Polymer Electrolyte Fuel Cell Membrane for High Temperature Operation

Introduction

As the natural resource depletion is accelerated, new energy sources are needed more desperately. Fuel cell is one of the promising substitutes for new energy supply. There are several different kinds of fuel cells that can be divided by operation temperature, electrolytes and conducting ions which transfer through the electrolytes. Among the fuel cells, polymer electrolyte fuel cells (PEFCs) are spotlighted because of their broad potential application for portable electrical devices, automobiles and residential usages.

Hydrogen and other hydrocarbon such as alcohol, gasoline and natural gases can be used as a fuel for PEFCs. The PEFCs are divided by the kind of the fuel for an operation. A pure hydrogen or refomate gas is used for the cell operation in proton exchange membrane fuel cell (PEMFC). Methanol is used directly for direct methanol fuel cell (DMFC). Most components in PEFCs are very expensive. Also, some of them need to be replaced for commercialization. Especially, fuel cell membrane has to be improved for good performance and long term usage. Nafion type perfluorosulfonated polymers were employed for PEMFC and DMFC membrane. Because of their inertness, high mechanical properties and high proton conductivity, they were studied for a long time. However, the conductivity of Nafion type polymers is not high enough to be used for fuel cell operations at high temperature under low humidity because they are dried under the conditions.[1,2]

Acid-doped poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (polybezimidazole, PBI) and poly[2,5-benzimidazole] (ABPBI) have been synthesized to replace Nafion type polymers. In the early report,[3] the PBIs' conductivity ranged from $2x10^{-4}$ to $8x10^{-4}$ S/cm at the relative humidities between 0 and 100%. However, after doping with strong inorganic acid, the PBIs can have proton conductivity up to $3.5x10^{-2}$ S/cm at 190 °C.[4] The ionic conductivity of PBIs was first discovered by Aharoni and Litt.[5] They also found out that the conductivity of the PBIs increased as the doping acid concentration increased. PBI membrane was doped with phosphoric acid or sulfuric acid and formed single-phase polymer electrolyte to yield ionic conductivity.[6] The nature of the acid influences the conductivity of the acid-doped PBIs, and after contact with acid of high concentration, the conductivity follows the order $H_2SO_4 > H_3PO_4 > HNO_3 > HClO_4 > HCl$ (Table 1).[7] This report presents the PBI utilization for fuel cell membrane. It contains brief history of PBI production, PBI membrane fabrication, synthesis of several different kinds of PBI derivatives, PBI blends and application of PBIs for DMFC and PEMFC.

History of Polybenzimidazoles (PBIs)

Polybenzimidazole is produced from the condensation reaction of 3,3'-diaminobenzidine and diphenyl isophthalate.[8,9] It proceeds by two consecutive nucleophilic reaction (a nucleophilic substitution to form an amine-amide followed by cyclization via nucleophilic addition) (Scheme 1). Also, PBI can be synthesized with 3,3'-diaminobenzidine and isophthalic acid in the reaction medium of polyphosphoric acid or the mixture of P_2O_5 and methanesulfonic acid.[10] The structures of other PBIs are presented in Figure 1.

The PBI is commercially available in the forms of fiber, composite resin and membrane (trade name; Celazole from Celanese). It has good stability and mechanical properties up to 300 °C and higher (about 25 °C higher than thermo-stable polyimides). PBI has better hydrolytic stability than aromatic polyamides and polyimides. It has been used for astronaut suit because of the properties. Sulfonated PBI has been used for protective clothing for fight fighters. PBI itself does not have appropriate properties for the usage because it undergoes extensive shrinkage when exposed to heat. However, the sulfonic acid on the PBI reduces the shrinkage problem. Other applications of PBI are hot-melt adhesives, hollow fibers and flat membranes for reverse osmosis.

Recently, H.-J. Kim et al. synthesized poly[2,5-benzimidazole] (ABPBI), which is one of the PBI derivatives, using a reaction medium of P_2O_5 and CH_3SO_3H.[11] The ABPBI membrane was cast directly from the polymerization solution (mixture of P_2O_5 and CH_3SO_3H). Proton conductivities of the ABPBI membranes ranged from 0.02 to 0.06 $S{\cdot}cm^{-1}$ at the temperatures above 100 °C without external humidification. They also made normal PBI (poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole]) using a reaction medium of P_2O_5, CF_3SO_3H and CH_3SO_3H.[12] It was used as a binding material for catalyst slurry for a membrane electrode assembly (MEA).

PBI Membrane Fabrication

It is not easy to make PBI solution and there are very limited numbers of solution preparation methods for membrane fabrication because of the PBI's structural rigidity. PBI solution was prepared from the 3 to 5% suspension of PBI in DMAc with 2% LiCl.[13] It was heated at 240 °C under pressure for several hours, filtered and concentrated by evaporation to 20% for film casting. The solution was cast on a glass plate using a Gardener knife and the solvent was removed under reduced pressure at 120 °C. The membrane was washed with boiling water to remove LiCl.

A second method is to reflux a 5 – 10% suspension of the PBI in NaOH/ethanol overnight.[14] The NaOH concentration needs to be about 2.5 – 3% to get full solution, independent of the PBI concentration. The polymer solution was then filtered through a coarse sintered glass filter and stored. During reflux and storage, the solution was kept under nitrogen to prevent polymer oxidation. The solution was cast on a glass plate in a globe box under a gentle stream of nitrogen. After the membrane dried, it was washed with water to remove NaOH. This membrane fabrication method can be applied to ABPBI. Acid-doped PBI membrane can be made directly from the mixture of CF_3CO_2H and phosphoric acid.[15,16] 10 wt% of PBI in TFA was refluxed under nitrogen for several hours, then 15 wt% of phosphoric acid was added to get a solution. The solution was cast on a glass plate in a globe box under a stream of nitrogen to get dried film. It was dried further by keeping it under vacuum for a day at room temperature to remove the trace of CF_3CO_2H.

Synthesis of Sulfonated PBIs

[(PBI)-(hydrogen sulfate)] complex is formed when PBI membrane is cast from sulfuric acid or the membrane is immersed in sulfuric acid. Sulfonated PBI can be obtained by thermal treatment of the complex (Scheme 2).[17] The introduction of sulfonic acid group on the PBI backbone produces outstanding mechanical and chemical properties for the PBI. However, the sulfonated PBI becomes insoluble and the membrane is getting brittle, which could be explained by cross-linking reaction during the sulfonation.

An alternative approach for the introduction of sulfonic acid group to PBI is developed by several different groups.[18,19,20] This method (Scheme 3) allows control of the degree of sulfonation, compared to the previous synthetic methods as mentioned above. It was developed as a route for further improving the chemical stability of PBI by introduction into the imidazole ring of groups less reactive than the imidazole hydrogen and provides the opportunity of tuning the properties of the polymer by the choice of substituent. The synthesis and electrochemical characterization of benzylsulfonate N-substituted PBI was recently described.[18,21] In this synthesis, a PBI anion is formed by reaction with a soluble base, such as an alkali metal hydride, followed by reaction with sodium (4-bromomethyl)benzenesulfonate.

In most cases, water content of polymer electrolyte is proportional to the sulfonation degree in the polymeric repeating unit. As the water amount increases, the conductivity increases. Proton conductivity of the sulfonated PBI also showed same tendency. The water uptake corresponded to 4, 7, 9 and 11 water molecules per PBI repeating unit with degrees of sulfonation of 0, 50, 65 and 75%, respectively.[18] The conductivity of sulfonated PBI ranged from $3x10^{-3}$ to $2x10^{-2}$ S/cm, lower than that of Nafion ($1x10^{-1}$ to $3x10^{-2}$ S/cm) and is significantly higher than that of PBI, which is doped by phosphoric acid.[22] The sulfonated PBI displays high proton conductivity as long as the polymer films are maintained in an environment of high relative humidity condition.

PBI Blends

PBI is relatively expensive. Also, it has low mechanical properties when it is doped with acid. PBI was blended with several different sulfonated polymers such as sulfonated polysulfone (sPS) and sulfonated poly(etheretherketone) (sPEEK).[23,24,25] sPS and sPEEK are cheap and have good mechanical properties even though they become brittle when drying out which can happen in fuel cell application under intermittent conditions. To overcome the disadvantages and develop the advantages of each PBI and sulfonated polymers, they were blended for fuel cell membrane application.

It was found that the blends of PBI with sPS show miscibility depending on the composition of the blends and the sulfonation degree of the sPS.[26] PBI-rich blends appeared to be one compound system, as opposed to the sPS-rich blends where two phases were observed. Acid-doped PBI-blend membrane exhibited proton conductivity over 10^{-2} S/cm, which is higher than pure PBI membranes under same doping condition. However, its conductivity decreased remarkably during the first 4 h. Also, the conductivity was almost similar to that of pure PBI membranes under same doping condition after 20 h. This behavior conforms that the higher conductivity of blends measured under a humidified condition should be attributed to the retention of water in the membrane. Sulfonic acid groups might interact with water and in this way the conductivity of blends is significantly influenced.

PBIs for DMFC and PEMFC Membrane

Fuel cell membrane works as a proton conducting medium and a barrier for fuel and oxidant. Commercially available Nafion type perfluorinated sulfonated polymers' conductivity is high, but its methanol permeability is high. Therefore, it does not perform the role in DMFC. To overcome Nafion's drawback, PBI was studied for DMFC application.[4,27] Importantly, for fuel cell operation above 100 °C, the electro-osmotic drag number of H_3PO_4 doped PBI is almost zero.[28] A low level gas hydration can therefore be used without drying out of the membrane, which may also assist in reducing reactant crossover. Table 2 presents the methanol and oxygen permeability of H_3PO_4 doped PBI and compares the values with those of Nafion 117.[29] Based on the permeation data, a DMFC using a H_3PO_4 doped PBI membrane and operating on a 50/50 methanol/ water feed to anode at 150 °C would have a methanol crossover equivalent to less than 10 mA/cm^2,[6] which can be compared with crossover rates in excess of 100 mA/cm^2 when Nafion is employed.

Recently, composite Nafion/zirconium phosphate membrane was fabricated for DMFC operation at high temperature.[30] Typical cell resistance of 0.08 Ωcm^{-2} were observed under cell operation at 140 – 150 °C. Maximum power densities of 380 and 260 mW/cm^2 were achieved under oxygen and air feed, respectively. There are several advantages for operating

PEMFC at high temperature. It makes easier the water management because water molecules exist as a gas state. Secondly, the high temperature operation enhances the catalytic activity at the electrodes. Also, the poisoning by CO from reformate gas is reduced drastically. Q. Li et al. carried out experiments for CO poisoning effect in PEMFC using PBI membranes.[31] There was no significant performance decrease for single cell operation at 175 °C, even if 1% CO was contained in the fuel feed of hydrogen. H.-J. Kim et al. also tested ABPBI membranes under similar conditions and obtained same results.[12]

References

1 V. Mehta and J. S. Cooper, J. Power Sources, 114, 32 (2003)

2 M. Rikukawa and K. Sanui, Prog. Polym. Sci., 25, 1463 (2000).

3 D. Hoel and E. Grunwald, J. Phys. Chem., 81, 2135 (1977).

4 J. Wainwright, J.-T. Wang, D. Weng, R. F. Savinell and M. H. Litt, J. Electrochem. Soc., 142, L121 (1995).

5 S. M. Aharoni and M. H. Litt, J. Polym. Sci., Chem. Ed., A3, 417 (1974).

6 J. Wainright, J.-T. Wang, R. F. Savinell, M. H. Litt, H. Moaddel and C. Rogers, in Electrode Materials and Processes for Energy Conversion and Storage, S. Srinivan, D. D. Macdonald and A. C. Khandkar Eds, 94, p255, The Electrochemical Society Proceedings Series, Pennington, NJ (1994).

7 B. Xing and O. Savadogo, J. New Mater. Electrochem Syst., 2, 95 (1999).

8 C. S. Marvel, J. Macromol. Sci. Rev. Macromol. Chem., C13, 219 (1975).

9 M. Ueda, M. Sato and A. Mochizuki, Macromolecules, 18, 2723 (1985).

１０ G. G. Odian, Principles of Polymerization, 3rd Edn., p 168, Wiley, New York (1991).

１１ H.-J. Kim, S. Y. Cho, S. J. An, Y. C. Eun, J.-Y. Kim, H.-K. Yoon, H.-J. Kweon and K. H. Yew, Macromol. Rapid Commu., 25, 894 (2004).

１２ H.-J. Kim, S. J. An, J.-Y. Kim, J. K. Moon, S. Y. Cho, Y. C. Eun, H.-K. Yoon, Y. Park, H.-J. Kweon and E.-M. Shin, Macromol. Rapid Commu., 25, 1410 (2004).

１３ M. H. Litt, R. Ameri, Y. Wang, R. Savinell and J. wainwright, *Mat. Res. Soc. Symp. Proc.* **1999**, *548*, 313.

１４ Y. Wang, MS Thesis, case Western Reserve, Cleveland, Ohio, USA, (1997).

１５ R. F. Savinell and M. H. Litt, US patent 6,025,085 (2000).

１６ R. F. Savinell and M. H. Litt, US patent 5,716727 (1998).

１７ E.J. Power and G.A. Serad, in High Performance Polymers: Their Origin and Development, R. B. Seymour and G. S. Kirschenbaum Eds, p355, Elsevier, Amsterdam

(1986)

１８ X. Glipa, M. El Haddad, D. J. Jones and J. Rozière, Solid State Ionics, 97, 323 (1997).

１９ P. M. Preston, D. M. Smith and G. Tennant, Benzimidazoles and Congeneric Tricycle Compounds, Part I, Wiley, New York (1981)

２０ M. J. Sansone, US Patent 4,898,917 (1990)

２１ M. Gieselman and J. R. Reynolds, Macromolecules, 25, 4832 (1992).

２２ X. Glipa, PhD Theis, Université, Montpellier II (1998).

２３ C. Hasiotis, V. Deimede and C. Kontoyannis, Electrochimica Acta, 46, 2401, (2001).

２４ V. Deimede, G. A. voyiatzis, J. K. Kallitsis, L. Qingfeng and N. J. Bjerrum, Macromolecules, 33, 7609 (2000).

２５ J. Kerres, A. Ullrich, F. Meier and T. Häring, Solid State Ionics, 125, 243 (1999).

２６ C. Hasiotis, L. Qingfeng, V. Deimede, J. K. Kallitsis, C. G. Kontoyannis and N. J. Bjerrum, J. Electrochem. Soc., 148, A513 (2001).

２７ J.-T. Wang, J. Wainright, R. F. Savinell and M. H. Litt, J. Appl. Electrochem., 26, 751 (1996).

２８ D. Weng, J. Wainright, U. Landau and R. F. Savinell, J. Electrochem. Soc., 143, 1260 (1996).

２９ T. Sakai, H. Takenaka, N. Wakabayashi, Y. Kawami and E. Torikai, J. Electrochem. Soc., 132, 1328 (1985).

３０ C. Yang, S.Srinivasan, A. S. Aricò, P. Cretì, V. Baglio and V. Antonucci, Electrochemical and Solid-State Letter, 4, A31 (2001).

３１ Q. Li, R. He, J.-A. Gao, J. O. Jensen and N. J. Bjerrum, J. Electrochem. Soc., 150, A1599 (2003).

Table 1. Conductivity of PBI with different inorganic doping material.

Acid	Concentration of acid solution (mol/dm^{-3})	Conductivity (S/cm)
HCl	11.8	1.4×10^{-3}
$HClO_4$	11.6	1.6×10^{-3}
HNO_3	15.8	1.8×10^{-3}
H_3PO_4	14.4	1.9×10^{-2}
H_2SO_4	16.0	6.0×10^{-2}

PBI membrane was immersed for 10 days before the conductivity measurement.

The test was performed at room temperature.

Table 2. Permeability of H_3PO_4 doped PBI and Nafion 117 to methanol and oxygen.

Electrolyte	Test material	Temperature (°C)	Permeability (barrer)*
H_3PO_4/PBI	Methanol	80	270
H_3PO_4/PBI	Oxygen	150	10
Nafion 117	Methanol	80	80000
Nafion 117	Oxygen	80	90

* 1 barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg

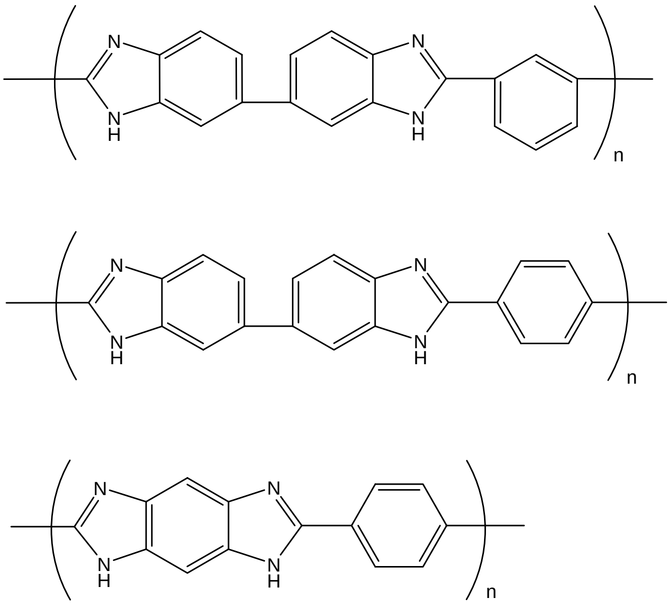
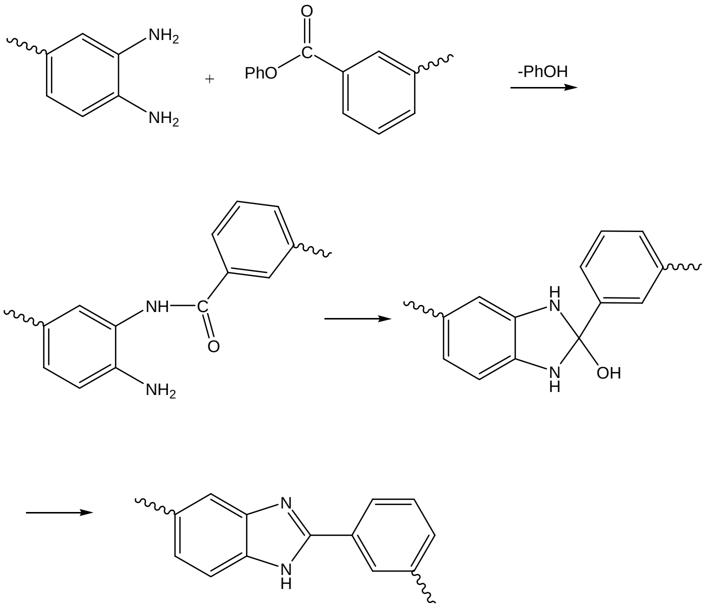
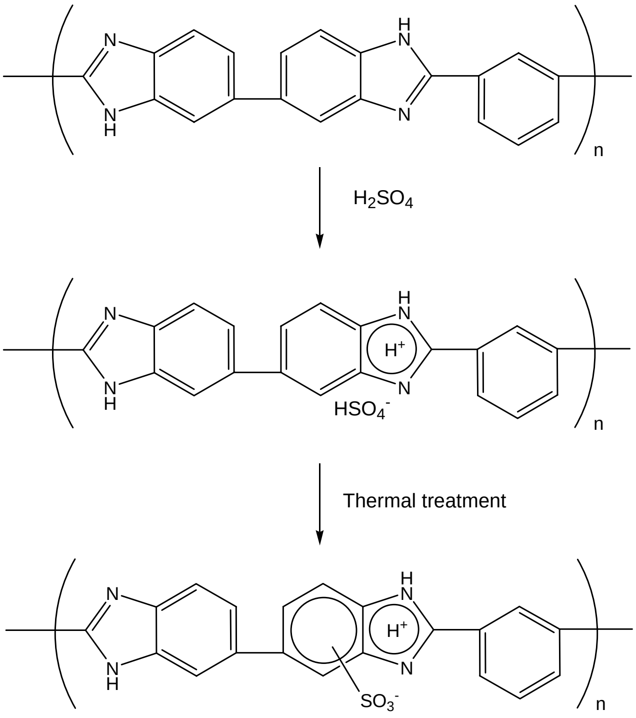


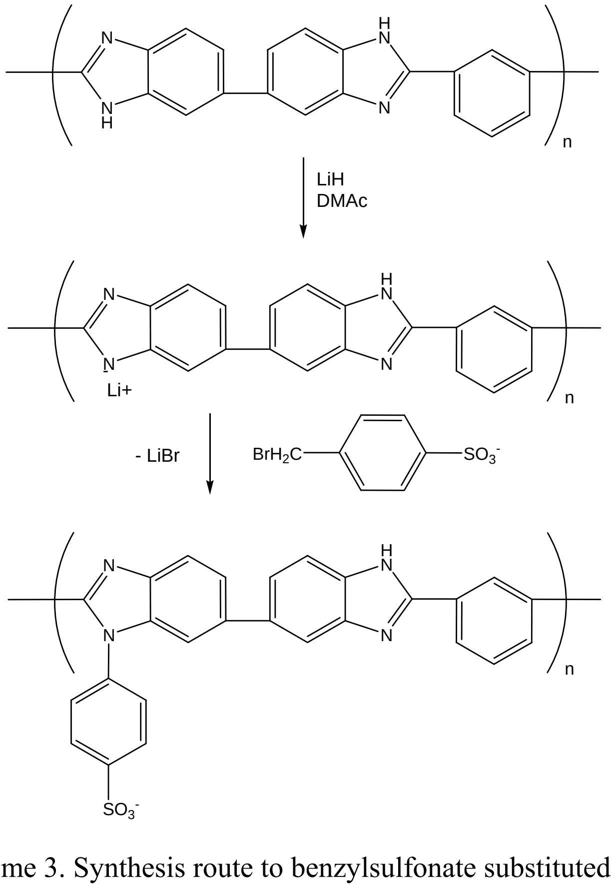
Figure 1. Structures of several PBIs.



Scheme 1. Synthesis of PBI



Scheme 2. Synthesis of sulfonated PBI.



Scheme 3. Synthesis route to benzylsulfonate substituted PBI