



Electrochemical properties of the polyethylene oxide–Li(CF₃SO₂)₂N and ionic liquid composite electrolyte

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HIGHLIGHTS

- ▶ The electrical conductivity of PEO₁₈LiTFSI–*x*PP13FSI increased with *x*.
- ▶ The lowest interface resistance of lithium electrode was observed in the range of *x* = 1.2–1.44.
- ▶ Lithium dendrite formation was suppressed by the addition of PP13FSI into PEO₁₈LiTFSI.

ARTICLE INFO

Article history:

Received 16 February 2012

Received in revised form

5 May 2012

Accepted 10 July 2012

Available online 17 July 2012

Keywords:

Dendrite

Ionic liquid

Lithium metal

Lithium air battery

ABSTRACT

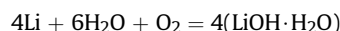
The electrical conductivity and lithium ion transport properties of the polyethylene oxide (PEO) with lithium salt Li(CF₃SO₂)₂N (LiTFSI) and a room temperature ionic liquid of *N*-methyl-*N*-propylpiperdinium bis(fluorosulfonyl)imide (PP13FSI) were examined as a function of the ionic liquid content. The electrical conductivity of PEO₁₈LiTFSI–*x*PP13FSI increased and the lithium ion transport number decreased with increasing the ionic liquid content. The interface resistance between PEO₁₈LiTFSI–*x*PP13FSI and lithium metal was dependent on *x* and the lowest interface resistance was observed in the range of *x* = 1.2–1.44. The critical current density of lithium deposition and dissolution on lithium metal was reduced and lithium dendrite formation was suppressed by the addition of PP13FSI into PEO₁₈LiTFSI.

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1. Introduction

Lithium–air rechargeable batteries are considered as a promising battery system with high specific energy density due to the extremely high theoretical energy density of 11,426 W h kg^{−1} (excluding oxygen), which is comparable with that of gasoline [1]. These batteries are attracting growing attention and much R&D effort as a possible power source for electric vehicles. The system mainly consists of a lithium metal negative electrode, an electrolyte and a carbon–air positive electrode. Two types of lithium–air batteries have been developed; non-aqueous and aqueous electrolyte types. The non-aqueous system exhibits higher specific energy density than the aqueous system, but has some severe problems that must still be addressed, such as lithium metal corrosion by water, CO₂ ingress when operated in air and high polarization during the charge and discharge processes. The energy density of the aqueous system is lower than that of the non-

aqueous system by the 2371 W h kg^{−1} (excluding oxygen), because water is involved in the cell reaction as follows;



However, these problems observed in the non-aqueous system are not present or have been solved in the aqueous system. The key component of aqueous-type lithium–air batteries is the water-stable lithium-conducting solid electrolyte, since lithium metal reacts severely with water. At present, the Li_{1+x}Ti_{2−x}Al_xP₃O₁₂ (LTAP) NASICON-type solid electrolyte is the only reported water-stable lithium-conducting solid electrolyte [2]. The use of a water-stable lithium electrode for lithium–air batteries was proposed by Visco et al. [3], and Imanishi and his colleagues [4]. The water stable lithium electrode proposed by Imanishi and co-workers consisted of a lithium metal negative electrode, a PEO-based lithium-conducting polymer electrolyte of PEO–Li(CF₃SO₂)₂N (LiTFSI), and LTAP, where the polymer electrolyte is used to prevent direct contact between the lithium metal and LTAP, because LTAP is unstable in contact with lithium metal [4].

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The polymer electrolyte acts as a protective layer for the water-stable lithium metal electrode in aqueous lithium–air batteries and should meet requirements such as high lithium ionic conductivity, stability with lithium metal, and a low interface resistance between lithium metal and the polymer electrolyte. Kim et al. [5] reported interesting results on a composite polymer electrolyte (CPE) based on PEO and a room temperature ionic liquid of *N*-alkyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR_{1A}TFSI). The addition of PYR_{1A}TFSI into PEO–LiTFSI resulted in a large increase of the ionic conductivity and in a decrease of the interface resistance between lithium metal and the CPE. Shin et al. [6] reported that *N*-methyl-*N*-propylpyrrolidinium TFSI (PYR13TFSI) addition into PEO inhibited the formation of crystalline polymer–salt phases and an increased fraction of amorphous region present in the CPE. Recently, Imanishi and his colleagues [7–9] have made some progress on this issue using a PEO-based polymer electrolyte with a SiO₂ nano-filler and a room temperature ionic liquid of *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP13TFSI). Addition of the ionic liquid into PEO₁₈LiTFSI improved the lithium ion conductivity and reduced the interface resistance between lithium and the CPE, where ionic liquids have the same anion as that of the lithium salt in the polymer electrolyte to interact with lithium cations located in the polymer chains, which hinders the formation of crystalline phases [10].

Although a polymer electrolyte with high ionic conductivity and a low interface resistance between lithium metal and the polymer electrolyte can be achieved by the addition of room temperature ionic liquids and nano-fillers, lithium dendrite formation during the lithium deposition process is another important subject to consider for a polymer electrolyte aimed at application in lithium–air and lithium–polymer batteries. Lithium metal is the best negative electrode candidate for high energy density batteries, because it has a very high theoretical specific capacity of 3861 mA h g⁻¹ and a high negative potential of –3.05 V vs. NHE. However, the formation of dendrites during lithium deposition limits the use of lithium metal as a negative electrode in lithium

batteries. This phenomenon occurs even with polymer electrolytes, although to a lesser extent than that with liquid electrolytes [11,12]. Brissot et al. [11] reported in detail on the lithium dendrite formation mechanism for Li/PEO₁₈LiTFSI/Li. Our previous results confirmed that the addition of an appropriate amount of PP13TFSI into PEO₁₈LiTFSI significantly suppressed the dendrite formation onset time [8].

In this study, the ionic conductivity and interface resistance between lithium metal and a CPE consisting of PEO₁₈LiTFSI–*x**N*-methyl-*N*-propylpiperidinium bis(fluorosulfonyl)imide (PP13FSI) are examined as a function of *x*, in addition to dendrite formation during the lithium deposition process dependent on the thickness of the CPE. These properties of PEO₁₈LiTFSI–*x*PP13FSI were compared with those of PEO₁₈LiTFSI–*x*PP13TFSI. An ionic liquid with FSI anions was considered due to the fact that it exhibits lower viscosity and higher ionic conductivity than that with TFSI anions and the Li/PP13FSI–LiTFSI/LiCoO₂ cell showed better high rate charge and discharge performances than that of the Li/PP13TFSI–LiTFSI/LiCoO₂ cell [13].

2. Experimental

PEO₁₈LiTFSI–*x*PP13FSI CPEs were prepared using a casting method. PEO (Sigma–Aldrich, Mv = 600,000) was dissolved in anhydrous acetonitrile (AN) and LiTFSI (Wako Chemicals, Japan) and PP13FSI (Dai-ichi Kogyo-Seiyaku Co. Ltd., Japan) were then added to obtain an O/Li⁺ mole ratio in PEO–LiTFSI of 18. The mixed solution was stirred at room temperature for 24 h and then cast into a clean Teflon dish. The AN solvent was evaporated slowly at room temperature in an Ar-filled dry glove box. After AN was completely evaporated, the Teflon dish was transferred to a vacuum oven to dry at 100 °C for 24 h to remove the residual AN. The thicknesses of the CPEs were in the range of 100–300 μm.

The microstructure of the CPEs was observed using an optical microscope (Keyence VHX-1000) at room temperature and 60 °C. Electrical conductivity measurements of CPE were performed using

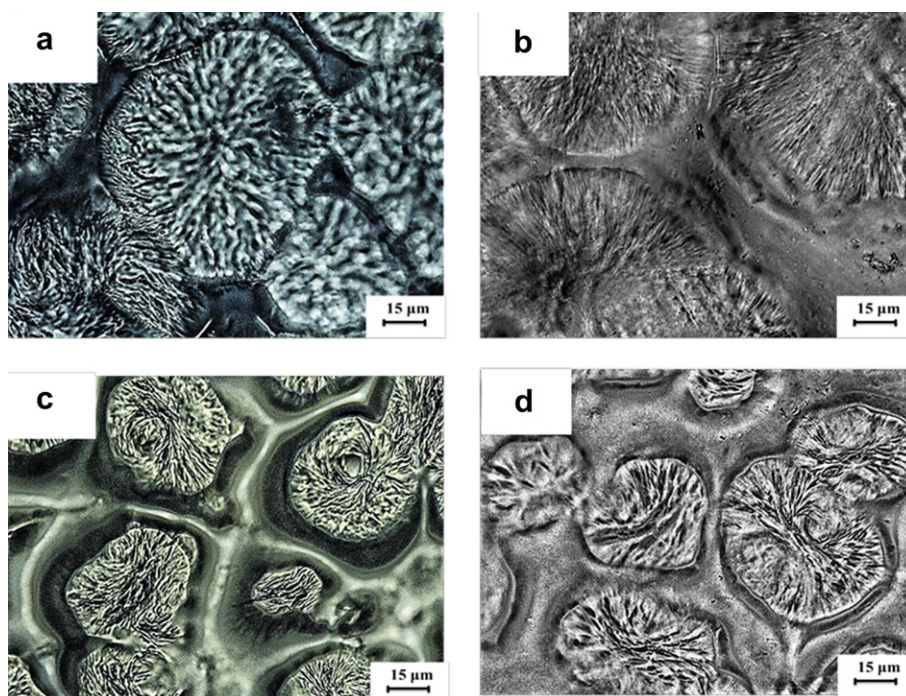


Fig. 1. Optical photographs of (a) PEO₁₈LiTFSI at room temperature, (b) PEO₁₈LiTFSI at 60 °C, (c) PEO₁₈LiTFSI–1.44PP13FSI at room temperature and (d) PEO₁₈LiTFSI–1.44PP13FSI at 60 °C.

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