Supporting Information

Activating the high-potential V^{4+}/V^{5+} redox couple for an advanced NASICON sodium-ion cathode

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Experimental Section

Material Preparation

The NVCTP-0, NVCTP-2, and NVCTP-4 composites were synthesized using a spray drying technique followed by a post-annealing process. All chemicals were used without further purification. The preparation method of the precursor solution is as follows: First, vanadium (IV)oxy acetylacetone ($C_{10}H_{14}O_5V$), tetrabutyl titanate ($C_{16}H_{36}O_4Ti$) and chromic nitrate ($Cr(NO_3)_3{\cdot}9H_2O$) are dissolved in 70 ml ethanol solution according to the stoichiometric ratio and vigorous stirring at 80°C. The solution was supplemented with 6.3 g of citric acid ($C_6H_8O_7$) as a chelating agent and carbon source. Sodium acetate ($C_2H_3NaO_2$) and phosphoric acid (H_3PO_4) were sequentially added into the mixed solution formed above. The precursor solution was then treated with spray drying, and the inlet temperatures were set to 170°C. Finally, the dried precursor was followed by annealing at 800℃ for 5 h in a tube furnace with Ar/H_2 (95:5 vol: vol) atmosphere. NVCTP-0 is prepared by a similar approach except without adding $Cr(NO_3)_3{\cdot}9H_2O$.

Material Characterizations

The chemical composition and crystal structure of the resulting materials were analyzed using X-ray diffraction (XRD, Rigaku/Ultima IV) and refined by Rietveld with the GSAS software. The property analyses of the carbon layer were undertaken on a laser micro-Raman spectrometer (Raman, Renishaw/inVia Reflex) with a laser wavelength of 532 nm, and the carbon contents were further tested by a thermogravimetric analyzer (TGA, Henven/HCT-1) from 30°C to 800°C with a ramping rate of 10°C min^{-1} in air. The specific calculation criterion of carbon content is based on the mass loss of between 300 and 550 °C, corresponding to the decomposition temperature of carbon in the air.[1] X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific/ESCALAB250Xi) was performed to confirm the valence state of transition metals. The morphologies and microstructure images of the synthesized cathodes were observed by scanning electron microscope (SEM, JEOL/JSM-7610FPlus) and transmission electron microscope (TEM, JEM-2100F).

Electrochemical Measurements

The electrochemical performance experiments were carried out by assembling 2016-type coin cells in an Argon-fulled glove box. Using NVCTP-x as working electrodes, sodium metal as counter electrodes, and glass fiber filters as separators. The electrolyte was 1M $NaClO_4$ dissolved in the mixed

solvent of propylene carbonate (PC) and 5% fluoroethylene carbonate (FEC) additive. To prepare a typical half-cell, the active material, Super P, and polyvinylidene fluoride (PVDF) were mixed in N-methyl-2-pyrrolidone (NMP) solvent at a mass ratio of 70:20:10. The obtained slurry was uniformly coated onto an Al foil and dried at 80°C under vacuum over 6 h. Afterward, the cathode was cut into circular electrodes (12 mm in diameter), and the loading mass of the active material was about 1.5-2.0 mg cm^{-2}. To demonstrate the practical feasibility, CR2025 coin cells were further assembled using commercial hard carbon (HC, Kureha Carbotron P) as the anode and NVCTP-2 as the cathode. HC electrode was prepared by mixing with HC (92 wt%), super P (3 wt%), and CMC-SBR (5 wt%) in water followed by coating on Cu foil. To complete the presodiation process, the HC anode wet with the electrolyte was kept in contact with the metallic sodium for approximately 2 h. Notably, the loading of the NVCTP-2 electrode is approximately 1.5 times that of the HC electrode to match the capacity of full cells.

All assembled cells were aged over 6 h before electrochemical measurements. Galvanostatic charge-discharge (GCD) tests between 1.5-4.3 V (vs Na^+/Na) were carried out on a Neware CT-3008W battery testing system. The parameters of the galvanostatic intermittent titration technique (GITT) were set with a current pulse duration of 0.5 h at 20 mA g^{-1} and a further interval time of 2 h. Cyclic voltammetry (CV) curves were recorded on the CHI660e electrochemical workstation.

Calculation methods

The DFT method, as implemented in the Vienna ab initio Simulation Package (VASP), was utilized for all calculations. The ion-electron interaction was handled via the projector augmented wave (PAW) scheme. To further enhance the description of d orbitals in transition metals, we employed the GGA+U method (U values for V, Ti and Cr are 4.2, 4.0 and 3.7 eV, respectively). The plane-wave energy cutoff and the force convergence criterion were set to 500 eV and 0.02 eV $Å^{-1}$ respectively.

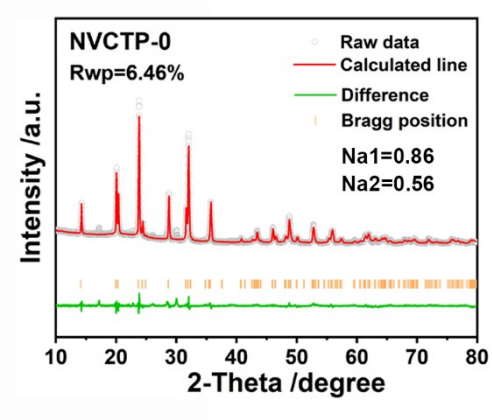

Fig. S1. XRD Rietveld refinement of NVCTP-0 sample.

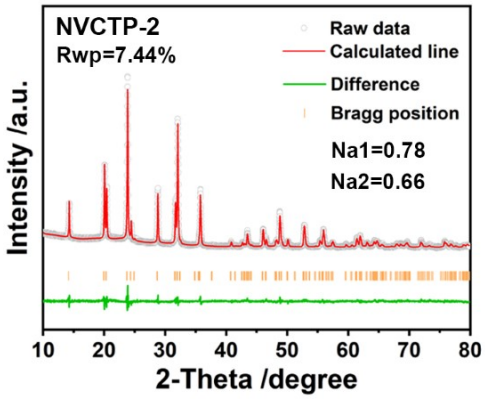

Fig. S2. XRD Rietveld refinement of NVCTP-2 sample.

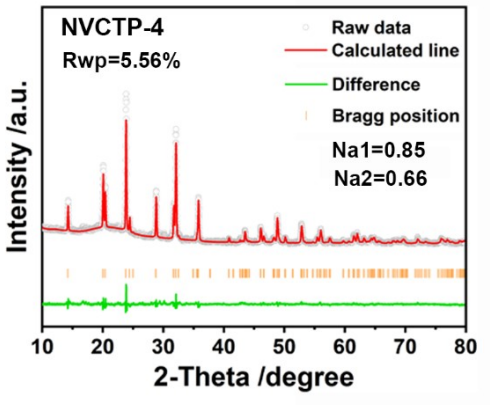

Fig. S3. XRD Rietveld refinement of NVCTP-4 sample.

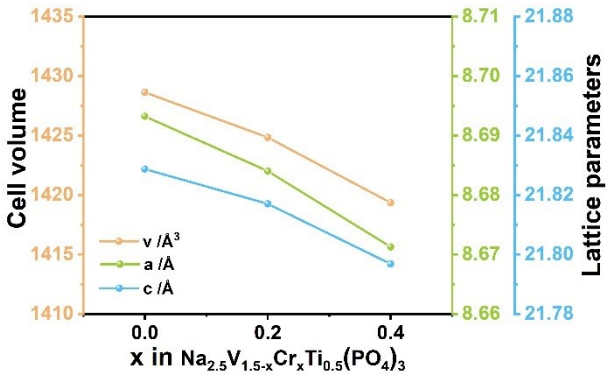

Fig. S4. Cell volume and Lattice parameter variation of NVCTP-x samples.

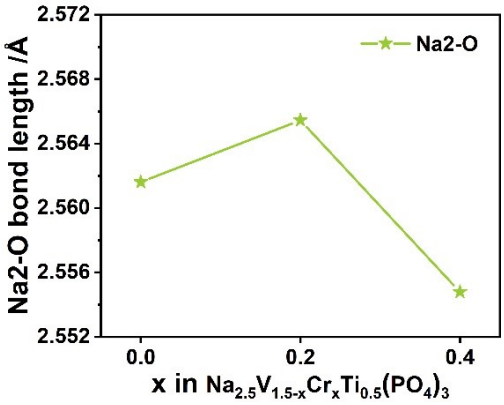

Fig. S5. Bond length of Na2-O in NVCTP-x samples.

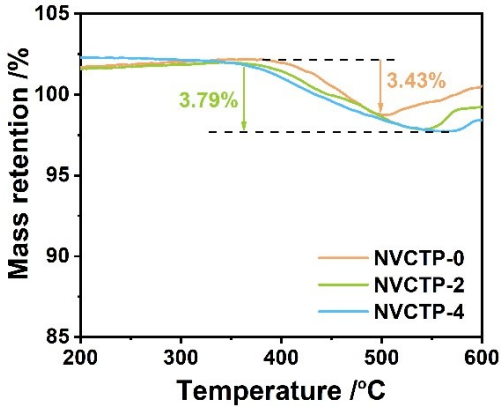

Fig. S6. TG curves of NVCTP-0, NVCTP-2, and NVCTP-4 samples.

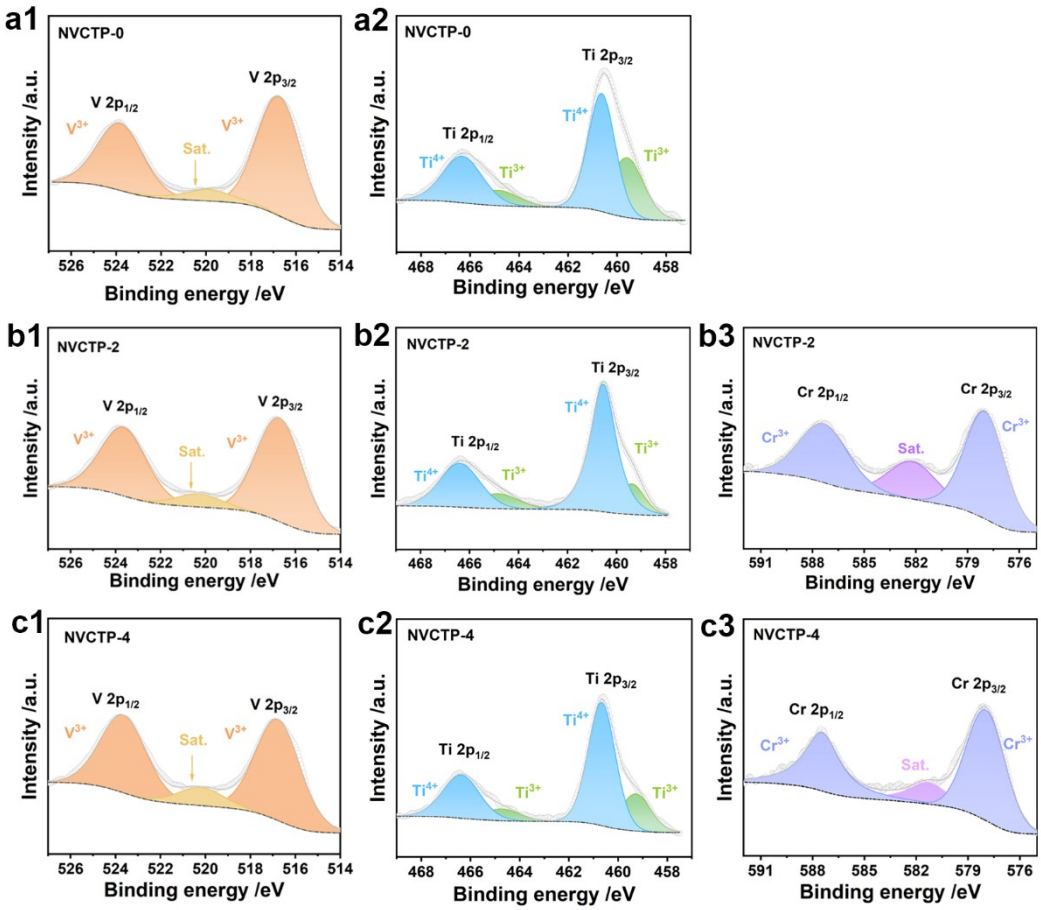

Fig. S7. High-resolution spectra of V 2p, Ti 2p and Cr 2p for (a) NVCTP-0, (b) NVCTP-2 and (c) NVCTP-4 samples.

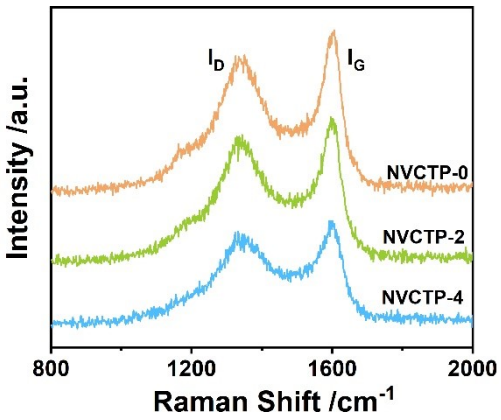

Fig. S8. Raman spectra of NVCTP-0, NVCTP-2, and NVCTP-4 samples.

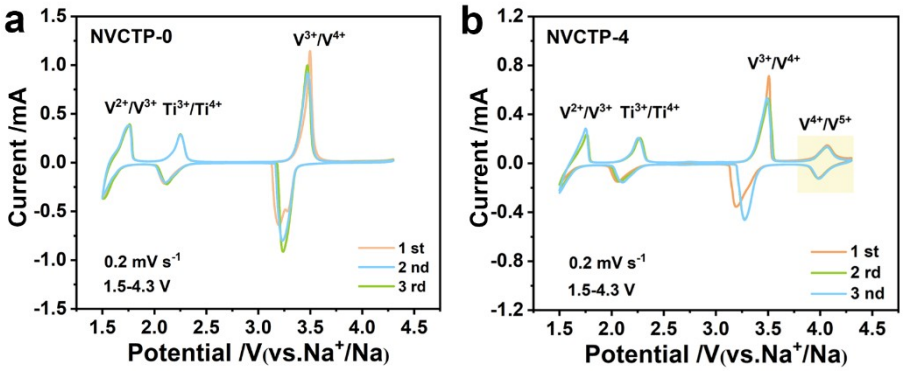

Fig. S9. CV curves of (a) NVCTP-0 and (b) NVCTP-4 electrodes.

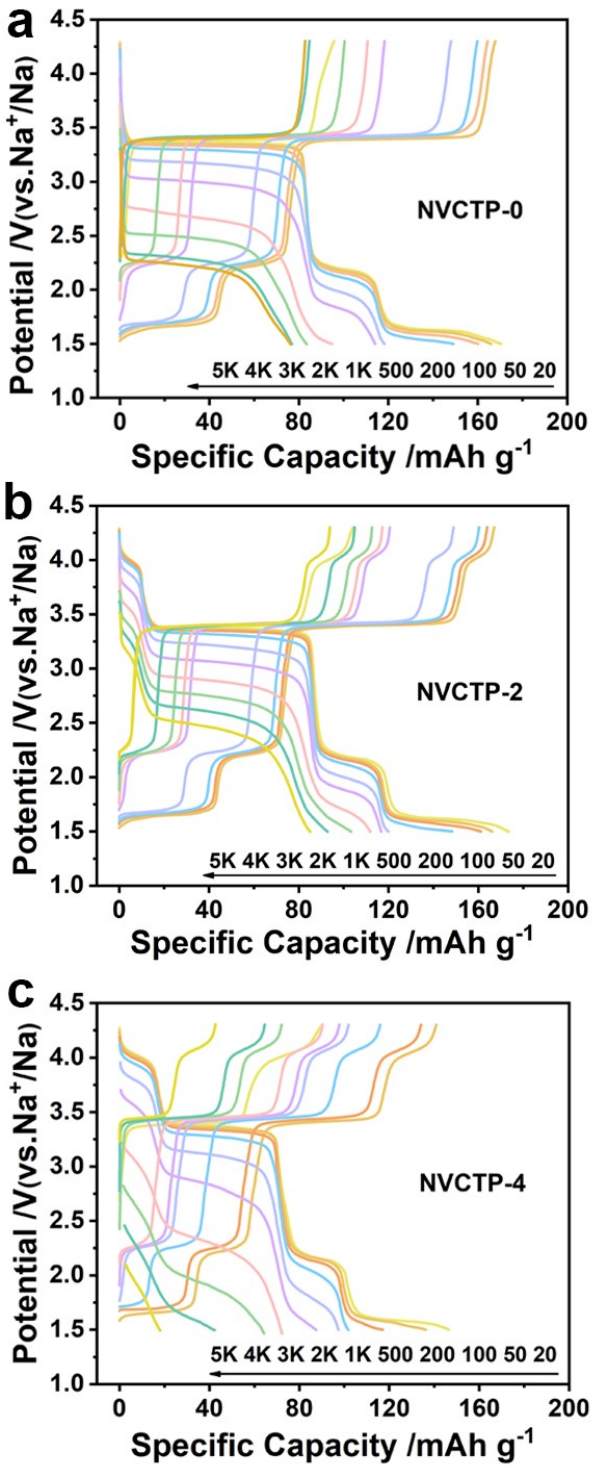

Fig. S10. The GCD curves of (a) NVCTP-0, (b) NVCTP-2 and (c) NVCTP-4 cathodes from 20 to 5000 mA g^{-1}.

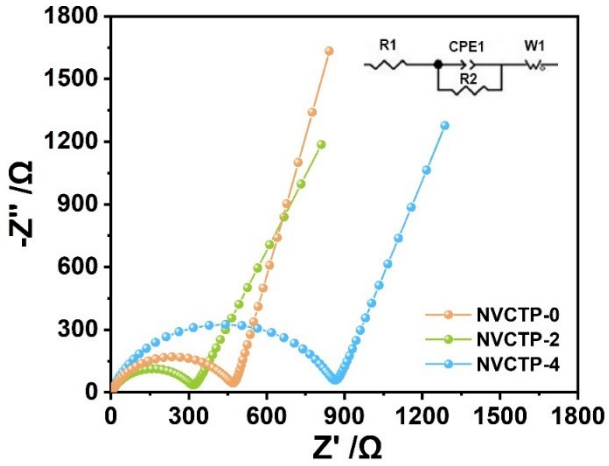

Fig. S11. EIS spectra of NVCTP-0, NVCTP-2 and NVCTP-4.

The Nyquist plots consist of a semicircle in the high-frequency region, which corresponds to the charge transfer resistance(R_{ct}), and a sloping line relating to the Warburg impedance (Z_w) in the low-frequency region.[2,3] The inset shows a characteristic EIS equivalent circuit fitting that includes an electrolyte resistor (R_1), a charge transfer resistor (R_2), and a constant phase angle element (CPE).[4]

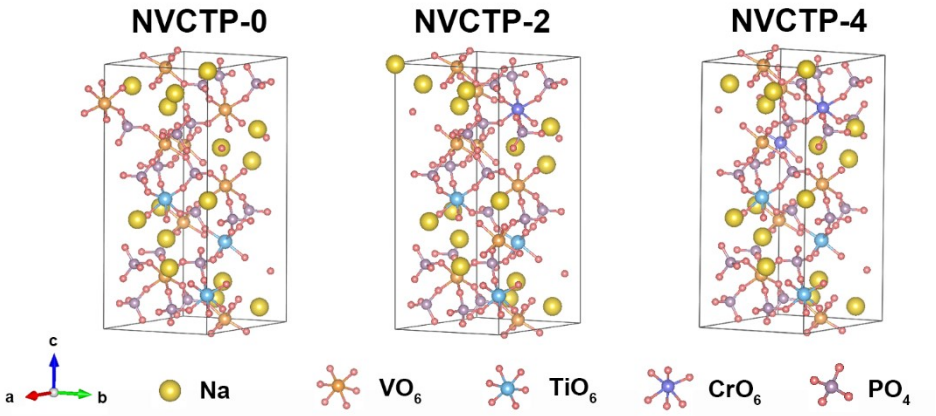

Fig. S12. Optimized crystal structure of NVCTP-0, NVCTP-2 and NVCTP-4.

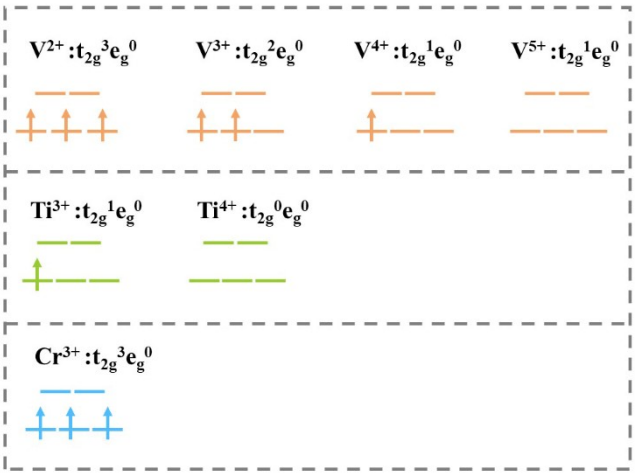

Fig. S13. Schematic view of the electronic configurations of transition-metal ions.

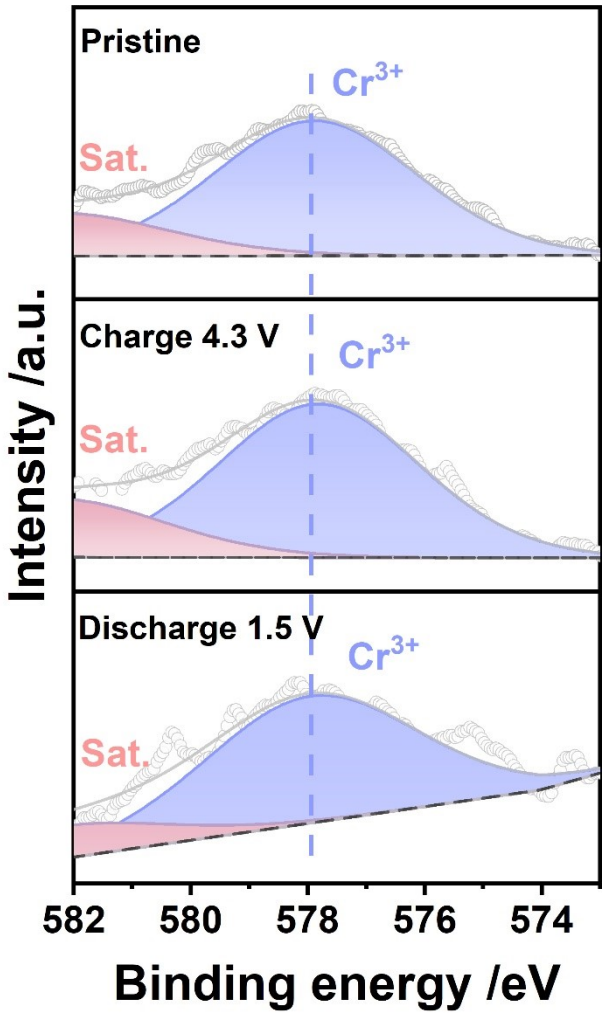

Fig. S14. Ex-situ XPS spectra of Cr $2p_{3/2}$ for NVCTP-2.

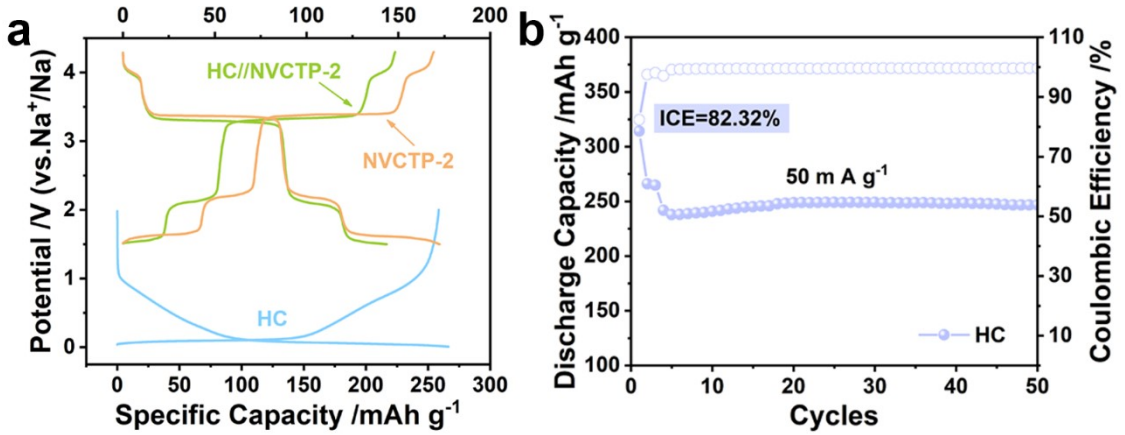

Fig. S15. (a) GCD profiles of NVCTP-2 cathode, HC anode, HC//NVCTP-2 full cell. (b) Long-term cyclability of HC in the voltage range of 0.01-2 V.

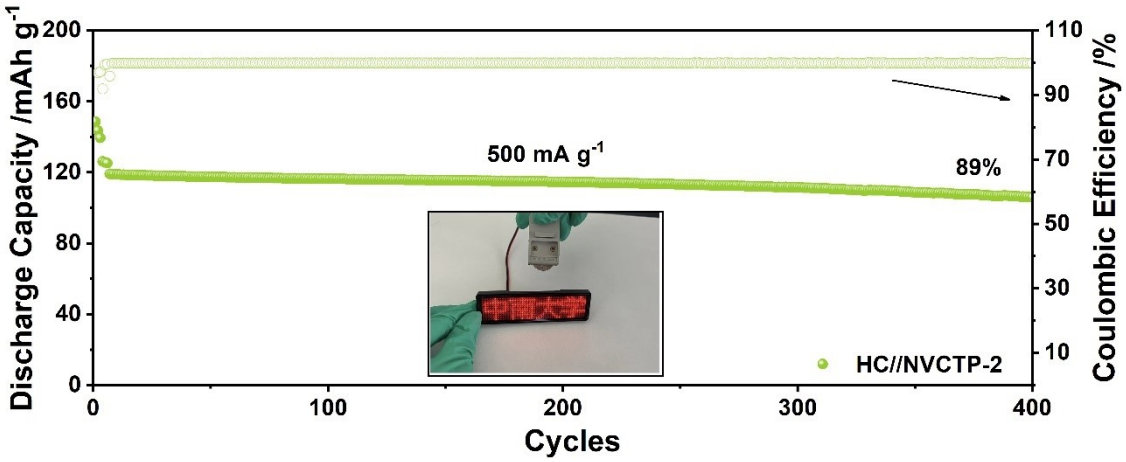

Fig. S16. Long-term cycling stability of HC//NVCTP-2 at 500 mA g^{-1}.

Calculation process for the D_{Na+} values through GITT tests:

The diffusion coefficient (D_{Na+}) of the as-prepared cathodes is calculated from the GITT potential profiles using Fick's second law. The calculation formula is as follows:

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

where τ represents the duration of the current pulse; m_B is the mass loading of the electrode material; S is the geometric area of the electrode; $^{\Delta E_S}$ is the quasi-thermodynamic equilibrium potential difference between before and after the current pulse; $^{\Delta E_\tau}$ is the potential difference during the current pulse; V_m is the molar volume of the electrode material; and M_B is the molar mass of the electrode material.

Table S1. Rietveld structure information of the NVCTP-0 sample.

Space group=R-3c		Rwp=6.46%		
a(Å)=b(Å)= 8.69323		c(Å)= 21.82872		V(Å^3)= 1428.634
α (°)=90		β(°)=90		γ(°)=120
Atom	x	y	z	frac
Na1	0.333300	0.666700	0.166700	0.8579
Na2	0.666700	0.969951	0.083300	0.5555
V	0.333300	0.666700	0.019775	0.7500
Ti	0.333300	0.666700	0.020030	0.2500
P	-0.043082	0.333300	0.083300	1.0000
O1	0.143080	0.499067	0.080704	1.0000
O2	0.540597	0.842954	-0.025611	1.0000

Table S2. Rietveld structure information of the NVCTP-2 sample.

Space group=R-3c		Rwp=7.44%		
a(Å)=b(Å)= 8.68402		c(Å)= 21.81703		V(Å^3)= 1424.846
α(°)=90		β(°)=90		γ(°)=120
Atom	x	y	z	frac
Na1	0.33330	0.66670	0.16670	0.7816
Na2	0.66670	0.96103	0.08330	0.6561
V	0.33330	0.66670	0.02122	0.6500
Ti	0.33330	0.66670	0.02004	0.2500
Cr	0.33330	0.66670	0.02122	0.1000
P	-0.04215	0.33330	0.08330	1.0000
O1	0.14572	0.49818	0.07945	1.0000
O2	0.53776	0.84147	-0.02638	1.0000

Table S3. Rietveld structure information of the NVCTP-4 sample.

Space group=R-3c		Rwp=5.56%		
a(Å)=b(Å)= 8.67127		c(Å)= 21.79682		V(Å^3)= 1419.350
α (°)=90		β(°)=90		γ(°)=120
Atom	x	y	z	frac
Na1	0.33330	0.66670	0.16670	0.8531
Na2	0.66670	0.96422	0.08330	0.6555
V	0.33330	0.66670	0.02100	0.5500
Ti	0.33330	0.66670	0.01941	0.2500
Cr	0.33333	0.66670	0.02040	0.2000
P	-0.04588	0.33330	0.08330	1.0000
O1	0.14436	0.49592	0.07925	0.9962
O2	0.54087	0.84116	-0.02663	1.0000

Table S4. Rietveld structure information of the NVCTP-2 cathode at pristine, 4.3 V and 1.5 V.

State	Rwp (%)	a,b (Å)	c (Å)	V (Å^3)
Pristine	3.45	8.6796	21.8113	1423.009
4.3 V	8.02	8.5849	21.7851	1390.483
1.5 V	2.42	8.6896	21.8252	1425.899

Reference:

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