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A facile method for the preparation of poly(vinylidene fluoride) membranes filled with cross-linked sulfonated polystyrene

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ABSTRACT

Pores of poly(vinylidene fluoride) (PVDF) membranes were filled with tetrabutylammonium 4-vinylbenzene sulfonate (TVS), a cross-linking agent, and a radical initiator in dimethyl sulfoxide, followed by radical polymerization and subsequent replacement of tetrabutylammonium ions by protons. This pore-filling method using an organic-soluble sulfonate monomer was very efficient and convenient, as it avoids the highly acidic sulfonation step. The dimensional changes in the length of the PVDF membranes filled with cross-linked sulfonated polystyrene were similar to Nafion 212, but their water uptakes were higher and they exhibited greatly improved mechanical moduli and elongations. Proton conductivities of the modified membranes were also higher than Nafion 212 under identical conditions.

1. Introduction

Perfluorosulfonic acid membranes, such as Nafion, have been widely used in polymer electrolyte membrane fuel cells (PEMFCs) because of their good mechanical properties, high thermal and chemical stability, high proton conductivity, and long-term durability [1–3]. However, those polymer membranes have some limitations such as high cost and low conductivity at high temperatures due to decreased humidity [4,5]. In order to overcome these limitations, alternative membranes such as poly(ether sulfone), poly(ether ketone), poly(phenylene), polyimide, poly(ether ether ketone) and polybenzimidazole have been developed [6–11]. Aromatic hydrocarbon polymers have appreciable thermal and chemical stability, and exhibit high proton conductivity when highly sulfonated. However, in general, such highly sulfonated polymer membranes exhibit severely decreased dimensional stability and mechanical strength due to excessive water uptake [12,13]. In order to overcome issues associated with excessive water uptake, cross-linked membranes, inorganic/polymer nanocomposite membranes, grafted membranes, and pore-filled membranes have been actively investigated [12–18].

Poly(vinylidene fluoride) (PVDF) membranes have been extensively used for scientific research and industrial processes because of their good mechanical properties and high thermal and chemical stability [19–21]. Yamaguchi et al. successfully imparted a proton-conducting property as well as hydrophilicity to porous PVDF membranes via pore-filling polymerization [18,22]. PVDF membranes filled with sulfonated polystyrene have also been prepared by filling the pores with styrene, irradiating with an electron beam, and sulfonating with chlorosulfonic acid [23]. Dobrovolsky and coworkers reported that PVDF membranes could be filled with a solution of styrene and divinylbenzene in toluene, followed by radical polymerization and subsequent sulfonation with sulfuric acid to prepare PVDF membranes filled with sulfonated polystyrene [24]. In these studies, sulfonic acid groups were incorporated into the PVDF membranes filled with polystyrene using sulfuric acid or chlorosulfonic acid. One problem associated with these pore-filling methods is degradation of the polymer chains [25].

The highly acidic sulfonation step would be avoided if styrene was replaced by sodium 4-vinylbenzene sulfonate. In other words, polymerization of PVDF membranes filled with sodium 4-vinylbenzene sulfonate would obviate the need of a sulfonation step. The ionic monomer, however, is not compatible with the hydrophobic PVDF membrane and does not efficiently fill the membrane pores. One possible way to overcome this pore-filling problem is to replace the sodium counterion with tetrabutylammonium ion, because the resulting ion-pair monomer, tetrabutylammonium 4-vinylbenzene sulfonate (TVS), will be organic-soluble.

In this study, sodium 4-vinylbenzene sulfonate was treated with tetrabutylammonium hydroxide to synthesize organic-soluble TVS. PVDF membranes were filled with TVS, *N*,*N*′-methylenebisacrylamide (cross-linking agent), and 2,2′-azobisisobutyronitrile (AIBN, initiator)

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in dimethyl sulfoxide (DMSO), followed by radical polymerization and subsequent washing with dilute HCl solution to replace the tetrabutylammonium ions with protons and to remove any unreacted cross-linking agent together with the monomer (Scheme 1). To the best of our knowledge, this is the first study of its kind where PVDF membranes filled with cross-linked sulfonated polystyrene (CSPS) were directly prepared using an organic-soluble sulfonate monomer without the highly acidic sulfonation step. In this study, the preparation of PVDF membranes filled with CSPS is described, together with their properties such as ion- exchange capacity (IEC), dimensional stability, thermal stability, mechanical properties, oxidative stability, and proton conductivity.

2. Experimental

2.1. Materials

PVDF membranes (thickness: 90 μm, porosity: 80%) were provided by Amogreentech, South Korea. Sodium 4-vinylbenzene sulfonate, DMSO, and *N*,*N*′-methylenebisacrylamide were purchased from Sigma-Aldrich Chemical Co. Tetrabutylammonium bromide was purchased from Sejinci Co. Hydrochloric acid (35–37%), 1.0 N hydrochloric acid solution, magnesium sulfate, sodium chloride, sodium hydroxide, methylene chloride, and acetone were purchased from Samchun Pure Chemical Co., Ltd. AIBN, aqueous phenolphthalein (1%), and hydrogen peroxide (35%) solutions were purchased from Dae-Jung Chemicals & Metals Co., Ltd. All the aforementioned chemical reagents and solvents were used as received.

2.2. Synthesis of TVS

Sodium 4-vinylbenzene sulfonate (1.0 g, 4.85 mmol) and tetrabutylammonium bromide (1.55 g, 4.85 mmol) were dissolved in water (6 mL) and acetone (5 mL), respectively, and the two solutions were mixed in a two-neck flask. The solution was left undisturbed at room temperature for 6 h under an argon atmosphere. Then, excess acetone was added to the reaction mixture to precipitate sodium bromide, and unreacted acetone was evaporated using a rotary evaporator. The residue was extracted with methylene chloride, and the mixture of organic solutions was dried over magnesium sulfate and concentrated using a rotary evaporator to yield a yellow gel-like product (2.0 g, 95%). ^{1}H nuclear magnetic resonance (NMR) (400 MHz, $CDCl_3$, ppm): 7.8–7.83 (d, 2H), 7.24–7.33 (d, 2H), 6.62–6.69 (dd, 1H), 5.68–5.73 (d, 1H), 5.19–5.27 (d, 1H), 3.19–3.24 (t, 8H), 1.53–1.61 (m, 8H), 1.32–1.41 (m, 8H), 0.92–0.95 (t, 12H). Elemental analysis: calculated for $C_{24}H_{43}NO_3S$: C 67.72%; H 10.18%; N 3.29% and S 7.53%. Found: C 67.10%; H 10.87%; N 3.46% and S 6.99%.

2.3. Preparation of PVDF–CSPS

PVDF membranes were immersed in a solution of TVS, *N*,*N*′-methylenebisacrylamide (cross-linking agent), and AIBN (radical initiator, 0.5 wt.% with respect to the total amount of TVS and cross-linking agent) in DMSO for 3 h. The following three weight ratios of TVS to *N*,*N*′-methylenebisacrylamide were used: 90:10, 85:15, and 80:20. The membranes were sealed between two glass plates, polymerized at 70 °C for 12 h in an oven, and then washed with methylene chloride to remove any unreacted compounds. The resulting membranes were immersed in a 1.0 N HCl solution and kept for 24 h to replace tetrabutylammonium ions with protons, washed with water, and dried in a vacuum oven. The resulting membranes filled with CSPS were designated PVDF–CSPS-10, PVDF–CSPS-15, and PVDF–CSPS-20, respectively, where the numbers indicate the loading of cross-linking agent with respect to the TVS used.

2.4. Instruments

Fourier-transform infrared (FTIR) spectra were recorded on a JASCO 4100E FTIR spectrometer under ambient conditions over the wave number range of 4000–600 cm^{-1}. ^{1}H NMR spectra were recorded on a JEOL FT-NMR (400 MHz) spectrometer in $CDCl_3$. Sample membranes were dried in a vacuum oven at 80 °C for 24 h before measurement, and the contact angles were measured directly after dropping water on the membrane surface (Surface Electro Optics Phoenix 150). Thermal stability of the sample membranes was measured on a SDT Q600 Thermogravimetric Analyzer at a heating rate of 10 °C/min under nitrogen atmosphere. Mechanical properties of the membranes (60 × 5 mm) were measured on a universal testing machine (UTM, LR5K Plus, Lloyd Instruments). All values were calculated thrice and their averages were measured. Membrane surface images were recorded on a field emission scanning electron microscope (FESEM, Hitachi SU-70).

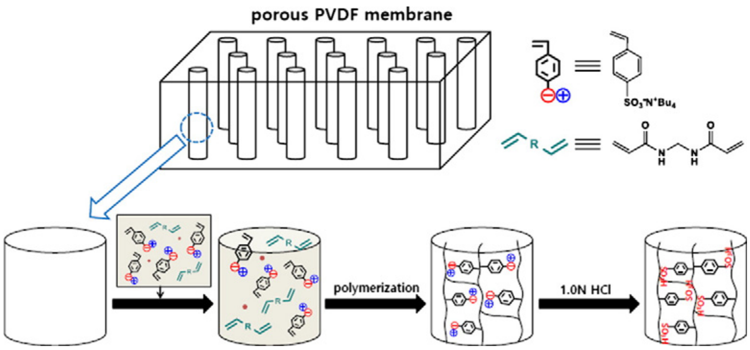
2.5. Measurements

2.5.1. Ion exchange capacity

The PVDF–CSPS membranes were immersed in a 2.0 N HCl solution and kept for 24 h. After washing several times with water, the samples were placed in an aqueous 3.0 M NaCl solution for 24 h, and then removed. The resulting solution was titrated with 0.01 N NaOH, and the IEC values were calculated from the following equation:

$$\mathrm{IEC\ (mmol/g)} = [C_{NaOH} \times V_{NaOH}]/W_{dry},$$

where C_{NaOH} is the concentration of NaOH solution, V_{NaOH} is the volume of NaOH solution, and W_{dry} is the weight of sample membranes.



Scheme 1. Experimental procedure for the preparation of PVDF membranes filled with cross-linked sulfonated polystyrene using organic-soluble TVS.

2.5.2. Dimensional stability and water uptake

The sample membranes were dried in a vacuum oven at 80 °C for 24 h, and then immersed in deionized water at 25 °C or 80 °C and kept for 1 day. Dimensional stability and water uptake of the membranes were calculated from the following equations:

$$\Delta L(\%) = \left[L_{wet} - L_{dry}\right]/L_{dry} \times 100$$
$$\text{Water uptake}(\%) = \left[W_{wet} - W_{dry}\right]/W_{dry} \times 100$$

where L_{wet} and L_{dry} are the lengths of the wet and dry membranes, and W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively.

2.5.3. Oxidative stability

The membranes were immersed in Fenton's reagent (3-wt.% H_2O_2 aqueous solution containing 2-ppm $FeSO_4$) at 80 °C and room temperature. Oxidative stability was calculated using the following equation:

$$\text{Oxidative stability }(\%) = [W/W_o] \times 100,$$

where W_o and W are the weights of the initial and remaining membrane, respectively.

2.5.4. Proton conductivity

Proton conductivity experiment was conducted on a SI-1260 (Solartron Company, USA). Impedance measurements were conducted on a four-electrode system over a frequency range of 0.01–100 kHz. The formula to calculate proton conductivity is as follows:

$$\sigma\ (S/cm) = L/AR,$$

where L is the distance between the two electrodes (cm), A is the cross-sectional area of the membranes (cm^2), and R is the electrical resistance of the membranes (Ω).

3. Results and discussion

TVS was prepared from sodium 4-vinylbenzene sulfonate and tetrabutylammonium bromide via ion exchange. The NMR spectrum (Fig. 1) and elemental analysis data confirmed that TVS was successfully synthesized with high purity. The obtained TVS was dissolved well in organic solvents such as methylene chloride, toluene, and DMSO.

In order to determine the pore-filling efficiency of TVS on the PVDF membranes, they were immersed in a solution containing TVS or sodium 4-vinylbenzene sulfonate together with *N*,*N′*-methylenebisacrylamide in water or DMSO at room temperature and kept for 3 h. The contents of the monomer and cross-linking agent in the water and DMSO solutions were 27 and 50 wt.%, respectively. Weight ratio of the monomers to the cross-linking agent was 90:10. The PVDF membranes filled with monomers and cross-linking agent were polymerized and purified using a method similar to the preparation of PVDF–CSPS membranes. As expected, TVS filled the PVDF membrane pores more efficiently than sodium 4-vinylbenzene sulfonate (42 vs. 0% in water; 62% vs. 29% in DMSO), because it is more organic-soluble than the latter. Weight increase of the membranes was higher in DMSO, because the monomers and cross-linking agent could be more highly concentrated in DMSO (27 wt.% in water vs. 50 wt.% in DMSO) due to its higher solubility, and the PVDF membranes are more wetted by DMSO.

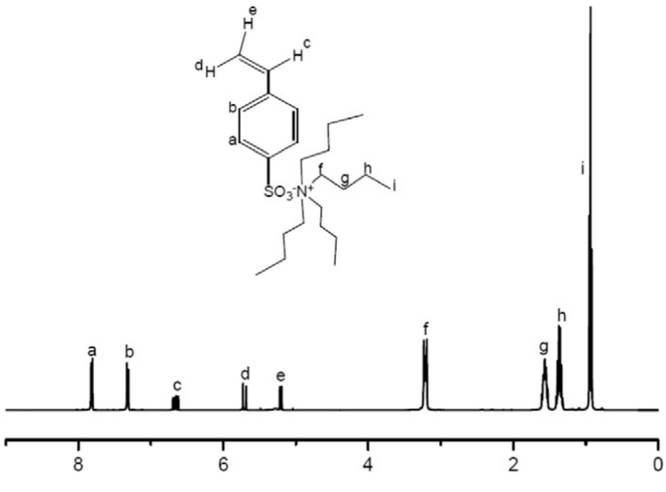


Fig. 1. ^1H NMR spectrum of TVS in $CDCl_3$.

Fig. 2 presents the weight increase of the membranes after pore-filling polymerization but before ion exchange with aqueous HCl solution. Initially, the weight of the membranes increased from 21% to 105% as the polymerization time extended from 2 to 8 h, and no considerable change was observed with further extension of polymerization time, up to 12 h. Thus, polymerization time was fixed at 12 h for this experiment.

The increase of weight due to CSPS with tetrabutylammonium ions filled in the membranes ranged from 97% to 105%. In order to replace tetrabutylammonium ions with protons, the membranes were immersed in 1.0 N HCl solution and kept for 1 day, washed with water, and dried. This decreased the weight of the membranes by 20–22% (calculated weight reduction: 22–26%), and the net weight increase was 57–62%. Dobrovolsky and coworkers reported that the weight increase of PVDF membranes (thickness: 90 µm, porosity: not provided) after polymerization of styrene and divinylbenzene for 12 h was approximately 40%, corresponding to a weight increase of about 50% after 100% sulfonation [24].

SEM images of the membranes indicated that the highly porous PVDF membrane was almost completely filled by CSPS (Fig. 3). After treatment with HCl solution, the membranes appear to be slightly less completely filled due to replacement of the large tetrabutylammonium ions with protons. In order to achieve complete filling of the membranes, the pore-filling procedure (pore-filling, polymerization, and treatment with HCl solution) was repeated for PVDF–CSPS-10. The weight increase of the twice pore-filled membrane was 81% with respect to the original PVDF. A SEM image indicated that the twice-polymerized membrane surface appears to be more completely filled even after treatment with HCl solution. However, the increment in water uptake was about 85%, indicating that the repeated pore-filling polymerization process significantly increased water uptake.

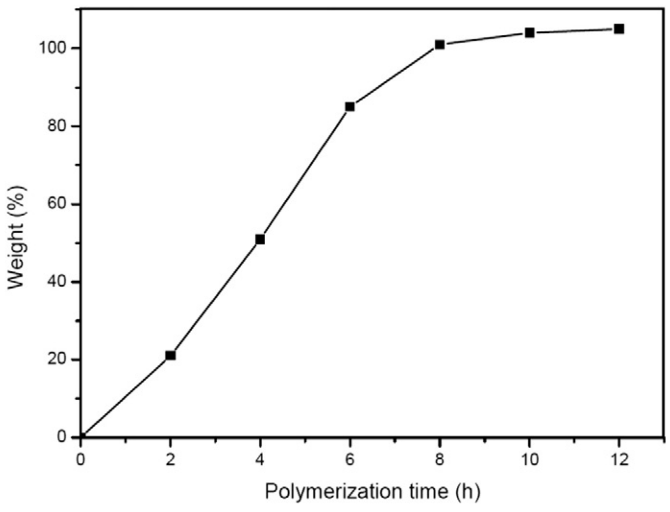


Fig. 2. Weight increase of PVDF–CSPS-10 membranes from the original PVDF membrane at different polymerization times (before replacement of tetrabutylammonium ions with protons).

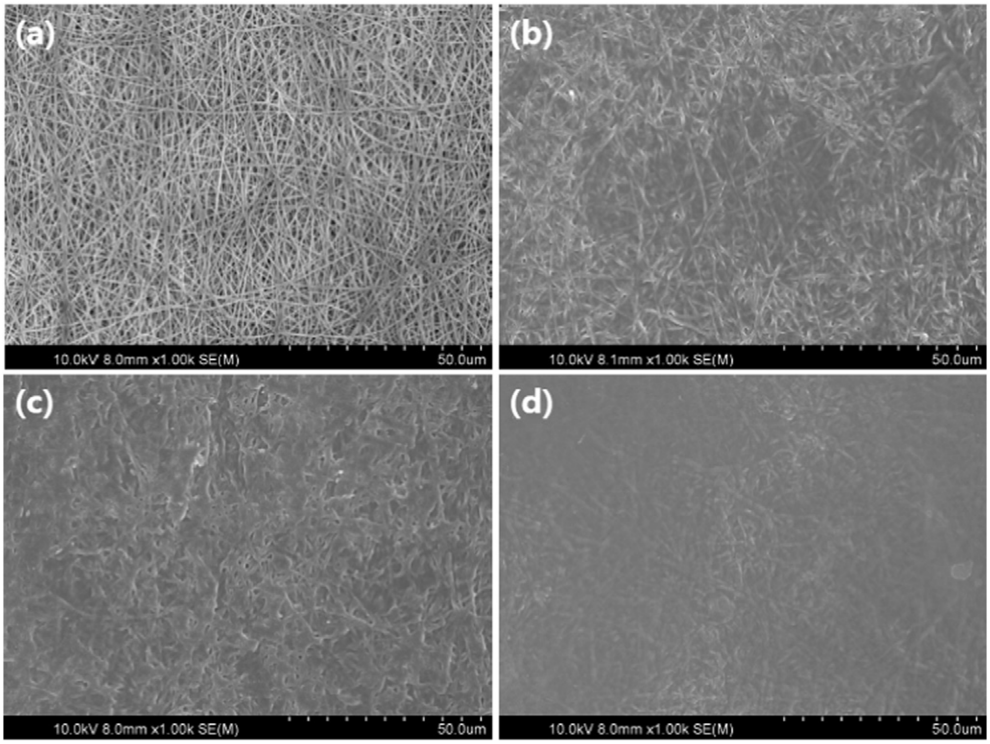


Fig. 3. SEM images of membrane surfaces: (a) original PVDF, (b) initial PVDF–CSPS-10, (c) PVDF–CSPS-10 after washing with 1.0 N HCl solution, and (d) PVDF–CSPS-10 after the second pore-filling polymerization and subsequent treatment with 1.0 N HCl solution.

Furthermore, the membranes became brittle. These results are probably due to the increased CSPS content in the PVDF membrane (62% vs. 81%). Thence, twofold pore-filling polymerization was not performed.

FTIR spectra of PVDF and PVDF–CSPS-10 membranes were recorded in attenuated total reflection (ATR) mode, and the results are shown in Fig. 4. The peaks due to C–F stretching vibrations of the PVDF membrane are observed at 1171 and 1121 cm^{-1} [26]. These membranes showed characteristic peaks for the sulfonic acid group at 1034 and 1006 cm^{-1}, an sp^2 C–H stretching peak at 3000 cm^{-1}, and aromatic C═C stretching peaks in the range of 1450–1600 cm^{-1}. A broad absorption peak in the range of 1700–1590 cm^{-1} may be due to amide carbonyl groups derived from the cross-linking agent. After replacing tetrabutylammonium ions with protons, the intensities of the sp^3 C–H stretching peaks decreased significantly, indicating the efficient removal of the former by HCl treatment.

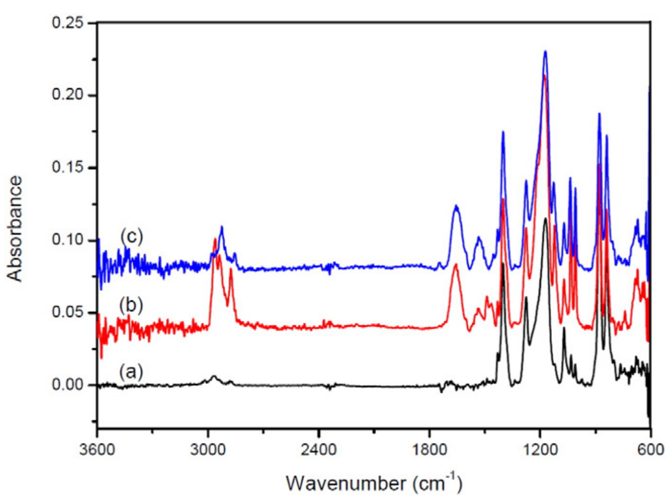


Fig. 4. FTIR spectra: (a) original PVDF and PVDF–CSPS-10 membranes (b) before and (c) after replacement of tetrabutylammonium ions with protons.

Experiments to determine thermal degradation behavior of PVDF and PVDF–CSPS membranes were conducted under nitrogen atmosphere, and the results are shown in Fig. 5. The weight of the PVDF membrane remained unchanged up to 400 °C and decreased rapidly by approximately 45% above 430 °C. On the contrary, the PVDF–CSPS membranes showed a two-step degradation behavior: (1) weight loss at 200–430 °C due to elimination of CSPS and (2) weight loss above 430 °C due to decomposition of the PVDF membranes. The degradation onset temperatures of the PVDF–CSPS membranes were not considerably affected by the content of cross-linking agent.

The IEC values of PVDF–CSPS-10, PVDF–CSPS-15, and PVDF–CSPS-20 were determined to be 2.1, 2.0, and 1.7 mmol/g, respectively (Table 1). The theoretical IEC value decreased from 2.9 to 2.3 mmol/g as the loading of the cross-linking agent was increased from 10 to 20 wt%, because

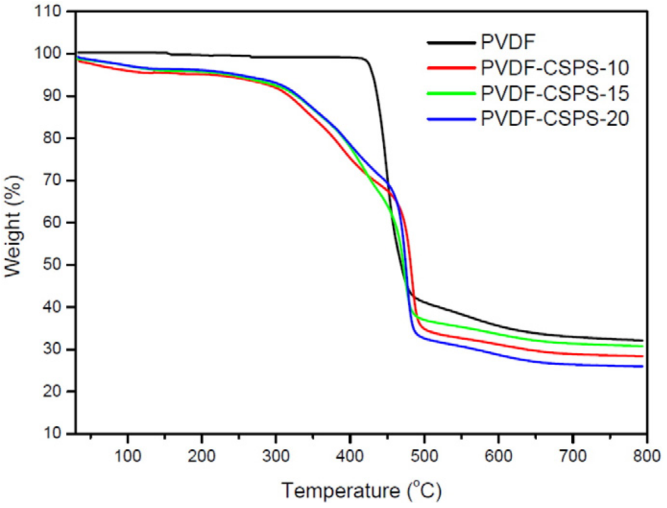


Fig. 5. TGA curves of the original PVDF and PVDF–CSPS membranes under nitrogen atmosphere (heating rate: 10 °C/min).

Table 1
IEC values, contact angles, dimensional stability, and water uptake of original PVDF, PVDF–CSPS, and Nafion 212 membranes.

Sample	IEC (mmol/g)		Contact angle (°)	ΔL (%)		Water uptake (%)	
	Calculated	Measured		25 °C	80 °C	25 °C	80 °C
PVDF	–	–	98	–	–	–	–
PVDF–CSPS-10	2.9	2.1	41	12	24	45	67
PVDF–CSPS-15	2.6	2.0	50	10	16	33	54
PVDF–CSPS-20	2.3	1.7	60	9	12	27	36
Nafion 212	–	0.9	–	5	20	16	20

of the decreased content of sulfonic acid groups at higher loadings of cross-linking agent. The experimental values of IEC were smaller than the theoretical counterparts. This is probably due to incomplete ion exchange between the sulfonic acid groups within the cross-linked membranes and NaCl [27]. Trace amounts of water present in the membranes even after drying in a vacuum oven may also contribute to the discrepancy. Dobrovolsky and coworkers reported IEC values of 2–2.4 mmol/g when the weight increment of cross-linked polystyrene was 40%, which is close to our IEC values [24]. However, it is difficult to directly compare our IEC values with those reported by the Dobrovolsky group because the loading of divinylbenzene and degree of sulfonation of polystyrene were not reported in their study.

The water contact angle was 98° on the original PVDF membrane surface (Table 1), but it decreased significantly on the pore-filled membranes. This indicates that the hydrophobic PVDF membranes became more hydrophilic after the pore-filling process, because the ionic polymer (CSPS) filled in the membranes is hydrophilic. As the content of the cross-linking agent increased from 10 to 20 wt.%, the water contact angle increased from 41° to 60°. This is probably because of the fact that hydrophobicity of the pore-filled PVDF membranes increases with an increase of the cross-linking agent content. This can be understood, as because the cross-linking agents are less hydrophilic than the sulfonated styrenes in the CSPS. The dimensional changes in length and water uptake of the membranes were measured at 25 °C and 80 °C in water, and the results are summarized in Table 1. It is evident from the table that the length increment and water uptake of the pore-filled PVDF membranes decreased with increased loading of cross-linking agent, because of increased cross-linking density. The dimensional changes in length of the membranes were similar to Nafion 212, but their water uptakes were relatively higher.

Mechanical properties of the PVDF, pore-filled PVDF, and Nafion 212 membranes were measured and listed in Table 2. The pore-filling polymerization process improved the tensile strength, but more significantly Young's modulus of the PVDF membrane. The improved tensile strength and Young's modulus of the pore-filled membranes can be attributed to the cross-linked network of the membranes. The elongations at break of the pore-filled PVDF membranes were also much higher than the original PVDF membranes. This might be due to moisture captured by sulfonic acid groups under experimental conditions. The elongation gradually decreased with an increase of cross-linking agent content, because of the increased cross-linking network and more restricted chain mobility between the polymer chains [27].

Oxidative stabilities of the membranes were measured using Fenton's reagent (2-ppm $FeSO_4$ + 3-wt.% H_2O_2) at 80 °C (Fig. 6a). The weight losses of PVDF–CSPS-10, PVDF–CSPS-15, and PVDF–CSPS-20 after 4 h were 28%, 15% and 4%, respectively. The increase of stability with cross-linking agent content is due to the more compact structure that restricts the diffusion of hydroxyl radical into the membrane. However, irrespective of the cross-linking agent content, the CSPS chains were almost completely lost from the PVDF membranes after 1 day. This indicates that the sulfonated polystyrene chains are decomposed and removed from the membranes under such conditions. Polystyrene-grafted poly(ethylene-*co*-tetrafluoroethylene) membranes were reported to be decomposed in 3-wt.% H_2O_2 + Fe^{2+} at 60 °C after several hours, and their oxidative stabilities were tested in 3-wt.%

Table 2
Mechanical properties and proton conductivities of PVDF, PVDF–CSPS and Nafion 212 membranes.

Sample	Mechanical property			Proton conductivity (S/cm)					
	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)	90% RH					30% RH
				30 °C	45 °C	60 °C	75 °C	90 °C	75 °C
PVDF	41	32	170	–	–	–	–	–	–
PVDF–CSPS-10	48	121	271	0.13	0.14	0.18	0.21	0.22	0.0104
PVDF–CSPS-15	55	152	268	0.1	0.12	0.15	0.19	0.21	0.0078
PVDF–CSPS-20	54	157	253	0.06	0.1	0.14	0.17	0.19	0.0034
Nafion 212	–	–	–	0.05	0.09	0.11	0.13	0.14	0.0068

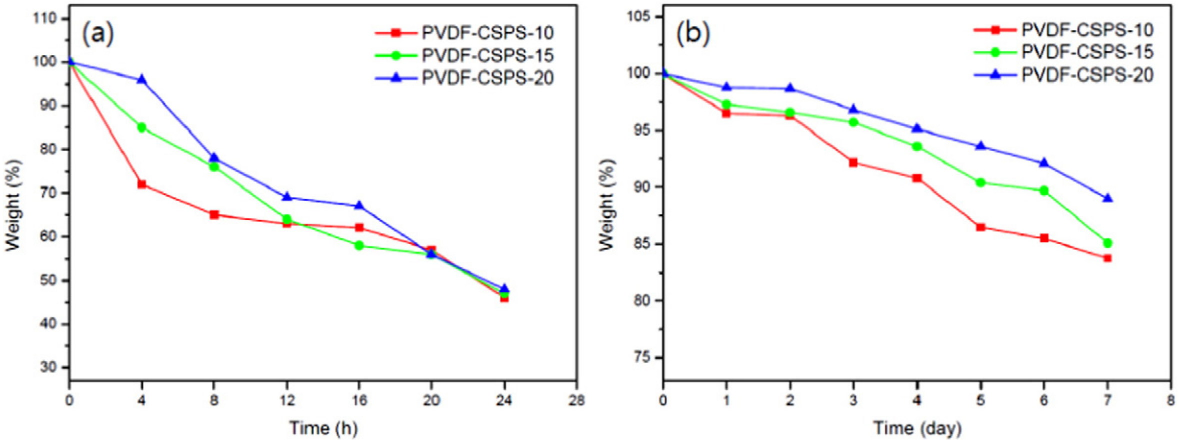


Fig. 6. Changes in the weight of PVDF–CSPS membranes with Fenton's reagent (2-ppm Fe^{2+} + 3-wt.% H_2O_2) at (a) 80 °C and (b) room temperature.

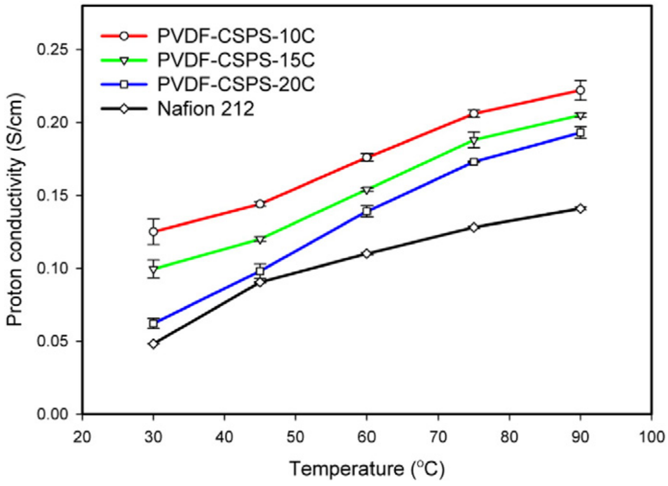


Fig. 7. Proton conductivities of pore-filled PVDF and Nafion 212 membranes.

H_2O_2 (without Fe^{2+}) at 60 °C [28]. Moon and coworkers also conducted experiments to determine the oxidative stability of sulfonated polystyrene/poly(vinyl chloride) composite membranes under similar conditions without Fe^{2+} [29], suggesting that our oxidation conditions might be too much accelerating. Thus, we repeated the stability test, but at room temperature, whose results are shown in Fig. 6b. After 7 days, the weight losses of PVDF–CSPS-10 and PVDF–CSPS-20 were only 16% and 11%, respectively. This clearly shows that the weight loss of the membranes could be decreased under mild reaction conditions and with increasing cross-linking agent content.

Proton conductivities of the pore-filled PVDF membranes, measured at various temperatures and a relative humidity (RH) of 90%, are presented in Fig. 7 and Table 2. It is thus evident that these values tended to decrease with an increased loading of cross-linking agent, as it decreases the IEC and increases the hydrophobic domain in the membranes, leading to a decreased water uptake. However, all of the pore-filled PVDF membranes exhibited higher proton conductivities than Nafion 212 at 90% RH in the temperature range studied, which might be due to their higher IEC values. A similar conclusion was also drawn by Dobrovolsky and coworkers, as the proton conductivity of their membranes with an IEC of ~2 mmol/g was slightly higher than that of Nafion 115 (0.015 vs. 0.011 S/cm at 30 °C and 75% RH) [24]. Proton conductivities of the PVDF membranes were also measured at 30% RH and 75 °C. As described earlier, these values decreased with an increase of the cross-linking agent content. However, they are found to be much lesser than those measured at 90% RH. This can be understood, as the membranes do not contain any additive that can retain water molecules under low humidity conditions.

4. Conclusions

TVS was synthesized and successfully used in the preparation of PVDF–CSPS membranes, which circumvented the need of a highly acidic sulfonation step. The increase of weight due to CSPS filled in the membranes ranged from 57% to 62%. The PVDF–CSPS membranes exhibited slightly higher water uptake and lower dimensional stability than Nafion 212. However, the mechanical properties and elongation at break from the original PVDF membranes were considerably improved. In addition, proton conductivities of the PVDF–CSPS membranes were found to be higher than Nafion 212 under identical conditions. The sulfonated polystyrene chains filled in the PVDF membrane pores were slowly decomposed under the oxidation-accelerating conditions (2-ppm Fe^{2+} + 3-wt.% H_2O_2) even at room temperature. However, these polymer membranes can find applications where high oxidation stability is not required. This strategy can be widely used for the preparation of polymer membranes filled with various types of ionic polymers.

Acknowledgments

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References

[1] K.A. Mauritz, R.B. Moore, State of understanding of Nafion, Chem. Rev. 104 (2004) 4535–4585.
[2] B. Smitha, S. Sridhar, A.A. Khan, Solid polymer electrolyte membranes for fuel cell applications—a review, J. Membr. Sci. 259 (2005) 10–26.
[3] N.W. Deluca, Y.A. Elabd, Polymer electrolyte membranes for the direct methanol fuel cell: a review, J. Polym. Sci. B Polym. Phys. 44 (2006) 2201–2225.
[4] M. Díaz, A. Ortiz, I. Ortiz, Progress in the use of ionic liquids as electrolyte membranes in fuel cell, J. Membr. Sci. 469 (2014) 379–396.
[5] M. Rikukawa, K. Sanui, Proton-conducting polymer electrolyte membranes based on hydrocarbon polymers, Prog. Polym. Sci. 25 (2000) 1463–1502.
[6] C.H. Park, C.H. Lee, M.D. Guiver, Y.M. Lee, Sulfonated hydrocarbon membranes for medium-temperature and low-humidity proton exchange membrane fuel cells (PEMFCs), Prog. Polym. Sci. 36 (2011) 1443–1498.
[7] C. Iojoiu, F. Chabert, M. Maréchal, N.El. Kissi, J. Guindet, J.-Y. Sanchez, From polymer chemistry to membrane elaboration: A global approach of fuel cell polymeric electrolytes, J. Power Sources 153 (2006) 198–209.
[8] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Alternative polymer systems for proton exchange membranes (PEMs), Chem. Rev. 104 (2004) 4587–4612.
[9] Q. Li, R. He, J.O. Jensen, N.J. Bjerrum, Approaches and recent development of polymer electrolyte membranes for fuel cells operating above 100 °C, Chem. Mater. 15 (2003) 4896–4915.
[10] R.Y.M. Huang, P. Shao, C.M. Burns, X. Feng, Sulfonation of poly (ether ether ketone) (PEEK): kinetic study and characterization, J. Appl. Polym. Sci. 82 (2001) 2651–2660.
[11] S. Han, M.-S. Zhang, J. Shin, Y.-S. Lee, 1,6-bis(4-vinylphenyl)hexane as a crosslinking agent for the preparation of crosslinked sulfonated poly(ether ether ketone) membranes by EB irradiation, Radiat. Phys. Chem. 97 (2014) 313–318.
[12] M. Han, G. Zhang, M. Li, S. Wang, Y. Zhang, H. Li, C.M. Lew, H. Na, Considerations of the morphology in the design of proton exchange membranes: cross-linked sulfonated poly(ether ether ketone)s using a new carboxyl-terminated benzimidazole as the cross-linker for PEMFCs, J. Hydrog. Energy 36 (2011) 2197–2206.
[13] C. Vogel, H. Komber, A. Quetschke, W. Butwilowski, A. Pötschke, K. Schlenstedt, J. Meier-Haack, Side-chain sulfonated random and multiblock poly(ether sulfone)s for PEM applications, React. Funct. Polym. 71 (2011) 828–842.
[14] A. Jasti, S. Prakash, V.K. Shahi, Stable zirconium hydrogen phosphate-silica nanocomposite membranes with high degree of bound water for fuel cell, React. Funct. Polym. 72 (2012) 115–121.
[15] D. Gupta, V. Choudhary, Non-fluorinated hybrid composite membranes based on polyethylene glycol functionalized polyhedral oligomeric silsesquioxane [PPOSS] and sulfonated poly(ether ether ketone) [SPEEK] for fuel cell applications, React. Funct. Polym. 73 (2013) 1268–1280.
[16] I. Honma, H. Nakajima, O. Nishikawa, T. Sugimoto, S. Nomura, Organic/inorganic nano-composites for high temperature proton conducting polymer electrolytes, Solid State Ionics 162 (2003) 237–245.
[17] K. Kato, E. Uchida, E.-T. Kang, Y. Uyama, Y. Ikada, Polymer surface with graft chains, Prog. Polym. Sci. 28 (2003) 209–259.
[18] T. Yamaguchi, F. Miyata, S. Nakao, Pore-filling type polymer electrolyte membranes for a direct methanol fuel cell, J. Membr. Sci. 214 (2003) 283–292.
[19] F. Liu, N.A. Hashim, Y. Liu, M.R.M. Abed, K. Li, Progress in the production and modification of PVDF membranes, J. Membr. Sci. 375 (2011) 1–27.
[20] G. Kang, Y. Cao, Application and modification of poly(vinylidene fluoride) (PVDF) membranes—a review, J. Membr. Sci. 463 (2014) 145–165.
[21] X. Chen, B. Zhao, P. Han, W. Fu, L. Chen, Temperature- and pH-sensitive membrane formed from blends of poly(vinylidene fluoride)-graft-poly(N-isopropylacrylamide) and poly(acrylic acid) microgels, React. Funct. Polym. 84 (2014) 10–20.
[22] H. Kang, M.-S. Lee, W.-J. Sim, T.-H. Yang, K.-H. Shin, Y.-G. Shul, Y.-W. Choi, Effect of number of cross-linkable sites on proton conducting pore-filling membranes, J. Membr. Sci. 460 (2014) 178–184.
[23] M.M. Nasef, N.A. Zubir, A.F. Ismail, M. Khayet, K.Z.M. Dahlan, H. Saidi, R. Rohani, T.I.S. Ngah, N.A. Sulaiman, PSSA pore-filled PVDF membranes by simultaneous electron beam irradiation: preparation and transport characteristics of proton and methanol, J. Membr. Sci. 268 (2006) 96–108.
[24] E.F. Abdrashitov, V.C. Bokun, D.A. Kritskaya, E.A. Sanginov, A.N. Ponomarev, Y.A. Dobrovosky, Synthesis and properties of the PVDF-based proton exchange membranes with incorporated cross-linked sulphonated polystyrene for fuel cells, Solid State Ionics 251 (2013) 9–12.
[25] K.G. Reed, The Development and Implementation of High-Throughput Tools for Discovery and Characterization of Proton Exchange Membranes(Doctoral Thesis) Georgia Institute of Technology, 2009.

[26] J. Sauk, J. Byun, H. Kim, Grafting of styrene on to Nafion membranes using supercritical CO_2 impregnation for direct methanol fuel cells, J. Power Sources 132 (2004) 59–63.
[27] E.-B. Lee, Q.B. Meng, J. Shin, Y.-S. Lee, Preparation and characterization of crosslinked sulfonated poly(ether ether ketone) membranes using 4-vinylbenzyl chloride via electron beam irradiation and subsequent friedel-craft reaction, Macromol. Res. 22 (2014) 1090–1095.
[28] J. Chen, M. Asano, T. Yamaki, M. Yoshida, Preparation and characterization of chemically stable polymer electrolyte membranes by radiation-induced graft copolymerization of four monomers into ETFE films, J. Membr. Sci. 269 (2006) 194–204.
[29] R.-Q. Fu, J.-J. Woo, S.-J. Seo, J.-S. Lee, S.-H. Moon, Sulfonated polystyrene/polyvinyl chloride composite membranes for PEMFC applications, J. Membr. Sci. 309 (2008) 156–164.