



Highly efficient mixed Li^+ transport in ion gel polycationic electrolytes



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ABSTRACT

Outstanding Li^+ conductivity and diffusivity have been achieved in free-standing ion gel electrolytes synthesized by in-situ photopolymerization of 1-(2-methacryloyloxy)ethyl-3-butylimidazolium bis(trifluoromethane sulfonyl)imide (IMMA) and/or poly(ethylene glycol) methacrylate (EGMA), in the presence of the room temperature ionic liquids 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMIFSI), 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide (BMPFSI) and bis(trifluoromethane)sulfonimide lithium salt (LiTFSI). The membranes are easy to handle and thermally stable up to 200 °C. Those containing IMMA in the polymer chain present liquid-like ionic conductivities (up to 10 mS cm^{-1} at 25 °C), and liquid-like Li^+ diffusivities and conductivities ($D_{\text{Li}} \approx 4 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $\sigma_{\text{Li}} \approx 1.4 \text{ mS cm}^{-1}$ at 25 °C) unreported so far in a solid electrolyte. D_{Li} is not only very high but significantly higher than its counteranions' diffusivity, D_{FSI} or D_{TFSI} , a very rare behavior in electrolytes where transport is, in principle, ruled by viscosity. It is proposed that in these polycationic electrolytes the motion of Li^+ occurs via two different transport mechanisms, the well-known viscosity-governed transport and an additional anion-exchange mechanism that enables very fast Li^+ diffusion. This combination has high practical relevance for Li^+ batteries as it implies a high contribution of σ_{Li} to the overall electrolyte's conductivity, and it constitutes a breakthrough in the design of polymer-based solid electrolytes for Li.

1. Introduction

The design of solid electrolytes with electrochemical characteristics comparable to those of liquid ones is a very challenging endeavor for materials scientists, for it requires producing a self-standing material with a local mobility comparable to that of a liquid. Such a material must combine high ionic diffusivity (and hence high ionic conductivity) and dimensional stability, and for the last decade the best candidates have been polymer based materials [1]. Solid polymer electrolytes include polymer 3D networks swollen with ad-hoc liquids [2,3] to produce chemically [1] or physically crosslinked gels [4–6]. For the sake of electrochemical and thermal stability in the last years the soaking liquid has frequently been a room temperature ionic liquid (RTIL) [7,8]. Particularly interesting for electrochemical applications are RTILs containing bis(fluorosulfonyl)imide anion (FSI), because of its low viscosity, and because it has been demonstrated that the viscosity increase arising from the incorporation of a Li salt to an ionic liquid is much lower when the anion is FSI [9].

To date, the highest reported conductivity in a polymer gel electrolyte with RTIL (N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)imide, PMPFSI) has been 1.6 mS cm^{-1} at 20 °C [10], of which only a small part is actually Li ion conductivity. As Li^+ has a characteristic large solvation shell [11] D_{Li} is smaller than its counteranions [12,13],

most frequently FSI or bis(trifluoromethane)sulfonimide (TFSI), and hence the contribution of Li to the overall conductivity is small. In this connection, polymer ion gels where the polymer scaffold is a polyelectrolyte made of a polymerizable ionic liquid are of great interest [12,14], not only because of their well-known advantages as regards safety, but because polycationic scaffolds seem to enhance Li^+ mobility (diffusivity) under certain conditions [13]. On the other hand, in liquid Li^+ electrolytes containing the FSI anion some authors [15,16] have recently found that for Li^+ electrolytes containing FSI D_{Li} can be slightly higher than D_{FSI} (\approx a 10%) at sufficiently high temperature and high Li salt concentration. In these works, it is proposed that an anion exchange transport mechanism appears that increases the Li^+ mobility with respect to the rest of ions in the electrolyte [17].

In the light of the Li^+ mobility enhancement promoted by both polycationic scaffolds and the presence of the anion FSI in the liquid phase of the electrolyte, in this work we present free standing ion gel electrolytes which consist of crosslinked polymethacrylates with imidazolium pendant groups and RTILs containing FSI as liquid phase. These new self-standing ion gels present a combination of properties unreported to date, with ionic conductivity and D_{Li} significantly higher than analogous liquid electrolytes [16] and where D_{Li} is up to a 40% higher than D_{FSI} (and 80% higher than D_{TFSI}) at 25 °C.

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Table 1Gel electrolyte composition (wt%), thermal stability (T_5) in air, elastic shear modulus (G'), 0.1 Hz and 0.1% strain, and strain (%) at which $G' = G''$ at 1 Hz and 25 °C.

Electrolyte	monomers		LiTFSI wt%	RTIL wt%	TGA T_5 (°C)	G' (Pa)	$G' = G''$ 1 Hz Strain %
	IMMA wt%	EGMA wt%					
PEGMA	–	30.8	0	69.2	238	2411	> 100
PEGMA/Li	–	24.5	20.2	55.3	228	3382	56
PIMMA	30.8	–	0	69.2	296	1704	21
PIMMA/Li	24.5	–	20.2	55.3	235	1290	24
PIMMA/MIX ^a	30.8	–	0	69.2	296	–	–
PIMMA/MIX/Li ^a	24.5	–	20.2	55.3	247	–	–
COPO	23.1	7.7	0	69.2	272	1655	70
COPO/Li	18.4	6.1	20.2	55.3	227	1897	27

^a electrolytes PIMMA/MIX and PIMMAMIX/Li contain a 1:1 wt. mixture of EMIFSI and BMPFSI. In the rest the RTIL is EMIFSI.

2. Experimental part

2.1. Materials and methods

2.1.1. Materials

All reactants and solvents were commercially available and used as received: 2-bromoethanol (Aldrich, 95%), triethylamine (Sigma Aldrich, 99%), methacryloyl chloride (Aldrich, 97%), 1-butylimidazole (Aldrich, 98%), hydroquinone (Panreac, 99.5%), poly(ethylene glycol) methylether methacrylate (Aldrich, Average Mn 300), ethyleneglycol dimethacrylate (Aldrich, 98%), 1-ethyl-3-methylimidazolium bis (fluorosulfonyl)imide (Solvionic, 99.5%), 1-butyl-1-methylpyrrolidinium bis (fluorosulfonyl)imide (Solvionic, 99.5%), bis(trifluoromethane)sulfonamide lithium salt (Aldrich, 99.95%), milliQ water, dichloromethane (Aldrich, 99.99%), hexane (Scharlau, 99.8%). [¹³C]O₂ labeled 99% was of Cambridge Isotopes Laboratories, Andover, MA.

2.1.2. Synthesis of 1-(2-methacryloyloxy)ethyl-3-butylimidazolium bis (trifluoromethane sulfonyl)imide (IMMA)

2.1.2.1. Synthesis of 2-bromoethyl methacrylate (M1) [18,19]. In an ace round-bottom pressure flask a solution of 2-bromoethanol (7.0 g, 0.055 mol) in 75 mL of dichloromethane was added. Then, a solution of methacryloyl chloride (5.6 mL, 0.06 mol) in 5 mL of dichloromethane was gradually added to the mixture at 0 °C over 10 min. After addition, the reaction mixture was continuously stirred for 30 min and triethylamine (4.04 mL, 0.06 mol) in 4 mL of dichloromethane was added dropwise at 0 °C for 15 min. The reaction mixture was stirred overnight at room temperature and then filtered. The filtrate was washed thoroughly using 3 × 100 mL of deionized H₂O and dried by anhydrous magnesium sulfate. The solvent was removed under vacuum below 30 °C. Yield: 8.92 g (85%) (M1). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 6.12 (s, 1H), 5.57 (s, 1H), 4.40 (t, $J = 6.1$ Hz, 2H), 3.51 (t, $J = 6.1$ Hz, 2H), 1.91 (s, 3H). ¹³C NMR (400 MHz, CDCl₃) δ (ppm) 166.74, 135.82, 126.23, 63.96, 28.80, 18.20. FTIR (wavenumber, cm⁻¹): st(C=O) 1718; st(C=C) 1637; st (C-O) 1153.

2.1.2.2. Synthesis of 1-(2-methacryloyloxy)ethyl-3-butylimidazolium bromide (M2) [20]. In an ace round-bottom pressure flask, a mixture of 2-bromoethyl methacrylate (M1) (1 g., 0.008 mol) and 1-butylimidazole (1.55 g., 0.008 mol) with a small amount of hydroquinone to inhibit the thermal polymerization of the resulting monomer, was stirred at 40 °C for 72 h. The reaction mixture was dissolved in 5 mL of dichloromethane and poured into 250 mL of hexane to give a viscous white precipitate. The product was collected and dried in vacuum. Yield: 2.28 g. (90%) (M2). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 9.52 (s, 1H), 7.92 (m, 2H), 6.02 (s, 1H), 5.68 (s, 1H), 4.64–4.57 (m, 2H), 4.52–4.41 (m, 2H), 4.23 (t, $J = 7.0$ Hz, 2H), 1.76 (s, 3H), 1.21 (m, 2H), 0.85 (t, $J = 7.3$ Hz, 3H). ¹³C NMR (400 MHz, DMSO-*d*₆) δ (ppm) 165.91, 136.55, 135.10, 126.56,

122.73, 122.52, 62.49, 48.56, 47.98, 31.31, 18.62, 17.80, 13.18. FTIR (wavenumbers, cm⁻¹): st(C=O) 1718; st(C=C) 1637; st (C-O) 1155; st (C=C) 1559; st (C=N) 1452; st (C-N) 1297; st (C-H) 2940; st (=C-H) 3200-3000.

2.1.2.3. Synthesis of 1-(2-methacryloyloxy)ethyl-3-butylimidazolium bis (trifluoromethane sulfonyl)imide (IMMA) [20]. In an ace round-bottom pressure flask, a mixture of M2 (1.69 g., 0.0053 mol) and bis (trifluoromethane) sulfonimide lithium salt (LiTFSI, 1.40 g., 0.0048 mol) were diluted in 80 mL of milliQ H₂O, and was stirred at 25 °C for 3 days to induce a liquid-liquid phase separation. The organic layer was isolated and diluted with dichloromethane (15 mL). This solution was washed with water (3 × 30 mL). The product was concentrated under reduced pressure to obtain a viscous light brown oil, IMMA. Yield: 2.1 g. (77%). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 9.24 (s, 1H), 7.80 (m, 2H), 6.03 (s, 1H), 5.69 (s, 1H), 4.52 (m, 2H), 4.48 (m, 2H), 4.19 (t, $J = 7.0$ Hz, 2H), 1.84 (s, 3H), 1.76 (m, 2H), 1.24 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H). ¹³C NMR (400 MHz, DMSO-*d*₆) δ (ppm) 165.96, 136.52, 135.24, 126.40, 122.84, 122.54, 62.40, 48.73, 48.12, 31.33, 18.68, 17.73, 13.06. Quartet arising from CF₃ in the TFSI anion 124.31, 121.11, 117.91, 114.7. FTIR (wavenumbers, cm⁻¹): st(C=O) 1726; st(C=C) 1640; st (C-O) 1153; st (C=C) 1559; st (C=N) 1460; st (C-N) 1295; st (C-H) 2970; st(=C-H) 3150-3000.

2.1.3. Synthesis of the gel electrolytes

The conductive gel electrolytes were prepared by radical polymerization of IMMA and/or poly(ethylene glycol) methylether methacrylate (EGMA) using ethylene glycol dimethacrylate (EGDMA) as cross-linking agent (1 wt%), Irgacure 651 (1 wt%) as photo-initiator and in the presence of LiTFSI and EMIFSI or mixtures of EMIFSI/BMPFSI (see the different compositions in Table 1). The homogenous solution comprising all components, were transferred to a glass vial, degassed by nitrogen bubbling and ultrasounds for 10 min. After that, 825 μ L of the mixture was injected into an oxygen-free atmosphere in a circular teflon mould of 2.5 cm of diameter. In this mould, the photo-initiated bulk polymerization was performed by irradiation with UV light (365 nm) at RT for 55 min. Then, the gel electrolyte was demoulded and conditioned at RT. GPEs of \approx 1300 μ m thick were obtained. The chemical structures of all the components are depicted in Scheme 1. More details on the composition, thermal stability and rheology of the gel electrolytes appear in Table 1.

2.2. Characterization

2.2.1. ATR-FTIR

IR spectra were recorded on the surface of the electrolytes using a PerkinElmer BX-FTIR spectrometer coupled with a MIRacle™ ATR accessory from PIKE Technologies, with 10 scans and resolution 2 cm⁻¹.

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