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Supporting Information for

A new Na[(FSO$_2$)(*n*-C$_4$F$_9$SO$_2$)N]-based polymer electrolyte for solid-state sodium batteries

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Experimental Section

Chemicals and Materials

Poly(ethylene oxide) (PEO, $M_w = 6 \times 10^5$ g mol^{-1}, Acros) was dried at 50 °C for 12 hours under high vacuum conditions. Na_2CO_3 (99.5%, Alpha), CuO (99%, Alpha), NiO (99%, Alpha), Fe_2O_3 (99.5%, Alpha), and MnO_2 (98%, Alpha) were used as received. Potassium (fluorosulfonyl)(*n*-nonafluorobutanesulfonyl)imide (KFNFSI) (99%, Suzhou Fluolyte Co., Ltd., China) were used as received without further treatment. Sodium perchlorate ($NaClO_4$) (99%, Alpha) was dried at 110 °C for 24 hours before use. Anhydrous acetonitrile (99.9%, Alpha Aesar) was dried by 4 Å molecular sieves for 48 hours before use. All the procedures related to the handing moisture or oxygen sensitive materials were carried out in an argon-filled glove box (MBraun, H_2O and $O_2 < 1$ ppm).

Synthesis of Sodium (fluorosulfonyl)(*n*-nonafluorobutanesulfonyl)imide (NaFNFSI)

NaFNFSI was synthesized by a metathesis reaction between KFNFSI and $NaClO_4$. KFNFSI (25.00 g) was dissolved in a quantitative acetonitrile (100 mL), and then $NaClO_4$ (7.30 g) was added slowly in an argon-filled glove box. The mixture was stirred at room temperature for 24 hours. The product was isolated by filtration through a poly(tetrafluoroethylene) (PTFE) membrane filter (pore size ≈ 1 μm). To depress $KClO_4$ contamination in the resulting salt, the powder obtained was recrystallized from acetonitrile/toluene under stirring conditions and filtered through a PTFE membrane filter (pore size ≈ 0.2 μm). The highly pure NaFNFSI salt was obtained as white powder after drying at 80 °C for 48 hours under high vacuum conditions. The above synthetic procedures are similar to the preparation of lithium (fluorosulfonyl)(*n*-nonafluorobutanesulfonyl)imide (LiFNFSI), as described in the literature.[1]

Fabrication of Polymer Electrolyte Membrane.

The membrane of the NaFNFSI/PEO ($EO/Na^+ = 15$, by molar ratio) blended polymer electrolyte was prepared by a solution-casting technique. First, NaFNFSI (1.00 g) and PEO (1.64 g) were mixed and dissolved in dried acetonitrile (60 mL) in an argon-filled glove box. Second, The mixture was continuously stirred at 60 °C for 24 hours to obtain a homogeneous viscous solution. Finally, the as-prepared solution was spread onto a Teflon plate and dried at 60 °C for 48 hours under high vacuum conditions to remove any residual solvent.

Synthesis of Cathode Material.

The $NaCu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}O_2$ (NCNFM) composite was synthesized by a simple solid-state reaction according to our previous report.[2]. The starting materials (Na_2CO_3, CuO, NiO, Fe_2O_3, and MnO_2) were ball-milled on the planetary ball mill apparatus (PM100) at a rotation speed of 400 rpm for 5 h and pressed into pellets under pressure of 10 MPa. Then the pellets were heated at 850 °C for 16 hours in air.

Fabrication of Cathode Sheet.

The cathode sheets of NCNFM composite were fabricated by mixing the NCNFM composite (65 wt.%), super P (10 wt.%), NaFNFSI/PEO ($EO/Na^+ = 15$) SPE (20 wt.%), and PVDF (5 wt.%) in a quantitative acetonitrile under strong agitation. The obtained slurry was cast onto a carbon-coated aluminum foil with doctor blade, and dried at 60 °C for 12 hours under high vacuum conditions.

Characterization of Polymer Electrolyte.

Scanning electron microscopy (SEM, Hitachi S-4800) was utilized to observe the morphology for the membrane of the NaFNFSI/PEO ($EO/Na^+ = 15$) blended polymer electrolyte. The sample was sealed in a vacuum transfer box and transferred to the SEM chamber without exposure to air.

Differential scanning calorimeter (DSC, Netzsch 200 F3) was employed to measure the phase transition behaviors of the as-prepared NaFNFSI/PEO ($EO/Na^+ = 15$) blended polymer electrolyte. The sample of 5–10 mg was hermetically sealed in an aluminum pan and placed at room temperature for 10 days prior to measurement in an argon-filled glove box. The sample was heated from −150 to 150 °C (or 250 °C) at a rate of 10 °C min^{-1} under a flow of nitrogen.

Thermal decomposition temperature of the NaFNFSI/PEO ($EO/Na^+ = 15$) blended polymer electrolyte was obtained using a thermal gravimetric analysis (TGA, NETZSCH STA 449C). The sample of 5–10 mg was put into an aluminum pan and heated from 30 to 600 °C at a ratio of 10 °C min^{-1} under a flow of argon.

X-ray diffraction (XRD) was used to identify the crystalline phases of the NaFNFSI/PEO ($EO/Na^+ = 15$) blended polymer electrolyte, which was performed on a D8 X-ray diffractometer (Bruker) equipped with Cu Kα radiation ($\lambda = 1.54$ Å) in the 2θ range from 5 to 90° at 40 mA and 40 kV.

The ionic conductivities of the NaFNFSI/PEO (EO/Na^+ = 15) blended polymer electrolyte were measured using AC impedance with an amplitude of 5 mV, which was carried out on an Autolab PGSTAT128N workstation (Netherland) over the frequency range from 0.01 to 10^6 Hz. The membrane of NaFNFSI/PEO electrolyte was sandwiched between two stainless steel blocking electrodes and heated to 80 °C for 2 hours to obtain good contact between the electrolytes and electrodes, and was then placed at room temperature for 10 days prior to the measurement in an argon-filled glove box.[3] Afterwards, the measurements were performed in the temperature range from 25 to 90 °C for the heating scan. The sample was thermally equilibrated at each temperature at least for 1 hour prior to the measurement.

Linear sweep voltammetry (LSV, Shanghai Chenhua CHI627D) was adopted to investigate the anodic electrochemical stability of the NaFNFSI/PEO (EO/Na^+ = 15) blended polymer electrolyte. The Na|SPE|SS coin-type cell was assembled in an argon-filled glove box and measured over a wide range of potentials from the open circuit potential (OCP) to 6.0 V vs. Na^+/Na at a scan rate of 1 mV s^{-1} at 80 °C.

The Na-ion transference number (t_{Na^+}) of the NaFNFSI/PEO (EO/Na^+ = 15) blended polymer electrolyte was evaluated using a combination measurement of AC impedance and DC polarization, which were proposed by Bruce and Abraham.[4,5] The symmetric Na|SPE|Na coin-type cell was first heated to 80 °C for 2 hours to obtain good contact between the electrolytes and electrodes. Then, a DC voltage of 10 mV was applied to the cell to obtain the initial and steady currents. Meanwhile, the EIS spectra of the same cell before and after the DC polarization were also monitored using AC impedance with an amplitude of 5 mV over the frequency range from 0.05 to 10^6 Hz.

Cell Fabrication and Evaluation.

The 2032 coin-type cells were assembled by using the NCNFM composite cathode, SPE (NaFNFSI/PEO, EO/Na^+ = 15), and Na-metal anode in an argon-filled glove box. The applied currents and specific capacities of the cells were calculated based on the mass of cathode active material. The active material mass loading on the electrode was ca. 1.8 mg cm^{-2}. The galvanostatic charge/discharge measurements were carried out on a Land CT2001A battery test system (Wuhan, China) at various current rates at 80 °C. The symmetric Na|SPE|Na coin-type cells were assembled by using Na metal as the working and counter electrodes, which were charged/discharged at a current density of 0.1 mA cm^{-2} at 80 °C.

Table S1 The characterization data for phase transition behaviors of the NaFNFSI/PEO (EO/Na$^+$ = 15) blended polymer electrolyte, as well as the neat PEO and NaFNFSI.

Samples	$T_{s\text{-}s}$[a] / °C	T_g[b] / °C	T_m[c] / °C	T_d[d] / °C	ΔH_m[e] / J g^{-1}	χ_c[f] / %
NaFNFSI	160.2		189.9	251.5	38.4	
NaFNFSI/PEO		−36.3	61.0	312.1	37.1	18.3
PEO[3]			70.1	359.6	122.2	60.2

[a] Solid-solid transition temperature (DSC, the peak of the heat capacity change).

[b] Glass transition temperature (DSC, the onset of the heat capacity change).

[c] Melting point (DSC, the peak of the heat capacity change).

[d] Decomposition temperature (TGA, 1% weight loss).

[e] Enthalpy of melting (DSC).

[f] The crystallinity (χ_c) of the blended polymer electrolyte is calculated by: $\chi_c = (\Delta H_m/\Delta H_o) \times 100\%$, where ΔH_m is the melting enthalpy of per unit mass of PEO, and ΔH_o is the value of 203.0 J g^{-1} reported in the literature[6] for the melting enthalpy of 100 % crystalline PEO.

Table S2 Measured values for the parameters in **Equation (S1)** and the corresponding calculated values of Na-ion transference number (t_{Na^+}) at 80 °C.

Samples	EO/Na$^+$	I_o (μA)	I_s (μA)	R_i (Ω)	R_f (Ω)	R_l^o (Ω)	R_l^s (Ω)	ΔV (mV)	t_{Na^+}
NaFNFSI/PEO	15	45.34	35.11	7.38	7.48	196.08	182.87	10	0.24
NaFSI/PEO[7]	20	23.78	11.97	13.83	13.16	342.00	359.72	10	0.16

$$t_{Na^+} = \frac{I_s R_f [\Delta V - I_o R_l^o]}{I_o R_i [\Delta V - I_s R_l^s]} \tag{S1}$$

Where ΔV is the DC potential applied across the cell; I_s and I_o are the steady-state and the initial currents determined by the DC polarization, respectively; R_l^o and R_l^s are the interface resistances measured by the AC impedance method before and after polarization, respectively; R_i and R_f are the initial and final resistances of the electrolytes, respectively.

Table S3 Comparison of electrochemical performances of PEO-based electrolytes for sodium batteries.

Samples	Cell	Discharge specific capacity	Cycle number	Capacity retention rate	Ref.
$NaCF_3SO_3$/PEO (SPE)	Na|S (90 °C)	505 mA h g^{-1} (0.144 mA cm^{-2})	10	33%	[8]
$NaClO_4$/PEO-NaCMC (CPE)	Na|$NaFePO_4$ (60 °C)	~ 90 mA h g^{-1} (0.2C)	20	87%	[9]
$NaClO_4$/PEO-TiO_2 (CPE)	Na|$Na_{2/3}Co_{2/3}Mn_{1/3}O_2$ (60 °C)	49.2 mA h g^{-1} (0.1C)	25	91%	[10]
NaFSI/PEO (SPE)	Na|$Na_3V_2(PO_4)_3$ (80 °C)	85 mA h g^{-1} (0.2C)	30	84%	[7]
NaFSI/PEO-NZSP (CPE)	Na|$Na_3V_2(PO_4)_3$ (80 °C)	~ 102 mA h g^{-1} (0.1C)	120	78%	[11]
$NaClO_4$/PEO-SiO_2-EMIFSI (CPE)	Na|NZY (60 °C)	212.5 mA h g^{-1} (0.5C)	100	30%	[12]
NaFNFSI/PEO (SPE)	Na|NCNFM (80 °C)	104.7 mA h g^{-1} (1C)	150	70%	**This work**

"SPE" represents solid polymer electrolyte; "CPE" represents composite polymer electrolyte;

"NZSP" represents $Na_3Zr_2Si_2PO_{12}$; "EMIFSI" represents 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide;

"NZY" represents yttrium-doping sodium zirconate; "NCNFM" represents $NaCu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}O_2$.

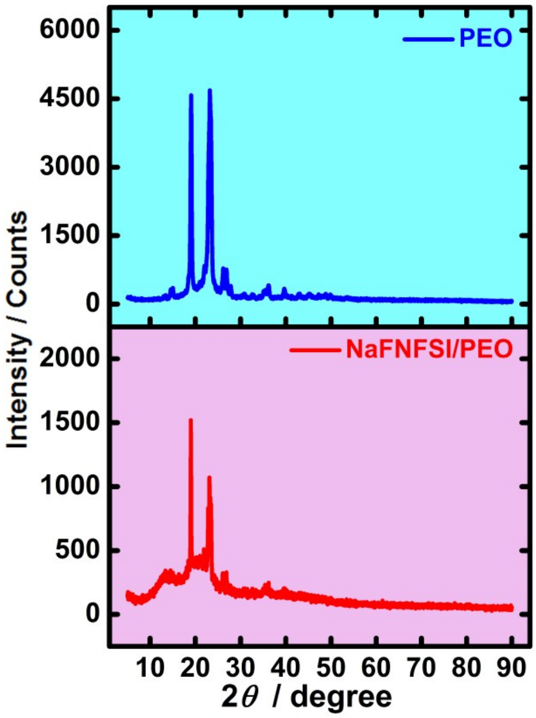

Figure S1. XRD patterns of the neat PEO and NaFNFSI/PEO (EO/Na^+ = 15) blended polymer electrolyte.

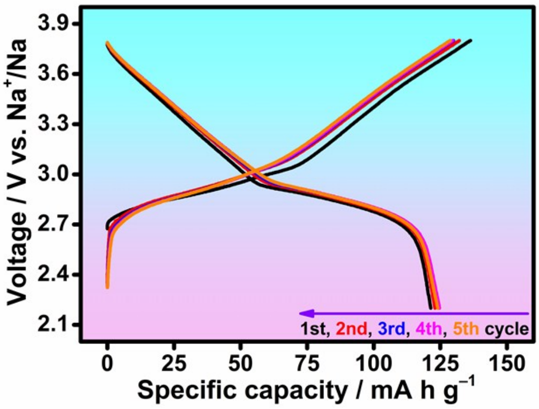

Figure S2. Voltage profiles of the Na|SPE|$NaCu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}O_2$ cell with the NaFNFSI/PEO (EO/Na^+ = 15) blended polymer electrolyte at 0.1C at 80 °C.

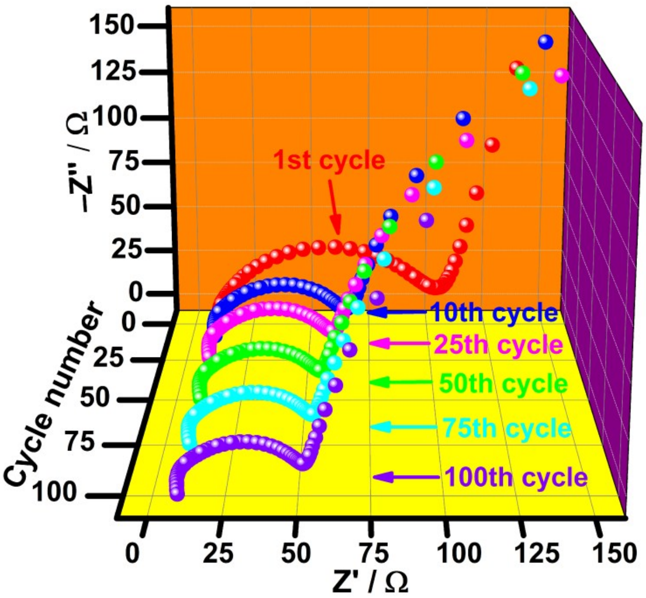

Figure S3. EIS spectra of the Na|SPE|$NaCu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}O_2$ cell with the NaFNFSI/PEO ($EO/Na^+ = 15$) blended polymer electrolyte at 1C (after 5 cycles for activation at 0.1C) at 80 °C.

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