

Characterization of sulfonated poly(styrene-co-pyrrolidone) pore-filling membranes for fuel cell applications

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Abstract Pore-filling membranes using three monomers, i.e., styrene, N-vinyl pyrrolidone (VP), and divinylbenzene (DVB), are prepared for polymer electrolyte fuel cell (PEFC) applications. A porous polyethylene (PE) film substrate is used to enhance the dimensional stability of the prepared membranes. The proton conductivity and the water uptake of the styrene/VP/DVB membranes are similar to those of the styrene/DVB membranes, even though their ion exchange capacity is slightly lesser than that of the styrene/DVB membranes. Furthermore, the thermal stability of the styrene/VP/DVB membranes is higher than that of the styrene/DVB membranes, and, for the same DVB content, the membranes containing VP exhibit better oxidative stability. VP increases the membrane's water-absorbing ability due to its intrinsic hydrophilic property and decreases weak α -hydrogen derived from the sulfonated styrene. Finally, the membrane-electrode assembly (MEA) using the 80/10/10 (Styrene/VP/DVB in weight percentage) membrane shows better performance than that using the 90/0/10 membrane.

Keywords Styrene · N-vinyl pyrrolidone · Pore-filling membrane · Polymer electrolyte fuel cell · Oxidative stability

1 Introduction

Polymer electrolyte fuel cells (PEFCs) are considered as energy-efficient and environmentally friendly power source. PEFC systems contain a proton exchange membrane (PEM), which is essential for proton conduction and electron insulation. Common commercial PEM, or Nafion[®] (Dupont), which is a perfluorinated sulfonic acid polymer, is generally used in PEFCs due to its excellent oxidative stability and proton conductivity ($\sim 0.12 \text{ S cm}^{-1}$ at operating temperatures of PEFCs). However, its high cost and environmentally harmful by-products have limited its industrial application on a large scale. Thus, the development of alternative PEM materials has attracted considerable attention [1]. Accordingly, most studies have recently focused on the development of low-cost high-performance membranes. These studies have yielded various types of sulfonated hydrocarbon polymers such as ionomer membranes [2, 3], organic/inorganic hybrid membranes [4–8], and reinforced membranes [9–17]. Among the various types of PEMs, reinforced membranes are prepared using porous or non-porous polymer films such as polyethylene (PE), polytetrafluoroethylene (PTFE), and poly(ethylene-alt-tetrafluoroethylene) (ETFE). The reinforcement of the polymer films is associated with the improvement in mechanical strength and dimensional stability of the membranes by restricting membrane swelling in a wet state. Electrolyte monomers are introduced into the films by monomer sorption (to form the semi-interpenetrating network structure) or by the pore-filling method (to form

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the electrolyte-filling structure in porous polymer films). They are then synthesized by radiation grafting, thermal and/or photo polymerization, etc.

Styrene has been widely used as a monomer for the preparation of polymer electrolytes because it can be easily polymerized and sulfonated. However, the polymer electrolyte synthesized by styrene is so brittle that it hardly forms a film-type membrane. In addition, due to the weak benzylic hydrogen at the α -position of sulfonated polystyrene, it can be readily degraded by radical attack (HO^\bullet and/or HOO^\bullet) during PEFC operations (see Scheme 1a), resulting in poor durability [18]. Thus, many researchers have made an intensive effort to enhance the oxidative stability and the mechanical strength of styrene-based membranes without the loss of proton conductivity, using membrane reinforcing methods. Schmidt et al. prepared FEP-grafted membranes using DVB as a crosslinker. They reported the influence of cross-linking on the fuel cell performance of the membranes. The crosslinked membranes were more stable than the non-crosslinked membranes over the same period of time [10]. Fu et al. reported that the use of DVB greatly improved the oxidative stability of the styrene-based membranes but also resulted in a significant decrease in proton conductivity. The highly crosslinked membranes are chemically stable because they have an elaborated structure, restricting the diffusion of HO^\bullet radicals into the membranes. This chemically stable structure, however, limits the proton mobility in the polymer chain, resulting in a decrease in the proton conductivity of the highly crosslinked membranes [11]. Other approaches include the use of substituted styrene monomers in the polymer backbone. The substitution of the styrene monomers with protected α -positions or substituted aromatic rings, e.g., *m,p*-methylstyrene (MeSt) [12, 13], *p-tert*-butylstyrene (*t*BuSt) [12, 13], α -methylstyrene (AMS) [14], and α,β,β -trifluorostyrene (TFS) [19], along with crosslinkers such as divinylbenzene (DVB) and/or bis(*p,p*-vinyl phenyl) ethane (BVPE), improved the oxidative stability, with only a small loss in proton conductivity. Chen et al. prepared reinforced membranes using the substituted styrene monomers such as MeSt and *t*BuSt along with crosslinkers, DVB and BVPE, by radiation grafting and reported that these membranes have higher chemical stability than styrene-based membranes. Inclusion of *tert*-butyl on *t*BuSt has significantly increased the stability of α -hydrogen due to the different electronic structure of the benzene rings [12, 13]. Gubler et al. demonstrated that the use of AMS (with protected α -position) and DVB also led to an increase in membrane durability but caused IEC loss after the cell tests [13]. HOOKER Chemicals & Plastic Co. and RAI Co. used TFS to prepare grafted membranes that are chemically more stable. Severe oxidation tests demonstrated that the weight

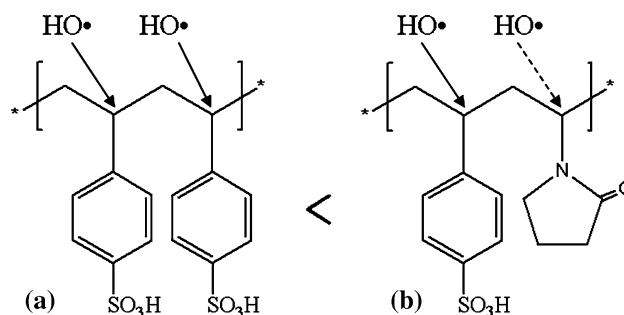
loss in the styrene membranes was much greater than that in the TFS-based membranes [19]. Thus, new styrene alternatives, which are chemically stable and minimize the decrease in ionic conductivity, are necessary for facilitating the use of styrene-based membranes in fuel cell applications.

In this study, we used N-vinyl pyrrolidone (VP) while preparing membranes by a pore-filling method to increase the oxidative stability while minimizing the conductivity loss of membranes. Styrene and DVB were used as a monomer and a crosslinker, respectively. VP was chosen as a substituting monomer because it has a stronger α -hydrogen position (see Scheme 1b) as well as remarkable water-absorbing properties with thermal stability. According to the results of previous studies [20–22], we expected that the use of VP would improve the chemical and thermal stability of the copolymers prepared in this study and result in a more homogenous distribution of the proton-conducting domain the membranes in order to minimize the loss of proton conductivity. Effects of VP on membrane properties such as proton conductivity, water uptake, thermal stability, and oxidative stability were investigated.

2 Experimental

2.1 Materials

A porous PE film (thickness 20 μm , porosity 38%, mean pore size 0.03 μm , SK energy, Republic of Korea) was rinsed with acetone and employed as a substrate. Styrene (inhibited by 4-*tert*-butylcatechol, Cat. No. S4972, Aldrich, 99%) and divinylbenzene (inhibited by 4-*tert*-butylcatechol, Cat. No. 169099, Fluka, 55 wt% isomer mixtures) (DVB) were used after purification using 6 M NaOH to remove the inhibitor in both monomer solutions. N-vinyl-2-pyrrolidone (VP), 2,2-azobis(isobutyronitrile) (AIBN), chlorosulfonic acid (97%), sulfuric acid (95%), NaOH, and HCl (37%) were used as received from Junsei Chemical.



Scheme 1 Possible sites for HO^\bullet radical attack on (a) sulfonated polystyrene and (b) sulfonated poly(styrene-co-vinyl pyrrolidone) (the dotted line represents the attack of the radical at the relatively strong α -position)

2.2 Preparation of pore-filling membranes

The porous PE film was immersed in monomer solutions for more than 5 min to fill the pores completely. The monomer solutions were prepared by mixing styrene, VP, and DVB with various compositions, as listed in Table 1. The monomer solution contained 0.25 wt% AIBN as an initiator for polymerization. After immersing the film in the solution, the monomer-impregnated PE was sandwiched between polyethyleneterephthalate (PET) films and thermally polymerized at 110 °C for 3 h under a nitrogen atmosphere.

2.3 Sulfonation of pore-filling membranes

The poly(styrene-co-vinyl pyrrolidone-co-divinyl benzene)/PE membranes were sulfonated using a chlorosulfonic acid/sulfuric acid mixture at 50 °C for 10 h. It is known that membranes sulfonated by excessive chlorosulfonic acid can be severely damaged by direct contact with cleaning water due to the high heat of dilution (560.12 kJ mol⁻¹) and the ensuing osmotic shock [23]. Thus, to prevent damage, the sulfonated pore-filling membranes were immersed in a 50 wt% dilute sulfuric acid solution for 1 h and then washed with deionized (DI) water several times. In order to convert the sulfonyl chloride groups (–SO₂Cl) into sulfonic acid groups (–SO₃H), the membranes were hydrolyzed in a 2 M NaOH solution for 6 h and then protonized in a 2 M HCl solution for 12 h. The sulfonated membranes were again washed several times with DI water to remove the remaining acid on the surface of the membranes. Finally, all the samples were immersed in toluene for 24 h to remove the unreacted monomers and were then washed with DI water several times.

2.4 Characterization of membranes

All the samples of the pore-filling membranes prepared in this study were named as x/y/(100-x-y), in order to represent the weight percentage of the styrene/VP/DVB mixture.

2.4.1 Measurement of scanning electron microscopy (SEM) and Fourier transform infrared attenuated total reflectance (FT-IR/ATR) spectroscopy

For SEM measurements, the samples, dried at 80 °C for 24 h under vacuum, were cryogenically fractured in liquid nitrogen and were then vacuum-sputtered with Pt/Pd. Each sample was characterized by scanning electron microscopy (S-4700, HITACHI).

The FT-IR/ATR analysis of the samples was carried out using a Nicolet 5700 to confirm the polymerization.

2.4.2 Thermal analysis

TGA analysis was carried out on a TGA 2050 instrument (TA Instruments) under a nitrogen atmosphere. Before the measurement, the samples were dried in a vacuum oven at 80 °C for 24 h to remove the residual water of the samples. The TGA chamber was heated up to 500 °C at a rate of 10 °C min⁻¹.

2.4.3 Water uptake

The water uptake of the samples was determined from the difference in sample weight before and after hydration. The samples were dried in a vacuum oven at 80 °C for 24 h and their weights (W_{dry}) were determined. The samples were then immersed in DI water for 24 h at room temperature. Water was removed from the sample surfaces, and the

Table 1 Monomer ratios for the prepared membranes and their properties compared with the properties of Nafion 112

Membranes	Monomer ratio (wt%)			Ion exchange capacity (meq g ⁻¹) ^a	Proton conductivity (S cm ⁻¹) ^b	Water uptake (%) ^c
	St	VP	DVB			
1	70	0	30	1.63	0.0326	27
2	70	10	20	1.66	0.0376	27
3	70	20	10	1.77	0.0419	26
4	70	25	5	1.78	0.0427	28
5	80	0	20	2.26	0.0451	34
6	80	10	10	2.32	0.0701	35
7 ^b	90	0	10	2.55	0.0729	40
Nafion 112	–	–	–	0.91	0.0802	22

^a Measured by the automatic titrator, Metrohm 848 TITRINO plus; calculated on the basis of the weight of dry membranes

^b Measured at room temperature

^c Used to test TGA and oxidative stability

weights of the samples (W_{wet}) were immediately determined. Water uptake was calculated using the following equation:

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

2.4.4 Ion exchange capacity

The ion exchange capacity of the membranes was determined through an acid–base titration with an automatic titrator Metrohm 848 TITRINO plus. The dry membrane was immersed in a 1 M NaCl solution, and this solution was titrated with 0.01 M NaOH solution to neutralize exchanged H^+ . Plotting the pH variation and the added titrant volume, the titrant volume at the equivalent point was determined. The ion exchange capacity (IEC) was calculated using the following equation:

$$\text{IEC} = \frac{V \times M}{m_{\text{dry}}} \quad (2)$$

where IEC is the ion exchange capacity (meq g^{-1}); V is the volume of the titrant added at the equivalent point (mL); M is the molar concentration of the titrant; and m_{dry} is the dry mass of the sample (g).

2.4.5 Proton conductivity

To measure proton conductivity, the samples were soaked in DI water for 24 h. The samples were 5 cm long and 5 cm wide. The proton conductivity of the samples was measured by impedance spectroscopy on a Solartron 1260 gain phase analyzer interfaced to a Solartron 1480 multi-stat. The measurement was carried out in potentiostatic mode in the frequency range of 0.1 Hz–10 MHz with 5 mV of oscillating voltage. A laboratory-made conductivity cell was used. The detailed configuration of this cell is found elsewhere [4]. The proton conductivity of the samples was calculated using the following equation:

$$\sigma = \frac{L}{RWd} \quad (3)$$

where σ is the proton conductivity of the samples, L the length of a voltage-detecting platinum wire, R the membrane resistance derived from the impedance value at zero phase angle, W the width between two voltage-detecting platinum wires, and d is the sample thickness.

2.4.6 Dimensional stability

The dimensional stability of the samples was characterized by measuring the thickness and area change of the samples from the dry state to the swollen state at room temperature. Two types of samples, i.e., a pore-filling membrane

(sulfonated hydrocarbon with the substrate) and Nafion 112, were used for the measurements. The initial sample size was 5' 5 cm.

2.4.7 Oxidative stability

The oxidative stability was characterized by measuring the weight loss of the samples with a size of 5' 5 cm, soaked in a 3 wt% H_2O_2 aqueous solution at room temperature. The samples were taken out of the solution and weighed immediately after removing the surface water every 12 h.

2.4.8 Membrane-electrode assemblies (MEA) fabrication and single cell test

The samples, i.e., 90/0/10, 80/10/10, and Nafion 112 membranes, were employed for single cell tests. The catalyst slurry was prepared using the mixture of Pt/C catalyst (40 wt%, Johnson Matthey), water, isopropyl alcohol (IPA) and Nafion solution (EW 1100, 5 wt%, Dupont) and was sonicated for 1 h. The Nafion solution was used as the ionomer binder in the electrodes for all the MEAs fabricated in this study. The gas diffusion electrodes (GDEs) were prepared by spraying the catalyst slurry onto the gas diffusion layer (25BC GDL, SGL Company). The loading amount of Pt catalyst at each electrode was 0.4 mg cm^{-2} . The MEAs were prepared by hot pressing at $120 \text{ }^\circ\text{C}$ under 30 kgf cm^{-2} . The effective cell area was 10 cm^2 . The unit cell was operated at $70 \text{ }^\circ\text{C}$ under atmospheric pressure with fully hydrated H_2/air (stoichiometry = 1.5/2.0). Prior to the measurement of the MEA polarization curves, all the MEAs were repeatedly conditioned by the activation procedure (OCV for 5 min, 0.7 V for 1 h, and 0.4 V for 1 h) until a constant current at 0.4 V was attained.

3 Results and discussion

The characteristics of the styrene/VP/DVB membranes mainly used in this study are summarized in Table 1.

3.1 FT-IR and SEM analyses

The successful polymerization was confirmed by the FT-IR spectra as shown in Fig. 1. All the prepared membranes exhibit the same absorption bands of styrene at 1,600 and $1,492 \text{ cm}^{-1}$ which are assigned to the stretching vibration of the skeletal benzene ring [11]. The absorption band at $1,510 \text{ cm}^{-1}$ (see Fig. 1a) is attributed to the bis-substituted structure of the benzene ring in DVB, and the band at $1,685 \text{ cm}^{-1}$ (see Fig. 1b) represents the amide carbonyl band of VP [24], indicating the successful polymerization of VP with styrene and DVB. For the sulfonated

membranes as shown in Fig. 1c, the absorption bands assigned to the sulfonic acid groups are observed at 1,006 and 1,033 cm^{-1} . The stretching vibrations of S=O are observed at 1,126 and 1,168 cm^{-1} .

Figure 2 shows the surface SEM images of the porous PE and the pore-filling membranes after sulfonation. Figure 2a presents the porous structure of the PE substrate. Figure 2b indicates that the porous substrate is completely filled by the sulfonated copolymer after the pore-filling and sulfonation steps.

3.2 Ion exchange capacity, proton conductivity, and water uptake

The proton conductivity, IEC, and the water uptake of the membranes are summarized in Table 1 and plotted in Fig. 3. Many researchers have reported that the IEC value of the styrene/DVB membranes decreased by increasing the amount of DVB [16, 25, 26]. This result indicates that only the mono-substituted benzene ring of styrene can be fully sulfonated. Therefore, it is assumed in this study that all the membranes containing the same styrene content would have nearly the same degree of sulfonation (DS). However, as shown in Fig. 3a, except water uptake, the IEC and the proton conductivity of the membranes having the same DS (i.e., the same styrene composition) increases when the amount of DVB decreases and accordingly the amount of VP increases, which differs from results of previous studies [16, 25, 26]. In case of the membranes containing 70 wt% styrene, the proton conductivity

increases from 0.0326 to 0.0427 S cm^{-1} and the IEC from 1.63 to 1.78 meq g^{-1} of dry membrane while the amount of DVB decreases from 30 to 5 wt%. The membranes containing 80 wt% styrene also show a similar trend. The styrene-based membranes with the same DS show no significant difference in the water uptake while the amount of DVB decreases (i.e., a decrease in the crosslinking density). Sawada et al. have reported the relationship between the crosslinking density and the water transport properties. As the crosslinking density decreased, the self-diffusion coefficient of water molecules increased, resulting in better channeling and clustering for proton transport by increasing the number of water molecules in each sulfonic acid (SO_3H) group. Consequently, the proton conductivity and the water uptake of the membranes increased as the crosslinking density decreased [27]. In this study, on the other hand, there was no significant change in water uptake. Although the amount of DVB decreased, it is due to the fact that the amount of VP accordingly increased and the amount of styrene was kept.

For the same DVB content (in other words, at the same crosslinking density), an increase in the amount of styrene implies that the number of sulfonation-available sites in the membrane increased. Similarly, it is observed that the proton conductivity increased with an increase in the amount of styrene, as shown in Fig. 3b. Interestingly, it is noted that the change in proton conductivity between the 80/0/20 and the 90/0/10 membranes in Fig. 3b is much greater than that between the 80/10/10 and the 90/0/10 membranes in Fig. 3b. This indicates that VP serves as a

Fig. 1 FT-IR/ATR spectra of the (a) styrene/DVB, (b) styrene/VP/DVB, and (c) sulfonated membrane

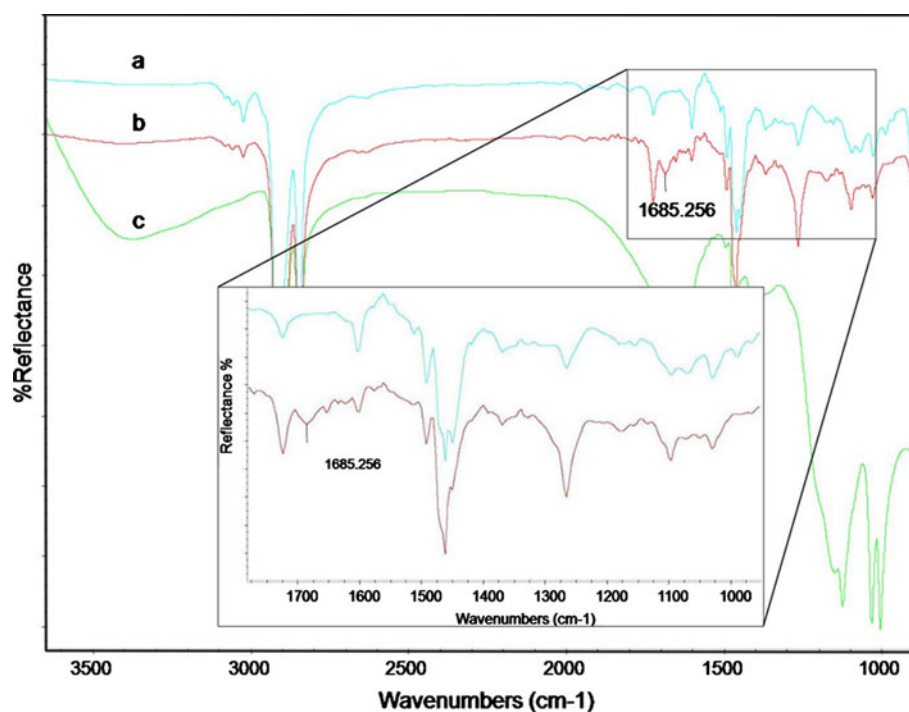


Fig. 2 Surface SEM images of **a** the substrate and **b** the sulfonated pore-filling membrane

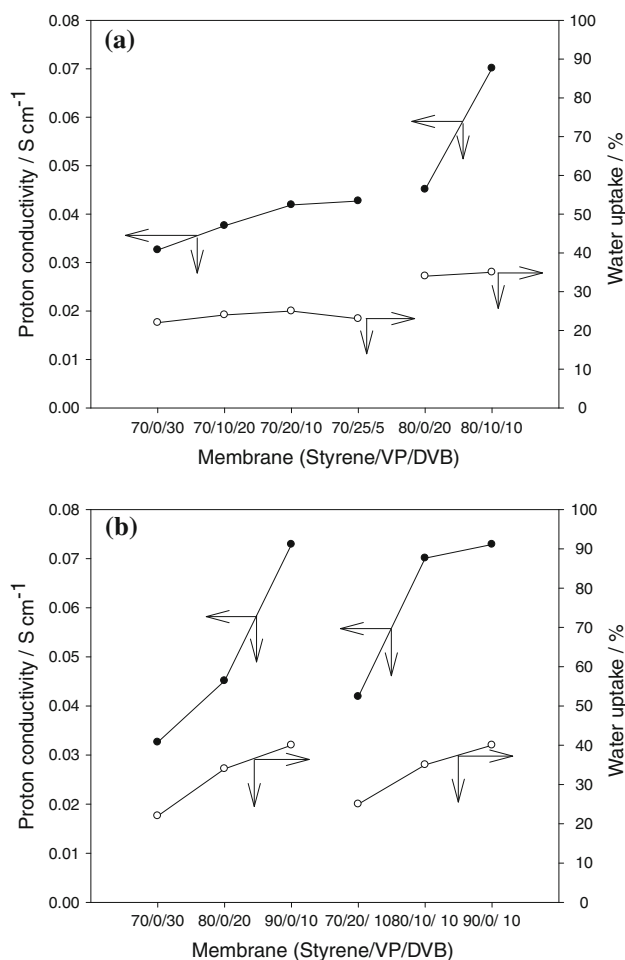
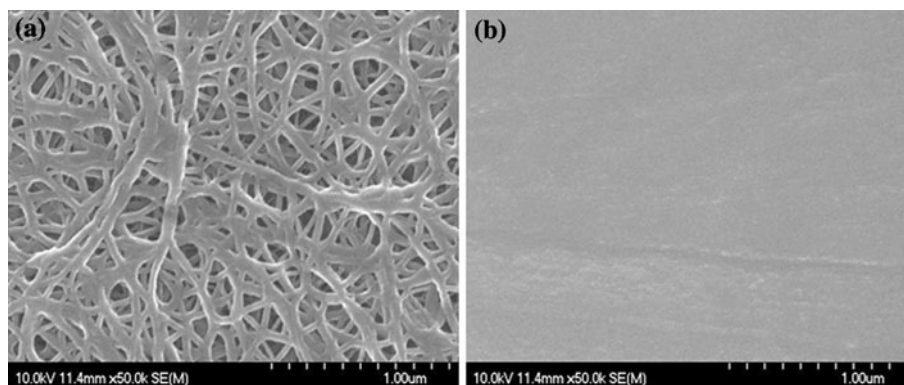


Fig. 3 Proton conductivity and water uptake of the prepared membranes at the same styrene content: **a** 70 wt% of styrene and 80 wt% of styrene, **b** no VP, and different VPs at the same DVB content

styrene alternative to decrease the crosslinking density and increase proton conductivity.

It is well known that VP is a hygroscopic material as discussed earlier. In this study, however, it is observed in Fig. 3a that the water uptake of the membranes containing VP does not increase with an increase in the amount of VP.

This indicates that the amount of VP introduced in this study is not sufficient for absorbing water. However, from Fig. 3, we found that the membranes containing VP showed higher proton conductivity at the same DS and decreased differences in proton conductivity between the 80/10/10 and 90/0/10 membranes as compared to the 80/0/20 and 90/0/10 membranes. It is implied that the membranes containing VP might have better inner water distribution even though total water content of those membranes is similar. Accordingly, the water-absorbed VP might contribute to water channeling and clustering, allowing for easier proton transport.

3.3 TGA analysis

As shown in Fig. 4, the thermal stability of the membranes copolymerized by VP and styrene with DVB was greater than that of styrene-DVB membranes. Some researchers have reported that the glass transition temperature, T_g , of membranes increased with increasing DVB or VP contents in the polymer composition [16, 22]. The TGA curves of the membranes (70/20/10, 80/10/10, and 90/0/10) are shown in Fig. 4. Only the membrane samples with a fixed amount of DVB were examined. The original PE film shows good thermal stability up to 400 °C and decomposes quickly above 450 °C. The pore-filling membranes show a broad decomposition peak of the electrolyte at 200–330 °C and the PE decomposition peak above 400 °C. This broad peak is present because the amount of polymer in the membranes is too small to distinguish each peak caused by desulfonation and backbone decomposition. In addition, it was found that the sulfonated membranes had approximately 20 wt% residuals above 500 °C, but the PE substrate decomposed completely. Chen et al. [12] and Nasef et al. [17] also found that the sulfonated membranes yielded about 20% residual character at the final heating temperature.

According to the TGA spectra, the temperatures of the 90/0/10, 80/10/10, and 70/20/10 membranes corresponding to 5% weight loss are 232, 248, and 254 °C, respectively.

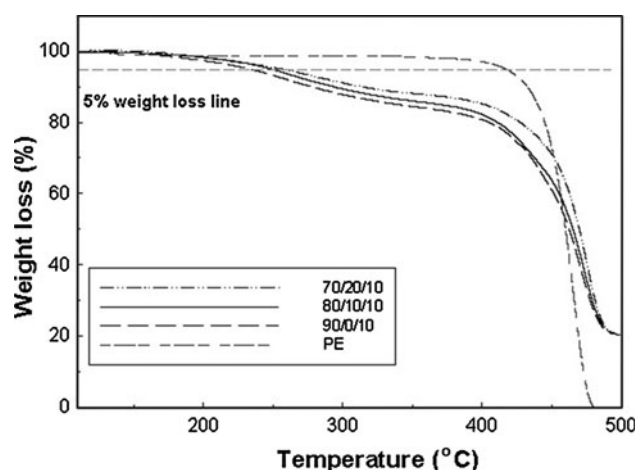


Fig. 4 TGA curves of the prepared membranes (Styrene/VP/DVB) at the same DVB content

The 70/20/10 membrane has good thermal stability but low proton conductivity. Inversely, the 90/0/10 membrane has good proton conductivity but low thermal stability. On the other hand, the 80/10/10 membrane has proton conductivity similar to the 90/0/10 membrane (see Fig. 4b) and similar thermal stability to the 70/20/10 membrane (see Fig. 5) due to the effect of VP.

3.4 Oxidative stability

During PEFC operations, styrene-based membranes are rapidly decomposed by the radical attack from HO^\bullet and/or HOO^\bullet , which is produced by the diffusion of oxygen through polymeric membranes from the cathode and/or by its incomplete reaction at the anode. It has been reported that membrane degradation by the radical attack

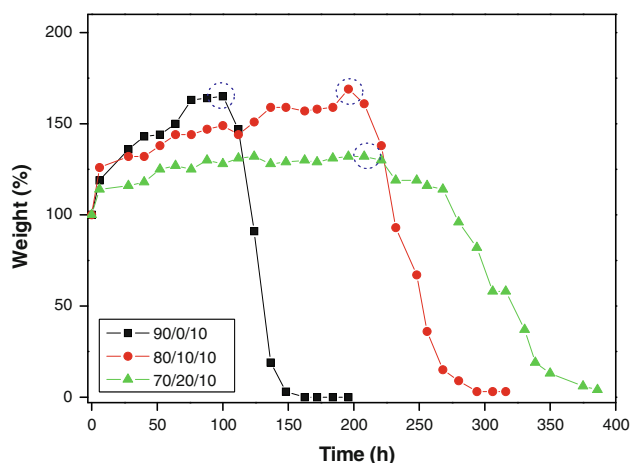


Fig. 5 Oxidative stability of the prepared membranes (Styrene/VP/DVB) at the same DVB content (the dotted circles represent the onset time of decomposition)

significantly reduced the durability of fuel cells for commercial applications [18]. As discussed earlier, the α -hydrogen derived from sulfonated polystyrene membranes is subjected to this radical attack, resulting in serious degradation of membranes. The effect of VP on the oxidative stability was investigated using membranes with the same DVB content (10 wt%), as shown in Fig. 5. The weight change of the membranes was measured as a function of reaction time in a 3 wt% H_2O_2 solution at room temperature. As a result, the oxidative stability of the 80/10/10 membrane containing VP was significantly improved, compared to the 90/0/10 membrane. Although the VP-containing membranes also have α -hydrogen in their backbone, the VP membrane has a stronger electronic structure, which can enhance the stability of α -hydrogen (see Scheme 1). In this study, the improvement in oxidative stability was due to the reduction of the α -hydrogen derived from sulfonated styrene by increasing the amount of unsulfonated VP and accordingly decreasing the styrene content.

3.5 MEA performance

In order to achieve high proton conductivity of styrene-based membranes, low crosslinking density and suitable styrene contents have been required so far. In this study, it is shown that the 80/10/10 membrane has fairly good proton conductivity, thermal stability, and oxidative stability, compared to the styrene-based membranes containing no VP (i.e., the 90/0/10 membrane). To assess the suitability of this membrane for PEFC applications, the polarization curves of the Nafion 112 and the prepared membranes (90/0/10 and 80/10/10) were measured, as shown in Fig. 6. Nafion 112 was used for reference cell performance. The current densities of the 90/0/10 and the 80/10/10 membranes at 0.6 V are approximately 160 and 290 mA cm^{-2} , respectively. Although the 90/0/10 membrane exhibits slightly higher proton conductivity than the 80/10/10 membrane, the 80/10/10 membrane showed better cell performance than the 90/0/10 membrane. In fuel cell operation, water for the hydration of electrolyte membranes is commonly fed by humidified fuel and air. The pore-filling membranes used in this study might easily be dehydrated during cell operation due to their low thickness (20 μm in this study). Compared to the 90/0/10 membrane, the 80/10/10 membrane, which has hydrophilic VPs in their backbone, is less sensitive to dehydration due to its water-absorbing ability. This could be the reason accounting for the enhanced cell performance of the 80/10/10 membrane. Another reason could be that decomposition of the 80/10/10 membrane, which might occur during the aforementioned repeated activation steps, was less due to its enhanced oxidative stability Fig. 7.

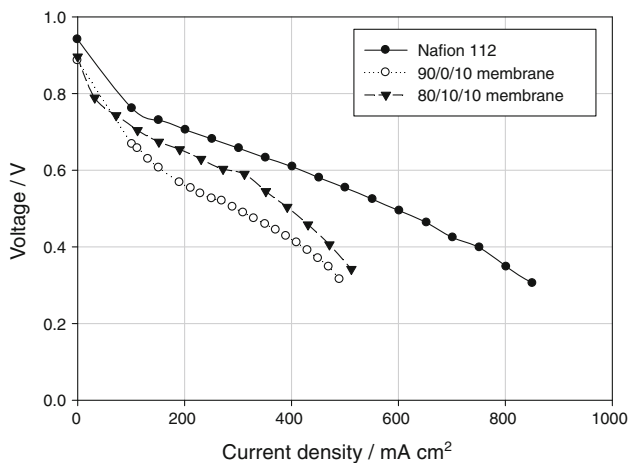


Fig. 6 Single cell performance of the Nafion 112 and prepared membranes (Styrene/VP/DVB) (0.4 mg cm^{-2} Pt/C, H_2/Air at 100% RH)

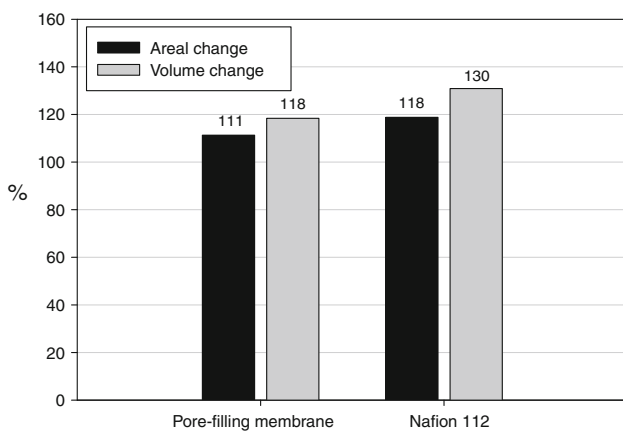


Fig. 7 Dimensional stability of the pore-filling membrane (Styrene/VP/DVB = 80/10/10) prepared in this study and Nafion 112

In comparison of the performance of Nafion 112, the activation overpotential of the 80/10/10 and 90/0/10 membranes (i.e., the voltage drop at the high voltage region from OCV (0.9 V) to 0.65 V) is higher than that of Nafion 112 (i.e., the voltage drop at the high voltage region from OCV (0.95 V) to 0.77 V). In addition, the mass transfer overpotential for the 90/0/10 and 80/10/10 membranes, which is defined by another voltage drop at high current density, begins at $\sim 400 \text{ mA cm}^{-2}$, but at $\sim 800 \text{ mA cm}^{-2}$ for Nafion 112. These high overpotentials of the styrene-based membranes may be due to the interfacial incompatibility between the hydrocarbon membrane and the perfluorinated ionomer binder arising from bad inter-adhesion. Lee et al. have reported the effect of the types of ionomer binders (SPEEK vs. Nafion) used in electrodes on the fuel cell performance of SPEEK membranes [28]. The MEAs using SPEEK ionomer

binders in the electrodes exhibited better performance than those using Nafion binders [28]. This result indicates that the use of the same type of polymers for the membrane and ionomer binder would decrease the interfacial incompatibility. In addition, Park et al. have reported that electrodes using the same type of ionomer binder as the electrolyte in MEAs required an optimal content of ionomer binders to achieve their best performance [29]. In the case of MEAs using different types of polymers for ionomer binders and electrolyte, higher activation and/or mass transfer overpotential can be obtained due to differential proton transfer, water drag, and water back diffusion between the electrolyte and electrode. Thus, if the electrodes in the MEAs fabricated in this study are optimized, the performance in the case of the styrene-based pore-filling membranes would be similar to that in the case of Nafion 112 (it should be noted that the proton conductivity of Nafion 112 is similar to that of the 80/10/10 and 90/0/10 membranes, as summarized in Table 1).

The dimension stability of MEAs during PEFC operations experiencing hydration/dehydration cycles is highly dependent on the dimensional stability of electrolyte membranes. As shown in Fig. 7, the pore-filling membrane (80/10/10) shows better areal and volumetric dimension stability than Nafion 112.

4 Conclusion

It was reported in this study that the pore-filling membrane prepared by styrene polymerization and subsequent sulfonation was a good candidate for PEFCs due to its low cost and ease of synthesis. In addition, a novel approach was employed for enhancing the oxidative stability of this membrane using VP. The introduction of VP, which is not sulfonated, increased the oxidative stability due to the reduction of the α -hydrogen derived from sulfonated styrene and minimized the loss of proton conductivity. In addition, the pore-filling concept might result in better durability for PEFC operations due to the enhancement of dimensional stability. It can be concluded that the introduction of VP and pore-filling concepts into styrene-based membranes can provide good electrolytes for PEFC applications. As a result, the 80/10/10 (Styrene/VP/DVB) membrane was considered to be an optimal electrolyte for PEFC operations.

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