Secondary Battery Performance of Solid Polymer Electrolyte Membranes Based on Lithium Ion Conductive Polyimide Nanofibers

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Poly(ethylene oxide) (PEO)-based solid polymer electrolytes have been investigated for the applications to all-solid-state lithium ion batteries. However, the lithium ion conductivities of the present electrolyte membranes are insufficient for practical applications. In our previous study, composite membranes composed of PEO-grafted polyimide (PI-g-PEO) nanofibers showed good electrolyte characteristics. In this study, a series of PI-g-PEO with various PEO lengths and grafting ratios were synthesized and converted to nanofibers. The nanofiber frameworks (NfFs) with high PEO weight fractions showed much higher ion conductivity than the corresponding membranes. The NfF composite membrane was fabricated by composing the best NfF and the PEO/Li matrix electrolyte. The NfF composite membrane showed high ion conductivity at low temperatures and good secondary battery performances.

**Keywords:** Ion conductivity, Lithium ion, Nanofiber, Secondary battery, Solid polymer electrolyte

1. Introduction

During the past decades, lithium ion conductive solid polymer electrolytes have been widely investigated for all-solid-state lithium ion batteries (ASS-LIBs) that have higher safety and durability than conventional LIBs [1]. Poly(ethylene oxide) (PEO)-based solid polymer electrolytes have been studied for long years and are still one of the most promising materials for the ASS-LIBs [2]. In the PEO type membranes containing lithium salts, ether oxygen coordination sites dissociate the lithium salts and the segmental motion of the polymer chains leads the lithium ion conduction [3-5]. In most cases, however, the ion conductivity significantly decreases at ambient temperature due to the crystallization of the PEO polymer chains. In order to increase the conductivity, a number of research groups reported various approaches, such as PEO-based block copolymers, grafted polymers, and network polymers with more flexible oligomeric PEO side chains [6-9]. However, the lithium ion conductivities of the present electrolyte membranes are insufficient for the practical ASS-LIB applications.

Recently, polymer nanofibers have been investigated as reinforcing composite materials for solid polymer electrolytes [10,11]. In contrast, our group designed and fabricated ion conductive polymer nanofibers as a framework to construct outstanding ion conductive pathways [12,13]. The polymer electrolyte membranes composed of the lithium ion conductive nanofiber framework (NfF) and matrix polymer electrolyte showed improved ion conductivity and good all-solid-state secondary battery performance [14]. However, a relationship between nanofiber structure and lithium ion conductive property has not been clearly revealed.

This study reports the fabrication and
characterizations of NfFs consisted of lithium salt-containing various PEO-grafted polyimides (PI-g-PEO) with different PEO lengths and grafting ratios. The obtained NfFs were combined with a typical polymer electrolyte (PEO/Li) matrix to provide dense composite membranes. Their lithium ion conductive characteristics and secondary battery performances were also investigated.

2. Experimental

A series of PEO-grafted polyimide (PI-g-PEO) with various PEO lengths and various grafting ratios were synthesized based on our previous report [14] (Fig. 1). A typical synthetic procedure of PI-g-PEO (a) with PEO length ($m$) of 12 and grafting ratio ($n$) of 0.44 is as follows: The main-chain polymer, 6FDA-DABA, was synthesized by the polycondensation of the equimolar of purified 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane di-anhydride (6FDA, Central Glass Co.) and 3,5-diaminobenzoic acid (DABA, Sigma-Aldrich) in N, N-dimethylacetamide (DMAc, Kanto Chemical), and the followed chemical imidization using acetic anhydride and trimethylamine. Then, into the anhydrous DMAc solution of 6FDA-DABA, the PEO side chain (poly(ethylene glycol) methyl ether, average $M_n = 550$, Sigma-Aldrich, 1.0 equivalent to the 6FDA-DABA repeating unit) was added under nitrogen at 0 °C in the presence of condensation reagents, N, N'-dicyclohexylcarbodiimide (TCI Co.), N-hydroxysuccinimide (TCI Co.), and the followed chemical imidization using acetic anhydride and trimethylamine. Then, into the anhydrous DMAc solution of 6FDA-DABA, the PEO side chain (poly(ethylene glycol) methyl ether, average $M_n = 550$, Sigma-Aldrich, 1.0 equivalent to the 6FDA-DABA repeating unit) was added under nitrogen at 0 °C in the presence of condensation reagents, N, N'-dicyclohexylcarbodiimide (TCI Co.), N-hydroxysuccinimide (TCI Co.), and N, N-dimethyl-4-aminopyridine (TCI Co.). The mixture solution was stirred under nitrogen at room temperature for 48 h, and the resulted PI-g-PEO was precipitated in methanol and dried in a vacuum oven at 40 °C overnight. The obtained PI-g-PEO was characterized by $^1$H NMR (Bruker AVANCE III 500) and gel-permeation chromatography (GPC, detector: JASCO 860-RI monitor) using Shodex SB-806HQ and SB-804HQ columns. Other PI-g-PEO (b)-(g) were also obtained by using different PEO (poly(ethylene glycol) methyl ether, average $M_n = 550, 750$, or 2000, Sigma-Aldrich) and each appropriate grafting reaction condition.

The PI-g-PEO nanofibers containing lithium salt was were prepared by the electrospinning apparatus (ES-1000, Fuence, Co., Ltd., Tokyo, Japan). First, anhydrous N, N-dimethylformamide (DMF, Kanto Chemical) was added to PI-g-PEO at a polymer concentration of 20 wt%, and the solution was stirred at 60 °C for 24 h. Then, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Aldrich) was added in the solution and stirred at 30 °C for 48 h. The ratio of Li$^+$ and ethylene oxide (EO) unit of PEO was set as $[\text{Li}]/[\text{EO}] = 1/24$. Typical ES conditions were as follows: Squeezing speed of polymer solution = 6.0 $\mu$L min$^{-1}$, voltage = 20 kV, distance between syringe and collector = 10 cm, temperature and humidity = 20 °C, 10% RH. For comparison, PI-g-PEO membranes were also prepared by a solvent casting method.

The nanofiber composite membranes were prepared by combining the PI-g-PEO NfF and the PEO/LiTFSI ($[\text{Li}]/[\text{EO}] = 1/24$) matrix. Appropriate
amounts of PEO/LiTFSI corresponding to the void volumes of the NfFs were dissolved in deionized water and were poured onto the NfFs. By evaporating the solvent, dense NfF composite membranes with their thicknesses in the range of 30-60 \( \mu \)m were obtained.

The surface and cross-sectional morphologies of the NfFs and the NfF composite membranes were examined by scanning electron microscopy (SEM, JXP-6100P, JEOL, Tokyo, Japan). The nanofiber diameters were determined by the SEM observation and an image analysis software (Image J). The ion conductivity of the samples sandwiched between two blocking stainless steel (SS) electrodes was measured by electrochemical impedance spectroscopy at the frequency between 0.1 Hz and 5 MHz (VersaSTAT3, Tokyo, Japan) in a temperature-controlled chamber. Ion conductivity \( \sigma (\text{S cm}^{-1}) \) was calculated from the resistance and the sample dimensions (thickness and area) using the following equation (1):

\[
\sigma = \frac{t}{A R_b}
\]

where \( t \) is the sample thickness (cm), \( A \) is the sample area (cm\(^2\)), and \( R_b \) is the bulk resistance (\( \Omega \)) of each electrolyte membrane. The secondary battery performance of an assembled LiFePO\(_4\) (Hosen Co) | NfF composite membrane | Li (Honjo Metal Co.) in a CR 2032-coin cell was evaluated by TOSCAT-3000 (Toyo system, Fukushima, Japan) under argon atmosphere. The cells were cycled at a constant charge/discharge current density of 0.01, 0.02, or 0.05 C over a voltage range between 2.8 and 3.9 V at 60 °C.

3. Results and discussion

3.1. Synthesis and nanofiber fabrication

The \(^1\)H NMR spectroscopy and the GPC measurement revealed the successful synthesis of a series of PI-g-PEO with the expected chemical structures (For example, in the case of PI-g-PEO (a): (CDCl\(_3\), \( \delta \) in ppm) 8.6-7.7 (m, 9H, Ph), 3.7-3.2 (m, 19.6H, -CH\(_2\)CH\(_2\)O-), 2.8 (s, 1.3H, -OCH\(_3\)) with high molecular weights (\( M_w > 10^5 \)). By considering the PEO length and grafting ratio, the weight fraction of PEO of each PI-g-PEO was estimated in the range from 30 wt% to 71 wt% (Fig. 1(b)). The ES method was attempted to all the PI-g-PEO to obtain nanofibers. The PI-g-PEO (g) and (e) with high PEO weight fractions (71 and 49 wt%) gave thick fibers with welded structures. In addition, these fiber structures became disrupted after heating at 80 °C. On the contrary, the PI-g-PEO (b) with a relatively high PEO weight fraction (47 wt%) gave nanofibers with their average diameters of 151 ± 18 nm and retained the nanofiber structures after heating at 80 °C. PI-g-PEO (a), (c), (d), and (f) also successfully produced smooth and thin nanofibers (Fig. 2).

![Fig. 2. SEM images and average fiber diameters of the PI-g-PEO (a) - (g) NfFs.](image)

3.2. Ion conductive characteristics

Temperature dependence of ion conductivity on the PI-g-PEO NfF and the corresponding PI-g-PEO membranes were shown in Fig. 3(a). The PI-g-PEO NfFs with high PEO weight fractions (PI-g-PEO NfF (b) and (d)) indicated 10-25 times higher ion conductivity than the corresponding membranes. As discussed in our previous paper [14], it is considered that the unique nanofiber characteristics including lower crystallinity and higher polymer chain mobility than the corresponding membrane enhanced the ion conductive properties. Interestingly, on the other hand, the ion conductivity of the PI-g-PEO NfF with low PEO weight fraction (PI-g-PEO NfF (a), (c), and (f)) were lower than those of the corresponding membranes. These results indicate that sufficient PEO weight fraction is required to construct effective ion transport pathways in the NfFs. To reveal the connectivity of the ion transport pathway among the nanofibers, water contact angle measurements were conducted. As shown in Fig. 3(b), the PI-g-PEO NfF (b) and (d) indicated lower water contact angles than the corresponding membranes. Since it is known that the nanofibers enhanced hydrophilicity or hydrophobicity due to the Cassie-Baxter model [15,16], suggesting that the hydrophilic PEO units exited at the surface of nanofibers. In contrast, the contact angles of the PI-g-PEO NfF (a), (c), and (f) were higher than those of the corresponding membranes. That is to say, increasing PEO content in the nanofibers promoted surface hydrophilicity of nanofibers, indicating that effective ion transport channel fabricated by grafted PEO could be formed on the interface among the
Fig. 3. (a) Ion conductivity and (b) water contact angle of the PI-g-PEO NfFs and membranes. (c) Ion conductivity of the PI-g-PEO NfF, PI-g-PEO NfF composite membrane, and PEO/Li membrane. These trends have good agreement with the ion conductivity results of the NfFs.

The PI-g-PEO (d) NfF, which showed the highest ion conductivity among the NfFs, was combined with POE/Li matrix electrolyte to provide a PI-g-PEO (d) NfF composite membrane. Figure 3(c) shows the ion conductivity of the composite membrane, along with a typical PEO/Li membrane without nanofibers and the PI-g-PEO (d) NfF. The NfF composite membrane indicated higher ion conductivity at low temperatures because of relatively high ion conductive characteristics of the PI-g-PEO NfF and the suppression effect of the PEO crystal formation by the NfF structure.

3.3. Secondary battery performance

As an all-solid-state lithium ion battery, a coin cell was fabricated using the PI-g-PEO (d) NfF composite membrane as an electrolyte, Li metal as an anode, and LiFePO₄ as a cathode. Figure 4 represents the discharge capacity of the cell as a function of the charge-discharge cycle number. The cell showed stable charge-discharge cycles with reasonable capacities (ca. 140 mAh g⁻¹, which was close to the theoretical value of LiFePO₄: 170 mAh g⁻¹). It is considered that the high ion conductivity and good mechanical strength based on the lithium ion conductive NfF led to such distinguished secondary battery performance. It is expected that further study on the polymer structures and optimization of electrodes and cell fabrication can improve the secondary battery performance in the future.

Fig. 4. Secondary battery cycle test of the cell using the PI-g-PEO NfF composite membrane as a solid electrolyte. (Inset) Charge-discharge curves.

4. Conclusion

A series of PI-g-PEO with various PEO lengths and grafting ratios were synthesized and converted to NfFs. The NfF with high PEO weight fractions showed much higher ion conductivity than the corresponding membranes. The NfF composite membrane was fabricated from the best NfF and the PEO/Li matrix electrolyte. The NfF composite
membrane showed high ion conductivity at low temperatures and good battery performances. The improved secondary performance is expected by further study.

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