



A novel organic/inorganic polymer membrane based on poly(vinyl alcohol)/poly(2-acrylamido-2-methyl-1-propanesulfonic acid/3-glycidyloxypropyl trimethoxysilane polymer electrolyte membrane for direct methanol fuel cells

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ABSTRACT

Poly(vinyl alcohol)/poly(2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPS)/3-glycidyloxypropyl)trimethoxysilane (PVA/PAMPS/GPTMS) organic/inorganic proton-conducting polymer membranes are prepared by a solution casting method. PAMPS is a polymeric acid commonly used as a primary proton donor, while 3-(glycidyloxypropyl)trimethoxysilane (GPTMS) is an inorganic precursor forming a semi-interpenetrating network (SIPN). Varying amounts of sulfosuccinic acid (SSA) are used as the cross-linker and secondary proton source. The characteristic properties of PVA/PAMPS/GPTMS composite membranes are investigated by thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), micro-Raman spectroscopy and the AC impedance method. Direct methanol fuel cells (DMFCs) made of PVA/PAMPS/GPTMS composite membranes are assembled and examined. Experimental results indicate that DMFCs employing an inexpensive, non-perfluorinated, organic/inorganic SIPN membrane achieve good electrochemical performance. The highest peak power density of a DMFC using PVA/PAMPS/GPTMS composite membrane with 2 M CH₃OH solution fuel at ambient temperature is 23.63 mW cm⁻². The proposed organic/inorganic proton-conducting membrane based on PVA/PAMPS/GPTMS appears to be a viable candidate for future DMFC applications.

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1. Introduction

Methanol is often used as a fuel in fuel cells. Direct methanol fuel cells (DMFCs) have recently gained much attention for their great potential as portable power sources for cellular phones, notebook computers, etc. Research on DMFCs is ongoing, and has generated many advancements in the past few years [1–17]. However, the mass production of DMFCs has been hindered by several serious problems, including slow methanol oxidation kinetics and incomplete electrooxidation of methanol, the poisoning of adsorbed intermediate species on the Pt surface, high methanol crossover rate through Nafion polymer membrane, and the high costs of Nafion polymer membranes and Pt catalysts.

Perfluorosulfonate ionomer membranes, such as Nafion membranes (DuPont), are the primary polymer membranes currently used in DMFCs. However, commercial Nafion polymer membranes create a serious methanol crossover problem, in which methanol permeates from the anode to the cathode. This methanol permeation not only causes a loss of fuel, but also forms a mixed potential

at the cathode that decreases electrochemical performance. Thus, for a liquid methanol fuel cell, it is imperative that the solid polymer membrane has a low methanol permeability rate, i.e., has no methanol crossover problem and a higher ionic conductivity. Researchers have used various types of ceramic fillers to reduce the methanol crossover rate: TiO₂ (PVA/TiO₂) [8], SiO₂ (PEG/SiO₂ and PVA/SiO₂) [9], hydroxyapatite (PVA/HAP) [10]. When fillers with a high specific surface area act as stiffer materials in the PVA polymer matrix, they effectively reduced the methanol permeability of the composite polymer membrane [1,9,10].

Yang et al. [1] prepared a PVA/MMT composite polymer membrane for DMFCs. However, the challenge of creating a PVA-based polymer membrane is that it shows a poor proton conductivity and acidic electrolytes, i.e., inorganic acid: H₂SO₄, H₃PO₄, may easily leak out from the PVA polymer membranes. This is primarily because the PVA polymer itself does not contain any negatively charged ions or negative organic functional groups, such as the carboxylic (–COOH) or sulfonic acid (–SO₃H) groups. To use a PVA polymer membrane in an acidic DMFC, some negatively charged ions would need to be grafted or blended on the PVA polymer host. Rhim et al. [2] prepared a PVA/sulfosuccinic acid (SSA) proton-conducting polymer membrane. In this design, the SSA contained both –SO₃H and –COOH groups, which var-

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ied in the range of 5–30 wt.%, and served as a crosslinking agent and proton donor. Okada et al. [3–5] studied a proton-conducting membranes based on PVA and poly(2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPS) for low temperature DMFC applications.

Recently, Kumar et al. [6] examined poly(vinyl alcohol)/para toluene sulfonic acid (PVA/PTSA) polymer membranes for a DMFC. By introducing a suitable amount of the $-SO_3H$ group as a proton charge carrier, this hydrophilic PTSA enhanced the ionic conductivity of the PVA/PTSA polymer membrane. These PVA/10 wt.%PTSA membranes exhibited a high selectivity in the range of $12.7 \times 10^7 \text{ mS s cm}^{-3}$, which is more than three times greater than that of a Nafion 117 membrane. Sahu et al. [7] investigated the effect of poly(styrene sulfonic acid) content on the PVA/PSSA composite membrane and its application for a hydrogen–oxygen polymer electrolyte membrane fuel cell (PEMFC). They found that the maximum proton conductivity of the PVA/PSSA membrane occurred at 35 wt.%PSSA. The PEMFC with the optimized PVA/PSSA polymer membrane achieved a peak power density of 210 mW cm^{-2} at 500 mA cm^{-2} at 75°C , compared with a peak power density of only 38 mW cm^{-2} at 80 mA cm^{-2} for a PEMFC with the pristine PVA membrane.

The experiments in this study use poly(2-acrylamido-2-methyl-1-propanesulfonic acid (PAMPS) as the primary proton donor because it allows reasonable proton conductivity in the PVA/PAMPS composite membrane. Sulfosuccinic acid (SSA) was used as a crosslinking agent for PVA polymer instead of glutaraldehyde (GA), which can also be a proton donor. In addition, 3-(glycidyloxypropyl)trimethoxysilane (GPTMS) provided inorganic Si. The addition of GPTMS to the PVA/PAMPS polymer matrix to form a semi-interpenetrating network (SIPN) membrane through a sol–gel process greatly decreased the methanol permeability and enhance the mechanical strength and thermal properties. A fixed amount of PAMPS and GPTMS was added to the PVA host (i.e., PVA:PAMPS:GPTMS = 10:2:1 in mass ratio).

Fig. 1 shows the chemical structure of the PVA, PAMPS, GPTMS and SSA. The PVA polymer served as a primary proton conducting ingredient, and was trapped inside the PVA matrix to offer the excellent ionic conductivity without an acid leakage problem. PAMPS has good chemical stability and can form excellent proton-conducting gel polymers [3–5]. GPTMS can also provide a Si–O–Si network through hydrolysis and condensation reactions. The epoxy content of the GPTMS can also improve the mechanical properties and form a 3D semi-interpenetrating network (SIPN) membrane. The SSA cross-linking agent bridge between PVA molecules to form crosslinking network, and also provides an additional proton conducting path ($-SO_3H$ functional group). Fig. 2 illustrates a possible structure for the PVA/PAMPS/GPTMS composite membrane.

TGA was used to analyze the thermal stability properties of the PVA/PAMPS/GPTMS composite membrane, while SEM was employed to examine the surface morphology. Micro-Raman spectroscopy was used to investigate the chemical properties of PVA/PAMPS/GPTMS composite membranes. A diffusion cell was designed to measure the methanol permeability of PVA/PAMPS/GPTMS membranes. The ionic conductivity of PVA/PAMPS/GPTMS polymer electrolytes was measured by AC impedance spectroscopy. The characteristic properties of the crosslinked PVA/PAMPS/GPTMS composite membranes with different amounts (5–20 wt.%) of SSA were examined and discussed. Finally, a DMFC consisting of the air cathode, the PtRu anode, and PVA/PAMPS/GPTMS composite membrane, was assembled and investigated. For comparison, the methanol concentration was varied in the range of 1–4 M. The electrochemical characteristics of the DMFC were measured by its linear polarization, especially for the peak power density of the DMFC.

2. Experimental

2.1. Preparation of the PVA/PAMPS/GPTMS composite membrane

PVA (M.W. = $130,000 \text{ g mol}^{-1}$, Aldrich), PAMPS (M.W. = $2,000,000 \text{ g mol}^{-1}$, Aldrich), GPTMS (Trade name: KH-560, Aldrich) and SSA (70 wt.% in water, Aldrich) were used as received without further purification. The degree of polymerization and saponification of PVA were 1700 and 98–99%, respectively. The PVA/PAMPS/GPTMS composite membrane was prepared by a solution casting method. The PVA polymer solution was stirred continuously at 90°C for 2 h until it became homogeneous and viscous. The fixed amounts of PAMPS and GPTMS were added to the PVA polymer host under a constant stirring condition. The chemical composition of PVA:PAMPS:GTPMS was 10:2:1 (in a mass ratio). Various amounts of 5–20 wt.% SSA were added to the viscous mixture polymer solution to carry out the cross-linking reaction. The resulting viscous composite polymer solution was coated onto a glass plate.

The wet composite polymer membrane ranged from 0.200 to 0.400 mm thick. The glass plate with viscous PVA/PAMPS/GPTMS/SSA sample was weighed and then excess water was allowed to evaporate slowly at 60°C at a relative humidity of 30%. After the water solvent evaporated, the glass plate with the composite membrane was weighed again. The thickness of the dried composite membrane was controlled between 0.120 and 0.140 mm. Previous research reports the details of preparing the composite polymer membranes based on PVA using a solution casting method [1,10].

2.2. Surface morphology and thermal properties

The surface morphology of the PVA/PAMPS/GPTMS composite membrane was investigated using a Hitachi S-2600H scanning electron microscope (SEM). TGA thermal analysis was carried out using a Mettler Toledo TGA/SDT 851 system. Measurements were carried out at temperatures ranging from 25 to 600°C under N_2 atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ using a 10 mg sample.

2.3. Ionic conductivity and methanol permeability measurements

The conductivity of the PVA/PAMPS/GPTMS composite membranes was measured using the AC impedance method. The PVA/PAMPS/GPTMS composite membranes were first immersed in a 2 M H_2SO_4 solution for at least 24 h, and then washed with D.I. water several times before testing. The composite membranes were clamped between stainless steel (SS304), ion-blocking electrodes, each with the surface area of 1.32 cm^2 , in a spring-loaded glass holder. A thermocouple was kept in close proximity to the polymer electrolyte membrane for temperature measurement. Each sample was equilibrated at the experimental temperature for at least 60 min before measurement. AC impedance measurements were carried out using an Autolab PGSTAT-30 (Eco Chemie B.V., Netherlands), and the AC spectra were recorded in the range of 1 MHz to 10 Hz at an excitation signal of 5 mV. The AC impedance spectra of the composite polymer membrane were recorded at a temperature range between 30 and 70°C . Experimental temperatures were maintained within $\pm 0.5^\circ\text{C}$ using a convection oven. The PVA/PAMPS/GPTMS composite membranes were examined at least three times.

Methanol permeability measurements were also conducted using a diffusion cell [1]. The cell was divided into two compartments, in which one compartment was filled with D.I. water (compartment B) and the other compartment was filled with a 20 wt.% methanol aqueous solution (compartment A). Prior to the test, the PVA/PAMPS/GPTMS composite electrolyte membrane was

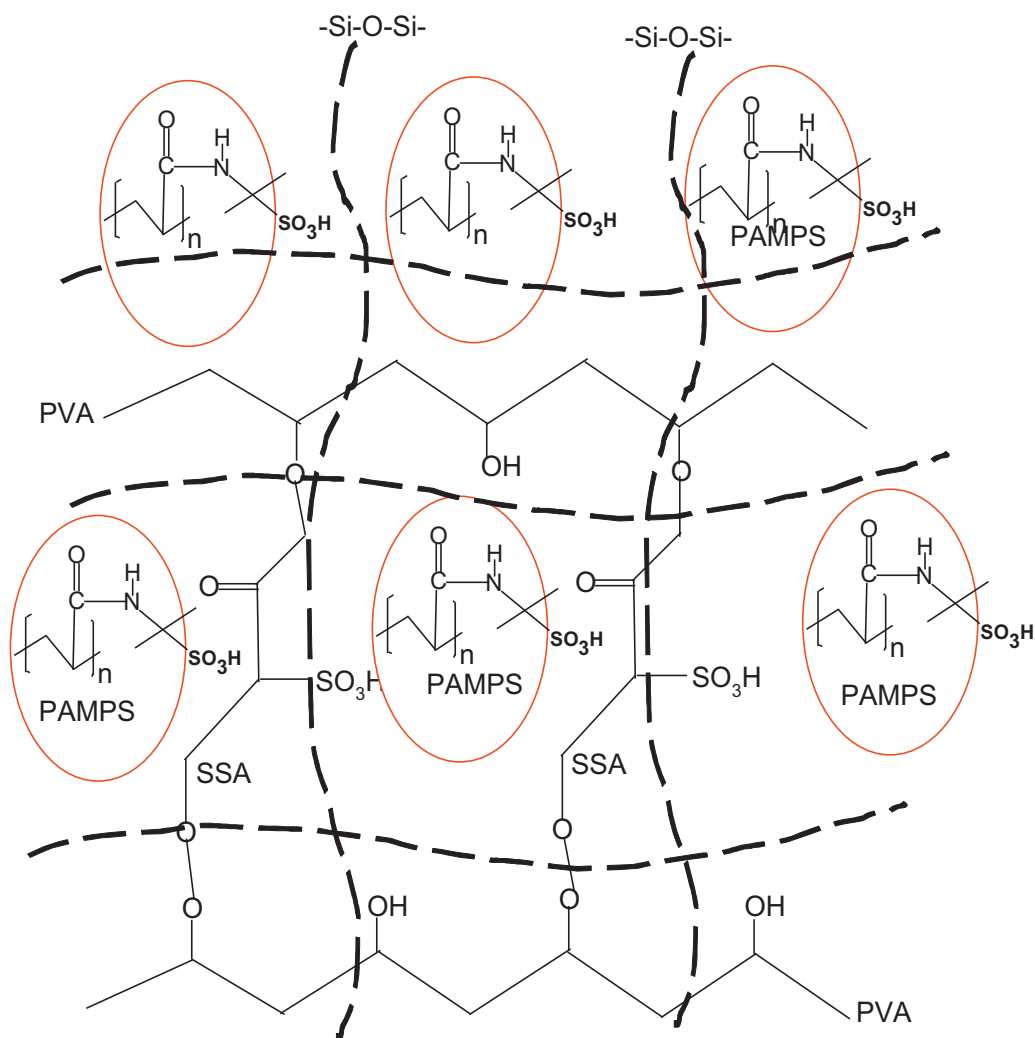


Fig. 2. The possible structure of PVA/PAMPS/GPTMS/SSA SIPN membrane.

of PVA/PAMPS/GPTMS membranes show four major weight loss regions, which appear as the four major peaks in the DTG curves (data not shown here). The pure PVA polymer remained fairly stable up to 300 °C. However, when PAMPS and SSA were added to the PVA matrix, the resulting blend membranes exhibited a lower thermal stability, as Fig. 3 clearly shows. For PVA/PAMPS/GPTMS/Xwt.%SSA membranes, the first region at 80–120 °C ($T_{p,1} = 100$ °C) is due to the evaporation of weakly physical and strongly chemical bound H₂O; the inset of Fig. 3 shows that the weight loss of the membrane is about 4–5 wt.%. The second transition region at approximately 130–200 °C ($T_{p,2} = 170$ °C) is due to the degradation of the sulfonic groups (–SO₃H) in PAMPS and the degradation of the PVA main chain. The total weight loss corresponding to this phase is approximately 24–26 wt.%. The peak of the third transition at 220–350 °C ($T_{p,3} = 290$ °C) is due to the cleavage of the side-chain of PVA polymer, with a total weight loss of about 41–43 wt.% at 350 °C. The fourth transition region at 350–470 °C ($T_{p,4} = 420$ °C) is due to the cleavage of the backbone of the PVA polymer membrane, and reflects a total weight loss of approximately 82–83 wt.% at 600 °C.

The degradation peaks of the PVA/PAMPS/GPTMS/SSA proton-conducting composite membranes are less intense and shift towards a higher temperature. This implied that the improvement in thermal stability is likely due to the cross-linked reaction between the PVA and SSA and the formation of a Si–O–Si network system (SIPN), as shown in Fig. 2.

3.2. Surface morphology

Fig. 4 shows SEM photographs of the top and cross-sections views of the PVA/PAMPS/GPTMS composite membrane. The PVA/PAMPS/GPTMS composite membranes exhibited a uniform and compact morphology without any phase separation or voids. These SEM results indicated that the GPTMS was distributed uniformly into the PVA/PAMPS matrix, forming a Si–O–Si crosslinking network due to the sol–gel process used here.

Both the PVA/PAMPS polymer matrix and the GPTMS inorganic material were homogeneous and fully compatible without any phase separation occurring. The cross-linking reaction of SSA and PVA greatly enhanced the mechanical strength and reduced the swelling ratio, forming a stable interfacial phase at the electrolyte/electrode that indirectly decreased the methanol crossover rate. The PVA/PAMPS/GPTMS polymer membrane also formed a semi-interpenetrating network (SIPN) structure that improved the mechanical and thermal properties. This is because the SIPN structure had high cross-linking density and formed strong covalent bonds between the inorganic and organic interfaces.

3.3. Micro-Raman analysis

Fig. 5 shows the micro-Raman spectra of SSA, PAMPS, PVA, PVA/PAMPS/GPTMS, and PVA/PAMPS/GPTMS/Xwt.%SSA composite

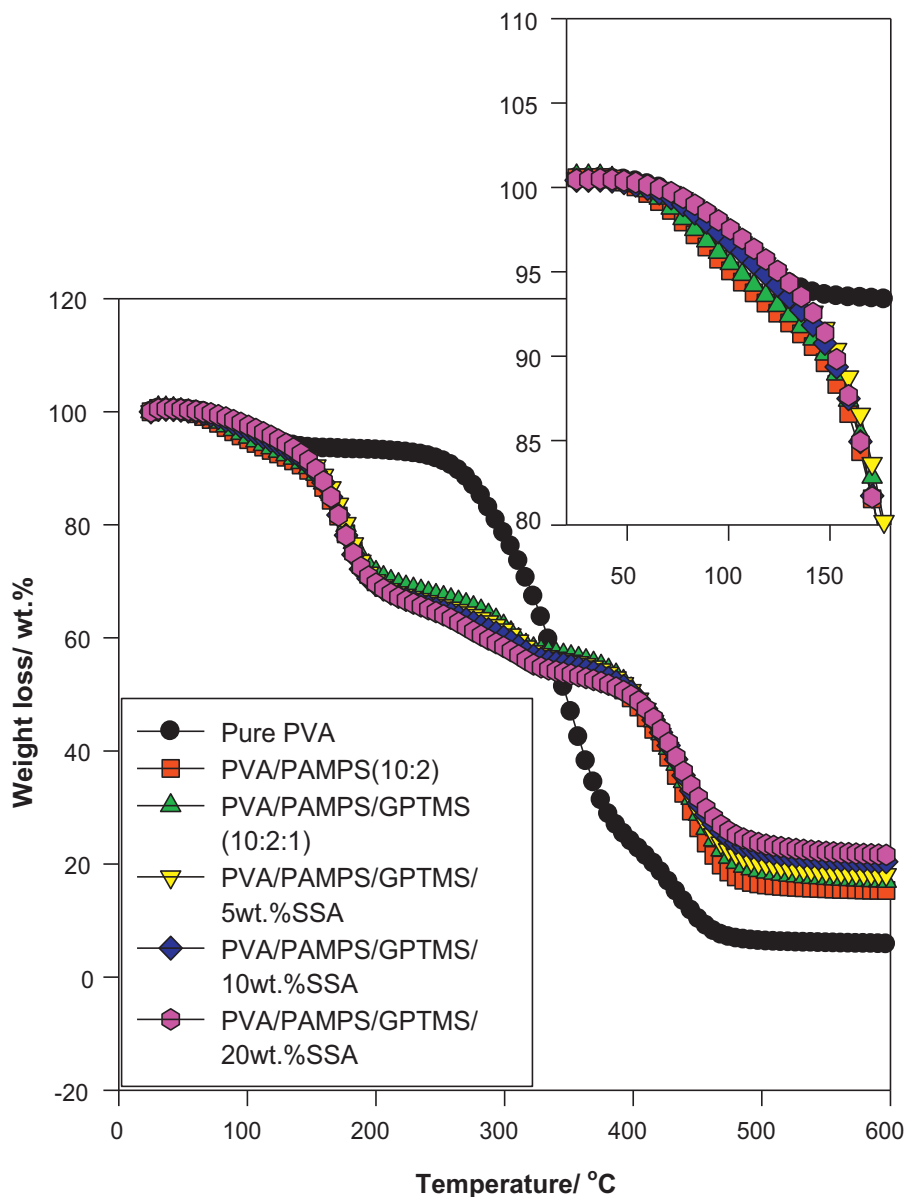


Fig. 3. TGA thermograph for PVA/PAMPS/GPTMS/Xwt.%SSA composite polymer membranes; the inset for a temperature range of 25–150 °C.

membranes. The SSA cross-linker exhibited four strong characteristic scattering peaks at 1043, 918, 845 and 715 cm^{-1} . The PAMPS showed three strong characteristic scattering peaks at 1434, 1294, and 769 cm^{-1} . The spectra showed several strong characteristic scattering peaks for the PVA polymer at 1440, 1258, 1146, 919, and 860 cm^{-1} [1,10]. Fig. 5 also shows two more strong characteristic scattering peaks at 1041 and 770 cm^{-1} . One represents the $-\text{SO}_3^-$ symmetric stretching band at 1041 cm^{-1} , which is due to the SSA; the other was identified for the NH stretching band at 770 cm^{-1} , which is primarily due to the PAMPS polymeric acid.

In addition, the intensity of the 1041 cm^{-1} peak was enhanced as the amount of the added SSA crosslinking agent increased. This is due to the increased amount of the $-\text{SO}_3\text{H}$ group (SSA) in the PVA/PAMPS/GPTMS composite membranes. The most important finding of micro-Raman analysis was the intensities of these characteristic vibrational peaks for PVA/PAMPS/GPTMS/SSA composite membranes slightly shifted; the vibrational peak of the $-\text{SO}_3^-$ at 1041 cm^{-1} is also an indicator for PAMPS and SSA compounds [3–5]. In other words, the ionic group ($-\text{SO}_3^-$) exists in the PVA/PAMPS/GPTMS/SSA composite membrane. The PAMPS poly-

mer (as a polymeric acid) containing the sulfonic group was trapped inside the PVA matrix, enhancing the proton conductivity. More importantly, it also prevented proton charge carriers from being lost from the polymer electrolyte membrane due to the formation of the SIPN network structure.

3.4. Ionic conductivity and methanol permeability

The typical AC impedance spectra of the PVA/PAMPS/GPTMS composite membrane were measured at different temperatures. The AC spectra are typically non-vertical spikes for stainless steel (SS) blocking electrodes, i.e., a SS|PVA/PAMPS/GPTMS SPE|SS cell. Analysis of the spectra yields information about the properties of the PVA/PAMPS/GPTMS electrolyte membrane, such as the membrane resistance, R . The membrane resistance associated the electrolyte membrane conductivity was measured using the high-frequency intercept of the impedance with real axis. Accounting for the thickness of the electrolyte membranes, the ionic conductivity (σ) was calculated from the R value, using the following equation: $\sigma = L/R \cdot A$, where σ is the proton conductivity of the

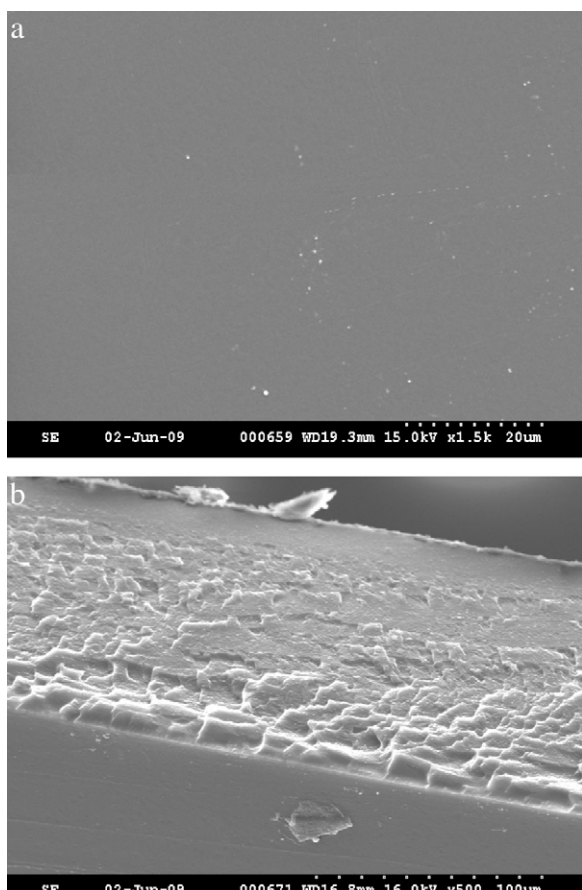


Fig. 4. SEM photographs (top view and cross-section view) for PVA/PAMPS/GPTMS composite polymer membrane.

electrolyte membrane (Scm^{-1}), L is the thickness (cm) of the PVA/PAMPS/GPTMS electrolyte membrane, A is the cross-sectional area of the blocking electrode (cm^2), and R is the resistance (ohm) of a proton-conducting composite electrolyte membrane.

The R_b values of PVA/PAMPS/GPTMS electrolyte membranes typically range from 4 to 16 Ω and are highly dependent on the contents of SSA. Note that these composite electrolyte membranes were immersed in D.I. water for 24 h before measurement [1].

Table 1 lists the ionic conductivities of PVA/PAMPS/GPTMS/Xwt.%SSA electrolyte membranes at different temperatures in water. The ionic conductivity value of PVA/PAMPS/GPTMS electrolyte membranes (without SSA cross-linker) in water was $3.18 \times 10^{-2} \text{Scm}^{-1}$ at 30 °C. In contrast, the ionic conductivity values for PVA/PAMPS/GPTMS/Xwt.%SSA electrolyte membranes with 5, 10, and 20 wt.% SSA were 1.58×10^{-2} , 1.93×10^{-2} , and $2.95 \times 10^{-2} \text{Scm}^{-1}$ at 30 °C, respectively. The PVA/PAMPS/GPTMS/20 wt.%SSA composite membrane achieved the highest ionic conductivity,

Table 1
The ionic conductivities for the PVA/PAMPS/GPTMS/Xwt.%SSA composite membranes at various temperatures.

Films	Para. L (cm)	Conductivity ($\times 10^{-2} \text{Scm}^{-1}$)				
		30 °C	40 °C	50 °C	60 °C	70 °C
		0 wt.%SSA	0.0123	3.18	4.17	4.77
5 wt.%SSA	0.0140	1.58	1.79	1.91	2.12	2.34
10 wt.%SSA	0.0135	1.93	2.09	2.29	2.51	2.65
20 wt.%SSA	0.0140	2.95	3.08	3.26	3.46	3.61

Table 2

The E_a , ionic conductivity, methanol permeabilities and selectivity values for PVA/PAMPS/GPTMS/Xwt.%SSA composite membranes.

Temp.	Para.			
	0 wt.%	5 wt.%	10 wt.%	20 wt.%
$\sigma_{30^\circ\text{C}}$ (Scm^{-1})	0.0318	0.0158	0.0193	0.0295
P ($\text{cm}^2 \text{s}^{-1}$)	9.54×10^{-7}	5.01×10^{-7}	3.66×10^{-7}	1.96×10^{-7}
S^* (Scm^{-3})	3.3×10^4	3.1×10^4	5.3×10^4	1.51×10^5
E_a (kJ mol^{-1})	4.52	8.30	10.57	12.80

* Note: Selectivity ($S = \sigma/P$).

$\sigma = 2.95 \times 10^{-2} \text{Scm}^{-1}$, at ambient temperature. These results clearly show that the ionic conductivity of the PVA/PAMPS/GPTMS/Xwt.%SSA membrane increased when the content of added SSA increased.

Sahu et al. [7] achieved an ionic conductivity of $1.30 \times 10^{-3} \text{Scm}^{-1}$ for a PVA/PSSA membrane in fully humidified conditions at 30 °C. They also showed that the ionic conductivity of a pristine PVA membrane was only $1.0 \times 10^{-5} \text{Scm}^{-1}$ [7]. Compared with the data of other literature data, Rhim et al. [2] also reported the cross-linked PVA membranes using sulfosuccinic acid (SSA), as a cross-linking agent, achieved proton conductivity and methanol permeability ranging from 10^{-3} to 10^{-2}Scm^{-1} and 10^{-7} to $10^{-6} \text{cm}^2 \text{s}^{-1}$, respectively, at a range of 25–50 °C. Huang et al. [12] also studied the proton-conducting polymer membrane based on PVA and poly(vinyl pyrrolidone) (PVP) with SSA for DMFCs. They also showed a proton conductivity on the order of 10^{-2}Scm^{-1} and a methanol permeability of 10^{-8} – $10^{-7} \text{cm}^2 \text{s}^{-1}$ for PVA/PVP/SSA composite membranes.

The results above indicate that the ionic conductivities of all PVA/PAMPS/GPTMS/Xwt.% SSA composite electrolyte membranes in water were on the order of 10^{-2}Scm^{-1} at ambient temperature. The temperature dependence of the ionic conductivity was of the Arrhenius type: $\sigma = \sigma_0 \exp(-E_a/RT)$, where σ_0 is a pre-exponential factor, E_a is the activation energy, and T is the temperature in Kelvin. From the $\log_{10}(\sigma)$ vs. $1/T$ plots, the activation energy (E_a) can be obtained for the PVA/PAMPS/GPTMS/Xwt.%SSA composite electrolyte membranes, which is highly dependent on the SSA content. Table 2 also shows the E_a value of PVA/PAMPS/GPTMS/Xwt.%SSA composite electrolyte membrane is approximately 4.52–12.8 kJ mol^{-1} , which is better than the general crosslinked composite electrolyte membrane based on PVA having E_a value over 14–20 kJ mol^{-1} [13]. The proton transport follows two mechanisms. One is the Grotthus mechanism, which can be explained as a proton jump from one solvent molecule to the next through hydrogen bonds. The other is the vehicle mechanism, which assume that the proton diffuses together with solvent molecules by forming a complex (i.e., H_3O^+) and then diffusing intact. This study assumes that both the Grotthus and vehicle mechanisms may be responsible for the composite polymer membrane proton transfer.

The methanol permeabilities of the crosslinked PVA/PAMPS/GPTMS composite membranes were obtained from the slopes of the straight line for the methanol concentration vs. time curves. The methanol permeabilities of the crosslinked PVA/PAMPS/GPTMS composite membranes were 9.54×10^{-7} – $1.96 \times 10^{-7} \text{cm}^2 \text{s}^{-1}$. The PVA/PAMPS/GPTMS/20 wt.%SSA composite membranes with the highest selectivity ($S = \sigma/P$) was about 1.51×10^5 , which is much higher than that of Nafion membrane [16]. Table 2 also compares the ionic conductivity (at 30 °C), the methanol permeability, selectivity and E_a values for all PVA/PAMPS/GPTMS composite membranes. The methanol permeability of the crosslinked PVA/PAMPS/GPTMS composite membrane, measured to be on the order of $10^{-7} \text{cm}^2 \text{s}^{-1}$ in this study, was lower than

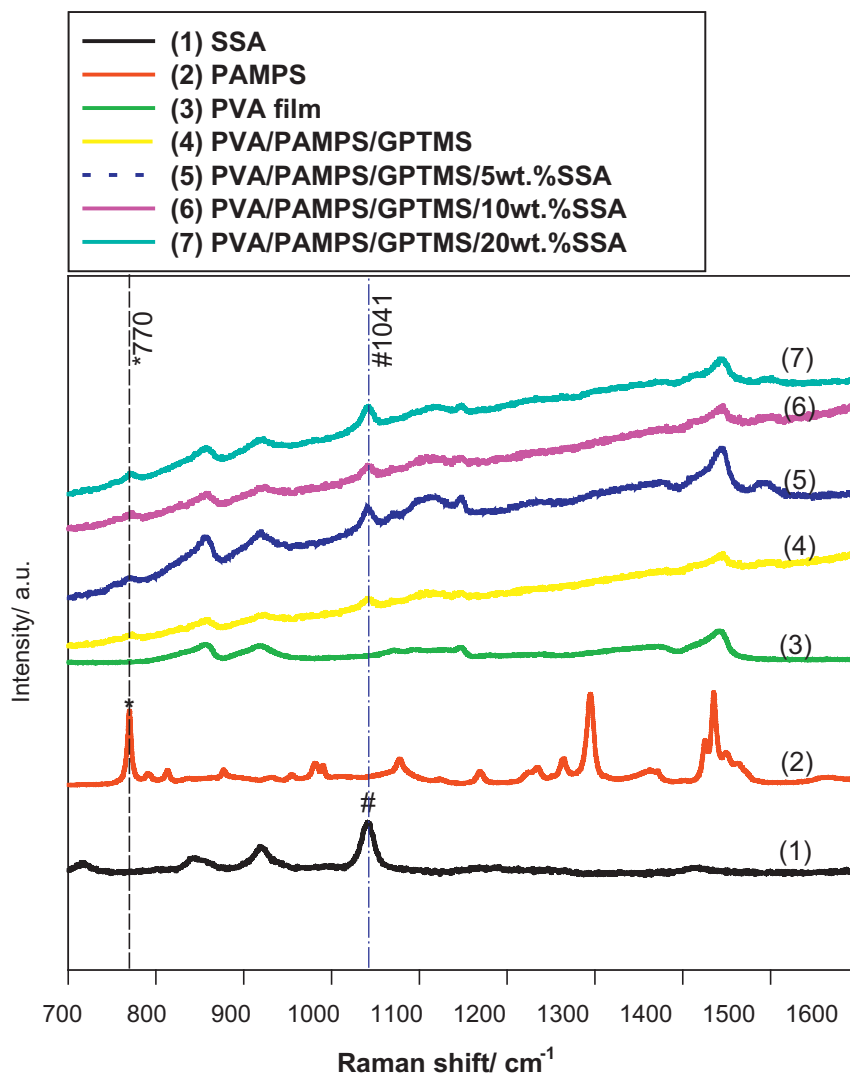


Fig. 5. Micro-Raman spectra for various PVA/PAMPS/GPTMS/Xwt.%SSA composite polymer membranes.

that of the Nafion 117 membrane, which was on the order of $2.91 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [8].

Water uptake (A) and dimensional stability (S) are also important parameters for the polymer membrane applications. The A and S values were defined as follows: $A\% = (W_{\text{wet}} - W_{\text{dry}}/W_{\text{wet}}) \times 100$; $S\% = (W_{\text{wet}} - W_{\text{dry}}/W_{\text{dry}}) \times 100$, where W_{wet} is the weight of the wet membrane and W_{dry} is the weight of the dry membrane [1]. Table 3 compares the $A\%$ and $S\%$ values of all PVA/PAMPS/GPTMS composite membranes and Nafion 117 polymer membrane in three different solutions, i.e., H_2O , H_2SO_4 , and methanol. Compared with the other

PVA-based composite membranes, there are higher $A\%$ and $S\%$ values for Nafion 117 membrane in methanol. This is why the Nafion membrane has a high methanol crossover rate. The swelling ratio in D.I. water can be significantly reduced by increasing the SSA content. Clearly, the mechanical strength and dimensional stability can be well controlled through a SSA crosslinking reaction.

3.5. Electrochemical measurements

Fig. 6 shows the potential–current density (I – V) and the power density–current density curves for an air-breathing DMFC with 1, 2, and 4 M methanol fuels at 25°C , respectively. The highest peak power density of 23.63 mW cm^{-2} was achieved for the DMFC employing PVA/PAMPS/GPTMS/20 wt.%SSA membrane and a 2 M methanol fuel was achieved at $E_{p,\text{max}} = 0.202 \text{ V}$ with a peak current density ($i_{p,\text{max}}$) of $117.16 \text{ mA cm}^{-2}$. By comparison, the peak power density of a similar DMFC, only using a 1 M methanol fuel, was 19.52 mW cm^{-2} at $E_{p,\text{max}} = 0.218 \text{ V}$ with a peak current density of 89.45 mA cm^{-2} . Measurements were made at 25°C and 1 atm. The peak power density of the DMFC with a 4 M methanol fuel was 18.72 mW cm^{-2} at $E_{p,\text{max}} = 0.192 \text{ V}$ with a peak current density of 97.65 mA cm^{-2} . As a result, the peak power densities followed the order of 2 M methanol > 1 M methanol > 4 M methanol. The DMFC with 2 M methanol fuel showed the highest power density

Table 3

The values of absorption ratio ($A\%$) and swelling ratio ($S\%$) for PVA/PAMPS/GPTMS/Xwt.%SSA composite polymer membrane in varied solutions.

Films	Para.					
	D.I. water		2 M H_2SO_4		99 wt.% CH_3OH	
	$A\%$	$S\%$	$A\%$	$S\%$	$A\%$	$S\%$
Nafion 117	14	16	4	9	31	44
PVA film	69	221	67	199	0.52	0.52
0 wt.%SSA	91	1081	68	217	13.23	15.25
5 wt.%SSA	83	523	61	156	12.36	14.11
10 wt.%SSA	87	391	62	165	12.10	13.77
20 wt.%SSA	89	215	62	165	12.50	14.29

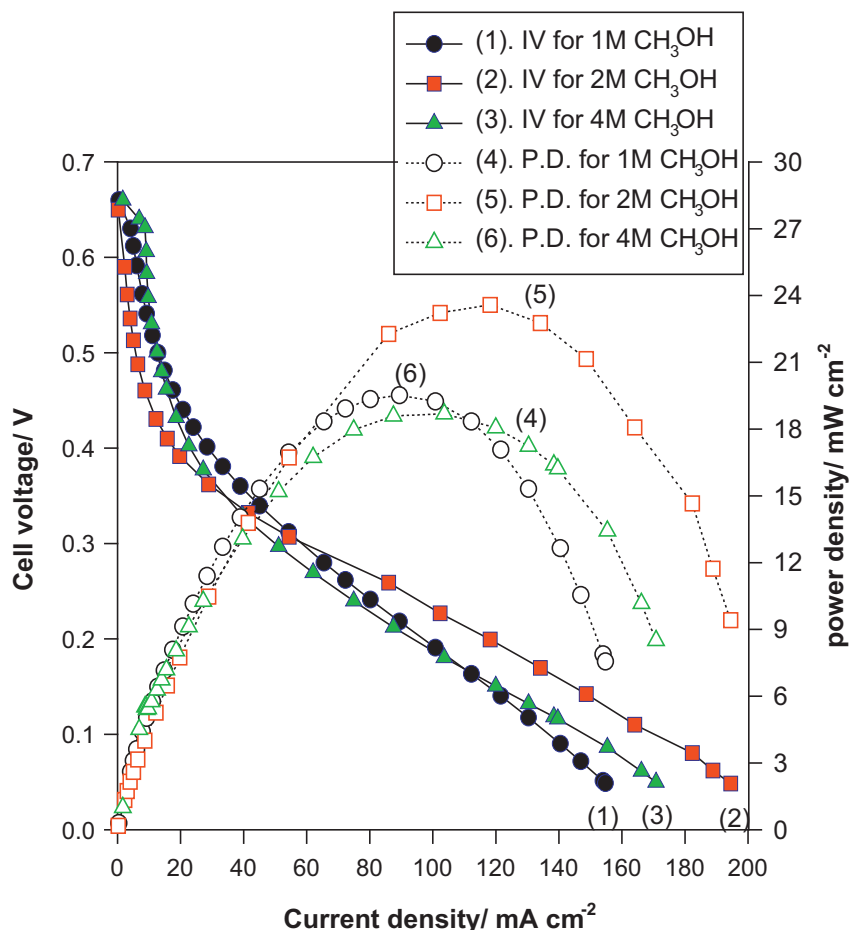


Fig. 6. The I–V and P.D. curves for the DMFC using PVA/PAMPS/GPTMS/20 wt.%SSA composite polymer membrane at 25 °C and in ambient air.

(P.D. = 23.63 mW cm⁻²) of these methanol concentrations, indicating an optimal range under these conditions.

Qiao et al. [4,5] prepared the proton-conducting composite membranes based on high molecular weight PVA and poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) ($\sigma = 0.06\text{--}0.10\text{ S cm}^{-1}$) for DMFC applications. The peak power density of the DMFC fabricated with the acidic PVA/PAMPS membrane was 15.8 mW cm⁻² at 30 °C, and reached 42.9 mW cm⁻² at 80 °C. Yang [13] studied a composite polymer membrane based on sulfonated poly(ether ether ketone) and sulfated poly(vinyl alcohol), i.e., SPEEK/PVA, for an acidic DMFC. They showed a peak power density value of approximately 21 mW cm⁻² for a DMFC with a 2 M methanol/air at 80 °C.

Lin et al. [14] prepared proton-conducting hybrid membranes consisting of PVA and phosphotungstic acid (PWA) for a DMFC. The electrochemical performance of PVA/PWA membrane and Nafion 115 membrane exhibited almost equal peak power density of 5 mW cm⁻², at 20 mA cm⁻² under ambient conditions. Lin et al. [15] also synthesized a semi-interpenetrating network (SIPN) membrane by using PVA with sulfosuccinic acid (SSA) as a cross-linking agent and poly(styrene sulfonic acid-co-maleic acid) (PSSA/MA) as a proton source. The peak power density of the DMFC with the SIPN membrane using 2 M methanol and oxygen gas exceeded 100 mW cm⁻² at 80 °C. Yang [16] studied a composite membrane based on PVA and sulfated β -cyclodextrin for a DMFC. Yang found that the peak power densities of the DMFCs with these composite membranes were increased from 14.34 mW cm⁻² to 18.56 mW cm⁻² under ambient conditions when the content of sulfated β -cyclodextrin increased from 10 to 23 wt.%.

Bhat et al. [17] studied a poly(vinyl alcohol)/polystyrene sulfonic acid/mordenite (PVA/PSSA/MOR) composite blend membrane for DMFCs. A peak power density of 74 mW cm⁻² was achieved for the DMFC using PVA/PSSA electrolyte with 50% degree of sulfonation and 10 wt.% mordenite (MOR) at 70 °C. These results indicate that a DMFC comprised of the PVA/PAMPS/GPTMS composite membrane achieved good electrochemical performance under ambient conditions. Sahu et al. [18] prepared organic-inorganic composite membranes based on Nafion using silica, mesoporous zirconium phosphate (MZP), and mesoporous titanium phosphate (MTP) fillers for DMFCs. Their results show a peak power-density of 110 mW cm⁻² for the DMFC with Nafion 117 membrane at 70 °C using 2 M methanol and pure oxygen feeds. In contrast, the peak power-densities of 140 mW cm⁻², 125 mW cm⁻² and 140 mW cm⁻² for DMFCs were achieved based on Nafion-silica (10 wt.%), Nafion-MZP (5 wt.%) and Nafion-MTP (5 wt.%) composite membranes, respectively. Note that these modified Nafion-based composite membranes show good electrochemical performances for DMFCs at a higher operating temperature (70 °C).

Table 4 compares the peak power density (P.D.) results of different studies under different operation conditions. This table shows that the electrochemical performances of the proposed DMFC are superior to previous design under ambient operation conditions.

As Fig. 7 shows the peak power density (P.D.) of the DMFC using the PVA/PAMPS/GPTMS/20%SSA composite membrane (peak P.D. = 23.632 mW cm⁻²) was much better than that of the DMFC using Nafion 117 membrane (peak P.D. = 8.33 mW cm⁻²), though both used a 2 M methanol fuel at ambient conditions. Clearly, the proposed PVA/PAMPS/GPTMS composite membrane is a cheaper

Table 4
Comparison of peak power densities for some alkaline DMFC presented in the literature (data classified accordingly to electrolyte phase, temperature, methanol concentrations).

Polymer membranes	Operation conditions				Peak power density(mW cm^{-2})	Reference
	Anode catalyst (loading in mg cm^{-2})	T ($^{\circ}\text{C}$)	Anode feed MeOH	Cathode feed		
SPEEK/50 wt.%sulfated-PVA(SSP50)	Pt/C (0.3)	80	2 M	air	21.10	[13]
			8 M		23.32	
PVA/PWA(80 wt.%)	PtRu	25	2 M	O_2	5	[14]
PVA/PSSA-MA/SSA	PtRu (3)	2,580	2 M	O_2	<20,100	[15]
PVA/ β -cyclodextrun(23 wt.%)	Pt (0.3)	25	2 M	air	18.56	[16]
PVA/PSS(50%)A/Mordenite(10%)	PtRu (2)	70	2 M	air	74	[17]
Nafion/Silica(10 wt.%), Nafion/MZP(5 wt.%), Nafion/MTP(5 wt.%)	PtRu (2)	70	2 M	O_2	140	[18]
					125	
					140	
PVA/PAMPS/GPTMS	PtRu (4)	25	2 M	air	23.63	This work

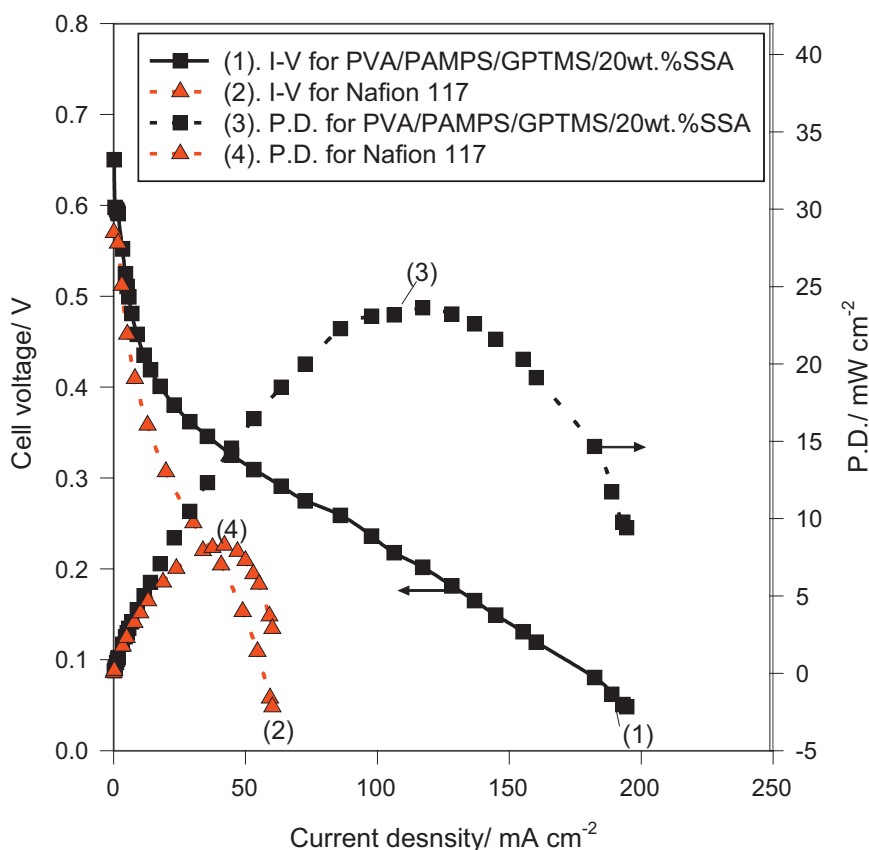


Fig. 7. Comparison of I–V and PD curves for the DMFC using PVA/PAMPS/GPTMS/20 wt.%SSA composite polymer membrane and Nafion 117 membrane, at 2 M methanol fuel at 25 °C and in ambient air.

non-perfluorosulfonated polymer membrane alternative to Nafion 117 membrane; which is an expensive fully perfluorosulfonated polymer membrane.

4. Conclusions

This study reports the preparation of an organic/inorganic proton-conducting composite membrane based on the PVA, PAMPS, GPTMS and SSA using a simple solution casting method. The ionic conductivities of the composite membranes were on the order of $10^{-2} \text{ s cm}^{-1}$ in water at ambient temperature. The methanol permeability of the crosslinked PVA/PAMPS/GPTMS composite membrane (on the order of $10^{-7} \text{ cm}^2 \text{ s}^{-1}$) was much lower than that of Nafion 117 membrane (on the order of $10^{-6} \text{ cm}^2 \text{ s}^{-1}$). An air-breathing direct methanol fuel cell consist-

ing of PVA/PAMPS/GPTMS composite membrane was assembled and systematically examined. The highest peak power density of the DMFC achieved with a 2 M methanol fuel. Moreover, the peak power densities at ambient conditions followed the order of 2 M methanol >1 M methanol >4 M methanol.

The electrochemical performance, in terms of the peak power density, of the DMFC with the PVA/PAMPS/GPTMS/20 wt.%SSA composite membrane (peak P.D. = 23.63 mW cm^{-2}) was several times greater than that of the DMFC with Nafion 117 membrane (peak P.D. = 8.33 mW cm^{-2}), though both used a 2 M methanol fuel and operated under similar conditions. The addition of GPTMS in the PVA/PAMPS polymer membrane to form a semi-interpenetrating network (SIPN) enhanced the mechanical and thermal properties of the device and greatly reduced methanol permeability. In summary, the proposed PVA/PAMPS/GPTMS

composite membrane is a viable candidate for DMFC applications.

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