Supporting Information

Supported Ionic Liquid Gel Membrane Electrolytes for a Safe and Flexible Sodium Metal Battery

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Materials

N-Propyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide ([C₃mpyr][FSI]) (> 99.5 wt %) and sodium bis(fluorosulfonyl)imide (NaFSI, > 99.7 wt %) were purchased from Solvionic. Poly(vinylidene fluoride-co-hexafluoropropylene) polymer (P(VdF-co-HFP), average Mw ~455,000, average Mn ~110,000, pellets) and dimethylformamide (DMF, > 99.9 wt %) and PVDF powder were obtained from Sigma-Aldrich. Carbon black (Vulcan XR-72R) was purchased from the Fuel Cell Store. The porous support, obtained from Whatman, is a glass fiber with a pore size of 1.6 μm and average thickness of 260 μm. All chemicals were used as received without further purification.

Preparation of ionogels

Ionogels were prepared by a two-step method. Firstly, the measured amounts of P(VdF-co-HFP) were dissolved in DMF, and vigorously stirred at 80 °C for 12 h until a clear and homogenous solution was obtained. In another vial, the NaFSI was dissolved in [C₃mpyr][FSI]) at room temperature (inside Ar glovebox). The concentration of NaFSI was 0.8 mol/kg in respect to [C₃mpyr][FSI]). In a second step, both solutions were mixed together and then kept at 80 °C to obtain a homogenous solution. The solution was dried in a Schlenk line at 0.15 mbar and 50 °C until no further bubbles could be observed. The samples are transparent or opaque (See Figure S1). The ionogels used in this paper are 0.8 mol/kg in (C₃mpyr)(FSI)/P(VdF-co-HFP). The polymer composition in the gel corresponds to 6% and the Na-containing ionic liquid is equal to 94% (6/94 w/w %).
Preparation of SILGMs

A melt-infusion method was used to prepare the SILGMs. Briefly, ionogels were impregnated into the porous glass fiber by first heating slowly the ionogel at 125-130 °C in the argon glove box. The ionogel melted, the resulting liquid was collected with a preheated pipette and the liquid was subsequently dropped on the top of a glass fibre separator/membrane. The molten ionogel spontaneously wetted the membrane and percolated inside the pores of the support via capillary forces. The resulting dense membranes were then naturally cooled to room temperature, followed by the crystallization of the gel upon cooling.

Synthesis of carbon-coated Na$_3$V$_2$(PO$_4$)$_3$

The synthesis of carbon-coated Na$_3$V$_2$(PO$_4$)$_3$ (NVP) was prepared as reported elsewhere.$^1$ Briefly, V$_2$O$_5$ and H$_2$C$_2$O$_4$·2H$_2$O were dissolved into deionized water and vigorously stirred at 70 °C for 1 h to obtain a VOC$_2$O$_4$ solution, followed by adding NaH$_2$PO$_4$ and glucose into the solution. Then N-propanol was further added under
stirring for 30 min, followed by drying at 70 °C to obtain the precursor. Finally, Na$_3$V$_2$(PO$_4$)$_3$/C micro-composites were obtained by preheating the precursor at 400 °C for 4 h and annealing at 750 °C for 8 h under inert atmosphere (Ar) with a heating rate of 5 °C/min.

**Characterization**

*Ionic conductivity*

Ionic conductivities of samples were measured at room temperature by the AC impedance spectroscopy with the frequency ranging from 10 MHz to 1.0 Hz using a signal voltage of 0.1 V. A 2-electrode Pt wire dip cell and barrel cell were used for the ionic conductivity measurements of ionic liquid or gels/membranes, respectively. The constant of the dip cell was calibrated using a 0.01 mol·L$^{-1}$ KCl solution (with an ionic conductivity of 1.41 mS·cm$^{-1}$ at 25 °C) before measurements of the ionogels. For the SILGMs measurements, the membranes were sandwiched between two stainless steel electrodes of 23 mm in diameter. The results can be found in Table S1.

**Table S1.** Ionic conductivities of samples at room temperature (23 °C).

| Samples                        | Ionic conductivity (mS/cm) |
|--------------------------------|---------------------------|
| pure C$_3$mpyrFSI              | 10.0                      |
| 0.8 mol/kg NaFSI in C$_3$mpyrFSI | 7.1                       |
| supported C$_3$mpyrFSI membrane | 4.3                       |
| ionogel (0.8 mol/kg NaFSI in P(VdF- | 6.4                       |
co-HFP)\([\text{C}_3\text{mpyr}[\text{FSI}]}\) (6/94 w/w) )

*a supported ionic liquid gel membrane (SILGM)

*a Glass fiber separator was used as support.

*Phase Behaviour*

Differential scanning calorimetry (DSC) was performed with a TA-Q100 instrument at a scan rate of 10 °C·min⁻¹. Samples were first cooled down from room temperature to −150 °C, followed by heating to 250 °C. A second cooling and heating cycle was performed and the reported thermal behavior were collected from the second heating traces. The DSC of neat C₃mpyrFSI, pure PVDF-co-HFP, and ionogel are displayed in Figure S2.

![Figure S2](image.png)

**Figure S2.** DSC of pure C₃mpyrFSI and for the 0.8 mol/kg NaFSI in P(VdF-co-HFP)\([\text{C}_3\text{mPyr}[\text{FSI}]}\) (6/94 w/w) ionogel.
The DSC curve of the neat ionic liquid reveals multiple endothermic transitions, which are rather different from other traditional ionic liquids (e.g. imidazolium-based ones). Firstly, upon heating the material, a low energy related to a solid—solid phase transition is observed at -82 °C (phase 3 to phase 2). The second phase transition takes place at -18 °C (phase 2 to phase 1) and subsequently the ionic liquid melts at -9 °C. Additionally, a very interesting behavior is spotted at the temperature range from -60°C to -35°C; at around -49°C, a broad endothermic peak comes out followed by an exothermic peak at -43°C. Such response is still not well understood but it is believed that the broad endothermic peak at -49°C may correspond to the melting of another (kinetic) phase and then readily crystalizes into a more thermodynamically stable phase (as phase 2 with exothermic peak at -43°C). This behavior was firstly observed and discussed by Passerini et al, and the results obtained here support very well their findings with a nearly identical DSC trace.²

Concerning the DSC trace for the ionogel, a glass transition (Tg) is observed at -60 °C, suggesting that the polymer is allowing glass formation in the ionic liquid. For the pure P(VDF-HFP) polymer, the glass transition is timidly situated at -40 °C. The higher Tg of the polymer when compared to the ionogel is expected; this is due to the fact that the addition of polymer inhibits the movement of the ionic liquid and consequently decreases the overall mobility. Besides, the addition of the mixture NaFSI-C₃mpyrFSI to the polymer (ionogel) shifts the melting point to lower temperatures, from 154 °C to 129 °C, showing that the polymer destabilizes the crystalline phase due to interactions with the ionic liquid. The ionogel has a good
thermal stability and can be heated up to 160°C, after this point, as shown in Figure S1, the material starts to decompose, most likely due to the decomposition of the sodium salt.

**NVP Cathode Material**

The structural characterization of the NVP materials was investigated by X-ray Diffraction (XRD, Rigaku Dmax Ultima + X-ray diffractometer) with CuKα radiation at 40 kV and 40 mA, in the 2θ ranging from 10° to 100° at a scan rate of 0.5 °C/min. The nanostructure of the NVP@C was assessed by transmission electron microscopy (TEM). The TEM images of NVP@C material were obtained by using the microscope FEI TECNAI T20 operating at 200 kV. Raman spectra analysis was carried out by using a Renishaw in via microscope, the wavelength of the applied laser was 514 nm (Ar-laser).

**Electrochemical measurements**

Electrochemical performance testings, including cyclic voltammetry, impedance analysis, and galvanostatic charge–discharge cycling were carried out using a CR2032 coin-cell half-cell configuration. For the cathode electrode preparation, a slurry containing 80% of NVP@C, 10% PVDF and 10% carbon black was prepared by mixing the materials with NMP solvent until a homogenous paste was formed. The paste was coated on Aluminium current collector, dried, punched into disks and finally applied as the cathode, the mass of the coated cathode material was in the range of 2.4–2.7 mg.cm⁻². A piece of sodium metal (disk) was used as the counter/reference electrode. SILGMs were sandwiched between two electrodes as both the electrolyte and separator in the
coin cells, which were assembled under inert condition in an argon glove with low level of O\(_2\) (<0.2 ppm) and humidity (H\(_2\)O <0.1 ppm). Charge-discharge tests, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were performed using a VMP-2 battery testing unit at room temperature. The batteries were galvanostatically cycled using a potential range of 2.5 V-3.8 V.

**Electrochemical impedance spectroscopy (EIS)**

The EIS obtained before and after cycling was recorded at OCP by applying an amplitude of 10 mV in the frequency range from 10\(^6\) Hz-10\(^{-2}\) Hz.

As mentioned, the figure 3 in the main manuscript shows the fitting of the EIS spectra before and after cycling the sodium battery. The calculated parameters after fitting is provided in table S2 below:

**Table S2 - EIS parameters after fitting.**

|                | \(R_b\) (Ω) | \(R_{SEI}\) (Ω) | \(R_{CT}\) (Ω) |
|----------------|-------------|----------------|-----------------|
| Before cycling  | 8.3         | -              | 246.0           |
| After 500 cycles | 8.4       | 1248.1         | 297.0           |

**Safety Procedures – Exposing and handling sodium metal to the atmosphere**

It is important to note that whenever sodium metal and/or sodium metal-containing
devices are to be handled outside of a glovebox, safety procedures should always be taken at all times since sodium metal can readily react with moisture and is an immediate hazard, possibly starting a fire with catastrophic results. In handling the flexible battery as shown in the attached video we always applied the safety procedures:

- Wear full personal protective equipment (safety glasses, lab coat and gloves).
- Have ready a bucket full of sand. Pour the sand on the fire immediately if sodium ignites.
- Have also nearby an extinguisher compatible with metal-related fires (Dry powder). Do not use water or CO₂ or any halogenated extinguishing agents whatsoever.

*First aid measures to treat sodium metal injuries*

- If there is eye irritation, immediately flush eyes with plenty of water for 15 minutes at least. Call for medical aid as soon as possible.
- Skin must be washed with large amounts of water for as long as possible.
- Inhaled sodium must be treated by inhaling fresh air immediately. Artificial respiration is advisable and if breathing is difficult, oxygen must be applied. Seek professional medical aid immediately.

**REFERENCES**

(1) Li, Y.; An, Q.; Cheng, Y.; Liang, Y.; Ren, Y.; Sun, C.-J.; Dong, H.; Tang, Z.; Li,
(2) Zhou, Q.; Henderson, W. A.; Appetecchi, G. B.; Montanino, M.; Passerini, S. Physical and Electrochemical Properties of N-Alkyl-N-Methylpyrrolidinium Bis(Fluorosulfonyl)Imide Ionic Liquids: Py$_{13}$fsi and Py$_{14}$fsi. *J. Phys. Chem. B* **2008**, *112*, 13577-13580.