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Electronic Supplementary Information

Ionic liquid functionalized electrospun gel polymer electrolyte for high-performance lithium metal battery

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Experimental Section

Materials. 1-methylpiperidine (purity: 97%), (3-chloropropyl) trimethoxysilane (98%), N, N-dimethylformamide (DMF, 99.5%) and N-Methyl-2-pyrrolidone (NMP, 99.5%) were purchased from Aladdin Industrial Inc. Colloidal silica (LUDOX® SM-30) was purchased from Sigma Aldrich. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was received from Rhodia R&D center. Polyvinylidene difluoride (PVDF, Solef® 6012) and poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP, SOLEF® 21216/1001) were provided by Solvay, Belgium. Lithium hexafluorophosphate ($LiPF_6$) was supplied by Morita Chemical Industries, Japan. Lithium difluoro(oxalato)borate (LiDFOB) was provided by Fosai Chemical Inc., China. The cathode material, $LiNi_{0.5}Mn_{1.5}O_4$ was supplied by Xingneng New Material Co., Ltd., China. Super P (TIMCAL) was provided by Imerys Graphite & Carbon, Switzerland. All these materials were used as received without further purification. The carbonates including dimethyl carbonate (DMC), ethylene carbonate (EC) and fluoroethylene carbonate (FEC) were supplied by Shida Shenghua Chem. Group, China. The carbonates were treated by 4 Å molecular sieve to remove the residue moisture before using, in which the water content was less than 10 ppm.

Synthesis and characterization of SiO_2PPTFSI. SiO_2PPTFSI was synthesized by a three-step method as reported by Lu et al.[1] Firstly, 1-methylpiperidine and (3-chloropropyl) trimethoxysilane with a mole ratio of 1:1.1 were reacted in DMF in nitrogen atmosphere at 80 ^{o}C for 24 h to obtain 1-methyl-1-propylpiperidinium chloride (PPCl). Secondly, PPCl was tethered to colloidal silica (0.15:1, wt. ratio) by a reaction in deionized water with pH<2. At last, SiO_2PPTFSI was synthesized by the reaction between silica tethered PPCl nanoparticles (SiO_2PPCl) and LiTFSI in deionized water through an ion exchange reaction. The final product of SiO_2PPTFSI (NanoIL) was dried in a vacuum oven and then stored in the argon filled glovebox. Purity and structure of the product PPCl were characterized in previous work.[2] Purity, structure and thermal stability of SiO_2PPTFSI was tested by the solid state ^{29}Si NMR on a Bruker AVANCE NMR spectrometer (600 MHz) and Thermo Gravimetric Analyzer (TGA, SDT-Q600), respectively, as shown in Fig. S1.

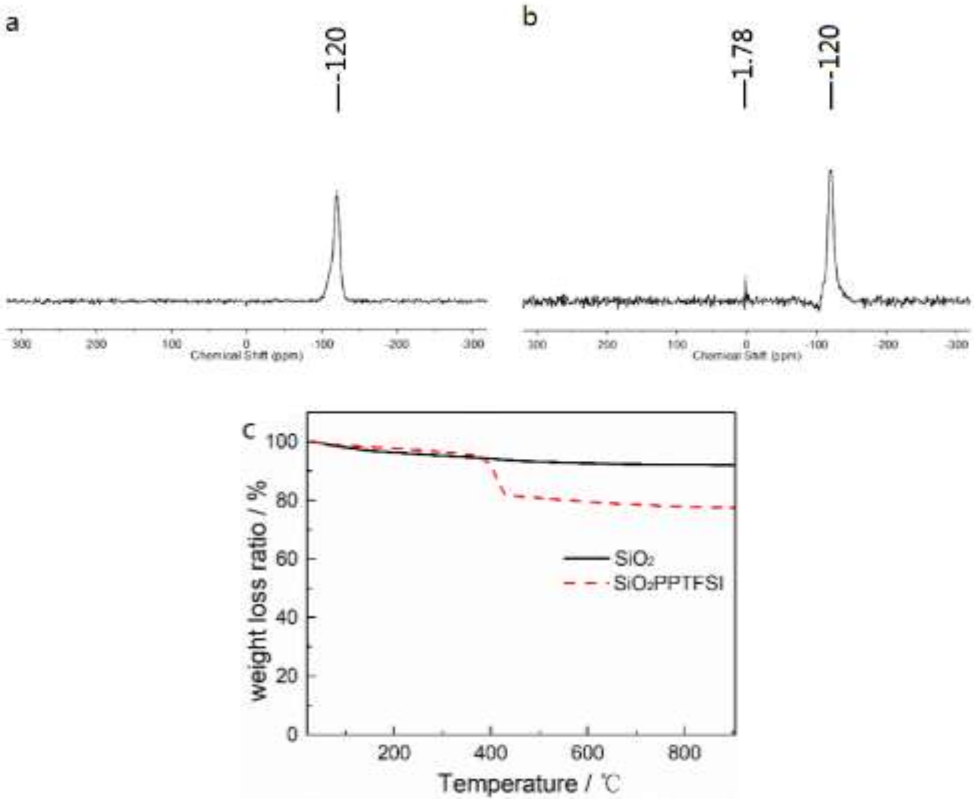


Fig. S1 Solid-state ^{29}Si MAS NMR spectra of (a) SiO_2, (b) SiO_2PPTFSI, (c) TGA curves of the resultants SiO_2 and SiO_2PPTFSI.

^{29}Si NMR chemical shifts, SiO_2: δ= -120 ppm, SiO_2PPTFSI: δ= -120, -1.78 ppm.[3] A peak -1.78 ppm was assigned to the resonance of PPTFSI on the surface of silicon nucleus.

The thermal property of SiO_2PPTFSI was tested by Thermo Gravimetric Analyzer (TGA, SDT-Q600).

The test was performed between 25 and 900 °C with a heating rate of 10 °C/min, under nitrogen atmosphere. These results show that SiO_2PPTFSI exhibits thermal stability up to 350 °C.

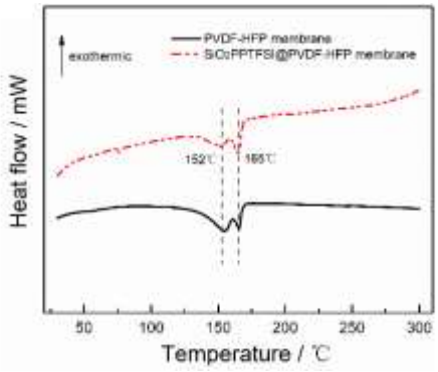
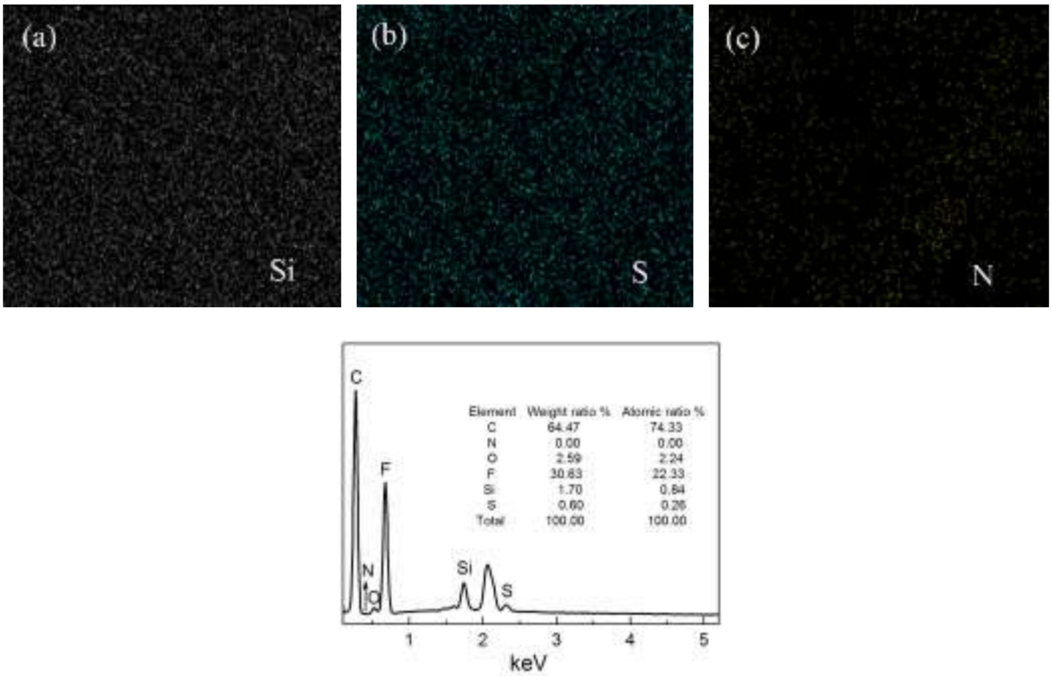


Fig. S2 DSC curves of PVDF-HFP and SiO_2PPTFSI/PVDF-HFP nanofibrous membranes.

The thermal properties of PVDF-HFP and SiO_2PPTFSI/PVDF-HFP nanofibrous membranes were tested by Differential scanning calorimetry (DSC1, Mettler-Toledo, Switzerland). The test temperature was from 30 to 300 °C with a heating rate of 5 °C/min, under nitrogen atmosphere.



Element	Weight ratio %	Atomic ratio %
C	64.47	74.33
N	0.00	0.00
O	2.59	2.24
F	30.63	22.33
Si	1.70	0.84
S	0.60	0.26
Total	100.00	100.00

Fig. S3 Elemental analysis spectrograms of SiO_2PPTFSI/PVDF-HFP membrane by EDS.

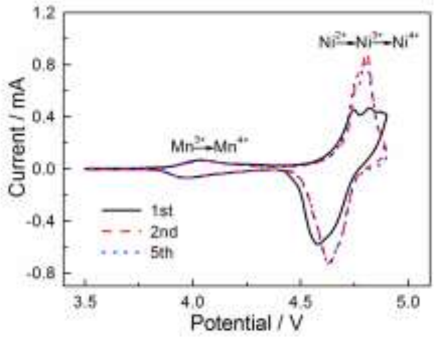


Fig. S4 Cyclic voltammetry curves of Li/NanoIL GPE/$LiNi_{0.5}Mn_{1.5}O_4$ battery at a scanning rate of 0.1 mV s^{-1}.

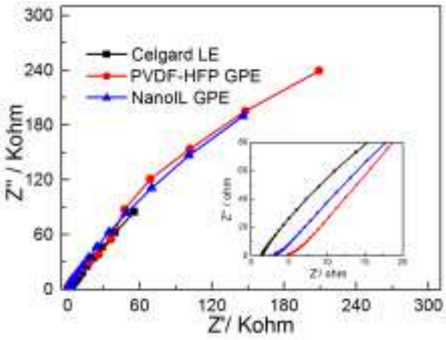


Fig. S5 Impedance evolution of SS/electrolyte/SS cells of ionic conductivity at 25 °C.

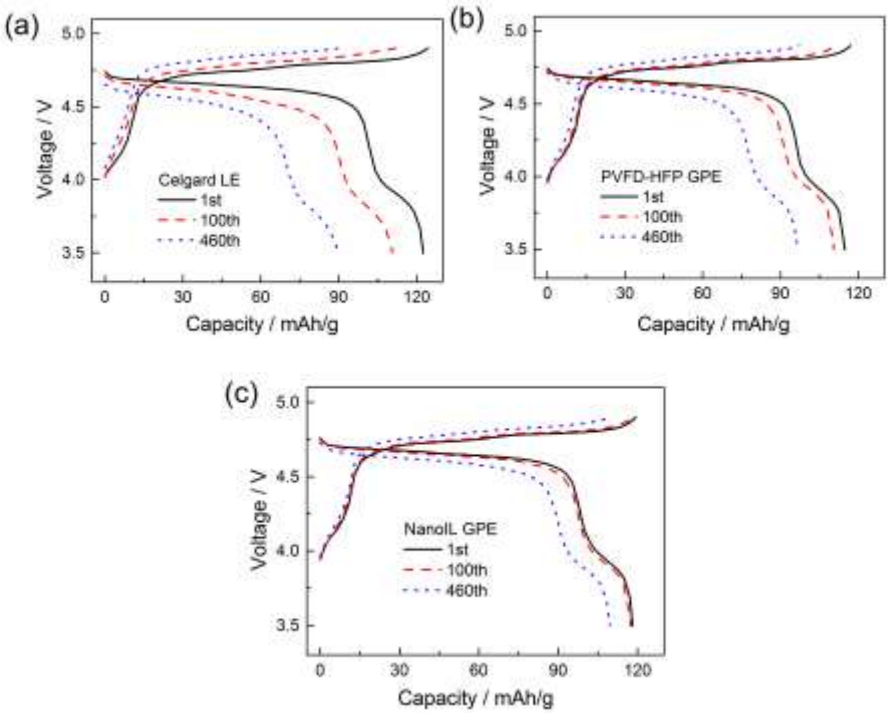
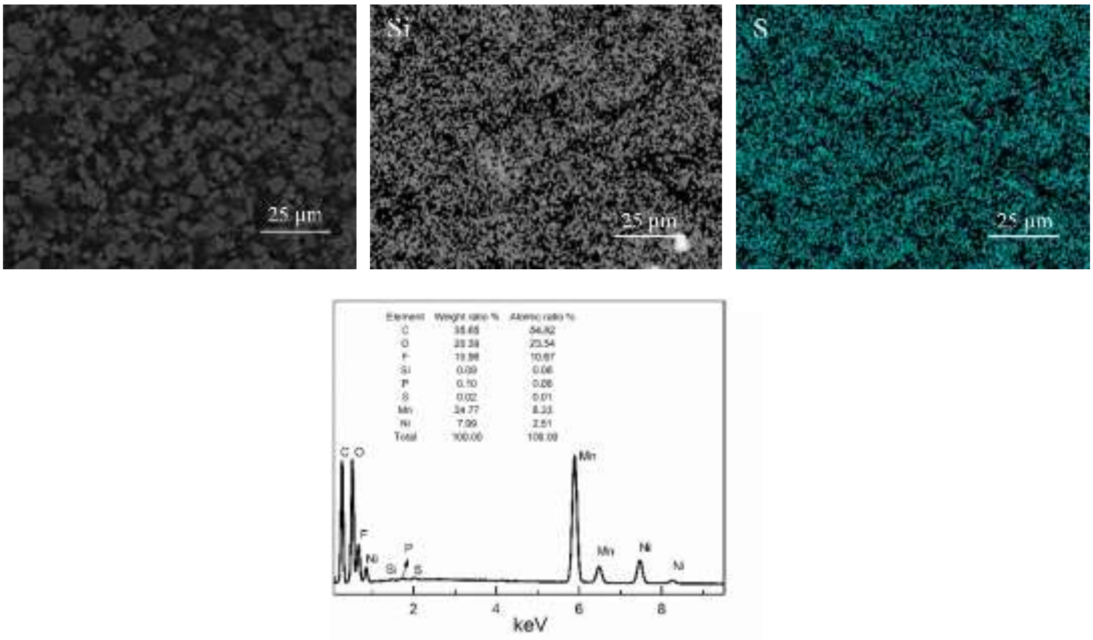


Fig. S6 Discharge-charge voltage profiles of (a) Celgard LE (b) PVDF-HFP GPE (c) NanoIL GPE at the 1st, 100th and 460th cycles at 1 C rate.



Element	Weight ratio %	Atomic ratio %
C	35.65	54.82
O	23.38	23.54
F	19.98	10.67
Si	0.09	0.06
P	0.10	0.06
S	0.02	0.01
Mn	34.77	8.33
Ni	7.99	2.51
Total	100.00	100.00

Fig. S7 Elemental analysis spectrograms of cathode of Li/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cell with NanoIL GPE by EDS.

Li/LiNi$_{0.5}$Mn$_{1.5}$O$_4$ cell with NanoIL GPE was disassembled after cycling. The cathode was washed by DMC, dried to remove the solvent, and then investigated by EDS. EDS data is shown in Fig. S7. There is a small amount of Si and S on the surface of the cathode, and their molar ratio is different. The results indicate SiO$_2$PPTFSI could release TFSI$^-$, which would participate in the formation of solid electrolyte interface (SEI) other than physical deposition.

Reference

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3 L. Lee, I.J. Kim, S. Yang, S. Kim, *Res. Chem. Intermediat.*, 2013, 39, 3279-3290.