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Electrochemical and mechanical properties of polyolefin hard segment with polyethylene oxide conductive phase block copolymers

MengXuan Tang [a,d], Hui Wang [a], Yong-Gun Lee [b], Yasuo Takeda [a], Osamu Yamamoto [a,*], Jiaqiang Xu [c], Anbao Yuan [c], Nobuyuki Imanishi [a]

[a] *Graduate School of Engineering, Mie University, Tsu 514-8507, Japan*
[b] *SAIT, Samsung Electronics Co., 129 Samsung Ro, Keonton-Gun, Suwon-city, Gyeonggi-Do, 443-742, South Korea*
[c] *Department of Chemistry, College of Science, Shanghai University, Shanghai 200444, China*
[d] *Department of Physics, College of Science, Shanghai University, Shanghai 200444, China*

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ABSTRACT

A high lithium ion conductivity polymer electrolyte with excellent mechanical properties was developed in a polyolefin hard segment with a polyethylene oxide conducting phase block copolymer (OEO) and tetraethylene glycol dimethyl ether (G4) composite polymer with lithium bis(fluorosulfonyl)imide (LiFSI). The effect of the modulus of polymers on the ionic conductivity is generally controversial; high ion conducting polymer electrolyte typically exhibit poor mechanical properties. The composite polymer electrolytes developed in this study have ion conductivities in the range of 10^{-5} to 4×10^{-4} S cm^{-1} and tensile strengths in the range of 1 to 12 MPa at room temperature. 10OEO-1.4LiFSI-2.5G4, where OEO is based on ethylene oxide (EO) units, has ionic conductivity of 1.3×10^{-4} S cm^{-1} and tensile strength of 5.1 MPa at room temperature. The high G4 content composite of 10OEO-3.0LiFSI-4.0G4 has a high ion conductivity of 4.0×10^{-4} S cm^{-1}, but a low tensile strength of 1.0 MPa at room temperature. The OEO-LiFSI-G4 composite polymer with high conductivity and high tensile strength is an attractive candidate for the electrolyte in lithium polymer batteries.

1. Introduction

The electrolytes in the most commonly used lithium-ion batteries for mobile phones, lap-top computers and electric vehicles contain flammable non-aqueous solvents and lithium salts. However, the use of flammable solvents has safety issues, especially in large size batteries for electric vehicles. Therefore, replacement of the flammable solvent electrolyte with a solid electrolyte has the potential to improve the safety characteristics of lithium-ion batteries [1].

Various types of high lithium ion conductivity solid electrolytes have been reported, such as the layered-type structure of Li_3N [2], Li_2S based glasses and glass ceramics [3], perovskite-type $La_{2/3-x}Li_{3x}TiO_3$ (LLTO) [4], NASICON-type $Li_{1+x}A_xTi_{2-x}(PO_4)_3$ (A=Al, Fe, Sc, etc.) (LATP) [5], garnet-type $Li_7La_3Zr_2O_{12}$ (LLZ) [6], and poly(ethylene) oxide (PEO)-based polymer electrolytes [7,8]. Lithium sulfide based conductors are stable in contact with lithium metal, but are quite hydroscopic. Li_3N also shows a low decomposition potential. LLTO and LATP are unstable in contact with lithium metal. Ta-doped LLZ exhibits a high lithium conductivity of 1×10^{-3} S cm^{-1} at room temperature and is stable in contact with lithium metal; however, lithium dendrites are formed for polarization times as short as 100–200 s at 0.5 mA cm^{-2} [9]. Polymer electrolytes are stable in contact with lithium metal and are not so sensitive to the atmosphere; however, their room temperature conductivity is low [8].

Lithium is the most attractive anode material for batteries because of its high specific capacity (3861 mAh g^{-1}) and low potential (−3.04 V vs. NHE). However, the formation of lithium dendrites during lithium deposition in a liquid electrolyte leads to serious safety problems; therefore, lithium rechargeable batteries with lithium anodes have not been commercialized. Research on rechargeable lithium batteries has thus focused on the development of true solid state electrolytes with high conductivity and limited reactivity with the lithium metal anode. Monroe and Newman [10] predicted that if a homogeneous solid electrolyte with a modulus of 6 GPa was obtained, the lithium dendrite problem would be solved. However, such hard solid electrolytes have a serious problem for the interface between the lithium electrode and solid electrolyte. In practice, the lithium metal anode recedes by several microns as the battery discharges and the solid electrolyte must adhere to the electrode as it recedes, which is not possible if the electrolyte is a simple solid with a modulus of 6 GPa [11]. It is well known that the efficacy of adhesives is lost if the modulus exceeds a few MPa [12]. Polymer electrolytes are the best candidates for high energy density lithium rechargeable batteries with respect to safety and adhesion with the lithium metal electrode.

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* Corresponding author.
E-mail address: yamamoto@chem.mie-u.ac.jp (O. Yamamoto).

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After a report by Wright on ionic conducting polymers in 1975 [13], many researchers have attempted to develop high lithium ion conducting polymer electrolytes. However, high lithium ion conducting polymer electrolytes with excellent mechanical properties at room temperature have not been reported to date. The cation transport in the polymer electrolyte is intimately coupled to the segmental motion of the polymer chain [14]. High ionic conductivity is obtained in soft polymers such as in the high temperature PEO phase. In this study, we aim to develop a high lithium ion conductivity solid polymer electrolyte with excellent mechanical properties. Several researchers have studied PEO-containing polystyrene block copolymers with high ionic conductivity and excellent mechanical properties [11,15–18]. In these systems, the conducting pathways are provided by an ethylene oxide (EO) containing block, while the non-conducting block of polystyrene imparts the desired mechanical properties. Niitani et al. [17] reported an ionic conductivity of 1×10^{-4} S cm^{-1} and a tensile strength of ca. 3 MPa at room temperature for a polystyrene hard segment with a PEO ion conducting phase containing $LiClO_4$. Wang et al. [15] also reported a high conductivity of 10^{-4} S cm^{-1} and a high dynamic Young's modulus of 10^9 dyn cm^{-2} at 60 °C for a polystyrene-block-polyethylene block polymer electrolyte containing lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).

Here, we investigate the ionic conductivity and tensile strength of a new class of block copolymer electrolyte that consists of a polyolefin hard segment and a PEO conductive phase with a lithium salt. To enhance the ionic conductivity, a composite electrolyte consisting of the block copolymer electrolyte and less flammable tetraethylene glycol dimethyl ether (G4) with the lithium salt of lithium bis(fluorosulfonyl)imide ($Li(FSO_2)_2N$; LiFSI) is examined.

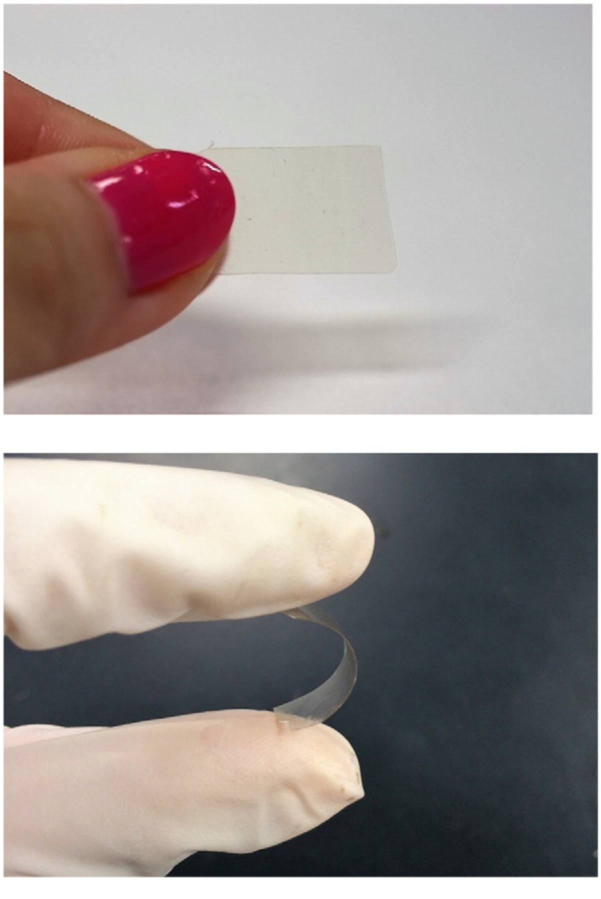

Fig. 1. Photographs of the 10OEO-1.4-LiFSI-2.8G4 film.

2. Experimental

The non-conducting polyolefin block-conducting PEO block copolymers (OEO) were supplied from Sanyo Chemical Ltd., Japan. The non-conducting polyolefin block is maleic acid-modified polypropylene (molecular weight: 3000, average number of maleic acid groups per molecule: 1.7) and the conducting PEO block is 3400 average molecular weight of EO chain. So, an average molecular weight of the block copolymer is 22,000 consisting of 62 wt.% of the non-conducting polyolefin block and 38 wt.% of the conducting PEO block. The polyolefin hard segment block copolymers were dissolved in xylene at 90 °C for 1–2 h and then LiFSI was added into the solution and stirred for 4 h at 90 °C under Ar gas flow. The obtained solutions were dried for 20 h under vacuum in a Teflon dish.

The composite electrolyte films of OEO block polymers and G4 were prepared by the following method. OEO, LiFSI and G4 were added to xylene in a round-bottom flask. The mixture was stirred and homogenized at 90 °C for 4 h and was then transferred rapidly into a Teflon dish in an in-house-built stainless steel drying box. All of these operations were performed under Ar gas. It is worth mentioning that even trace amount of water in the solution can largely influence the formation of the final films since G4 is very sensitive to water. So the control of humidity and the protection of Argon gas are the vital factors in the synthesis leading to the perfect films. After that, the enclosed box was dried at 80 °C under vacuum (0.2 MPa/cm^2) for approximately 24 h. Approximately 150 μm thick transparent composite polymer films as shown in Fig. 1 were obtained by this careful preparation method.

The ionic conductivity was measured using gold plate electrodes. The Au/electrolyte/Au sandwich cells with copper foil leads were placed into an envelope, which was then evacuated and heat-sealed. The cells were isotactically pressed at 150 MPa to ensure good contact between the gold plate electrodes and electrolyte. The impedance of the pouch type Au/electrolyte/Au cells was measured using a frequency analyzer (Solartron, 1250) in the temperature range of −20 to 80 °C and the frequency range of 1 MHz to 0.1 Hz. The bulk and grain boundary conductivities of the samples were calculated from complex impedance plots using Zview 2 software (Scribner Associates). The mechanical properties of the polymer electrolytes were measured using an in-house-built tensiometer at a stretching speed of 10 cm min^{-1} in a glove box under an Ar atmosphere. The stability of the composite polymer electrolyte in contact with lithium metal was tested using an in-house-built Swagelok-type cell with lithium electrodes. The change in cell impedance during storage at 60 °C was also measured. Electrochemical tests of the Li/electrolyte/Li cell were conducted using the Swagelok-type cell and a potentio/galvanostat (Hokuto Denko, HJ 10015DS).

3. Results and discussion

Fig. 2 shows a typical impedance profile for 10OEO-1.4LiFSI at 25 °C. The EO/Li ratio is the solubility limit of LiTFSI in PEO [19]. A large semicircle was observed, which may be due to the contribution of grain boundary resistance in the polymer electrolyte. The bulk, grain boundary and total conductivities were estimated to be 5.8×10^{-5}, 4.6×10^{-7} and 4.61×10^{-7} S cm^{-1}, respectively at 25 °C. A similar large semicircle was observed in the impedance profile for 18PEO-LiTFSI [20], where the bulk, grain boundary and total conductivities were 8.9×10^{-5}, 6.0×10^{-6} and 5.6×10^{-6} S cm^{-1} at 25 °C, respectively. The total conductivity of 10OEO-1.4LiFSI is lower than that of 18PEO-LiTFSI, although the bulk conductivity of 10OEO-1.4LiTFSI is comparable to that of 18PEO-LiTFSI. However, the tensile strength of 10OEO-1.4LiFSI was as high as 13 MPa at 25 °C, which is in contrast to that for the PEO-based lithium ion conducting electrolyte of 3.6 MPa [21]. The tensile strength of 10OEO-1.4LiSFI was measured using a tensiometer in an Ar-filled glove box to avoid the effect of moisture in the air. Fig. 3 shows the temperature dependence of the bulk and grain boundary conductivity for 10OEO-1.4LiTFSI. No clear bulk and grain boundary