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Short communication

Novel proton-conducting polymer electrolyte membranes based on PVA/PAMPS/PEG400 blend

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Abstract

Polyvinyl alcohol/poly-2-acrylamide-2-methyl propane sulfonic acid/polyethylene glycol blend membranes were cross-linked by glutaraldehyde in acetone to give water-insoluble film with an excellent ionic conductivity. The water-swelling ratio (WSR) of the membranes was decreased by treating with glutaraldehyde accompanied by increasing proton conductivity. Excellent proton conductivities (0.02–0.083 S cm^{-1}) were obtained for the resulted cross-linked blend membranes. Methanol permeability of the cross-linked film was significantly low, around one-fifth as low as that of Nafion.
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1. Introduction

Low-temperature proton exchange membrane fuel cells (PEMFCs) fuelled directly by methanol are gaining more and more attention for their large potential application to fuel cell vehicles, onsite power generators and portable power sources [1]. Generally, perfluorinated ion exchange membranes in their proton-exchanged form such as Nafion are being used as polymer membrane materials, which combine the required chemical, electrochemical and mechanical stability with high proton conductivity. However, they have some disadvantageous features of high cost, and additionally of high permeability of methanol, which reduces considerably the fuel efficiency. Thus alternatives to membrane materials are strongly desired which enable high proton conductivity with minimum methanol permeability.

In our research of new membrane materials for PEM-FCs, we noticed the importance of utilizing polyvinyl alcohol (PVA), which is known to have good film-forming and good chemical-resistant properties. PVA is also known to be an alcohol-barrier membrane because of its dense structure by strong intra- and inter-molecular hydrogen bonding [2,3]. Rhim et al. [3] reported that the permeability of alcohol in water–alcohol mixed solvent was suppressed by modifying PVA film through cross-linking. Based on these trends, we report here a new series of polymer electrolyte membranes using PVA main chain, introducing sulfonic acid groups through another polymer by a technique of polymer blending. Polymer electrolytes made by blending are reported, for example, PVA doped with inorganic acids [4] or PVA and polystyrene blends [5], but there are only a few successful membranes possessing high proton conductivities together with chemical stability.

In this work, a new polymer, poly-2-acrylamide-2-methyl propane sulfonic acid (PAMPS), as a second ingredient, is used to first prepare a blend membrane with PVA, because the former one is known to be one of the excellent proton-conducting polymers [6–13] and miscible easily with the latter one. When polyethylene glycol (PEG) is further mixed into this blend polymer, the resulted membrane is found to improve better in the screening experiment. Thus PEG is further added as the third ingredient, in order to improve the membrane property and obtain flexible ternary

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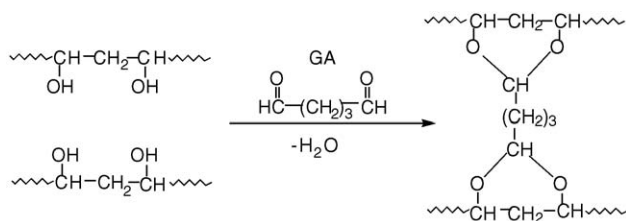
Scheme 1.

blend membranes. The membrane structure is finished by cross-linking the PVA main chain with acetal ring formation using aldehyde cross linkers. The cross-linking reaction by GA is illustrated in Scheme 1, as has been proposed by many researchers [14,16–19].

2. Experimental

Molecular weight of PVA was in the range $M_w = 124,000$ to 186,000 (Aldrich), that of PAMPS was $M_w = 2,000,000$ (Aldrich) and that of PEG was 400 (Aldrich), which was determined after optimisation. Especially the molecular weight and content of PEG affected strongly the membrane flexibility and conductivity. Aqueous solutions of 6 wt.% PVA, 15 wt.% PAMPS and 7.5 wt.% PEG were mixed and spread on a Teflon sheet. The cast film was dried for 2–3 days. This process of film formation was followed by cross-linking by 6 wt.% glutaraldehyde (GA) in acetone at room temperature. The formation of ether bonds between the hydroxyl groups of PVA and the aldehyde groups of GA, proceeded without any additional acid but with the catalytic effect of PAMPS [20]. When the film was cross-linked in water, reaction occurred immediately and the resulting membranes were gel-like but stiff and brittle after drying.

Water-swelling ratio (WSR) of the ternary-composed membrane, PVA-PAMPS-PEG, was calculated from the following equation:

$$WSR = (W_{wet} - W_{dry})/W_{dry}$$

where W_{wet} and W_{dry} are wet and dried membrane weight, respectively [14]. The proton conductivity of the membrane was evaluated by AC impedance method [15]. The samples were conditioned in pure water overnight, and the membrane impedance was measured in a hydrated state by contacting with pure water.

Methanol permeation of the blend membrane was measured by a cup method. The membrane was attached upper side of the cup containing liquid methanol. Then, the cup was placed in a desiccator containing silica gel and the amount of methanol permeation was determined gravimetrically at 25 °C.

As the durability test, in order to see if the main chain dissolves ultimately or sulfonic acid groups release from the polymer, water or acid soaking in 1 mol dm^{-3} HCl were conducted for 14 days at 25 °C in a temperature-controlled

chamber, and WSR and membrane conductivity were monitored. Also, thermal decomposition behaviour was measured by thermogravimetry (TG) using Seiko Instruments model TG/TDA 6200 with a heating rate of 5 °C min^{-1}.

3. Results and discussion

Acetalization that occurred intermolecularly between PVA and GA was identified from the decrease of hydroxyl groups (3300–3450 cm^{-1}) and the increase of ether bonds (970–1400 cm^{-1}) through the reaction as shown by the IR spectra in Fig. 1. The possibility about the progress of nucleophilic addition of –NH from PAMPS to GA was not evidenced in the spectra.

Untreated blend membrane absorbed water vigorously in hydrated state, more than 20 times as much as the weight of the membrane in dried state. The extent of cross-linking was evaluated from the value of WSR. The higher the extent of cross-linking, the lower value took WSR. Fig. 2 shows the WSR and conductivity of the cross-linked membrane obtained by the reaction with GA (6 wt.%) in acetone solution, which were plotted against the reaction time. WSR decreased rapidly by the reaction with GA and reached nearly constant after 7 h, while the conductivity increased gradually and reached a plateau after nearly the same time.
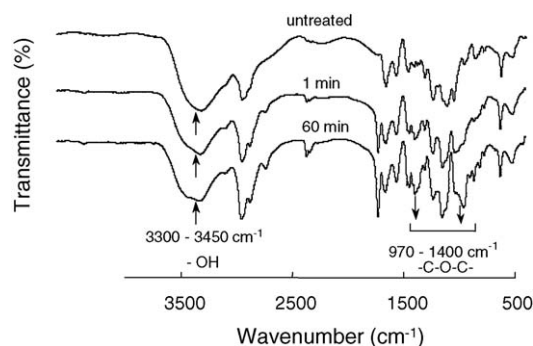

Fig. 1. IR spectra of PVA/PAMPS/PEG400 blend membranes (1:1:0.5 in mass) before and after the cross-linking with 6 wt.% glutaraldehyde in acetone, with the cross-linking time as a parameter.
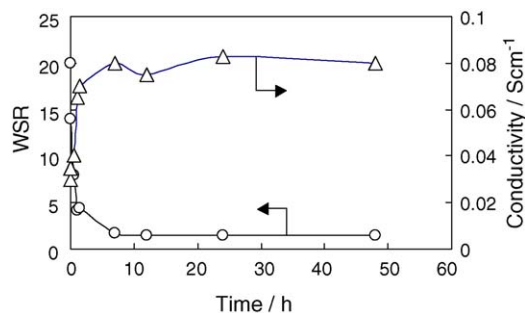

Fig. 2. Conductivity and water-swelling ratio (WSR) of the PVA/PAMPS/PEG400 cross-linked membrane (1:1:0.5 in mass) obtained by treating with 6 wt.% glutaraldehyde in acetone for various treating times. All measured at 25 °C.
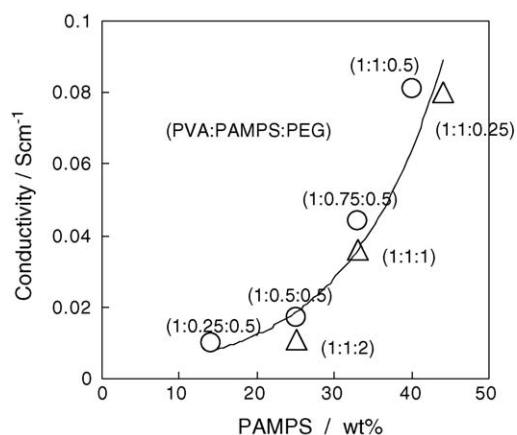
Fig. 3. Effect of PAMPS content on the ionic conductivity of the cross-linked membrane at 25 °C. The mass ratio of the blend polymer PVA/PAMPS/PEG400 is indicated in the parenthesis.

Fig. 4. Durability test of cross-linked PVA/PAMPS/PEG400 blend membranes (1:1:0.5 in mass) soaked in 1 mol dm^{-3} HCl at 25 °C, shown as the change of water-swelling ratio (a) and proton conductivity at 25 °C (b) in the time course. (●) PVA/PAMPS/PEG400, (▲) Nafion 117.

In acetone the cross-linking occurred gradually from the surface to the interior, but the homogeneity of cross-linking distribution was not identified at this stage. When the extent of cross-linking was low, the membrane was gel in hydrated state but brittle after drying. Well cross-linked membrane was fairly intense mechanically and showed a high proton conductivity (around 0.083 S cm^{-1}), which is comparable to the commercial available Nafion 117 (0.091 S cm^{-1}) in its fully hydrated state under the same measuring conditions. Hereafter the cross-linking time was fixed to 24 h.

PEG was found to play a decisive role in proving the membrane performances. Ternary-composed (PVA/PAMPS/PEG400) cross-linked membrane was robust and flexible, while the binary-composed (PVA/PAMPS) one was rather stiff and brittle. This could be ascribed to the special plasticizing effect of PEG, where the presence of hydrophilic and hydrophobic moieties in PEG gives it unique ability to be soluble in both aqueous and organic solvents, and to be blended with other polymers such as PVA [21–23]. Without PEG, the WSR was more than twice of that with PEG showing extreme water swelling, and no stable membranes were obtained for conductivity measurements. On the other hand, when the amount of PAMPS was reduced, the membrane flexibility and mechanical properties were improved while conductivity was tremendously reduced.

Fig. 3 illustrates the relation between the conductivity and the PAMPS content of the cross-linked membranes prepared where the content of PEG or PAMPS was changed. The con-
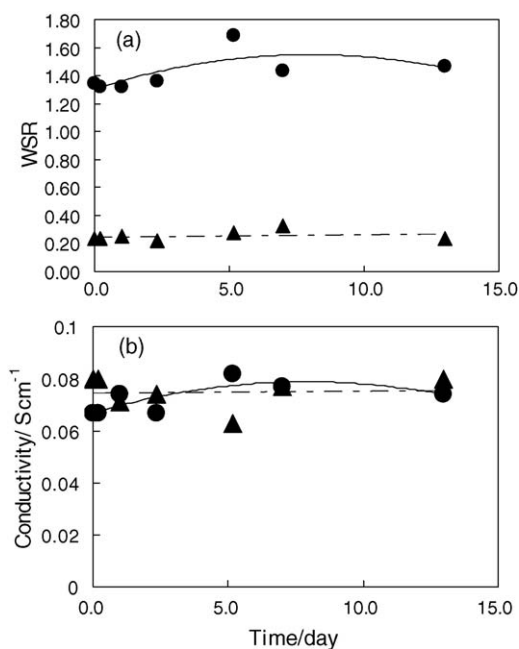
ductivity increased with the content of PAMPS irrespective of the character of matrix (membrane composition). However, it was found that there was a limit of PAMPS in a net dry polymer content, and exceeding 40 wt.% of which resulted in the membrane to become rapidly fragile. For a good mechanical strength, optimal membrane composition should be in the range of 5–25 wt.% for PEG and less than 40 wt.% for PAMPS.

Table 1 shows the methanol permeability of the blend membrane measured by a cup method. The methanol permeation coefficient of the blend membrane was appreciably small compared to that of Nafion. It was further decreased through cross-linking. Although this measurement is not a direct consequence of methanol permeability in contact with aqueous solution, the trend shows that cross-linking further improves methanol barrier performance of the membrane.

The membrane durability against acid decomposition was checked in 1 mol dm^{-3} HCl aqueous solution at 25 °C. Fig. 4(a) and (b) shows the WSR and membrane conductivity measured for 14 days. Also membrane swelling was checked by soaking in pure water. No serious degradation

Table 1
Permeability coefficient of methanol through PVA/PAMPS/PEG400 blend membranes

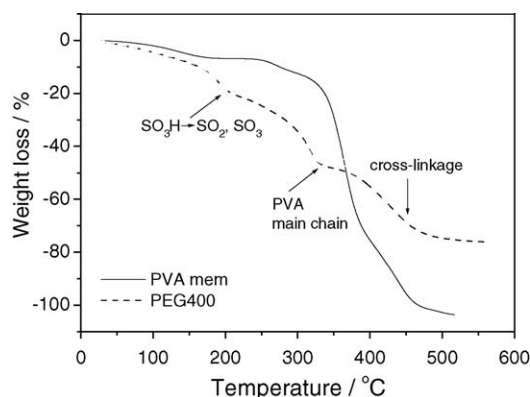|	Membrane thickness (μm)	Permeability	
		Rate ($\times 10^3$ g min^{-1})	Coefficient ($\times 10^7$ cm^2 min^{-1} cmHg^{-1})
Nafion 117	175	8.5	22.85
PVA	85	0.017	0.02
PVA/PAMPS/PEG400 (non-cross-linking)	115	3.33	5.88
PVA/PAMPS/PEG400 (treated with GA)	151	1.8	4.18

Fig. 5. TG profiles of cross-linked PVA/PAMPS/PEG400 blend membranes (1:1:0.5 in mass), together with that of PVA. Heating rate: $5\,^{\circ}\mathrm{C}\,\mathrm{min}^{-1}$.

was observed during the testing period. Thus the acetalization of PVA with cross-linker, GA, was assumed to be complete and the main chain was resistant to the acid decomposition, hence no leaching of sulfonic acid groups from PAMPS was anticipated in this degradation test. It can be assumed that the acetal ring is maintained in equilibrium with the acid environment, and does not decompose in this moderate temperature. However, at present, we do not assert that these membranes have relatively better hydrolytic durability than other aliphatic membranes at a high temperature.

The thermogravimetry (TG) behaviour of PVA/PAMPS/PEG400 membrane is shown in Fig. 5, together with that of PVA. There were observed three major steps of thermal decomposition. In the temperature range $80–150\,^{\circ}\mathrm{C}$, water desorption occurred (10%). Then through $190–330\,^{\circ}\mathrm{C}$, PAMPS ad PVA decomposed with a weight loss of 45%, followed by a major degradation of cross-linking bridge and polymer backbone through $330–500\,^{\circ}\mathrm{C}$. For PVA alone, very large decomposition was observed between 330 and $500\,^{\circ}\mathrm{C}$, and more than 80% of the polymer decomposed almost completely.

Conclusively, resulted (PVA/PAMPS/PEG400) cross-linked membranes possess the following advantages:

(1) Easy of the membrane preparation (only mixing of each polymer solution), which leads to a good cost performance, since each polymer is well-known material and low cost.

(2) Robustness and flexibility of the membranes due to the plasticizing effect of PEG.
(3) Excellent proton conductivity ($0.083\,\mathrm{S}\,\mathrm{cm}^{-1}$) comparable to that of Nafion 117.
(4) Rather low methanol permeability (one-fifth) compared to that of Nafion 117.

Therefore, it might be expected that ternary-composed (PVA/PAMPS/PEG400) cross-linked membranes will be promising in low-temperature DMFC applications.

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