

# New highly proton-conducting membrane poly(vinylpyrrolidone)(PVP) modified poly(vinyl alcohol)/2-acrylamido-2-methyl-1-propanesulfonic acid (PVA–PAMPS) for low temperature direct methanol fuel cells (DMFCs)

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## Abstract

A new type of chemically cross-linked polymer blend membranes consisting of poly(vinyl alcohol) (PVA), 2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPS) and poly(vinylpyrrolidone) (PVP) have been prepared and evaluated as proton conducting polymer electrolytes. The proton conductivity ( $\sigma$ ) of the membranes was investigated as a function of cross-linking time, blending composition, water content and ion exchange capacity (IEC). Membranes were also characterized by FT-IR spectroscopy, thermogravimetric analysis (TGA), and the differential scanning calorimetry (DSC). Membrane swelling decreased with cross-linking time, accompanied by an improvement in mechanical properties and a small decrease in proton conductivity due to the reduced water absorption. The membranes attained  $0.088 \text{ S cm}^{-1}$  of the proton conductivity and  $1.63 \text{ mequiv g}^{-1}$  of IEC at  $25 \pm 2 \text{ }^\circ\text{C}$  for a polymer composition PVA–PAMPS–PVP being 1:1:0.5 in mass, and a methanol permeability of  $6.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ , which showed a comparable proton conductivity to Nafion 117, but only one third of Nafion 117 methanol permeability under the same measuring conditions. The membranes displayed a relatively high oxidative durability without weight loss of the membranes (e.g. 100 h in 3%  $\text{H}_2\text{O}_2$  solution and 20 h in 10%  $\text{H}_2\text{O}_2$  solution at  $60 \text{ }^\circ\text{C}$ ). PVP, as a modifier, was found to play a crucial role in improving the above membrane performances.

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*Keywords:* Proton-conducting polymer membrane; Polymer blend; Chemical cross-linking

## 1. Introduction

Proton-conducting polymer electrolytes have so far been given much attention due to their possible applications in such electrochemical devices as fuel cells, humidity and gas sensors, capacitors, and electrochemical displays that work from sub-ambient to moderately high temperatures. Among them, Nafion<sup>®</sup>, a perfluorinated ionomer, developed by DuPont, evoked the greatest interest because of its combined chemical, electrochemical, and mechanical stabilities with high proton conductivity (ca.  $10^{-1} \text{ S cm}^{-1}$ ) at ambient temperature [1]. However, this still limits the wide applications due to its high cost, high methanol permeability and difficulty in synthesis and processing [2–4]. Therefore, fabrication of novel proton-conducting membranes to replace Nafion<sup>®</sup> has been the subject

of continuous research. In recent years, some new conducting polymer membranes have been successfully proposed such as the sulfonated aromatic polymers [5,6], irradiation graft polymers [7,8], cross-linked [9–11] and blending polymers [11,12].

In fuel cell applications, the water management is a key issue, because both drying and flooding of the membrane during operation are problems. Chemical cross-linking is a highly versatile method to create and modify polymers, in particular, to limit the swelling, since the networks formed are insoluble due to the presence of chemical cross-links, which renders the membrane to be thermodynamically compatible with water [13,14]. In addition, the methanol permeation barrier and proton conductivity can also be improved by adjusting the cross-linking density of the membranes prepared. Therefore, for proton exchange membrane fuel cells, in particular, for DMFC applications at low operating temperatures with a liquid methanol feed system, cross-linking techniques have received attention owing to their low cost and easy processing [5,9–11,15,16].

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Polymer blend is attracting intense interest in recent years owing to its potential feature of combining the good characteristics of each blend component while at the same time reducing their deficient characteristics [12,17]. Not only from the viewpoint of cost effective materials and improved toughness of the membranes, but also the synergistic effects are important considerations that are not equal to the ‘physical’ average. However, binary blends of immiscible polymers generally exhibit poor mechanical properties due to a coarse and often unstable morphology, especially when swollen in water [18]. The preferred route to overcome these problems has been to add the third component, for example, a polymer, as a stabilizer to improve the membrane performances, and the use of terpolymers has been successfully reported for the modification of polyamide [18,19].

In this work we report a new proton-conducting ternary blend polymer membrane with poly(vinyl alcohol)/2-acrylamido-2-methyl-1-propanesulfonic acid/poly(vinylpyrrolidone) (PVA–PAMPS–PVP) in combination with chemical cross-linking. PVA shows superior methanol barrier properties to Nafion<sup>®</sup> [20], while PAMPS was found to be a high proton conductor comparable to partially hydrated Nafion<sup>®</sup> due to their sulfonic acid groups in its chemical structure [21]. Unfortunately, little was reported on their proton conducting behavior especially in solid state because of the high water solubility of PAMPS. Controlling the morphology of the membrane, for example, by the introduction of another copolymer seems to be an effective way to controlling their extensive swelling [21,22]. By blending PVP as the third component, the membrane performances, such as the mechanical property and the oxidative stability would be improved greatly.

Through chemical cross-linking reactions between the hydroxyl groups (–OH) of the polyhydroxy polymer PVA and the aldehyde groups (–CHO) of glutaraldehyde cross-linker, the swelling property of PVA was effectively controlled because of the increased cross-linking density. PAMPS, besides its proton conductivity, was used as a catalyst for the acetalization reaction instead of traditional HCl [10]. The resultant PVA–PAMPS–PVP blend membranes are thus capable of possessing all the required properties of a proton exchange membrane, namely, reasonable swelling, good

mechanical strength, excellent stability toward water and oxidative substances, and low methanol permeability along with the high proton conductivity due to ‘trapped’ PAMPS chains in the PVA network.

## 2. Experimental

### 2.1. Materials and membrane preparation

Polymer blends were prepared by solution casting method. Water solutions of PVA and PVP were separately prepared. First, PVA (99% hydrolyzed, average  $M_w = 124,000$ – $186,000$ , Aldrich) was fully dissolved in water at 70 °C and then cooled to room temperature. Appropriate amounts of the two solutions were then mixed with PAMPS (15% water solution, average  $M_w = 2,000,000$ , Aldrich). After removing the air in a vacuum, the well-mixed solution was transferred to plastic petri dishes and the water was evaporated at ambient temperature. When visually dry, the membrane was peeled off from the plastic substrate easily with a thickness of about 100  $\mu\text{m}$ .

### 2.2. Chemical cross-linking of PVA–PAMPS–PVP blend membranes

Samples of square pieces of polymer membranes ( $1 \times 1.5 \text{ cm}^2$ ) were soaked in a reaction solution that contained 10 mass% of glutaraldehyde (GA) (15 wt% solution in water, Wako) in acetone at room temperature. During this process, the chemical modification occurred in the membrane. The cross-linking took place between the –OH of PVA and the –CHO of GA in the membrane due to an acid-catalyzed reaction by PAMPS. Fig. 1 shows the structure of chemically cross-linked PVA–PAMPS–PVP blend membranes. The schematic process for the membrane preparation is illustrated in Fig. 2.

### 2.3. Characterization of chemically cross-linked PVA–PAMPS–PVP blend membranes

The membranes were examined by the Fourier transform infrared (FT-IR) spectra in order to characterize the molecular structure after chemical modifications. IR spectra were recorded on a spectrometer (FTIR-4200, Shimadzu) with

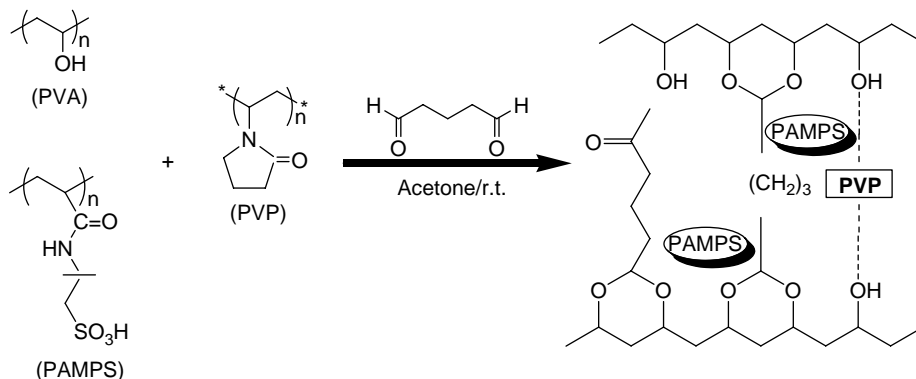


Fig. 1. Structure of chemically cross-linked PVA–PAMPS–PVP blend membranes. Here, PVA served as cross-linking network; GA as a cross-linking agent; PAMPS as a proton conductor, and PVP as a polymer stabilizer.

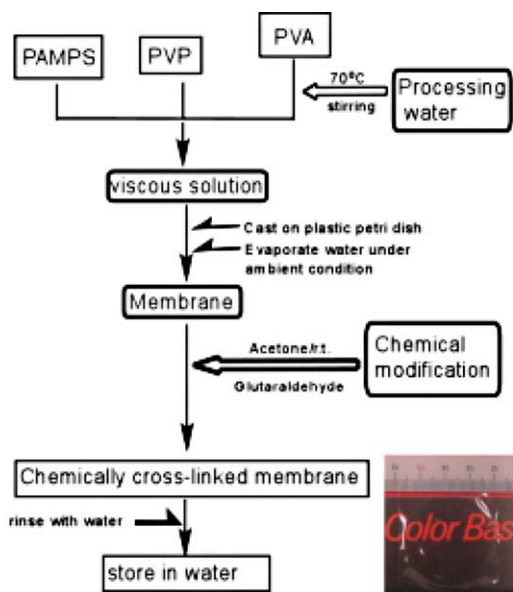


Fig. 2. Schematic presentation for the preparation of chemically cross-linked PVA–PAMPS–PVP blend membranes.

a wavenumber resolution of  $4\text{ cm}^{-1}$  in the range of  $400\text{--}4000\text{ cm}^{-1}$ . Samples with a form of thin film were sandwiched between two KBr plates and placed in the cell to be measured. Air was employed as background references.

#### 2.4. Thermal analysis

Thermal analysis of the polymer membranes was performed using both differential scanning calorimetry (DSC-6200 SII Nano Tec. Inc) and thermogravimetry (TG/DTA 6200 SII Nano Tec. Inc.). All measurements were performed under nitrogen. The thermal degradation onset temperature of the samples on TGA was used as references for DSC measurements. DSC measurements were carried out in a dry nitrogen atmosphere from  $-50$  to  $250\text{ }^{\circ}\text{C}$ . The samples of about  $10\text{--}20\text{ mg}$  were loaded into aluminium pans, and then heated to the desired temperature with a heating rate of  $5\text{ }^{\circ}\text{C min}^{-1}$ . The second heating curve was evaluated. The empty aluminium pan was used as a reference during the whole experiment.

#### 2.5. Water uptake and ion exchange capacity

The water uptake (WU) of the membranes ( $\text{g g}^{-1}$ ) was evaluated from the mass change before and after the complete dryness of the membrane. A dry membrane was swelled in deionized water for a day, then the surface water was wiped carefully with a filter paper, and it was immediately weighed. After drying the sample overnight in a vacuum oven at  $60\text{ }^{\circ}\text{C}$ , the water uptake (WU), was calculated using the expression:

$$\text{WU} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}}$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  are the mass of fully hydrated membrane, and of the dry membrane, respectively.

The ion exchange capacity (IEC,  $\text{mequiv g}^{-1}$ ) of the membranes was determined titrimetrically. Square pieces of each membrane were soaked in  $20\text{ ml}$  of a  $2\text{ M NaCl}$  solution and equilibrated for at least  $24\text{ h}$  to replace the protons by sodium ions. The remaining solution was then titrated with a  $0.01\text{ M NaOH}$  solution using phenolphthalein as an indicator. The IEC is defined as  $\text{mequiv}$  of sulfonic groups per gram of dried sample.

#### 2.6. Proton conductivity

Proton conductivity was measured by an AC impedance technique using an electrochemical impedance analyzer (S-1260, Solartron), where the AC frequency was scanned from  $100\text{ kHz}$  to  $0.1\text{ Hz}$  at a voltage amplitude of  $10\text{ mV}$ . Fully hydrated membranes were sandwiched in a Teflon conductivity cell equipped with Pt foil contacts on which Pt black was plated [23]. The impedance was measured by placing the cell in a temperature-controlled chamber under a temperature range of  $5\text{--}50\text{ }^{\circ}\text{C}$ . The membrane was in contact with water over the measurements.

#### 2.7. Methanol permeability measurement

Methanol permeability of the PVA–PAMPS–PVP membranes was measured using a home-made liquid diffusion cell which was composed of two glass compartments, each with a capacity of approximately  $80\text{ ml}$ , separated by a vertical membrane (effective area  $5.72\text{ cm}^2$ ). The membranes were equilibrated in deionized water for at least  $24\text{ h}$  prior to the test. One compartment ( $V_1$ ) was filled with a  $10\text{ wt}\%$  methanol–water solutions ( $\text{CH}_3\text{OH}$ : chromatographic grade, Wako). The other one ( $V_2$ ) was filled with pure deionized water. Methanol was diffused from  $V_1$  to  $V_2$  by the concentration difference between the two compartments, which were well-stirred during the test. The concentration of methanol in the receptor compartment was measured automatically by IR absorption methanol sensor (FCD-100, FC Development Co. Ltd, Hitachi) equipped with  $3\text{ mm}$  diameter column packed with a peristaltic pump, GILSON minipuls 2. Methanol permeability was then determined from the slope of the plot of methanol concentration in the receptor compartment versus time as described elsewhere [24–26].

### 3. Results and discussion

#### 3.1. FT-IR spectra

Fig. 3 shows the typical FT-IR spectra measured for PVA–PAMPS–PVP blend membranes before and after chemical cross-linking. As the analytical bands, strong peaks at around  $1562$  and  $1655\text{ cm}^{-1}$  were clearly observed based on the vibrational mode of amide groups of PAMPS unit in the host polymer [27]. Two sharp peaks at  $1039$  and  $1221\text{ cm}^{-1}$  were also clearly observed due to the S–O stretching of sulfonic acid groups [27,28]. Additional characteristic peaks of the C–N group and C=O group of PVP could not be unambiguously

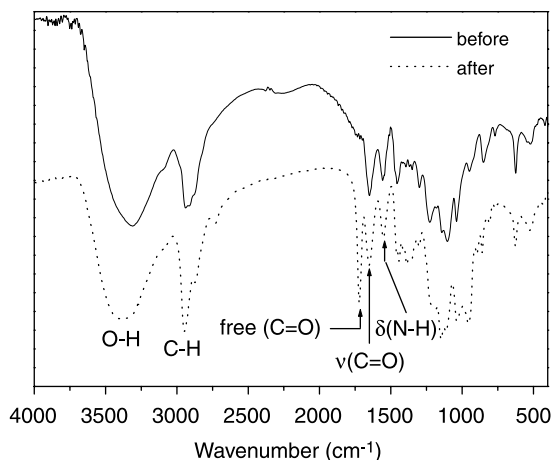


Fig. 3. FT-IR spectra of PVA–PAMPS–PVP blend membranes before and after chemical cross-linking. Polymer composition of PVA:PAMPS:PVP=1:1:0.5 in mass.

assigned due to the overlapping by the signals of amide  $\nu$  (C–N) II peak ( $1560\text{ cm}^{-1}$ ) and  $\nu$  (C=O) I peak ( $1657\text{ cm}^{-1}$ ) of pristine PAMPS. However, the presence of the cross-links in the membrane have been proven by IR measurements, where the appearance of a  $\nu$  (C–O) ester mode centered at  $1105\text{ cm}^{-1}$  increased greatly due to the etherification of –OH along the polymer chain of PVA with –CHO in GA (Fig. 3). Another interesting point may be the fact that we observed a large decrease in the intensity of the O–H of PVA after chemical cross-linking, which was accompanied by the appearance of a sharp absorption band at  $1724\text{ cm}^{-1}$ . The latter was ascribed to the ‘free’ –CHO attached to GA and, which indicates a reduced accessibility of the reactive groups caused by an increase of the network density [23].

### 3.2. Thermal analysis

In Fig. 4, the thermal degradation of PVA–PAMPS–PVP blend membranes was studied by TG, changing the PAMPS and PVP contents. The pristine PVA remains stable up to  $330\text{ }^{\circ}\text{C}$  [23], and pristine PVP to  $413\text{ }^{\circ}\text{C}$  [29]. When PAMPS was incorporated into polymer matrices, the resulting blend exhibited a lower thermal stability than either of PVP or PVA. In this figure, the dehydration that occurs first accounts for 2–5% mass loss and ceases at about  $190\text{ }^{\circ}\text{C}$ . Then, a major weight-drop begins at  $200\text{ }^{\circ}\text{C}$ , which is attributed to the decomposition of sulfonic acid groups ( $\text{SO}_2$  and  $\text{SO}_3$ ) and the splitting of the PVA main chain. This was followed by a final destruction of cross-linking bridges between  $400$  and  $500\text{ }^{\circ}\text{C}$  with a further 15% weight loss.

By a further thermal analysis from a derivative of weight loss (DTG) (the figure was not provided), one can perceive that increased content of PAMPS in the polymer blend leads to an early onset of degradation, but the mass loss becomes gradual (Fig. 4(a)). The weight drop of the composition, PVA:PAMPS:PVP=1:1:0.5 in mass, for example, was much lower than that of the PVA:PAMPS:PVP=1:0.25:0.5 in mass.

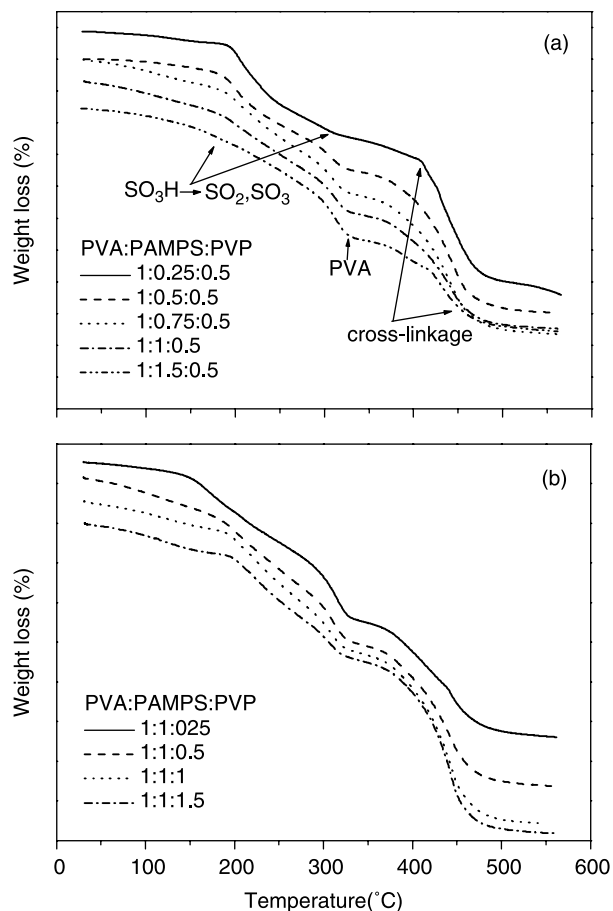


Fig. 4. TGA thermograms of the chemically cross-linked PVA–PAMPS–PVP blend membranes with different contents of (a) PAMPS and (b) PVP.

Obviously, an interaction between PVP and PAMPS as well as PVA would best explain the outcome.

Contrary to this, a reverse effect was observed by addition of PVP in the polymer blend. An increase of the PVP content leads to a higher onset temperature of decomposition. As shown in Fig. 4(b), the onset of decomposition temperature has been shifted by  $44\text{ }^{\circ}\text{C}$  (from  $155\text{ }^{\circ}\text{C}$  for the polymer containing 11 mass% of PVP to  $199\text{ }^{\circ}\text{C}$  for the sample containing 43 mass% of PVP) as a result of strengthened hydrogen-bonding interaction between PVP and PAMPS. That is, the thermal stability of the membrane was greatly improved by blending with PVP.

Fig. 5 shows the DSC traces of PVA–PAMPS–PVP blend membranes with different PAMPS and PVP contents. For the samples with different PAMPS content, the glass transition temperature ( $T_g$ ) appearing around  $35\text{ }^{\circ}\text{C}$ , slightly shifted to lower temperature for higher PAMPS content, suggesting the plasticizing effect of PAMPS (Fig. 5(a)). In contrast, the samples exhibited glass transition temperature ( $T_g$ ) at slightly higher values with increasing PVP content (Fig. 5(b)). In some DSC traces there are second  $T_g$ s visible around  $-25\text{ }^{\circ}\text{C}$ , which may be the glass transition of water containing PVA. This may exclude an assumption of total homogeneity and compatibility among components of the blend, although a wholly optical

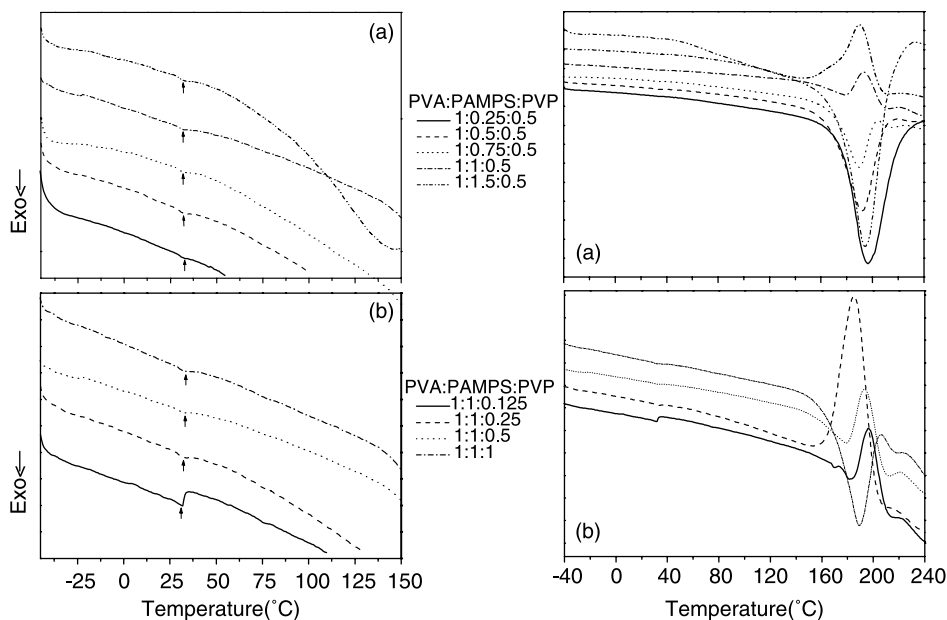


Fig. 5. DSC curves of the chemically cross-linked PVA–PAMPS–PVP blend membranes with different contents of (a) PAMPS and (b) PVP.

transparency of the membranes was obtained after they are dried in ambient condition (Fig. 2, inserted picture). Above this temperature a series of peaks appeared around 190 °C that was probably due to the loss of water and the onset of the thermal decomposition of PAMPS just as the TG profiles showed.

### 3.3. Dependence of conductivity on the polymer composition

Fig. 6 shows typically the effect of cross-linking time on the water uptake and the proton conductivity of PVA–PAMPS–PVP blend membranes in a polymer composition of 1:1:0.5. The water uptake (WU), expressed as grams of water incorporated per gram of dry membrane, was evaluated as a measure of cross-linking density. As shown in Fig. 6, the cross-linking density of the membranes strongly depended on the cross-linking time. It increased with cross-linking time, accompanied by an improvement in mechanical properties and a small decrease in proton conductivity due to the reduced

water absorption. The optimal reaction time was determined as 3–4 h in terms of membrane performances with both high conductivity and good mechanical stability.

Fig. 7 shows the changes in proton conductivity of PVA–PAMPS–PVP blend membranes with different PAMPS and PVP contents. The proton conductivity increased with the content of PAMPS due to the higher concentration of sulfonic acid groups, and reached a plateau with further increase in PAMPS content (Fig. 7, curve (a)). The effect of PVP content in the blend on the proton conductivity of PVA–PAMPS–PVP membranes is shown in Fig. 7, curve (b). Similarly, the proton conductivity of the membranes increased with the content of PVP and reached a maximum of 0.088 S cm<sup>-1</sup> as the mass ratio of PVA:PVP was increased from 1:0.125 to 1:0.5, then experienced a decrease when the mass ratio of PVA:PVP was above 1:1.

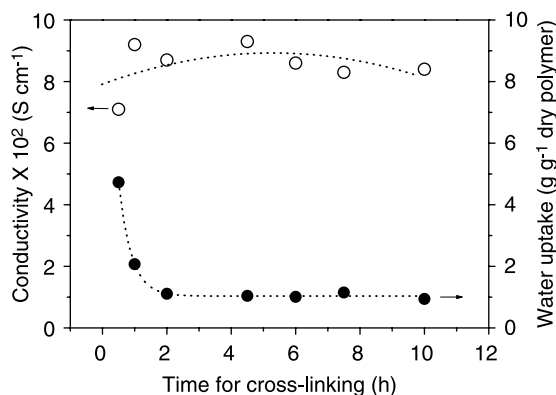


Fig. 6. Plots of the proton conductivity and the water uptake of chemically cross-linked PVA–PAMPS–PVP blend membranes as a function of time for chemical cross-linking. Polymer composition of PVA:PAMPS:PVP = 1:1:0.5 in mass.

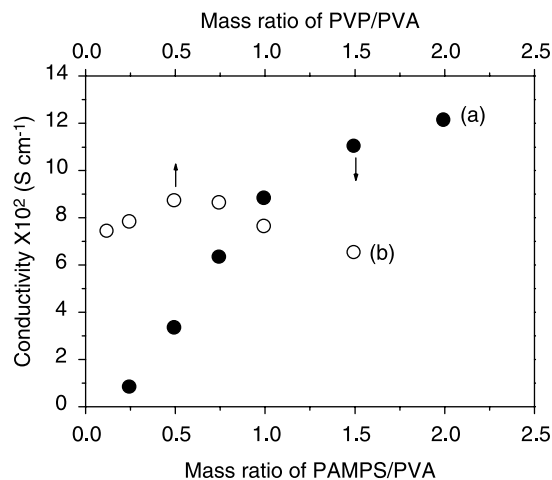


Fig. 7. Proton conductivity of the chemically cross-linked PVA–PAMPS–PVP membranes for different (a) PAMPS and (b) PVP contents in the blend. (a) PVA:PVP = 1:0.5 in mass. (b) PVA:PAMPS = 1:1 in mass.



It should be noted that PAMPS has a large influence on the mechanical stability of the blend membranes other than its effect on the proton conductivity. The membranes would become too brittle to endure even a slightly hard handling if the membrane was prepared from only PVA and PAMPS components. The addition of PVP to the blend was found to assist the relaxation of the polymer chains through its plasticizing effect, together with water molecules. The membranes obtained showed good mechanical property, wholly transparent appearance and high proton conductivity. In short, such a behavior may result from the opposing effect of water uptake (WU) and ion exchange capacity (IEC) of the PVA–PAMPS–PVP membranes, which will be discussed thoroughly in Section 3.4.

### 3.4. Water uptake (WU) and ion exchange capacity (IEC)

WU and IEC are known to have the profound effects on membrane conductivity. The proton conductivity will increase with increasing WU because the mobility of ions in the water phase increases with increasing water content (volume). Also, the proton conductivity increases with increasing IEC because of the high charge density of the membranes. Figs. 8 and 9 present the WU and IEC of the PVA–PAMPS–PVP membranes plotted as a function of PAMPS and PVP content in the polymer blend, respectively. The water uptake of PVA–PAMPS–PVP membranes increased gradually with PAMPS doping due to the strong hydrophilicity of the sulfonic acid groups (Fig. 8), if the cases at lower content of PAMPS were ignored, where a random water uptake at low PAMPS content was probably due to a phase separation. The IEC increased with increasing PAMPS content in the blend and then leveled off. This coincides with the proton conductivity as Fig. 7 shows, which indicates that a large PAMPS content plays a major role in controlling the proton conduction due to the increased sulfonic acid groups in the membrane. Thus, the maximum proton conductivity of  $0.088 \text{ S cm}^{-1}$  at  $25 \text{ }^\circ\text{C}$  in a polymer composition of PVA:PAMPS:PVP being 1:1:0.5 in mass, is the best value considering the practical usage, where the membrane becomes brittle with mass ratio of PAMPS:PVP above 1: 1.5 as described previously.

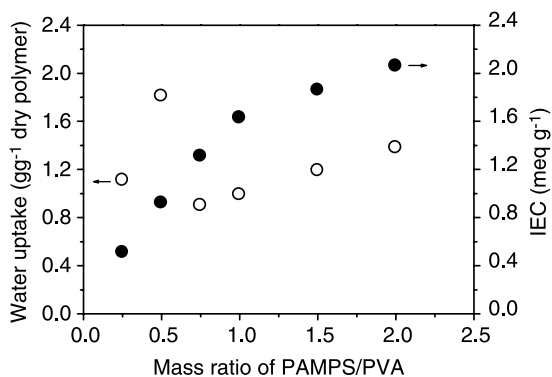


Fig. 8. Water uptake and IEC of the chemically cross-linked PVA–PAMPS–PVP membranes plotted as a function of PAMPS content in the blend. Here, PVA: PVP=1:0.5 in mass.

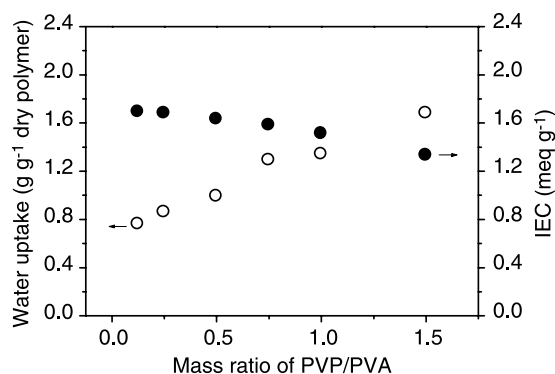


Fig. 9. Water uptake and IEC of the chemically cross-linked PVA–PAMPS–PVP membranes plotted as a function of PVP content in the blend. Here, PVA: PAMPS=1:1 in mass.

The conductivity profile related to PVP in Fig. 7 could also be explainable by the changes in the water uptake and the ion exchange capacity (IEC) as shown in Fig. 9. It should be noticed that the water uptake in the blend increased almost linearly with the content of PVP, however, the ion exchange capacity of the membranes changed inversely. This fact suggests that when the water content in the membranes is low at low PVP content, it is not enough to dissociate the  $\text{SO}_3\text{H}^+$  completely, which results in the decrease in the proton conductivity due to the associated ion pairs. In the opposite sense, large sorption of water at high content of PVP, does not simply give an improved proton conductivity but rather a dilution of charge carries like the cases for high content of PAMPS, thus the energy barrier for the proton transport increases, which would also lead to a decrease in proton conductivity. In other words, the density of charge carriers would decrease because of the increased hydrophilic effect of PVP, although the proton hopping in the blend may occur due to the protophilic nature (or basicity) of PVP.

### 3.5. Temperature dependence of proton conductivity

The temperature dependences of the proton conductivity of PVA–PAMPS–PVP blend membranes are illustrated in Fig. 10(a) and (b), where the membranes are prepared from different PAMPS and PVP contents, respectively. The membranes were tested from  $5$  to  $50 \text{ }^\circ\text{C}$ . All the membrane samples exhibited positive temperature-conductivity dependencies, which suggests a thermally activated process. The activation energy values  $E_a$  fall into the range of  $13$ – $16 \text{ kJ mol}^{-1}$  derived from the slope of  $\log \sigma \sim 1/T$  plots. These are similar to the  $E_a$  of Nafion 117, for which  $E_a = 14.6 \text{ kJ mol}^{-1}$  in its fully hydrated state obtained under the same measuring conditions. Because of the amide groups ( $-\text{C}-\text{NH}$ ) of PAMPS and the carbonyl groups ( $\text{C}=\text{O}$ ) of PVP and the cross-linker, GA, after chemical cross-linking (Figs. 1 and 3), it is reasonable to assume that the proton conduction occurs by two routes, that is, the protons transport via acid groups and amide groups of the polymer molecules through hydrogen bonding.

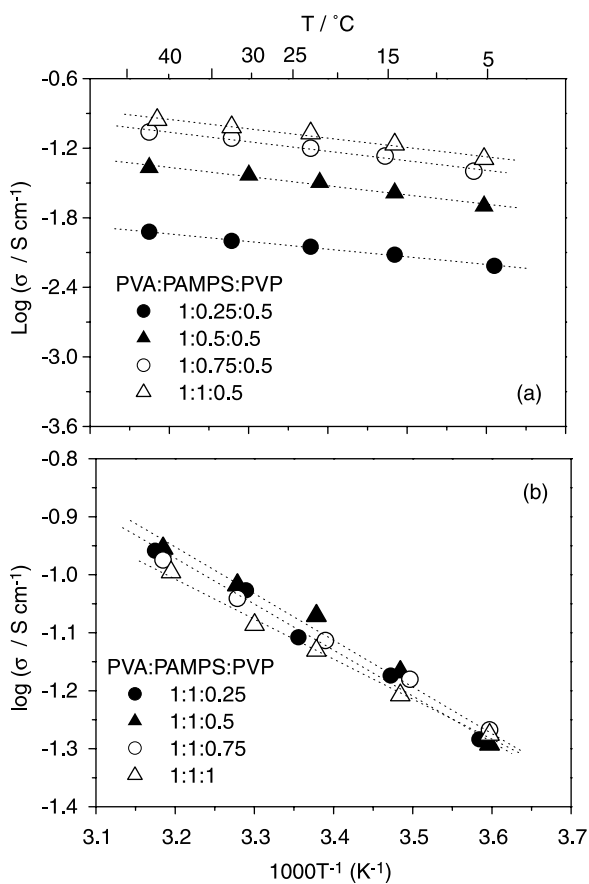


Fig. 10. Temperature dependences of the proton conductivity of chemically cross-linked PVA–PAMPS–PVP membranes with different (a) PAMPS and (b) PVP contents in the blend. (a) PVA:PVP=1:0.5 in mass. (b) PVA:PAMPS=1:1 in mass.

### 3.6. Membrane stability

To evaluate the stability of PVA–PAMPS–PVP blend membranes after chemical cross-linking, time dependent measurements of the proton conductivity at 25 °C and, the weight changes in 3 and 10%  $\text{H}_2\text{O}_2$  solutions at an elevated temperature of 60 °C were carried out, respectively. As an example, Fig. 11 shows the variation in the proton conductivity with time measured at 25 °C for the sample of PVA:PAMPS:PVP (1:1:0.5 in mass) soaked in pure water. As shown in Fig. 11, PVA–PAMPS–PVP membranes showed an excellent stability toward water for a long time without any decrease in proton conductivity (e.g. for 240 h, 25 °C). In fact, all the membrane samples exhibited a good hydrolytic stability without any changes in original appearance, flexibility, and toughness even after they had been immersed in 50 °C water more than a month, although both their WU and IEC are higher than that of Nafion 117. It can be assumed that the acetal ring is maintained and does not decompose in this moderate temperature. However, we do not assert that these membranes have relatively better hydrolytic durability than other aliphatic membranes in a diluted aqueous acid hot solution, on which the hydrolysis would be favored.

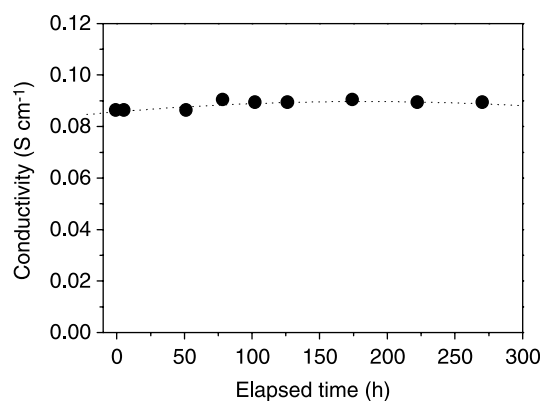


Fig. 11. Time course of the proton conductivity for chemically cross-linked PVA–PAMPS–PVP blend membranes soaked in pure water at  $25 \pm 2$  °C. Polymer composition of PVA:PAMPS:PVP=1:1:0.5 in mass.

The membrane samples showed a relatively high oxidative durability after they were immersed in  $\text{H}_2\text{O}_2$  solutions (Fig. 12). No noticeable weight change was observed after the membrane sample was immersed in 3%  $\text{H}_2\text{O}_2$  solution up to 100 h at 60 °C, and about 15% weight loss was observed after 240 h. When the membrane sample was immersed in 10%  $\text{H}_2\text{O}_2$  solution, an initial sharp decrease in weight percentage (30%) was observed within 20 h, and then the sample weight tends to maintain a constant value of about 60 wt% with no further weight losses again. Obviously, the chemical cross-linking modification, and especially the presence of PVP would play an important role in improving the membrane performances.

### 3.7. Methanol permeability

Fig. 13 gives the methanol permeability through PVA–PAMPS–PVP membranes, which are plotted as a function of both PAMPS (curve (a)) and PVP (curve (b)) content in the blend. For a comparison, methanol permeability of Nafion117 was measured under the same experimental conditions. The methanol permeability of Nafion 117 reported as  $1.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  at room temperature [30] is in good agreement

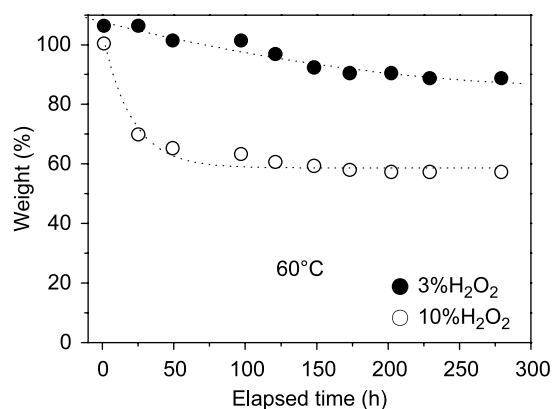


Fig. 12. Oxidative durability of the chemically cross-linked PVA–PAMPS–PVP blend membranes in 3 and 10%  $\text{H}_2\text{O}_2$  solutions at 60 °C, respectively. Polymer composition of PVA:PAMPS:PVP=1:1:0.5 in mass.

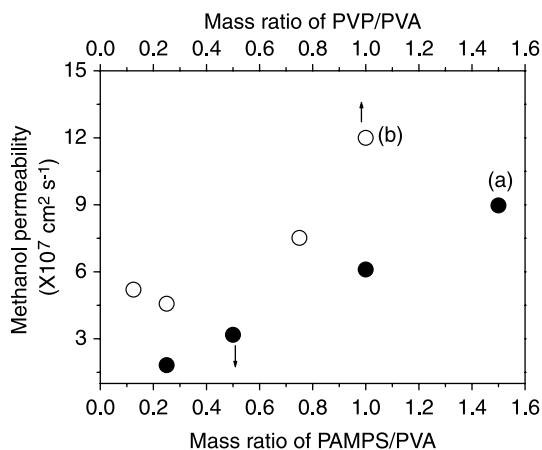


Fig. 13. Methanol permeability of the chemically cross-linked PVA–PAMPS–PVP membranes with different (a) PAMPS and (b) PVP contents in the blend. (a) PVA:PVP=1:0.5 in mass. (b) PVA:PAMPS=1:1 in mass.

with the present value of  $1.83 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  at  $24^\circ \text{C}$ . For PVA–PAMPS–PVP membranes, the methanol permeability increased with PAMPS content, due to an increased sulfonic acid groups attached to PAMPS. Similarly, methanol permeability also increased with additional high content of PVP owing to the hydrophilic property of PVP.

Generally, the methanol permeability was found to be proportional to the proton conductivity. As described in Section 3.6, the PVA–PAMPS–PVP membranes showed much larger water uptake than Nafion 117 ( $0.34 \text{ g g}^{-1}$  dry film, measured in this work). However, PVA–PAMPS–PVP membranes showed much lower methanol permeability than Nafion 117, even for the sample, where a polymer composition PVA:PAMPS:PVP was 1:1.5:0.5 or 1:1:1.5 in mass (where the membranes showed about 3.5 and 4.7 times larger WU value than Nafion 117, respectively) (Figs. 8 and 9). It can be concluded, therefore, that the effect of cross-linking in PVA–PAMPS–PVP membranes overcomes the swelling effect due to hydrophilic domains in the PAMPS. In particular, the addition of PVP was found to effectively inhibit the methanol permeation through the membranes, which is probably due to the strengthened hydrogen-bonding interaction with water. Eventually, the methanol permeability through PVA–PAMPS–PVP membranes is only one third of that of Nafion 117.

#### 4. Conclusions

New highly proton conductive polymer membranes PVA–PAMPS–PVP have been successfully developed using blending and chemical cross-linking procedures. The membrane showed the best proton conductivity of  $0.088 \text{ S cm}^{-1}$  at  $25^\circ \text{C}$  with a polymer composition PVA:PAMPS:PVP being 1:1:0.5

in mass, which is comparable to commercially available Nafion 117. Such an enhancement of proton conductivity can be attributed to the high water uptake and IEC. PVA–PAMPS–PVP blend membranes share not only excellent water stability at room temperature but also a relatively high oxidative durability at  $60^\circ \text{C}$ . In spite of their high WU and IEC, the PVA–PAMPS–PVP membranes revealed an effective methanol barrier. As a stabilizer, PVP plays an important role in providing the above membrane performances, and the methanol permeability ranged in  $10^{-7} \text{ cm}^2 \text{ s}$ , which is about one third of Nafion 117. Therefore, these novel proton-conducting membranes are potential candidates as polymer electrolytes for low temperature DMFC applications.

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