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Polymerized ionic liquid diblock copolymer as solid-state electrolyte and separator in lithium-ion battery

Jacob R. Nykaza [a], Alice M. Savage [b], Qiwei Pan [c], Shijun Wang [c], Frederick L. Beyer [b], Maureen H. Tang [a], Christopher Y. Li [c], Yossef A. Elabd [d, *]

[a] Department of Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States
[b] Army Research Laboratory, Aberdeen Proving Ground, MD 21005, United States
[c] Department of Material Science and Engineering, Drexel University, Philadelphia, PA, 19104, United States
[d] Department of Chemical Engineering, Texas A&M University, College Station, TX 77843, United States

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ABSTRACT

A polymerized ionic liquid diblock copolymer (PILBCP-TFSI), poly(MMA-*b*-MUBIm-TFSI), consisting of an ionic liquid monomer, (1-[(2-methacryloyloxy)undecyl]-3-butylimidazolium bis(trifluoromethane)sulfonamide) (MUBIm-TFSI), and a non-ionic monomer, methyl methacrylate (MMA), was synthesized *via* reverse addition fragmentation chain transfer polymerization followed by anion exchange metathesis. Free standing, mechanically stable transparent solid polymer films were produced with PILBCP-TFSI containing 1 M lithium bis(trifluoromethane)sulfonamide in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Li-TFSI/EMIm-TFSI). The resulting PILBCP-TFSI + Li-TFSI/EMIm-TFSI films possessed ion conductivities from 1 to 10 mS cm^{-1} from 25 °C to 105 °C. Solid-state lithium-ion coin cell batteries were assembled and tested at room temperature with PILBCP-TFSI + Li-TFSI/EMIm-TFSI films as the solid-state electrolyte and separator and resulted in a maximum discharge capacity of 112 mAh g^{-1} at 0.1 C with a Coulombic efficiency greater than 94% over 100 cycles. For the first time, these results demonstrate the feasibility of PIL block copolymers as solid-state electrolytes and separators in lithium-ion batteries.

1. Introduction

Recently, solid polymer electrolytes (SPEs) have been explored as solid-state ion conducting electrolytes and separators in lithium-ion batteries due to their improved flammability safety compared to traditional liquid electrolytes [1–3]. Other advantages include suppression of dendrite growth, better shape flexibility, and improved electrochemical stability when compared to typical liquid electrolytes [4]. One primary drawback to SPEs is the relatively low ionic conductivity, specifically at room temperature, where traditionally the ionic conductivity must be on the order of 1 mS cm^{-1} or higher for practical battery applications [5]. Many SPEs currently fail to meet this conductivity criterion, which prevents their commercialization. The ideal SPE for an all solid-state battery would have the high room temperature ionic conductivity of a liquid (for high overall storage capacity, energy and power), the mechanical properties of a solid (for improved stability and cyclability), and the formability of a thermoplastic (for good processability and flexibility).

Polymerized ionic liquids (PILs), a new class of polymer electrolyte (a polymeric form of ionic liquids (ILs)), have recently been explored as SPEs for electrolytes and separators in solid-state lithium-ion batteries [6,7]. PILs possess unique properties, such as high solid-state ionic conductivity, high chemical, electrochemical, and thermal stability, and a widely tunable chemical platform, where significant changes in physical properties have been observed with subtle changes in chemistry [8–10]. PILs and their corresponding ILs have strong affinity for one another, compared to other polymers, which allows for complete compatibility or miscibility [11]. The use of ILs within PIL-based SPEs is known to be stable, which minimizes phase separation and IL leakage. The use of ILs as electrolytes in lithium-ion batteries has been well documented in the literature, where the benefits over traditional liquid electrolytes include non-flammability and non-volatility, as well as having similar properties as PILs as described above [12–14]. One should note that in many of these previous reports for lithium-ion

* Corresponding author.
E-mail address: elabd@tamu.edu (Y.A. Elabd).

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battery applications, a source of lithium ions is typically a lithium salt (*e.g.*, lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI)) dissolved in an IL [6].

To date, there are only a few reports of PILs as solid-state electrolytes and separators in batteries, where the PIL SPE typically consists of a mixture of lithium salt and IL imbibed in the film [6,15–19]. Most of these studies have examined PIL homopolymers, where an IL monomer is polymerized using free-radical polymerization to produce a PIL as the SPE. Appetecchi et al. [17] synthesized a poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl) imide PIL and incorporated the PYR_{14}-TFSI IL with Li-TFSI salt within the SPE. The PIL with 60 wt% IL/salt had a conductivity of 0.5 mS cm^{-1} at 40 °C and a Li/$LiFePO_4$ solid-state battery capacity of 82.3% of the theoretical capacity at 40 °C. Sato et al. [18] synthesized an ammonium-based PIL, poly(*N*,*N*-diethyl-*N*-(2-methacryloylethyl)-*N*-methylammonium bis(trifluoromethylsulfonyl)imide) (poly(-DEMM-TFSI)), and added a mixture of DEME-TFSI/Li-TFSI and achieved a discharge capacity of 97.7% of the theoretical capacity and a 97% Coulombic efficiency at 40 °C with this PIL + IL/salt as the electrolyte and separator in a battery using $Li_4Ti_5O_{12}$ and $LiMn_2O_4$ as the anode and cathode, respectively. However, the use of homopolymers can lead to battery failure over time due to the low mechanical properties of some homopolymers. Li et al. [15] copolymerized a guanidinium-based IL monomer with methyl acrylate to form a random copolymer. This PIL random copolymer acted as a host for a guanidinium-based IL, Li-TFSI salt, and nano-sized SiO_2 and was incorporated as the solid-state electrolyte and separator in Li/$LiFePO_4$ batteries. This SPE had a relatively low ionic conductivity of 0.117 mS cm^{-1} even at a high temperature of 80 °C. Therefore, batteries tests were conducted at this high temperature of 80 °C with a discharge capacity of 93% of the theoretical capacity and capacity fade of 0.27 mAh g^{-1} per cycle.

The use of block copolymers, instead of random copolymers, can assist in improving properties and can potentially provide the desired orthogonal properties of high ion conduction and high mechanical strength in the solid-state and have been explored for battery applications [20–24]. One recent example includes work by Bouchet et al. [25] in which they synthesized a single-ion conductor triblock copolymer with a conductivity of 0.013 mS cm^{-1} at 60 °C and a discharge capacity of >88% of the theoretical capacity at 60 °C with lithium metal anodes and $LiFePO_4$ cathodes.

PIL block copolymers (PILBCPs) are a new distinct class of block copolymer that combines the properties of PILs and block copolymers, where the latter is known to self-assemble into a variety of different nanostructures (*e.g.*, body centered cubic spheres, hexagonal packed cylinders, and lamellae) [11]. A recent report has shown that when PILs self-assemble into continuous ion-rich microdomains within block copolymer morphologies, accelerated ion transport within these continuous nanostructured ion-channels can occur [9]. Ye et al. [10] compared a single-ion conductor PIL block copolymer to its analogous PIL random copolymer at the same PIL composition and showed that the ionic conductivity of the block copolymer was 2 orders of magnitude higher than the random copolymer, which was due to the microphase separated morphology in the block copolymer. Although there are now a number of recent studies on the conductivity and morphology of PILBCPs [11,26–31], there are few that examine the conductivity of lithium ions in PILBCPs. Recent work by Wang et al. [7] reports on the ionic conductivity (0.47 mS cm^{-1} at 100 °C) and electrochemical stability of (4.2 V *versus* Li/Li^+) of a PILBCP with additional PIL (50.7 mol%) and Li-TFSI (5 wt%). However, they did not report on battery performance for this PILBCP. To date, there are no reports of a PILBCP as the electrolyte and separator in a lithium-ion battery.

In this work, a PIL diblock copolymer, poly(MMA-*b*-MUBIm-Br) (denoted as PILBCP-Br), was synthesized *via* the reverse addition fragmentation chain transfer (RAFT) polymerization technique at a single composition (20.0 mol% PIL) and then was subsequently ion exchanged to the bis(trifluoromethane)sulfonamide (TFSI) form, poly(MMA-*b*-MUBIm-TFSI) (denoted as PILBCP-TFSI). PILBCP-TFSI was then imbibed with a 1.0 M solution of LiTFSI in EMIm-TFSI (denoted as Li-TFSI/EMIm-TFSI) to produce the lithium-conducting PILBCP SPE (denoted as PILBCP-TFSI + LiTFSI/EMIm-TFSI). The glass transition temperatures, thermal degradation temperature, and ionic conductivity of the new PILBCP-TFSI and PILBCP-TFSI + LiTFSI/EMIm-TFSI SPEs were measured. The morphology was invested using small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). The electrochemical stability and lithium-ion battery performance of PILBCP-TFSI + LiTFSI/EMIm-TFSI as the solid-state electrolyte and separator were investigated. To our knowledge, this is the first report of lithium-ion battery performance of a PIL block copolymer.

2. Experimental

2.1. Materials

Acetonitrile (anhydrous, 99.8%), bis(trifluoromethane)sulfonamide lithium salt (Li-TFSI, 99.95%), 1-methyl-2-pyrrolidinone (NMP; anhydrous, 99.5%), platinum foil (Pt; 0.125–0.135 mm, 99.99%), and silver foil (Ag; 0.5 mm, 99.99%) were used as received from Sigma-Aldrich. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm-TFSI, >99%) was used as received from Iolitec. Lithium titanate ($Li_4Ti_5O_{12}$; >98%), conductive graphite (≥99.98%), polyvinylidene fluoride (PVDF; ≥99.5%), and lithium cobalt oxide ($LiCoO_2$) pre-coated Al current collector (single sided) were used after drying at 100 °C under vacuum for 12 h from MTI Corporation. CR2032 Coin Cell Cases (20 mm D × 3.2 mm T) with O-rings for battery research, stainless steel spacer for CR2032 Cell (15.5 mm D × 0.5 mm T), stainless steel wave spring for CR2032 Case were used as received from MTI Corporation. Ultrapure deionized (DI) water with resistivity ≈ 16 MΩ cm was used as appropriate. The polymerized ionic liquid (PIL) diblock copolymer, PILBCP-TFSI, was synthesized by anion exchange from its precursor form, PILBCP-Br, which was prepared according to literature and is described below [32,33].

2.2. Synthesis of PIL diblock copolymer: PILBCP-TFSI

Imidazolium-based PIL diblock copolymer, poly(methyl methacrylate-block-1-[(2-methacryloyloxy)undecyl]-3-bromide (referred to as PILBCP-Br), was used as the precursor polymer in this study (left structure in Scheme 1) and was synthesized previously from an ionic liquid monomer, 1-[(2-methacryloyloxy) undecyl]-3-butylimidazolium bromide (MUBIm-Br), and a non-ionic monomer, methyl methacrylate (MMA), *via* the reverse addition fragmentation chain transfer (RAFT) polymerization technique [32,33]. Herein, this PIL block copolymer is reported at a single PIL composition of 20.0 mol%, in which its synthesis and characterization were previously described in detail in literature [33]. The bis(trifluoromethylsulfonyl)imide ($TFSI^-$)-exchanged PIL diblock copolymer, PILBCP-TFSI (M_n = 40.6 kg/mol), used in this study, was prepared *via* ion exchange metathesis of the precursor PIL diblock copolymers, PILBCP-Br, as shown in Scheme 1. This exchange was performed in the solid state (films; see section below for details on film casting procedure). Scheme 1 provides details of the ion exchange metathesis, where films were placed in a well-mixed 0.1 M Li-TFSI aqueous solution for 12 h. The Li-TFSI solution was replaced with a freshly prepared solution every 4 h and repeated 3 times. The $TFSI^-$-exchanged films were then soaked in fresh DI water for 30 min and repeated 3 times to remove excess