



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Highly conductive solvent-free polymer electrolyte membrane for lithium-ion batteries: Effect of prepolymer molecular weight

Ruixuan He^a, Mauricio Echeverri^{a,1}, Daniel Ward^{b,2}, Yu Zhu^c, Thein Kyu^{a,*}

^a Department of Polymer Engineering, University of Akron, Akron, OH 44325, USA

^b Department of Chemical Engineering, Miami University, Oxford, OH 45056, USA

^c Department of Polymer Science, University of Akron, Akron, OH 44325, USA

ARTICLE INFO

Article history:

Received 13 July 2015

Received in revised form

3 September 2015

Accepted 4 October 2015

Available online 8 October 2015

Keywords:

Solvent-free

Solid-state polymer electrolyte membrane

Molecular weight effect

Photopolymerization

Lithium-ion battery

ABSTRACT

The present article demonstrates the effects of molecular weight of network precursor on properties of solid-state polymer electrolyte membrane (PEM) comprised of poly (ethylene glycol) diacrylate (PEGDA) prepolymer, succinonitrile (SCN) plasticizer, and lithium bis(trifluoromethane sulphonyl) imide (LiTFSI) salt using two different PEGDA molecular weights. To provide guidance for crosslinking reaction, ternary phase diagrams of the PEM precursor mixtures were established. Upon photopolymerization within the wide isotropic region, completely amorphous membranes were obtained in several compositions. The PEM having a higher PEGDA molecular weight (i.e., 6000 g/mol) revealed both improved impact strength with an elongation at break of ~80 % and higher ambient temperature ionic conductivity ($\sim 1.4 \times 10^{-3} \text{ S cm}^{-1}$) relative to the low molecular weight counterpart (i.e., 700 g/mol). Both PEMs exhibited excellent electrochemical (4.8 V/Li/Li⁺) and thermal (140 °C) stabilities. Specific discharge capacities of the PEM containing half-cells using LiFePO₄ or Li₄Ti₅O₁₂ electrodes against lithium electrode reached the level of ~140 mAh g⁻¹ at 0.2 °C, indicating potential applications in all solid-state lithium-ion batteries.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

A conventional wisdom in the design of an ideal polymer electrolyte membrane (PEM) for lithium-ion batteries is to fabricate all solid-state, shape-conformable membrane having ionic conductivity in a superionic range (i.e., $> 10^{-3} \text{ S cm}^{-1}$ at room temperature), electrochemical stability with a wide operating voltage range ($> 5 \text{ V}$), thermal stability ($> 100 \text{ °C}$), and mechanical sturdiness [1,2]. The first-generation PEM was fabricated by mixing poly(ethylene) oxide (PEO) with lithium salts [3]. Although mechanical strength of the PEO-based electrolyte membrane reached an acceptable level, the room temperature ionic conductivity (i.e., $\sim 10^{-6}$ to $10^{-5} \text{ S cm}^{-1}$) [4,5] was too low for practical purposes due to restricted segmental motion of PEO chains which are closely related to PEO crystals [6–8]. To improve the ionic conductivity, organic liquid plasticizers such as ethylene carbonate (EC) and dimethyl carbonate (DMC) had to be compounded usually into the PEM [9,10]. The addition of such small

organic molecules into thermoplastic matrices made these PEMs to be physically weak having paste-like appearance and flammable. However, the incorporation of solid plasticizer (e.g., succinonitrile) into PEO-based PEM afforded self-standing films with reasonably high room temperature ionic conductivity on the order of $10^{-4} \text{ S cm}^{-1}$, but these films were brittle [11–13].

Crosslinking of thermosetting polymers is an alternative strategy that can provide mechanical support, while ionic salts and plasticizers can be contained in the polymer networks. Among many strategies, ultraviolet (UV) crosslinking is one of the methodologies that has been widely practiced as a means of producing a so-called ‘polymer gel electrolyte’ [14,15]. The trapped solvent additives not only plasticize polymer chains, but also dissociate lithium ions from the lithium salt. The room temperature ionic conductivity of polymer gel electrolyte can reach $10^{-3} \text{ S cm}^{-1}$ [16], which certainly meets the targeted value for lithium-ion batteries. A notable example is due to Song et al. who prepared thermoset/thermoplastic blends via UV-curing of PEGDA gel in the presence of poly(vinylidene fluoride) (PVDF) and liquid plasticizers such as ethylene carbonate (EC)/dimethyl carbonate (DMC). These authors showed that the PEGDA/PVDF (50/50) blend containing EC/DMC revealed a room temperature ionic conductivity on the order of $10^{-3} \text{ S cm}^{-1}$ and an elongation at break of 60% [17]. However, their polymer gel electrolyte must be sealed in bulky metal or

* Corresponding author. Fax: +1 3309725290.

E-mail address: tkyu@uakron.edu (T. Kyu).

¹ Present address: Kent Displays Inc., 343 Portage Boulevard, Kent, OH 44220, USA

² Present address: Vanderbilt University Law School, Nashville, TN 37203, USA

plastic containers due to sizable amount of organic solvent incorporated, which can be as high as 400 wt% of the dry polymer mass. Moreover, the volatility of organic solvent presents potential risk of smoking, ignition and even combustion, especially at elevated temperatures above 80 °C. Hence, there is a growing demand for development of solvent-free solid polymer electrolyte with reasonably strong mechanical strength and elongation.

Incorporating succinonitrile (SCN) in lieu of liquid plasticizers (EC or DMC) into crosslinked PEM is an effective way to prepare solvent free, solid PEM [18,19]. SCN is a plastic crystal at room temperature with a crystal-plastic crystal transition at –40 °C and plastic crystal-isotropic melt transition at 58 °C [20]. More importantly, SCN serves as an effective plasticizer to the polymer matrix as well as efficient ionizer to the lithium salt [21]. By incorporating LiTFSI and SCN blend into UV-cured ethoxylated trimethylolpropane triacrylate networks, a PEM having satisfactory ionic conductivity ($\sim 10^{-3}$ S cm⁻¹) at 30 °C can be fabricated although the membrane exhibited moderate tensile strength of 0.13 MPa and elongation at break is of only $\sim 20\%$ [18]. However, a pronounced capacity decay (56% after 30 cycles) of such solid PEM has prevented full utilization in lithium-ion batteries [19].

In our previous work, ionic conductivity of UV-cured PEGDA700 (PEGDA with a molecular weight of 700 g/mol)/SCN/LiTFSI polymer electrolyte membrane was systematically studied in reference to the ternary phase diagram. Self-standing solid-state, completely amorphous polymer electrolyte membranes were then fabricated by UV-curing the ternary mixtures within the isotropic region without requiring any solvent [22], and superionic ionic conductivity ($\sim 10^{-3}$ S cm⁻¹) was achieved at room temperature. With increasing SCN amount, ionic conductivity increases further, but it occurs at the expense of lowering mechanical strength and modulus. This observation is in line with a general notion that ionic conductivity and mechanical properties of the membranes operate in diametrically opposing way.

In the present study, to improve the toughness of the superionic conductive polymer electrolyte membrane, PEGDA having a higher molecular weight of 6000 g/mol (labeled as PEGDA6000) was used as network precursor, while SCN and LiTFSI were kept in the same ratio as that of the PEGDA700-PEM formulation. Room temperature ternary phase diagrams of PEM precursor mixtures were established to provide the melt processable window for the UV crosslinking reaction. Conversion of the reaction was determined from the photo-DSC experiment. The tensile properties of PEGDA6000-PEM were investigated in comparison with those of PEGDA700-PEM. Of particular interest is that our amorphous PEGDA6000-PEM showed higher tensile strength of 0.24 MPa and superior elongation at break of $\sim 84\%$ relative to that of Ha et al. [18]. While the impact strength of the PEM can be significantly enhanced by incorporating a higher molecular weight prepolymer, ionic conductivity was also improved at the same time. The dual improvements in toughness and ionic conductivity are seemingly afforded by the longer chain between crosslinked junctions of the loose PEGDA6000-PEM network. The thermal and electrochemical stabilities of PEM were discussed, and galvanostatic charge-discharge cyclic behaviors of PEM containing half-cells were further examined. To our knowledge, the present study is the first in demonstrating the effects of molecular weight of PEGDA network precursor on simultaneous improvement of electrochemical, mechanical, and thermal performance of the solvent-free, photopolymerized solid PEMs.

2. Experimental

2.1. Materials and sample preparation

PEGDA having molecular weights of 700 g/mol and 6000 g/mol, LiTFSI (99.95%) and SCN (99%) were purchased from Sigma-Aldrich Company. Photoinitiator Irgacure[®] 819 (*bis* (2,4,6-trimethylbenzoyl)-phenylphosphine oxide) was obtained from Ciba Company. LiTFSI was dried at 130 °C for at least 24 h before use and other materials were used as received. Electrode materials used were LiFePO₄ and Li₄Ti₅O₁₂ from MTI Corp., which were compounded with acetylene black (AB from MTI) to improve electron conductivity and poly (vinylidene fluoride) (PVDF from Sigma-Aldrich) as a binder in anhydrous (99.5%) 1-methyl-2-pyrrolidinone (NMP) (Sigma-Aldrich) solvent.

Ternary mixtures containing desired ratios of PEGDA700/SCN/LiTFSI or PEGDA6000/SCN/LiTFSI were prepared in a nitrogen filled glovebox. These samples were labeled according to the mass fraction of individual component in feed; for instant, 20/40/40 PEGDA6000/SCN/LiTFSI indicates the composition to have 20 wt% PEGDA6000, 40 wt% SCN and 40 wt% LiTFSI. Regarding the phase diagram determination, blend materials were first dissolved in a 40/1 (v/v) methyl dichloride/acetonitrile co-solvent. After vigorously stirring, solution casting was carried out in a hot stage at 80 °C under continuous nitrogen flow for 1 h. It should be emphasized that solvent blending was performed only in the determination of phase diagrams.

In the preparation of solvent-free polymer electrolyte membrane, photoinitiator Irgacure[®] 819 was added into the liquid mixture within the isotropic region of the ternary phase diagram at room temperature. The amount of photoinitiator was 2 wt% with respect to the amount of PEGDA incorporated. After vigorous stirring, the photoinitiator was well dissolved in the liquid mixture. After pouring the above liquid into a rectangular spacer frame, photopolymerization takes place upon UV exposure at a wavelength of 350 nm and an intensity of 5 mW/cm² for 15 min in a nitrogen gas filled glovebox. Transparent solvent-free solid polymer electrolyte membranes were finally obtained.

2.2. Sample characterization

In the construction of ternary phase diagram, thermal transitions of the precursor mixtures were determined by differential scanning calorimetry (DSC, TA Q200, TA Instruments, Inc.) by ramping from –50 °C to 80 °C at a scan rate of 10 °C/min. In photo-DSC experiments, liquid sample was placed in an open aluminum pan while the temperature was kept at 25 °C. The UV-lamp shutter was synchronized with the DSC controller. Both sample and reference materials were exposed to UV-light under the same condition described above. In the determination of glass transition temperature of the neat photopolymerized PEGDA, DSC scans were ramped from –75 °C to 0 °C at a rate of 2 °C/min.

Tensile test was conducted by means of dynamic mechanical analyzer (DMA, TA Q800, TA Instruments, Inc.) Samples with dimensions of 15.0 × 5.0 × 0.6 mm³ were stretched at a constant strain rate at 1 mm/min at 25 °C in air until break. Thermal gravimetric analysis (TGA, TA Q50, TA Instruments Inc.) was conducted to determine thermal stability of neat materials and of PEMs. Each sample was weighed to the recommended amount of 10–15 mg. The temperature was raised from 25 °C to 500 °C at a rate of 10 °C/min, under dry nitrogen gas circulation.

AC Impedance, linear sweep voltammetry and cyclic voltammetry tests were performed at ambient temperature using SI 1260 Impedance/Gain Phase Analyzer and SI 1287 Electrochemical Interface (Solartron Analytical Inc.). In the ionic conductivity

Download English Version:

<https://daneshyari.com/en/article/632821>

Download Persian Version:

<https://daneshyari.com/article/632821>

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