Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Electronic Supplementary Information

A NASICON-Type $Na_{3.67}Cu_{0.17}Fe_{0.5}V_{1.33}(PO_4)_3$ Cathode with Multi-Electron Reaction for High-Density Sodium-Ion Battery

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Experimental Section

Characterization. X-ray diffraction (XRD) measurements are performed on a Bruker D8 Discover utilizing the X-ray diffractometer with Cu Kα X-ray source (λ = 1.5406 Å). Scanning electron microscope (SEM) images are collected using a JEOL-7100F microscope. Transmission electron microscopy (TEM) images and energy dispersive spectroscopy (EDS) mappings are collected on a JEOL JEM - 2100F STEM/EDS microscope. Raman spectroscopy is performed with the Horiba LabRAM HREvolution. The chemical bonding information of the materials is obtained by Fourier Transform Infrared Spectroscopy (FT-IR, Nicolet iS50). X-ray photoelectron spectroscopy (XPS) spectra are collected with a VG Multilab 2000. An ASAP 2020 analyser is used to acquire nitrogen adsorption-desorption isotherms to assess the BET specific surface area and pore size distribution of the materials. Thermogravimetric analysis (TGA) tests are performed using a thermogravimetric analyzer type STA-449C in an air with a ramp rate of 10 °C min^{-1}.

Electrochemical Characterization. The electrochemical properties are tested in CR2016 coin-type cells. To prepare the slurry, the active material (70 wt.%), acetylene black (20 wt.%), and polyvinylidene fluoride (10 wt.%) are dispersed in N-methyl-pyrrolidone. After stirring for 12 hours, the slurry is coated onto aluminum foil, and dried in vacuum for 12 hours. The cathode is punched into electrode sheets with a diameter of 10 mm and the areal mass loading of the active material is 0.9-1.5 mg cm^{-2}. Sodium disks of 14 mm diameter are used as reference and counter electrodes. 1.0 M $NaPF_6$ in vinyl carbonate/polycarbonate (1:1 w/w) with 1 wt.% $NaClO_4$ is used as the electrolyte.

Whatman GF/D glass fibre diaphragm is used as the separator. Galvanostatic charge/discharge testing in the 1.5-3.8V *vs.* Na/Na^+ potential window is carried out using a multi-channel battery test equipment (LAND CT2001A). Cyclic voltammetry (CV) tests and electrochemical impedance (EIS) tests at frequencies ranging from 0.1 Hz to 100 kHz are performed using the Autolab PGSTAT 302N electrochemical workstation.

The full cells are assembled with NCFVP as the cathode, pre-sodiated hard carbon (HC) as the anode, Whatman GF/D glass fibre diaphragm as the separator, and 1.0 M $NaPF_6$ dissolved in vinyl carbonate/polycarbonate (1:1 w/w) with 1 wt.% $NaClO_4$ as the electrolyte. The HC anodes are prepared by dispersing commercial hard carbon (70 wt.%), acetylene black (20 wt.%), and polyvinylidene fluoride (10 wt.%) in N-methyl pyrrolidone, and then coated onto a copper foil and vacuum-dried at 100 °C for 12 h. The HC electrodes are 12 mm diameter discs with area load in the range of 0.5-0.7 mg cm^{-2}. For the pre-sodiumation of HC, CR2016 cells are assembled using HC as the work electrode, Na as the counter electrode, Whatman GF/D glass fibre diaphragm as the separator, and 1.0 M $NaPF_6$ in tetrahydrofuran as the electrolyte. After three cycles at a current density of 15 mA g^{-1} in a potential window of 0.01-2.0 V, the HC electrodes are disassembled from the coin cell for full cell assembly.

In-situ XRD measurements are carried out on a Bruker D8 Discover X-ray diffractometer with a planar detector. The cathode, which contains polytetrafluoroethylene (10 wt.%), acetylene black (20 wt.%), and active material (70 wt.%), is divided into square sheets with a surface area of around 1 cm^2 and a thickness of roughly 0.1 mm. The cathode is positioned on the backside of an X-ray transparent Be

window that also acts as the current collector. During the charge/discharge procedures, the in-situ XRD signals are gathered in the 2θ range of 20^{o} to 50^{o} with a still mode and each pattern is captured in 120 s.

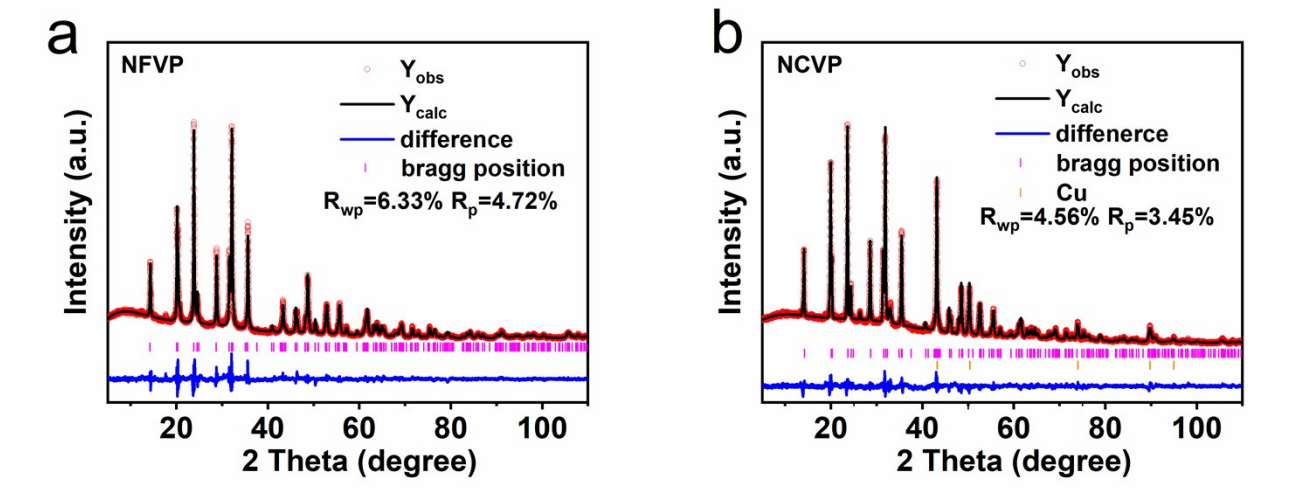

Figure S1. Rietveld refinement of the XRD patterns of (a) NFVP and (b) NCVP.

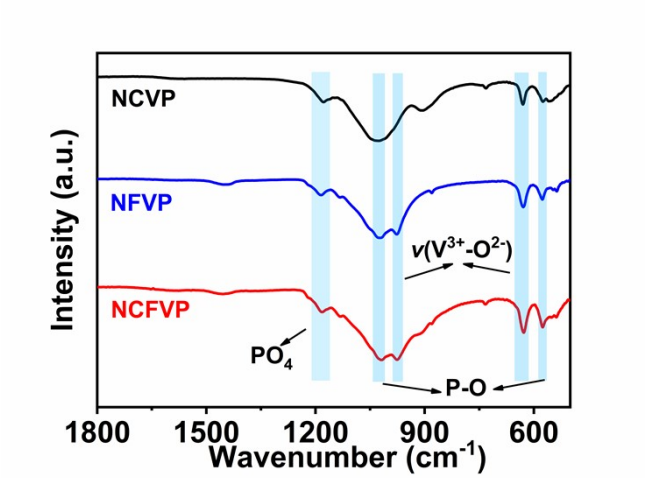

Figure S2. FI-IR spectra of NCFVP, NFVP, and NCVP.

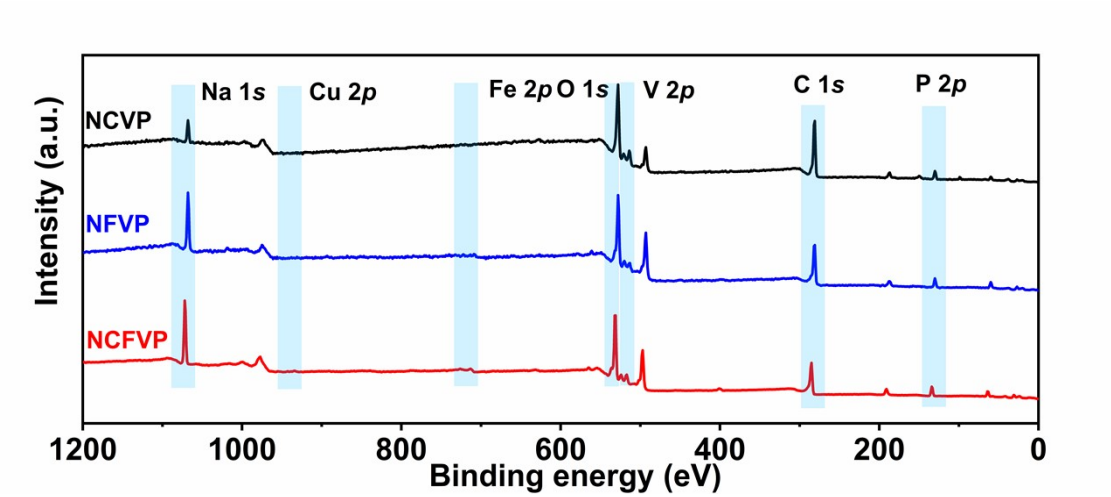

Figure S3. XPS survey spectra of the NCFVP, NFVP, and NCVP.

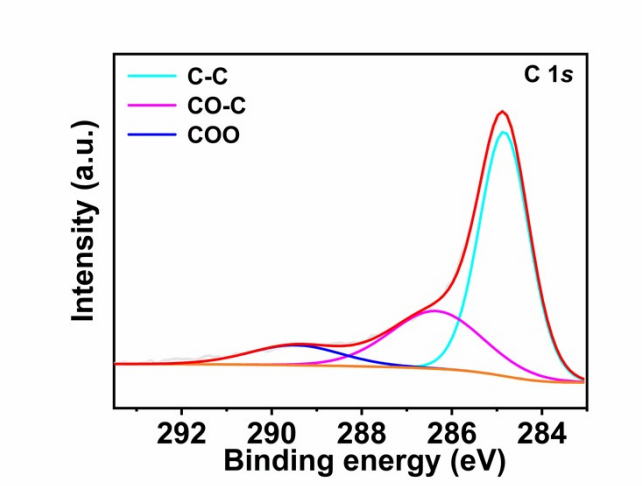

Figure S4. C 1*s* XPS spectra of NCFVP.

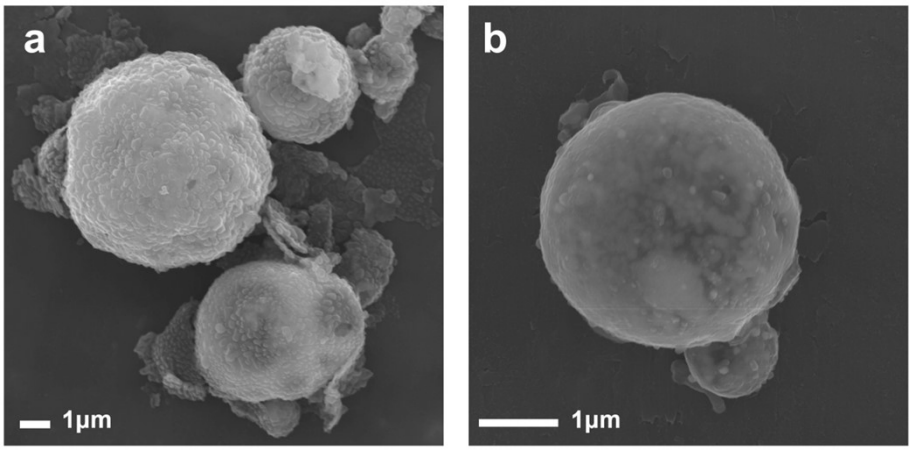

Figure S5. SEM images of (a) NFVP and (b) NCVP.

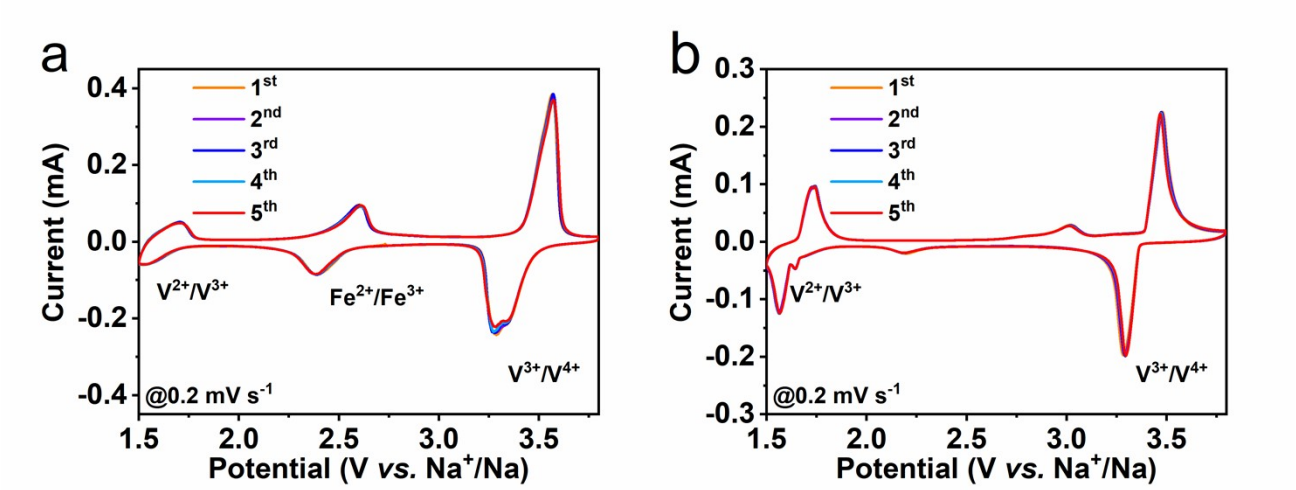

Figure S6. CV profiles of (a) NFVP and (b) NCVP at 0.2 mV s^{-1}.

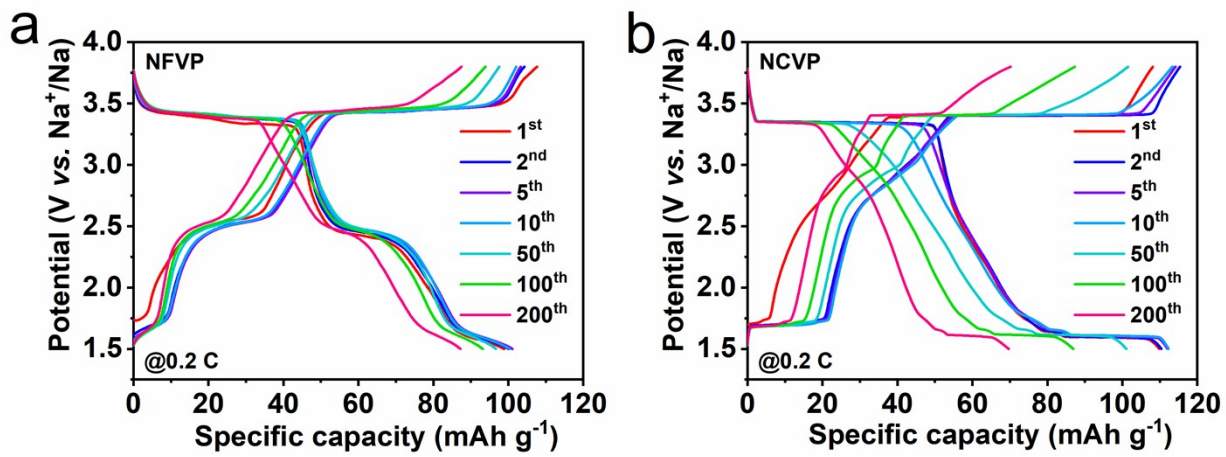

Figure S7. (a) GCD curves of (a) NFVP and (b) NCVP at 0.2 C.

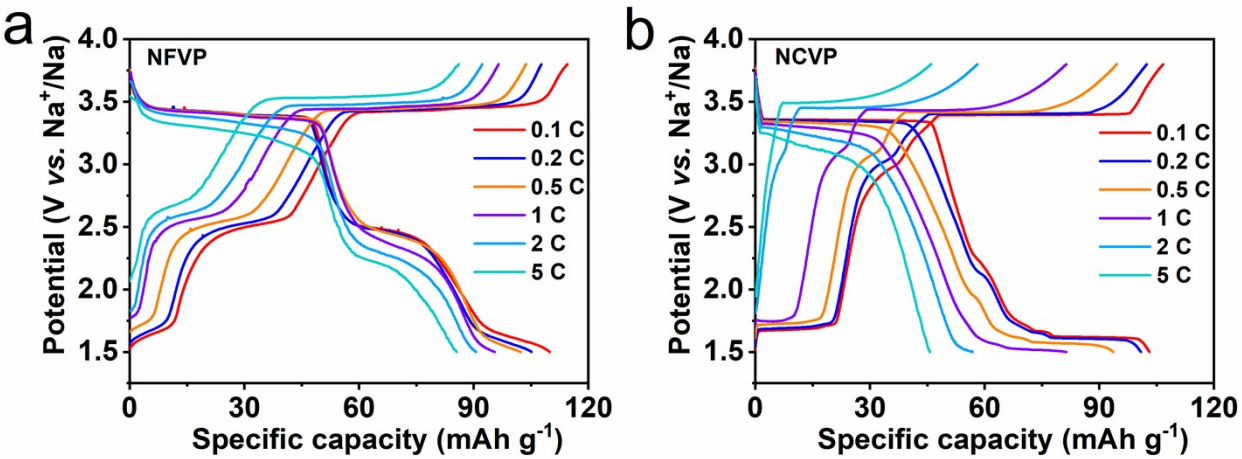

Figure S8. GCD curves of (a) NFVP and (b) NCVP at different C-rates.

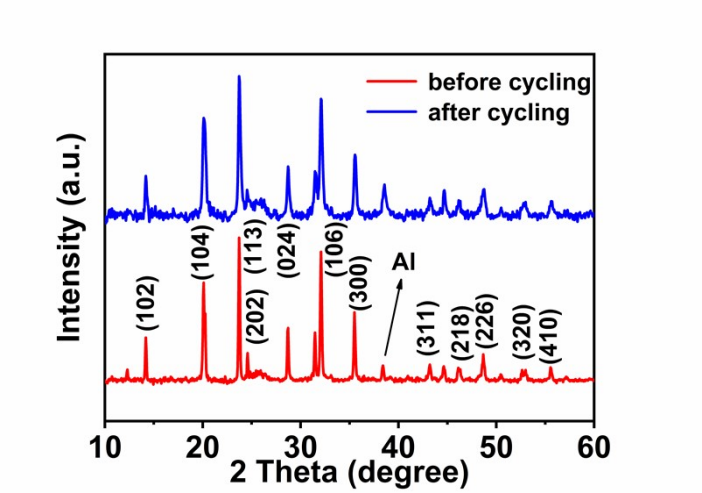

Figure S9. XRD patterns of the electrode before and after cycling.

The D_{Na^+} values can be calculated based on the following equation：

$$D_{Na+} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \qquad \left(\tau \ll \frac{L^2}{D_{Na+}}\right)$$

where τ is the relaxation time, S is the electrode/electrolyte contact area, m_B, M_B and V_M are the active material mass, molar mass, and molar volume of the electrode, respectively, L is the average radius of the material particles, ΔE_τ is the variation of the voltage during the constant current pulse, and ΔE_s is the difference in the voltage during the open-circuit period.

A linear relationship is fitted between the peak current (I_p) and the square root of the scan rate (v), according to the Randles-Sevick equation.

$$Ip = 269000 n^{\frac{3}{2}} A D_{Na+}^{\frac{1}{2}} C_{Na+} v^{\frac{1}{2}}$$

where Ip is the peak current, n is the number of electrons transferred by the NCFVP during charge/discharge process, A is the area of the NCFVP electrode, D_{Na^+} is the diffusion coefficient, C_{Na^+} is the concentration of Na^+, and v is the scan rate.

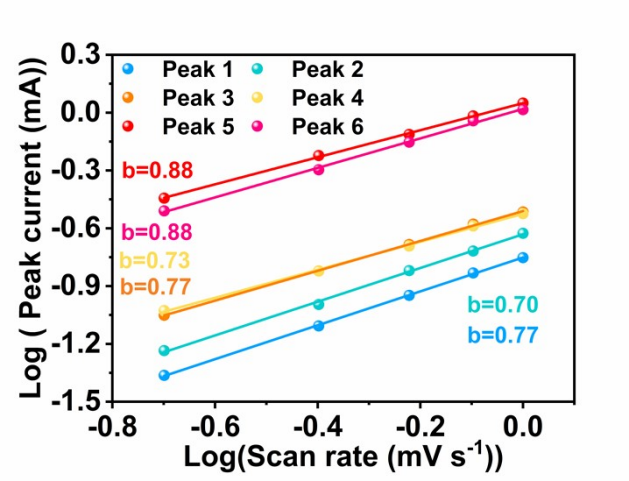

Figure S10. The Log (peak current) as a function of Log (scan rate).

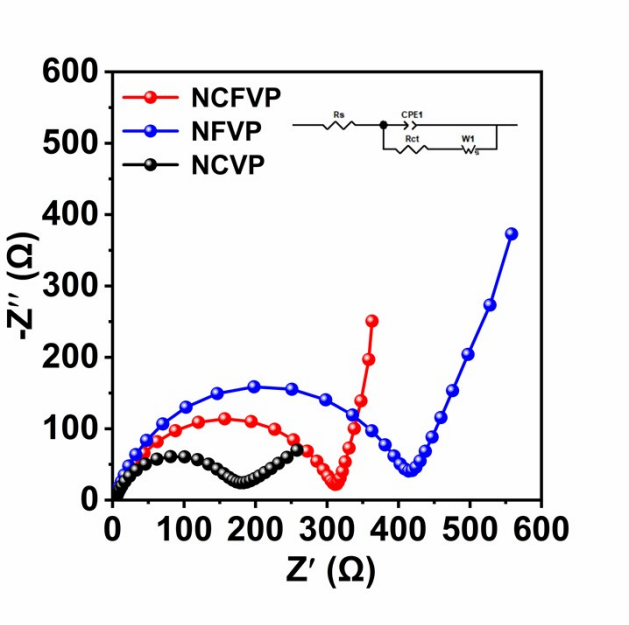

Figure S11. EIS plots of the NCFVP, NFVP, and NCVP.

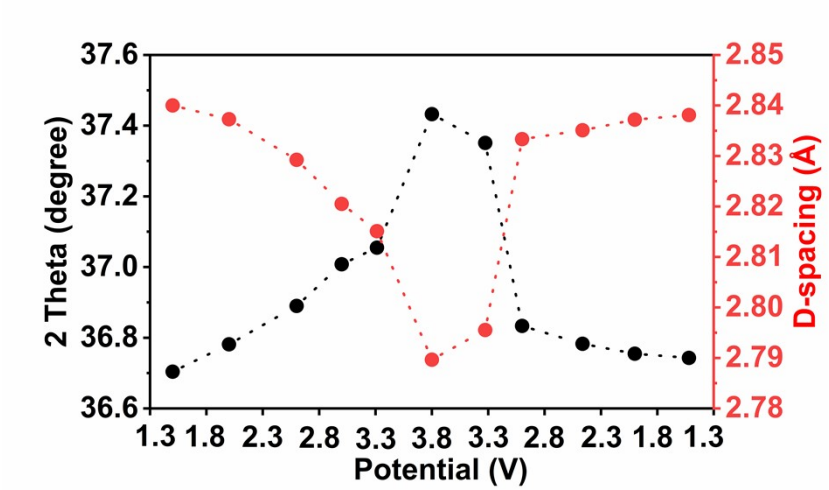

Figure S12. The (116) peak locations and corresponding D-spacings of NCFVP as a function of charge/discharge potential.

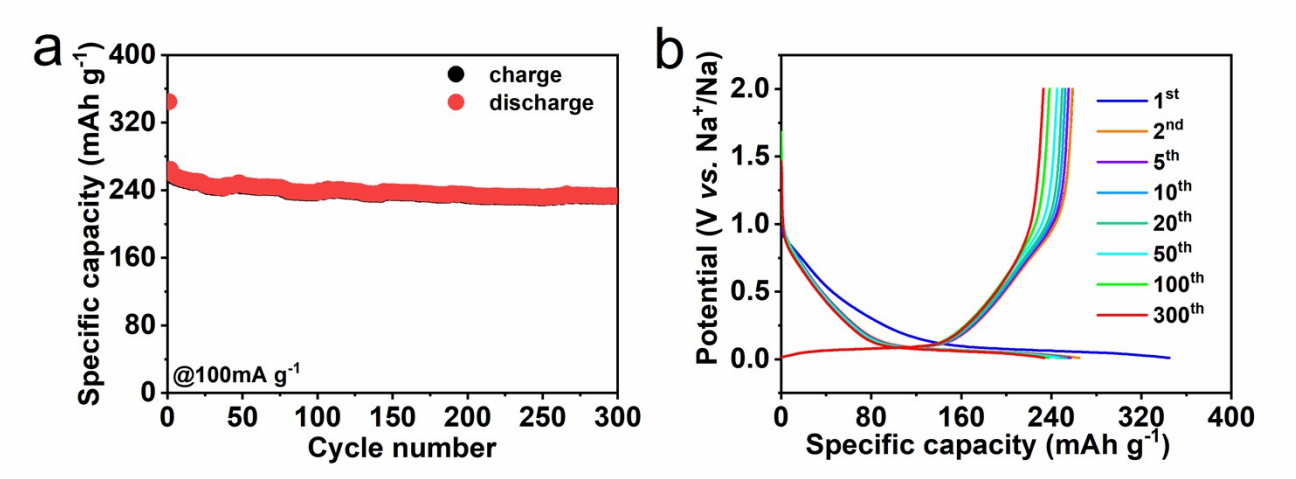

Figure S13. (a) the cycling performance and (b) selected charge/discharge curves of commercial hard carbon at 100 mA g^{-1}.

Table S1. Detailed structural information of NCFVP derived from Rietveld Refinement

Space group = *R-3c*	R_{wp} = 5.63%	R_p = 4.28%		
a = 8.75006 Å	c = 21.67872 Å	a/b = 1		
b/c = 0.403	c/a = 2.478	V = 1437.439 $Å^3$		
Atom	Wyckoff	X	Y	Z
Na1	6b	0.33333	0.66667	0.16667
Na2	18e	0.66667	0.96568	0.08333
V1	12c	0.33333	0.66667	0.01984
Fe1	12c	0.33333	0.66667	0.01984
Cu1	12c	0.33333	0.66667	0.01984
P1	18e	0.95638	0.33333	0.08333
O1	36f	0.14379	0.50043	0.07970
O2	36f	0.53562	0.84648	0.97534

Table S2. Detailed structural information of NFVP derived from Rietveld Refinement

Space group = *R-3c*	R_{wp} = 6.33%	R_p = 4.72%		
a = 8.74462 Å	c = 21.76200 Å	a/b = 1		
b/c = 0.401	c/a = 2.489	V = 1441.157 $Å^3$		
Atom	Wyckoff	X	Y	Z
Na1	6b	0.33333	0.66667	0.16667
Na2	18e	0.66667	0.96708	0.08333
V1	12c	0.33333	0.66667	0.01842
Fe1	12c	0.33333	0.66667	0.01842
P1	18e	0.95490	0.33333	0.08333
O1	36f	0.14268	0.50129	0.07838
O2	36f	0.53902	0.84457	0.97416

Table S3. Detailed structural information of NCVP derived from Rietveld Refinement

Space group = *R-3c*	R_{wp} = 6.33%	R_p = 4.72%		
a = 8.73751 Å	c = 21.82902 Å	a/b = 1		
b/c = 0.400	c/a = 2.498	V = 1443.245 $Å^3$		
Atom	Wyckoff	X	Y	Z
Na1	6b	0.33333	0.66667	0.16667
Na2	18e	0.66667	0.96276	0.08333
V1	12c	0.33333	0.66667	0.01953
Cu1	12c	0.33333	0.66667	0.01953
P1	18e	0.95505	0.33333	0.08333
O1	36f	0.14535	0.49991	0.07835
O2	36f	0.53760	0.84307	0.97534