

## Supporting Information

### 2. Experiments

#### 2.1 Sample preparation

##### 2.1.1 The preparation of Zn<sup>2+</sup>-doped NVP.

The experimental process is shown in Scheme 1. Experimental sample Na<sub>3</sub>V<sub>2-x</sub>Zn<sub>x</sub>(PO<sub>4</sub>)<sub>3</sub> (x=0.01, 0.04, 0.07, 0.1) was synthesized by the traditional liquid phase method. It is named NVP/C-Zn<sub>x</sub>@CHACC (x=0.01, 0.04, 0.07, 0.1) according to the different amount of Zn doping. Taking NVP/C-Zn0.07@CHACC as an example. Firstly, place NH<sub>4</sub>VO<sub>3</sub> (99%, Aladdin), NaH<sub>2</sub>PO<sub>4</sub> (99%, Aladdin) and Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (99%, Aladdin) into 60ml deionized water in a beaker at the corresponding stoichiometric ratio, a certain amount of monohydrate citric acid mixing in the beaker.

##### 2.1.2 The preparation of Zn<sup>2+</sup>-crosslinked CHACC.

Chitosan quaternary ammonium salt (HACC) (2.00g) and deionized water (200.00 mL) are stirred in a beaker with magnetic stirrers. Stir them at 70 °C until the solution is clear. Subsequently, the pH of the solution in the beaker was adjusted to 10 with a 1.00 mol/L sodium hydroxide solution. Epichlorohydrin (4.00g) is added to the beaker as a crosslinking agent. Then the PH of the solution was tested every 30 minutes and the PH of the solution in the beaker was adjusted to 10 by using NaOH solution. Keep stirring during this process for 24 hours. Subsequently, based on the molar mass of Zn<sup>2+</sup> used for NVP preparation in different samples, we calculated the doping amount to be 5% and added it to the prepared CHACC. The mixture was continuously stirred for 24 hours to ensure sufficient crosslinking between the metal

ions and CHACC.

### **2.1.3 Powder sample preparation process.**

Add a quarter of the preformed CHACC solution to the beaker. And stir in a beaker on a magnetic mixer for 10 h. When all raw materials were mixed uniformly as turbid liquid, we transferred it to the drum wind oven. After undergoing at 120 °C for 24 h, the precursor was dried until the anhydrous powders were acquired. Subsequently, it was sintered in N<sub>2</sub> atmosphere in a tube furnace in two steps at 450 °C for 4 hours and 700 °C for 6 hours respectively. After sintering, the sample was ground to obtain the final sample.

## **2.2 Characterization**

The crystal structure of all samples was determined using X-ray diffraction (XRD) measurements on an Ultima IV diffractometer. The XRD data for all samples was collected at a rate of 10 degrees per minute with a step size of 0.02 degrees in the range of 10 to 80 degrees. The microscopic morphology of the sample and the morphology of the carbon layer will be examined using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) on an SU8010 and Tecnai G2 F20 S-TWIN TMP, respectively. The valence states of Na, C, V, O, and K in the NVP/C-Zn<sub>0.07</sub>@CHACC sample will be analyzed using X-ray photoelectron diffraction (XPS). The presence and amount of carbon in the NVP/C-Zn<sub>0.07</sub>@CHACC sample will be determined through a TGA test, followed by a Raman test to analyze the properties of the carbon particles designed in the sample.

## **2.3 Electrochemical measurement**

The electrochemical performance of NVP/C-Znx@CHACC was evaluated using a CR2025 half cell assembled in an argon glove box. The cathode material consists of active material, acetylene carbon black, and polyvinylidene chloride (PVDF) in a mass ratio of 7:2:1. The raw materials were proportionately fed into a ball mill tank and ball milled on a planetary ball mill for 5 hours to obtain a slurry. The slurry was then coated onto suitable aluminum foil and vacuum dried at 120 °C for 12 hours to obtain the final positive electrode. The resulting electrodes were drilled into 16mm diameter disks with an average loading density of 1.5 mg cm<sup>-2</sup>. The electrolyte used was 1 M NaClO<sub>4</sub> in Propylene carbonate (PC) with 2 vol% ethylene fluoride (FEC). Celgard 2400 membrane was utilized as the separator. A round metal sodium block with a diameter of 14 mm and a thickness of 1.4 mm served as the negative electrode. The half-cell cyclic voltammetry and electrochemical impedance spectroscopy tests were conducted using an Electrochemical workstation (AUIVIUM). Cyclic voltammetry was performed at a scanning rate of 0.1 mV s<sup>-1</sup> in the voltage range of 2.3 to 4.1 V. Electrochemical impedance spectroscopy was analyzed with a 10 mV AC amplitude in the frequency range of 0.01 Hz to 100 kHz. Constant current charge-discharge measurements and constant current intermittent titration (gitt) technique were carried out in the LAND battery system within a specified voltage window.

After this, the NVP/C-Zn0.07@CHACC sample was cut into 16 mm electrode pieces to make both positive electrode and negative electrode to make a symmetric full battery. The electrolyte used was the same as the above half battery, and the test

procedure was the same. However, the voltage interval is changed to 0-3 V.

Following the half-cell evaluation, the synthesized cathode sheet was paired with commercial hard carbon (CHC) and assembled into a full battery for electrochemical testing. The mass ratio of commercial hard carbon and super P to carboxymethyl cellulose (CMC) mixed with conductive carbon black and sodium was 8:1:1. Take an A4 size copper foil and cut into 1/4 size. The uniformly mixed negative slurry was evenly coated onto copper foil and dried at the aforementioned temperature. The dried negative electrode plate was cut into a 14 mm diameter circle with a cutting machine, and then assembled with a pure Na plate for pre-sodium plating. Two charge and discharge cycles were performed at a rate of 0.1 C for pre-natrization. Upon completion, the assembled battery was taken out of the glove box and the negative electrode sheet after the pre-natrization process was immediately removed. The positive and negative electrodes, diaphragm, and electrolyte were then packaged into a CR2025 full battery and a constant current charge and discharge test was conducted.

#### **2.4 Thermal safety performance test**

The two cathode materials containing the sodium metal anode were assembled into CR2025-shaped coin batteries and performed 10 cycles of charge-discharge processes at 0.1 C using the LAND testing system. Finally, when the charge state of the coin cell reached 100%, the anode sheet was removed from the testing system. Subsequently, only the short-circuited battery consisting of the cathode material and electrolyte was placed in the accelerating rate calorimeter(ARC) for testing. The electrolyte used in this process was the same as in the experimental procedure

described above.

## 2.5 Calculation method

The effects of  $\text{Zn}^{2+}$  introduction on the structure of  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  were studied by applying the Vienna Ab initio Software package (VASP), based on the density functional theory (DFT). The electron exchange correlation interaction was described by the Perdew-Burke-Ernzerhof for solids (PBEsol) functional under the generalized gradient approximation (GGA) with the projector augmented wave (PAW) method. To eliminate the strong interaction between electrons, vanadium atoms were treated by adding  $U$ , where  $U$  value was 4.2 eV. The cut-off energy of the plane waves was set as 500 eV and the Brillouin zone integrals used a  $2 \times 2 \times 1$ k-point sampling of Monkhorst-Pack grid for the supercell. Convergence was judged when the force and energy reached 0.02 eV/Å and  $10^{-5}$  eV, respectively. To analyze the diffusion mechanism of sodium ions, the possible diffusion path of sodium ions and the corresponding migration energy barrier was calculated by using the climbing image nudged elastic band (CINEB) method.

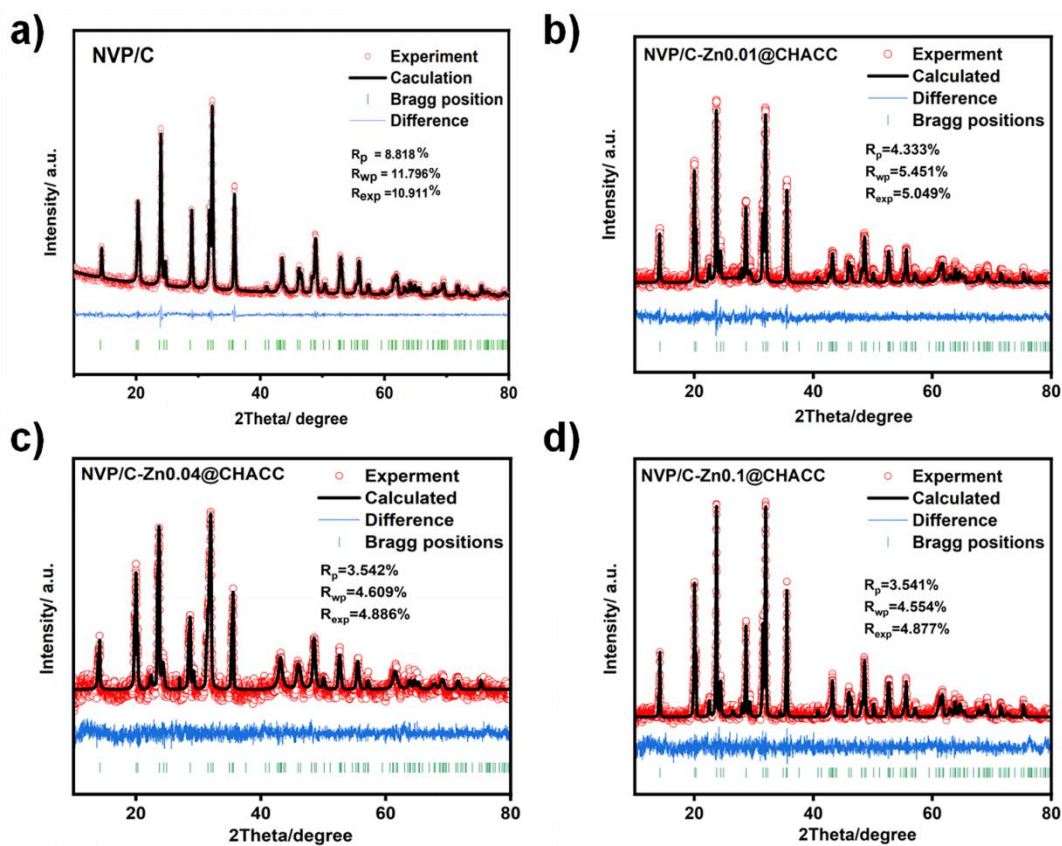


Fig.S1 The refinement map of XRD structure of (a) NVP/C, (b) NVP/C-Zn0.01@CHACC, (c) NVP/C-Zn0.04@CHACC, (d) NVP/C-Zn0.1@CHACC.

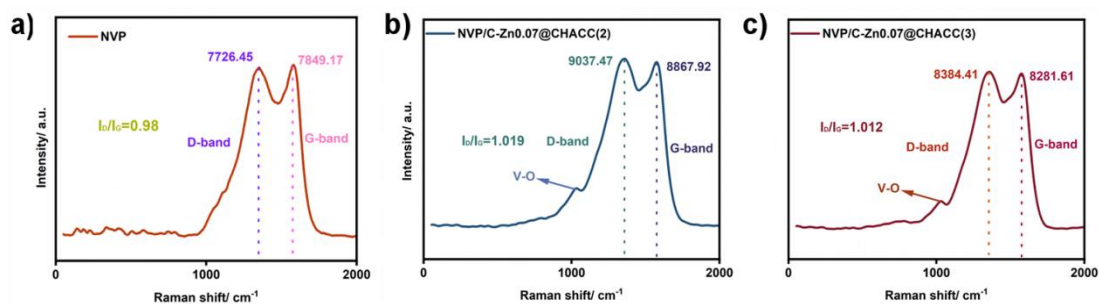


Fig.S2 (a) Raman spectra of the other two points of the NVP/C. (b) (c) Raman spectra of the other two points of the NVP/C-Zn0.07@CHACC sample.

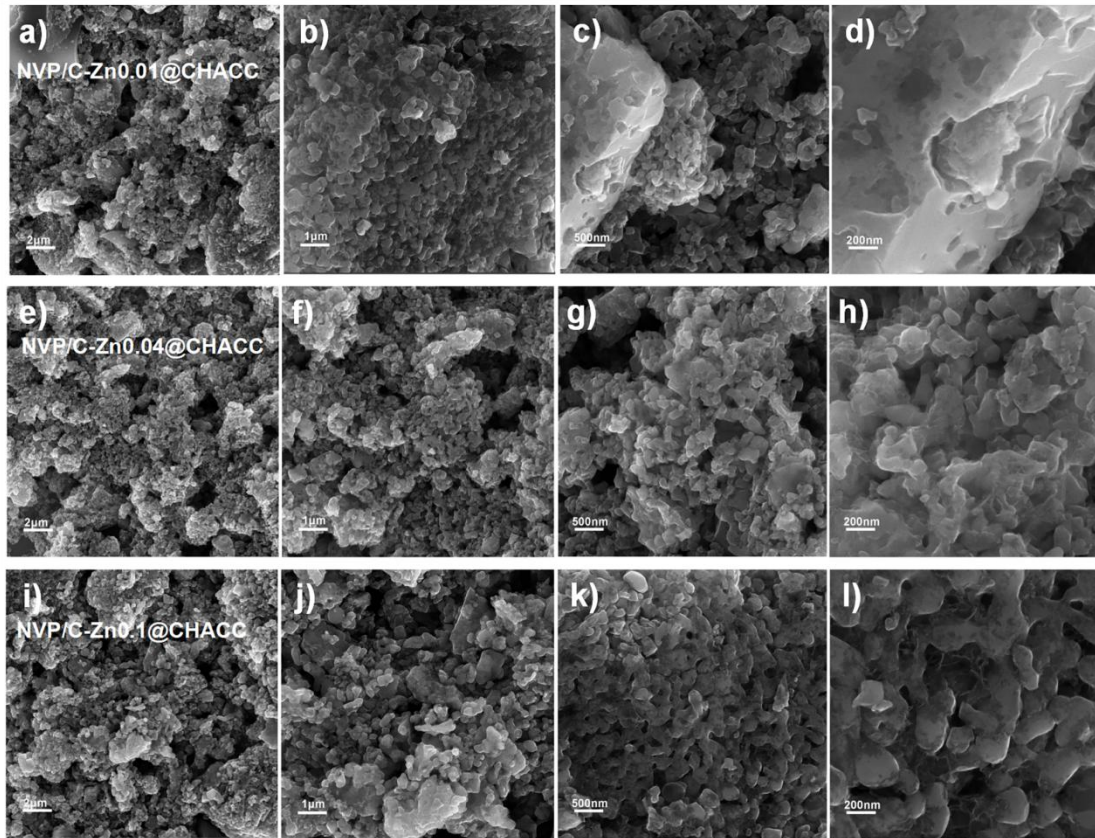


Fig.S3 (a, b, c and d) SEM images of NVP/C-Zn0.01@CHACC at different resolutions. (e, f, g and h) SEM images of NVP/C-Zn0.04@CHACC at different resolutions. (i, j, k and l) SEM images of NVP/C-Zn0.1@CHACC at different resolutions.

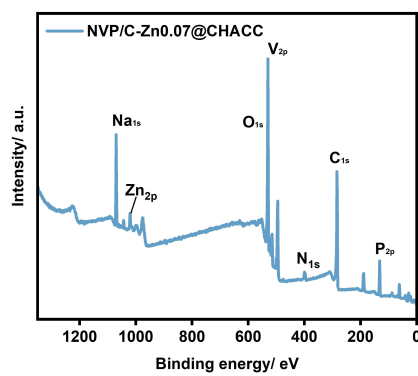


Fig.S4 Total XPS test profiles of the NVP/C-Zn0.07@CHACC sample.

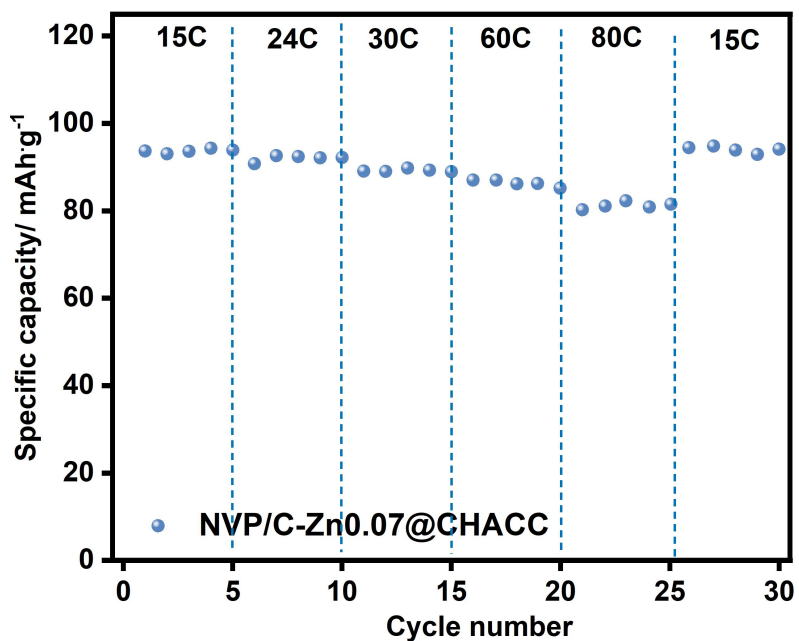


Fig.S5 Testing of the NVP/C-Zn0.07@CHACC sample at different large magnification.

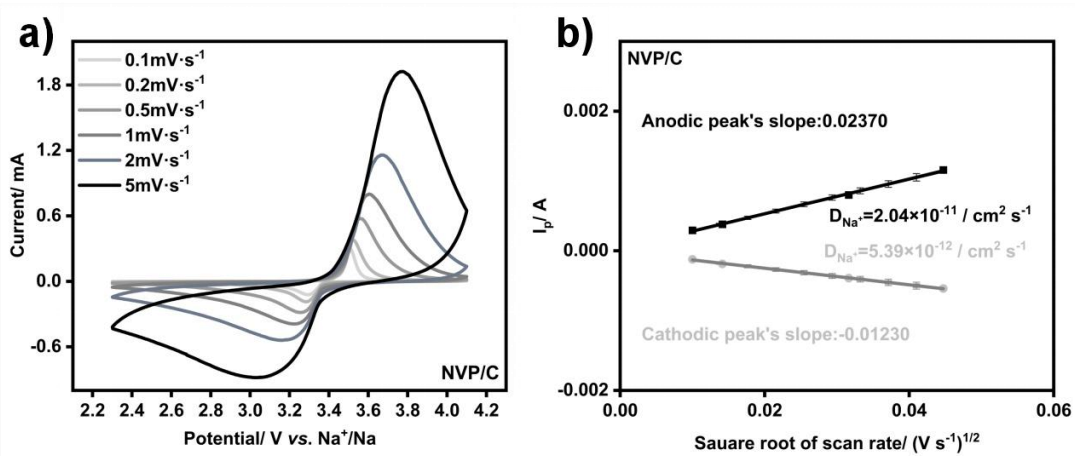


Fig.S6 (a) The CV curves obtained from the raw NVP/C tested at different sweeps. (b) ‘ $I_p$  vs  $v^{1/2}$ ’ curve.



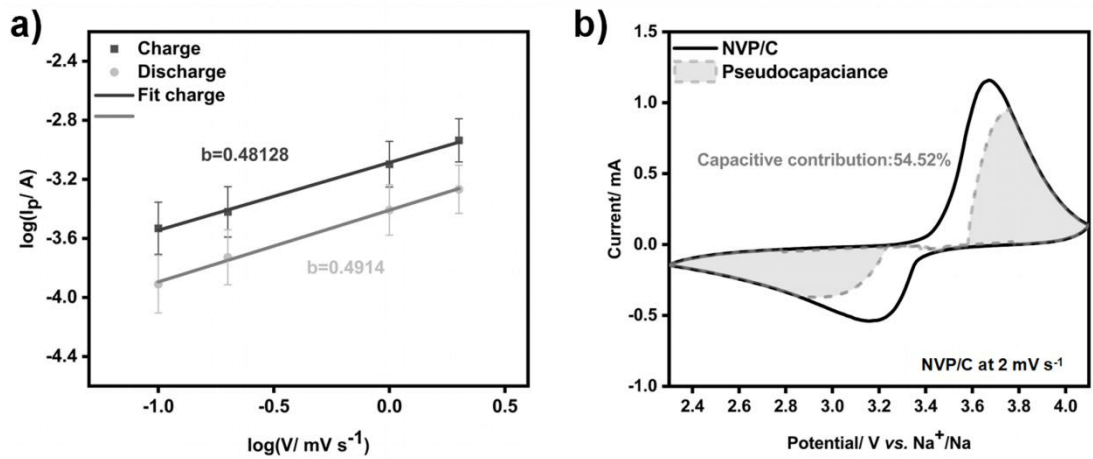


Fig.S7 The ‘log I vs. log v’ curves of NVP/C (a). The capacity contribution analysis of NVP/C (b).

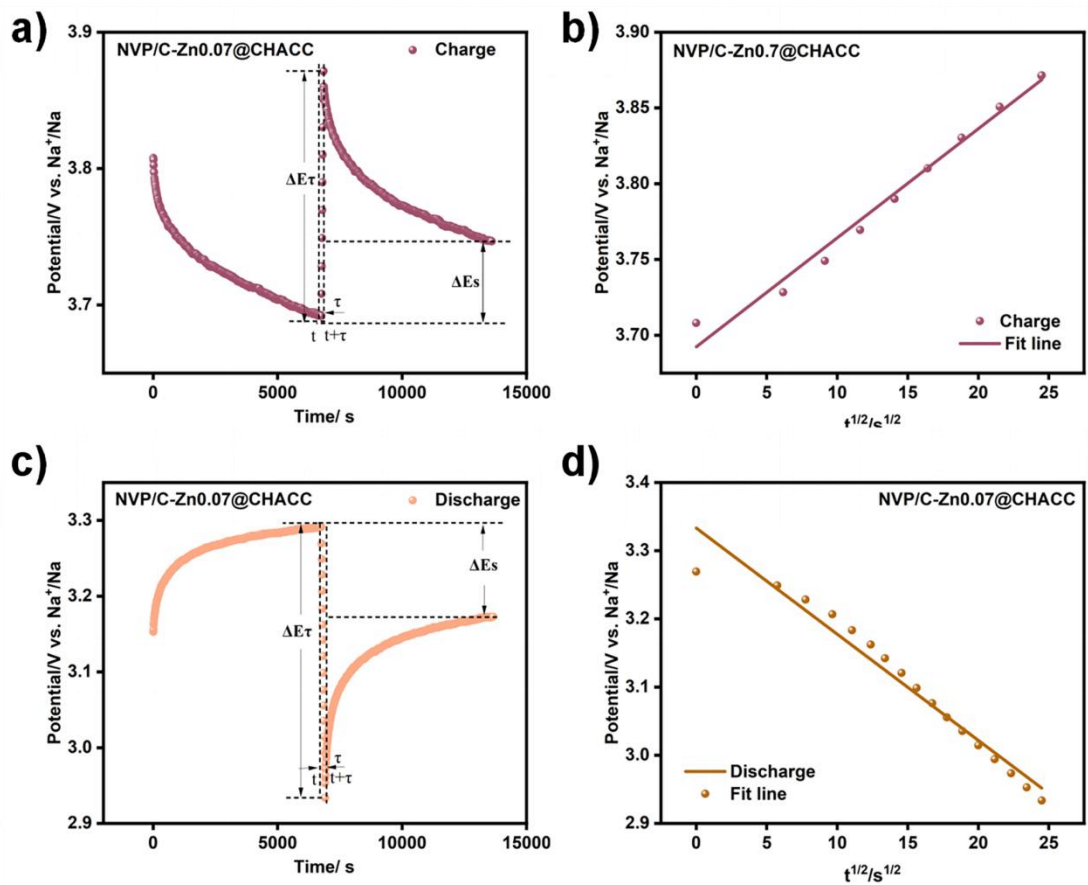


Fig.S8 The plot in a single period during charge (a) and discharge (c) process. The linear relationship of ‘V vs  $\tau^{1/2}$ ’ (b and d).

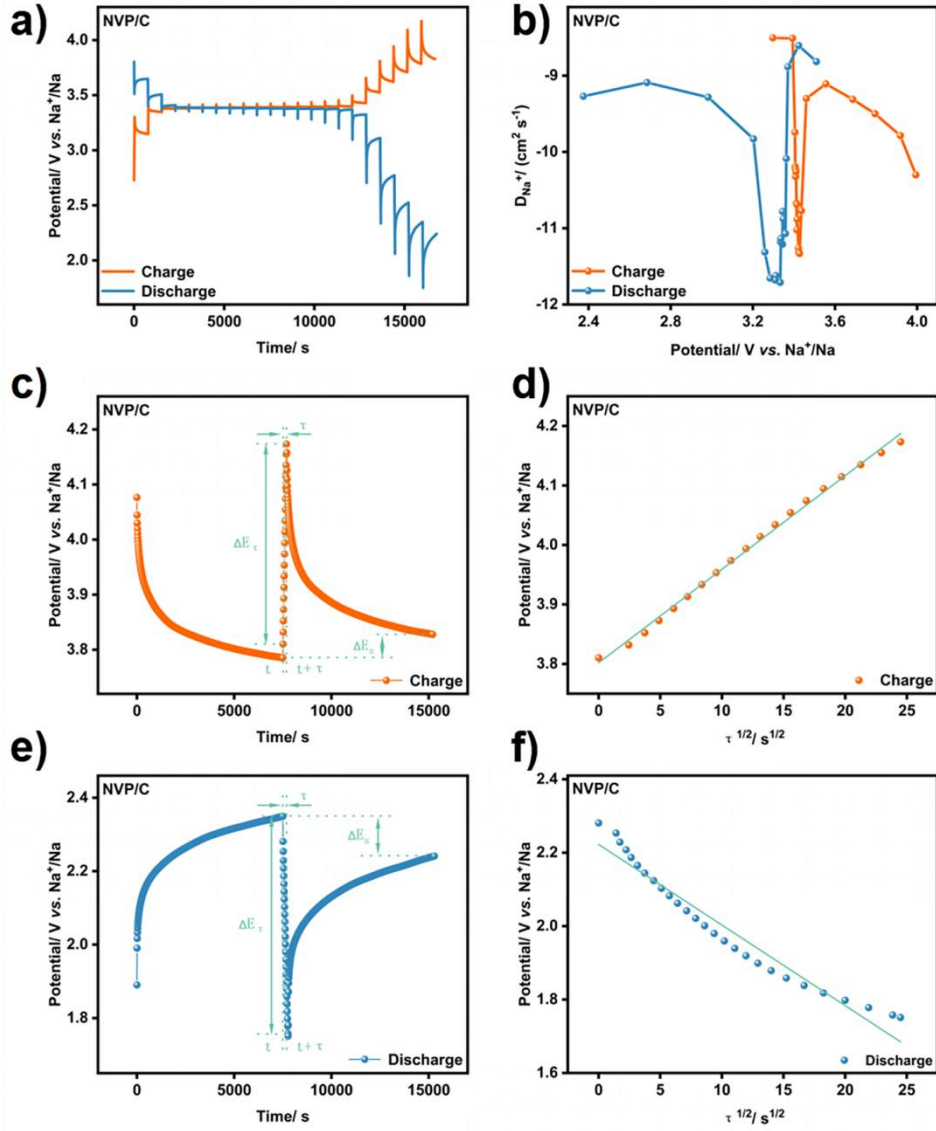


Fig.S9 (a) The GITT curves during charge/discharge process. (b) The calculated  $D_{Na^+}$  during charge/discharge process of NVP/C. The plot in a single period during charge (c) and discharge (e) process. The linear relationship of 'v vs  $\tau^{1/2}$ ' (d) and (f).

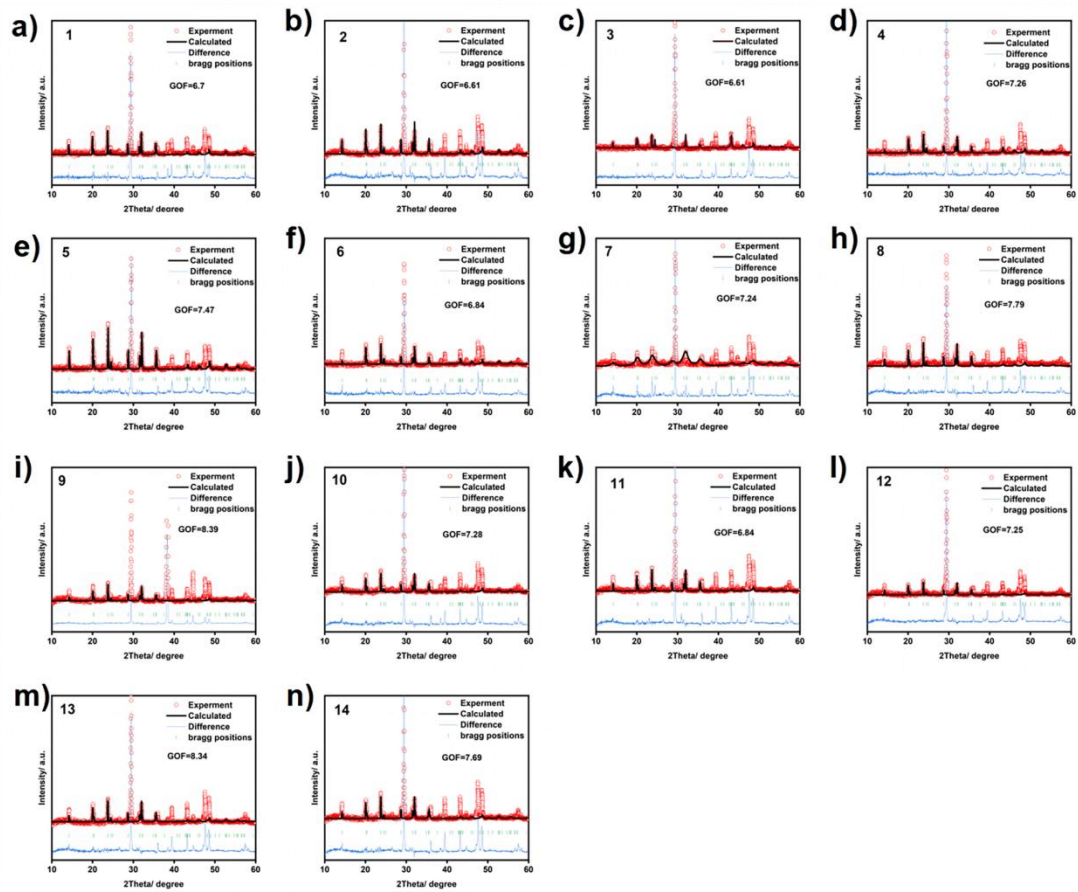


Fig.S10 Images of samples at 14 points in the ex-situ XRD test.

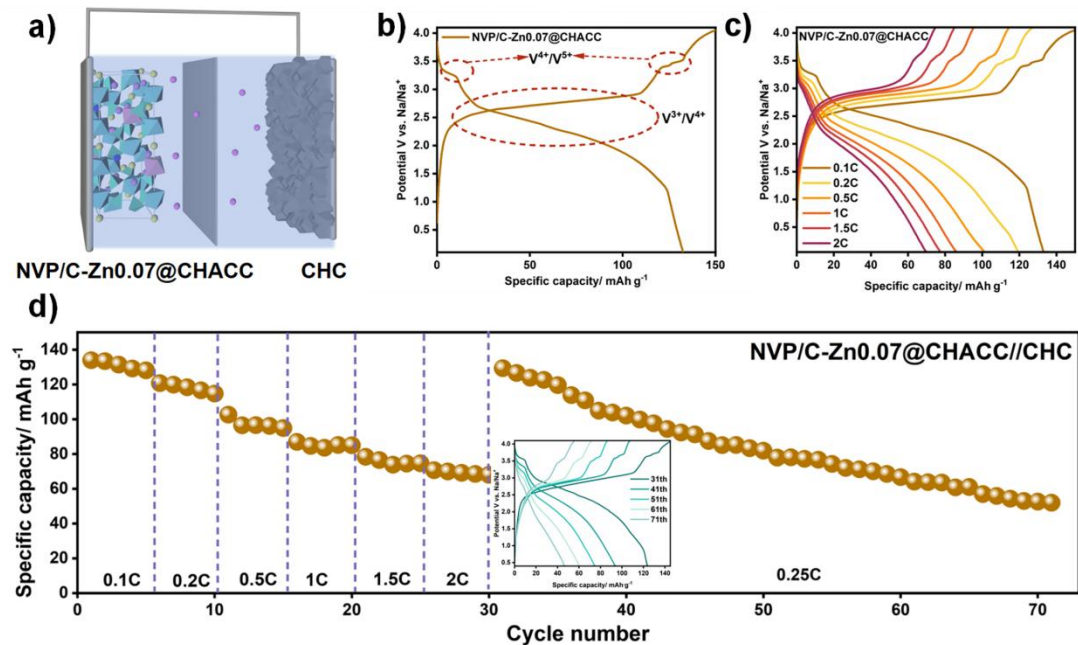


Fig.S11 (a) Schematic diagram of NVP/C-Zn0.07@CHACC//CHC full battery. (b) The first turn charge and discharge curve and the light bulb with full battery. (c) GCD curves at different multiples of NVP/C-Zn0.07@CHACC//CHC. (d) Electrochemical performance diagram of

assembled full battery and the GCD curve of this whole-cell in the late cycle.

Table S1 Structural refinement data at different points obtained after ex-situ XRD testing.

Samples	a=b/ Å	C/ Å	V/ Å <sup>3</sup>
1	8.725	21.773	1435.709
2	8.728	21.765	1436.002
3	8.727	21.773	1436.343
4	8.728	21.782	1437.177
5	8.730	21.778	1437.456
6	8.727	21.778	1436.490
7	8.725	21.773	1435.502
8	8.723	21.770	1434.711
9	8.726	21.776	1435.241
10	8.726	21.781	1436.544
11	8.727	21.780	1436.812
12	8.730	21.781	1437.885
13	8.729	21.780	1437.518
14	8.728	21.778	1436.819

Table S2 The share of Na<sup>+</sup> at each point after intensive repair.

Samples	Name	x	y	z	Occ.
1	Na(1)	0.3333	0.6667	0.1667	0.8053
	Na(2)	0.6667	0.9672	0.0833	0.7312
2	Na(1)	0.3333	0.6667	0.1667	0.8124
	Na(2)	0.6667	0.9672	0.0833	0.7023
3	Na(1)	0.3333	0.6667	0.1667	0.8164
	Na(2)	0.6667	0.9672	0.0833	0.5124

4	Na(1)	0.3333	0.6667	0.1667	0.8037
	Na(2)	0.6667	0.9672	0.0833	0.2647
5	Na(1)	0.3333	0.6667	0.1667	0.8124
	Na(2)	0.6667	0.9672	0.0833	0.2234
6	Na(1)	0.3333	0.6667	0.1667	0.7534
	Na(2)	0.6667	0.9672	0.0833	0.1843
7	Na(1)	0.3333	0.6667	0.1667	0.6834
	Na(2)	0.6667	0.9672	0.0833	0.1275
8	Na(1)	0.3333	0.6667	0.1667	0.6357
	Na(2)	0.6667	0.9672	0.0833	0.0954
9	Na(1)	0.3333	0.6667	0.1667	0.7346
	Na(2)	0.6667	0.9672	0.0833	0.1365
10	Na(1)	0.3333	0.6667	0.1667	0.8376
	Na(2)	0.6667	0.9672	0.0833	0.1786
11	Na(1)	0.3333	0.6667	0.1667	0.8224
	Na(2)	0.6667	0.9672	0.0833	0.3745
12	Na(1)	0.3333	0.6667	0.1667	0.8324
	Na(2)	0.6667	0.9672	0.0833	0.5984
13	Na(1)	0.3333	0.6667	0.1667	0.8165
	Na(2)	0.6667	0.9672	0.0833	0.6954
14	Na(1)	0.3333	0.6667	0.1667	0.8276
	Na(2)	0.6667	0.9672	0.0833	0.7684

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