Journal of Membrane Science 362 (2010) 29–37

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Preparation and characterization of high-durability zwitterionic crosslinked proton exchange membranes

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ARTICLE INFO

Article history:
Received 28 November 2009
Received in revised form 31 May 2010
Accepted 2 June 2010
Available online 9 June 2010

Keywords:
Fuel cells
Polymer-electrolyte membrane
Sulfonated polymer
Crosslinked membranes
Proton conductor

ABSTRACT

The present paper describes the development of a novel proton exchange membrane comprising a poly (styrene sulfonic acid-co-4-vinylpyridine) copolymer that was crosslinked with a haloalkyl crosslinker through the formation of ionic bonding linkages. The nucleophilic substitution of these crosslinked membranes as well as a model reaction between pyridine and 1-bromobutane was confirmed by nuclear magnetic resonance (NMR). Tough and flexible membranes of a high mechanical strength were prepared. They demonstrated very elevated thermal, hydrolytic and oxidative stabilities as compared to other sulfonated polymers. The crosslinked membrane composed of zwitterionic molecules with a crosslinking fraction of 90.3, denoted SP-1, exhibited a proton conductivity of ca. 7.1×10^{-2} S cm^{-1} at 30 °C under 90% relative humidity; a value comparable to that of Nafion 117. Moreover, the crosslinked SP-1 membrane possessed the highest selectivity for methanol fuel cells (3.38×10^5 S cm^{-3} s), approximately five times that of Nafion 117, thus implying its potential for practical use in high-energy-density devices.

1. Introduction

Proton exchange membranes (PEMs) are key components in solid polymer electrolyte fuel cells (PEFCs) in which they provide an ionic pathway for proton transfer and prevent mixing of the reactant gases [1–4]. A large number of PEMs have been prepared from sulfonated aromatic polymers, including sulfonated poly(aryl ether sulfone) (SPES) [5,6], sulfonated polyphosphazene (SPOP) [7], poly(benzimidazole) (SPBI) [8,9], sulfonated polyimide (SPI) [10–12], and sulfonated poly(ether ether ketone) (SPEEK) [13,14]. In view of improving the performance of PEMs, crosslinking appears to be an efficient and simple approach for reducing the degrees of methanol diffusion and water uptake while enhancing the mechanical properties and dimensional stability. Numerous reports have been dedicated to the methods for crosslinking polymer-electrolyte membranes, and techniques include the ionic crosslinking of acid/base blend membranes (e.g., Nafion/polyaniline composites) [15], the sulfonation of polysulfone/polybenzimidazole (SPSF/PBI) [16] the UV-assisted photo-crosslinking of SPEEK [17–20], the sulfonation of poly(phthalazinone ether ketone) (SPPEK) [21], the covalent crosslinked polyvinyl alcohol (PVA) [22,23], and the covalent crosslinked SPEEK [24,25]. Nevertheless, these crosslinked polymer-electrolyte membranes usually display significant losses in proton conductivity due to low water uptake values caused by the crosslinking structure. Consequently, improving the chemical and mechanical stabilities of sulfonated polymer membranes without detrimentally affecting their proton conductivity and methanol crossover still remains an important challenge.

Although polymers derived from 4-vinylpyridine (4VP) have been quaternized with alkyl halides [26,27] to form crosslinked polymers for use in anion-exchange membranes [28,29], relatively few studies have exploited the role of zwitterionic crosslinked membranes in PEMs [30]. The present study describes the synthesis of poly(styrene sulfonic acid-co-vinylpyridine) (NaSS-4VP) and its reaction with a crosslinker containing haloalkyl groups with the aim of forming zwitterionic crosslinked membranes exhibiting high oxidative and hydrolytic stabilities, adequate mechanical properties, a high proton conductivity, and a low methanol crossover relative to those of other sulfonated polymers.

2. Experimental

2.1. Materials

4-Styrenesulfonic acid sodium salt hydrate (NaSS), 4-vinylpyridine (4VP), poly(4-vinylpyridine) (P4VP), potassium disulfite ($K_2S_2O_5$) and 1,10-dibromodecane were purchased from

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doi:10.1016/j.memsci.2010.06.004

Sigma–Aldrich. All other chemicals were of reagent grade, obtained from Sigma–Aldrich and used as received.

2.2. Synthesis of poly(styrene sulfonic acid-co-vinylpyridine) (NaSS-4VP)

The NaSS-4VP copolymer was synthesized according to Scheme 1 through a free radical polymerization in deionized water at 70 °C under a nitrogen atmosphere for 8 h. The chosen reaction conditions were: $[M]_{total}$ = 4.5 M, the initiator of $[K_2S_2O_5]$ = 1 wt%, and monomer feed ratios of ([NaSS]:[4VP] = 3:2 mol%). The resulting solution was precipitated into acetone and the NaSS-4VP polymer was filtered off, washed three times with acetone, and then dried under vacuum at 80 °C for 12 h. The copolymer structure and compositions were determining ^{1}H NMR (using integral area of chemical shifts of monomer functional groups for quantitative analysis). The mole ratio of NaSS to 4VP was determined to be 1.58:1 (25 °C, d_6-DMSO).

^{1}H NMR (DMSO-d_6): δ = 0.65–2.39 (d), 6.05–7.15 (c), 7.15–7.89 (a), 7.89–8.81 (b) ppm; ^{13}C NMR (DMSO-d_6): δ = 122.8–124.5 (f), 125.6–126.9 (b), 126.9–128.2 (c) 144.9–147.2 (a and d), 149.3–151.2 (e), 153.2–155.0 (g) ppm; IR: 1555 ($\nu_{C=N}$ pyridine), 1040 (ν_{asym} S=O), 1010 (ν_{sym} S=O) cm^{-1}; Intrinsic viscosity (IV, in DMSO at 30 °C): 2.83 dl g^{-1}.

2.3. Film casting and membrane acidification

Desired amounts of NaSS-4VP and the haloalkyl crosslinker 1,10-dibromodecane (cf. Table 1; molar ratio of pyridine groups of NaSS-4VP to 1, 10-dibromobutane for SP-1, SP-2, SP-3 and SP-4 was 1:1, 4:3, 2:1 and 4:1) were dissolved in order to give rise to a 10 wt% solution in DMSO at room temperature which was then stirred for 2 h. The resulting solution was cast onto a glass plate and heated at 60 °C for 48 h in order to complete the crosslinking reaction. The dried membrane was soaked in methanol at room temperature to remove the residual solvent, and then peeled from the glass plate upon immersion in deionized water. The crosslinked NaSS-4VP membrane in acidic form (SS-4VP) was obtained after immersion in a 2 M HCl solution for 48 h and washing with deionized water until the pH reached 6–7.

2.4. Characterization of the membranes

2.4.1. Copolymer characterization

^{1}H NMR spectra were recorded at 25 °C using an INOVA 500 MHz NMR spectrometer. FTIR spectra were obtained with a Nicolet Avatar 320 FTIR spectrometer; 32 scans were collected at a spectral resolution of 1 cm^{-1} (25 °C, d_6-DMSO).

2.4.2. Water uptake and ion-exchange capacity of the membranes

The ion-exchange capacities (IECs) were determined by titration. A membrane in H^+ form was first equilibrated in 1.0 M NaCl solution for 24 h to exchange the protons with sodium ions. Subsequently, the membrane was removed and rinsed with deionized water. The rinse water was then collected and combined with the NaCl solution, which was titrated with 0.01 mol L^{-1} NaOH using a 0.1% phenolphthalein solution in ethanol/water as the end-point of exchangeable protons to the weight of the dry membrane (W_{dry}, g).

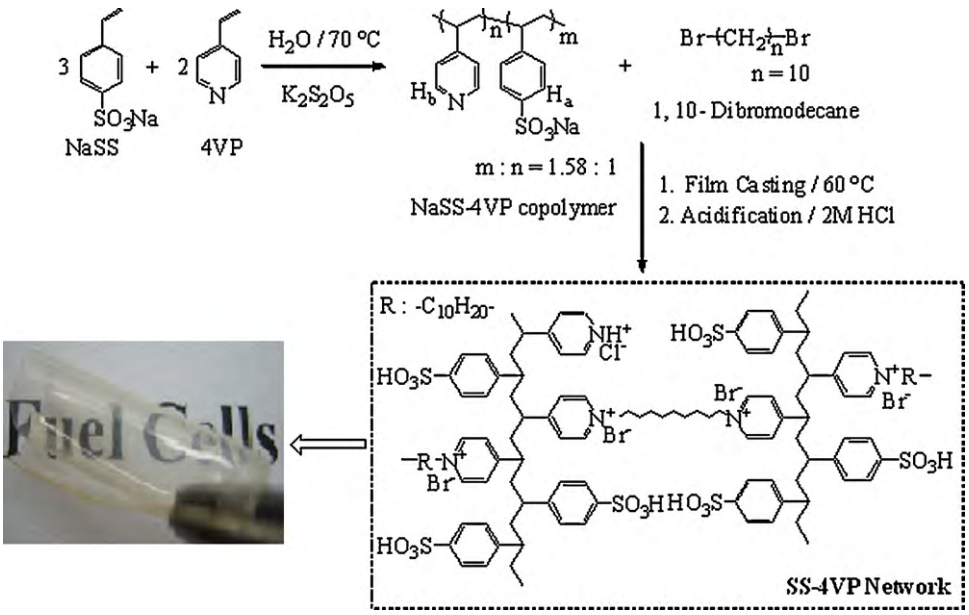
$$\mathrm{IEC} = \frac{C_{\mathrm{NaOH}} V_{\mathrm{NaOH}}}{W_{\mathrm{dry}}} \quad (1)$$

The completely dry crosslinked SS-4VP membranes were immersed in deionized water at room temperature for 24 h and were then swiftly extracted, blotted with filter paper to remove any excess water from the membrane surfaces, and immediately weighed to obtain their wet masses (W_{wet}). Subsequently, the

Table 1
Characteristics of the crosslinked SS-4VP membranes.

Sample	Polymer content (wt%)	Crosslinker content (wt%)	Crosslinking fraction (mol%)[a]	Ion-exchange capacity (mequiv g^{-1})		Water uptake (%)	Methanol uptake (%)	Proton conductivity (S cm^{-1})[d]	Methanol permeability × 10^{-6} (cm^2 s^{-1})	Selectivity × 10^5 (S cm^{-3} s)
				Calculated IEC_{th}[b]	Titration IEC_{tit}[c]					
SP-1	74.6	25.4	90.3	2.52	2.41	53.1	24.5	0.071	0.21	3.38
SP-2	79.5	20.5	72.8	2.84	2.65	62.5	26.1	0.082	0.39	2.10
SP-3	85.5	14.5	48.1	3.42	3.33	86.3	28.9	0.110	1.75	0.63
SP-4	92.2	7.8	23.9	4.06	3.83	142.4	30.2	0.143	6.46	0.22
Nafion 117	–	–	–	–	1.02	35.6	62.1	0.093	1.31	0.71

[a] Molar ratio of crosslinked pyridine units to total pyridine units.
[b] IEC calculated from DS.
[c] IEC measured with titration.
[d] Measured at 30 °C and 90% RH.



Scheme 1. The network structure of the crosslinked SS-4VP membranes.

membranes were dried at 120 °C for 24 h before their dry weights (W_{dry}) were measured. The water uptake (WU %) was calculated according to the following equation:

$$\text{WU}\ (\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (2)$$

2.4.3. Mechanical and thermal properties

The mechanical properties of the wet membranes were measured by Instron-1211 at the test speed of 2 mm/min, the size of the specie is 60 mm × 10 mm. For each testing, three measurements at least were recorded and average value was calculated. A DuPont Q100 thermogravimetric analyzer (TGA) was utilized to investigate the thermal stability of the membranes; the samples (~10 mg)were preheated to 150 °C for 15 min to remove resdiual water before measured, then heated from ambient temperature to 850 °C under a nitrogen atmosphere at a heating rate of 20 °C/min.

2.4.4. Oxidative and hydrolytic stability

Oxidative stability of the membranes was tested by immersing the films into Fenton's reagent (30 wt% H_2O_2 containing 30 ppm ferrous ammonium sulfate) at 80 °C. The oxidatve stability was evaluated by recording the time when the membranes was dissolved completely. The proton conductivities of membranes plotted with respect to the time they were exposed to Fenton's reagent (30 wt% H_2O_2 containing 30 ppm ferrous ammonium sulfate) at 30 °C. The resultiing membranes were immersed in deionized water at room temperature for 12 h and were then measured using an electrode system. Hydrolytic stability of the membranes was tested proton conductivities and weight loss for membrane after soaking in water at 100 °C. The proton conductivity of these membranes was measured at 30 °C and 90% RH. The electrode system and electrochemical procedure was according Section 2.4.5.

2.4.5. Proton conductivity

The proton conductivity of the membrane was determined with an ac electrochemical impedance analyzer (PGSTAT 30), and the experiments involved scanning the ac frequency from 100 kHz to 10 Hz at a voltage amplitude of 10 mV. The membrane (1 cm in diameter) was sandwiched between two smooth stainless steel disk electrodes in a cylindrical PTFE holder. The cell was placed in a thermal and humid controlled chamber for measurement. At a given temperature and humidity, the samples were equilibrated for at least 30 min before any measurement. Repeated measurements were taken at that given temperature with 10 min interval until no more change in conductivity was observed. The proton conductivity of the membrane was calculated from the observed sample resistance from the relationship:

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

where σ is the proton conductivity (in S cm^{-1}), L is the distance between the electrodes used to measure the potential (L = 1 cm). R is the impedance of the membrane (in ohm), which was measured at the frequency that produced the minimum imaginary response, and A is the membrane section area (in cm^2)

The activation energy (E_a, kJ mol^{-1}), which is the minimum energy required for proton transport, was obtained for each membrane from the gradients of Arrhenius plots based on the following equation:

$$\sigma = \frac{-E_a}{RT} \quad (4)$$

Here, σ is the proton conductivity (in S cm^{-1}), R is the universal gas constant (8.314 J mol^{-1} K), and T is the absolute temperature (K).

2.4.6. Methanol permeability and water desorption

The methanol diffusion coefficient of the membrane was measured using a two-chamber liquid permeability cell. A detailed description of this cell can be found elsewhere [22–25]. Water desorption measurements were carried out on a TGA Q100 to determine the weight change of the sample over time at 60 °C. The water diffusion coefficient was calculated according Ref [34].

2.4.7. Membrane morphology

The membrane morphologies were characterized using a JEOL JEM-1200CX-II transmission electron microscope (TEM) operated at 120 kV. To stain the hydrophilic domains, the membrane was converted into its Pb^{2+} form by immersing in 1 N $Pb(Ac)_2$ [lead(II) acetate] solution overnight and then rinsing with water. The membrane was dried under vacuum at 80 °C for 12 h and then the sample

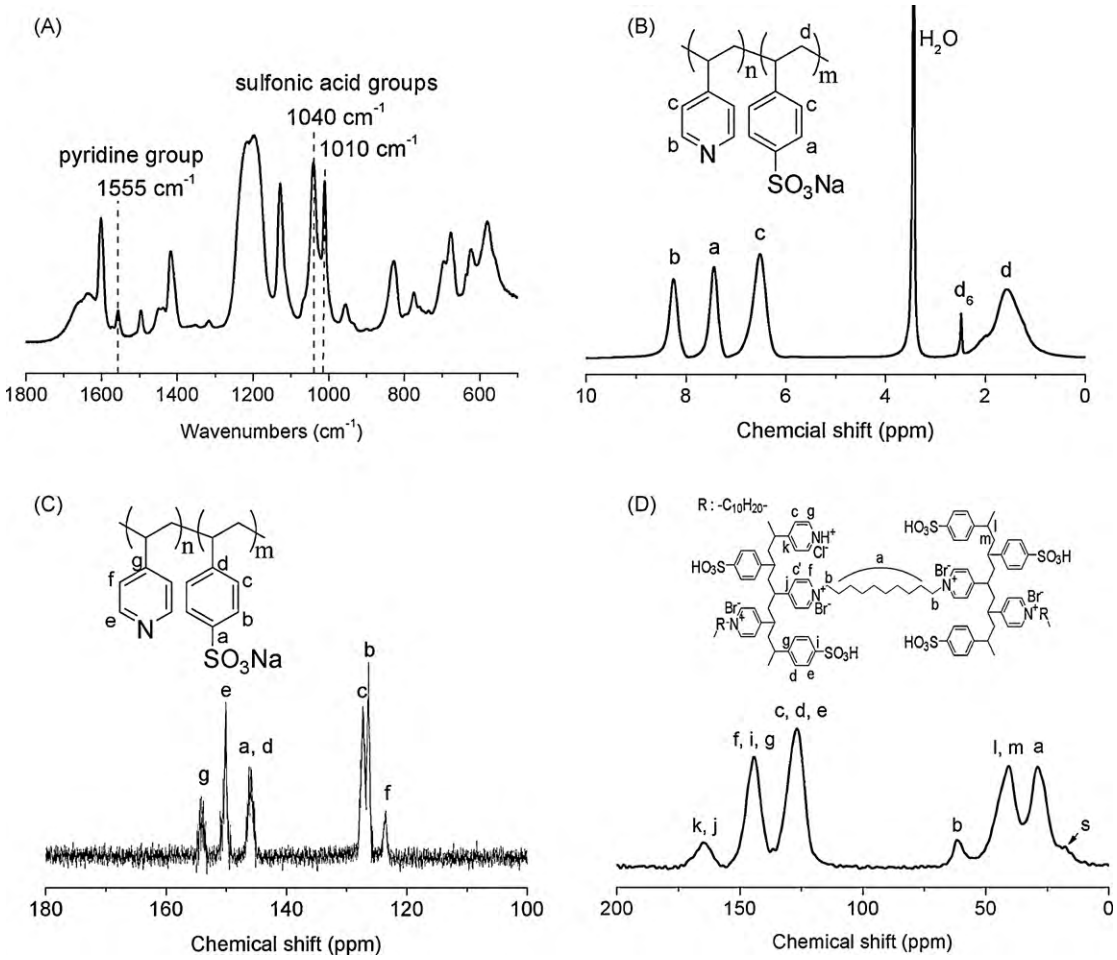


Fig. 1. (A) FTIR, (B) ^{1}H NMR and (C) ^{13}C NMR spectra of the NaSS-4VP copolymer. (D) A^{13}C NMR spectrum of SP-2 (25 °C, d_6-DMSO).

was sectioned into 50-nm slices using an ultramicrotome. The slices were picked up with 200-mesh copper grids for TEM observation.

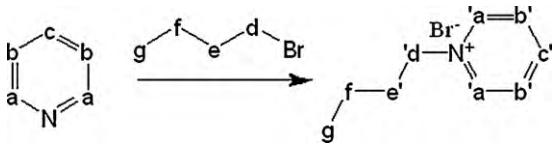
3. Results and discussion

3.1. Characterization and crosslinking reaction

^{1}H NMR, ^{13}C NMR (d_6-DMSO, 25 °C), and FTIR experiments were performed in order to confirm the structure of the copolymer. Fig. 1(A) shows the FTIR spectrum of the copolymers. The sharp peak at 1555 cm^{-1} was attributed to the pyridine group, and the peaks at 1040 and 1010 cm^{-1} were assigned to the vibration of sulfonic acid groups. In Fig. 1(B), the peaks at 6.6 ppm corresponded to meta protons [marked as 'c' in the molecular formula in Fig. 1(B)] on the phenyl ring in NaSS-4VP, the peaks at 7.5 and 8.3 ppm were assigned to the protons adjacent to the sulfonated group ('a') and pyridine nitrogen atom ('b'), respectively, and the peak at 1.5 ppm was believed to represent the protons of methane and methylene groups ('d'). In addition, the ^{13}C NMR spectrum of the NaSS-4VP copolymer [Fig. 1(C)] illustrated the characteristic carbons adjacent to the sulfonated group and pyridine nitrogen atom at 150.2 [marked as 'b' in the molecular formula in Fig. 1(C)] and 126.1 ppm ('e'), respectively.

The pyridine groups of the NaSS-4VP copolymer were able to interact with the 1-bromobutane thereby forming pyridinium salts via nucleophilic substitution as previously reported [26–29] To study the processes, model reactions of 1-bromobutane with pyridine (Scheme 2) in DMSO-d_6 at 60 °C were investigated by means of ^{1}H NMR spectroscopy and the results are presented in Fig. 2. As displayed in the ^{1}H NMR spectrum, the formation of pyridinium salts was revealed by the shift of the signals from the protons of pyridine (7.37, 7.75 and 8.62) and alkyl group (1.78 and 3.46) to 8.34, 8.81 and 9.54, and 1.96 and 4.91, respectively. These results confirmed that the 1-bromidebutane was almost completely reacted with pyridine via nucleophilic substitution after 400 min. In the nucleophilic substitution reaction, the formation of pyridinium salts would occur if a haloalkyl group's monomer was employed.

In the present study, ^{1}H NMR spectroscopy was also utilized to analyze the degree of crosslinking between the pyridine groups of NaSS-4VP and the haloalkyl groups. Table 1 displays the relative ratios of crosslinked pyridine units to the total number of pyridine groups determined from integration of the corresponding signals in each ^{1}H NMR spectrum. One can observe that the nucleophilic substitution reaction occurred during the solvent evaporation process. The degree of crosslinking increased relatively slowly upon increasing the content of the haloalkyl crosslinker as a result of the crosslinking reaction being inhibited by the network structure.



Scheme 2. The reaction of 1-bromobutane with pyridine (model compound).

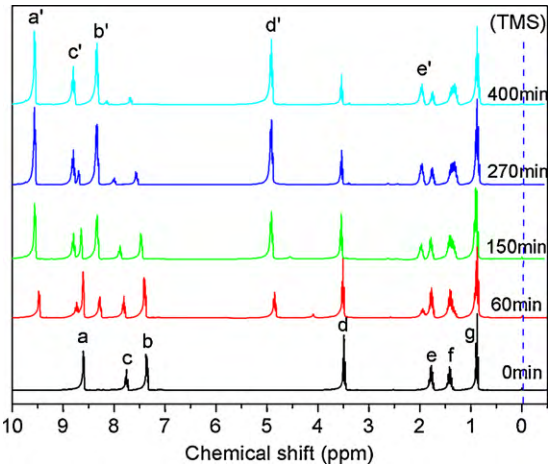


Fig. 2. Model reactions of 1-bromobutane with pyridine in d_6-DMSO at 60 °C: the evolution of the ^{1}H NMR spectra of the reaction mixture with time (the designated signals belong to protons from the starting halide and the formed pyridinium salt, as indicated in Scheme 2).

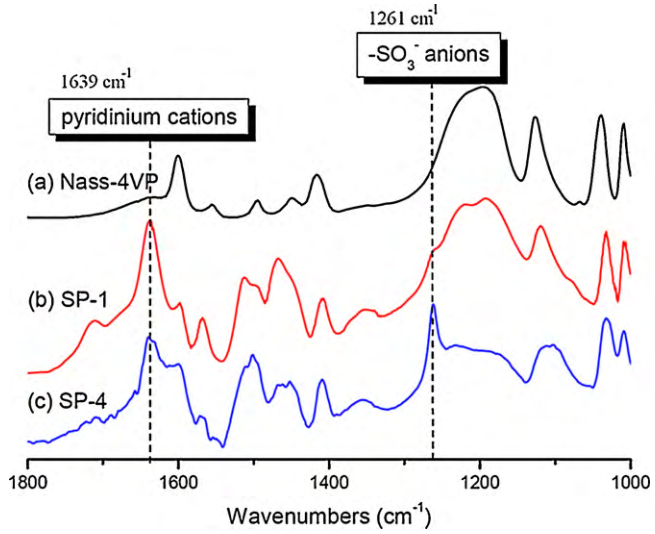


Fig. 3. FTIR spectra of NaSS-4VP, SP-1 and SP-4.

Further evidence of a crosslinked SS-4VP structure was obtained from ^{13}C NMR analysis. The ^{13}C NMR spectrum of SP-2 [Fig. 1(D)] indicates the presence of the alkane group of carbons adjacent to the pyridinium salt at 62.2 ppm [marked as 'b' in the molecular formula in Fig. 1(D)]. These results suggest that the crosslinked SS-4VP structure was obtained after the solvent evaporation process.

In addition, the effect of interaction between the pyridinium cation and sulfonated anion on the crosslinked SS-4VP membrane was also investigated by FTIR spectra. Fig. 3 shows the spectra of pure NaSS-4VP, SP-1 and SP-4 membranes, indicating that the intensity of the peak at 1639 cm^{-1} increased after the crosslinking reaction and acid treatment. According to previous studies [31,32], this peak can be assigned to a ring vibration of the pyridinium cations, which were produced through proton transfer from the sulfonic acid groups and hydrochloric acid to the pyridine groups. In the spectrum of SS-4VP membranes, a new peak appeared at 1261 cm^{-1} and its intensity increased with the reduction of the crosslinking density. The absorption band at 1261 cm^{-1} was assigned to the absorption arising from the asymmetric stretching of the $-SO_3^-$ anions as previously described [33]. With the reduction of crosslinking density, more pyridinium cations were produced through proton transfer from the sulfonic acid groups. Therefore, we conclude that $-SO_3^-$ anions and pyridinium cations can attach to one another in the crosslinked SS-4VP to form ion pairs, which also give rise to the formation of ionic interaction of the polymer chains.

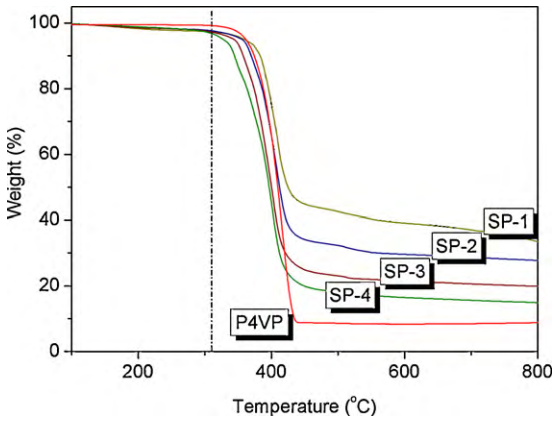


Fig. 4. TGA curves of P4VP and the crosslinked SS-4VP membranes.

3.2. Thermal and mechanical properties

The thermal stabilities of crosslinked SS-4VP membranes were determined by TGA and DSC. The TGA curves for the crosslinked SS-4VP are given in Fig. 4. As shown in Fig. 4, the thermal degradation of the crosslinked SS-4VP copolymer increased upon increasing the crosslinker content. The degradation temperatures of crosslinked SS-4VP membranes were all higher than 300 °C, suggesting that the presence of the alkane crosslinking structure and the interaction between acidic (sulfonic acid groups) and basic (basic nitrogen) units in the membrane improved the thermal stability of SS-4VP. As disclosed by the DSC measurements, no glass transition temperature (T_g) was observed for any of the crosslinked SS-4VP membranes in the temperature range from 30 to 300 °C. The absence of a glass transition temperature originated from the nature of the ionomer, with its elevated ion concentration [35]. Such improved thermal properties are very desirable for electrolyte materials used in PEFCs.

It is essential for PEMs to possess adequate mechanical integrity to withstand fabrication of the membrane electrode assembly. When subjected to hot pressing, the electrodes could be easily peeled away from the MEA due to the deformation of the membrane. The experimental results on mechanical modulus, strength and elongation properties for the crosslinked SS-4VP membranes at room temperature were summarized in Table 2. In the wet state, the sample showed superior mechanical properties, as opposed to Nafion 117, with tensile stress values in the range of 29.6–51.6 MPa, elongation at break values of 2.2–6.3% and values of Young's modulus of 1.3–2.4 GPa. The mechanical properties of the crosslinked SS-4VP membranes increased upon increasing the crosslinking density, i.e., the presence of the crosslinking structure enhanced the strength of the membranes. In addition, it is assumed that the acid–base interaction restrict the molecular motion of the polymer chains resulting in stronger membranes.

These data presented in Table 2 indicated that the addition of alkane crosslinker enhanced the mechanical properties of the resulting membranes to some extent, respective of the ratio of alkane crosslinker. The membranes obtained good mechanical properties and were strong and tough enough to be used as functional PEM materials.

Table 2
The oxidative stabilities and mechanical properties of crosslinked SS-4VP membranes.

Sample	Oxidative Stability (h)[a]	Tensile strength (MPa)[b]	Young's modulus (GPa)[b]	Elongation at break (%)[b]
SP-1	13.5	51.6	2.4	2.2
SP-2	11	43.4	2.1	3.1
SP-3	8.5	39.1	1.7	3.4
SP-4	4.5	29.6	1.3	6.3
Nafion 117	–	28.4[c]	0.1[c]	329[c]

[a] The oxidative stability of the crosslinked SS-4VP membranes were tested using Fenton's reagent at 80 °C.
[b] Measured in the hydrated state.
[c] According to Ref. [57].

3.3. Ion-exchange capacity (IEC) and water uptake (WU)

IEC is a quantification of the ion-exchangeable sulfonic acid groups and pyridinium salts in the membranes. The measured IEC value of the crosslinked SS-4VP membranes are listed in Table 1. The IEC value for Nafion 117 was also measured and found to be 1.02 mequiv g^{-1}—a result that agreed well with previously reported data [36]. The reliability of the measurement method could thus be validated. The IEC values of the crosslinked SS-4VP membranes ranged from 2.41 to 3.83 mequiv g^{-1}. The decrease in IEC values with the increase in crosslinker content was caused by the decrease in the overall sulfonic acid content. Theoretical IEC values could be calculated based on the composition of the starting mixture and the following assumptions: (i) that no residual crosslinker was left in the membranes; (ii) that the weight variations due to the nucleophilic substitution reaction were negligible; (iii) that all of the sulfonic acid groups in SS-4VP contributed to the IEC; (iv) that all of the residual pyridinium salts contributed to the IEC.

Previous studies have indicated that the formation of the acid–base complexes within PEMs give rise to perturbations when measuring the IEC. This is the result of the exchange of the acid protons of the PEMs being more difficult as compared to for other kinds of sulfonated polymers [37–40], which was also the case in the present study. To eliminate this effect, the membrane was kept in the titration solution until the measurement was completed.

The WU of sulfonated polymers is known to have a profound effect on membrane conductivity and mechanical properties [4]. However, excessively high WU levels can result in membrane fragility and dimensional changes, which leads to the loss of mechanical properties. Basically, the amount of WU in the crosslinked sulfonated polymers is strongly dependent upon the amount of crosslinker and is also related to IEC values. The WU was determined from the ratio of the weight of the water absorbed by the membrane when immersed in water, with respect to the dry membrane weight. The WU of the crosslinked SS-4VP membranes was evaluated at 30 °C and is presented in Table 1. As expected, the crosslinking caused a significant suppression of the membrane swelling and the water uptake in the crosslinked membranes was thus lower, presumably because of the decrease in the overall sulfonic acid content and the reduced free volume within the PEM. The water retention of membranes could provide indirect evidence of the variation in the WU with the increase in temperature and reduction in relative humidity (RH). Moreover, it is a very important parameter in view of their application in PEFCs.

The water desorption curves of crosslinked SS-4VP membranes are shown in Fig. 5. As can be seen, the water diffusion coefficients of the crosslinked SS-4VP membranes demonstrate considerable decreases with an increasing crosslinker content. As the increase in crosslinking density, the water mobility decreased and hence the penetration of the water molecules through the membrane became difficult. In addition, the crosslinked materials were pyridinium salts (Scheme 1), and as such provided additional sites for water absorption giving rise to an improved ability for water retention. The lower the diffusion coefficient, the stronger the membranes were able to hold water, and the more water remained in the membranes. Thus, the crosslinked SS-4VP membranes exhibited superior degrees of water sorption and water retention.

3.4. Proton conductivity and methanol permeability

The type of crosslinker, the crosslinking density, and the microstructural change that occurs after crosslinking all have dramatic effects on the water uptake, the state of water, and the proton conductivity of crosslinked membranes [17–25]. The proton conductivities of the crosslinked SS-4VP membranes decreased with the crosslinker content and the associated decrease in water content. Nevertheless, although the SP-1 membrane exhibited the highest crosslinking density among all of the membranes, it still presented an adequate conductivity that was close to that of Nafion 117 (i.e., 7.1×10^{-2} S cm^{-1} for SP-1 and 9.3×10^{-2} S cm^{-1} for Nafion 117). Furthermore, the proton conductivity of the SP-1 membrane surpassed that of Nafion 117 and reached a value of 0.14 S cm^{-1} at 60 °C. The presence of both hydrogen bonds and ionic interactions in the membrane (Section 3.1) led to the formation of a random proton conductive pathway that facilitated proton transfer [40–42]. In addition, the introduction of the alkane and long crosslinker was believed to induce the formation of efficient hydrophilic channels within the polymer matrix, thereby enhancing the proton conductivity [43]. TEM micrographs of the SP-1 membrane (Fig. 6) also indicate that the addition of crosslinker in the membrane results in a better distribution of the ionic clusters.

Fig. 7 presents Arrhenius plots of the proton conductivities measured at various temperatures. The proton conductivity of the crosslinked SS-4VP membrane was thermally stimulated since higher proton conductivities were expected at higher temperatures.

The activation energy (E_a) of these crosslinked SS-4VP membranes (SP-1 and SP-2), obtained from the Arrhenius plots, lay

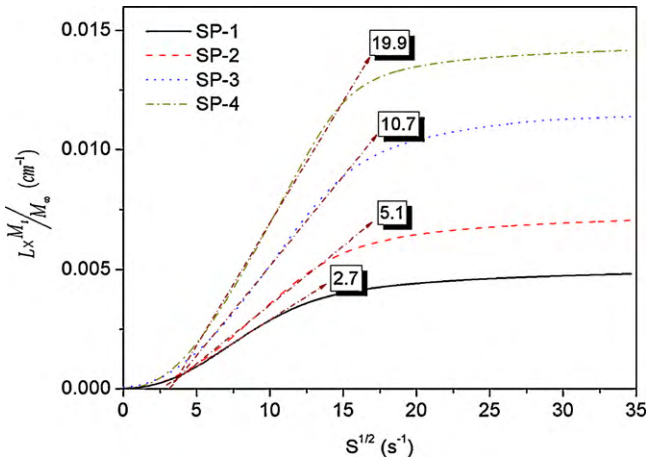


Fig. 5. The water desorption of the crosslinked SS-4VP membranes. The numbers in the boxes correspond to the water diffusion coefficients ($\times 10^{-5}$ cm^{-2} s^{-1}).

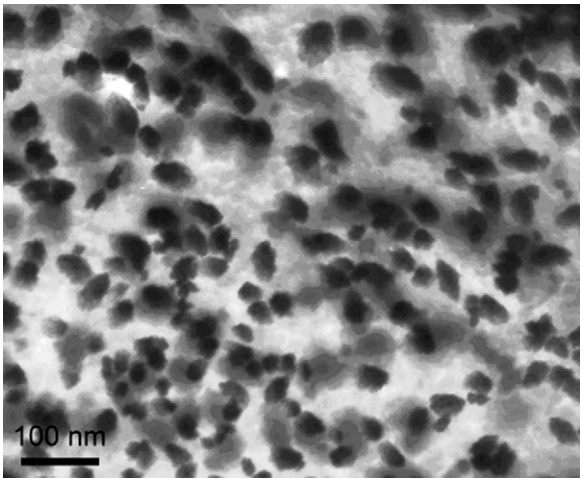


Fig. 6. TEM image of SP-1 membrane.

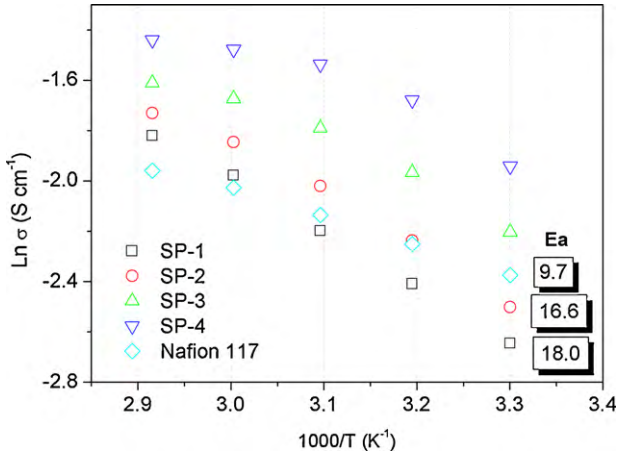


Fig. 7. Proton conductivities of the crosslinked SS-4VP membranes and Nafion 117, plotted as functions of the inverse temperature. The numbers in the boxes correspond to the activation energies (E_a, kJ mol^{-1}).

within the range of 14–40 kJ mol^{-1}. This was in decent agreement with the results from the Grotthus-type mechanism [43]. The E_a-value of the SP-1 membrane (i.e., 18.0 kJ mol^{-1}) was the highest among all the investigated composites. This was a result of the higher amount of dense alkane network structure retarding the evaporation of water at high temperatures [10], and thus resulting in a less dramatic reduction of the proton conductivity. However, for SP-3 and SP-4, the plots of the conductivity vs. temperature cannot fit Arrhenius equation (non-linear relationship). This is probably because the membranes highly swelled under the conductivity test environment.

The proton conductivity of the crosslinked SS-4VP membranes as a function of the relative humidity (RH) at 60 °C is presented in Fig. 8. For all crosslinked SS-4VP membranes, the proton conductivity decreased drastically as the RH decreased; a common phenomenon that has been observed for many other sulfonated polymer membranes. However, the relationship between the proton conductivity and the RH indicates that the reduction of the proton conductivity was less dramatic when increasing the crosslinker content at low RH and 60 °C, which also implied that the dense alkane network, acid–base complex and additional pyridinium salts displayed a higher propensity for retaining water, thus limiting the dependence of the proton conductivity on hydration. On the other hand, the proton conductivity of the SP-1 was maintained at 6.4×10^{-3} S cm^{-1} at 50% RH—a result comparable to that

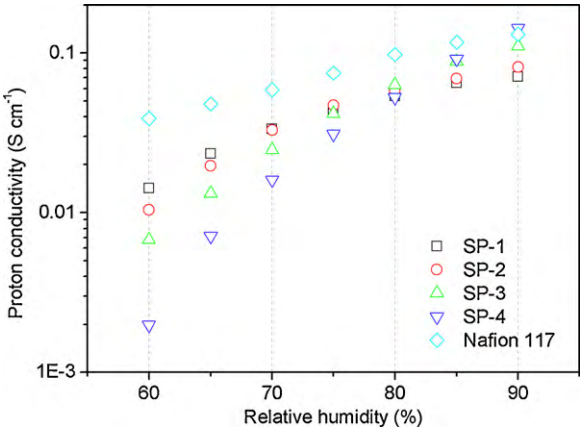


Fig. 8. Conductivities of the crosslinked SS-4VP membranes plotted as functions of the relative humidity at 60 °C.

of Nafion 117. These findings were in good agreement with the water desorption data mentioned above. In addition, the proton conductivity was measured at low RH, and the proton transport therefore depended strongly on the distance between the hopping sites. However, since the crosslinked SS-4VP membranes comprised a combination of acidic and basic sites and thus acted as a proton transfer medium, the site-to-site jumping distances were minimized and the proton transfer processes were facilitated under low RH conditions [44–46].

Methanol permeability is an important membrane property in DMFC applications since the crossover of methanol from the anode to the cathode leads to a lower cell voltage and a decreased fuel efficiency. As can be seen in Table 1, the methanol permeability of the crosslinked SS-4VP membranes decreased upon increasing the crosslinking density. This was due to the presence of the crosslinker between the polymer chains preventing excessive water swelling while simultaneously retarding the degree of methanol crossover [17–25]. The methanol permeability of the SP-1 membrane was a mere 16% of that of Nafion 117 under equivalent conditions (i.e., 2.10×10^{-7} cm^2 s^{-1} for SP-1 and 1.31×10^{-6} cm^2 s^{-1} for Nafion 117), despite that it absorbed more water. The underlying reason was presumed to be the lower methanol uptake behavior (Table 1) and the acid–base interaction acting as a methanol barrier [37].

For practical PEFC applications, PEMs need to exhibit high proton conductivities (>10^{-2} S cm^{-1}) and low methanol permeabilities (<10^{-6} cm^2 s^{-1}). The ratio of the proton conductivity to the methanol permeability, known as the selectivity (Φ), is thus an effective parameter for evaluating membrane performance in DMFCs. The selectivity of the SP-1 membrane was found to be ca. 5 times that of Nafion 117, as can be seen in Table 1, indicating that the SP-1 membrane provided a superior performance as opposed to Nafion 117 with regard to being used in DMFCs.

3.5. Hydrolytic and oxidative stability

The oxidative stability of the crosslinked SS-4VP membranes was determined using Fention's reagent at both 25 and 80 °C (Table 2). Fenton's reagent is often employed to simulate the oxidative reactions from radical species, such as OH$^\bullet$ and HOO$^\bullet$, during fuel cell operation. In the present case, the choice was made to utilize a higher concentration of Fenton's reagent (i.e., 30 wt% H_2O_2 and 30 ppm $FeSO_4$) than what had been used in previous studies (i.e., 3 wt% H_2O_2 and 2 ppm $FeSO_4$) to measure the oxidative stability [45–48]. Despite that the non-crosslinked SS-4VP copolymer was water-soluble, all of the crosslinked SS-4VP membranes were either completely insoluble or became decomposed in Fenton's reagent, even after 500 h at 25 °C, thus

Table 3
Proton conductivities and weight loss for the SP-1 membrane after soaking in water at 100 °C.

Sample	Soaking time (day)	Decrease in weight (%)	Proton conductivity ($S\,cm^{-1}$)[a]
SP-1	0	0	0.071
	1	0	0.071
	6	0	0.068
	12	1.0	0.064
	28	1.9	0.055

[a] The proton conductivity of the crosslinked SS-4VP membranes were measured at 30 °C and 90% RH.

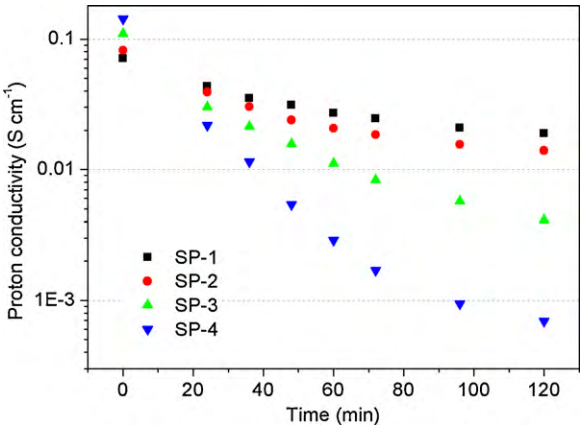


Fig. 9. Proton conductivities of the crosslinked SS-4VP membranes plotted as functions of the time they were exposed to Fenton's reagent at 25 °C. (The conductivity of SS-4VP membrane was measured at 30 °C and 90% RH.)

revealing that the oxidative stability of the crosslinked SS-4VP membranes was superior to that previously reported for sulfonated polymers [47–56]. The test carried out at 80 °C indicated that the oxidative stability of the crosslinked SS-4VP membranes increased as the crosslinking density was raised due to the crosslinking structure retarding the permeation of H_2O_2 into the membrane. The crosslinked SS-4VP membranes also possessed the potential of providing matrices with higher chemical stability due to the zwitterionic throughout the membrane [21]. The hydrolytic stability of a PEM is a crucial property for long-term fuel cell operation, and the testing of this characteristic for the crosslinked SS-4VP membranes was performed by immersing them in deionized water at 100 °C and determining the time that elapsed before the hydrated membranes began to lose their proton conductivity.

Table 3 lists the proton conductivity and weight loss data of the SP-1 membrane before and after the aging tests. No changes in either shape or appearance were observed in the membrane up to after 6 days, thus demonstrating that there was no obvious hydrolysis during the treatment. Moreover, the SP-1 membrane retained more than 98.1% of its original weight after soaking in water for 28 days at 100 °C, and the membranes maintained high proton conductivities of $5.5 \times 10^{-2}\,S\,cm^{-1}$ (to be compared to the initial proton conductivity of $7.1 \times 10^{-2}\,S\,cm^{-1}$) thus revealing their hydrolytic stability at high temperatures. Fig. 9 illustrates the proton conductivities of the crosslinked SS-4VP membranes plotted with respect to the time they were exposed to Fenton's reagent (30 wt% H_2O_2 containing 30 ppm ferrous ammonium sulfate at 30 °C). The SP-1 membrane maintained adequate proton conductivities (>0.01 $S\,cm^{-1}$) after 120 h (The conductivity of SS-4VP membrane was measured at 30 °C and 90% RH). In contrast, other sulfonated polymers [45–54] have been seen to decompose after 24–60 h under similar testing conditions. Such oxidative and hydrolytic stabilities have rarely been observed for PEMs with non-fluorinated hydrocarbon skeletons.

4. Conclusions

In conclusion, a novel sulfonated poly (styrene sulfonic acid-*co*-4-vinylpyridine) copolymer could be prepared through direct free radical polymerization of styrene sulfonic acid and 4-vinylpyridine in water. Crosslinked SS-4VP membranes were achieved with a haloalkyl crosslinker and the degree of crosslinking could be controlled. The crosslinked SP-1 membrane demonstrated an excellent hydrolytic stability with only slight changes in weight and proton conductivity after 28 days of testing in water at 100 °C. The dense alkane network structure and strong acid–base interaction were believed to be the reason for the high thermal stability, excellent hydrolytic and oxidative stability, as well as low methanol permeability of the crosslinked SP-1 membranes despite their high IEC values. The proton conductivity was comparable or even superior to that of Nafion 117 at high temperatures and 90% RH. The crosslinked SP-1 membrane possessed the highest selectivity (i.e., $3.38 \times 10^5\,S\,cm^{-3}\,s$); a result approximately five times that of Nafion 117, thus implying its potential for practical applications in high-energy-density devices.

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