

고체 알칼리 연료전지용 음이온 교환 세공충진막의 제조 및 특성

*최 영우, 박 구곤, 임 성대, 이 미순, 양 태현, **김 창수

Preparation of pore-filling membranes for polymer electrolyte fuel cells and their cell performances

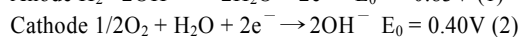
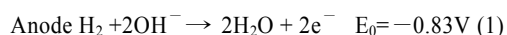
*Young-Woo Choi, Gu-Gon Park, Sung-Dae Yim, Mi-Soon Lee,
Tae-Hyun Yang, **Chang-Soo Kim

Abstract : Anion exchange polymer electrolyte pore-filling membranes consisting of the whole hydrocarbon materials were prepared by photo polymerization with various quaternary ammonium cationic monomers and characterized on the properties for applying to solid alkali fuel cell (SAFC). Hydrocarbon porous substrates such as polyethylene were used for the preparation of the pore-filling membranes. The hydroxyl ion conductivity of the polymer electrolyte membranes prepared in this research was dependent on the composition ratio of an electrolyte monomer and crosslinking agents used for polymerization. Furthermore, these pore-filling membranes have commonly excellent properties such as smaller dimensional affects when swollen in solvents, higher mechanical strength, lower fuel crossover through the membranes, and easier preparation process than those of traditional cast membranes.

Key words : Pore-filling membrane(세공충진막), Polymer electrolyte(고분자 전해질), Solid Alkaline Fuel cell(고체 알칼리 연료전지), Anion exchange membrane(음이온 교환막), Hydrocarbon polymer(탄화수소 고분자)

1. Introduction

Limitation of the use of acidic polymeric electrolytes (e.g., in polymer electrolyte membrane fuel cells and direct methanol fuel cells) - (i) slow electrode-kinetics, (ii) CO poisoning of Pt and Pt-based electrocatalysts at low temperatures and (iii) high costs of the membrane, catalyst - - can be overcome by using alkaline polymeric electrolytes (i.e., anion-exchange membranes, AEMs). It is well known that electro-kinetics of oxygen reduction in an alkaline medium is much enhanced in comparison with an acid medium as shown in the following equations:



It leads to use non-precious catalysts (e.g., Ni, Ag, perovskite-type oxides, etc.)^[1-4]. Fuel cells using AEMs have the electrochemical and structural analogy with alkaline fuel cells (AFCs) except the use of solid-state electrolytes instead of liquid alkaline solutions, e.g.,

KOH(l). That is why it can be called as solid alkaline fuel cells (SAFCs) as shown in Fig. 1. The use of AEMs prevents undesirable formation of carbonate/bicarbonate in the liquid alkaline solutions due to CO₂ reactions from the oxidant gas stream at cathodes of AFCs. For good SAFC operations good membrane-electrode assemblies (MEAs) are required. An MEA consists of a membrane, two electrodes, and two pieces of gas diffusion layer (e.g., carbon paper, felt or cloth). One of main components in MEAs is a membrane, i.e., anion-exchange membrane. AEMs with good properties such as high OH⁻ conductivity and good thermal and chemical stability are essential. Many researchers have reported anion-exchange membranes for fuel cell applications^[1,3-5] because most commercial available AEMs are too much thick (200-300μm) for fuel cell applications and have problems on (i) the chemical stability, i.e., nucleophilic displacement by the hydroxyl

* 주저자의 소속 : 한국에너지기술연구원

E-mail : cozmoz67@kier.re.kr

Tel : (042)860-3586 Fax : (042)860-3104

** 교신저자의 소속 : 한국에너지기술연구원

E-mail : cskim@kier.re.kr

Tel : (042)860-3573 Fax : (042)860-3104

ions for the quaternary ammonium functional groups and (ii) the thermal stability of styrene-type backbone.

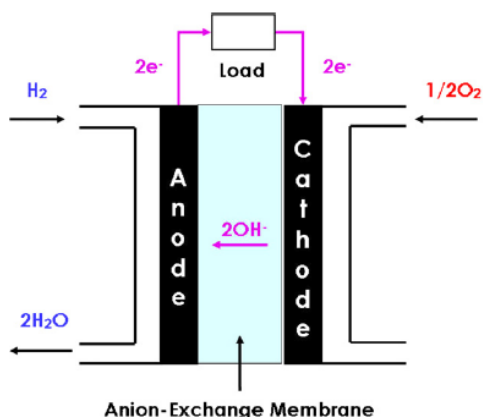


Fig. 1. A schematic diagram of solid alkaline fuel cells (SAFCs) using anion-exchange membranes.

A new concept of ion exchange membranes has been developed in which a controlled amount of polyelectrolyte was anchored within the pores of a porous membrane⁽⁶⁾. The general principle behind this new concept of a pore-filling electrolyte membrane is predicted on combining the most desirable properties of two materials, which are a porous substrate and a polymer that fill the pores of the base substrates. The porous support in these membranes functions as an inert “rigid” host or shell that constrains the polyelectrolyte, and limiting its swelling, thus provides mechanical strength for the membrane.

Yamaguchi et al. have proposed a pore-filling electrolyte membrane concept for fuel cell applications, that was originally developed for liquid separation⁽⁶⁾. The pore-filling electrolyte membrane is composed of two materials: a porous substrate having pore sizes of one micron or less, and a polymer that fills the pores of the substrate, as shown in Fig. 2. The porous substrate must be completely inert to liquid fuels and gas. In addition, the substrate must be mechanically strong, to homogeneously suppress the swelling of the filling polymer in it. To achieve this, pore sizes should be small. Small amounts of water can be contained in the filling polymer electrolyte for hydroxyl ion migration. The filling polymer exhibits hydroxyl ion conductivity, and the porous substrate matrix mechanically prevents excess swelling of the filling polymer, which can otherwise lead to high fuel crossover. Hydrocarbon materials were employed because of their low cost and environmental friendliness, unlike perfluorinated carbons. In addition, the substrate matrix restricts the change in membrane area between the dry and the swollen state. Several benefits of pore-filling electrolyte membranes have been confirmed^{(8), (9), and (10)}.

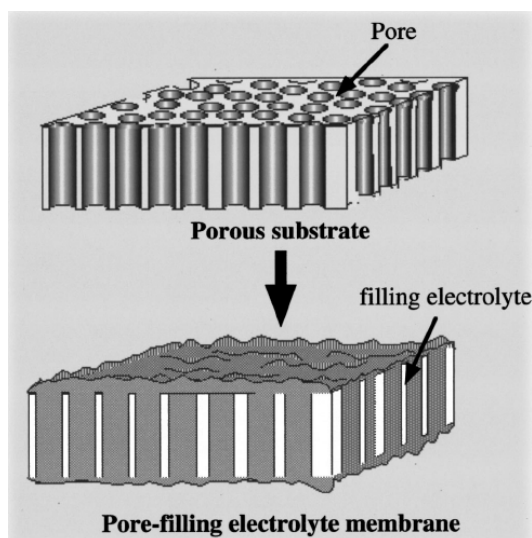


Fig. 2. The concept of the pore-filling membranes⁽⁷⁾.

Hence, in this research, we report the work done on the preparation methodology of pore-filling electrolyte membranes by particularly using all hydrocarbon polymers and solid alkaline fuel cell performances with the membranes. The physico-chemical properties of the prepared electrolyte membranes such as swelling behavior, ion exchange capacity and ionic conductivity were also investigated in correlation with the electrolyte composition.

2. Experimental

2.1. Membrane preparation

A microporous high-density polyethylene film was used as the substrate. The substrate was obtained from Asahi Chemicals Co. Ltd., and was of 25 μm thickness, 70 nm mean pore diameter, and 47% porosity. An anhydrous monomer containing sulfonic acid was employed as a proton conducting electrolyte. The pore-filling membrane is produced by impregnating a mixed solution of a quaternary ammonium based electrolyte monomer, several crosslinking agents and a photoinitiator into a microporous polymer support, polymerizing the monomer, and simultaneously photocrosslinking the polymer to form a chemically crosslinked polymer electrolyte membrane which is also physically crosslinked with the porous substrate.

2.2. Ion exchange capacity (IEC)

The ion exchange capacities (meq/g) of the prepared pore-filling membranes were determined by acid-base titration technique. The dried

membrane samples (5 cm × 5 cm) in acid form were equilibrated in 50 ml of 0.5 M KOH overnight at room temperature with frequent stirring. The amount of hydroxyl ion released in the solution was then titrated with 0.05 M HCl. After titration, the membrane samples were converted into base form again by boiling with 3.5 M KOH for 3 h and washed free of base. The membrane samples were then dried in vacuum oven (1.333224×10^2 Pa [1 Torr], 60 °C) overnight. The dry weight of the membranes was determined after keeping it in a desiccator at ambient temperature over fresh silica gel for 30 min. The ion exchange capacity (IEC) of the dry membrane per unit mass (meq/g) was calculated from the following relationship:

$$IEC_{\text{experimental}} = \frac{V_{\text{HCl}} \times 0.05}{m_{\text{dry}}} \quad (2.1)$$

where V_{HCl} is the volume of HCl consumed and m_{dry} , the mass of the dried sample. The degree of quaternary amine was defined as an ion exchange capacity (IEC) equivalent to one quaternary amine group per the repeat unit of electrolyte monomer:

$$\text{Quaternary amine yield}(\%) = \frac{IEC_{\text{experimental}} \times 100}{IEC_{\text{theory}}} \quad (2.2)$$

where IEC_{theory} is the ion exchange capacity calculated from the content of electrolyte monomer which was given by the following equation:

$$IEC_{\text{theory}} = \frac{9.62Y}{100 + 1.77Y} \quad (2.3)$$

where Y is the content of the electrolyte monomer into the pore-filling membrane. The equivalent weight (EW) was calculated from the following equation.

$$EW = \frac{1000}{IEC} \quad (2.4)$$

2.3. Water uptake and change in membrane area ratio

The water uptake of the prepared membrane was measured by soaking the samples overnight in water at 25 °C. The samples were then taken out of the water, and any excess surface water wiped off using wet filter paper. Then, the

swollen sample weight was measured. The water uptake, ϕ_w (%), in the sample is defined by Eq. (2.5). For the membranes, the substrate weight was subtracted to evaluate the water uptake of the filling polymer

$$\phi_w = \frac{w_{\text{fp}}^s - w_{\text{fp}}^d}{w_{\text{fp}}^s} \times 100 \quad (2.5)$$

where w_{fp}^s is the swollen polymer weight, and w_{fp}^d is the dry polymer weight. The membrane area was measured in water, and the change in membrane area ratio between the swollen state and the dry substrate, ϕ_a (%), was evaluated. The entire membrane area was measured, including that of the substrate

$$\phi_a = \frac{S_{\text{mem}}^s - S_{\text{sub}}^d}{S_{\text{sub}}^d} \times 100 \quad (2.6)$$

where S_{mem}^s is the membrane area in swollen state, and S_{sub}^d is the dry substrate area.

2.5. OH⁻ conductivity measurements

The prepared membranes (5 cm x 5 cm) were dipped in distilled water at 25 °C for 1 hour and was then interposed between two glass substrates, to which a rectangular platinum electrode was fixed, without removing water from the surface. The alternating current impedance of the membrane was measured at 100 Hz - 4 MHz to determine the proton conductivities of the membranes.

2.6. Performance of fuel cells

Solid Alkaline fuel cells (SAFCs) were fabricated using the membranes to be the conductivities of 0.005 - 0.025 S/cm. Specifically, each of the membranes was joined to two electrodes containing Pt/C (1 mg/cm²), respectively, in order to construct a membrane electrode assembly (MEA) having an effective area of 10cm². The membrane electrode assembly was mounted on an apparatus for evaluating the performance of a unit cell. Fully humidified hydrogen gas and air (or oxygen gas) were allowed with stoichiometric flow rates through the fuel electrode and the air electrode at 60 °C, respectively, to determine the performance of the fuel cell.

3. Summary

Anion exchange polymer electrolyte pore-filling membranes consisting of the whole hydrocarbon materials were prepared by photo polymerization with various quaternary ammonium cationic monomers and characterized on the properties for applying to solid alkali fuel cell (SAFC). Hydrocarbon porous (SAFC). H (on ps polyethylene were used for ton with variation of the pore-filling membranes. The hydroxyl ion conductivity of the polymer electrolyte membranes prepared in this research was dependent on the composition ratio of an electrolyte monomer and crosslinking agent used for polymerization. Furthermore, these pore-filling membranes have commonly excellent properties (on physical and chemical aspects) when used in solid, high mechanical strength, lower fuel crossover through the membranes, and easier preparation process than those of traditional cast membranes.

References

- [1] J.-S. Park, G.-G. Park, S.-H. Park, Y.-G. Yoon, C.-S. Kim, W.-Y. Lee, *Macromol. Symp.* 249/250 (2007) 174-82.
- [2] J.R. Varcoe, R.C.T. Slade, *Fuel Cells* 5 (2005) 187-200.
- [3] E. Agel, J. Bouet, J.F. Fauvarque, *J. Power Sources* 101 (2001) 267-274.
- [4] J.R. Varcoe, R.C.T. Slade, G.L. Wright, Y. Chen, *J. Phys. Chem. Part B: Condens. Matter. Surf. Interf. Biophys.* 110 (2006) 21041-1049.
- [5] T.N. Danks, R.C.T. Slade, J.R. Varcoe, *J. Mater. Chem.* 13 (2003) 712-21.
- [6] T. Yamaguchi, F. Miyata and S. Nakao, 2003. "Pore-filling type polymer electrolyte membranes for a direct methanol fuel cell", *J. Membr. Sci.*, 214, pp. 283-292.
- [7] T. Yamaguchi, S. Nakao, S. Kimura, 1991. *Macromolecules*, 24, p. 5522.
- [8] T. Yamaguchi, M. Ibe, B.N. Nair, S. Nakao, 2002. *J. Electrochem. Soc.*, 149, A1448.
- [9] T. Yamaguchi, H. Hayashi, S. Kasahara, S. Nakao, 2002. *Electrochemistry*, 70, p. 950.
- [10] T. Yamaguchi, F. Miyata, S. Nakao, 2003. *Adv. Mater.*, 15, p. 1198.