



Design of polymers with an intrinsic disordered framework for Li-ion conducting solid polymer electrolytes



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ABSTRACT

Polymers with phosphorus in the main chain with intrinsic disordered framework for lithium-ion conductivity were synthesized. Conductivity of one of the solid polymer electrolytes prepared from those polymers with 40 wt% of LiTFSI was $8.9 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C and $5.3 \times 10^{-3} \text{ S cm}^{-1}$ at 80 °C. The impressive conductivity is explained by the availability of high conduction pathways provided by frozen chain disorder.

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1. Introduction

Advanced materials and molecules for energy harvesting and storage devices are in demand to improve their performance and efficiency. Case in point, the Li-ion batteries are fast developing as replacement to lead-acid batteries to run automobiles [1]. However, some of its disadvantages – such as high cost and more weight of the Li-ion batteries – and the imperatives to increase its energy density and working temperature necessitate further evolution of new electrode materials and polymer electrolyte systems [2]. Further, there is a need for a thorough understanding of the conduction mechanism to focus on improving ionic conductivities of solid polymer electrolytes [3].

According to the conventional theory, amorphous polymers exhibit ionic conductivity whereas crystalline polymers most likely behave as insulator. The ionic conductivity in amorphous polymer is due to the movement of ions, ensued by the local segmental motion of the polymer chain particularly above its glass transition temperature (T_g). Above T_g , the superstructure of polymers has disordered and flexible environment. Since the polymer chains are in constant motion above its T_g , a vacant space would continually create and disappear, through which an ion move by coordination. It means an ion has to wait to find a new coordination site and a free volume for hopping. This clearly describes that the rate of ion transport depends on local chain dynamics of polymer [4]. Our interest is creating a

fixed perpetual free space through which the ion can move without delay. It would improve the mobility of ion leading to higher ionic conductivity. For that, we have chosen to synthesize materials with a needed structural framework for better lithium ion transport [5].

Many efforts are directed toward synthesizing polymers for lithium ion transport without sacrificing their properties. One such approach is constructing a perfect polymer framework through a crystalline arrangement of polymer chains by either metal organic framework (MOFs) or covalent organic framework (COFs). MOFs and COFs are well known for applications in gas storage, catalysis and molecular separation [6]; but synthesizing the material by MOF and COF approach for lithium ion transport without sacrificing their desired properties is challenging. Alternatively, an amorphous covalent organic framework can be achieved in hyper-cross linked polymers or intrinsic porous polymers. Herein, we report the synthesis of soluble polymers with intrinsic disordered framework supportive of Li-ion conductivity.

2. Experimental section

2.1. Materials and instrumentation

All manipulations involving air and moisture sensitive compounds were carried out using standard Schlenk techniques under dry nitrogen. All solvents to be used under inert atmosphere were thoroughly deoxygenated using freeze–pump–thaw method before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen. The following drying agents were used: sodium benzophenoneketyl

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(hexane, toluene, tetrahydrofuran), P_2O_5 (triethylamine), $Mg(OMe)_2$ (methanol). The compounds, ferrocenylmethyl bis(hydroxymethyl)phosphine sulfide [7] (**M1**), benzyl bis(hydroxymethyl)phosphine sulfide [8] (**M2**) and 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene [9] (**M3**) were synthesized according to the literature procedures. The compound lithium bis(trifluoromethanesulfonyl)imide, $LiN(SO_2CF_3)_2$ purchased from Acros was used as received without purification.

Structures of all monomers and polymers were confirmed by 1H and ^{31}P NMR spectroscopy. All the NMR spectra were recorded on a Bruker Avance 400 MHz FT NMR spectrometer at room temperature. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane as reference for 1H and ^{13}C NMR. The ^{31}P (162 MHz) spectra were referred to 85% H_3PO_4 . The Netzsch STA 409 PC model was used for thermogravimetric and differential thermal analysis (TG–DTA) to examine the thermal stability. The decomposition behaviour of polymers was studied from 30 °C to 900 °C under the nitrogen flow with a heating rate of 10 °C/min. The temperature of 5% weight loss was chosen as onset point of decomposition (T_d). A Differential Scanning Calorimeter (DSC) from PerkinElmer (Pyris Diamond DSC 8000) was used to find the glass transition temperature (T_g). Measurements were performed at a heating rate of 10 °C/min from 25 °C to 240 °C in case of polymers and 25 °C–280 °C in case of solid polymer electrolytes (**SPEs**). Mass spectra was obtained using Shimadzu–LCMS–2010 instrument operating at an ionizing voltage of 70 eV using EI technique. Molecular weights of the polymers were determined by using Gel Permeation Chromatography (GPC) of Shimadzu 10AVP model equipped with refractive index (RI) detector. The separation was achieved using a Phenogel mixed bed column (300 × 7.80 mm) operated at 30 °C with a flow rate of 0.5 mL/min using tetrahydrofuran (THF) as the eluent and polystyrene as the standard.

2.2. General procedure for the synthesis of polymers P1–P4

To a solution of RP(S) (CH_2OH)₂ (7.7 mmol) and 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (2.46 g, 7.7 mmol) in N,N-dimethylacetamide (DMAc) (30 mL), 60% sodium hydride (0.77 g, 19.3 mmol) was added at 0 °C under nitrogen. The mixture was then allowed to warm to 25 °C within 1 h. After 40 h stirring at required temperature, the reaction mixture was poured into hydrochloric acid (3% v/v, 500 mL) to precipitate the polymer as powder. The product was purified by washing with methanol for 24 h using soxhlet apparatus to yield pure polymer.

Polymer 1 (**P1**): Yield 81%. 1H NMR (400 MHz, $CDCl_3$): δ 4.82–4.61 (m, 4H, OCH_2Ph), 4.30–4.03 (m, 9H, Fc), 3.96–3.77 (m, 4H, PCH_2O), 3.28–2.94 (m, 2H, $FcCH_2$), 2.47–2.07 (bs, 12H, CH_3). ^{31}P { 1H } NMR (162 MHz, $CDCl_3$): δ 45.44.

Polymer 2 (**P2**): Yield 72%. 1H NMR (400 MHz, $CDCl_3$): δ 7.67–7.27 (m, 5H, C_6H_5), 4.67–4.36 (m, 4H, OCH_2Ph), 4.18–3.68 (m, 4H, PCH_2O), 3.56–3.32 (m, 2H, $PhCH_2$), 2.47–1.96 (bs, 12H, CH_3). ^{31}P { 1H } NMR (162 MHz, $CDCl_3$): δ 47.94.

Polymer 3 (**P3**): Yield 78%. 1H NMR (400 MHz, $CDCl_3$): δ 4.83–4.56 (m, 4H, OCH_2Ph), 4.34–4.00 (m, 9H, Fc), 3.97–3.69 (m, 4H, PCH_2O), 3.23–2.86 (m, 2H, $FcCH_2$), 2.46–2.05 (bs, 12H, CH_3). ^{31}P { 1H } NMR (162 MHz, $CDCl_3$): δ 44.98 (m), 41.03 (m).

Polymer 4 (**P4**): Yield 75%. 1H NMR (400 MHz, $CDCl_3$): δ 7.76–7.35 (m, 5H, C_6H_5), 4.92–4.49 (m, 4H, OCH_2Ph), 4.03–3.53 (m, 4H, PCH_2O), 3.41–3.00 (m, 2H, $PhCH_2$), 2.42–1.99 (bs, 12H, CH_3). ^{31}P { 1H } NMR (162 MHz, $CDCl_3$): δ 46.19 (m), 42.84 (m).

2.3. Model reaction

To a solution of **M2** (0.20 g, 1 mmol) and benzyl bromide (0.34 g, 2 mmol) in DMAc (2.4 mL) was added sodium hydride (0.05 g,

2 mmol) at 0 °C under nitrogen. The mixture was then allowed to warm to 25 °C within 1 h. After 3 h stirring, methanol (1 mL) was added and the reaction mixture was poured in to water (25 mL). The reaction mixture was extracted with chloroform (20 mL × 3). The organic layer was washed with water (20 mL × 2). Solvent was evaporated to give the crude product, which was purified by column chromatography on silica gel eluting with hexane/ethyl acetate (9: 1). Yield 79%. 1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.32 (m, 10H, C_6H_5), 7.30–7.26 (m, 5H, C_6H_5), 4.65 (dd, $J = 21.4$ Hz, $J = 11.8$ Hz, 4H, OCH_2Ph), 3.95–3.84 (m, 4H, OCH_2P), 3.38 (d, $J = 13.8$ Hz, 2H, PCH_2Ph). ^{13}C { 1H } NMR (100 MHz, $CDCl_3$): δ 136.7, 130.2, 130.1, 128.9, 128.5, 128.4, 128.3, 128.2, 128.1, 127.3, 75.5 (d, $J = 10.3$ Hz), 67.3 (d, $J = 63.9$ Hz), 33.5 (d, $J = 44.2$ Hz). ^{31}P { 1H } NMR (162 MHz, $CDCl_3$): δ 43.50. EI–MS: m/z 397 ($M^+ + 1$).

2.4. Preparation of solid polymer electrolytes SPE1–SPE4

All manipulations were carried out in MBraun glove box filled with ultrapure nitrogen gas. The polymers (**P1–P4**) were dried at 90 °C under vacuum for 8 h. $LiN(SO_2CF_3)_2$ was dried at 150 °C under vacuum for 10 h before making **SPEs**. Initially, the films were made by dissolving the polymers and $LiN(SO_2CF_3)_2$ in a mixture of solvents THF/ $CHCl_3$ at room temperature. However, films of **SPEs** were brittle. Therefore, it was difficult to cut into a proper shape for conductivity studies. Hence, the **SPEs** in the form of pellets were prepared for impedance measurements.

The solid electrolytes with different ratio were prepared as follows. The polymer and lithium salt was ground together inside the glove box and then sealed. Then the flask containing the mixture was tied with a mechanical stirrer rotating at a constant speed (blending) for 24 h. The process was repeated for three times (Total 72 h). The homogeneities of the blended **SPEs** were confirmed as follows: After blending the polymer with lithium salt, samples were taken from the four different regions and their glass transition temperature (T_g) was examined. The T_g of all the samples were matching well with each other. In both cases, the solids were loaded in to a die and then pressed (5 ton) to make pellets of 0.07–0.08 cm thickness and 0.9 cm diameter were obtained for conductivity studies. The **SPE** pellets were sandwiched between two gold plated electrodes housed in a homemade cell.

2.5. Impedance measurements of polymer electrolytes

The impedance measurements and electrochemical stability studies of polymers and **SPEs** were performed in Zahner-Zennium electrochemical workstation with built-in Thales software for data acquisition. The measurements were done in the frequency range of 1 Hz–4 MHz. The measurement cell was constructed in such a way that it can hold specimen (pellet) tightly in order to achieve good interfacial contacts between the electrodes and electrolyte. The measurement cell was sealed completely to avoid contaminations. It was further upheld from the measurements using with different pellets of **SPE1**, which showed the same pattern of results and bulk resistance (R_b).

The conductivities were calculated [10] according to the equation $\sigma = d/(AR_b)$, where d is the thickness of the polymer electrolyte disc, 'A' is the surface area of the pellet and R_b is the bulk resistance value which can be calculated from the intercept of the curve with real axis. Further, an equivalent circuit model was obtained from the computerised least square parameters fitting. Then, the experimental bulk resistance (R_b) was compared with the bulk resistance (R_b) obtained from equivalent circuit model. The consistency of results was checked by repeating three times. The conductivity of blended **SPEs** and **SPEs** derived from evaporation method were in good agreement. For variable temperature

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