

Cross-linked poly(vinyl alcohol) and poly(styrene sulfonic acid-*co*-maleic anhydride)-based semi-interpenetrating network as proton-conducting membranes for direct methanol fuel cells

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Abstract

A series of semi-interpenetrating network (SIPN) membranes was synthesized by using poly(vinyl alcohol) (PVA) with sulfosuccinic acid (SSA) as a cross-linking agent and poly(styrene sulfonic acid-*co*-maleic acid) (PSSA-MA) as a proton source for direct methanol fuel cell (DMFC) application. A bridge of SSA between PVA molecules not only reinforced the network but also provided extra proton-conducting paths. PSSA-MA chains trapped in the network were the major proton conduction path of the membrane. The SIPN membranes with 80% PSSA-MA (SIPN-80) exhibited a higher proton conductivity value of $2.59 \times 10^{-2} \text{ S cm}^{-1}$ and very low methanol permeability ($4.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$). More specifically, the SIPN membranes exhibited very high selectivity (proton conductivity/methanol permeability). Membrane characteristics such as water uptake, proton conductivity and methanol permeability were evaluated to determine the effect of PVA molecular weights. The SIPN membranes with higher PVA molecular weight were also evaluated using methanol and oxygen gas in a single cell fuel cell at various temperatures. Power density value of over 100 mW cm^{-2} was obtained for SIPN membrane-based membrane electrode assembly at 80°C and using commercial binary alloy anode catalysts and 2 M methanol.

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Keywords: Proton-conducting membrane; Semi-interpenetrating network; Poly(vinyl alcohol); Membrane electrode assembly; Direct methanol fuel cells

1. Introduction

Direct methanol fuel cell (DMFC) is one of the most attractive power sources for widely differing applications, ranging from vehicles to portable devices, due to its inherently high efficiency and low emission [1,2]. Despite its advantages, there are several obstacles preventing commercialization of DMFC. The main issue is the non-availability of a suitable proton-conducting membrane due to the unacceptably high methanol crossover of currently used perfluorosulfonic acid membranes such as Nafion[®] (DuPont). This not only reduces the fuel efficiency but also causes performance loss at the cathode due to the consumption of oxygen and catalyst poisoning [3,4]. The polymer electrolyte is one of the critical components dictating the size, cost, power and efficiency of DMFCs. Early commercialization

of DMFC requires new proton-conducting membranes that can significantly reduce methanol permeability with suitable proton conductivity.

In the past, several attempts have been made by researchers around the world to minimize methanol crossover by developing new membranes from non-fluorinated and partially fluorinated hydrocarbon-based polymers [5–8] or by modifying Nafion[®] membranes [9–13]. Among the variety of different approaches to synthesizing new electrolyte membranes, acid–base polymer blends have become a favorite approach to the design of improved proton exchange membrane (PEM) materials due to the interaction (ionically cross-linked) between polymers. These interactions can significantly reduce the swelling and the methanol permeability of membranes [14,15]. However, membranes with physically cross-linked structure can become disentangled in water and even in methanol, resulting in large swelling and mechanical disintegration [16]. Specific attempts to reduce the excessive swelling of the membranes have been made, such as using chemical cross-linking structure

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and higher molecular weight polymers to modify membranes [16–19].

Poly(vinyl alcohol) (PVA) membranes are used in pervaporation-based dehydration of alcohols because they preferentially permeate water and retain alcohol [20–23]. Taking advantage of its high selectivity, Pivovar et al. [24] explored the possibility of using PVA as the proton exchange membrane in DMFC by using proton conductivity and methanol permeability experiments. They reported that the PVA membranes employed in pervaporation process were much better methanol barriers than Nafion® membranes.

A series of PVA acid–base polymer blends with poly(styrene sulfonic acid-*co*-maleic acid) (PSSA-MA), poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) and sulfonated phenolic resin (S-Ph) have also been investigated [25–28]. Recently, Rhim et al. [29,30] prepared and characterized cross-linked PVA membranes containing sulfonic acid group for DMFC applications. Most of the previous studies on PVA-based membranes have focused on preparation and transport properties but few of them were devoted to fabrication of membrane electrode assemblies (MEA) and evaluation of fuel cell performance [25–30]. In this paper, a series of semi-interpenetrating network (SIPN) membranes was synthesized by using poly(vinyl alcohol) with sulfosuccinic acid (SSA) as a cross-linking agent and poly(styrene sulfonic acid-*co*-maleic acid) (PSSA-MA) as proton sources, and their physico-chemical and electrochemical characterizations are reported. More importantly, the SIPN membranes with high molecular weight PVA were fabricated into membrane electrode assemblies for direct methanol fuel cell testing with methanol/O₂ at various temperatures and a power density of >100 mW cm⁻² at 80 °C was observed.

2. Experiment

2.1. Materials

Poly(vinyl alcohol) (Aldrich, average $M_W = 89,000$ – $98,000$ g mol⁻¹; degree of hydrolysis, 99%; Fluka, average $M_W = 130,000$ and $195,000$ g mol⁻¹; degree of hydrolysis, 88 and 99%, respectively), sulfosuccinic acid, as a cross-linking agent (SSA, 70 wt.% solution in water, Aldrich) and poly(styrene sulfonic acid-*co*-maleic acid) (sodium salt, the ratio of styrene sulfonic acid to maleic acid is 3/1, average $M_W = 20,000$ g mol⁻¹; Aldrich) were used to prepare proton-conducting polymers. All chemicals were used without further purification. Pt/C (46.4% Pt on carbon, TEC1050E) from Tanaka Kikinokogyo KK, Japan, was used as a cathode electrocatalyst and Pt–Ru (58.1% Pt:Ru on Vulcan XC-72; 1:1 a/o Pt:Ru, E-Tek, USA) was used as an anode electrocatalyst.

2.2. Membrane preparation

The SIPN membranes were prepared by casting PVA/SSA/PSSA-MA solutions onto Petri dishes and evaporating water at 60 °C in an oven for 1 day. The membranes were peeled off the dishes and then annealed at 120 °C for 1 h, described in

detail elsewhere [31]. The thicknesses of the membranes were controlled in a range of 100–120 μm.

2.3. Characterization of proton conductivity membrane

The water uptake of the membranes was determined by measuring the change in the weight before and after the hydration. Pre-dried membranes were immersed in de-ionized water for 24 h, and then surface-attached water onto the membrane was removed with filter paper. After that, the wetted membrane weight (W_{wet}) was determined as quickly as possible. The weight of the dry membrane (W_{dry}) was determined after completely drying it in vacuum at 60 °C for 24 h. The water uptake (%) value of the membranes was calculated by using the following equation [32]:

$$\text{water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

A titration method was used to determine the ion-exchange capacity (IEC). Each membrane was soaked in 1 M sodium chloride aqueous solution for 1 day to exchange protons with sodium ions. The ion-exchanged solution was then titrated with 0.005 M sodium hydroxide solution. The IEC value was calculated using the following equation [32]:

$$\text{IEC} = \frac{M_{i,\text{NaOH}} - M_{f,\text{NaOH}}}{W_{\text{dry}}} = \frac{H^+ (\text{mmol})}{W_{\text{dry}}}$$

where $M_{i,\text{NaOH}}$ is the initial mmol of NaOH of titration and $M_{f,\text{NaOH}}$ is the mmol (m_{eq}) of NaOH after equilibrium. In addition, H^+ is the molar number of proton sites presented in the membrane and W_{dry} is the weight of dry membrane.

Proton conductivity measurements were carried out at ambient temperature after equilibrating the membrane in de-ionized water for 1 day. The proton conductivity cell was composed of two 9.5 mm diameter stainless steel electrodes. The membrane sample was sandwiched between the stainless steel electrodes. The ac impedance spectra of the membranes were recorded from 200,000 to 100 Hz with amplitude of 5 mV by using an Autolab PGSTAT30 instrument. The resistance value associated with the membrane proton conductivity was determined from the high frequency intercept of the impedance with the real axis. The proton conductivity was calculated according to

$$\sigma = \frac{L}{RA}$$

where σ , L , R and A denote, respectively, the proton conductivity of the membrane, thickness of the membrane (which was measured with a micrometer in each case), the measured resistance of the membrane, and the cross-sectional area of the membrane perpendicular to current flow. The temperature dependence of proton conductivity was determined by using the same piece of membrane and controlling the temperature in a range starting from 20 to 50 °C. The conductivity at each temperature was measured several times until the reading remained unchanged.

Methanol permeability of membranes was determined by using a home-made side-by-side glass diffusion cell. Prior to all experiments, the membrane was equilibrated in water for

1 day at room temperature. Next, the membrane was clamped between well-stirred donor (A) and receptor (B) compartments with a membrane cross-sectional area of 3.19 cm^2 exposed to the solutions in both compartments. The receptor compartment ($V_B = 80 \text{ ml}$) was initially filled with water, while the donor compartment ($V_A = 80 \text{ ml}$) was charged with a methanol solution (3 wt.%). After closing the two compartments, the diffusion cell was kept in a thermostatically controlled device at 35°C . The difference in concentration between the two compartments leads to a flow of methanol across the membrane. The concentration of methanol in the receptor compartment was measured using a gas chromatograph (GC) (Shimadzu GC14) at regular intervals. Methanol permeability was determined from the slope of the plot of methanol concentration in the receptor compartment versus time.

2.4. Fabrication of MEAs and evaluation of single cell DMFC performance

Catalyst-coated membranes (CCM) with 5 cm^2 active area were fabricated using Pt–Ru/C and Pt/C catalyst slurries in isopropanol (20 ml for 1 g of electrocatalyst) and the microspray method for anode and cathode sides. The isopropanol was added after purging the catalyst powder in flowing nitrogen gas for about 30 min to avoid any flame/ignition. In order to extend the reaction zone of the catalyst layer, a 5% Nafion[®] solution (30 wt.% to Pt and Pt–Ru catalysts; 10 ml Nafion[®] solution for 1 mg of electrocatalyst) was added to the catalyst slurry. The membrane was fixed in a home-made fixture to ensure anode and cathode catalyst layers were exactly on the same area of the membrane. The catalyst loadings on the anode and cathode sides were about 3 mg Pt–Ru and 1 mg Pt cm^{-2} , respectively. The catalyst-coated SIPN membrane was vacuum dried at about 70°C for an hour before assembling it in the test cell. For comparison purposes, Nafion[®] 115-based MEA was also fabricated with the above procedure.

The gas diffusion layer (GDL) was prepared with a teflonized non-woven 7 mil carbon paper (P50T, Ballard Material Products Inc., Lowell, MA, USA) substrate. A slurry of graphitized carbon black grade PUREBLACK 205-110 carbon (Superior Graphite Co., Chicago, IL, USA) with PTFE (TE3859 Teflon suspension from Dupont) dispersion in a mixture of isopropanol and de-ionized water (80:20 volume ratio) was prepared by ultrasonication for 20 min followed by magnetic stirring for about 2 h. The micro-porous layer was fabricated by applying the slurry on the carbon paper by a microspraying method. Subsequently, the carbon paper with micro-porous layer was heat treated by sintering at 350°C in air for about 1 h. The carbon loading for the micro-porous layer was approximately 3 mg cm^{-2} and the PTFE content was 30 wt.%.

MEAs were assembled by sandwiching the catalyst-coated membrane with the GDLs inside the DMFC test cell (Fuel Cell Technologies). Gas sealing was carried out using silicone-coated fabric materials (Performance Plastics, CF1007) at a uniform torque of 40 lb in. Single cell fuel cell performance was evaluated using a Greenlight G40 (Hydrogenics Test Systems, Burnaby, Canada) Test Station at various temperatures using 2 M

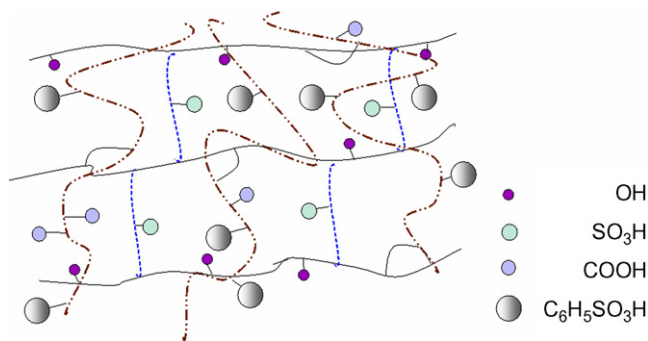


Fig. 1. The SIPN structural scheme of PVA/SSA/PSSA-MA membrane.

methanol/ O_2 under ambient pressure by galvanostatic polarization. The methanol flow rate was fixed at $1 \text{ cm}^3 \text{ min}^{-1}$ using a peristaltic pump and the oxygen flow rate was fixed at 200 sccm. The relative humidity of the oxidant was maintained at 100% by controlling the humidity bottle temperatures.

3. Results and discussion

3.1. Membrane characterization by IEC, solvent uptake, proton conductivity and methanol permeability

The SIPN structure has been confirmed by FT-IR spectra in our previous study [31] and the scheme of the SIPN structure is also shown in Fig. 1. According to our preliminary studies, an optimum cross-linking agent of SSA was determined to be 20 wt.% in terms of swelling level and mechanical property. In the present study, a fixed amount of SSA 20 wt.% was used to construct the PVA network. Due to the increase of sulfonic acid and maleic acid on PSSA-MA, the measured IEC values of the membranes increased from 1.1 to 1.86 mmol g^{-1} with an increase of PSSA-MA content varying from 20 to 80% as shown in Fig. 2.

Water uptake plays a critical role in proton conduction because it is the major carrier of protons. However, excess swelling in water reduces the membrane's mechanical strength. Fig. 2 also shows the water uptake as a function of PSSA-MA

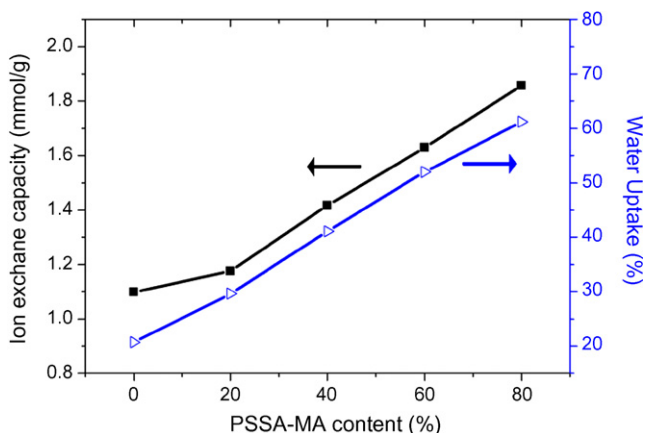


Fig. 2. IEC, water uptake of SIPN membranes based on PVA/SSA/20 with different amounts of PSSA-MA trapped in the network (PVA, M_w : 89,000–98,000 g mol^{-1}).

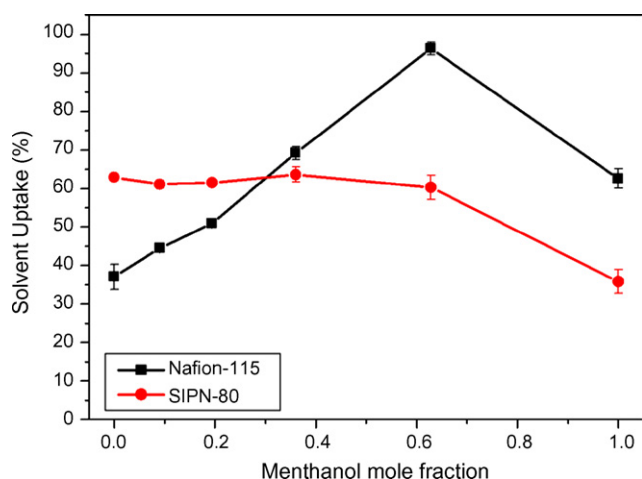


Fig. 3. Solvent uptakes of Nafion® 115 and SIPN-80 membranes (PVA, M_w : 89,000–98,000 g mol^{-1}) as a function of methanol concentration.

content. The water uptake increased from 20 to 60% as the PSSA-MA content increased from 0 to 80 wt.%, mainly due to the increase of the hydrophilic groups of PSSA-MA.

Fig. 3 shows the solvent uptake of Nafion® 115 and SIPN-80 as a function of methanol concentration. When the SIPN-80 membrane was swelled in pure water, it had higher water uptake than that of Nafion® 115 due to its higher IEC value. With an increase of methanol concentration, the solvent uptake of Nafion® 115 increased through a maximum value when methanol mole fraction is 0.63. This trend is in agreement with the finding of Skou et al. [33], who found the water content of Nafion® membrane was little affected by the uptake of methanol at lower methanol concentrations. However, water starts to be excluded at higher methanol concentrations. In contrast, the trend of solvent uptake of SIPN-80 decreased with the increase of methanol mole fraction, and the methanol uptake of the SIPN membrane was approximately one half lower than that of Nafion® 115. The two different behaviors can be explained by the chemical cross-linking structure of the SIPN membrane in contrast to the physical cross-linking structure of Nafion® 115. Moreover, the excellent methanol resistance of PVA is also an important factor [24].

Fig. 4(a) presents the proton conductivity of PVA/SSA20/PSSA-MA membranes as a function of PSSA-MA content at room temperature. As expected, the proton conductivity values increased with PSSA-MA content. The proton conductivity of Nafion® 115 measured under the same experimental conditions was $1.4 \times 10^{-2} \text{ S cm}^{-1}$, which is in agreement with literature [26,34–37]. When PSSA-MA content was up to 80%, the proton conductivity reached to $2.59 \times 10^{-2} \text{ S cm}^{-1}$, comparable to that of Nafion® 115. It is well known that both water uptake and IEC have profound effects on membrane conductivity. Higher water uptake promotes the transportation of protons more effectively, and higher IEC decreases the distance between anionic groups leading to faster proton conduction.

The temperature dependence of proton conductivity for several compositions of SIPN membrane samples are plotted in Fig. 4(b) along with that for the Nafion® 115 membrane.

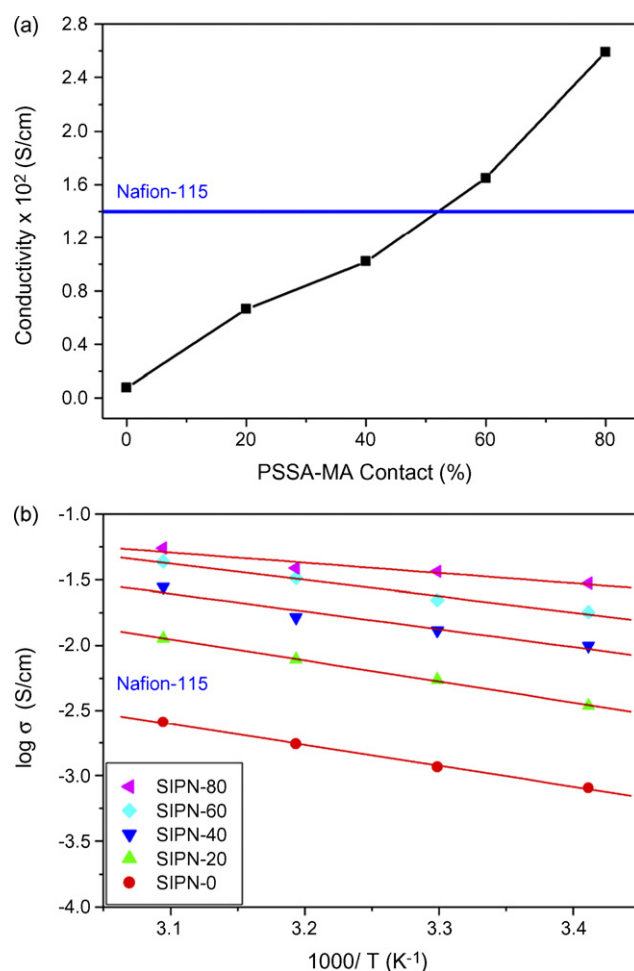


Fig. 4. (a) The proton conductivity of PVA/SSA20/PSSA-MA membranes (PVA, M_w : 89,000–98,000 g mol^{-1}) as a function of PSSA-MA amount and (b) temperature dependence of proton conductivity by plotting $\log(\sigma)$ vs. $1/T$.

Evidently, the change of proton conductivity with temperature follows the Arrhenius relationship in the experimental temperature range of 20–50 °C:

$$\sigma = \sigma_0 \exp\left(-\frac{E_{a,\text{cond}}}{kT}\right)$$

where k is the Boltzman constant, and $E_{a,\text{cond}}$ is the activation energy of proton conduction, that can be derived from the slope of $\log \sigma$ versus $1/T$ plots. All the membranes exhibited positive temperature–conductivity dependencies. The $E_{a,\text{cond}}$ for proton conduction decreased with an introduction of PSSA-MA into the SIPN membranes as shown in Table 1. The proton transport might occur by two mechanisms: (i) the Grotthuss mechanism, which can be idealized as the protons jump from one solvent molecule to the next through hydrogen bonds, or (ii) the vehicle mechanism, which assumes the proton diffuses together with solvent molecules by forming a complex such as H_3O^+ or H_5O_2^+ (hydronium ion) and then diffuses intact [38]. For the first mechanism, the activation energy for proton conduction was reported to be around 14–40 kJ mol^{-1} [39]. The measured $E_{a,\text{cond}}$ values for the SIPN membranes corresponded well to this range. Accordingly, it is deduced that the proton transfer in the SIPN

Table 1
Dependence of proton conductivity of PVA/SSA/PSSA-MA membranes as function of temperatures and activation energy calculated according to Arrhenius equation

Membrane	Proton conductivity (S cm^{-1})				Activation energy (kJ mol^{-1})
	20 °C	30 °C	40 °C	50 °C	
SIPN-0	8.04×10^{-4}	1.16×10^{-3}	1.75×10^{-3}	2.58×10^{-3}	30.76
SIPN-20	3.46×10^{-3}	5.47×10^{-3}	7.82×10^{-3}	1.13×10^{-2}	30.77
SIPN-40	9.94×10^{-3}	1.29×10^{-2}	1.63×10^{-2}	2.78×10^{-2}	25.99
SIPN-60	1.79×10^{-2}	2.22×10^{-2}	3.25×10^{-2}	4.35×10^{-2}	23.86
SIPN-80	2.96×10^{-2}	3.65×10^{-2}	3.88×10^{-2}	5.49×10^{-2}	14.98
Nafion® 115	1.95×10^{-2}	2.33×10^{-2}	2.56×10^{-2}	2.87×10^{-2}	9.90

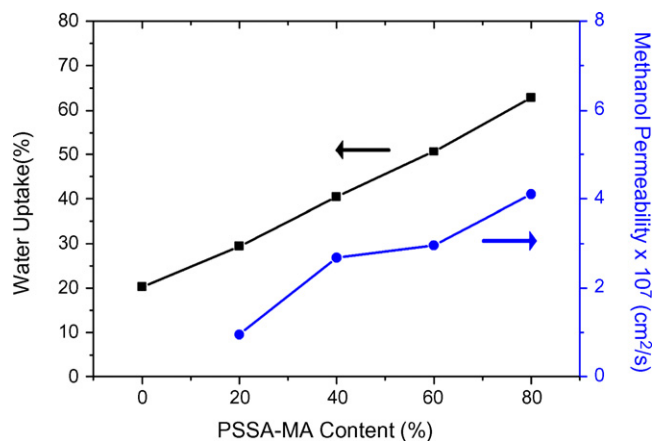


Fig. 5. Water uptake and methanol permeability of SIPN membranes based on PVA/SSA20 with different amounts of PSSA-MA trapped in the network (PVA, M_w : 89,000–98,000 g mol^{-1}).

membranes was mainly through the Grotthuss mechanism. On the other hand, the $E_{a,\text{cond}}$ for Nafion® 115 in this study measured a value of 9.9 kJ mol^{-1} , which is in good agreement with literature data [25,40], and it was well recognized that both the vehicle and Grotthuss mechanisms were responsible for Nafion®'s proton transfer [24].

Methanol permeability is a critical point affecting DMFC performance. The methanol permeability of the SIPN membranes as a function of PSSA-MA is presented in Fig. 5. The methanol permeability of the SIPN membranes increased with PSSA-MA content varying from 20 to 80%. Similar trends in the water uptake and methanol permeability are well correlated. For comparison, methanol permeability of Nafion® 115 was also measured under similar experimental conditions reported in this study as $1.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and is in agreement with literature [41].

Table 2
The measured water uptake, proton conductivity, methanol permeability and selectivity of various PVA/SSA20/PSSA-MA (PVA, M_w : 89,000–98,000 g mol^{-1}) and Nafion® 115 membranes

Membrane	Water uptake (wt.%)	Conductivity (S cm^{-1})	Methanol permeability ($\text{cm}^2 \text{ s}^{-1}$)	Selectivity, φ ($\times 10^4 \text{ S cm}^{-3} \text{ s}$)
SIPN-20	29.4	6.63×10^{-3}	9.56×10^{-8}	6.59
SIPN-40	40.4	1.02×10^{-2}	2.68×10^{-7}	3.81
SIPN-60	50.7	1.66×10^{-2}	2.96×10^{-7}	5.61
SIPN-80	62.9	2.59×10^{-2}	4.10×10^{-7}	6.32
Nafion® 115	37.0	1.4×10^{-2}	1.8×10^{-6}	0.78

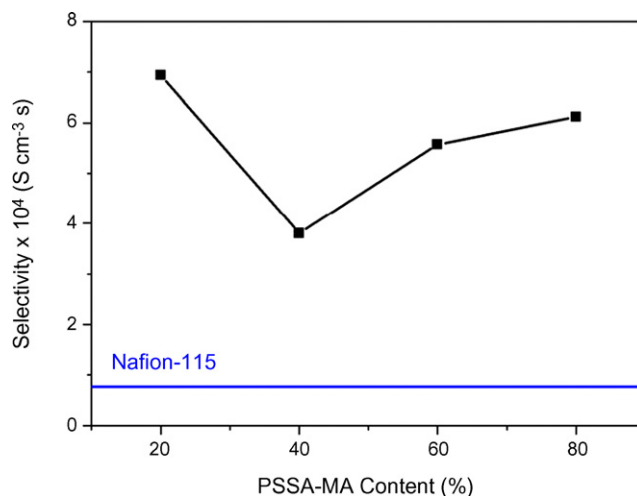


Fig. 6. Selectivity of SIPN membranes based on PVA/SSA20 with different amounts of PSSA-MA trapped in the network (PVA, M_w : 89,000–98,000 g mol^{-1}).

As shown in Table 2, all of the SIPN membranes show lower methanol permeability than Nafion® 115. The methanol permeability of the SIPN-80 membrane measures $4.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, about one-fourth lower than that of Nafion® 115. The lower methanol permeability of the SIPN membrane relates well to the lower methanol uptake behaviors of the SIPN membranes. The relationship shows that the SIPN membranes have better methanol resistance than Nafion® 115. In addition, it clearly indicates that methanol crossover can significantly be reduced if these SIPN membranes are used in DMFC.

For the purpose of exploring the possibility of the SIPN membranes using in DMFC, the selectivity of proton conductivity and methanol permeability should be analyzed. Fig. 6 shows the selectivity of the SIPN membranes with different PSSA-MA

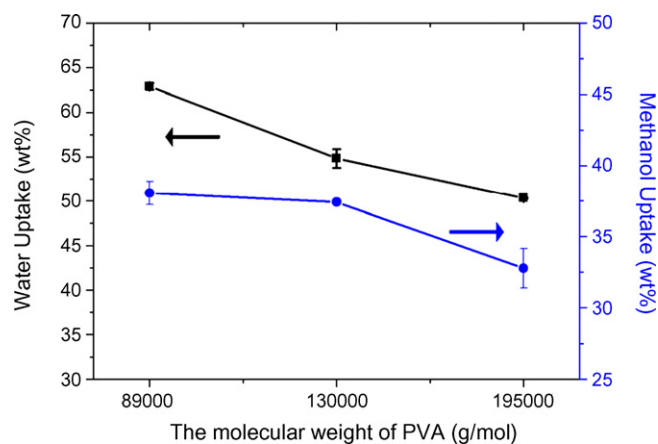


Fig. 7. Water and methanol uptakes of SIPN-80 membranes based on different PVA molecular weight.

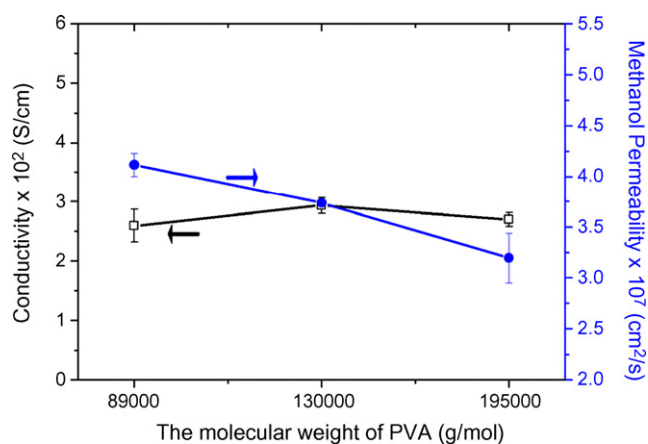


Fig. 8. Proton conductivity and methanol permeability of SIPN-80 membranes based on different PVA molecular weight.

content. Importantly, all of the SIPN membranes showed higher selectivity than that of Nafion[®] 115.

All the measured, important properties related to proton exchange membranes are summarized in Table 2. As shown in the table, it can be concluded that a higher PSSA-MA content plays a major role in controlling the proton conduction due to the increase of sulfonic acid and carboxylic groups in the membrane. However, the higher amounts of PSSA-MA also led to excessive swelling in water and caused undesired mechanical instability and methanol permeability of the membranes. In this context, the mechanical property of the SIPN membranes was improved by using a high molecular weight of PVA.

3.2. Effect of PVA molecular weight

The mechanical property of proton-conducting membranes is the key factor necessary to explore the possibility of membranes used in DMFC. However, high water uptake leading to high proton conductivity results in excessive swelling and poor dimensional stability of membranes.

Importantly, molecular weight is a fundamental parameter which affects all the mechanical properties of polymers. PVA with different molecular weights were adopted in order to improve the mechanical property of the SIPN membranes. Fig. 7 shows the water and methanol uptakes of SIPN-80 as a function of PVA molecular weight. The water uptake values decreased from 62.9 to 50.3 wt.% with an increase of PVA molecular weight from 89,000–98,000 to 195,000 g mol⁻¹. A similar trend was found in methanol uptake behavior. The methanol uptake decreased with an increase of PVA molecular weight. In addition,

the swelling of a membrane determines its mechanical properties and its dimensional stability [32]. More water uptake can lead to lower mechanical stability of polymeric membrane because the excess water may cause high stress on the local bonds of the membrane and interrupt the integration of the membrane structure. Therefore, it is reasonable to deduce that using PVA with higher molecular weight is helpful in preventing a deterioration of the mechanical stability of the membrane.

The proton conductivity and methanol permeability of SIPN-80 membranes with different PVA molecular weights are presented in Fig. 8. No significant effect of molecular weight on the proton conductivity of the membranes was found. In contrast, the methanol permeability of SIPN-80 membranes slightly decreased with the increase of PVA molecular weight. Some of the specific characteristics subject to the membranes SIPN-80 with various PVA molecular weights and Nafion[®] 115 were summarized in Table 3. It is worth noting that the membrane with higher molecular weight exhibited lower water and methanol uptakes. As a consequence of higher selectivity, it is therefore wise to select PVA with higher molecular weight for preparing SIPN membranes for DMFC applications.

3.3. DMFC performance

Fig. 9(a) shows fuel cell performance of an MEA using the SIPN-60 membrane (M_w : 195,000 g mol⁻¹; thickness: 70 μ m) at various temperatures (30, 40, 50, 60, 70 and 80 °C with 2 M methanol and humidified oxygen gas at ambient pressure). As can be seen, there is a consistent improvement in fuel cell performance as the cell temperature was increased

Table 3
Characteristics subject to the membranes SIPN-80 with various PVA molecular weights and Nafion[®] 115

Molecular weight of PVA (g mol ⁻¹)	Water uptake (wt.%)	Methanol uptake (wt.%)	Conductivity (S cm ⁻¹)	Methanol permeability (cm ² s ⁻¹)	Selectivity, ϕ ($\times 10^4$ S cm ⁻³ s)
89,000–98,000	62.9	38.0	2.59×10^{-2}	4.10×10^{-7}	6.32
130,000	54.8	37.4	2.93×10^{-2}	3.73×10^{-7}	7.86
195,000	50.3	32.8	2.69×10^{-2}	3.19×10^{-7}	8.43
Nafion [®] 115	37.0	62.6	1.4×10^{-2}	1.8×10^{-6}	0.78

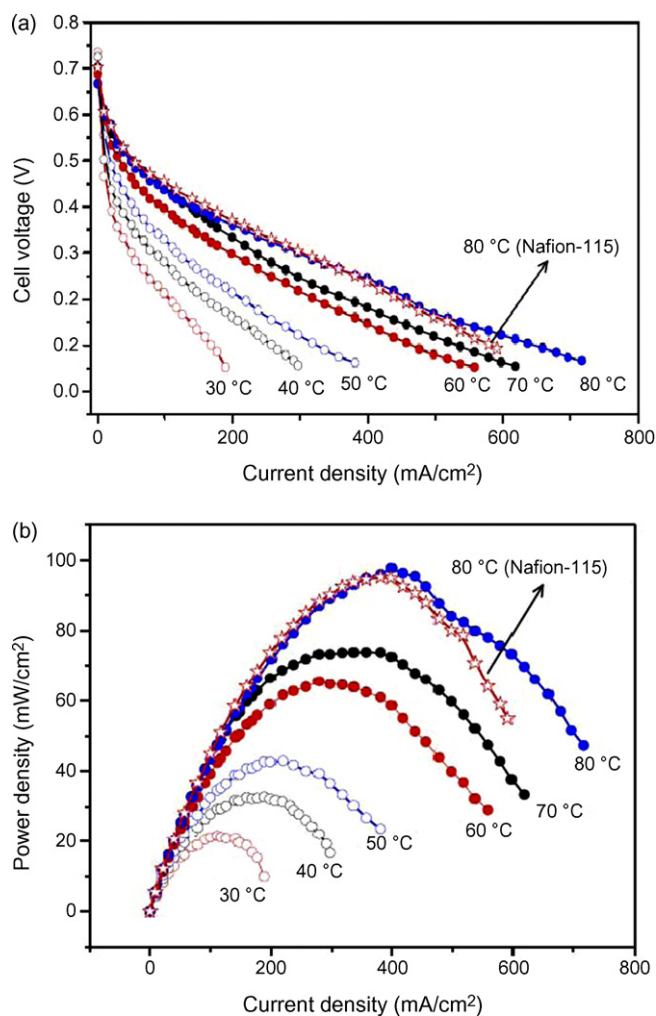


Fig. 9. Direct methanol fuel cell performance of a SIPN-60 membrane (thickness: 70 μm)-based MEA using 2 M methanol/ O_2 at various temperatures. (a) Polarization data and (b) power density data. FC performance for Nafion[®] 115-based MEA at 80 $^\circ\text{C}$ is given for comparison.

from 30 to 80 $^\circ\text{C}$. The power density data for the MEA based on SIPN-60 membrane is given in Fig. 9(b). A power density value of over 100 mW cm^{-2} was obtained at 80 $^\circ\text{C}$ using 2 M methanol/oxygen at 100% RH and ambient pressure. In order to compare the performance of the SIPN membrane-based MEAs for DMFC application, polarization data for the Nafion[®] 115 membrane-based MEA at 80 $^\circ\text{C}$ is also provided in Fig. 9(a) and (b). As can be seen from the data, the peak power (>100 mW cm^{-2}) of SIPN-based MEA is as high as that of the Nafion[®] 115 membrane. This clearly demonstrates the potential of SIPN membrane for DMFC applications.

4. Conclusions

In this study, a series of SIPN proton-conducting membranes have been prepared with PSSA-MA penetrating in a cross-linked PVA network. The measured IECs of the membranes increased with increase of the PSSA-MA content varying from 20 to 80% and it correlated well with water uptake and proton conductivity. The SIPN-60 and SIPN-80 membranes had higher proton

conductivity than Nafion[®] 115 with reasonable water uptake. Additionally, the methanol permeability of the SIPN membranes was much lower than that of Nafion[®] 115.

Moreover, a series of different PVA molecular weight-based SIPN membranes were synthesized. The measured methanol permeability of the membranes decreased with the increased PVA molecular weight and it correlated well with the water and methanol uptake. Furthermore, the molecular weight of PVA was found to have no obvious influence on proton conductivity under a fully hydrated state. The power density value of over 100 mW cm^{-2} was obtained for the electrode assembly consisting of the SIPN-60 membrane at 80 $^\circ\text{C}$, using commercial binary alloy anode catalysts and 2 M methanol.

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