Supplementary Information

Ionic liquid electrolytes supporting high energy density in sodium-ion batteries based on sodium vanadium phosphate composites

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Experimental Section:

NVP@C synthesis:

The NVP@C composite material was synthesized by a two-step, glucose-assisted solid-state reaction¹. Firstly, 0.3 mol oxalic acid dihydrate was dissolved in 50 mL distilled water, and 0.1 mol vanadium oxide powder was added. The solution was stirred at 120 °C for 5 hr to form a sticky blue gel, which was then dried overnight under vacuum at 80 °C. The obtained powder was ground and heated at 100 °C in air for 1 hr to form vanadium oxalate. In the second step, sodium nitrate, as-prepared vanadium oxalate and diammonium hydrogen phosphate (to give a mole ratio of Na: V: P of 3:2:3) and 17 wt% glucose were dispersed in alcohol and ball milled at 300 rpm for 8 hr. The obtained slurry was dried overnight under vacuum at 80 °C, ground for 1 hr in a mortar and pestle, and subjected to a two-stage calcination, at 350 °C for 5 hr and 850 °C for 8 hr in 5% H₂-95% N₂ atmosphere to obtain well-crystallized Na₃V₂(PO₄)₃/C. Details of this process and characterization of the products are in previous publications²⁻⁴.

Materials Characterizations:

A powder X-ray diffractometer with Cu K α radiation at 40 kV and 40 mA (Rigaku, Japan), measuring across a 2 θ range of 5–60 ° at a scan rate of 0.5 °C min⁻¹ was used to identify the crystalline phases within the NVP@C. Carbon content was determined by carbon hydrogen nitrogen analysis (CHN).

For *ex situ* measurements, electrodes were removed from their cells in an argon-filled glovebox, washed with dimethyl carbonate (DMC) and thoroughly dried. Field emission gun scanning electron microscopy (FEG-SEM, JSM-7600F, and Carl-Zeiss, Ultra-55) with energy dispersive X-ray spectroscopy (EDX) and high-resolution transmission electron microscopy (HR-TEM, Jeol-2100F) were employed to study the microstructure and passivation layers on the electrode surfaces. ATR-FTIR analysis was carried out on a Cary 640 FTIR spectrometer, Agilent. Raman analysis used a Renishaw *in via* microscope and applied laser excitation of 514

nm and 633 nm wavelengths. X-ray photoelectron spectroscopy (XPS) data were collected with a Thermo Scientific MultiLab spectrometer using a concentric hemispherical analyzer and a micro focused, monochromatic Al Kα x-ray source

Electrochemical Performances:

Electrochemical performance testing was carried out using a 2032 coin-cell half-cell configuration with NVP@C or hard carbon as the working electrode and one piece of sodium foil as the counter/reference electrode separated by a borosilicate glass fibre separator (GF/D, Whatman), soaked in electrolyte. To prepare the NVP@C cathode electrode, 80% active material, 10% carbon (carbon black, C-65, Timcal), and 10% PVDF binder (Sigma–Aldrich) were blended with N-methyl-2-pyrrolidone solvent and cast onto aluminium foil. To prepare the hard carbon electrode slurry, 80% commercial active material (Kuraha, China), 10% carbon (carbon black, C-65, Timcal), and 10% CMC (Sigma-Aldrich) binder, by mass, were blended with distilled water and cast onto aluminum foil. The solvent was removed under vacuum in an oven at 120 °C overnight, and the electrode cut into circular discs (10 mm or 12 mm diameter) for further use. Charge-discharge tests, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) tests on NVP@C and hard carbon were performed using a Biologic VMP-2 battery testing unit at 20 ± 5 °C. The scan rates for CV were 0.1 mV s⁻¹ for hard carbon and 0.01 mVs-1 for NVP@C materials. Electrochemical stability window tests were performed in a three-electrode Swagelok cell using Na as the counter and reference electrodes and aluminium foil as the working electrodes.

Sodiation of Hard carbon electrode experiment was performed by contacting the sodium metal for 30 minutes by wetting the both electrodes with ionic liquid electrolyte and experimental setup shown in Figure S1.



Figure S1: Experimental setup of sodiation of hard carbon electrode by sodium metal with ionic liquid electrolyte.

Charaterization of organic and ionic liquid electrolyte:

The thermogravimetric analysis (TGA) data for the organic (1M NaClO₄ in EC:PC(1:1)v/v) and ionic liquid electrolytes are shown in Figure S2. The organic electrolyte showed a significant mass loss of >85% when the temperature reached to 300°C, corresponding to the evaporation of organic solvents (EC and PC). In contrast, the ionic liquid electrolyte showed a mass losses of >5% when the temperature reached at 300 °C, indicating their higher thermal stability.



Figure S2:TGA measurements for organic and ionic liquid electrolytes

CV was used to evaluate the electrochemical oxidative stability for the electrolytes in contact with sodium metal (Figure S3). Ionic liquid electrolyte shows a higher oxidative stability than the organic electrolyte; the oxidative stability trends for ionic liquid electrolyte (5.2 V vs. Na⁺/Na) and organic electrolyte (4 V vs. Na^+ /Na).



Figure S3: Electrochemical oxidative stability tests were performed in three electrode swagelok cells at 10mVs⁻¹ scan rate.

NVP@C and hard carbon material characterization:



Figure S4: NVP@C cathode material structural and morphology analysis by: (a) XRD, (b) Raman spectrum, (c) SEM, (d) TEM.

The XRD pattern of as-prepared NVP@C is displayed in Figure S4a. The NVP@C diffraction patterns match with ICSDS data (card no-248410) and show the formation of a crystalline NASICON-type framework with an R- $\overline{3}$ C space group. NASICON-type Na₃V₂(PO₄)₃ has a 3-dimensional framework of VO₆ octahedra sharing all corners with PO₄; two different sodiumion sites occur: M1 sites, where Na1 ions are 6-fold coordinated, and M2 sites, where Na2 ions are 8-fold coordinated. Because of strong binding of the Na⁺ ions at M1 sites by the surrounding oxygen atoms, Na⁺ ions are extracted from and inserted into M2 sites during charging and discharging, respectively. The theoretical capacity for this structure is 117 mAhg⁻¹, based on the reversible insertion/extraction of the two Na⁺ ions at M2 sites².

The surface of NVP@C was investigated with Raman spectroscopy (Figure S4b). NVP@C displayed a vibration band around 1000 cm⁻¹, which corresponds to weak stretching vibrations of PO₄³⁻. The stronger peaks at 1316 cm⁻¹ and 1605 cm⁻¹ are related to the D and G bands intrinsic to residual carbon, confirming the presence of amorphous carbon in NVP@C. This is consistent with the elemental analysis, which found that NVP@C contains 4.2 wt% carbon. Figure S4c is an SEM image of as-prepared NVP@C powder, showing micron-sized particles. The TEM image in Figure S4d shows agglomerates of NVP@C particles partly coated with amorphous carbon.



Figure S5: Commercial hard carbon anode material morphology and structural information by (a) XRD, (b) Raman and (c) SEM.

Figure S5a shows the XRD pattern of commercial hard carbon anode material, which exhibited two broad peaks at 23° and 44°, corresponding to the (002) diffraction of the graphitic layer structures and the (101) diffraction of graphite, respectively⁵. Moreover, the Raman spectrum shows two broad bands: the defect-induced band at 1335 cm⁻¹ (D-band) and crystalline graphite band at 1587 cm⁻¹ (G-band) (Figure S5b). The intensity of the I_G/I_D ratios was 0.94, indicating that the graphene sheets in the material are highly defective⁶. An SEM image of the hard carbon (Figure S5c) shows sheet-like particles, with a wide range of sizes, in the material.

Electrochemical performance of NVP@C and hard carbon with Na metal:



Figure S6: Electrochemical characterization of NVP@C/IL/Na metal cell with ionic liquid electrolyte: (a) Potential vs. Specific capacity curves obtained at different rates for NVP@C/IL/Na cell, and (b) Charge-discharge cycling performance at the C/2 rate for 50 cycles

Figure S7 shows similar electrochemical performance measurements for the HC/IL/Na cell with ionic liquid electrolyte. The cyclic voltammetry of hard carbon was performed at 0.1 mVs⁻¹ scan rate in the potential interval of 0.01 to 2.5 V vs. Na/Na⁺ (Figure S7a). The hard carbon

anode material shows peaks at 0.5 V and 0.01 V vs. Na/Na⁺, which are related to the insertion and adsorption mechanism of sodium on the electrode material in SIBs^{6, 7}. This electrode material was then subjected to charge-discharge cycling at different rates with IL electrolyte, and showed discharge capacity values of 258, 250, 200, 150, 100, 50 mAhg⁻¹ at C/20, C/10, C/5, C/2, 1C, and 10C rates, respectively (Figure S7b). It shows that excellent rate capability and good capacity retention of 99% with ionic liquid electrolyte, and followed the similar trend with organic electrolyte^{2, 8}.



Figure S7: Electrochemical performance of HC/IL/Na cell with ionic liquid electrolyte (a) Cyclic voltammetry performed at a scan rate of 0.1 mVs⁻¹, (b) The charge-discharge cycling performance of hard carbon at different rates in the potential range of 0.01 to 2V vs Na/Na+, (c) Potential versus Capacity plot of hard carbon anode material for first and 100th cycle, (d) Charge-discharge cycling performance of hard carbon for 100 cycles at C/5 rate in the potential range of 0.01 to 2V vs Na/Na+.

Figure S7c and S7d show the charge-discharge cycling performance of hard carbon with sodium metal at the C/5 rate for 100 cycles in the potential range of 0.01 to 2 V vs. Na/Na⁺.

The potential versus capacity plot shows that first charge capacity value is less than the first discharge capacity, due to the formation of a solid electrolyte interface (SEI) on the surface of hard carbon. During the subsequent cycles, the capacity values stabilized and showed stable capacity values up to 100 cycles (Figure S7d). The charge-discharge cycling performance of hard carbon showed stable capacity values and excellent capacity retention of 99% for up to 100 cycles at a C/5 rate (Figure S5d).



Figure S8: Electrochemical characterization of NVP@C/IL/HC@Na cell with IL electrolyte for (a) Potential vs. specific capacity curve at different current densities, and (b) Charge-discharge cycling performance at C/2 rate for 100 cycles.



Figure S9: Electrochemical impedance measurements for NVP@C/IL/Na, Hard carbon/IL/Na, and NVP@C/IL/HC@Na cell at (a) after 5 cycles, (b) after 50 cycles with ionic liquid electrolyte.

SEI characterization of NVP@C and Hard carbon:



Figure S10: *Ex situ* FTIR spectrum of electrodes extracted from NVP@C/IL/HC@Na cells. (a) NVP@C, pristine and after 100 cycles; (b) hard carbon, pristine (without sodiated) and after 100 cycles.



Figure S11: Raman spectra of electrodes from NVP@C/IL/HC@Na cells. (a) NVP@C, pristine and after 100 cycles, (b) hard carbon, pristine (no sodiated) and after 100 cycles.

NVP@C electrode SEI composition's					
Raman Shift(cm ⁻¹)	Assigned to the compositions				
1039	H-F				
833	S-F, SO ₂ FSI				
563	S-F				
447	S-S				
332	С-Н				
231	C-N				
Hard carbon electrode SEI composition's					
Raman Shift(cm ⁻¹)	Assigned to the compositions				
1214	C-C				
1126	SO ₂				
1082	CF ₂				
1038	S-O				
968	С-Н				
902	C-F,S-F				
724	S-C,C-F				

Table S1: Listing of Raman peaks and their assignments for the spectra of the SEI layers on NVP@C and hard carbon electrodes after cycling with IL electrolyte.



Figure S12:XPS spectrums for pristine and after 100 cycled with organic and ionic liquid electrolytes for (a) NVP@C and(b) HC electrodes.

 Table S2: Summary of electrochemical performance of various sodium-ion batteries.

Sodium systems (Cathode/electrolyte/Anode)	Voltage (V)	Average Discharge Voltage(V)	Specific Energy discharge (Whkg ⁻¹) (C- rate) A+C (Both Anode and cathode mass included)	Capacity Retention (%) Cycle range	Reference
NVP@C/1M NaClO ₄ in EC:PC+2wt% FEC/Hard carbon	2–3.8	3.3	363 _c (0.5C)	57%(1– 100)	8
O3-Na _{0.5} Cu _{0.22} Fe _{0.3} Mn _{0.48} O ₂ /0.8M NaPF ₆ in EC/DMC (1:1)v/v /HC	1–4.05	3.2	210 _{A+C} (0.05C)	>95%(1– 100)	9
P2-Na _{7/9} CuO _{2/9} Fe _{1/9} Mn _{2/3} O ₂ /1M NaClO ₄ in EC/DEC(1:1)v/v /HC	1–4.2	3.5	195 _{A+C} (0.02C)	89%(1–50)	10
P2-Na _{2/3} Ni _{1/3} Mn _{2/3} O ₂ /1M NaClO ₄ in EC:PC(1:1)v/v+5wt% FEC/Sb	1.4-4.0	2.9	130 _{A+C} (0.5C)	94%(1– 110)	11
P2-Na _{0.7} CoO ₂ /1M NaClO ₄ in TEGDME/Graphite	0.5–3.7	2.2	60 _{A+C} (0.175C)	80(1–1250)	12

Symmetrical P2-Na $_{0.6}$ Cr $_{0.6}$ Ti $_{0.4}$ O $_2$ /1M NaClO $_4$ or 0.8M NaPF6 in EC:DEC(4:6)v/v	1.5–3.0	2.5	82 _{A+C} (0.106C)	84(1–100)	13
Na ₃ V ₂ (PO ₄) ₃ /1M NaPF ₆ in DEGDME/graphite	0.7–4.2	2.9	120 _{A+C} (0.1C)	70(1–250)	14
$Na_2FeP_2O_7/1M NaClO_4$ in PC+2vol% FEC/C-Fe_3O_4	1.1–4.2	2.3	142 _{A+C} (0.01C)	93.3(1– 100)	15
NaFePO ₄ /NASICON-based hybrid solid electrolyte/HC	1.5–4.0	2.6	312 _{A+C} (0.2C)	96(1–200)	16
R-Na _{2x} MnHCF/1M NaClO₄ in DEC/EC(1:1)+10wt% FEC/HC	1.5–3.8	3.2	448 _c (0.1C)	95(2–25)	17
P2/P3/O2- Na _{0.76} Mn _{0.5} Ni _{0.3} Fe _{0.1} Mg _{0.1} O ₂ /1M NaPF ₆ in PC/HC	2–4.2	3.3	180 _{A+C} (0.09C)	80(1–700)	18
NVP@C/1M NaFSI in P ₁₃ FSI/HC	2–3.8	3.3	368 _c (0.5C)	75(1–100)	This work*



Figure S13: NVP@C/IL/HC@Na full sodium-ion battery prototype demonstration video, showing an LED study lamp with a 2032 coin cell

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