Synthesis and Characterization of Phosphoric Acid-doped Poly(2,5-benzimidazole) Membrane for High Temperature Polymer Electrolyte Membrane Fuel Cells

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Abstract >> Phosphoric acid-doped poly (2,5-benzimidazole) (DABPBI) was prepared by condensation polymerization of 3,4-diaminobenzoic acid for high temperature proton electrolyte membrane fuel cells. The membranes were casted directly using a hot-press unit and characterized by fourier transform infrared spectroscopy, thermogravimetric analysis, conductivity measurement, scanning electron microscopy and tensile test. The proton conductivities of DABPBI are observed to be 0.062 and 0.018 S cm⁻¹ under 30 and 1% relative humidity, respectively at a temperature of 120°C which is appreciably higher than that of Nafion 115 under similar conditions. The DABPBI membrane has demonstrated excellent thermo- mechanical properties and proton conductivity suggesting its suitability as a high temperature membrane.

Key words : Poly(2,5-benzimidazole)(폴리(2,5-벤지이미다졸)), Membrane(전해질막), High temperature proton electrolyte membrane fuel cells(고온용 고분자 전해질막 연료전지), Mechanical property(기계적 특성), Proton conductivity(수소 이온 전도도)

1. Introduction

Proton exchange membrane fuel cell, also known as polymer electrolyte membrane fuel cell (PEMFC), is a type of fuel cell comprising of an anode, a cathode, and an electrolyte membrane13). The electrolyte membranes should demonstrate high proton conductivity along with substantial chemical and electrochemical stability in fuel cell operating conditions. The membrane should also exhibit extremely low permeability to reactant species in order to maximize the efficiency. Nafion is the most widely used polymer membrane for fuel cell
applications. It shows outstanding properties such as high proton conductivity at low temperature and high chemical inertness. However, it’s inferior properties at temperature above 90°C and high membrane cost has motivated many researchers to synthesize new varieties of membranes4-8).

In order to overcome the deficiencies associated with low temperature PEMFCs, such as CO catalyst poisoning, heat and water managements, high temperature PEMFCs are considered to be an alternative. Till date various types of membranes have been developed for high temperature PEMFCs (temperature ranging from 100-200°C9-12). Among the membranes, acid-doped polybenzimidazoles (PBI) have attracted much interest because of their high proton conductivity without humidification and their superior thermal stability13-15).

Poly (2,5-benzimidazole) (ABPBI) is a member of PBI family. ABPBI is preferred over PBI, since, it can be synthesized from a single monomer (3,4-diaminobenzoic acid) and in the process, the problems due to stoichiometric imbalance and monomer purification can be avoided. Owing to its structural difference, ABPBI can absorb more acid than PBI which leads to the superior proton conductivity of ABPBI membranes than that of the PBI membranes16-20). During normal fuel cell operation, polymer electrolyte membranes undergo creep under compressive stress between the bipolar plates. It causes failure leading to degradation in fuel cells. Therefore, the mechanical property of polymer electrolyte membrane is an important factor for fuel cell application. For this reason, the present work aims in improving the performance of the DABPBI membrane by improving its mechanical properties. Hence, the fabrication of DABPBI membrane is reported by direct casting method followed by detail investigation on the proton conductivity, morphology, thermal and mechanical stability of the same. The direct casting method is a one step process where the membrane is casted directly from the polymerization solution. It is fast and can effectively improve the proton conductivity of the membrane16,20).

2. Experimental

2.1 Materials

3,4-diaminobenzoic acid (DABA), polyphosphoric acid (PPA) and phosphoric acid were purchased from TCI, Japan and used without further purification. Phosphorous pentoxide (P_2O_5) was purchased from Sigma Aldrich, USA.

2.2 Polymer synthesis

PPA was heated under nitrogen atmosphere at 150°C for 30 minutes in order to reduce the viscosity. Then, weighed amount of DABA was added to PPA within a time span of 30 minutes. Then the temperature of the solution was raised to 200°C and the reaction was continued for one hour. After that P_2O_5 was added to this mixture. An increase in viscosity of the solution was noticed. The reaction temperature was maintained at 200°C for 3 hours more. As a result, a homogeneous and dark red polymer mixture was formed. This mixture was used to cast membrane directly using a hot-press.

2.3 Casting and doping of the ABPBI

For casting the membrane directly from the reaction mixture, the mixture was kept between two Teflon sheets and the entire assembly was heated to 120°C for 20 minutes under a pressure of 7 tons in a Carver hot press (Model 3721, USA). Membrane was detached from Teflon sheets using cold water. The film was then immersed in DI water in order to remove traces of PPA and P_2O_5. The resulting membrane was transparent, flexible and tough. Doping of the resulting membrane
was carried out by immersing the membrane in 60 wt.% phosphoric acid for 3 days at room temperature in order to ensure total saturation.

3. Characterizations

The fourier transform infrared spectroscopy (FTIR) of the membranes were performed on a NICOLET 6700 FTIR instrument (Thermo scientific, USA) within a range of 4000 - 700 cm\(^{-1}\). The morphologies of the cryo-fractured membranes were investigated using a field emission scanning electron microscope (FE-SEM, JEOL-JSM-6701F). The proton conductivity of the membrane was measured by the four-point-probe method using a Bekk Tech conductivity test cell in conjunction with a PGZ301 Dynamic EIS Voltammetric (Bekk Tech Lic Co, USA). The stress at break and the elongation at break of the membranes were measured at room temperature using a universal test machine (LR5K plusmodel, Lloyd. Co.) at a cross head speed of 5 mm min\(^{-1}\), according to ASTM D412. Dumbbell-shaped specimens were cut from the membranes for the measurement. Thermo gravimetric analysis (TGA) was carried out using a Q50 TGA (TA Instruments, USA), with a heating rate of 20°C min\(^{-1}\) over a temperature range of 30 to 900°C under nitrogen atmosphere.

4. Results and Discussion

4.1 FT-IR analysis

The FT-IR spectra of the ABPBI and DABPBI are shown in Fig. 1. The peaks at 3392 and 3177 cm\(^{-1}\) in the FTIR spectrum of ABPBI membrane indicates the free N-H\(_{\text{ar}}\) and hydrogen bonded N-H\(_{\text{in}}\) bands, respectively. The asymmetric and symmetric stretching vibrations of aromatic C-H groups are situated at 2917 and 2842 cm\(^{-1}\), respectively in the FTIR spectrum of ABPBI. Bands at 1630, 1574, 1453, and 1404 cm\(^{-1}\) can be assigned to the C=N and C=C stretching for ABPBI, however, for DABPBI membranes, these peaks are shifted to 1625, 1582, 1451, 1408 cm\(^{-1}\) respectively, corroborating the change in chemical environment after doping. Presence of a broad band in the region of 1250-750 cm\(^{-1}\) confirms the successful doping of ABPBI membrane using phosphoric acid. A broad band in the region of 4000-2000 cm\(^{-1}\) suggests the N\(^{+}\)-H stretching for DABPBI\(^{21}\).

4.2 Morphology observation

Fig. 2 shows the field emission scanning electron microscope (FE-SEM) images of ABPBI and DABPBI membranes. Fig. 2a and b show uniform surface morphology of ABPBI and DABPBI without pin hole defects. The white lines on the ABPBI membrane surface (Fig. 2a) is due to the presence of P\(_2\)O\(_5\) on the polymer. After doping with phosphoric acid, the presence of P\(_2\)O\(_5\) on the membrane surface is reduced due to the transformation of P\(_2\)O\(_5\) to phosphoric acid (Fig. 2b). Fig. 2c and d show the fracture surfaces of ABPBI and DABPBI membranes, respectively. DABPBI
membrane fracture surface is rougher compared to that of the ABPBI membrane, indicating improved adhesion between the polymer chains upon doping with phosphoric acid. This is possibly due to the realignment of the DABPBI chains after the hydrolysis of P₂O₅ upon doping.

4.3 Mechanical properties

Table 1 lists the mechanical properties of the ABPBI and DABPBI membranes. ABPBI membranes exhibit lower value of stress at break and elongation at break compared to that of DABPBI. Generally, for PBI type membranes, the stress at break decreases dramatically after doping with phosphoric acid 14. However, the attention-grabbing result in the present study is possibly due to the non-reinforcing nature of P₂O₅ present on ABPBI. However, the increased tensile properties of DABPBI may be due to the increased adhesion between

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress at break (MPa)</th>
<th>Elongation at break (%)</th>
<th>Young’s modulus (MPa)</th>
</tr>
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<tbody>
<tr>
<td>ABPBI</td>
<td>54.00 ± 3</td>
<td>7.73</td>
<td>223.97</td>
</tr>
<tr>
<td>DABPBI</td>
<td>83.00 ± 3</td>
<td>15.68</td>
<td>437.94</td>
</tr>
</tbody>
</table>
DABPBI chains upon phosphoric acid doping as evident from the SEM study (Fig. 2). The interaction between –N= and –NH- groups in imidazole rings results in close chain packing and thus results in enhanced mechanical strength of the membranes. In the current study, the presence of phosphoric acid inside the DABPBI membrane regulate the interaction between polymer chains, and the hydrogen bonding between nitrogen atoms and phosphoric acid increases the cohesion.

4.4 Thermo gravimetric analysis

The thermal stability of ABPBI and DABPBI membranes are shown in Fig. 3. ABPBI and DABPBI membranes are hygroscopic in nature. The initial weight loss below 150°C is due to elimination of absorbed water. As evident from TGA, ABPBI and DABPBI membranes lose 6 and 14% of water, respectively. Degradation of phosphoric acid is a two-step process commencing at 160 and 600°C, respectively. However, leaching of phosphoric acid from the membranes under consideration is very difficult. After subsequent washings, trace amount phosphoric acid still remains in ABPBI membranes (as evident from the slope of the TGA curve). Similar types of degradation behavior have been noted in both ABPBI and DABPBI membranes with a higher amount of weight loss in case of ABPBI compared to DABPBI membrane. This can be ascribed to the presence of additional phosphoric acid in DABPBI compared to that of the ABPBI.

4.5 Proton conductivity

The proton conductivity of Nafion 115, ABPBI and DABPBI membranes as a function of temperature for different relative humidity (RH) values are presented in Fig. 4. The proton conductivity of ABPBI is almost negligible at 90°C under 30% RH level. The value of the same at 120°C is determined to be $7 \times 10^{-5}$ S.cm$^{-1}$. However, the conductivities of the membranes increase to a significant extent upon doping with phosphoric acid. The DABPBI membranes show proton conductivities as high as 0.015 and 0.018 S.cm$^{-1}$ at 90°C and 120°C, respectively even at 1% RH. The proton conductivity of DABPBI increases with increasing temperature and humidity. The proton conductivities of DABPBI membranes at 90 and 120°C are determined...
to be 0.040 and 0.062 S.cm⁻¹, respectively at 30% RH. The presence of unbound and bound acid molecules and acidic anions play a predominant role in altering the proton conductivity of the membrane under consideration²⁴). The bound acid molecules and acidic anions contribute to the increment in the magnitude of proton conductivity via the Grothuss mechanism, whereas, the presence of unbound H₂PO₄⁻ ions is essential for the vehicle mechanism¹⁴). DABPBI membranes show better proton conductivity compared to Nafion 115 membrane, especially at low RH. The proton conductivity of Nafion type membranes is highly dependent on the humidity of the environment. The sulfonated side-chains absorb water and make water-filled clusters through which the proton is transported. The channels break under low humidity which drastically decreases the proton conductivity of the membrane. The Nafion membrane dehydrates above 100°C resulting in a decrease in proton conductivity that makes these kinds of membrane unsuitable for high temperature PEMFCs. The effect of humidity on the proton conductivity of DABPBI and Nafion 115 membranes at 120°C is shown in Fig. 5. The proton conductivity of Nafion 115 membrane increases with the increase in RH. However, the conductivity values remain lower than the DABPBI membranes irrespective of the RHs studied here. The reason for the humidity- dependant proton conductivity is the difference in proton transport mechanism, as discussed earlier. Hence, the membrane prepared in this study by direct casting method is suitable for high temperature applications under anhydrous conditions.

4. Conclusions

ABPBI membrane was fabricated successfully by condensation polymerization of 3,4- diaminobenzoic acid in polyphosphoric acid in presence of phosphorus pentoxide. The membranes were obtained by direct casting method using a hot-press unit. DABPBI membrane shows uniform surface and without pinhole defects. The presence of phosphoric acid inside the membrane induces not only morphologic changes but also major properties change. DABPBI membrane exhibits reasonable proton conductivities and endurable mechanical property. These features make the membrane (DABPBI), a suitable candidate for use as high temperature proton exchange membrane fuel cells.

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