Proton conductivity of zirconium tricarboxybutylphosphonate/PBI nanocomposite membrane

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Abstract

The preparation process and proton transport properties of zirconium tricarboxybutylphosphonate Zr(O$_3$PC(CH$_2$)$_3$(COOH)$_2$ (Zr(PBTC))/polybenzimidazole (PBI) composite membranes have been investigated with a view to developing a novel electrolyte for direct methanol fuel cells. A compacted Zr(PBTC) powder sample and a Zr(PBTC)/PBI composite membrane with 50 wt.% Zr(PBTC) content show conductivities of 6.74 $\times$ 10$^{-2}$ Sc m$^{-1}$ and 3.82 $\times$ 10$^{-3}$ Sc m$^{-1}$ at 200 °C under a fully humid condition, respectively. Post-sulfonation thermal treatment, which has a great effect on the ligand structure of PBI, gives a marked increase in the conductivity of the membrane by a factor of 2 in the same condition. This effect is mainly attributed to the proton transport via sulfonic acid groups bonded to the PBI unit.

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1. Introduction

Proton conductive membranes are currently being researched extensively due to their potential for use in direct methanol fuel cell (DMFC) applications [1–3]. The thermal stability extending up to 150 °C is clearly vital to the successful operation of DMFC since thermal effect facilitates an oxidation reaction of methanol fuel at the anode and suppresses the electrode flooding and methanol crossover processes [4]. One possible approach to realize such proton conductive membranes is to combine a highly proton conductive inorganic nanomaterial with a thermostable polymer—composite proton conductive membranes [5–7]. Recent experiments have shown that layered phosphonates Zr(O$_3$PR)$_2$ with an ionogenic $R$ group such as –SO$_3$H, –COOH, –PO$_3$H, etc. exhibit ionic conductivity and could be a prospective inorganic material for composite proton conductive membranes—see Fig. 1 [8,9].

In this study, we prepare several composite proton conductive membranes using inorganic zirconium tricarboxybutylphosphonate Zr(O$_3$PC(CH$_2$)$_3$(COOH)$_3$)$_2$ (Zr(PBTC)) and polybenzimidazole (PBI) as a binding polymer which shows high thermal and chemical stability and superior mechanical properties [10]. Furthermore, provided that electrically insulating PBI is modified with an organic acid, e.g. sulfuric or phosphoric acids, it becomes a proton conductor [11,12]. In this view, we also prepare a H$_3$PO$_4$-doped Zr(PBTC)/PBI membrane and a post-sulfonation thermal-treated Zr (PBTC)/PBI membrane. The proton conductivities of these membranes are measured and we find that the post-sulfonation thermal treatment gives a significant increase in the proton conductivity up to 8.14 $\times$ 10$^{-2}$ S cm$^{-1}$ at 200 °C under a fully humid condition.

2. Experimental

Zr(PBTC) powder was prepared using a method similar to that of the corresponding zirconium compound reported by Clearfield et al. [13]. ZrOCl$_2$·8H$_2$O of 0.02 mol was dissolved in distilled deionized water of 30 ml, and a 48% hydrofluoric acid of 15 ml was added to form a zirconium fluoro complex. A 2-phosphonobutane-1,2,4-tricarboxylic acid (OH)$_2$OPC(CH$_2$)$_3$(COOH)$_3$ (PBTC) of 0.04 mol was...
then added into the mixture at 80 °C. After heat treatment for 4 days, fine Zr(PBTC) powder precipitates. The Zr(PBTC) powder was dispersed in a PBI solution of N,N-dimethylacetamide following the procedure described by Staiti [14]. The dispersion was then spread on a substrate and turned into a Zr(PBTC)/PBI composite membrane with 50 wt.% of Zr(PBTC)—we term this Zr(PBTC)P50—by evaporating the solvent. Finally the membrane was treated with a 4 N HCl solution in order to introduce protons in the membrane.

The Zr(PBTC)P50 membrane was further phosphorated or sulfonated by immersing into H3PO4 or H2SO4 solutions. We term the products Zr(PBTC)P50/H3PO4 or Zr(PBTC)P50-S60, respectively. The Zr(PBTC)P50-S60 membrane was then thermally treated at 480 °C for 60 s. The detail is described in a US patent by Kuder and Chen [15].

The crystal and chemical structures of the membranes were characterized using X-ray diffraction (XRD) and Fourier transform infrared (FTIR) measurements, while the morphologies of the membranes were characterized using a scanning electron microscope (SEM). Thermograms were also employed in order to examine the thermal stability of the membranes.

The proton conductivities of compacted Zr(PBTC) powder, Zr(PBTC)P50, Zr(PBTC)P50/H3PO4, Zr(PBTC)P50-S60 membranes were measured using ac impedance spectroscopy at an oscillation amplitude of 100 mV in the frequency range 1–2.2 MHz [16]. For the measurements near room temperature, the samples were placed in a thermostatic compartment to which a mixture of dry and water-saturated air was introduced. For higher temperatures, the measurements were carried out in the saturated water vapor pressure at each measurement temperature.

3. Results and discussion

Fig. 2 shows a cross-sectional SEM image of a Zr(PBTC)/PBI membrane with 50 wt.% Zr(PBTC) content (Zr(PBTC)P50). Zr(PBTC) grains are embedded in a PBI polymer matrix uniformly. Small cracks are seen in the film, which were created due to the shrinkage of the PBI polymer when the sample was transferred into a high vacuum SEM chamber. Also Zr(PBTC) grains are inter-connected with each other so that conduction paths of protons between the grains are established via the PBI polymer over the whole membrane.

Fig. 3 shows the XRD patterns of Zr(PBTC) powder, PBI, Zr(PBTC)P50, Zr(PBTC)P50/H3PO4, Zr(PBTC)P50-S60 membrane samples. The XRD pattern of Zr(PBTC) powder sample has broad peaks and the first reflection corresponding to an interlayer spacing of 13.1 Å is assigned to be the (002) plane. The interlayer spacing changes when exposed to the air due to the presence of –COOH terminals and the interlayer spacing of a thoroughly dried sample was 11.1 Å. The PBI membrane shows a broad peak at 2θ = 24° associated with the convolution of an amorphous region and a crystalline region. The diffraction pattern of Zr(PBTC)P50 sample is basically understood in terms of a superposition of those of Zr(PBTC) powder and PBI polymer samples. On the other hand, the diffraction patterns of Zr(PBTC)P50/H3PO4, Zr(PBTC)P50-S60 membrane shows an increase in the reflection associated with the crystalline region at 2θ = 24°, indicating that the formation of inter-chain and intra-chain hydrogen bridge bonding due to the introduction of H3PO4/HSO3 in the polymetric chains of PBI. An enhancement in the crystalline characteristics of a non-symmetric polymer was also seen in the presence of hydrogen bridge bonding [17].

The FTIR spectra of compacted Zr(PBTC) powder, Zr(PBTC)P50, Zr(PBTC)P50/H3PO4, Zr(PBTC)P50-S60 membranes are shown in Fig. 4. For Zr(PBTC) powder sample, the absorptions at 1250 and 1400 cm⁻¹ are associated with C–O stretching vibration modes in the carboxylic acid, while the absorption at 1700 cm⁻¹ is due to

Fig. 1. A schematic diagram of the structure of zirconium tricarboxybutylphosphonate Zr(PBTC).

Fig. 2. A cross-sectional SEM image of a typical Zr(PBTC)/PBI membrane.

Fig. 3. A cross-sectional SEM image of a Zr(PBTC)/PBI membrane.
a C=O stretching vibration mode as reported previously [18]. The absorption spectrum of Zr(PBTC)P50 sample is quite similar to that of PBI over the wavenumber range examined, corroborating our picture that the Zr(PBTC)P50 is just a superposition of Zr(PBTC) and PBI and no significant chemical interaction between Zr(PBTC) and PBI exists. In contrast, the spectra for Zr(PBTC)P50/H3PO4, Zr(PBTC)P50-S60 membranes are remarkably different from that of PBI. The spectrum of Zr(PBTC)P50/H3PO4 sample shows peaks at 945, 1065, 1135 cm\(^{-1}\), which are believed to be characteristic features of HPO\(_4^{2-}\), P–OH, H\(_2\)PO\(_4\) [19–21]. A predominant feature of the spectrum of the Zr(PBTC)P50-S60 membrane is the appearance of a new band in the wavenumber range 1000–1250 cm\(^{-1}\). Gieselmann et al. [22] reported absorptions at 1040 and 1221 cm\(^{-1}\), which they attributed to a \(\nu(\text{SO}_3)\) vibration mode. Therefore, we assign the band in the 1000–1250 cm\(^{-1}\) region to the symmetric and asymmetric vibration modes of sulfonate groups introduced in the Zr(PBTC)P50-S60 membrane. It should also be noted that the spectrum of Zr(PBTC)P50-S60 sample is clearly different from that of Zr(PBTC)P50 even after boiled in water. This test indicates that C–S chemical bonding is established by the post-sulfonation thermal treatment [23].

Fig. 5 shows the conductivity of compacted Zr(PBTC) powder, Zr(PBTC)P50, Zr(PBTC)P50/H\(_3\)PO\(_4\), Zr(PBTC)P50-S60 membranes under a fully humid condition as a function of temperature. For comparison, the data for PBI membranes immersed in a H\(_3\)PO\(_4\) solution (PBI/H\(_3\)PO\(_4\)) and after the post-sulfonation thermal treatment (sPBI) are also shown. Although all the conductivities shown here increase with increasing temperature, the absolute values of the conductivity clearly vary with each other. The Zr(PBTC)P50 membrane shows a conductivity of 3.82 \(\times\) 10\(^{-3}\) S cm\(^{-1}\) at 200 °C, while Zr(PBTC)P50/H\(_3\)PO\(_4\) and Zr(PBTC)P50-S60 samples show higher conductivities of 5.24 \(\times\) 10\(^{-3}\) and 8.13 \(\times\) 10\(^{-3}\) S cm\(^{-1}\), respectively. The conductivity of Zr(PBTC)P50/H\(_3\)PO\(_4\) may be associated with proton transport between two H\(_3\)PO\(_4\) molecules which are coordinated with the imidazole groups of a PBI unit through another excess H\(_3\)PO\(_4\) molecule. Proton transport between H\(_3\)PO\(_4\) molecules in neighboring PBI units also occurs successively in a similar manner, resulting in an enhancement in the conductivity of the Zr(PBTC)P50/H\(_3\)PO\(_4\) membrane. The increase in the conductivity of the Zr(PBTC)P50-S60 membrane is also associated with the conductive network of sulfonic acids bonded with the imidazole groups via H\(_2\)SO\(_4\) molecules. On the other hand, sPBI shows a relatively low conductivity of...
2.34 × 10⁻⁴ S cm⁻¹ at 200 °C in accordance with the results reported by Staiti et al. [24]. We speculate that this could be due to the low degree of sulfonation of PBI and a resultant less amount of protons available for the transport in the membrane, since the sulfonic acid is tightly bonded with the imide rings.

Finally, we show TGA data for the compacted Zr(PBTC) powder, Zr(PBTC)/P50, Zr(PBTC)/P50/H₃PO₄, Zr(PBTC)/P50-S60 samples in order to examine the thermal stability of Zr(PBTC)/PBI composite membranes (Fig. 6). For the compacted Zr(PBTC) powder sample, a weight loss is seen in three different temperature range: (a) 0–190 °C, (b) 250–340 °C, and (c) 340–450 °C. Based on a quantitative calculation of weight loss, range (a) is found to be due to a water loss of 8.1% at the interlayer region. The range (b) originates from the thermal decomposition of CH₃ organic components and the most significant weight loss in the range (c) is due to the complete decomposition of the carboxyl group. On the other hand, Zr(PBTC)/P50, Zr(PBTC)/P50/H₃PO₄, Zr(PBTC)/P50-S60 membranes are more thermally stable than Zr(PBTC). One of the reasons for the thermal stability could be attributed to the fact that Zr(PBTC) grains are tightly surrounded by PBI. Also, rather strong hydrogen bonding due to the chemical modification of Zr(PBTC)/P50 by H₃PO₄ and H₂SO₄ is likely to contribute to the thermal stability.

4. Conclusion

We have shown that the preparation process and proton conductivity of Zr(PBTC)/PBI composite membranes. In spite of an insulating property of PBI, which has a conductivity of ∼10⁻¹² S cm⁻¹, a Zr(PBTC)/PBI composite membrane sample has a relatively high proton conductivity of 3.82 × 10⁻⁷ S cm⁻¹ in a fully humid condition at 200 °C, which we attribute to proton transport via hydrogen bonding between COOH, PBI and water. Moreover, an increase in the proton conductivity up to 5.24 × 10⁻³ and 8.13 × 10⁻³ S cm⁻¹ has been achieved after H₃PO₄ treatment and post-sulfonation thermal treatment, respectively. From these combined results, we conclude that Zr(PBTC)/PBI is a possible candidate for an electrolyte material for use in DMFC instead of expensive Nafion membranes.

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