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Effect of organo clay content on proton conductivity and methanol transport through crosslinked PVA hybrid membrane for direct methanol fuel cell

Dae Sik Kim [a], In Cheol Park [c], Hyun Il Cho [b], Dae Hoon Kim [b], Go Young Moon [c], Hyung Keun Lee [d], Ji Won Rhim [b,*]

[a] Institute for Chemical Process and Environmental Technology, National Research Council, 1200 Montreal Road, Ottawa, Ontario, K1A 0R6 Canada
[b] Department of Chemical Engineering, Hannam University, 461-6 Junmin-dong, Yuseong-gu, Daejeon 305-811, Republic of Korea
[c] LS Industrial Systems Co., Ltd., Advanced Sci. & Tech. Division, Gyeonggi-do, Anyang 431-080, Republic of Korea
[d] Korea Institute of Energy Research, 71-2 Jang-dong, Yuseong-gu, Daejeon 305-343, Republic of Korea

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ABSTRACT

In the present study, crosslinked poly(vinyl alcohol) (PVA) membranes were prepared using poly(styrene sulfonic acid-*co*-maleic acid) (PSSA_MA) (PVA:PSSA_MA = 1:7). The PSSA_MA was used both as a crosslinking agent and as a donor of the hydrophilic group (–SO_3H and/or –COOH). The hybrid membranes were prepared by modified clay such as Clay Na^+, Clay 30B, and Clay 15A. The thermal, water uptake, proton and methanol transport properties of the hybrid membrane were found to be sensitive to the clay type and content. The hybrid membrane with Clay 30B shows higher proton conductivity than other hybrid membranes due to hydroxyethyl group. The membrane with Clay 15A showed the lowest methanol permeability due to lower specific gravity than other clay. Compared to the membrane without modified, the PVA/PSSA_MA/Clay 15A containing 4 wt% of Clay 15A showed both high proton conductivity (0.023 S/cm) and low methanol permeability (2.19×10^{-7} cm^2/s).

1. Introduction

Poly(vinyl alcohol) (PVA) appears to be very attractive material for preparing proton exchange membrane (PEM) because this polymer can function as an excellent methanol barrier [1]. PVA also has both very good mechanical properties and chemical stability, which are adequate for preparing PEMs. Although PVA itself does not have fixed charges, several organic groups like hydroxyl, amine, carboxylate, sulfonate, and quaternary ammonium can be incorporated to impart hydrophilicity and/or ionic group [2]. Torres et al. [3] reported that it was assumed that the crosslinking of the completely miscible blend system occurs *via* dehydration between carboxylic acid and hydroxyl group, that is, esterification and bond formation during thermal activated reaction.

In our previous study, we reported the preparation of crosslinked membranes employing PVA as a base materials and sulfosuccinic acid (SSA) [4,5] or poly(acrylic acid-*co*-maleic acid) (PAM) [6] or poly(styrene sulfonic acid-co-maleic acid) [7] as both a crosslinking agent and as a donor of the hydrophilic group (–SO_3H) and/or carboxylic group(–COOH). Since a maleic acid group has two ion-exchangeable sites in its molecular structure and also could be crosslinked with –OH group of PVA, the introduction of PSSA_MA into the PVA polymer matrix can control the membrane charge density and also prevent excessive swelling.

The commercial Nafion membranes such as the fluorinated membrane from DuPont, Flemion from Asahi Glass and Neosepta from Tokuyama Soda have been intensively used as proton-conducting electrolyte membranes due to their chemical stability and high proton conductivity (>0.1 S/cm) in the fully hydrated state. However, the operational limit of these polymers is usually considered to be about 100 °C or lower because of the deterioration of proton transport and mechanical and electrochemical properties [8].

There has been considerable effort spent trying to reduce methanol crossover and to reach high proton conductivity. The organic–inorganic composite membranes containing Zr phosphonates, zeolites, and silica [9–12] have been investigated. Yeh et al. reported that an organic–inorganic hybrid nanocomposite membrane having exfoliated silicate layers of clay dispersed in the PVA matrix was successfully prepared [13].

The aim of this study was to prepare membranes for possible use in a DMFC. To do this, PVA/PSSA_MA/Clay hybrid membranes containing sulfonic acid and carboxylic acid groups were synthesized. Sulfonic acid groups were introduced into the PVA matrix by esterification with poly(styrene sulfonic acid-*co*-maleic acid) (PSSA_MA). In addition, the modified clay such as Clay Na^+, Clay

* Corresponding author. Tel.: +82 42 629 8839; fax: +82 42 629 8835.
E-mail address: jwrhim@hnu.kr (J.W. Rhim).

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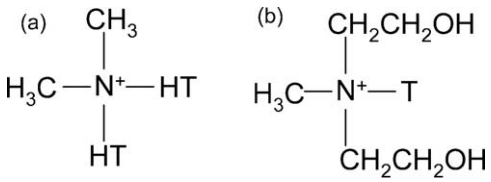

Scheme 1. Structural formula of Clay species (a) Closite® 15A, (b) Closite® 30B, where HT is Hydrogenated Tallow, T is tallow (~65 C18; ~30% C16; ~5% C14).

30B, and Clay 15A particles were dispersed into the polymer matrix. We expected that the crosslinked PVA hybrid membranes would lead to high proton conductivity due to the addition of the sulfonic acid, and low methanol permeability due to the crosslinking between the PVA and PSSA_MA, with the Clay providing a barrier to methanol. The content of clay was controlled to seek the best performance in terms of methanol permeability and proton conductivity measurements.

2. Experimental

2.1. Materials

Fully hydrolyzed PVA (99% hydrolyzed, average Mw = 89,000–98,000) and the PSSA_MA (sodium salt, styrene (Sty)-sulfonic acid:maleic acid = 3:1, average Mw = 20,000 g/mol) as a crosslinking agent and as a donor of the hydrophilic $-SO_3H$ and –COOH group were purchased from the Aldrich Chemical Co., Milwaukee, WI, USA. The organo Clay Closite Na^+, 15A and 30B were purchased from the Southern Clay Product, Inc., Gonzales, TX, USA. The structural formula and characterization of various clay species are shown in Scheme 1 and Table 1.

2.2. Membrane preparation

Aqueous 10 wt% PVA solutions were prepared by dissolving dry PVA in water and then refluxing at 90 °C for 6 h, and aqueous 10 wt% PSSA_MA solutions were prepared. The PVA solutions were mixed together along with PSSA_MA solution until forming a homogeneous solution for at least 1 day at room temperature. The amount of PSSA_MA was 7% by weight to PVA solution. Inorganic–organic hybrids using various clays were prepared by dispersing the clay in PVA/PSSA_MA solution using homogenizer. The amount of clay was 1–5% by weight to PVA weight. The solutions were then poured onto a plexiglass plate, and cast using the doctor blade process. The cast solutions were allowed to dry in air at room temperature. The fully dried membranes were peeled away from the glass plate, and then heated in a thermosetting oven. The prepared membranes were annealed at 120 °C for 1 h to induce crosslinking reaction. The reaction mechanism of PVA and PSSA_MA was reported [7].

2.3. Membrane characterization

The FT-IR spectra of the membranes were measured using a Nicolet IR 860 spectrometer (Thermo Nicolet, Madison, WI, USA) operating in the wavenumber range 4000–500 cm^{-1}. The degradation process and the thermal stability of the membranes were investigated using thermogravimetry (TGA) (TA Instruments TGA 2050, New Castle, DE, USA). The TGA measurements were carried out under a nitrogen atmosphere using a heating rate of 10 °C/min from 50 to 700 °C.

The water swelling ratio was measured by soaking the samples in distilled water for more than 24 h. After this period, they were wiped with a filter paper and then weighed immediately. The samples were then dried under vacuum until a constant weight was obtained. The water content (g H_2O/g membrane) was determined using the following equation:

$$\text{Water content} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}}$$

where W_{wet} and W_{dry} are the wet and dry membrane weights, respectively. The values of the water content reported are the mean of at least five measurements, and the average estimated error was ±5%.

The ion exchange capacity (also known as the IEC value) was measured using the classical titration technique (ASTM D2187) with 0.01 M NaOH and phenolphthalein as an indicator.

To investigate the morphology of the membranes, the fracture surfaces were investigated using field emission scanning electron microscopy (FE-SEM, Jeol Model JSF 6340F, Tokyo, Japan).

The proton conductivity of the membranes was measured using the normal four-point probe technique at RH (relative humidity) = 100%. The impedance of the membranes was determined using a Solatron Analytical Full Material Impedance System 12608W consisting of a Frequency Response Analyzer 1260 and Electrochemical Interface 1287 unit. Each sample was cut into sections 4 cm × 1 cm prior to being mounted on the cell. The proton conductivity (σ) was obtained using the following equation:

$$\sigma = \frac{l}{RS} \quad (1)$$

where σ is the proton conductivity (in S/cm), and l is the distance between the electrodes used to measure the potential (1 cm). R is the impedance of membrane (in Ω). S is the surface area required for a proton to penetrate the membrane (in cm^2). The impedance of each sample was measured five times to ensure good data reproducibility.

The methanol permeability of the membranes was determined using a diaphragm diffusion cell. This cell consisted of two reservoirs, each with a capacity of approximately 60 ml, separated by a vertical membrane. The membrane was clamped between the two reservoirs, the contents of which were stirred during the experiments. Prior to the test, the membranes were equilibrated in deionized water for at least 12 h. Initially, one reservoir (V_A) contained a 2 M methanol–water solution, and the other reservoir (V_B) contained pure deionized water. The increase in concentration of methanol in the initially pure water reservoir was measured against time using gas chromatography. In the gas chromatography measurements, 1-μl samples were analyzed using a Shimadzu GC-14B gas chromatograph. The methanol permeability was calculated [12]. In the permeability tests, the temperature was controlled using a thermostatic water bath at 30 °C.

Table 1
Structural formula and characterization of various clay species.

	Organic modifier	Modifier concentration	% moisture	% weight loss on ignition	Specific gravity (g/cm^3)
Closite® Na^+	None	92.6 mequiv./100 g clay	<2%	7%	2.86
Closite® 15A	2M2HT[a]	125 mequiv./100 g clay	<2%	43%	1.66
Closite® 30B	MT2EtOH[b]	90 mequiv./100 g clay	<2%	30%	1.98

[a] Dimethyl, dehydrogenated tallow, quaternary ammonium.
[b] Methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium.