Electronic Supplementary Material (ESI) for Dalton Transactions.


# Supporting Information

## Multi-heteroatom doped carbon coated $Na_3V_2(PO_4)_3$ derived from ionic liquid

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**Materials characterization**

The crystal structure of the as-prepared samples were characterized by powder X-ray diffraction (XRD, Rigaku RINT-2000) using Cu Kα radiation (λ= 1.5418 Å) in a 2$\theta$ range from 10 ° to 60 °. The morphology was observed by both a field emission scanning electron microscopy (FESEM, JSM-7500F, JEOL) and a transmission electron microscope (TEM, JEM-2100F, JEOL). The structure of residual carbon in samples was detected by a Raman spectrometer (LabRAM HR800, Horiba JobinYvon) equipped with a 532 nm laser and an output power of 5 mW, and the carbon content in samples was tested by an IR carbon/sulfur determinator with high-frequency induction combustion furnace (HW2000B, China). The chemical state of elements in NVP/C-ILs was investigated by X-ray photoelectron spectroscopy (XPS, MultiLab 2000, Thermo VG Scientific Inc.) with Al Kα radiation. The electronic conductivity of samples was investigated with a powder resistivity measurement system (FT-300I, Rico, China).

**Electrochemical measurements**

For fabricate working electrodes, 75 wt. % active material (i.e., NVP, NVP/C-1, NVP/C-2,NVP/ILs and NVP/C-ILs), 15 wt. % acetylene black as conducting agent and 10 wt. % polyvinylidene fluoride (PVDF) as binder were well mixed in N-methyl pyrrolidinone (NMP) solvent by stirring for 12 h. The obtained slurry was casted on aluminum foil as current collector to form uniform film. After drying, the film was cut into discs with a diameter of 14 mm. The discs were pressed at a pressure of ~6 MPa, and then dried in vacuum at 120 °C for 8 h to obtain the cathode electrodes.

The mass loading of cathode material is about ~1.0 mg $cm^{-1}$. The R2025 coin cells were assembled in an argon-filled glove box with oxygen and water contents lower than 1 ppm by using sodium foil as anode, Whatman GF/D glass membrane as separator, and 1 M $NaClO_4$ solution in propylene carbonate (PC) with 5 vol. % fluoroethylene carbonate (FEC) as electrolyte.

All electrochemical tests were performed at room temperature. Galvanostatic charge/discharge measurements were performed on a cell test system (LAND CT2001A, China) within a voltage range from 2.5 to 3.8 V (1 C = 117.6 mAh $g^{-1}$) (vs. $Na^+/Na$). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were carried out on an electrochemical workshop (CHI614C, China). EIS measurements were performed with an amplitude of 5 mV in the frequency range from 0.01 to 100 kHz.