# **Electronic Supporting Information (ESI)**

# Electrospun Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C Nanofibers as Stable Cathode Materials for Sodium-Ion Batteries

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## **Experimental methods**

#### Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C nanofibers fabrication

NaH<sub>2</sub>PO<sub>4</sub> (3.75 mmol), NH<sub>4</sub>VO<sub>3</sub> (2.5 mmol), citric acid (6.25 mmol) and 0.6 g polyethylene oxide (PEO, Mw = 600,000) were dissolved into 30 mL distiller water. After vigorous stirring for 12 h, the homogenous precursor solution was poured into a syringe connected to a plastic needle, while a copper wire attached to a high-voltage generator was placed in the solution. A direct current electric field of 20 kV was applied between the needle and the Al foil target used for collection. The as-collected electrospun fibers were calcined at 500 °C for 2 h and 800 °C for 10 h under Ar atmosphere to obtain Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C hierarchical nanofibers.

### Materials characterization

The collected products were characterized by an X-ray diffractometry (XRD) on a Rigaku-DMax 2400 diffractometer equipped with the graphite monochromatized Cu K $\alpha$  radiation flux at a scanning rate of 0.02°s<sup>-1</sup>. Scanning electron microscopy (SEM) analysis was carried using a Zeiss Gemini DSM 982 scanning electron microscope. The thermogravimetric analysis (TGA) was performed from room temperature to 800 °C at a ramp rate of 20 °C/min with an air flow rate of 20 mL/min using Q50 TGA. The structure of these Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C hierarchical nanofibers was investigated by means of transmission electron microscopy (TEM, JEOL 4000FX).

#### **Electrochemical test**

The electrochemical performances of the as-prepared products were measured by using two-electrode Swagelok-type cells. For the preparation of the working electrode, a mixture of Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/C hierarchical nanofibers, carbon black, and polyvinylidene fluoride (PVDF) in the weight ratio of 85:5:10 was ground in a mortar with *N*-methy1-2-pyrrolidone (NMP) as solvent to make slurry. For assembling Naion batteries, a Na foil was utilized as counter electrode and glass fiber (GF/D) from Whatman was used as a separator. The electrolyte was 1 M NaClO<sub>4</sub> in propylene carbonate (PC). The charge/discharge curves and cycling capacity were evaluated by an Arbin MSTAT battery test system in the cut-off voltages of 2.5 and 3.8 V. Cyclic voltammetry (CV) was performed using a VoltaLab 80 electrochemical workstation.