

## Supporting Information

### **Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> coated by N-doped Carbon from Ionic Liquid as Cathode Materials for High Rate and Long-Life Na-ion Batteries**

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### **Experimental Section**

#### *1. Synthesis of NVP@C-N*

In this work, four NVP-based electrode including NVP@C-N130, NVP@C-N150, NVP@C-N170 and NVP@C are prepared via a typical hydrothermal assisted sol-gel approach. First, V<sub>2</sub>O<sub>5</sub> (0.364 g, 2 mmol, 99.99%, Sigma-Aldrich), NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (0.69 g, 6 mmol, 99%, Sigma-Aldrich) and Na<sub>2</sub>CO<sub>3</sub> (0.318g, 3mmol, 99.5%, Sigma-Aldrich) were poured into 60 mL of deionized water and magnetically stirred at 60°C. Then, the ascorbic acid (0.528 g, 3 mmol, 98%, Sigma-Aldrich) and polyethylene glycol 400 (1.6 ml, 95%, Sigma-Aldrich) were mixed with the above solution, in which the reagents were stirred and dissolved about 30 minutes. Subsequently, the brown solution transformed into blue one. Before the succedent hydrothermal treatment, different amounts (130ul, 150ul, 170ul, 0ul) of EMIm-dca were added drop wise into the precursor solution, respectively, which was stirred for 40 minutes before being transferred to a 100 ml Teflon-lined autoclave. The sealed autoclave was kept at

180 °C for 40 hours, and then naturally cooled to room temperature. The obtained samples were named NVP@C-N130, NVP@C-N150, NVP@C-N170 and NVP@C, respectively, after freeze drying. Subsequently, the powder was thoroughly ground and preheated at 350 °C in ceramic ark for 4 hours in flowing Ar atmosphere and cooled to RT. Finally, the preheated samples were ground to tiny powders and finally calcined at 750 °C for 6 hours in flowing Ar atmosphere. Particularly, the NVP@C-C1 and NVP@C-C2 were prepared by the same way with the NVP@C, except the additive amount of the ascorbic acid (1.5 mmol for the NVP@C-C1 and 4.5 mmol for the NVP@C-C2, respectively).

## *2. Material characterization*

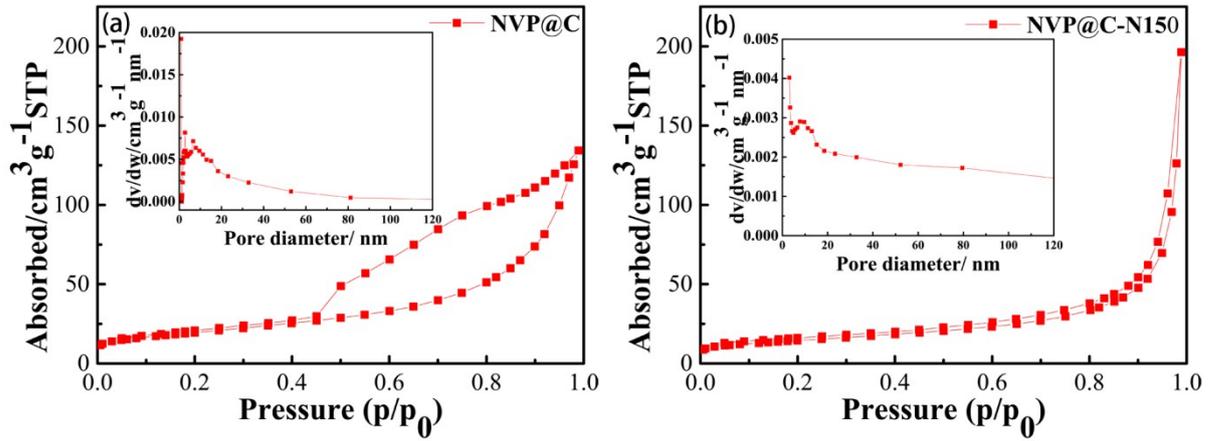
The crystal structure were characterized by means of X-ray powder diffraction (Philips X'Pert PRO SUPER X-ray diffractometer with Cu-K $\alpha$  radiation). The morphology and microstructure of Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> particles were investigated by using field-emission scanning electron microscopy (FESEM, JEOL, Tokyo, Japan), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). The EDX mapping was operated on a Hitachi S-4800 scanning electron microscope equipped with an energy dispersive X-ray analyzer (Horiba EMAX). Raman spectra were achieved via a LanRanHR (HORIBA Scientific, Paris, France) spectrometer which equipped with a 514 nm Ar-ion laser. X-ray photoelectron spectroscopy (XPS) data of the as-synthesized powder were obtained via a VG Microtech ESCA 2000 using a monochromic Al X-ray source (2kV, 1486 eV). The carbon content of the composites were measured by the thermogravimetry (TG) analyses. The nitrogen adsorption/desorption isotherms were determined by an ASAP 2020 Accelerated Surface Area and Porosimetry instrument.

### 3. Electrochemical investigation

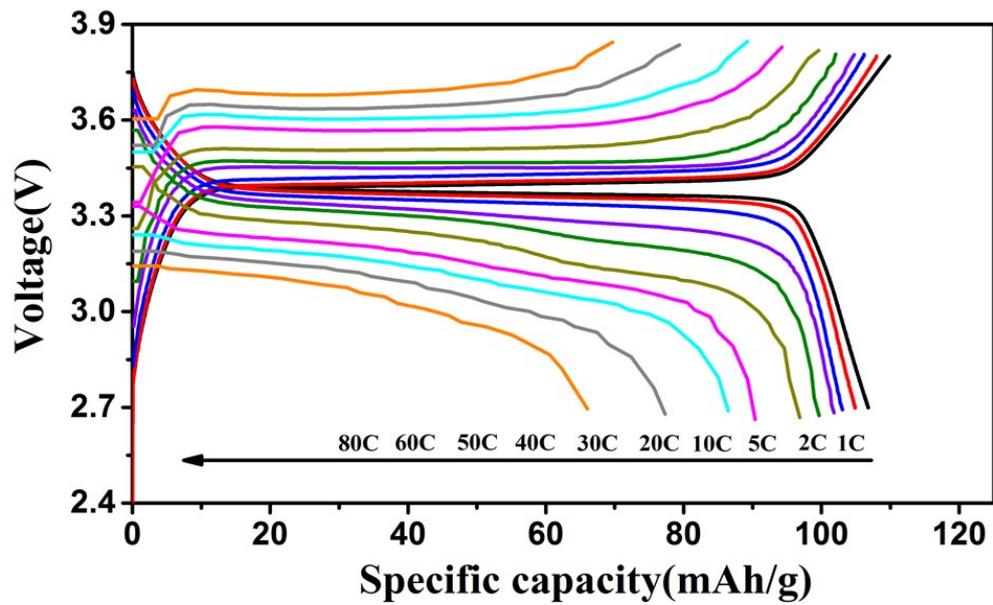
The electrochemical performance was measured with 2032 coin cells assembled in an argon-filled glove box which has strict limits on both moisture and oxygen levels. The active electrode was made by blending 70% active materials, 20% carbon black and 10% PVDF with an appropriate amount of N-methyl-2-pyrrolidone (NMP) as a solvent and pasted onto an aluminum foil. The electrolyte is composed of 1M NaClO<sub>4</sub> in propylene carbonate (PC) with 5% fluoroethylene carbonate (FEC) as additive. The glass fiber (Whatman) was employed as the separator. The electrode loading is about 0.9 mg cm<sup>-1</sup>. The specific capacity values of the cells were calculated on the basis of the active electrode. The galvanostatic charge-discharge tests were conducted on the Neware BTS-610 instrument at a voltage window of 2.7-3.8V. The cyclic voltammetry (CV) data were carried out with a scan rate of 0.2 mV s<sup>-1</sup> and electrochemical impedance spectrum (EIS) measurements were obtained using the CHI 660D electrochemical workstation.

**Table S1.** The weight ratio of carbon and nitrogen element of different NVP samples.

Element	NVP@C-N130	NVP@C-N150	NVP@C-N170	NVP@C	NVP@C-C1	NVP@C-C2
C(%)	14.02	14.45	14.93	11.20	8.62	14.30
N(%)	2.36	2.77	3.22	1.66	1.64	1.66



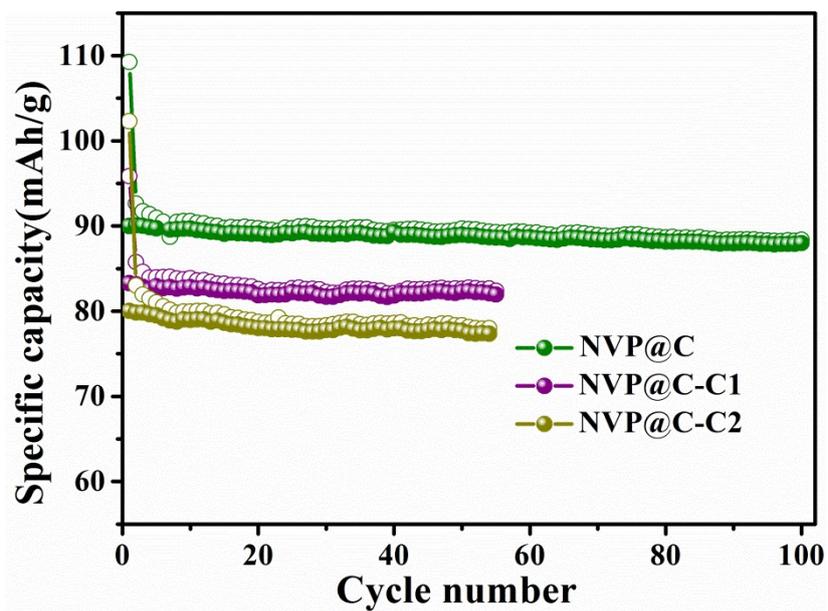
**Figure S1.** N<sub>2</sub> adsorption-desorption isotherm with the pore-size distribution curves of inset: (a) NVP@C and (b) NVP@C-N150.



**Figure S2.** The charge-discharge profiles from 1 C to 80 C of NVP@C-N150.

**Table S2.** The quantitative EDX results of NVP@C-N150 sample.

Element	C	N	Na	V	P	O
Weight %	17.57	2.78	41.25	6.97	20.65	10.78
Atomic %	28.62	3.87	46.88	4.97	12.52	3.14



**Figure S3** Cycle performance of NVP@C, NVP@C-C1 and NVP@C-C2 at 1C in the voltage range between 2.7V and 3.8V.