

Supplementary Information

Improvement in LiFePO₄/Li battery Performance via Poly(perfluoroalkylsulfonyl)imide (PFSI) Based Ionene Composite Binder

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Synthesis of PFSILi ionic polymer

The lithiated poly(perfluoroalkylsulfonyl)imide (PFSILi) ionomer was prepared from an iodo perfluorinated sulfonyl fluoride precursor (Shanghai Sino fluoro Scientific Co., Ltd, China) following the reaction scheme¹ presented in **Figure S1**. Sulfonyl fluoride (-SO₂F) group was converted to a sulfamide sodium salt (-SO₂NHNa) from liquid ammonia. Iodo group was transformed into the sodium salt of a sulfinic acid (-SO₂Na) via sulfinatodehalogenation method. The resulting compound was further chlorinated at 0 °C to obtain the monomer containing two reactive groups (-Cl and -NH₂). Next, the PFSI ionic polymer cesium salt was prepared through condensation polymerization using excess CsF (99.9%, Aladdin, China). To exchange Cs⁺ with Li⁺ in nearly quantitative yield, the polymer was dissolved and stirred in a solution of dry CH₃CN (HPLC, Aladdin, China) containing LiClO₄ (AR, Sinopharm, China) for 12 h at 50 °C.^{2,3} Cesium perchlorate white precipitate formed by a metathesis reaction was filtered out and the resulting lithiated ionic polymer was vacuum-dried at 100 °C for 24 h.

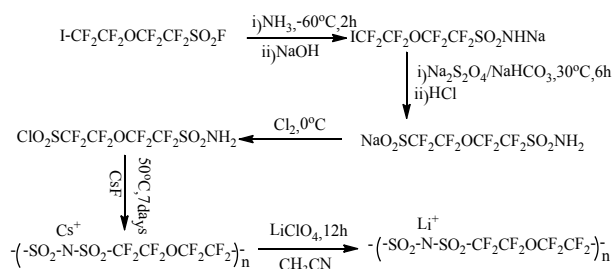


Figure S1. Synthesis of lithiated poly(perfluoroalkylsulfonyl)imide polymer (PFSILi).

Characterization of PFSILi

^{19}F NMR spectra were recorded for both the monomer and the polymer using a Bruker AV-400 spectrometer at 400 MHz using CD_3CN as lock solvent. As seen in **Figure S2**, the monomer exhibits four clean singlet peaks corresponding to the four CF_2 groups from the molecule. The ^{19}F NMR chemical shifts of -80.08 ppm and -81.71 ppm were attributed to CF_2OCF_2 , the peak at -109.58 ppm was for $\text{CF}_2\text{SO}_2\text{Cl}$, and the peak at -118.11 ppm was identified with CF_2NH_2 . The ^{19}F chemical shifts of the ionic polymer, with a backbone structure of a Bronsted super acid, tended to aggregate into two regions: CF_2O region around -81 ppm and CF_2S region around -117 ppm. Comparing the polymer with the monomer, the chemical shift at -109.58 ppm⁴ disappeared, which meant that the Cl on the SO_2Cl group had been substituted. The peak area ratio of CF_2O region to CF_2S region approached 1:1 while signals at both regions showed peak splitting that could be ascribed to ion coordination and the wide distribution of polymerization degree, which was further confirmed by GPC (Table1). The molecular weight ($M_n=209182$, $M_w=315775$) and molecular weight distribution ($M_w/M_n=1.51$) were determined using a HLC-8320(TOSOH) gel permeation chromatograph (GPC) operated at 40 °C with a mobile phase of 0.1 mol/L LiBr in DMF solution at a flow rate of 0.6 mL/min. The evaluation of M_n and M_w

values were derived from a conventional calibration based on the narrow-distribution polystyrene standard.

Thermal analysis was employed using a Perkin-Elementer Diamond TG/DTA (Switzerland) thermo-gravimetric analyzer at a heating rate of 10 °C /min in a nitrogen or air atmosphere. The thermal stability of PFSiLi ionic polymer was evaluated using the TGA test for further application in technological devices, and the result is presented in **Figure S3**. The ionic polymer was thermally stable up to 330 °C, which provide the needed stability for use at high temperatures.

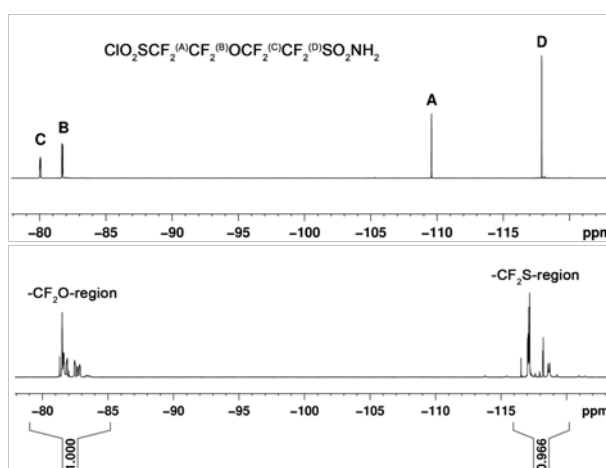


Figure S2. ^{19}F NMR spectra of monomer (top) and PFSiLi (bottom).

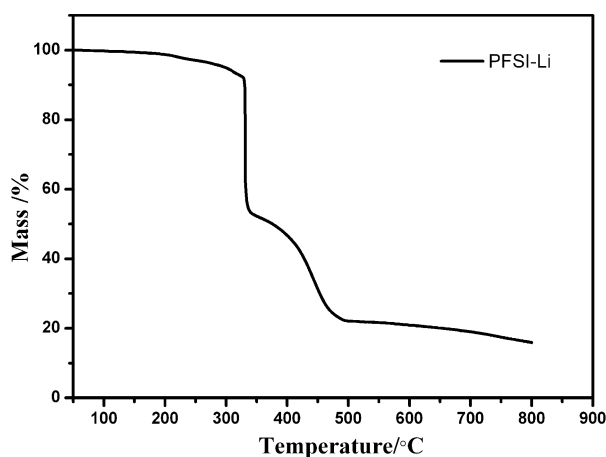


Figure S3. TGA curve of prepared PFSiLi ionic polymer.

Conductivity of PFSI-PVDF composite

Symmetrical stainless-steel/membrane/stainless-steel cell was assembled to determine the ionic conductivity of PFSI-PVDF composite with two electrodes AC impedance method using Zahner Zennium EL101 electrochemical station. The composite membrane was prepared by solution casting method. Prior to assemble into the cell, the composite membrane was removed from PC-EC solvent and blotted dry with filter paper in the glove-box. AC impedance experiments were performed over a frequency range of 100 mHz–1 MHz with a disturbing voltage of 10 mV in the temperature range of 20 °C to 80 °C. At each temperature, the cell was maintained for 1 h for stabilization before testing. The ionic conductivity was calculated from the bulk sample impedance at a zero-phase angle. Results are listed in **Table S1**.

Table S1 Conductivity of PFSI-PVDF composite at different temperatures.

Temperature/°C	R/Ω	d/μm	S/cm ²	$\sigma \times 10^{-4}$ S/cm
20	6.608	78.7	2	5.95
30	6.766	78.7	2	5.81
40	5.987	78.7	2	6.57
50	5.287	78.7	2	7.44
60	4.735	78.7	2	8.31
70	4.302	78.7	2	9.14
80	3.732	78.7	2	10.54

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) measurements were carried out to detect the difference in electrodes with PVDF and composite binder. It was performed using an AXIS ULTRA DLDS system with focused monochromatic Al K α radiation. As **Figure S4** showed, the XPS survey spectra were generally the same except the signals

from chemical elements in PFSiLi and no significant bonding change between active material, conductive additives and binder were observed.

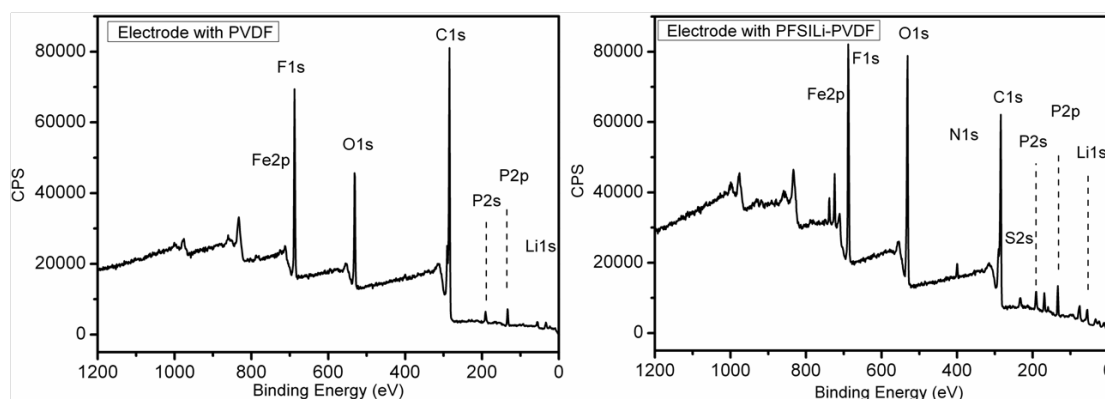


Figure S4. XPS spectra of electrode with different binders.

Reference

1. L. Xue, Doctor of Philosophy in Chemistry, Clemson University, 1996.
2. H. Han, J. Guo, D. Zhang, S. Feng, W. Feng, J. Nie and Z. Zhou, *Electrochem. Commun.*, 2011, **13**, 265.
3. S. Zhou, H. Han, J. Nie, M. Armand, Z. Zhou and X. Huang, *J. Electrochem. Soc.*, 2012, **159**, A1158.
4. L. Xue, ACS 12th Winter Fluorine Conference, Florida, January 22-27, 1995.