

Supporting Information

Safe and Flexible Ion Gel Based Composite Electrolyte for Lithium Batteries

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1. Experimental Part

1.1 Materials: 3-Bromo-1-propanol (97%), methacryloyl chloride (97%), triethylamine (> 99 %), anhydrous magnesium sulfate, 1-butylimidazole (98%), 1, 1, 4, 7, 10, 10-hexamethyl triethylene tetramine (HMTETA, Elf Atochem) were purchased from Energy Chemical. lithium bis(trifluoromethane sulfonyl)imide (LiTFSI, 98%), Lithium triflate (LiTf, 98%), copper(I) bromide (CuBr, 98%) and 1-Ethyl-3-methylimidazolium Bis(trifluoromethanesulfonyl)imide (98%) were purchased from Aldrich and used as received. LiFePO₄, PVDF binder, carbon black and lithium metal anode were Chemically Pure and purchased from Damao Chemicals, Tianjin, China. Dichloromethane, acetone, acetonitrile, diethyl ether, methyl alcohol, toluene, tetrahydrofuran (THF), dimethylformamid (DMF) and N, N-dimethylformamide (NMP) were purchased from Shanghai Reagent Co., Ltd. Ultrapure deionized (DI) water was used as appropriate.

1.2 Synthesis of imidazolium monomer

By the method shown in [Scheme S1](#), the imidazolium based monomer, 1-[(2-methacryloyloxy) propyl]-3-butylimidazolium bromide (MPBIm-Br), has been synthesized. 14.6 g (0.105 mol) 3-Bromo-1-propanol in 30 mL dichloromethane were added to a dry, two-neck 100-mL flask and stirred for 10 min in an ice bath. Then under N₂ atmosphere, 11.1 g (0.11 mol) of triethylamine along with 10 mL of dichloromethane was added slowly by a funnel. After stirring the mixture for 10 min, 10.5 g (0.1 mol) methacryloyl chloride in 10 mL dichloromethane was added dropwise. The reaction mixture was stirred 12 h at room temperature and then filtered. Washing the filtrate with 200 mL of DI water four times and collecting the organic layer. Remaining water was further dried with anhydrous magnesium sulfate. Then dichloromethane in the mixture was removed by vacuum, after which clear liquid 3-Bromopropyl methacrylate yielded (75% yield).

To obtain imidazolium bromide monomer ([Scheme S1](#)), a mixture consisting of 13.51

g (0.07 mol) 3-Bromopropyl methacrylate and 8.69 g (0.07 mol) 1-butyl imidazole and a small amount of 2,6-di-tertbutyl-4-methylphenol (inhibitor), was stirred in a 40 °C oil bath for 24 h, after which viscous liquid yied (80% yield). The resulting liquid was dissolved in 30 mL dichloromethane and re-precipitated in 200 mL diethyl ether in an ice bath. ¹H NMR (δppm, DMSO-d₆): 10.35 (s, 1H, N-CH=N), 7.36-7.45 (d, 2H, N-CH-CH-N), 6.03 (s, 1H, HCH=C(CH₃)), 5.51 (s, 1H, HCH=C(CH₃)), 4.36 (m, 2H, N-CH₂-CH₂-CH₂-O), 4.30 (m, 2H, N-CH₂-CH₂-CH₂-O) 4.07 (t, 2H, N-CH₂-CH₂-CH₂-CH₃), 2.30 (m, 2H, N-CH₂-CH₂-CH₂-O), 1.88 (s, 3H, CH₂=C(CH₃)), 1.65 (m, 2H, N-CH₂-CH₂-CH₂-CH₃), 1.37 (m, 2H, N-CH₂-CH₂-CH₂-CH₃), 0.92 (t, 3H, N-CH₂-CH₂-CH₂-CH₃).

1.3 Synthesis of three-arm imidazolium based polymerized ionic liquid (3P(MPBI_m-Br)) by Atom Transfer Radical Polymerization (ATRP)

Trimethylolpropane-tri(2-bromoisobutyrate) initiator (TMPBr₃) (0.058g, 0.3 mmequiv. Br) was synthesized by ATRP, the procedure of which is described in details elsewhere,¹ and ligand 1,1,4,7,10,10-hexamethyltriethylenetetramine (69mg, 0.3mmol) were added to a 50mL Schlenk flask, The flask was then degassed by three freeze–pump–thaw cycles. While the contents were frozen in liquid nitrogen, the flask was back filled with nitrogen and CuBr (43mg, 0.3mmol) was added. The flask was then degassed and backfilled with nitrogen thrice, after that imidazolium monomer (MPBI_m-Br) (3.41g, 10 mmol) and distilled toluene (10ml) were added via syringe. Then the flask was transferred to a thermostated oil bath at 80 °C. After 6 h of polymerization, the Schlenk flask was cooled down to room temperature. The polymer was precipitated in acetone, purified by dialysis (MWCO = 2 kpa) against methanol, and dried under vacuum at 50 °C.

1.4 Synthesis of three-arm poly (1-[(2-methacryloyloxy) propyl]-3-butylimidazolium bromide) X⁻ (3P(MPBI_m-X))

PILs with different anions were prepared by a simply ion-exchange method, as

illustrated in [Scheme S1](#). Briefly, LiCF_3SO_3 was added dropwise into homogeneous acetone solution of 3P(MPBI m -Br) with the anion mole ratio of $\text{CF}_3\text{SO}_3^-/\text{Br}^- = 3/1$, and stirred at room temperature. 6 h later, the solvent was removed and the raw product was collected. The raw product was removed via immersing and rinsing it in deionized water several times to remove the superfluous lithium salts and then filtered and dried in a vacuum oven until constant weight at 50°C . After that the pure 3P(MPBI m -Tf) was obtained. A titration test with the addition of AgNO_3 to a solution of the resulted polymer in acetone confirmed that no bromine anions remained in the PILs, for there is no precipitation of AgBr occurred.²⁻⁴ 3P(MPBI m -TFSI) was synthesized by the same simple procedure with LiTFSI salts.

2. Results and Discussion

2.1 Analysis of structural confirmation

As can be seen from [Fig. S1](#), the characteristic proton absorptions of 3P(MPBI m -Br) locate at 9.76 ppm (N-CH=N) and 7.94-8.04 ppm (N-CHCH-N). After anion exchange reaction, the obtained 3P(MPBI m -Tf) and 3P(MPBI m -TFSI) contains different counter-anions, which are CF_3SO_3^- , $(\text{CF}_3\text{SO}_3)_2\text{N}^-$ respectively. The anion exchange disturbs chemical shifts of the signal attributed to the midazolium ring protons ([Table S1](#)). These chemical shifts change to 9.10 ppm (N-CH=N), 7.69-7.76 ppm (N-CHCH-N) for 3P (MPBI m -Tf) and 9.14 ppm (N-CH=N), 7.66-7.75 ppm (N-CHCH-N) for 3P (MPBI m -TFSI). Proton absorption peak of N-CH=N (9.76 ppm) associated with Br shifted in the exchanged PIL indicates that Br^- has been replaced by other anion.

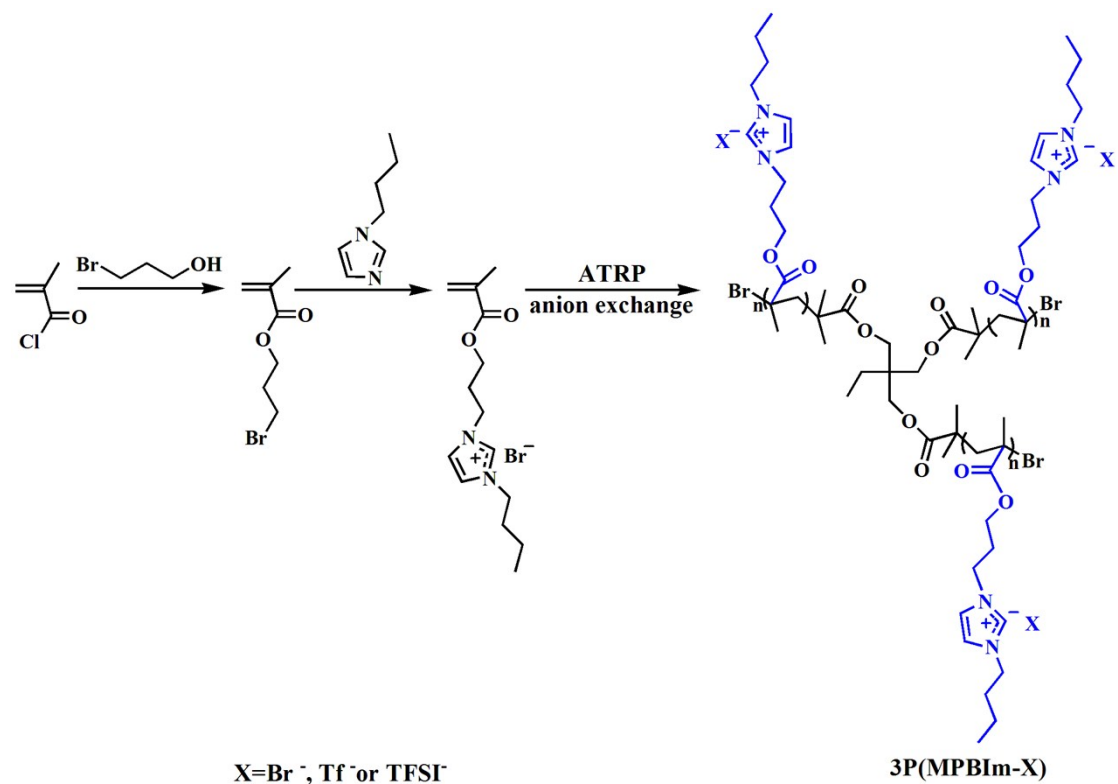
To further characterize the structure of midazolium PILs with different counter anion, ATR-FT IR spectroscopy was conducted. The frequency range shown in it describes the vibrational contributions arising from multiple sources including midazolium cations, different anions and methacrylate blocks. In [Fig. S2](#), all the polymers show characteristic bands at 1722 cm^{-1} and 1157 cm^{-1} for the C=O and C-O stretching vibration.⁵ These demonstrated that the structure of the polymer backbone is maintained after the anion exchange reaction. At the same time, the appearance of

new bands attributes to different anions, such as CF_3SO_3^- anion (1255 cm^{-1} , 1159 1031 cm^{-1})³ and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ anion (1350 , 1195 , 1135 and 1056 cm^{-1}).⁶ In addition, broad peaks near 3420 cm^{-1} in the FTIR spectra of 3P (MPBIm-Br) are from water,⁷ which do not appearance in the exchanged PILs. This owes to the high hydrophilic of 3P (MPBIm-Br). In conclusion, the FT-IR spectra provide a further evidence of the anion exchange successfully.

2.2 Effect of counter anions on solubility of 3P(MPBIm-X)

In the case of ionic liquids, anion exchange leads to hydrophobic liquids immiscible with water and miscible with organic solvents such as acetone, tetrahydrofuran, and dichloromethane.⁸⁻⁹ To investigate whether nature of counter anions affect the solubility of PILs, test were conducted. As shown in Table S1, 3P (MPBIm-Br) with bromide anions is soluble in water. However, when the halide anion is substituted by CF_3SO_3^- , the polymer can't dissolve in water anymore but show freely soluble in polar aprotic solvents such as acetone, dimethylsulfoxide and dimethyl formamide. The 3P(MPBIm-X) becomes soluble in less polar solvents such as tetrahydrofurane when the counter-anion are $(\text{CF}_3\text{SO}_2)_2\text{N}^-$. Combining with the similar behaviors that have been observed for the type of PILs having imidazolium, alkylammonium, pyridinium or guanidinium cationic backbones, it confirms that the nature of the anion has stronger influence on the solubility behavior of PILs.^{4, 10}

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Scheme S1. Schematic illustration for the synthesis of three-arm poly(1-[(2-methacryloyloxy) propyl]-3-butylimidazolium bromide) X^- (3P(MPBIIm- X)). X represents Br^- , Tf^- or TFSI^- .

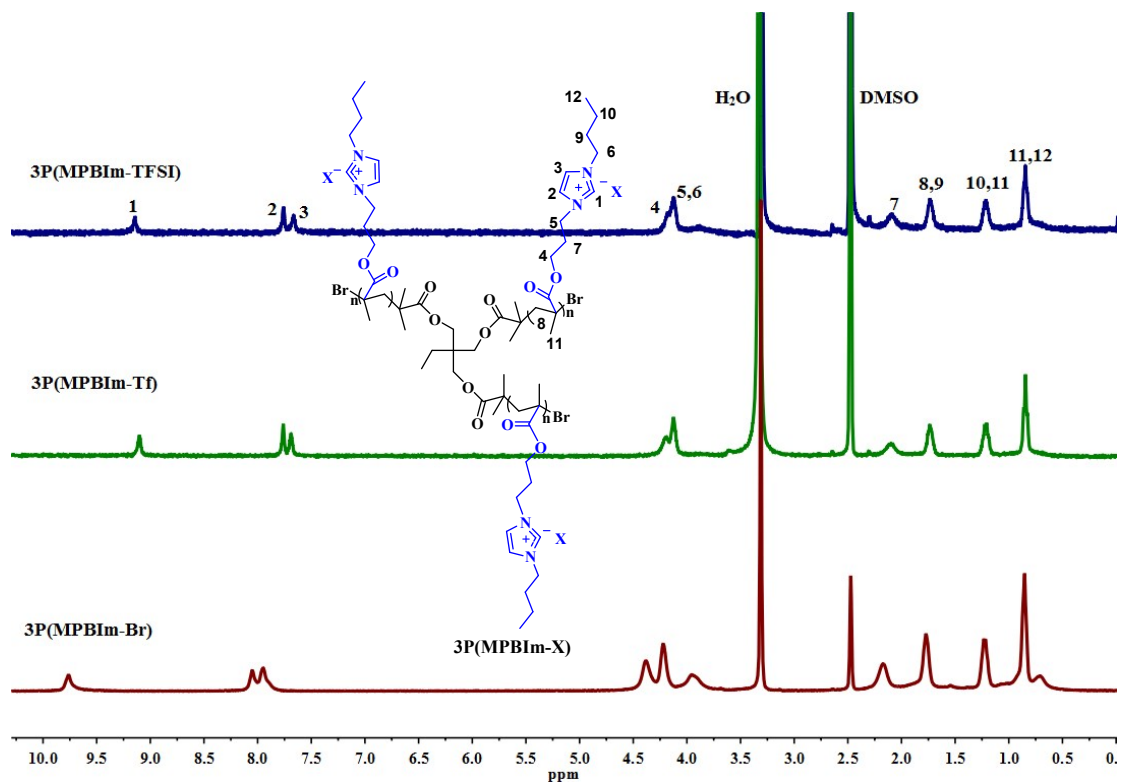


Fig. S1. ^1H NMR spectra of the 3P (MPBIm-X) in DMSO-d_6 , X represents the corresponding anion (Br^- , CF_3SO_3^- , $(\text{CF}_3\text{SO}_3)_2\text{N}^-$).

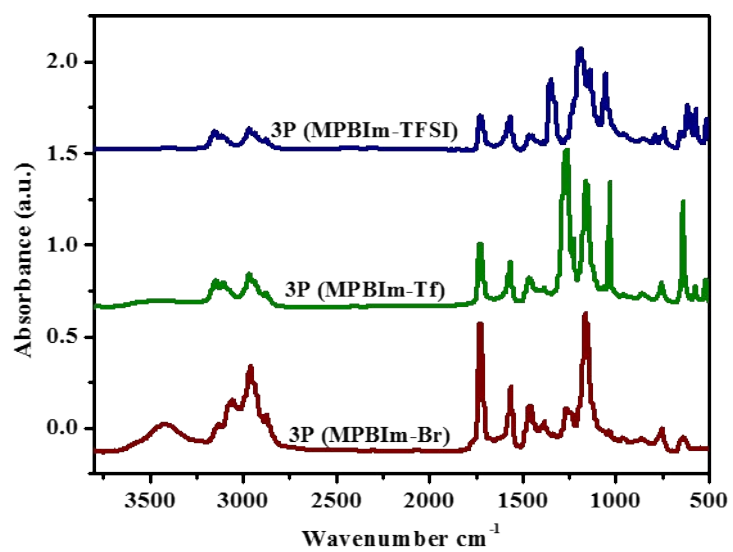


Fig. S2. Infrared spectra of 3P(MPBIIm-X) at ambient conditions.

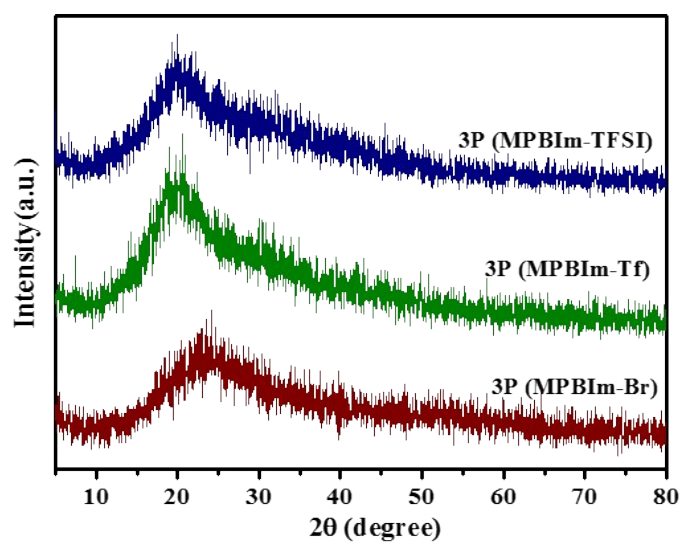


Fig. S3. XRD spectra of 3P(MPBIIm-Br), 3P(MPBIIm-Tf) and 3P(MPBIIm-TFSI), respectively.

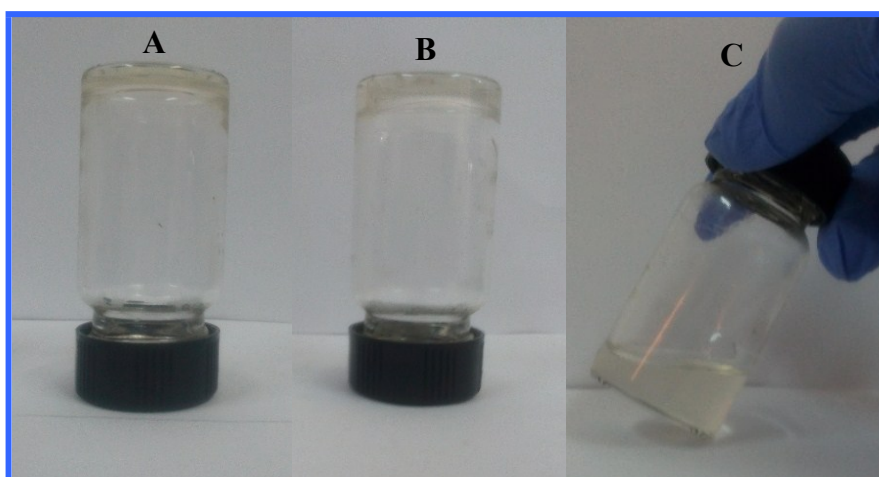


Fig. S4. Photographs of 3P(MPBI_m-TFSI)/LiTFSI/EMIM-TFSI hybrid complex containing different amounts of EMIM⁺TFSI⁻: (A) and (B) soft, sticky, and nonfluidic gel ($0 \leq x \leq 1.5$); (C) viscous and flowable gel ($x > 2$).

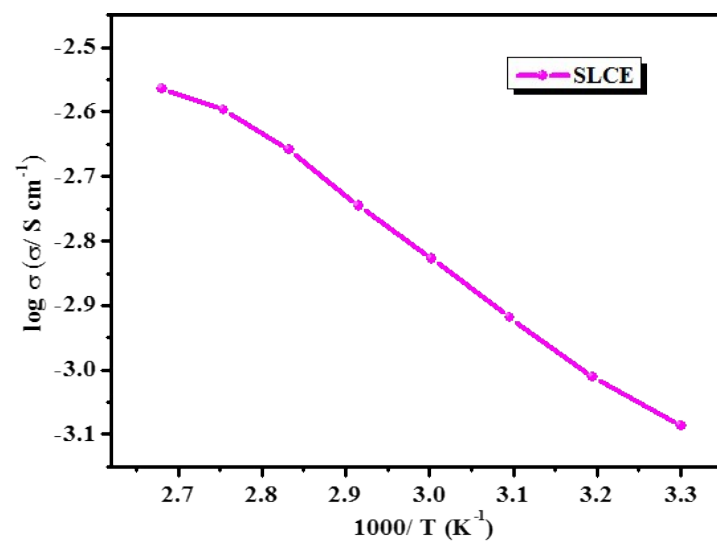


Fig. S5. Temperature-dependent ionic conductivity of the SLCE.

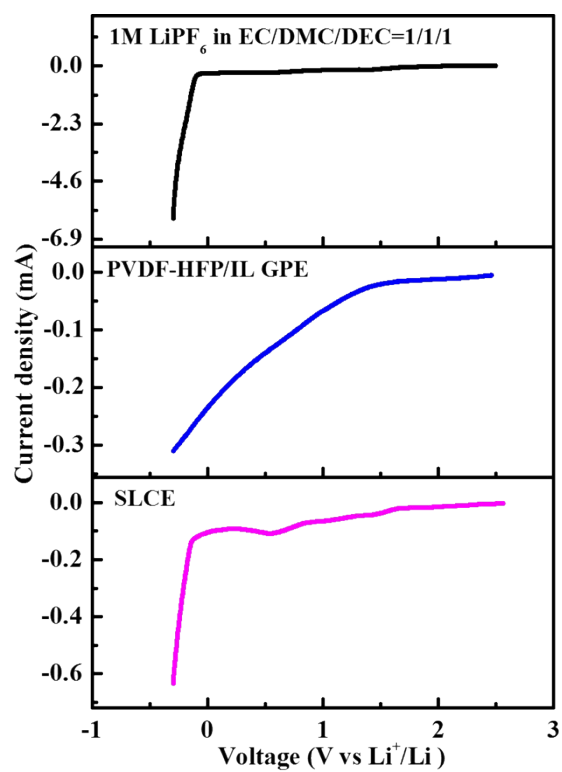


Fig. S6. Linear sweep voltammograms of SLCE, PVDF-HFP/IL GPE, carbonate-based liquid electrolyte for the cathodic sweeps from open circuit potential to -0.3V (5.0 mV s^{-1}).

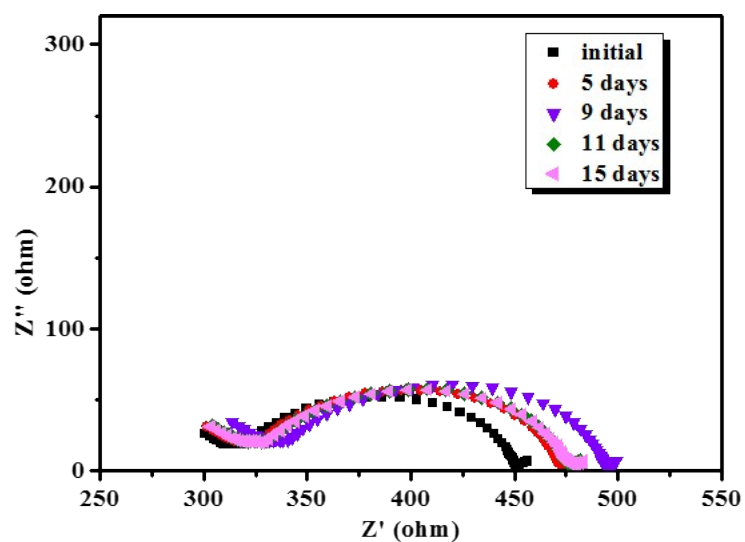


Fig. S7. Electrochemical impedance spectra of a symmetric cell (Li metal/3P(MPBI_m-TFSI) electrolyte/Li metal) versus time at 50 °C.

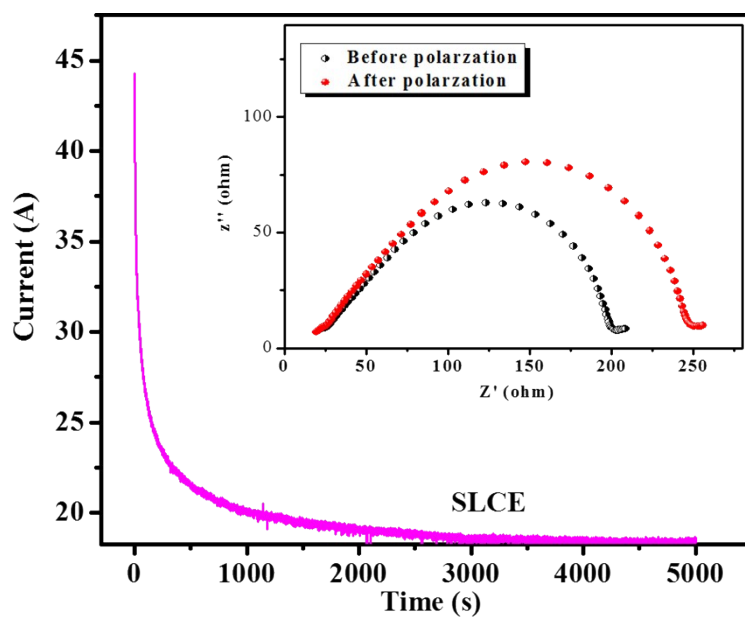


Fig. S8. Current-time curve following a DC polarization of 0.01 V of SLCE. Inset is Nyquist profiles of the cell electrochemical impedance spectroscopy response before and after polarization.

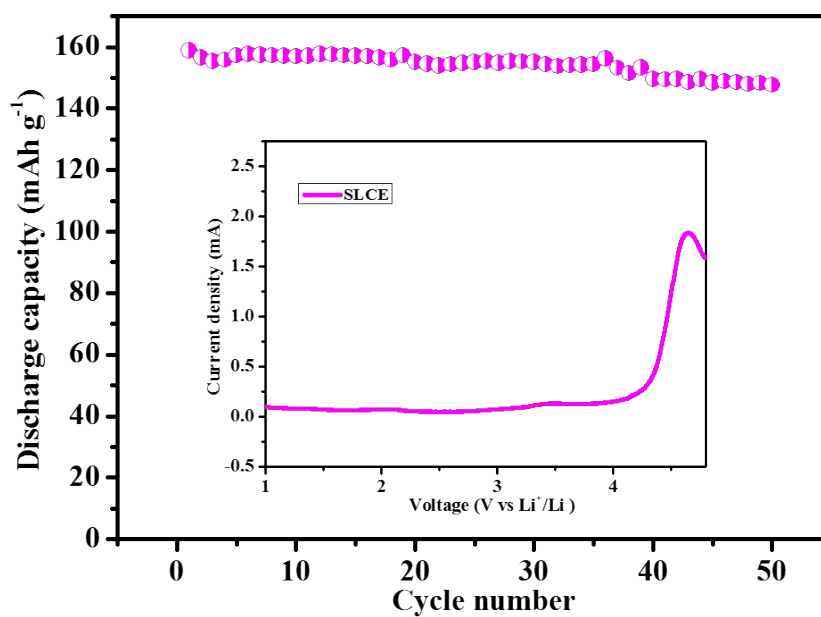


Fig. S9. Cycling performance of Li/SLCE/LiFePO₄ at 80 °C for 50 cycles (0.1C rate, 2.5-4 V) and linear sweep voltammograms of SLCE at 80 °C (inset).

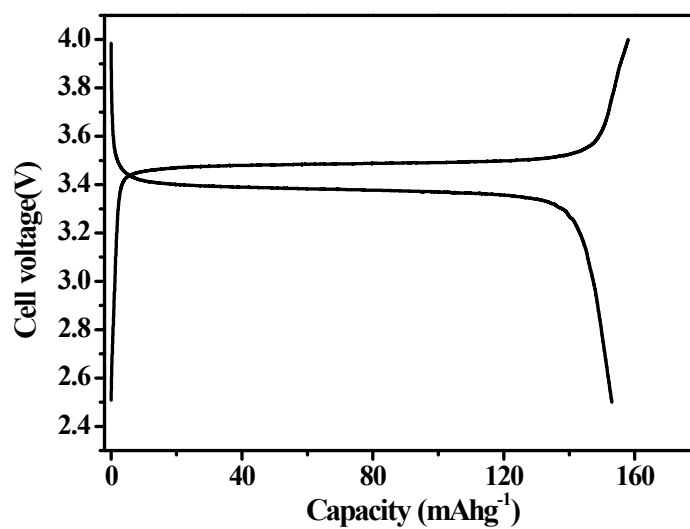


Fig. S10. Cycling performance of Li/LiFePO₄ cell with 3P(MPBIIm-TFSI) electrolyte at high temperature (80 °C) and low current rate (0.05C).

Table S1. Structure and thermal characters, t_{Li^+} and σ_{Li^+} of PILs with different counter anion.

PILs	Chemical shifts in 1H NMR spectra			Molecular weights and polydispersities		Thermal character			σ	t_{Li^+}	σ_{Li^+}
	N-CH=N (ppm)	N-CH=CH-N (ppm)		M_w	PDI	T_g ($^{\circ}C$)	T_m ($^{\circ}C$)	T_d ($^{\circ}C$)	50 $^{\circ}C$	50 $^{\circ}C$	50 $^{\circ}C$
		(Scm^{-1})	(Scm^{-1})						(Scm^{-1})		
3P(MPBIm-TFSI)	9.14	7.66	7.75	86700	1.50	3.3	-	365	1.4×10^{-4}	0.18	2.5×10^{-5}
3P(MPBIm-Tf)	9.10	7.69	7.76	77600	1.45	33.4	-	337	5.0×10^{-5}	0.19	9.5×10^{-6}
3P(MPBIm-Br)	9.76	7.94	8.04	74400	1.55	71.5	-	263	-	-	-

Table S2. Solubility of 3P(MPBI m -X) within different solvents^[a].

X ⁻	H ₂ O	MeOH	Acetone	THF	DMF	Toluene	EMIM-TFSI
Br ⁻	+	+	-	-	+	-	-
CF ₃ SO ₃ ⁻	-	+	+	-	+	-	+
(CF ₃ SO ₂)N ⁻	-	-	+	+	+	-	+

[a] + = soluble; - = insoluble