



Ionic liquid impregnated lithium ion conductive solid electrolytes based on poly(acetyl ethylene glycol methacrylate-co-methyl acrylate)



Shin Woo Choi, Dinh Xuan Luu, Anh Le Mong, Byungsan Kwon, Dukjoon Kim *

School of Chemical Engineering, Sungkyunkwan University, 300 Chunchun-dong, Jangan-gu, Suwon, Kyunggi 440-746, Republic of Korea

ARTICLE INFO

Article history:

Received 25 February 2015

Received in revised form 29 June 2015

Accepted 17 July 2015

Available online 28 July 2015

Keywords:

Solid electrolyte

Lithium battery

Poly(ethylene glycol)

Lithium ion conductivity

ABSTRACT

Poly(ethylene glycol)methacrylate (PEGMA) was modified with acetyl chloride to afford acetyl-poly(ethylene glycol)methacrylate (AEGMA) containing PEG and carbonyl groups at the pendant position. AEGMA was further reacted with methyl acrylate (MAc) to synthesize poly(AEGMA-co-MAc) copolymer containing additional carbonyl groups. When lithium salts such as lithium perchlorate (LiClO_4) and lithium bis(trifluoromethanesulfony)imides (LiTFSI) were introduced into the poly(AEGMA-co-MAc) membrane, the ionic conductivity increased with increasing lithium salt concentration up to 15 wt%, followed by a decrease because when the lithium ion concentration was above its saturation level, the excess lithium salts aggregated together exerting a negative effect on ion transport. The maximum ionic conductivity of the copolymer system containing lithium salt was $1.1 \times 10^{-4} \text{ S cm}^{-1}$ at 15 wt% MAc and 15 wt% of LiTFSI concentration. When room temperature ionic liquid (RTIL), PYR14-TFSI in addition to LiTFSI salt was introduced to the poly(AEGMA-co-MAc)-LiTFSI, the ionic conductivity increased monotonically with increasing salt/RTIL concentration. The maximum ionic conductivity of $1.2 \times 10^{-3} \text{ S cm}^{-1}$ was obtained at 70 wt% 0.5 M LiTFSI/PYR14-TFSI concentration.

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1. Introduction

As portable electronics become more integrated, the electrical energy consumption is an important issue to be addressed. As the lithium battery inherently generates high energy density, it is being applied in a variety of electronic devices. While its utilization is getting expanded, a serious problem associated with its safety is more confronted. The liquid electrolytes used in lithium battery possess an inherent danger of explosion because of its leakage caused by the swelling and external impact of the host materials during long-term use. As the high investment is required to minimize or prevent such problems, its production cost is increasing. The replacement of liquid electrolyte with solid electrolyte is a solution, and thus the polymer is a suitable solid material to be considered.

The transfer of alkali metal ions through the polymer electrolyte is possibly accomplished by the strong interaction between ion and polymer molecules and their segmental movement [1]. Among a number of polymers, poly(ethylene glycol) (PEG) has ether groups in the main chain, and thus they can form the coordinate bonds with lithium ions to establish great segmental movement [2]. However, high molecular weight PEG often shows the inclination of crystallization at low temperature, followed by significant reduction in ionic conductivity. A variety of methods such as blending [3,4], cross-linking [5,6], block copolymerization [7,8], plasticization [9,10], and inorganic composite fabrication

[11,12] were tried to reduce or prevent crystallization of PEG. A simple way to maintain PEG in amorphous state is to use relatively low molecular weight PEG.

The liquid electrolytes such as ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) used in lithium-ion battery commonly possess carbonyl group, as it has a unique characteristic of dissociating lithium salt. Recently, we reported a couple of copolymer electrolyte systems containing PEG and additional carbonyl groups on the pendant position to enhance the ionic conductivity based on the association-dissociation relationship between carbonyl group and lithium ions [13,14]. Those polymeric structures possibly reduced crystallinity of PEG and possessed high polarity to dissociate Li salts more feasibly, and thus enhanced the ion conductivity. Introduction of the monomers containing carbonyl groups increased the glass transition temperature (T_g) of polymer, and thus decreased the flexibility of polymer molecules. However, the resulting ion conductivity was still $<10^{-3} \text{ S cm}^{-1}$ at room temperature.

Room temperature ionic liquids (RTILs) are liquid-state salts at room temperature and are usually non-volatile, non-flammable, and thermally and chemically stable. Because of such unique properties, RTILs have also been largely investigated as electrolytes (or electrolyte components) for electrochemical applications such as electro-deposition of electropositive metals, photo electrochemical cells, double-layer capacitors, hybrid super capacitors, fuel cells, and rechargeable lithium batteries [15–25]. Moreover, RTILs have significant advantages over the common liquid electrolytes in consideration of safety when those are applied to lithium-ion battery. In this study, acetyl-poly(ethylene

* Corresponding author. Tel.: +82 31 290 6853.
E-mail address: djkim@skku.edu (D. Kim).

glycol)methacrylate (AEGMA) containing PEG and carbonyl groups at the pendant position was synthesized, followed by the copolymerization with methyl acrylate to introduce additional carbonyl groups. To this copolymer was added thermally and chemically stable RTIL to further enhance the ionic conductivity. As the RTILs have relatively high viscosity, minimization of its leakage from polymer membrane is also expected in addition to general abovementioned advantageous properties.

2. Experimental

2.1. Materials

Methyl acrylate (MAc), acetyl chloride, and poly(ethylene glycol)methacrylate (PEGMA, $M_n = 360 \text{ g mol}^{-1}$) were purchased from Sigma-Aldrich Chemical Company (Milwaukee, WI, USA), and acryloyl chloride was purchased from Tokyo Chemical Industry Co., Ltd. (TCI, Japan). 1-methylpyrrolidine, 2-bromo ethanol, triethylamine (TEA), *N*-methylpyrrolidine (NMP), 1-iodobutane, and lithium salts such as lithium perchlorate (LiClO_4) and lithium bis(trifluoromethylsulfonyl)imides (LiTFSI), were also purchased from Sigma-Aldrich. 2,2-Azobisisobutyronitrile (AIBN) and tert-butylperoxide (Aldrich) were used as the initiator for the polymerization. Tetrahydrofuran (THF), dichloromethane, ethyl acetate, and acetonitrile purchased from Sigma-Aldrich were used as the solvents.

2.2. Synthesis of lithium salt and RTIL

The RTIL precursor, 1-butyl-1-methylpyrrolidinium iodide (PYR14I), was first synthesized from *N*-methylpyrrolidine (PYR1) and 1-iodobutane. 1-iodobutane (57 g, 0.31 mol) dissolved in 30 mL THF was added drop wise to PYR1 (30 g, 0.34 mol, 10% PYR1 excess) dissolved in 70 mL ethyl acetate. The reaction mixture was stirred for 2 h at room temperature, and then heated at 50 °C for 5 h. A white PYR14I precipitate formed was filtrated and washed thrice with ethyl acetate. Finally, the PYR14I product was dried for 24 h at room temperature in vacuum.

1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (PYR14-TFSI) RTIL was then prepared from PYR14I precursor and LiTFSI.

PYR14I was added to a solution of LiTFSI (20 g) in water (18 g). The mixture was stirred for 4 h at room temperature. When the stirring was stopped, the phases were separated in a few minutes. The upper aqueous phase was mostly composed of LiI and excess LiTFSI, whereas the lower phase was mostly composed of PYR14-TFSI RTIL with a small amount of ethyl acetate and traces of water and lithium salts (LiI and LiTFSI). The rapid formation of two liquid phases clearly indicated that the reaction proceeds quickly. The PYR14-TFSI phase was separated and rinsed several times with cold water to remove the residue lithium salt. The PYR14-TFSI product was freeze-dried for 3 d. The reaction schemes for the synthesis of PYR14I and PYR14-TFSI are illustrated in Fig. 1a and b, respectively. Two different concentration of LiTFSI salt in RTIL electrolytes, 0.5 M LiTFSI/PYR14-TFSI and 1 M LiTFSI/PYR14-TFSI, were prepared by dissolving 1.435 g of LiTFSI in 10 mL and 5 mL of viscous PYR14-TFSI RTIL, respectively.

2.3. Preparation of the polymer electrolyte

A solution of acetyl chloride (11.8 g, 0.15 mol) in THF (30 mL) was added drop-wise over a period of 1 h to the mixture of PEGMA (36 g, 0.1 mol), TEA (15 g, 0.15 mol), and inhibitor copper wire (1 g) in 70 mL of THF in ice bath. The reaction mixture was stirred for ~3 h at room temperature and then heated at 60 °C for 12 h with continuous stirring. The crude acetyl poly(ethylene glycol)methacrylate (AEGMA) was obtained after filtering TEA hydrochloride and copper wire, followed by removing THF by vacuum evaporation using a rotary evaporator. The crude AEGMA was purified by cooling for 12 h in a refrigerator, followed by the filtration of any residual TEA hydrochloride salt. The corresponding reaction scheme is shown in Fig. 2a.

The lithium salt contained copolymer of AEGMA and MAc (poly(AEGMA-co MAc)) was prepared by dissolving MAc and AEGMA along with AIBN and LiClO_4 or LiTFSI in THF. The concentration of AIBN initiator was 0.3 wt% of the monomer in this copolymerization reaction. The mixed solution was stirred for 12 h at room temperature, and then casted on a glass dish for the polymerization at 60 °C for 12 h under vacuum. The synthetic scheme of poly(AEGMA-co-MAc) is shown in Fig. 2b. For the preparation of RTIL contained poly(AEGMA-co MAc) electrolytes, a desired amount of AEGMA and MAc along with PYR14-TFSI was dissolved in THF. The solution was casted on Teflon

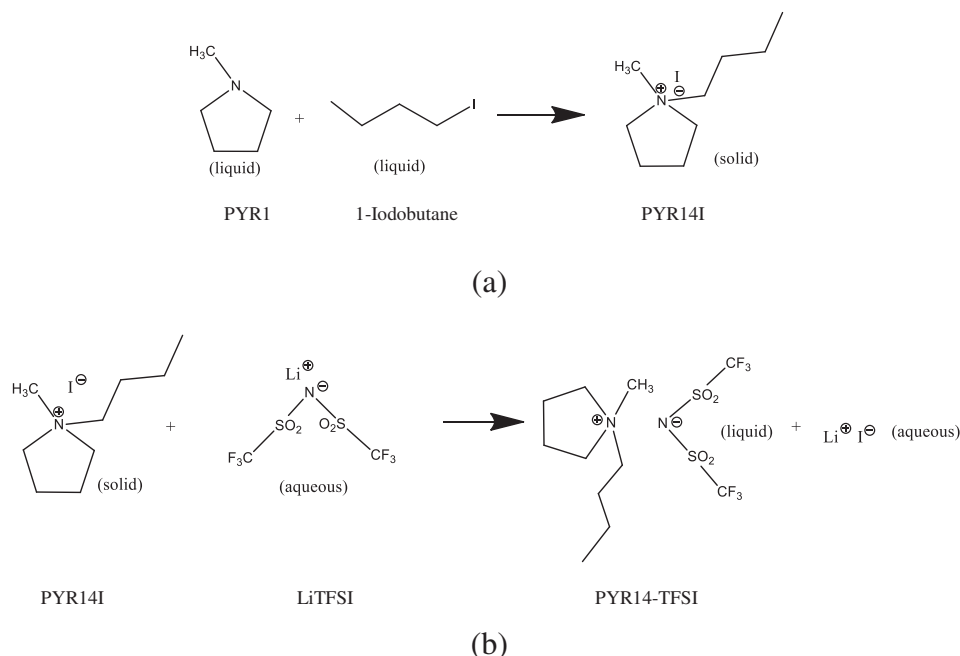


Fig. 1. Synthetic schemes of (a) PYR14I and (b) PYR14-TFSI.

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