Proton-Conducting Polymer Membranes for Direct Methanol Fuel Cells

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Summary: Three methods to block the methanol transport through proton-conducting polymer membranes while maintaining the proton conductivity unchanged have been conducted; 1) selective layer formation on the surface of the membrane, 2) prearation of nanoclay composite membrane providing tortuous pathway of methanol, 3) control and fixation of the proton transport channels. The methanol permeability through the membranes decreased significantly at the expense of the small decrease in the proton conductivity. It is thus concluded that both the structure and the fixation of the proton transport channels are crucial in optimizinging proton conducting membranes for direct methanol fuel cells.

Keywords: barrier; crosslinking; ionomers; membranes; organoclays

Introduction

Proton, in the form of a hydrogen atom without the electron, is the core material for all atoms. Polymer electrolytes are proton-conducting and plays is the key role in lots of electrochemical devices such as fuel cells. Low temperature fuel cells stem from the advantages of using a solid proton conducting polymer electrolyte. Solid polymer electrolytes form a thin but electronic insulator between the two electrodes while allowing rapid proton transport. Generally Nafion type perfluorinated polymer membranes, which have a phase-separated structure comparising a hydrophobic matrix and interconnected hydrophilic clusters, called ionic channels, are used as the electrolyte. The conductivities of proton through the perfluorinated membranes such as Nafion are strongly dependent on the characteristics of ionic channels. And the size of ionic channels depends on the structure of the polymer, degree of sulfonation, level of hydration,[1] and nano-phase separation into hydrophilic and hydrophobic domains. This is because of the mechanism of proton transport in solid polymer electrolytes; proton migrates through the sulfonic acid species and diffuses through the medium together with a H_2O in the form of H_3O^+.

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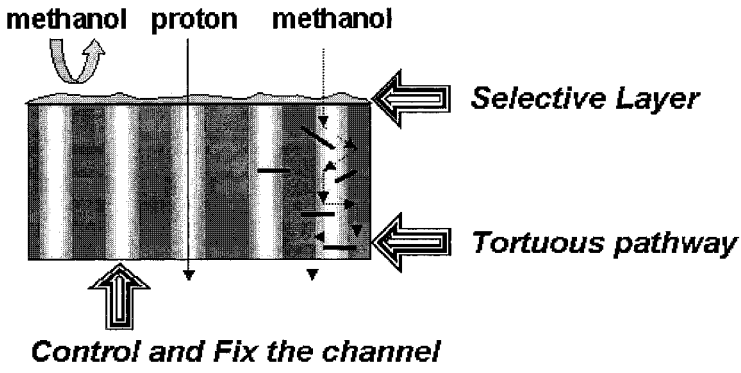
Therefore the migration of each proton will be linked with the transport of at least water molecule. In practical fuel cells, a mixed transport process is believed to be operating, leading to a certain electro-osmotic drag factor of water molecules per proton. This is thought to be on the order of 0.6 to 2.0.[1-2]

One of the critical problems hindering the commercialization of DMFC is high methanol permeation rate across electrolyte membranes.[3] Methanol crossover is caused by protonic drag of methanol, similar to electro-osmotic drag of water. As both water and methanol molecules behave similarly inside proton exchange membranes, i.e., reduced methanol permeability usually lowers water uptake into the membrane and hence conductivity.

The lack of selectivity for methanol of perfluorinated materials along with their high cost and recycling problem is all additional reasons for the development of new electrolyte membranes. Considerable effort is being paid to the development of lower cost, usually fluorine-free, hydrocarbon-based membrane materials. However, the concern remains about the long-term stability of membranes based on these materials, and methanol crossover.[4-10]

Here, in order to provide the selectivity of proton transport over methanol on the proton conducting membranes, three approaches are attempted. First, to modify the surface of the proton conducting membranes to block the methanol transport; second, to provide a tortuous pathway for a methanol with organoclays, and finally to control and fix the size of the proton transport channels using block copolymers and crosslinkage as shown in Scheme 1.



Scheme 1.

Experimental

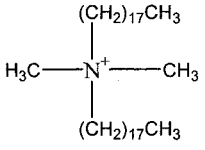
Materials

Sulfonated poly(styrene-*b*-(ethylene-*r*-butylene)-*b*-styrene) (sSEBS) solution in 1-propanol and dichloroethane (Mw ~ 80000, 28 wt% styrene and 45% of sulfonation; Aldrich), maleic anhydride (MAH; Junsei) and methanol (Merck, RPA) were purchased and used as received. Characteristics of the organoclay powders from Southern Clays, which were organically modified montmorillonite, are listed in Table 1. Nafion 115, 117 were used.

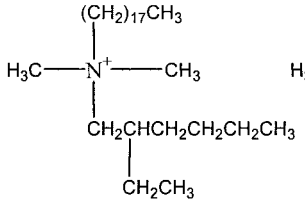
Poly(styrene-*b*-butadiene-*b*-styrene) (SBS) (Mw~140,000; 30 wt% styrene; Aldrich) was purchased and purified by precipitation in methanol in order to remove the stabilizer. The photoinitiator, 2,4,6-trimethylbenzoyldiphenylphosphine oxide (Lucirin TPO from BASF), was kindly provided by BASF Korea Co. H_2SO_4 (95%, Daejung), acetic anhydride (Daejung), toluene (Aldrich), 1,2-dichloroethane (DCE: Junsei) were used as received.

Table 1. Characteristics of organoclays.

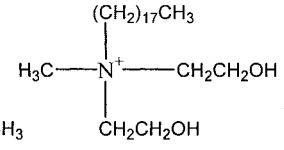
ID	Modifier	Modifier concentration Meq/100g
Na	-	-
6A	2M2HT	140
15A	2M2HT	125
20A	2M2HT	95
25A	2MHTL8	95
30B	MT2EtOH	95



2M2HT



2MHTL8



MT2EtOH

Preparation

Surface modification: sSEBS solution was poured into a Teflon dish and dried at room temperature until complete evaporation of the solvent. 50 mg of MAH were placed in a plasma reactor with sSEBS films in order to introduce succinic anhydride groups on the sSEBS film.[11] Plasma treatment was carried out using a R300A radio-frequency generator (Autoelectric, Seoul), operating at 13.56 MHz and setting at 50W. The membrane was glow-discharged in air for 20s under the pressure of 0.1 Torr[12] in a bell jar type reactor (6 cm radius x 11 cm deep). Inductively coupled plasma was generated by a circular coil connected to a radio-frequency generator.

Clay impregnation: All clays were washed with deionized water several times to remove freely existing excess ionic intercalants and impurities; this was followed by centrifugation and vacuum drying for overnight. Clays were dispersed by ultrasonication for several min in DMSO (or Toluene):Water (9:1) co-solvent and and the concentration of the clay solution was adjusted to be 5mg/5ml. The Nafion films swollen in DMSO for 24 hrs at 60° was immediately transfer into the clay solution for clay particles to be relocated or impregnated inside of the swollen Nafion membranes.

Control and fixation of the proton transport channel: A solution of 5 wt% SBS in toluene with 5 wt% of the photoinitiator of SBS was prepared and filtered. The solution was poured into a glass dish and held at room temperature to evaporate the solvent. The residual solvent was completely evaporated under vacuum. Membrane thickness was measured using a digital micrometer. Both sides of the samples were exposed to irradiation of 1700 $\mu W/cm^2$ for 120 min in a UV crosslinker (Spectrolinker XL-1000, Spectronics Co. New York) to obtain crosslinked SBS (cSBS) films. It is believed that crosslinking mainly occurred in the butadiene phase.

The appropriate amount of acetic anhydride in DCE was cooled below 0°C and the corresponding volume of sulfuric acid was added to form acetyl sulfate. The acetyl sulfate solution was maintained at 0°C in an ice bath until its addition to the reaction medium. The cSBS film was swollen in an excess amount of DCE overnight. The solution was heated to 50°C and purged with nitrogen for 30 min. Then the acetyl sulfate solution was added. Different mole ratios of acetyl sulfate to phenyl groups ($[CH_3CO_2SO_3H]/[C_6H_5]$) in the range of 0.01 to 2 were used. Fresh acetyl sulfate was prepared prior to each sulfonation reaction. The

solution was stirred for 4 h at this temperature, then the reaction was terminated by the addition of 2-propanol, resulting in a sulfonated SBS crosslinked membrane (scSBS).[13-15] The membrane was washed in boiling water and many times with cold water.

Characterization

Uptake content: The swelling characteristics of the membranes were determined by water or solvent uptake measurements. The samples were dried under vacuum for 24 h at 30°C and then weighed. They were then placed in deionized water or in each different ratio of methanol/water solution for a week at different temperature. Before sample weighing, the excess water or solvent on the membrane surface was removed with absorbent paper. The uptake content was calculated using the following relationship:

$$\text{uptake content } (\%) = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100 \quad (1)$$

where M_{wet} and M_{dry} are the weights of the wet and dried samples, respectively.

Proton conductivity: A two-point and a four-point probe methods were used to measure the proton conductivity of the membrane. It was found that a decrease in the conduction of 70% for Nafion tested in the transverse rather than the longitudinal direction.[16] Before the measurement of proton conductivity, the prepared membranes were equilibrated with deionized water. Complex impedance measurements were carried out in the frequency range of 1 Hz to 8 MHz at 25°C, using a ZAHNER IM-6 impedance analyzer.[17] The impedance spectra of the membranes can be used to generate Nyquist plots[18-19] to calculate the proton conductivity.

IR-spectra: FT-IR measurements were performed on a 6030 Galaxy Series FT-IR spectrometer (Mattson Instruments); 256 scans were signal-averaged at a resolution of 4 cm^{-1}. The ATR spectra were obtained using a KRS-5 prism with an incident angle of 45°. The degree of sulfonation was determined by elemental analysis and characterized by FT-IR.

Methanol permeability: The methanol permeability of the membranes was obtained using a diffusion cell described in the literature.[20-22] This cell consists of two reservoirs, each approximately 48 mL, separated by a vertical membrane. Each membrane is clamped between the two reservoirs, which are stirred during the experiment. Initially, one reservoir contains a

methanol-water mixture (10 wt% methanol) and the other reservoir only contains water. Increases of the concentration of methanol in the water reservoir with time were detected by gas chromatography (Gow-Mac Instrument Co.) and with a differential refractometer (RI750F by Young In Co.). Each reservoir has a capillary tube for sampling 1 μl for gas chromatography.[22-23] The uncertainty of the obtained values was less than 2%.

Morphology: Ultra-thin sections of the samples were prepared in order to observe their morphology. Sample films were imbedded into an epoxy resin, Epon-812, purchased from SPI. Ultra-thin cross-sections of the films of approximately 90 nm thickness were prepared at -90° by an ultramicrotome of model Ultracut-R made by Leica using a diamond knife. The thin-sectioned films were mounted on a copper grid and stained with OsO_4 vapor. Carbon was evaporated onto the specimens in order to prevent accumulation of electrons during TEM observation. Transmission electron microscopy was performed at 200 kV by a JEOL TEM, model JEM-2010.

Results and Discussion

Surface modification: The methanol-water uptakes of sSEBS membranes are plotted as a function of the methanol concentration in water and temperature in Figure 1. The methanol-water uptake generally increases with increasing methanol content and temperature. Block copolymer ionomers have a highly ordered sequence of both ionic and nonionic blocks unlike random ionomers, in which ionic groups are randomly distributed along with the polymer chain. Block copolymer ionomers promise as an althernative membrane for several reasons. First, the nonionic block can be designed to be a barrier for methanol, and second, block copolymer ionomers have the ability to self-assemble into unique nanostructured morphologies compared to random ionomers.

From the SAXS profiles for sSEBS membranes in the dried and water-swollen states, it can be seen that the membrane maintains its structure after swelling but the inter-domain spacing increases by approximately 680 Å, as does the cylindrical diameter, representing a significance increase in the size of the ionic channels. This significant swelling occurs because there is no permanent fixing of the structure in the linear sSEBS membranes, as demonstrated by the high water uptake values.

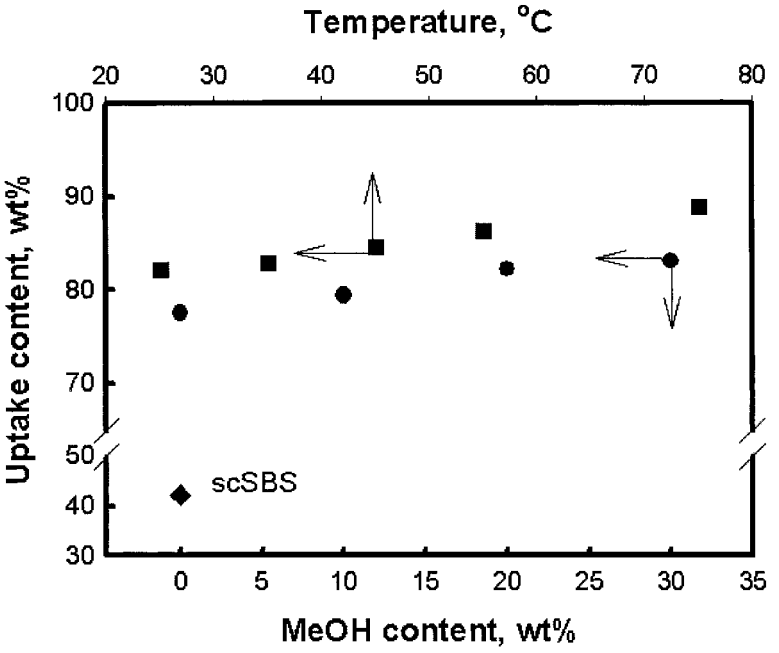


Fig. 1. Methanol-water uptakes as a function of methanol concentration at 25°C and temperature.

We have observed that the surface modification of the polymer membrane by plasma in the presence of MAH produces hydrophobic properties on the top of the polymer substrate, which may act as a barrier layer for methanol.[15,24] Succinic anhydride can be chemically bound to the surface of polymer substrate by plasma treatment with MAH.[25-27] ATR FT-IR spectroscopy provides information on the surface of the anhydride modified sSEBS film. The spectrum of the succinic anhydride layer on the plasma treated sSEBS membrane has three bands at 1844, 1778 and 1730 cm^{-1}, which can be attributed to the asymmetric and symmetric anhydride C=O stretching modes of succinic anhydride and the C=O stretching modes of the carboxyl group resulting most likely from the ring-opening reaction of anhydride on the surface, respectively. The intensity of the 1778 cm^{-1} is much stronger than that of the 1730 cm^{-1} band, meaning that the majority of the anhydride functionality is maintained during plasma treatment. Surface succinic anhydride layer having hydrophobic properties on the surface of sSEBS membrane will

operate as a barrier for methanol as well as for proton.

The deposited amount was detected by the thickness measurement of the loading amount of MAH in the plasma reactor. Although we have tried to measure the thickness dependence of the loading amount of MAH at lower concentration ranges, it was not detectable, being below the practical lower limit of the ellipsometry. The thickness of the anhydride layer was 440 ± 10 Å when the sample was plasma treated with 100 mg of MAH, and our previous result[15] showed that the deposited amount increases and then levels off, so the thickness must be less than 440 Å when the membrane is plasma treated with 50 mg of MAH. The relative permeability and conductivity to those of the pristine sSEBS membrane are plotted with respect to the loading amount of MAH in Figure 2. The relative permeability and conductivity values were calculated as the ratio of the value to the those of the pristine sSEBS membrane. The values decrease with the loading amount of MAH, i.e., thickness of selective layer on the surface of the membrane. The decreasing trend of conductivity is steeper than the one of permembility. This can be considered that the hydrophobicity of succinic anhydride hinders proton access to the surface. Although the surface modification by plasma treatment in this research provides the possibility of blocking methanol transport through sSEBS membrane, the application to the real fuel cell is not that promising as yet becasue of the significant swelling hysterisis of sSEBS membrane.

Clay impregnition:[28] The complete dispersion of nanolayers in a matrix provide a tortuous pathway for a permeant to transverse the nanocomposite membranes as shown in scheme 1. The x-ray diffraction patterns (XRD) spectra show that the clay was not dispersed completely inside of the Nafion membranes. It is not easy either to identify the exact position of the clay inside the membranes from XRD spectra. The opaqueness of the initially transparent membrane after immersed in the clay solution suggests that the clay is assumed to be located inside of the membranes in the form of aggregate as well as dispersed state.

The relative permeability and conductivity to those of the prostine Nafion 115 membrane are plotted in Figure 3. In all case, methanol permeability as well as the conductivity decreased with the insertion of clay inside of the membrane. The decreasing ratio of methanol permeabiloity is steeper than the one of conductivity, which suggests a very favorable way to prepare a membrane for direct methanol fuel cell.

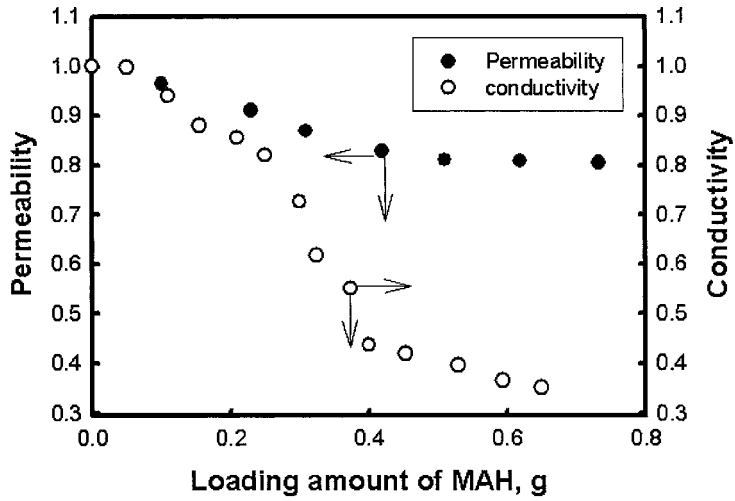


Fig. 2. Changes of MeOH permeability and proton conductivity of surface-modified sSEBS membranes after plasma treatment in the presence of MAH.

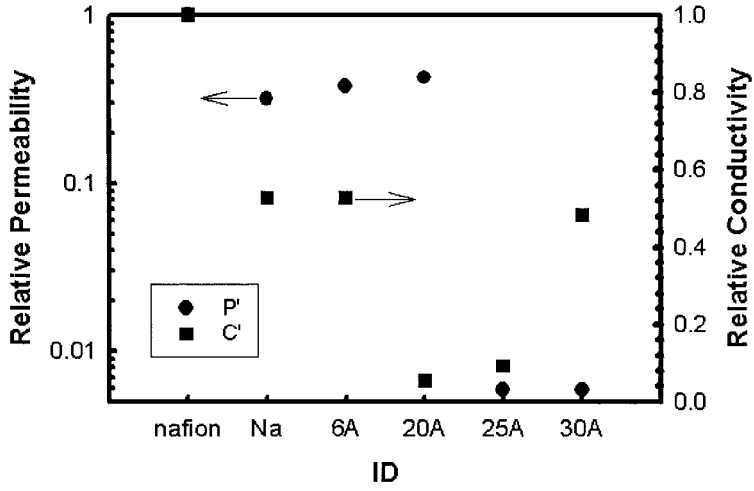
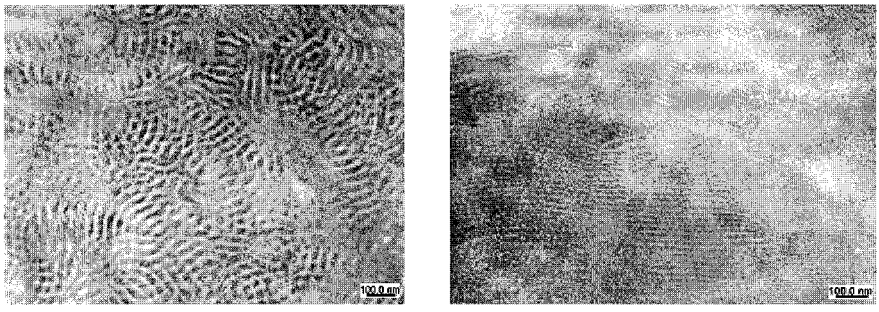


Fig. 3. Relative MeOH permeability and proton conductivity of clay composite Nafion 115 membranes.

Control and Fixation of proton transport membrane: We prepared SBS block copolymer membranes with various degrees of sulfonation. The extent of sulfonation was controlled by varying the molar ratio of acetyl sulfate to phenyl groups $[CH_3CO_2SO_3H]/[C_6H_5]$. The success of the sulfonation reaction was confirmed by detection of an absorbance peak around 1238 cm^{-1} by FT-IR spectra, which is due to the asymmetric stretching vibrations of sulfonate groups.[29] The water uptake of the scSBS membrane, which has a comparable conductivity with sSEBS, in water are plotted in Figure 1. Since scSBS and sSEBS are sulfonated "block" copolymers, they may have similar microdomain structures, but different swelling behavior due to the crosslinkage.

TEM is able to provide more localized information about selected areas of block copolymers (usually in the range of a few square micrometers). Figure 4 shows TEM micrographs of cSBS and scSBS membranes microtomed in arbitrarily chosen directions. The dark region corresponds to the PB phase selectively stained with OsO_4 and the bright region is associated with the unstained PS microdomain. These micrographs are in agreement with a microdomain arrangement consisting of hexagonal packing of cylinders by previous observations.[30-31] However, the specific structural domains for the highly sulfonated scSBS are indistinct.



(a) (b)

Fig. 4. TEM micrographs of (a) crosslinked SBS (cSBS) and (b) sulfonated crosslinked SBS (scSBS) membranes (IEC=37).

The proton conductivities of the sulfonated polymers were determined by impedance spectroscopy and plotted in Figure 5 along with methanol permeability.

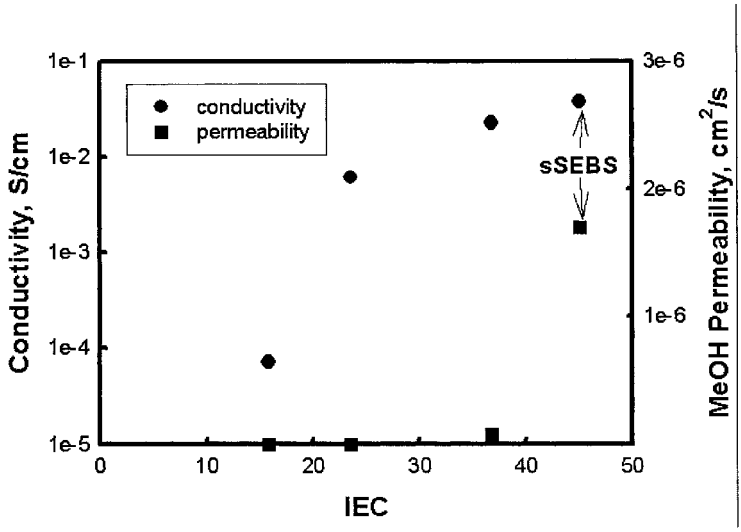


Fig. 5. Proton conductivity and MeOH permeability (10wt%) of the membranes as a function of ion exchange capacity (IEC).

The proton conductivity increased with ion exchange capacity (IEC), that is, with the degree of sulfonation. The IEC is calculated as the quotient of the molar content of the sulfonate groups and the membrane weight. It is generally known that the ionic conductivity and the degree of swelling of a membrane increase with the concentration of ionic sites for a given membrane structure.[32]

The permeances of 10 wt% methanol through the various membranes are given. It is clear that the crosslinked sulfonated membrane has low methanol permeability. When the scSBS and sSEBS membranes are compared, the degree of sulfonation and the proton conductivity are compatible, but the methanol permeability of the scSBS is almost two orders of magnitude lower than that of the sSEBS. Maintenance of the size of the ionic channels by permanent crosslinkages may be the main reason for this low methanol permeability; the methanol permeability may be reduced because of the reduced size of the ionic channel.

Compared with the high swelling behavior of sSEBS having no permanent fixing of the structure, the permanent crosslinkages prevent disentanglement of polymeric chains for swelling and reduce its swellability.

This result suggests the importance of the ionic channel size in determining methanol permeability. Therefore, it is possible to decrease the methanol permeability while maintaining the proton conductivity almost unchanged by reducing the ionic channel size and fixing the hydrophobic matrix with crosslinkages.

Conclusions

It is known that methanol primarily permeates through hydrophilic ionic channels, and that protons dominantly permeate by hopping between ionic sites. Thus, the methanol permeability strongly depends on the cross-sectional size of the ionic channels, but the proton conductivity does not. This can be achieved by introducing a selective layer on the surface of the membrane, by providing the tortuous pathway with organoclays and by reducing the size of the ionic channels.

Three methods to block the methanol transport through proton-conducting polymer membranes while maintaining the proton conductivity unchanged have been attempted; 1) selective layer formation on the surface of the membrane, 2) prearation of nanoclay composite membrane providing tortuous pathway of methanol, 3) control and fixation of the proton transport channels. It was found that the third method is the most effective among the three mentioned above in reducing the methanol permeability while maintaining the proton conductivity alsmot unchanged . This is because that methanol primarily permeates through hydrophilic ionic channels, and that protons dominantly permeate by hopping between ionic sites. It is thus concluded that both the structure and the fixation of the proton transport channels are crucial in optimizinging proton conducting membranes for direct methanol fuel cells.

Acknowledgement

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[1] T. A. Zawodzinski, Jr., T. E. Springer, J. Davey, R. Jestel, C. Lopez, J. Valerio, S. Gottesfeld, *J. Electrochem. Soc.* **1993**, *140*, 1981.
[2] T. F. Fuller, J. Newman, *J. Electrochem. Soc.* **1992**, *139*, 1332.
[3] M. K. Ravikumar and A. K. Shukla, *J. Electrochem. Soc.* **1996**, *143*, 2601.
[4] C. Pu, W. Huang, K. L. Ley, E. S. Smotkin, *J. Electrochem. Soc.* **1995**, *142*, 119.
[5] Z. Poltarzewskii, W. Wieczore k, J. Przyluski, V. Antonucci, *Solid State Ionics*, **1999**, *119*, 301.
[6] S. G. Ehrenberg, J. K. Serpico, G. E. Wnek, J. N. Rider, *US Patent,* 5,468,574 (1995).
[7] N. Rao, T. P. Andersen, P. Ge, *Solid State Ionics* **1994**, *72*, 334.
[8] V. Tricoli, in Second Int. Symp. Proton Conducting Membrane Fuel Cells II S. Gottesfeld, T. F. Fuller, Eds., Boston, MA, 1998, p358.
[9] T. J. Wang, S. Wasmus, R. F. Savinell, J. Electrochem. Soc. **1996**, *143*, 1233.
[10] J. Kerres, A. Ullrich, F. Meier, T. Häring, *Solid State Ionics* **1999**, *125*, 243.
[11] Scott R. Caboury, Marek W. Urban, *Langmuir* **1993**, *9*, 3225.
[12] P. L. Antonucci, A. S. Arocò, P. Cretì, E. Ramunni, V. Antonucci, *Solid Solid State Ionics*, **1999**, *125*, 431.
[13] Grot, W. *Chem. Ing. Tech.* **1978**, *50*, 299.
[14] M. W. Verbrugge, *J. Electrochem. Soc.* **1989**, *136*, 417.
[15] B. J. Cha, Y. S. Kang and J. Won, *Macromolecules*, **2001**, *34*, 6631.
[16] C. L. Gardner, A. V. Anantaraman, *J. Electroanal. Chem.* **1995**, *395*, 67.
[17] M. A. Vargas, R. A. Vargas, B.-F. Mellander, *Electochimica Acta* **1999**, *44*, 4227.
[18] R. A. Vargas, A. García, M. A. Vargas, M. A. *Electochimica Acta* **1998**, *43*, 1271.
[19] J. J. Fontanella, M. C. Wintersgill, J. S. Wainrght, R. F. Savinell, M. Litt, *Electochimica Acta* **1998**, *43*, 1289.
[20] J. Won, S. W. Choi, Y. S. Kang, H. Y. Ha, I.-H. Oh, H. S. Kim, K. T. Kim, W. H. Jo, *J. Membr. Sci.* **2003**, *214*, 245.
[21] V. Tricoli, *J. Electrochem. Soc.* **1998**, *145*, 3798.
[22] N. Carretta, V. Tricoli, F. Picchioni, *J. Membr. Sci.* **2000**, *166*, 189.
[23] B. S. Pivovar, Y. Wang, E. L. Cussler, *J. Membrane Sci.* **1999**, *154*, 155.
[24] J. Won, K. J. Ihn, Y. S. Kang, *Langmuir*, **2002**, *18*, 8246.
[25] M. E. Ryan, A. M. Hynes, J. P. S. Badyal, *Chem. Mater.*, **1996**, *8*, 37.
[26] S. R. Gaboury, M. W. Urban, *Langmuir*, **1993**, *9*, 3225.
[27] S. R. Gaboury, M. W. Urban, *Langmuir*, **1994**, *10*, 2289.
[28] J. Won, Y. S. Kang, I.-H. Oh, H. Y. Ha, B. Jung, J. W. Chun, S. W. Choi, Korea, applied Patent #01-54158.
[29] A. Mokrini, J. L. Acosta, *Polymer* **2001**, *42*, 9.
[30] Q. Zhang, O. K. C. Tsui, B. Du, F. Zhang, T. Tang, T. He, *Macromolecules* **2000**, *33*, 9561.
[31] C. Wang, *Macromolecules*, **2001**, *34*, 9006.
[32] P. Zchocke, D. Quellmalz, D. *J. Membr. Sci.* **1985**, *22*, 325.