

Supporting information

**High-performance aqueous sodium-ion battery using hybrid
electrolyte with wide electrochemical stability window**

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1. Theoretical simulations

DFT-MD simulations were conducted in generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) exchange correlation function using the DMol³ code. The canonical NVT ensemble for a few picoseconds with a time step of 1 fs was adopted in the DFT-MD simulation, and the temperature of the system was kept constant at 300 K.

2. Experimental

2.1 Synthesis of cathode material

1mM citric acid ($C_6H_8O_7 \cdot H_2O$) and 2 mM NH_4VO_3 were added to 15 mL distilled water and magnetically stirred for 0.5 h in a water bath at 80 °C. $C_6H_8O_7 \cdot H_2O$ was used not only as a carbon source but also as a chelator. Then, 3 mM NaH_2PO_4 , 2.85 mM NaOH and 0.15 mM KOH were added to the suspension, and the mixture was quickly stirred for 10 min. Afterwards, 50 mL N, N-Dimethylformamide (DMF) was added to the above solution and stirred continuously for 3 h. The resulting solution was put in an oven for drying at 70 °C for 12 h. After thoroughly ground, the resultant powder was heated at 400 °C for 4 h and 750 °C for 8 h with ramping rate of 5 °C min⁻¹ under the dilute H₂ flow of 120 cm³/min (H₂/Ar=5/95). The calcined product was referred to as $Na_{2.85}K_{0.15}V_2(PO_4)_3$ small particles (NKVP-SP).

The as-prepared NKVP-SP was then added to three hydroxyl methyl methane buffer (THAM) (75 mL, 0.5 M), which was dispersed ultrasonically for 30 min. HCl solution (1 M) was then injected drop by drop into the solution under magnetic stirring until the pH value of the solution reached 8-9. The dopamine hydrochloride (1:10 by weight to NKVP-SP) was added to the above solution and stirred vigorously for 24 h at room temperature. The resulting solution was centrifuged, and washed several times with deionized water and ethanol. Afterwards, the sediment was put in an oven for drying at 80 °C for 12 h. The dried product was then preheated at 400 °C for 4 h and 800 °C for 8 h with ramping rate of 5 °C min⁻¹ under the dilute H₂ flow of 120 cm³/min (H₂/Ar=5/95). The as-prepared product was referred to as carbon-coated $Na_{2.85}K_{0.15}V_2(PO_4)_3$ small particles (NKVP-SP-C).

2.2 Synthesis of anode materials

A appropriate amount of citric acid was added to 20 mL deionized water, until the pH value of the solution reached 4. Then, a stoichiometric amount of Na_2CO_3 , tetrabutyl titanate and $\text{NH}_4\text{H}_2\text{PO}_4$ were added, and stirred quickly for 10 min. 50 mL DMF was added to the above solution, and stirred magnetically for 4 h in an 80 °C water bath. The precursor brown powder was obtained after drying for 12 h in an oven at 120 °C. Then, the precursor was ground and calcined in a tubular furnace at 350 °C for 3 h and 750 °C for 12 h under Ar atmosphere with a ramping rate of 5 °C min^{-1} . The as-prepared product was $\text{NaTi}_2(\text{PO}_4)_3$ that was abbreviated as NTP in this work.

2.3. Material characterization

The crystal structure of the samples were characterized by X-ray diffraction (D8 Advance, Germany) equipped with a $\text{Cu-K}\alpha$ radiation at 40 kV, 30 mA. The morphology of the sample was observed by field emission scanning electron microscope (SEM, JSM-7900F, JEOL, Japan) with an energy dispersive X-ray spectrometry analyzer (EDS). The microstructure of the sample was observed by transmission electron microscopy (TEM, JEOL-2100UHR, JEOL, Japan). The Raman spectra of the electrolyte were recorded by using a 532 nm-laser excitation at room temperature (DXR, Thermo Fisher Scientific).

2.4. Electrochemical measurements

70 wt% active material, 20wt% carbon black and 10wt% polyvinylidene fluoride were mixed in an appropriate amount of N-methyl-2-pyrrolidone (NMP) solvent, forming a slurry. The slurry was then coated on a current collector and dried in an oven at 80 °C for 6 h, resulting in an electrode. A piece of carbon cloth (1 cm^2) and a piece of carbon nickel foam (1 cm^2) were used as current collectors of cathode and anode, respectively. The mass loading of active material is 1.0 mg. A three-electrode cell was assembled in $\text{NaClO}_4(\text{H}_2\text{O})_2(\text{AN})_{2.4}$ solution using the fabricated electrode, platinum plate, and SCE (saturated calomel electrode) as working electrode, counter electrode and reference electrode, respectively. A button cell comprising NKVP-SP-C cathode and NTP anode was assembled for full cell evaluation. The mass ratio of the cathode and anode active materials was 1:1.2 in button cell. Cycle voltammetry (CV) curves

were recorded by an electrochemical workstation (CHI660D). Galvanostatic charge/discharge curves were collected by a battery testing system (LAND CT2001A).

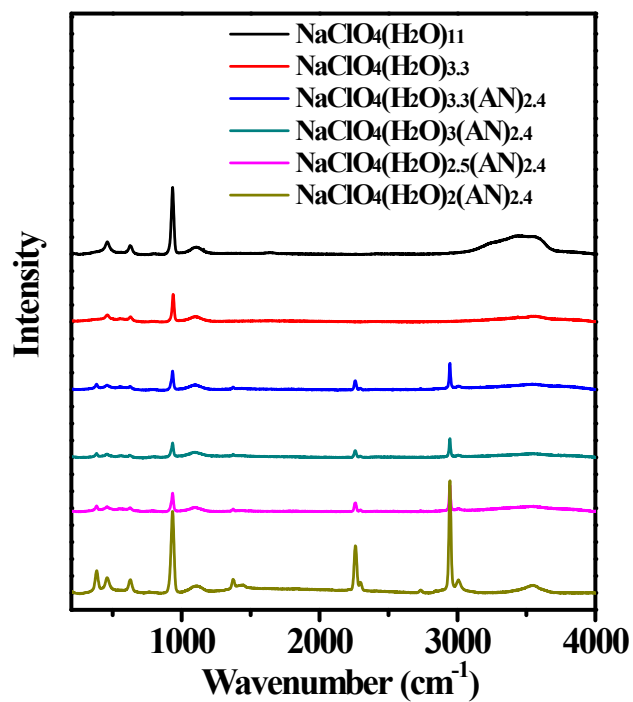


Fig. S1. Raman spectra of electrolytes with different compositions.

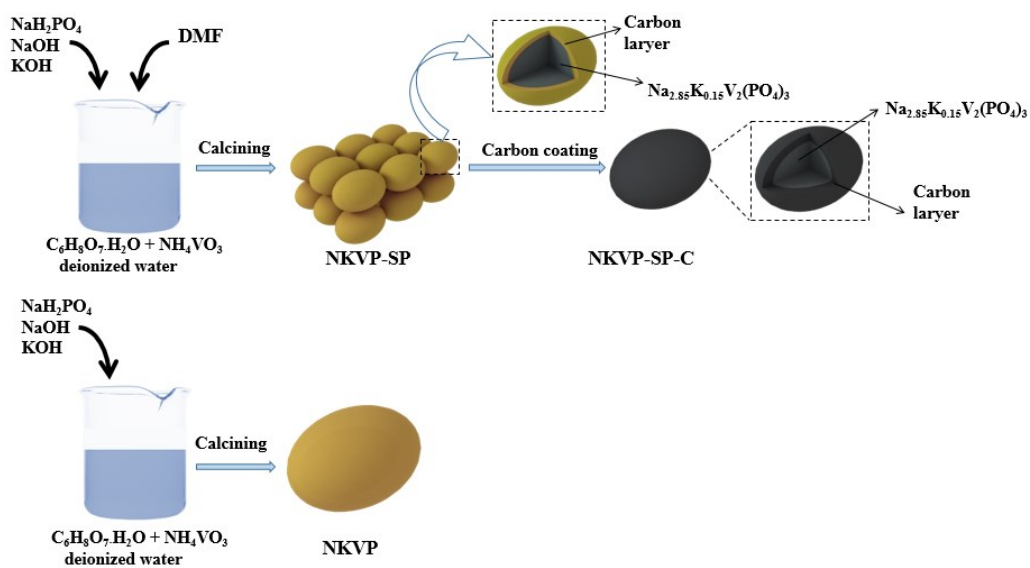


Fig. S2. Schematic diagram of synthetic strategy for NKVP-SP-C.

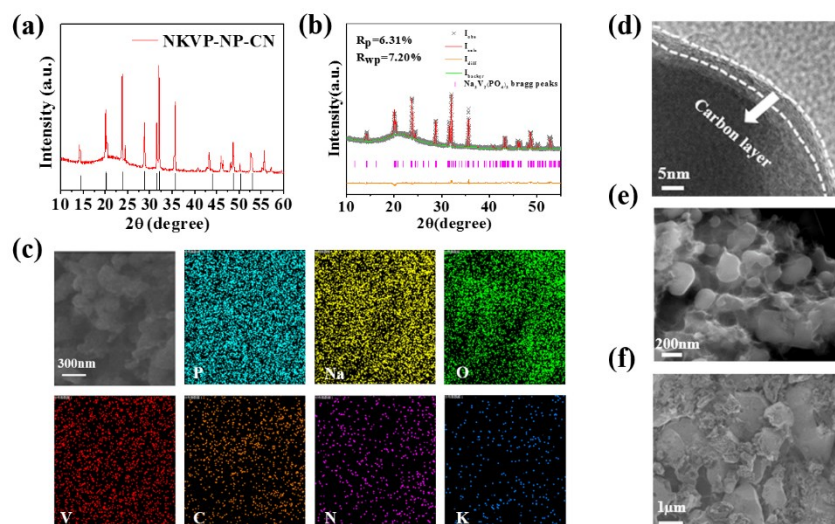


Fig.S3. (a) XRD pattern (b) refined XRD pattern (c) EDS maps (d) HRTEM image (e) micrograph of the NKVP-SP-C, (f) micrograph of NKVP.

The XRD pattern of NKVP-SP-C is shown in the Fig. S3a-b. All of the diffraction peaks can be indexed to the rhombohedral $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ structure (JCPDS No. 53-0018), suggesting that the crystal phase of the material do not change after modification. The grain surface of NKVP-SP-C was wrapped by dopamine-derived carbon layer, which was confirmed by TEM observation (Fig. S3d). This carbon layer would increase the electrical conductivity of the material. SEM image of NKVP-SP-C (Fig. S3e) clearly displayed the size of NKVP-SP-C was about 200 nm. This is greatly reduced compared to the size of NKVP (Fig. S3f). With the addition of antisolvent DMF in the preparation, the solubility of the solute is significantly lowered. This increased crystal nucleation rate rather than crystal growth rate, leading to such a smaller grain size of NKVP-SP-C. The corresponding energy dispersive spectrometry (EDS) element maps (Fig. S3d) show that Na, V, O, P, C, K and N are uniformly distributed in NKVP-SP-C.

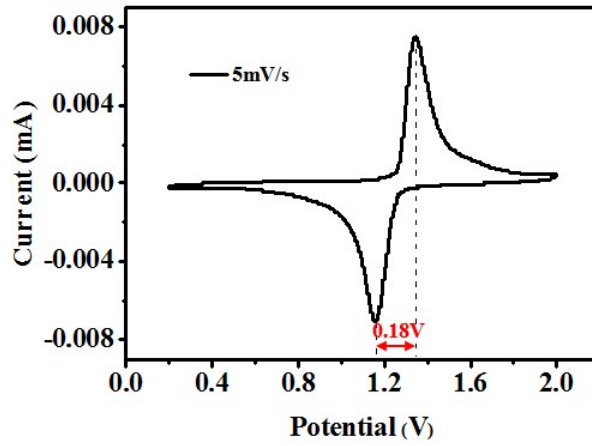


Fig. S4. The CV curve of the full cell at the scanning rate of 5 mV s^{-1} .

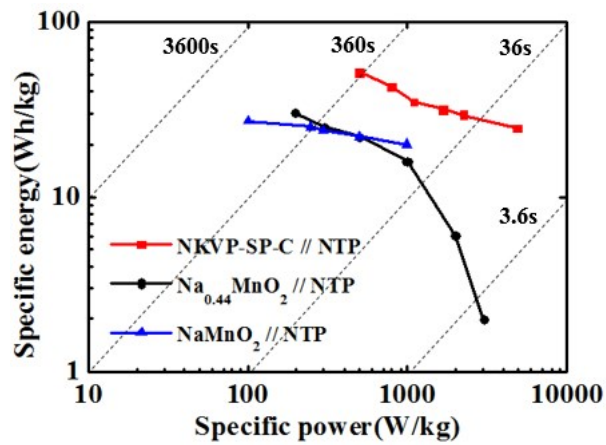


Fig.S5. Ragone plots of NaMnO_2 //NTP¹, $\text{Na}_{0.44}\text{MnO}_2$ //NTP², NKVP-SP-C//NTP (based on total mass of active cathode and anode).

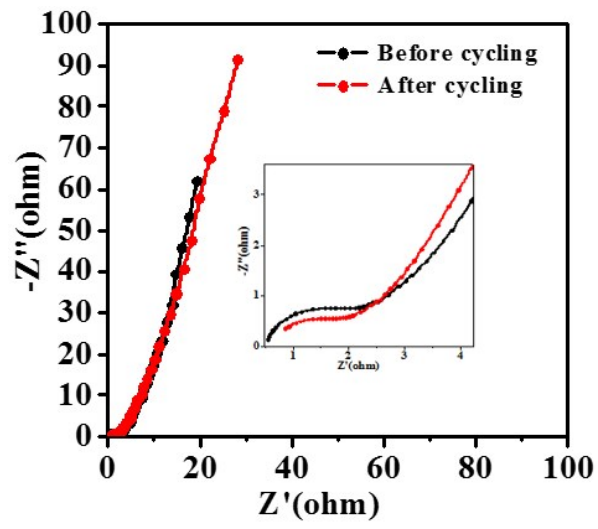


Fig. S6. Nyquist plots of the full cell.

Notes and references

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