



The effects of anion structure of lithium salts on the properties of in-situ polymerized thermoplastic polyurethane electrolytes

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ABSTRACT

Thermoplastic polyurethane (TPU) electrolytes with lithium salts were prepared by an in-situ polymerization method. Three different lithium salts were used to study the effects of the anion structure on the properties of polyurethane electrolytes: LiCl, LiClO₄, LiN(SO₂CF₃)₂ (LiTFSI). The effects of the anion structure on monomer (PTMG) prior to polymerization and on the properties of TPU electrolytes post polymerization were investigated. The anion structure of lithium salt has a significant influence on the ionic conductivity, thermal stability and tensile property of TPU electrolytes. The TPU electrolytes with LiTFSI demonstrated a high ionic conductivity up to 10⁻⁵ S/cm at 300 K. The ionic conductivity of polyurethane electrolytes with lithium salts is in the order: LiCl < LiClO₄ < LiTFSI. It was found that the lithium salts with larger anions were easily dissociated in TPU and had stronger interaction with TPU, which provided more charge carriers and gave higher ionic conductivity.

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1. Introduction

Solid polymer electrolytes (SPEs) are new generation solid ionic conductive materials, which have wide potential applications in electronic devices by replacing liquid electrolytes. They have many advantages over conventional liquid electrolytes and solid inorganic electrolytes in terms of their mechanical strength, processability, no-leakage, higher energy density, flexibility for cell design and non-combustible reaction products at the electrode surface existing, etc. [1,2]. SPEs are used as solid ionic conductive component in new power devices such as dye sensitized solar cells [3], polymer electrolyte membrane fuel cells [4], and lithium batteries [5]. For example, in the application of thin film lithium battery, solid polymer electrolyte film is sandwiched between a lithium metal anode and a composite cathode. The entire cell assembly can be produced as a laminated thin film by using proper coating process, and then rolled or folded into its finished shape as illustrated in Fig. 1 [6]. The most attractive characteristics of the polymer electrolyte membrane in the cell are its great capacity to tolerate shock, vibration, and mechanical deformation, its exceptionally long shelf-life, its wide operating temperature range, and its shape flexibility and manufacturing integrity [7]. The application of thin film lithium batteries in high value portable electronics zero-emission

vehicles, medical instruments, aerospace industry and military is starting to be realized [6]. The solid polymer electrolytes for the current battery applications are required to have high ionic conductivity (>10⁻⁵ S/cm at ambient temperature), good thermal dimensional stability, good electrochemical stability, easy processability, etc. [8].

In the last several decades, various polymer electrolytes have been studied, but most of them exhibit low ionic conductivity at ambient temperature. PEO based electrolytes were the first generation of polymer electrolytes and have been well studied [9,10]. They demonstrate a low ionic conductivity at temperatures below T_m (60 °C). Low ionic conductivity is believed to be associated with the low ion mobility in crystal lattice. At temperatures above its T_m , the ionic conductivity of PEO electrolytes significantly increases due to the melting of the crystal phase, but this also leads to its poor dimension stability [11]. Researchers attempted to tailor the chemical structure of the polymer used in polymer electrolytes to achieve both high ionic conductivity and good thermal dimensional stability. This approach utilizes polymers with electron donors other than oxygen such as poly(ethylene succinate) [12], poly(ethylene imine) [13] and poly(alkylene sulphide) [14]; polymers with block, branch or network structures [15,16]; polymer blends [17] and polymer/filler composites [18,19].

Considering that the mobility of the ions in polymer electrolyte is associated with the flexibility of the polymer segments and that the dimensional stability of the polymeric material depends on the rigidity of polymer segments, a polymer composed of hard segments and soft segments is helpful. Recently polyurethane

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¹ Sadly, Dr Kyonsuku Min died during the preparation of this article.

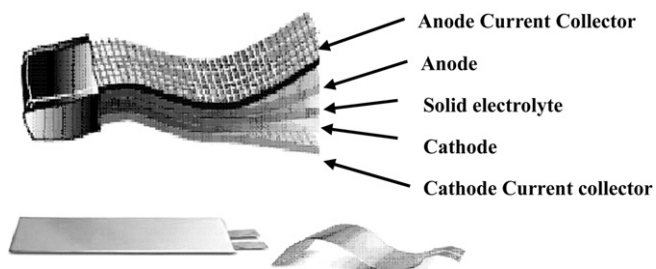


Fig. 1. Schematic diagram of basic construction of a film-like polymer electrolyte-based batteries [6].

based polymer electrolytes have attracted great attention [20–23]. The unique multiphase structure of polyether based thermoplastic polyurethane (TPU) makes it an interesting polymer matrix for polymer electrolytes. TPU is a block copolymer composed of soft segments and hard segments. The hydrogen bonding between the carbonyl group and N–H group in the hard segments leads to the formation of physically cross-linked hard domains [24]. The polyether-based soft segments act as polymer solvents to solvate the cations favoring the transportation of the ions and contribute to the conductivity of the polymer electrolyte. The hard segment is responsible for the dimensional stability acting as physical cross-link sites [25]. One great virtue of TPU is its property can span a wide range by tailoring the structure and the ratio of soft segment and hard segment [26]. Besides polymer matrix, the other important component in SPEs is salt. For the application in lithium battery, lithium salt is required in SPEs. It has been reported that the anion has significant effect on the ionic conductivity of PEO electrolytes [8]. For TPU based electrolytes, anion can affect the interactions between cation and polyurethane segments and impact on the morphology, ionic conductivity, dimensional stability, thermal stability and other properties of TPU electrolytes. So far, very few studies have been conducted on the effect of anion structure on the properties of TPU electrolytes.

As for the preparation method, most of the polymer electrolytes reported are prepared by solution cast method [27–30]. The intrinsic drawbacks of using the solution cast method to prepare polymer electrolytes are: 1) solvent residue left in the electrolyte film affects its thermal and ionic conductivity stability [8]; 2) a significant amount of solvent needs to be employed, which increases the manufacturing cost and safety risk in the mass production. The melt mixing method [31–33] and hot-pressing method [34] were also reported. In those methods, the solvation of salts in these films is poor because of the high viscosity of the polymer chain.

In this work, we proposed a novel solvent free method to prepare polyurethane electrolytes by using polymerization of the reactive monomer with the presence of lithium salts. The monomer of TPU, polyol, was mixed with salt before the reaction, then the other reactive components, isocyanate and chain extender, are added to initiate the polyurethane polymerization. The monomer functions as a common solvent to dissolve the salts and then after the polymerization it became part of the polymer. The prominent advantage of this method is that no volatile solvent used in the conventional solution cast method is needed and the ionic conductivity instability caused by the solvent residue is eliminated. Thermoplastic polyurethane electrolytes with three different lithium salts (LiCl, LiClO₄, and LiN(SO₂CF₃)₂ (LiTFSI)) were prepared by this in-situ method. The effect of anion structure of lithium salts on the ionic conductivity, thermal and tensile properties of TPU electrolytes and its mechanism was discussed. Before polymerization, the interaction between lithium salts with PTMG

was characterized by Optical Microscopy, Fourier Transform Infrared Spectroscopy (FTIR) and Differential Scanning Calorimetry (DSC). After polymerization, the interaction of ions with soft segments and hard segments of TPU was studied by using FTIR and DSC. Then, the property of TPU electrolytes including ionic conductivity, tensile property and thermal stability were investigated.

2. Experimental

2.1. Material

The thermoplastic polyurethane components were formulated with a low hard segment content and high soft segment content. The polyol used was polytetramethylene oxide glycol (PTMG) with molecular weight of 2000 g/mol from Sigma-Aldrich chemical company. The chain extender, 1,4 butanediol, was purchased from ARCO and diisocyanate, 4,4' diphenylmethane diisocyanate (MDI), was provided by Bayer. Three kind of lithium salts with different sized anions were used: lithium chloride LiCl, lithium perchlorate LiClO₄, lithium bistrifluoromethanesulfonimide LiN(SO₂CF₃)₂ (LiTFSI). They were all from Aldrich.

2.2. Procedure

2.2.1. Preparation of TPU electrolyte via the in-situ polymerization method

In the conventional solution cast method, the pre-synthesized TPU was mixed with salt in solvent and electrolyte films were formed by vaporization of the solvent. In this work, an in-situ polymerization method with polyurethane polymerization in the presence of salt was used. TPU was formulated with equimolar quantities of PTMG and BDO. The formulation of polyurethane component in the electrolytes contains 68.26% PTMG, 6.14% BDO and 25.60% MDI by mass when the stoichiometric ratio of hydroxyl to isocyanate functionality was maintained at unity. In the experiment, 2% excess of stoichiometry of MDI was used to compensate for trace amounts of residual water in the salt, and reactants. Prior to polymerization, the liquid PTMG was mixed with lithium salts by a magnetic stirrer at 60 °C for 1 day to make sure the salts completely dissolved and then dried under a vacuum at 80 °C. No solvent was used in this method; BDO was dried under a vacuum oven first and demoistured over 3 Å molecular sieves at room temperature prior to reaction; MDI was stored under vacuum at 0 °C before usages. In the polymerization, the premixed PTMG/salt mixture was poured into aluminum pan on a hot stage, and then BDO and MDI were added at 80 °C mixed by a stirrer. The reactive mixture then was poured in a plate made of Teflon coated aluminum sheet and put into a vacuum oven for 24 h at 100 °C for curing. The lithium salt concentration in the polymer electrolytes is represented by the stoichiometry ratio of ether unit in the polymer to Li in the lithium salt, [O:Li]. The polymer electrolytes of with [O:Li] equal to 8:1, 16:1, 32:1 were prepared.

2.2.2. Characterization

Prior to the polymerization, the PTMG/salt mixtures were investigated by a Lietz Laborlux polarized optical microscope equipped with a video camera. Thermal behavior of the PTMG/salt mixture was investigated by using a Thermal Advantage 2920 differential scanning calorimeter operating in the temperature scanning mode. Samples were scanned in the range of –120 to 200 °C. All the DSC thermograms were recorded at a scan rate of 20 °C/min. In the FTIR characterization of PTMG/salt mixtures, samples were melted to liquid state and then directly coated on the KBr Plate. The plates coated with samples were scanned over the

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