



Functionalized polystyrene based single ion conducting gel polymer electrolyte for lithium batteries



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ABSTRACT

Lithium poly(4-styrene sulfonyl (phenylsulfonyl)imide) (PSSPSI) was synthesized through the Hinsberg reaction. Since the bis(sulfonyl)imide anion is immobilized in the polymer chain, the lithium cation transference number was measured to be 0.87. The weight average number molecular weight (M_w) was found to be 105,343 determined by gel permeation chromatography (GPC). A gel polymer electrolyte membrane, comprising of PVDF and PSSPSI, was successfully prepared with the ionic conductivity of $1.1 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. The membrane exhibits a wide electrochemical window up to 4.5 V (vs. Li^+/Li) and is thermally and mechanically stable. The material is well suited for applications in lithium-ion batteries.

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1. Introduction

The steady exhaustion of fossil fuels and its adverse effects on the environment have compelled intense research efforts to search for clean energy resources and to improve energy efficiency to cope with the increasingly pressing energy demand [1,2]. To this end, renewable energy sources necessitate intermittent such as batteries and capacitors with high energy capacity, which require development of novel electrode materials and electrolytes to meet the market demands [3,4]. The high specific capacity (3.86 Ah g^{-1}) coupled with the low gravimetric density (0.534 g cm^{-3}) of lithium metal makes it a superior choice for negative electrode, in particular, to work with high capacity cathode materials in tandem [4]. However, the formation of lithium dendrites on the anode can be highly hazardous [1,5]. Furthermore, the movement of both cations and anions of a liquid electrolyte upon charging and discharging hampers the amount of useful work and ultimately the performance of battery devices [6].

Solid polymer electrolytes (SPE) provide an important alternative to conventional liquid electrolytes to address the issues on battery safety and efficiency. Unfortunately, the inability of achieving both high ionic conductivity and strong mechanical strength, coupled with the problem of concentration potential, impeded its chance to replace the liquid electrolytes [7]. The conductivity and mechanical robustness issues can be partially resolved by introducing either lithium ion salts in organic carbonate solvents, such as ethyl carbonate (EC) and propyl carbonate (PC), or ionic liquids into the polymer matrix such as polyethylene

oxide (PEO), polyvinylene difluoride (PVDF), which serve as a binder, to form gel polymer electrolytes (GPEs) [8–10]. Nevertheless, despite these improvements, the low transport number of cations still remains a serious issue affecting the battery performance. To deal with this problem, the concept of single-ion conducting electrolyte, with or without an organic solvent, was recently coined [6]. A single ion electrolyte is made of a polymeric or copolymeric lithium salt [11–20]. The polymeric part of the lithium salt serves as immobile anions in the framework and allows transport of lithium ions only upon charging or discharging. Consequently, the problem of concentration polarization is minimized [6].

In this paper, we report a synthesis of a novel polystyrene based single ion gel polymer electrolyte with ionic conductivity of $1.1 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. The ionic conductivity of the membrane is among the highest values of the single ion polymer electrolytes reported to date and comparable to the conductivity of liquid electrolytes [21–24]. The fabricated membrane displays a sufficiently high mechanical strength for serving as a separator to block lithium dendrite formation on anode and high electrochemical stability in the operating voltage range of lithium ion batteries.

2. Experimental

2.1. Materials

Polystyrene powder, M_w 65,000 g mol^{-1} (Alfa-Aesar), chlorosulfonic acid (Fluka), thionyl chloride (Tee Hai), benzenesulfonamide (Sigma-Aldrich), lithium hydroxide (Sigma-Aldrich), polyvinylidene fluoride (PVDF) (Solef 6020), M_w 680,000 g mol^{-1} (Solvay), dichloroethane (DCE) (Alfa-Aesar), ethoxylated natural fatty alcohol with 12 carbon atom chain based non-ionic surfactant (commercial name Brij L23)

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(Alfa-Aesar), dichloromethane (DCM) methanol, tetrahydrofuran THF, dimethyl sulfoxide (DMSO) (QRec), deionized water (molar resistivity 10–18 $\Omega \text{ cm}^{-1}$).

2.2. Synthesis of poly(4-styrene sulfonyl (phenylsulfonyl)imide) (PSSPSI)

2.2.1. Synthesis of poly(4-styrene sulfonyl chloride) (PSSC)

0.2 g of polystyrene powder (mol wt. 65,000 Da) was dissolved in 1, 2-dichloroethene (DCE) in argon environment with constant stirring at 40 °C and 10 ml concentrated chlorosulfonic acid was added by a constant pressure dropping funnel and stirring was continued for 16 h. 10 ml of chlorosulfonic acid was added further and stirring was continued for another 16 h. 12 ml of thionyl chloride was added slowly by the same constant pressure dropping funnel during the period. Upon completion, temperature was raised to 60 °C and the reaction continued for the next 16 h. The poly(4-styrene sulfonyl chloride) (PSSC) was washed by DCE, acetone and finally with methanol until the pH of the solution became 7. PSSC was dried in a vacuum oven at 80 °C for 12 h. Impurities were removed by dissolving PSSC in DMSO followed by re-precipitation with tetrahydrofuran (THF) for three times.

The peak positions and corresponding group frequencies for PSSC are assigned in Table 1 [25,26].

2.2.2. Lithium poly(4-styrene sulfonyl (phenylsulfonyl)imide) (PSSPSI)

3.25 g phenylsulfonamide (BSA) and 0.9 g of LiOH were dissolved in deionized water. 0.4 g PSSC was added to the solution at a constant but slow rate at 70 °C for 4 h. Wash steps were repeated and the poly (4-styrene sulfonyl (phenylsulfonyl)imide) (PSSPSI) was dried overnight in a vacuum oven at 80 °C for 24 h. The peak positions and corresponding group frequencies for PSSPSI are assigned in Table 2 [27].

2.2.3. Gel polymer electrolyte membrane preparation

0.1 g of PVDF, 0.2 g of PSSBSA, 0.026 g of Brij L23 and 6 ml of NMP solvent and a magnetic stirring bar were taken in a 25 ml glass beaker and heated to obtain a transparent solution. Subsequently, the liquid was drop-casted into a glass culture dish (7 cm diameter) and dried in an oven at 95 °C to vaporize the NMP solvent. The obtained film was further dried under vacuum at 70 °C for 24 h and then transferred to the glove box where it was punched to get a circular membrane. The membrane was subsequently placed in the EC/PC (1:1 volume ratio) solution for soaking.

2.3. Methods

All infrared spectra were taken with a Shimadzu 8400 FTIR spectrophotometer equipped with an attenuated total reflectance probe in the 600–4000 cm^{-1} frequency range.

Images of the polymer electrolyte microstructures were obtained by scanning electron microscopy (SEM) using Quanta 200 FEG. Samples were prepared by gold sputtering under 5×10^{-2} mbar at room temperature (20 s, 30 mA) with a Baltec SCD050 apparatus.

The material composition was calculated by elemental analysis. CHNS analysis (carbon, hydrogen, nitrogen and sulfur detection) technique was used for the organic part of the polymers while inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used for the detection of the metal part of the samples.

Table 1

Positions and assignment of peaks of PSSC.

FTIR peak positions (ν in cm^{-1})	Assignment of peaks
1636	C=C stretching
1355	SO ₂ asymmetrical stretching
1176	SO ₂ symmetrical stretching
1005	C–S stretching
834	C–H out of plane deformation

Table 2

Positions and assignment of peaks of PSSPSI.

FTIR peak positions (ν in cm^{-1})	Assignment of peaks
1646	C=C stretching (aromatic)
1496	C–H in plane deformation
1184	SO ₂ symmetrical stretching
1009	C–S stretching
837	C–H out of plane deformation
777	SNS stretching
680	CCC out of plane deformation

Molecular weight and polydispersity index (PDI) was measured by gel permeation chromatography (GPC) (Waters 515 HPLC Pump, Waters 2707 Autosampler, Waters 2414 Refractive Index Detector). Gel permeation chromatography, also known as size exclusion chromatography, is a widely used technique to determine molecular weight and molecular weight distribution parameters based on the hydrodynamic volume of polymers. It is a type of liquid chromatography for solid stationary and liquid mobile phase materials. Pure water was used as an eluent at a flow rate of 0.8 ml/min. The polyethylene oxide (PEO) standard was used for calibration.

Ion conductivity of the polymer electrolytes was measured by electrochemical impedance spectroscopy using a Zahner potentiostat-galvanostat model PGSTAT with the EIS module over a frequency range of 4×10^6 to 1 Hz with the oscillating voltage of 5 mV. The electrolyte membrane was placed inside a cylindrical stainless steel device with a cavity of 1.5 cm diameter. The measurement device was sealed in a glove box under argon and heated at 80 °C in an oven to ensure a maximum contact between the membrane and the surface of the device, prior to analysis. Electronic conductivity was also measured using a Keithley high resistance meter (Model 6517A).

The electrochemical stability test (linear voltammetry) was performed using scanning electrochemical microscope (SECM), of CH Instruments, Inc., in the voltage range of 2.8–7 V vs Li/Li⁺ with the same stainless steel device (EIS measurement). The potential (V) of the working electrode was varied linearly with time between two values i.e., the initial (E_i) and final (E_f), while the current (I) is measured as a function of the potential concurrently. Oxidation or reduction is recorded as a peak or trough in the current signal corresponding to the potential at which oxidation or reduction occurred. The resulting current–voltage plot is called linear sweep voltammogram [28,29]. A circular thin lithium foil and the electrolyte membrane were placed inside the cavity of the device sealed in a glove box under argon atmosphere.

Thermal degradation study was performed under inert atmosphere of N₂ (flow rate 60 $\text{cm}^3 \cdot \text{min}^{-1}$) at 10 °C $\cdot \text{min}^{-1}$ heating rate in a Thermo Gravimetric Analyzer (model TGA Q 50) of TA, Instruments. Experiment was conducted from room temperature to 900 °C.

The DSC study was carried out on a Differential Scanning Calorimeter (DSC-1 Star system), of Mettler Toledo. The experiments were carried out in an inert atmosphere from –50 °C to 300 °C at the heating rate of 10 °C min^{-1} .

3. Result & discussion

3.1. Synthesis and characterization of lithium poly(4-styrene sulfonyl (phenylsulfonyl)imide) (PSSPSI)

As depicted in Scheme 1, PSSPSI (c) was synthesized in three steps. In the first step, sulfonation of polystyrene takes place, which forms two products: polystyrene sulfonyl chloride (A) and polystyrene sulfonic acid (B). It is analogous to typical chlorosulfonation of benzene, which ends with two products benzenesulfonyl chloride and benzenesulfonic acid. The latter can be converted into the former upon reacting with an excess amount of thionyl chloride (SOCl₂). The same approach was

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