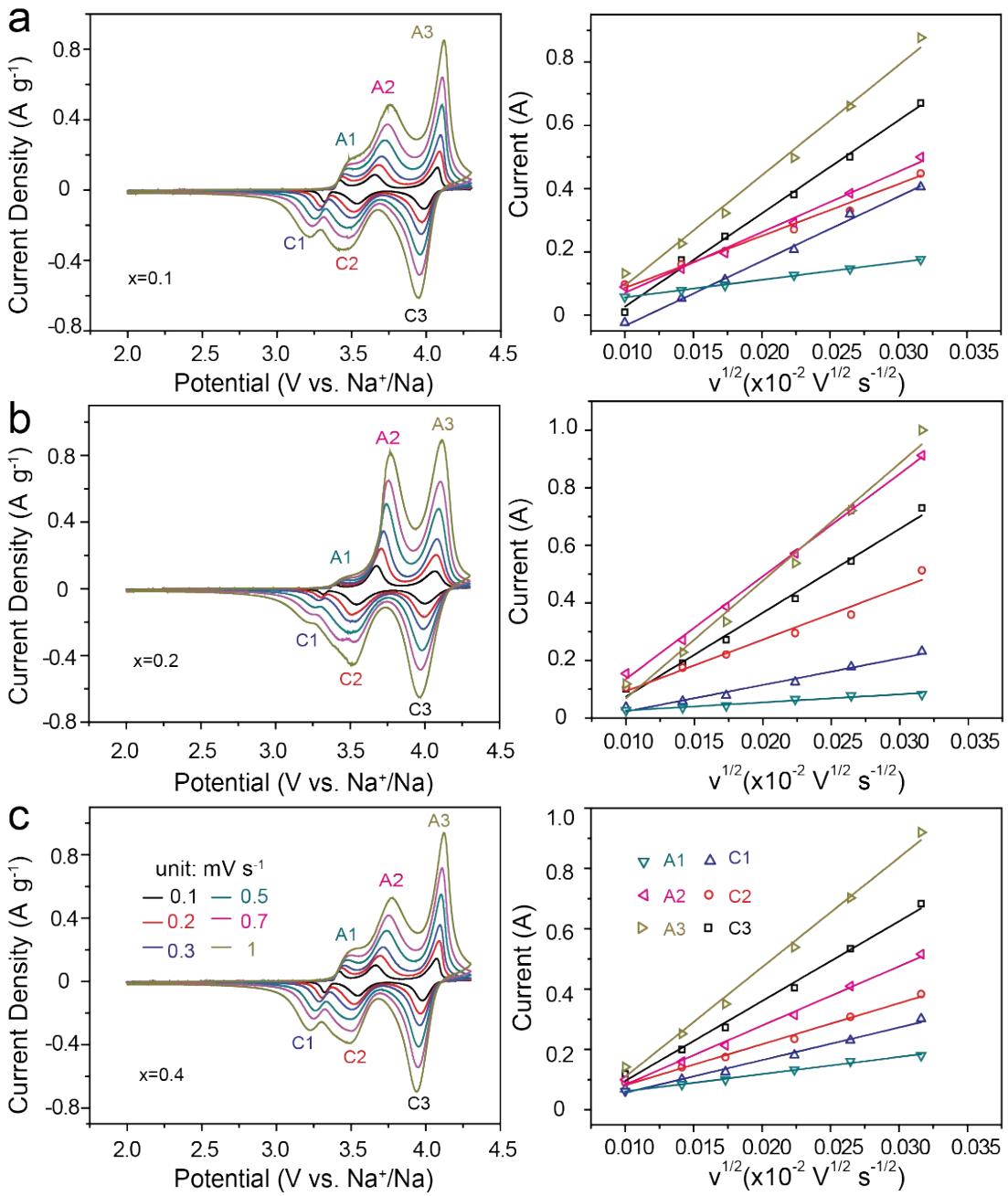

Figure S7 The CV test results and fitting curves of the $Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x}$ (x = 0.1, 0,2, 0,4).

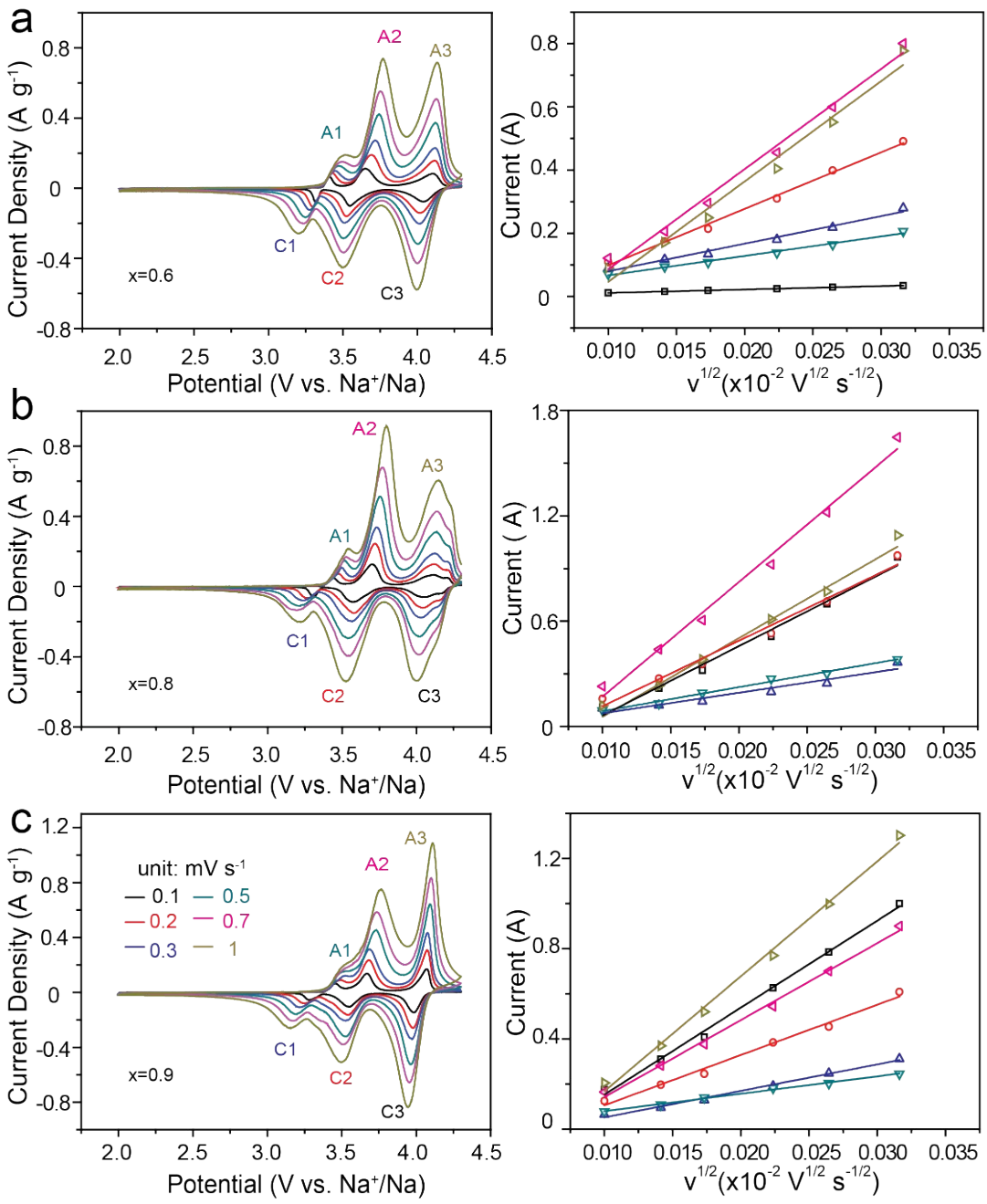

Figure S8 The CV test results and fitting curves of the $Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x}$ (x = 0.6, 0.8, 0.9).

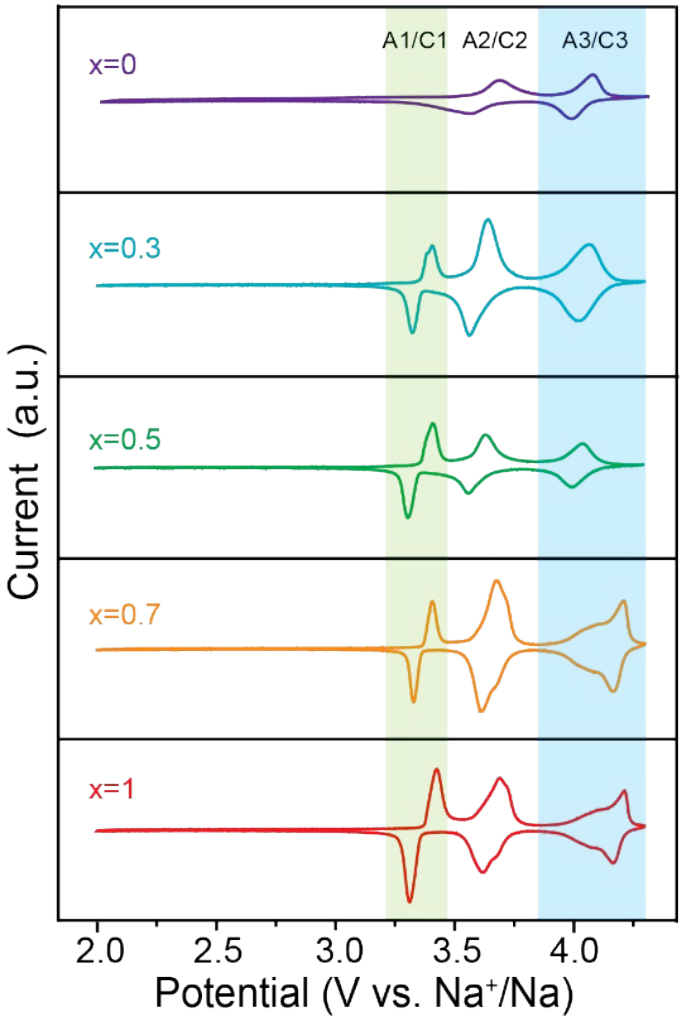

Figure S9 The CV test results of the $Na_3V_2(PO_4)_2O_{2-2x}F_{1+2x}$ (x = 0, 0.3, 0.5, 0.7, 1).

References

S1. Y.-U. Park, D.-H. Seo, H. Kim, J. Kim, S. Lee, B. Kim and K. Kang, A Family of High-Performance Cathode Materials for Na-ion Batteries, $Na_3(VO_{1-x}PO_4)_2F_{1+2x}$ ($0 \leq x \leq 1$): Combined First-Principles and Experimental Study, *Adv. Funct. Mater.*, 2014, **24**, 4603-4614.

S2. L. Q. Xu, J. Y. Li, Y. T. Li, P. Cai, C. Liu, G. Q. Zou, H. S. Hou, L. P. Huang and X. B. Ji, Nitrogen-doped Carbon Coated $Na_3V_2(PO_4)_3$ with Superior Sodium Storage Capability, *Chem. Res. Chin. Univ.*, 2020, **36**, 459-466.