

Effects of the Addition of TiO₂ Nanoparticles for Polymer Electrolytes Based on Porous Poly(vinylidene fluoride-co-hexafluoropropylene)/Poly(ethylene oxide-co-ethylene carbonate) Membranes

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ABSTRACT

We have attempted to combine a typical gel and a typical solvent-free polymer electrolyte through the conception of a pore-filling polymer electrolyte; instead of organic solvents, a viscous poly(ethylene oxide-co-ethylene carbonate) (P(EO-EC))/LiCF₃SO₃/TiO₂ electrolyte mixture is filled into the pores of a porous poly(vinylidene fluoride-co-hexafluoropropylene) (P(VdF-HFP))/P(EO-EC)/TiO₂ membrane. The porous membrane with 10 wt% TiO₂ showed better performance (*e.g.*, high uptake and good mechanical strength) than the others and was therefore selected as an optimal matrix to prepare a polymer electrolyte. All polymer electrolytes obeyed Arrhenius behavior and showed linear enhancement of ionic conductivity with increasing the temperature. In addition, maximum conductivity of 4.7×10^{-5} S cm⁻¹ at 25 °C was obtained for the polymer electrolyte containing 1.5 wt% TiO₂ in electrolyte mixture.

Keywords: porous membrane, polymer electrolyte, TiO₂ nanoparticle, ionic conductivity, rechargeable lithium battery

1 INTRODUCTION

During the last two decades, ion-conducting polymer electrolytes have continued to attract great interest from both scientific and industrial perspectives due to their growing application potentials in electronic devices such as rechargeable batteries, displays, fuel cells, and so forth [1]. Among these, solvent-free polymer electrolytes (SPEs) formed by complexes of a lithium salt (LiX) with a polyether such as poly(ethylene oxide) (PEO) have received considerable attention due to their advantages in terms of the ease of fabrication, flexibility in dimensions, good mechanical properties, safety features, and excellent stability at the lithium interface. However, their low ionic conductivity has been the reason for them not being used in practical applications for rechargeable lithium batteries that require a value of above 10^{-4} S cm⁻¹ at room temperature.

The ion transport of SPEs is induced via their rapid segmental motion combined with strong Lewis acid-base interactions between the cation and the donor atom present

in the amorphous phase. Therefore, most approaches for enhancing the conductivity of PEO-based systems have been focused on lowering the degree of PEO crystallinity or reducing the glass transition temperature, T_g , through the modification of the polymer structures and the incorporation of plasticizers or ceramic fillers [2,3].

In this study, in order to ameliorate the performance of SPEs, we report on a pore-filling polymer electrolyte filled with a viscous poly(ethylene oxide-co-ethylene carbonate) (P(EO-EC)) complexed with LiCF₃SO₃ into a porous poly(vinylidene fluoride-co-hexafluoropropylene) (P(VdF-HFP))/P(EO-EC) membrane. However, the pore-filling polymer electrolyte requires the modification to enhance its mechanical strength and ionic conductivity. In order to satisfy these requirements, TiO₂ nanoparticles are added to both a porous membrane and a viscous electrolyte mixture. Generally, it is reported [4] that there are weak coordination interactions between alkylene oxide segments and TiO₂, resulting in the increase of mechanical strength. Also, hydroxyl groups on the surface of TiO₂ and carbonyl groups in the polymer have interactions by the formation of hydrogen bonds [5]. From these reasons, it is expected that TiO₂ would be dispersed well in both a porous membrane and an electrolyte mixture due to the use of P(EO-EC), which contains carbonate and ether groups, causing the mechanical strength to be increased. On the other hand, the addition of TiO₂ induces improvement of ionic conductivity of polymer electrolytes. In general, it is widely accepted that the addition of TiO₂ into semi-crystalline polymers suppresses the crystallization and enlarges the amorphous phase, resulting in the enhancement of conductivity. In this study, in order to improve the conductivity of polymer electrolytes, TiO₂ nanoparticles are added into the amorphous polymer. Although there is not enough research concerned with the addition of TiO₂ on polymer electrolytes consisted of amorphous polymers, it is possible to enhance their ionic conductivity because the free volume, which is produced by the hydrogen bonds between hydroxyl groups on the surface of inorganic nanoparticles and ether groups in polymers is increased. Therefore, we focus on the improvement of mechanical strength and ionic conductivity of pore-filling polymer electrolytes by the addition of TiO₂ nanoparticles with various contents into both a porous membrane and an electrolyte mixture.

2 EXPERIMENTAL

2.1 Preparation of Porous Membranes and Polymer Electrolytes

Porous membranes were prepared by a phase inversion method. To prepare porous membranes with TiO₂ (ST-01, Ishihara Sangyo Kaisha), the weight ratio of polymers with TiO₂, a solvent, and a nonsolvent was optimized at 1:8:1. The proportion of P(VdF-HFP) ($M_w = 4.6 \times 10^5$ g mol⁻¹, Aldrich Chemicals) and P(EO-EC) ($M_n = 1800$ g mol⁻¹, synthesized in the laboratory) was chosen as 60 to 40 wt% in this study. TiO₂ content was varied as 0, 10, 20, 30, and 40 wt% in P(VdF-HFP)/P(EO-EC)/TiO₂. Firstly, a homogenous mixture was prepared in advance by dissolving P(VdF-HFP) and P(EO-EC) in acetone. Then, a measured amount of TiO₂ was added into TEA (nonsolvent) and acetone (solvent) mixture and dispersed by stirring and ultrasonication. Finally, the prepared TiO₂/TEA/acetone mixture was added into a homogenous P(VdF-HFP)/P(EO-EC) mixture. After complete dissolution, the solution degassed at 50 °C for 2 h was cast on a cleaned glass plate and desired thickness was made with a doctor blade. After a solution was stored at room temperature, the glass plate was put into steam atmosphere until the volatile acetone was evaporated, and then phase inversion occurred. TEA was removed by washing with methanol. After the residual solvent was allowed to slowly evaporate at room temperature, it was completely removed under vacuum at 50 °C for 24 h, thereby resulting in porous membranes. The resultant membranes had a thickness of 140–180 μm.

In order to prepare pore-filling polymer electrolytes, P(EO-EC) was first dissolved in acetone. After a homogenous solution was obtained, a measured amount of LiCF₃SO₃ (Aldrich Chemicals) and TiO₂ were added. TiO₂ content was varied as 0, 0.5, 1.0, 1.5, 2.0, 5.0, and 10.0 wt% in the P(EO-EC)/LiCF₃SO₃/TiO₂ mixture. Then, the solution was stirred until the LiCF₃SO₃ was completely dissolved. The resulting viscous solution was left to allow the acetone to evaporate under vacuum at room temperature. After perfect evaporation of acetone, porous membranes were filled for several times with the heated P(EO-EC)/LiCF₃SO₃/TiO₂ mixture by using a vacuum filter equipment, thereby producing pore-filling polymer electrolytes. The mixture remained on the surface was wiped with a filter paper. All procedures for preparing polymer electrolytes were carried out in a dry room.

2.2 Nomenclature

MTx denotes a porous Membrane with blend composition of P(VdF-HFP)/P(EO-EC) (the weight ratio of 6 to 4) containing x wt% TiO₂. Furthermore, ETx-y means a polymer Electrolyte filled with the P(EO-EC)/Li-salt mixture containing y wt% TiO₂ inside the pores of a MTx.

2.3 Characterization

The crystalline property of porous membranes was observed via a Perkin-Elmer GX IR spectrometer in the range of 400–4000 cm⁻¹. The uptake of P(EO-EC) in porous membranes was determined as follows:

$$\text{Uptake (\%)} = \frac{(W - W_0)}{W} \times 100 \quad (1)$$

where W and W_0 are the weights of the wet and dry membranes, respectively. Morphologies of porous membranes involving TiO₂ were investigated with a field emission scanning electron microscopy (FE-SEM) using JSM-6330F (JEOL, Japan), operating 5 kV, with the working distance of 15 mm. The mechanical properties of porous membranes were measured from stress-strain tests using a LLOYD LR10K universal testing instrument. Tensile load was measured by 100 N load cell, while air grips held the specimens. A standard ASTM D412-92T dumbbell was used with a 15.5 mm gauge length and a cross head speed of 20 mm min⁻¹.

The glass transition temperatures of electrolyte mixtures were determined by differential scanning calorimetry (DSC) with a TA instruments DSC 2920 at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The ionic conductivity of polymer electrolytes was measured using an ac impedance analyzer (Solartron 1260) within a temperature range of 5 to 95 °C and frequency range of 0.1 Hz to 1 MHz. The specimens were prepared by sandwiching the polymer electrolyte between two stainless steel (SS) electrodes. Each sample was allowed to equilibrate for 30 min at each temperature before the measurement was taken. All assemblies and testing operations of samples were carried out in a dry room.

3 RESULTS AND DISCUSSION

3.1 Porous Membranes

The Fourier transform infrared (FT-IR) spectra of pure TiO₂ and porous membranes including various contents of TiO₂ are shown in Fig. 1. The characteristic peaks of α-phase PVdF crystal were revealed at 531, 766, and 976 cm⁻¹. Also, the peaks at 484 and 840 cm⁻¹ responded to γ- and β-phase of PVdF crystal. The stretching mode vibration of Ti-O band at 1640, 800, 450 cm⁻¹ was occurred. The peak intensities corresponding to PVdF crystals were disappeared with the increase of TiO₂ content in porous membranes, except for the small remainder peak owing to α-phase of PVdF crystal at 976 cm⁻¹. The decrease of peak intensities was considered as the result from the fact that TiO₂ was blended within polymers very well, thereby bringing to a conclusion that TiO₂ dispersion in porous membranes was well established.

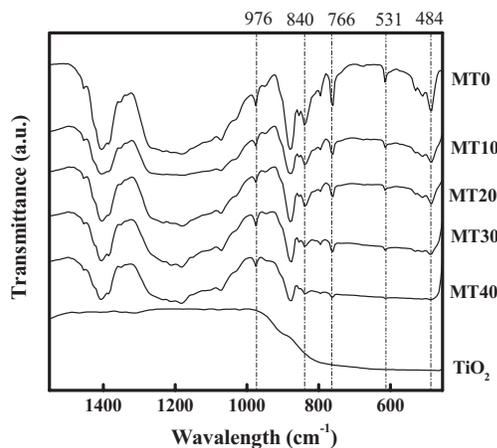


Figure 1: Infrared spectra of pure TiO_2 and porous membranes in the frequency of 1550–420 cm^{-1} .

The uptake of P(EO-EC) for porous membranes was measured. From the results, it was confirmed that the uptake of porous membranes was abruptly decreased above 30 wt% TiO_2 . Consequently, the appropriate amount of TiO_2 in membranes was considered as 10 and 20 wt% (*i.e.*, uptake of MT10 and MT20 was 62.3 and 62.2%, respectively).

The morphologies of porous membranes loading various contents of TiO_2 were investigated with the field emission scanning electron microscopy (FE-SEM). Figure 2 shows the images of selected samples. The porous membrane (Fig. 2(a)) is the matrix of a polymer electrolyte (Fig. 2(d)) and the viscous electrolyte mixture confined into the pores of a membrane plays a role as an ion conductor. On the other hand, the surfaces of membranes became rougher with the increase of TiO_2 content. Furthermore, it was definitely observed that the size of TiO_2 agglomerate was up to a few micrometers because TiO_2 in inorganic/organic composites prepared by mechanically mixing easily became agglomerates due to their low compatibility with the polymer matrix. The bigger size of TiO_2 was occurred in MT30 in contrary to the case of MT20. These agglomerates may reduce the efficiency of TiO_2 to enhance mechanical properties of porous membranes. From these results, 10 and 20 wt% TiO_2 were regarded as the appropriate amounts to obtain the porous membranes containing relatively well-dispersed TiO_2 . To confirm the presence and distribution of titanium in porous membranes, energy dispersive spectrometer (EDS) analysis was performed on the surface (Fig. 2(b)) and cross-section (Fig. 2(c)) of membranes. These images showed that TiO_2 in MT20 membrane had a homogenous distribution, implying that TiO_2 was well dispersed throughout the porous membrane.

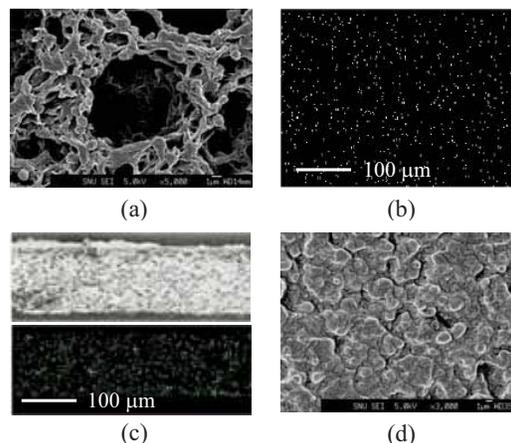


Figure 2: Typical micrographs of porous membranes and a polymer electrolyte: (a) MT0; (b) surface and (c) cross-section of MT20 measured using FE-SEM with EDS; (d) ETO.

The stress-strain data of porous membranes are described in Fig. 3. The maximum stress and tensile modulus values of porous membranes were increased up to 2.0 and 41.0 MPa until using 30 wt% TiO_2 , respectively. This is due to the fact that TiO_2 nanoparticles play a role as a crosslinker, thereby resulting in the increase of mechanical strength. Then, they were decreased up to 1.2 and 34.5 MPa, respectively, when adding 40 wt% TiO_2 . The strain values became decreased more and more as the increase of TiO_2 content in porous membranes. These results indicate that the addition of TiO_2 up to 20 wt% has an effect on the enhancement of mechanical properties of porous membranes as a result from the formation of interaction between TiO_2 nanoparticles and polymers. Overall, MT10 was chosen as the best one when considering the way to minimize the preparing cost.

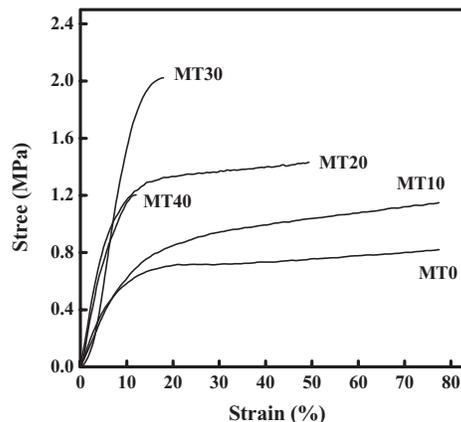


Figure 3: Stress-strain curves of porous membranes with different TiO_2 content.

3.2 Polymer Electrolytes

Ionic conductivity, σ of polymer electrolytes prepared by filling a P(EO-EC)/LiCF₃SO₃/TiO₂ mixture into the pores of a porous membrane was measured using an impedance analyzer. All polymer electrolytes with the optimized Li-salt concentration of 1.5 mmol LiCF₃SO₃/g-P(EO-EC) obeyed Arrhenius behavior and showed linear enhancement of ionic conductivity with increasing the temperature. In addition, maximum conductivity of $4.7 \times 10^{-5} \text{ S cm}^{-1}$ at 25 °C was obtained for ET10-1.5 containing 1.5 wt% TiO₂ in electrolyte mixtures (Fig. 4). Generally, the increase of ionic conductivity for PEO-based polymer electrolytes is attributed to the role of ceramic filler in inhibition of crystallization of polymers from the amorphous state. However, P(EO-EC), which plays an important role as an ion conductor in this study, is so amorphous that the theory mentioned above is not suitable. Another role of ceramic fillers in the increase of ionic conductivity is the formation of Lewis acid-base interaction between oxide groups of polymers and hydroxyl groups of ceramic fillers such as TiO₂ [6]. To better investigate the role of TiO₂, thermal analysis using differential scanning calorimetry (DSC) was conducted.

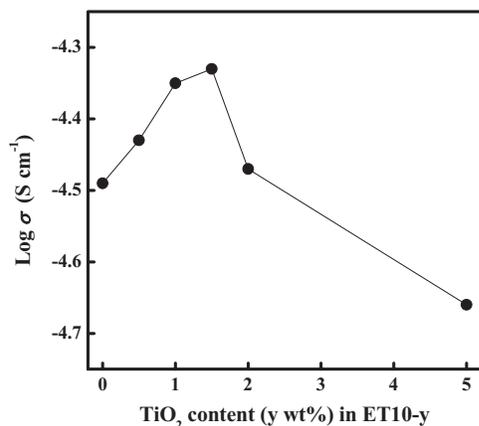


Figure 4: TiO₂ content dependence of ionic conductivity for polymer electrolytes (ET10-y).

The value of T_g was increased markedly by LiCF₃SO₃, *i.e.*, from *ca.* -42 to -23 °C. However, the value was lowered by the addition of TiO₂ (up to 1.5 wt%, see Fig. 5) due to the presence of the Lewis acid-base interaction between P(EO-EC) and TiO₂, which leads to weaker interaction between ether groups of the polymer and Li-ions. The decrease of T_g is contributed to the enhancement of conductivity through the weakened interaction between Li-ion and oxide groups in polymers as well as the increase of free volume among polymer segments. However, further addition of TiO₂ (above 1.5 wt%) caused the T_g to increase. This is supposed as a result of the TiO₂ agglomerates.

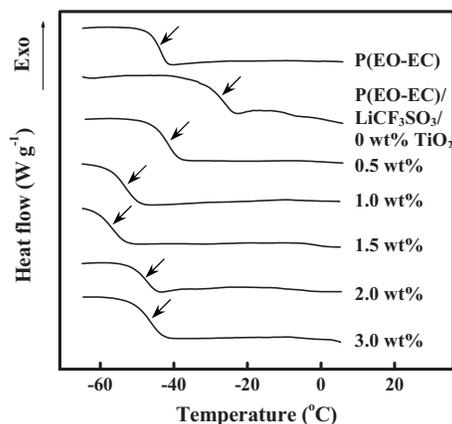


Figure 5: Changes in T_g with TiO₂ addition to P(EO-EC)/LiCF₃SO₃ complex.

4 CONCLUSIONS

This study has been focused on the characterization of the pore-filling polymer electrolyte with TiO₂ nanoparticles. From FT-IR results, it was confirmed that TiO₂ was well blended with polymers in porous membranes as the peak intensity of polymers became smaller with the increasing the TiO₂ content. The MT10 membrane showed better performance (*e.g.*, high uptake and good mechanical strength) than the others and was therefore selected as an optimal matrix to prepare the polymer electrolyte. The maximum conductivity of $4.7 \times 10^{-5} \text{ S cm}^{-1}$ at 25 °C was obtained for ET10-1.5. The T_g was increased markedly by LiCF₃SO₃ and then lowered by the addition of TiO₂ (up to 1.5 wt%), which was in good agreement with the ionic conductivity data.

Overall, these results indicate that pore-filling polymer electrolytes involving TiO₂ nanoparticles can be potentially useful as a new class of SPEs for rechargeable lithium batteries.

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