Preparation of Sulfonated PVA-TMSP Membranes for Direct Methanol Fuel Cell

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Abstract

Novel preparation and characterization of sulfonated polyvinyl alcohol (PVA)–trimethoxysilyl propanethiol (TMSP) membranes for direct methanol fuel cell (DMFC) application have been investigated. Preparation of sulfonated PVA-TMSP membrane was conducted by crosslinking steps using sol-gel method and a catalyst of concentrated HCl. TMSP concentrations were varied from 1% to 3%. The gel solution was cast on to the membrane metal plate to obtain membrane sheets. The membrane was then oxidized in H_2O_2 concentrations of (10-30%) to convert the mercapto groups into sulfonate group. Investigations of the cross-linking process and the existence of sulfonate group were conducted by infrared spectroscopy as shown for frequencies at 1140–1200/cm and 1200–1145/cm respectively. The scanning electron microscope–energy dispersive X-rays (SEM–EDX) of the membranes indicated that the distribution of silica particles from sol–gel reaction products was uneven due to the fast exchange rate of condensation. The degree of swelling decreased as methanol concentrations increase for sulfonated PVA–TMSP membrane which opposed toward the value of commercial Nafion membrane. The maximum value of ion exchange capacity of the membrane was 1.82 mmol/g whereas the highest proton conductivity was 3.9 x 10^{-4} S/cm. Therefore it can be concluded that the membrane was a potential candidate for application in DMFC.

Abstrak

Pembuatan Membran PVA-TMSP Tersulfonasi untuk Sel Bahan Bakar Methanol (DMFC). Metode baru dan karakterisasi membran komposit PVA-TMSP tersulfonasi untuk aplikasi sel bahan bakar metanol langsung (DMFC) telah diinvestigasi. Pembuatan membran PVA-TMSP tersulfonasi dilakukan melalui tahapan pengikatan silang antara larutan PVA dan *trimethoxysilyl propanethiol* (TMSP) dengan metode sol-gel dan katalis HCl pekat. Konsentrasi TMSP divariasikan dari 1% hingga 3%. Larutan dalam bentuk gel dituangkan di atas lembaran logam untuk mendapatkan lembaran tipis membran. Membran tersebut kemudian dioksidasi dengan H_2O_2 pada berbagai variasi konsentrasi (10-30%), untuk mengkonversi gugus merkapto menjadi gugus sulfonat. Pengamatan terhadap proses pengikatan silang serta keberadaan gugus sulfonat, dilakukan dengan teknik spektroskopi inframerah, yang hasilnya ditunjukkan dengan frekuensi vibrasi masing-masing pada 1140-1200/cm and 1200-1145/cm. Pengamatan membran dengan SEM-EDX menunjukkan hasil bahwa distribusi partikel silika dalam reaksi sol-gel tidak merata yang disebabkan oleh cepatnya laju pertukaran reaksi kondensasi. Nilai derajat pengembangan menurun drastis seiring dengan meningkatnya konsentrasi metanol di dalam membran PVA-TMSP tersulfonasi, yang berkebalikan dengan nilai derajat pengembangan untuk membran komersial Nafion. Nilai maksimum kapasitas penukar ion dari membran adalah 1,82 mmol/g sedangkan konduktivitas proton tertinggi sebesar 3,9 x 10^{-4} S/cm. Dengan demikian dapat disimpulkan bahwa membran tersebut berpotensi untuk diaplikasikan di dalam sistem DMFC.

Keywords: DMFC, fuel cell, nafion, PVA, TMSP

1. Introduction

Direct methanol fuel cells (DMFC) have attracted considerable attention for several applications in view of their lower weight, high efficiency and low toxic emissions [1–4]. The usage of liquid fuel in DMFC simplifies the problems of delivery and storage and, because of its very high theoretical mass energy, density (3000 Whkg[−1]). More importantly, liquid fuel can be used at ambient temperature and pressure, which makes the DMFC easy to use with portable electronic devices [1–12]. Perfluorosulfonate ionomer membranes, such as Nafion membranes, are the major membranes used in polymer electrolyte membrane fuel cells at present.

However, large-scale applications of these membranes are limited by their high cost and poor barrier to methanol crossover. Therefore it is essential to find novel proton conductive membranes with low cost and low methanol permeability. For the above objects, many kinds of proton exchange membranes have been developed. The development of a PVA membrane for DMFC applications is of interest because the polymer is inexpensive and has been used to separate alcohol from water in a pervaporization process [5]. Furthermore, proton conductivity in PVA membranes can be induced by modification of the chemical structure of the polymer through sulfonation [6].

A solid proton conductor was developed by mixing poly (vinyl alcohol) (PVA) and phosphoric acid in 1985 [7]. Since that time, a number of research groups have investigated several combinations of PVA and acid or salts for obtaining solid polymeric ionic conductors [8]. In some articles [8-9], membranes based on PVA have been studied in alkaline condition. In other articles [9-16], PVA membranes doped with H_3PO_2 or H_3PO_4 have been made. Lei Li *et al*. [17] have made PVA membranes doped with phosphotungstic acid (PWA) with a reagent of dimethylsulfoxide (DMSO). But PVA membranes doped with PWA swell too strongly to be used. Deng *et al*. [18] have found that silica in PVA membrane can improve the thermal stability of the membrane. Smitha *et al*. [19] also prepared PVA blended with chitosan and sodium alginate membranes for DMFC applications. Although the membranes have good thermal stability and lower methanol permeability, the ion exchange capacity and proton conductivity were still low as compared to the Nafion membrane. Recently, Duangkaew *et al*. [20] also found that PVA-layered silica nanocomposite membranes can reduce methanol permeability and the degree of swelling though proton conductivity also decreases after the additional layered silicate (CloisiteNa) of 2%.

In this work, a series of new proton conductivity composite PVA-silica sulfonated membranes for direct methanol fuel cells are fabricated using the trimethoxysilylpropanethiol (TMSP) sol-gel process in the presence of PVA solution followed by solution casting of the membranes and oxidation stage. The resulting membranes are characterized by FTIR spectrometry, X-ray diffraction (XRD), degree of swelling (DS), proton conductivity and ion exchange capacity (IEC).

2. Experiment

Materials. Poly(vinyl alcohol) (PVA, 98% hydrolyzed, average molecular weight = 60,000 g/mol, from MERCK). Trimethoxysilylpropanethiol (TMSP), 98% v/v from Sigma Aldrich Chemicals). H_2O_2 and methanol (AR grade from Fisher-Chemicals). All chemicals were used as received.

Preparation of the sulfonated PVA-TMSP membranes. The PVA-TMSP membranes were commenced by preparing 10% aqueous solution of PVA and then heated at 90 °C for 6 h. Then, a given amount of trimethoxysilylpropanethiol (TMSP) a crosslinking agent (ranged between 1 and 3% by weight of the PVA) mixed by water (mol ratio of 1:4) was added to the solution drop-wise. HCl was also added as the catalyst. After that, the solution was stirred at room temperature for 24 h. After carrying out the chemical reaction for a given time, the PVA-TMSP solution was cast onto an acrylic sheet. After that, the membrane was peeled off from the substrate and then rinsed with de-ionized water to remove some residual acid. The cast membrane was allowed to dry at 60 °C for 12 h. Finally, the dry membrane was sulfonated by oxidizing the mercapto group on the TMSP using H_2O_2 (ranged between 10 and 30%) for 24 hours to complete the sulfonation. After that the membranes were rinsed with de-ionized water to remove some residual peroxide. The sulfonated PVA-TMSP membranes were dried at 110 °C for 4 h. Thickness of the casted membrane was about 80-100 mm. The sulfonated PVA-TMSP membranes were then characterised and analysed by physical and chemical instrumentation.

For simplification, the prepared membrane has been labelled as follow: M1-10% denotes that the PVA membrane was prepared by adding 1% by weight of TMSP and oxidised using 10% H_2O_2.

Characterizations by FTIR and SEM-EDX. Changes in the chemical structure of PVA after the sulfonation were followed with the Fourier transform infrared (FTIR) spectrometer technique with FTIR Shimadzu 8400. The sample was prepared in the form of a thin film. The spectrum was recorded over wave numbers ranging from 4000 to 400/cm.

The cross-sectional view and top surface morphologies and microstructures of all PVA -TMSP membranes composite polymer membranes were investigated by JSM-35 C scanning electron microscope-energy dispersive X-ray (SEM-EDX). The membranes were coated by gold-palladium (Au: 80%–Pd: 20%).

Degree of Swelling (DS). Measurements of water uptake or degree of swelling (DS) values of sulfonated PVA-TMSP membranes were conducted by immersing the membrane into the de-ionized water at 25 °C for 24 h. After that, the water swollen membrane was taken out, wiped with tissue paper, and immediately weighed. The water uptake (W) was then calculated from the following equation;

$$DS\ (\%) = [(W_{wet} - W_{dry})/W_{dry}] \times 100 \qquad (1)$$

where W_{dry} and W_{wet} are the weights of dry and water swollen membranes, respectively.

Ion exchange capacity (IEC). Ion exchange capacity (IEC) of the membrane was measured by a titrimetric analysis. About 0.3–0.5 g of the sample was immersed in 0.1M of NaCl solution for 24 h to allow exchange between protons and sodium ions. After that, the solution was titrated with 0.1 M NaOH aqueous solution to evaluate the amount of HCl generated from the exchange process. From the titration, the IEC value was then calculated by using the following equation;

$$IEC = M_{NaOH} / W_{dry} \qquad (2)$$

where M_{NaOH}, is the mol equivalent (mequiv) of NaOH and W_{dry}, the weight of the dry membrane.

Proton Conductivity Measurements. Proton conductivity tests of Precision LC meter, were carried out on sulfonated PVA-TMSP membranes that were synthesized in the Chemistry Department ITB laboratory. To verify the experimental procedures and interpretation of data, tests were also done on Nafion-112 membranes supplied by Aldrich Chemicals Singapore. Measurements were carried out in both two- and four-point-probe conductivity cells that were designed and constructed in-house. The four-point-probe conductivity cell frame was made of two Teflon blocks, with an open 'window-like structure' employed to allow determinations of the conductivity of fully- and partially-hydrated membranes. Two, stainless-steel, wire electrodes were used to apply a current to the ends of the membrane sample, while another pair of electrodes (2.25 cm apart) was used to measure the voltage drop along the film near the centre of the sample. The membrane samples were sandwiched between the two blocks that were pressed together by four screws fastened with approximately the same torque to ensure good electrode–membrane contact.

3. Results and Discussion

Fourier transform infrared spectroscopy. Figure 1 and 2 shows the FTIR spectra of the PVA-silica nanocomposite membranes both before and after the sulfonation. The broad absorption peaks at 3100-3400/cm are the stretching vibration of (OH)-hydroxyl groups from PVA. The peak at 2900/cm could be ascribed as the symetric stretching of CH_2 from the chain of RCH_2R- The crosslinking process between PVA and TMSP occurs during the sol-gel process which leads to the formation of Si-O-C assymmetric stretching bond at 1140–1200/cm whereas Si-O bond could be observed at 1654/cm. Some new absorption peaks occurred after the sulfonation process, including the peaks at 1216 and 690/cm. These peaks could be ascribed to the S=O (symmetric stretching) bonds and S=O (asymmetric stretching) bonds, respectively. The results suggest that PVA was sulfonated.
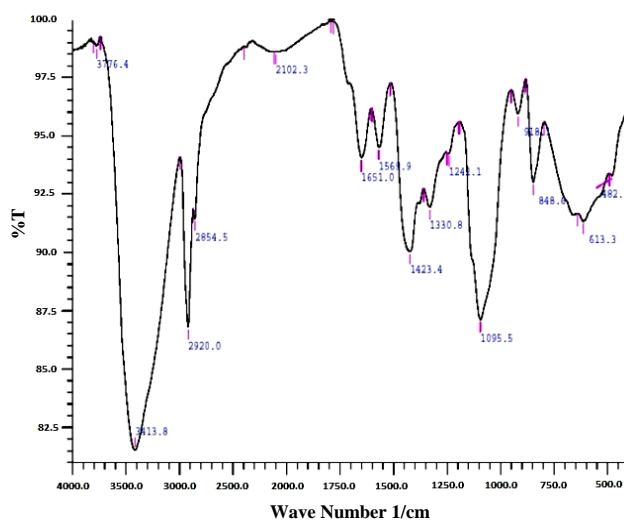
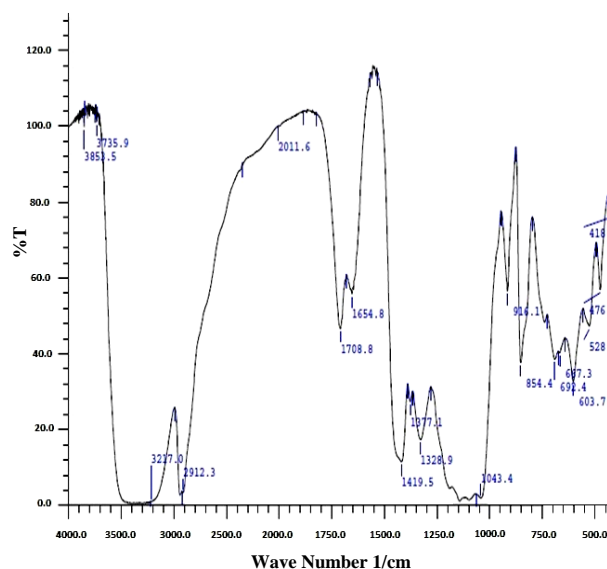**Figure 1. FTIR Spectrum of PVA Membrane**

Figure 2. FTIR Spectrum of PVA-TMSP after Sulfonation (M3-10%)

Scanning electron microscope–energy dispersive X-rays (SEM-EDX). The SEM photographs of the surfaces and cross-sections of sulfonated PVA-silica (PVA-TMSP) membrane is shown in Figure 3. Generally the membrane prepared by casting on the plane surface and followed by drying surface resulted in dense membrane which indicated no pore formation. It was also observed that silica particles were homogeneously dispersed in the hybrid membrane, leading to the fact that no phase separation occured during the condensation reaction of sol-gel process. Therefore by introducing TMSP into PVA, homogeneous dispersion of silica particles at nanoscale level in the nanocomposite membrane was observed. It was reasonably assumed that the hydrolyzed silanol of TMSP could react with the hydroxyl group at the

surface of silica particles formed from sol–gel process of TMSP. This reaction lowered the surface energy of the silica particles and thus prevented their aggregation. Moreover, SEM photographs on the surface of the PVA-TMSP membrane after sulfonation through oxidation of mercapto group to sulfonate group also shows the similar morphology as the prestine PVA-TMSP membrane. Therefore, it can be concluded that the sulfonation process to the PVA-TMSP membrane using H_2O_2 as an oxidator did not change the morphology of the membrane structure.

From the cross sectional view as depicted in Figure 4, it could be seen that the characteristics of the membrane are dense and homogenous in structure. The membrane thickness can be estimated of 80 μm.

The SEM-EDX observation also provided information about the elements present on the surface of the nanocomposite membrane. As depicted in Figure 5, It can be seen that the main component in the matrix structure of the membrane is the carbon and oxygen from the PVA polymer chains. The presence of silicon due to the results of hydrolysis and condensation reaction between TMSP and PVA through sol gel process.
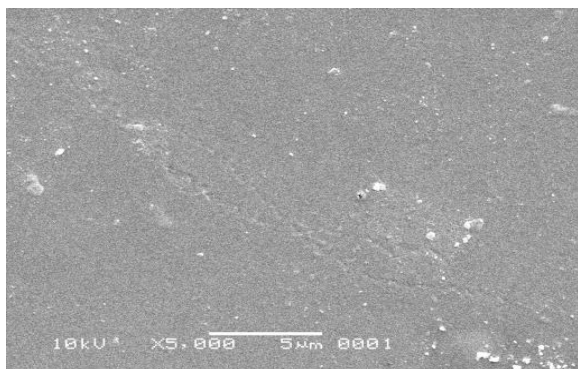

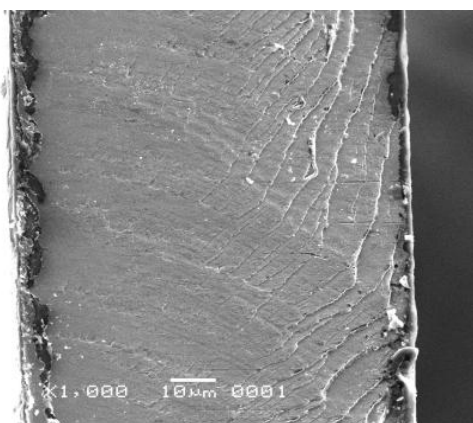**Figure 3. SEM Photograph of Top Surface on Sulfonated PVA-TMSP Membrane (M3-10%)**

Figure 4. SEM Photograph of Cross Sectional View of Sulfonated PVA-TMSP Membrane (M3-10%)

Degree of swelling. Uptake behavior of the membrane has great effects on the properties of proton exchange membrane (PEM). In general, higher uptake is desirable to achieve the most efficient DMFC. Higher uptake facilitates the transport of the protons, which significantly improves the efficiency of the fuel cells. The dimension expansion of the composite membrane induced by water uptake would have the adverse effect on the membrane electrode assembly (MEA). The excessive expansion in plane direction would loosen the contact of catalyst layer and PEM, which could increase the resistance to proton transfer. Therefore, it is expected that the composite membrane exhibit high water uptake and low dimension expansion in plane direction simultaneously. Uptake and swelling behavior results from water and methanol solution are shown in Figure 6.
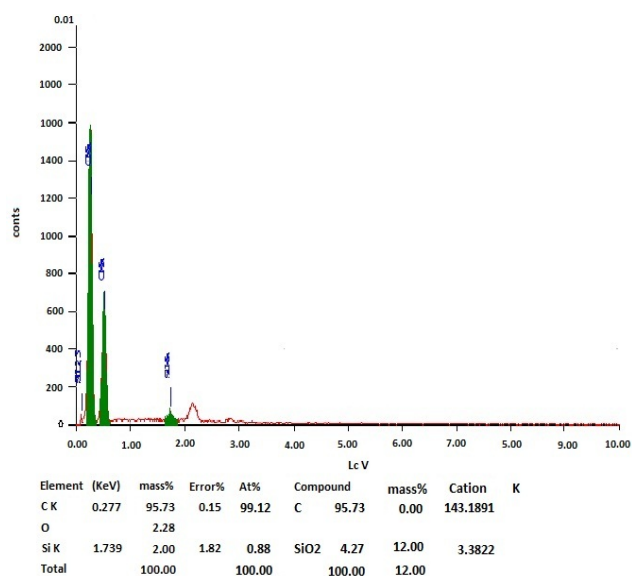

Element	(KeV)	mass%	Error%	At%	Compound	mass%	Cation	K
C K	0.277	95.73	0.15	99.12	C	95.73	0.00	143.1891
O		2.28						
Si K	1.739	2.00	1.82	0.88	SiO2	4.27	12.00	3.3822
Total		100.00		100.00		100.00	12.00	

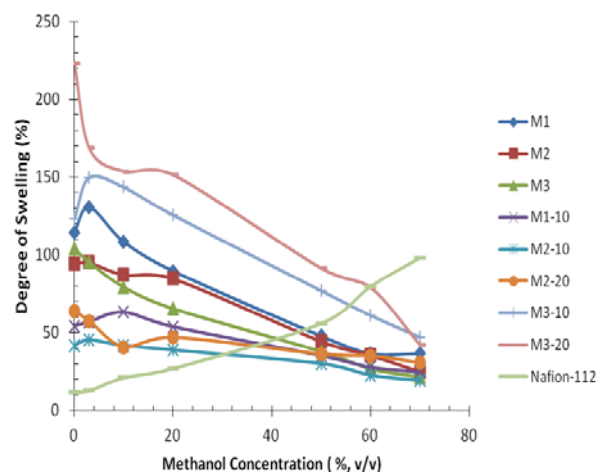**Figure 5. EDX Spectrum of Sulfonated PVA-TMSP Membrane (M3-10%)**

Figure 6. Degree of Swelling of PVA-TMSP and Sulfonated PVA-TMSP Membranes

It can be seen that the degree of swelling (DS) of PVA-TMSP membranes decreased with increasing the methanol concentration up to 70% v/v.

The DS of PVA-TMSP in water is about 95 to 115% for various TMSP concentrations from 1 to 3% w/w. The uptake decreased up to 80% as the concentration of TMSP increased as shown in Figure 6. These results can be explained by the incursion of methanol molecules. Similarly, the degree of swelling of sulfonated PVA-TMSP membranes decreased with increasing the methanol concentration, the uptake of sulfonated-PVA-TMSP in water is about 40 to 50%, which decreased down to the range of 19–30% as methanol concentration increased to 70% (v/v) for TMSP concentrations of 1 and 2% (w/w). The sulfonated-PVA-TMSP at TMSP concentration of 3% (w/w) exhibits high water loading due to the hydrophilic hydroxyls, whereas, the hydroxyls can withstand the incursion of methanol molecules effectively. This can also be related to the relatively high crosslink density of the membranes, overriding the contributory effect of the high polarity to the water uptake values. However, it can also be seen that the DS of sulfonated-PVA-TMSP in methanol solution is slightly lower than that of PVA-TMSP. This may be due to the presence of SO_4H group in sulfonated-PVA. Many researches proved that the introduction of a sulfuric group in polymer can increase methanol permeability [21-22]. For comparison, the degree of swelling of Nafion 112, as a reference of DMFC membrane, tends to increase as the concentration of methanol increased up to 70% (v/v). This might suggest that only at lower methanol concentration, Nafion 112 membrane can be applied as the solid polymer electrolyte due to higher methanol uptake and lead to contribute significantly to the problem of methanol crossover for DMFC system.

Ion exchange capacity (IEC). Ion exchange capacity is one of the parameters that indicate the potential of the membrane to be applied as the solid electrolyte in DMFC or PEMFC systems. Ion exchange capacity (IEC) is defined as the fixed milliequivalents of exchangeable group per gram of polymer, which is usually considered to correspond to the amount of sites for proton transfer and has great relation to the proton conductivity. Table 1 shows IEC of the composite sulfonated PVA-TMSP membranes at their indicated compositions. It can be seen that M3-10% or sulfonated PVA-TMSP membrane having 3% of TMSP and oxidized by 10% H_2O_2 shows the largest IEC of 1.82 mmol/g. This value is even larger than the standard Nafion-112 membrane for DMFC systems, leading to potential application in the PEM (proton exchange membrane) system.

Proton conductivity. Table 2 shows proton conductivity values of the sulfonated PVA-TMSP membranes modified

Table 1. IEC of Sulfonated PVA-TMSP Membranes

Type of Membrane	IEC (mmol/g)
M1-10%	0.87
M2-10%	0.88
M3-10%	1.82
M2-20%	0.60
M3-20%	0.76
Nafion-112	0.99

Table 2. Proton Conductivity of Sulfonated PVA-TMSP Membranes

Type of Membrane	Proton Conductivity, (S/cm)
M1-10%	3.0×10^{-5}
M2-10%	5.5×10^{-5}
M3-10%	3.9×10^{-4}
M2-20%	3.7×10^{-5}
M3-20%	2.6×10^{-5}
Nafion-112	5.9×10^{-3}

with various amounts of TMSP and H_2O_2 as an oxidator. Proton conductivities of the membranes are not linearly related to the amounts of both TMSP and H_2O_2 agents used. The conductivities initially increased with the amount of TMSP, up to the maximum value of 3.9×10^{-4} S/cm as the amount of TMSP increased at 10% H_2O_2. After that, the proton conductivity of the sulfonated PVA-TMSP membranes decreased again as the amount of H_2O_2 used was above 10%. The maximum proton conductivity value herein is ten times less to that of the Nafion-112 membrane measured in this study (5.9×10^{-3} S/cm). The initial increase in proton conductivity of the membrane can be ascribed to the greater content of sulfonic acid groups in the sulfonated PVA-TMSP molecules, which is responsible for conducting protons. However, the proton conductivity of a membrane is not only dependent on the degree of sulfonation of the polymer, it also changes with water uptake of the membrane. In this study, the optimum value of the amount of the TMSP and H_2O_2 are 3% by weight and 10% v/v respectively.

4. Conclusions

The novel composite polymer membranes of sulfonated-PVA using various TMSP concentrations have been prepared using the sol-gel method. The oxidation of mercapto group in TMSP leads to the formation of sulfonate groups within the PVA membrane matrices as indicated by FTIR spectroscopy, ion exchange capacity and proton conductivity measurements. From the morphology observation, it can be concluded that the sulfonated PVA-TMSP membranes are dense membrane types which are suited for proton exchange membrane applications. It was also found that the composite membranes showed an increase in methanol

resistance with increasing TMSP content especially at high methanol concentration. The maximum ion exchange capacity and proton conductivity are 1.82 mmol/g and 3.94 x 10^{-4} S/cm respectivly. These values of ion exchange capacity and proton conductivity are close to the standard values of Nafion-112 commercial membrane. Therefore, it can be implied that the novel composite polymer membranes of sulfonated PVA-TMSP show potential application in DMFC.

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