



Highly conductive solid polymer electrolyte membranes based on polyethylene glycol-*bis*-carbamate dimethacrylate networks



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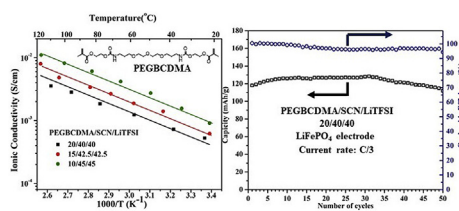
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HIGHLIGHTS

- As-synthesized PEGBCDMA is thermally stable and mechanically sturdy.
- Room temperature ionic conductivity of our solid PEM reaches 10^{-3} S/cm.
- The present solid PEM exhibits a wide electrochemical stability window.
- High capacity retention has been achieved in charge/discharge cycling tests.

GRAPHICAL ABSTRACT



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ABSTRACT

In an effort to fabricate highly conductive, stable solid-state polymer electrolyte membranes (PEM), polyethylene glycol *bis*-carbamate (PEGBC) was synthesized via condensation reaction between polyethylene glycol diamine and ethylene carbonate. Subsequently, dimethacrylate groups were chemically attached to both ends of PEGBC to afford polyethylene glycol-*bis*-carbamate dimethacrylate (PEGBCDMA) precursor having crosslinking capability. The melt-mixed ternary mixtures consisting of PEGBCDMA, succinonitrile plasticizer, and lithium trifluorosulphonyl imide salt were completely miscible in a wide compositional range. Upon photo-crosslinking, the neat PEGBCDMA network was completely amorphous exhibiting higher tensile strength, modulus, and extensibility relative to polyethylene glycol diacrylate (PEGDA) counterpart. Likewise, the succinonitrile-plasticized PEM network containing PEGBCDMA remained completely amorphous and transparent upon photo-crosslinking, showing superionic conductivity, improved thermal stability, and superior tensile properties with improved capacity retention during charge/discharge cycling as compared to the PEGDA-based PEM.

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1. Introduction

Lithium-ion batteries have gained increasing recognition due to their wide variety of applications including electric vehicles, electronics, and implantable medical devices [1–4]. Most lithium-ion

batteries in use today consist of a lithium salt dissolved in a mixture of cyclic/acyclic organic carbonate solvents, capable of facilitating fast diffusion of lithium ions [5]. However, these mixed organic liquids, being volatile and flammable by virtue of their low flash points and poor thermal management, have resulted in battery explosion and catching fires [6,7]. One strategy is to replace the volatile carbonate solvent with a nonvolatile, solid electrolyte system that allows for fast ion movement and also binds well with

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the electrodes [8,9]. Wright and co-workers reported that the ether-based polymer, viz., polyethylene oxide (PEO) was capable of dissolving inorganic salts and thus afforded ion conduction, albeit low [10,11]. Some recent works have shown that doping a plastic crystal such as succinonitrile (SCN) into a polymer electrolyte membrane (PEM) can achieve a high ionic conductivity in excess of 10^{-3} S/cm [12–14]. The feasibility of producing solvent-free solid electrolyte was demonstrated by utilizing PEO as matrix and doping with SCN plastic crystals for lithium ion transport. It was found that this polymer electrolyte achieved reasonably high ionic conductivity in the order of 10^{-4} S/cm at room temperature, despite the fact that SCN itself is a poor ionic conductor. However, such PEO based PEM containing lithium salt (LiTFSI) is a waxy substance without sustainable mechanical strength or integrity, thereby preventing its full utilization as solid electrolyte [15,16]. Upon replacing PEO with photo-curable poly(ethylene glycol) diacrylate (PEGDA), the tensile strength of the photo-cured PEM has improved to 0.10 MPa while the network plasticization by SCN expedites the lithium ion transport [17–19].

In solid-state battery applications, the performance of the PEM depends not only on their electrochemical properties, but also on their mechanical properties such as tensile strength, modulus, and elongation at break. During the repeated charge/discharge cycling of the conventional liquid electrolyte battery, lithium dendrite was found to grow on the negative electrode, which eventually reached the cathode resulting in short-circuiting, thereby compromising safety [20]. Such dendrite growth may be prevented by using mechanically tougher PEM without compromising high ionic conductivity [21,22]. Photopolymerized polyethylene glycol diacrylate (PEGDA) networks have shown improved mechanical strength and modulus while imparting flame retardant property and chemical stability to the solid PEM. However, room temperature ionic conductivity of neat PEGDA based binary PEMs is inherently low and thus plasticization of these PEM networks is desirable to reach the level of superionic conductivity, viz., $>10^{-3}$ S/cm. It was demonstrated that small-molecule plasticizers such as succinonitrile (SCN) can boost not only ionic conductivity, but also enhance the dissociation (i.e., ionization) of the lithium salt in the solid-state polymer electrolyte membranes.

In this paper, polyethylene glycol (PEG) containing telechelic amine groups were end-linked with cyclic ethylene carbonate via ring-opening reaction to afford polyethylene glycol bis-carbamate (PEGBC). Subsequently, UV-curable methacrylate groups were further attached at both chain ends to form polyethylene glycol-bis-carbamate dimethacrylate (PEGBCDMA) to impart crosslinking capability. By virtue of the low glass transition, the urethane segments in PEGBC further promotes the ionic conductivity, while the photo-cured PEGBCDMA has achieved high tensile strength, modulus, and extensibility. Of particular interest is that the electrochemical performance including high ionic conductivity and capacity retention with improved thermal stability has been achieved with the present PEGBCDMA based solid PEMs.

2. Experimental section

Materials. Lithium bis(trifluoromethane) sulfonimide (LiTFSI) having a purity of 99.9%, succinonitrile (SCN) (>99%), ethylene carbonate (EC, 99%), 4,7,10-trioxa-1,13-tridecanediamine (TTDDA, 97%, also known as PEG diamine), 4-(dimethyl-amino) pyridine (DMAP, 99%), hydroquinone (99%), triethylamine (TEA, 99%) and methacrylic anhydride (MAA, 94%) were purchased from Sigma-Aldrich Co. The solvents such as dichloromethane (99.9%), methylene chloride (99.9%) and acetone (99.9%) were bought from Fisher Scientific Co. The electrode materials LiFePO_4 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and acetylene black powders were purchased from MTI Corp. Poly

(vinylidene fluoride) (PVDF having Mw ~534,000) binder and 1-methyl-2-pyrrolidinone (NMP) solvent were obtained from Sigma-Aldrich.

Sample Preparation. The LiTFSI salt was dried at 170 °C under vacuum for 24 h before blending. Varying weight percentages of PEGBC and LiTFSI mixtures were prepared by dissolving in the mixed dichloromethane/acetone (40/1 w/w) solvent in a nitrogen-purged glove box. Solution casting of the blend solution was carried out at 80 °C for under continuous nitrogen flow. Subsequently, these PEGBC/LiTFSI blends were further dried at 150 °C in a vacuum oven for 12 h.

In the fabrication of solid PEM films, several compositions of PEGBCDMA/SCN/LiTFSI were selected that correspond to the isotropic region of the ternary phase diagram (figure not included). Melt-mixing was performed at room temperature by mechanically stirring without using any solvent. 2 wt% of Irgacure 819[®] with respect to the PEGBCDMA amount was added to the above mixtures during melt mixing. The homogeneous mixture thus obtained was placed on a glass slide within a tape frame spacer having a square shape with a dimension of $10 \times 10 \text{ mm}^2$, and then covered with a transparent cover glass. Subsequently, UV polymerization was performed at room temperature (25 °C) by illuminating with a UV Cure Lamp (Bondwand 350 nm) at an intensity of 5 mWcm^{-2} for 15 min in a glove box under nitrogen atmosphere. The thickness of the photocured transparent film was approximately 0.2 mm.

For electrochemical measurements, the working electrodes were prepared by mixing active materials (lithium iron phosphate (LiFePO_4) or lithium titanium oxide ($\text{Li}_4\text{Ti}_5\text{O}_{12}$)), acetylene black, and polyvinylidene fluoride (PVDF) polymer binder in NMP solvent at a weight ratio of 8:1:1. The slurry mixture was coated onto stainless steel and current collectors such as aluminum or copper foil, and then dried at 160 °C in vacuum for 24 h. The coin-cell batteries were assembled in half-cell configurations using a lithium metal foil (Alfa Aesar Co.) as the counter (or reference) electrode in an argon gas-filled glovebox. In the battery assembling process, the polymer electrolyte membrane was placed on top of the electrode by applying a very light pressure to improve the contact between the cathode and PEM.

Sample characterization. Thermal properties of the samples were examined using a thermogravimetric analyzer (TGA; Model Q50, TA Instruments) at a heating rate of 10 °C/min from room temperature to 600 °C under a nitrogen atmosphere. The glass transition temperatures of the PEM samples were determined using differential scanning calorimetry (DSC) (Model Q200, TA Instruments) in which the blend samples weighing 5 mg were hermetically sealed with aluminum lids in a glovebox under nitrogen to alleviate moisture absorption. All DSC scans were acquired at a ramp rate of 10 °C/min unless indicated otherwise. Fourier transform infrared (FTIR) spectra were acquired by means of an FTIR spectrometer (Alpha-P, Bruker Optics) in a transmission mode. The tensile properties of neat polymer matrices were evaluated using a tensile tester (Model 5900, Instron) at a constant displacement rate of 10 mm/min. The typical size of all the samples for the tensile test was $4 \times 10 \text{ mm}^2$ and the film thickness was approximately 1 mm. For softer plasticized PEM films, tensile measurements were performed using a dynamic mechanical analyzer (DMA Q800 TA instruments) at a constant stress rate of 0.1 MPa/min. All tensile tests were conducted at ambient temperature.

Ionic conductivities were determined by using an AC impedance analyzer (HP4192A LF, Hewlett Packard). Samples were sealed between two parallel stainless steel polished plates with an area of $10 \times 10 \text{ cm}^2$ and ~0.2 mm in thickness. Sample loading was undertaken in a glovebox to prevent moisture absorption, if any. The frequency sweep was carried out from 13 MHz to 5 Hz with a

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