



Single Ion Conducting Polymer Electrolytes Based On Versatile Polyurethanes



Luca Porcarelli^{a,b,*}, Kasina Manojkumar^c, Haritz Sardon^{a,d}, Oihane Llorente^a, Alexander S. Shaplov^{e,f}, Kari Vijayakrishna^c, Claudio Gerbaldi^b, David Mecerreyes^{a,d,*}

^a POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 72, 20018 Donostia-San Sebastian Spain

^b GAME Lab, Department of Applied Science and Technology (DISAT), Politecnico di Torino, C.so Duca degli Abruzzi 24, Turin 10129, Italy

^c Department of Chemistry, School of Advanced Sciences, VIT University, Vellore, 632 014, Tamil Nadu India

^d IKERBASQUE, Basque Foundation for Science, Bilbao Spain

^e A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences (INEOS RAS), Vavilov str. 28, 119991 Moscow Russia

^f Luxembourg Institute of Science and Technology (LIST), 5 Avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette Luxembourg

ARTICLE INFO

Article history:

Received 8 January 2017

Received in revised form 23 April 2017

Accepted 25 April 2017

Available online 26 April 2017

Keywords:

polymer electrolytes
polyurethanes
single ion conductors
lithium metal batteries

ABSTRACT

Single-ion polymer electrolytes are expected to play an important role in the development of next-generation lithium metal batteries. In this paper, the synthesis and characterization of single-ion conducting polyurethanes (SIPUs) based on PEG and a specifically designed ionic liquid monomer (bis-MPTFSI) is presented. Exploiting the flexible chemistry of polyurethanes, it was possible to tailor the composition and chemical structure of SIPE, obtaining both segmented and crosslinked lithium ion-conductive ($\sigma = 10^{-8} - 10^{-4} \text{ S cm}^{-1}$) and free-standing films with the lithium transference number close to unity. Finally, the performances of gel polymer electrolytes based on SIPUs for lithium metal batteries operating at room temperature were investigated (80 cycles at C/10 with nearly 100% efficiency). To the best of our knowledge, these SIPUs represent one of the first examples of polyurethane-based poly(ionic liquid)s for application in the field of battery science.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Next-generation batteries technologies (i.e., Li-metal, Li-Sulfur, and Li-Air) are expected to play an important role in the emerging energy economy based on renewable sources [1,2]. However, safety concerns related to the use of flammable and toxic liquid electrolytes are posing serious obstacles to the implementation of lithium metal electrodes [3,4]. Polymer electrolytes have long been recognized as intrinsically safer alternatives to liquid electrolytes owing to their non-flammability, non-volatility, wide electrochemical stability window, and good mechanical properties [5]. In addition, the chemical structure of polymer electrolytes can be tailored in order to display unique properties such as lithium-ion transference number (t_{Li^+}) approaching unity, not otherwise achievable with conventional electrolytes. Interestingly, the use of high t_{Li^+} electrolytes can theoretically reduce salt concentration

gradients during battery operation and improve performances. These advantages include the reduction of polarization losses and limitations of the maximum current sustainable by the battery, as well as the suppression of lithium dendrites growth on lithium metal electrodes [6–9].

This class of polymer electrolytes, namely single-ion conductors, was first proposed in the early 80's [10–12] and it is attracting growing interest in recent years due to the introduction of ionic liquid monomers based on highly delocalized anions [13,14]. A number of polymer families have been explored as single-ion conducting polymer electrolytes, such as acrylic [15], methacrylic [16,17], styrenic [18–21], silanes [22–24], and polyethers [25,26]. In particular, lithium poly(styrenesulfonyl(trifluoromethylsulfonyl)imide) has received broad interest from the scientific community since its first report by Armand and coworkers [27].

Fewer attentions have been devoted to polymer electrolytes based on polyurethanes (PU) despite the large number of uses of this versatile class of polymeric materials for other applications, such as foams, adhesive, coatings, binders, and elastomers. Early works dealing with PU ionomers focused on the incorporation of sulfonate [28–31], phosphate [32] and carboxylate groups [33–37] into the polymer backbone. Nevertheless, ionic conductivity (σ)

* Corresponding authors at: POLYMAT, University of the Basque Country UPV/EHU, Joxe Mari Korta Center, Avda. Tolosa 72, 20018, Donostia-San Sebastian, Spain.

E-mail addresses: luca_porcarelli001@ehu.es (L. Porcarelli), david.mecerreyes@ehu.es (D. Mecerreyes).

values were typically limited far below $10^{-5} \text{ S cm}^{-1}$ at 25°C [38–40]. Several research works demonstrated that lithium ion diffusion is strongly correlated with the local segmental motion [41], thus reducing the glass transition temperature may increase the ionic conductivity. Moreover, crystalline phases represent other strong obstacles to fast lithium-ion diffusion, as in the case of systems containing low- T_g polyethylene oxide (PEO) [42,43]. A solution to this issue has been the incorporation of plasticizers or high boiling point solvents, thus forming gel-polymer matrices [44]. However, to the best of our knowledge, no attempts have been made in order to incorporate highly delocalized anionic species, such as TFSI, into a PU ionomer.

In this paper, we present the synthesis and characterization of single-ion conducting polyurethanes (SIPUs) based on isophorone diisocyanate (IPDI), soft polyethylene glycol (PEG) blocks and a specifically designed ester functionalized anionic diol (bis-MPTFSI) having a pendant TFSI group and lithium-ion counter ions. By means of the versatile polyurethane chemistry, it was possible to tailor the composition and chemical structure of SIPE, obtaining both segmented and crosslinked lithium ion-conductive and free-standing films with the lithium transference number close to unity. Finally, gel polymer electrolytes based on SIPUs were prepared and their performances for lithium metal batteries operating at room temperature were investigated.

2. Experimental

2.1. Materials and methods

PEG diols (PEG600, PEG1000, and PEG1500 of $M_n = 600, 1000,$ and 1500 g mol^{-1} respectively) were dried by azeotropic distillation in toluene. Isophorone diisocyanate (IPDI, Sigma) and 2-hydroxyethyl methacrylate (HEMA, Sigma) were dried by stirring with CaH_2 in anhydrous dichloromethane (DCM), followed by filtration and solvent removal in vacuo. Dibutyltin diacetate (DBTDA, Sigma) was directly transferred inside the N_2 -filled glove-box (MBRAUN LABstar). Trifluoromethanesulfonamide (97%, ABCR), carbon-coated lithium iron phosphate (LiFePO_4 , Advanced Lithium Electrochemistry Co. Ltd.), carbon black C_{65} (Timcal), carbon coated aluminum current collector (Showa Denko), lithium metal foil (Chemetall Foote Corporation) were used without further purification. All other materials were purchased from Sigma and used as received.

2.2. Synthesis of potassium 3-chloropropanesulfonyltrifluoromethanesulfonylimide

Potassium 3-chloropropanesulfonyltrifluoromethanesulfonylimide has been synthesized according to the previous literature with minor modifications.[25] 6.72 g (45.1 mmol) of trifluoromethanesulfonamide was taken in a clean 500 mL flask containing 100 mL of anhydrous acetonitrile. To the above solution, 5 g (90 mmol) of potassium hydroxide was added in the presence of argon atmosphere under cold conditions and stirred for 30 minutes. Later, 8 g (45.1 mmol) of 3-chloropropanesulfonyl chloride dissolved in 100 mL of anhydrous acetonitrile was added drop-wise to the reaction mixture under cold conditions and stirred for 13 h at room temperature. Then, the reaction mixture was filtered and the residue was washed with 50 mL of anhydrous acetonitrile. The filtrate was dried with sodium sulfate, filtered, rotary evaporated and vacuum dried. The resultant solids were washed with excess of dichloromethane and ether for two times to remove the starting materials and then, vacuum dried to afford a fine white solid (11.35 g, 76.79% yield). $^1\text{H NMR}$ (400 MHz, DMSO-d_6): δ 3.74 (t, 2H, $\text{CH}_2\text{-SO}_2$), 3.24–2.94 (t, 2H, $\text{CH}_2\text{-Cl}$), 2.24–1.97 (m,

2H, $\text{CH}_2\text{-CH}_2\text{-CH}_2$). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6): δ 124.98–118.54 (CF_3), 52.00 ($\text{CH}_2\text{-SO}_2$), 43.72 ($\text{CH}_2\text{-Cl}$), 27.38 ($\text{CH}_2\text{-CH}_2\text{-CH}_2$).

2.3. Synthesis of potassium 2, 2-bis(hydroxymethyl)propanoate (bis-MPA potassium salt)

10 g (74.55 mmol) of 2, 2-bis(hydroxymethyl)propionic acid (bis-MPA) was dissolved in 80 mL of water followed by the addition of an aqueous solution of KOH (3.97 g, 70.82 mmol). The solution was stirred overnight at room temperature followed by evaporation of water using rotary evaporator and then dried under high vacuum at 50°C overnight. The solids were washed twice with ether (100 mL x 2) under vigorous stirring for one hour and the solids were dried under high vacuum which afforded fine crystalline white powder (12 g, 94% yield).

2.4. Synthesis of potassium ((3-((3-hydroxy-2-(hydroxymethyl)-2-methylpropanoyloxy)propyl)sulfonyl) ((trifluoromethyl)sulfonyl) amide (bis-MPTFSI)

6.3 g (36.6 mmol) of bis-MPA potassium salt and 10 g (30.5 mmol) of potassium-3-chloropropanesulfonyltrifluoromethanesulfonylimide were taken in a flask under argon atmosphere containing 50 mL of dry DMF. The reaction mixture was stirred under an oil bath maintained at 100°C overnight and then, the solvent was removed using rotary evaporator and dried overnight under high vacuum at 60°C . The residue was dissolved in 100 mL of anhydrous acetonitrile to precipitate KCl which was filtered. The filtrate was concentrated and purified using column chromatography on silica gel with 20 v.% methanol in ethyl acetate as eluent (11.54 g, 89% yield). $^1\text{H NMR}$ (400 MHz, DMSO-d_6): δ 4.66 (t, 2H, $\text{CH}_2\text{-OH}$), 4.06 (t, 2H, $-\text{CH}_2\text{-O}$), 3.49–3.41 (m, 4H, $\text{CH}_2\text{-OH}$), 3.09–2.96 (t, 2H, $\text{CH}_2\text{-SO}_2$), 1.96 (t, 2H, $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 1.04 (s, 3H, CH_3). $^{13}\text{C NMR}$ (101 MHz, DMSO-d_6): δ 174.56 ($-\text{COO}$), 121.71–118.49 (CF_3), 63.85 ($\text{CH}_2\text{-OH}$), 62.12 ($\text{CH}_2\text{-O}$), 51.36 ($\text{CH}_2\text{-SO}_2$), 50.20 ($\text{CH}_3\text{-C}$), 23.50 ($\text{CH}_2\text{-CH}_2\text{-CH}_2$), 16.82 (CH_3).

2.5. Synthesis of segmented polyurethanes based on IPDI, PEG and bis-MPTFSI monomers (SIPUs)

The following examples is given for the polymerization of sample SIPU-4, polymerization was performed inside the N_2 -filled glovebox to avoid moisture contamination. PEG600 (0.67 g, 1.2 mmol, 1.5 equiv.) and IPDI (0.33 g, 1.5 mmol, 2.0 equiv.) were dissolved in 6.7 mL of dry ACN. A solution of DBTDA in dry ACN (0.1 mL) was added (1 mg, 0.003 mmol; 0.02 mol.%) and the reaction vessel was transferred into an oil bath preheated at 60°C for three hours. Then a solution of bis-MPTFSI (0.16 g, 0.38 mmol, 0.5 equiv.) in dry ACN (1.1 mL) was feeded to the reaction vessel and the reaction vessel. The conversion was judged to be complete within 6 h, determined by FTIR and $^1\text{H NMR}$ analysis. $^1\text{H NMR}$ (DMSO-d_6 , 400 MHz): δ 7.20–7.07 (m, NH), 4.09 (m, $\text{COO-CH}_2\text{-O}$), 4.03 (m, NHCOOCH_2), 3.51 (t, OCH_2), 3.03 (t, $\text{CH}_2\text{-SO}_2$), 2.72 (m, OOCNHCH_2), 1.98 (m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.44–0.87 (m, $\text{OCONHCH}_2\text{CH}_2$), (m, $\text{OCONHCH}_2\text{CH}_2$) (m, CH_3) (m, CH_3) (m, CH_3) ppm. Detailed polymerization conditions for the SIPUs serie are presented in Table 1.

2.6. Synthesis of crosslinkable polyurethanes based on IPDI, PEG, bis-MPTFSI, and HEMA monomers (UV-SIPUs)

The synthesis of UV-curable SIPUs was performed inside the N_2 -filled glovebox to avoid moisture contamination. First, linear SIPUs having an excess of NCO-terminations were prepared via the two step procedure described in the previous section, the following amounts of reactants were used: IPDI (0.33 g, 1.5 mmol, 2.0 equiv.),

Download English Version:

<https://daneshyari.com/en/article/4767042>

Download Persian Version:

<https://daneshyari.com/article/4767042>

[Daneshyari.com](https://daneshyari.com)