Preparation of Poly Eter Eter Keton as Alternative Membrane for Direct Methanol Fuel Cell (DMFC)

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Abstract: The objective of this study focuses on the characterization of polyetheretherketone (PEEK) membranes for direct methanol fuel cells (DMFC) application. The PEEK membrane was modified with sulfonation and charged surface modifying macromolecule (cSMM) using MDI, DEG and HBS in NMP solvent. The characterized of membrane were done using Scanning Electron Microscopy (SEM), water uptake, contact angle, thermal stability, methanol permeability, proton conductivity and DMFC test. DMFC tests were performed at room temperature to obtain polarization curves that show voltages and power density of each variable. The results showed that the cSMM methode of the polymer increases water uptake, thermal stability, methanol permeability and proton conductivity. In terms of morphology, it was found that cSMM method can be applied for membrane modification for DMFC application. In terms of the DMFC tests of the membranes, SPEEK without modification proved to have the best performance in stability because of its low methanol permeability. In contrast, the best performance was achieved by the SPEEK/cSMM (with modification) in highest voltage and power density because of its high proton conductivity.

Key words: Charged Surface Modifying Macromelecule · DMFC · Methanol permeability · Polarization curves · Proton conductivity · SPEEK

INTRODUCTION

One of the most important challenges that our world will face in the twenty-first century will be continuing to meet the ever increasing energy needs of its citizens. Along with the need to find a renewable long term energy source is the need to find a more environmental friendly one. One of the promising candidates as a power source solution for the future world energy problem is fuel cell. A fuel cell is an electrochemical device that converts chemical energy directly into electrical energy from an electrochemical reaction. It produces electricity, water and heat from the reaction of fuel and oxygen without any burning thus greatly reducing the pollutants and inefficiencies brought about by combustion. Unlike dry-cell battery, fuel cell does not require recharging and operates as long as fuel is available [1-8]. The fuel is typically hydrogen.

The basic advantages of fuel cells are the potential for a high operating efficiency (up to 50-70%) and near zero green house emissions. Secondly, fuel cell systems provide quiet and vibration free operation. Thirdly, a fuel cell system is a highly scalable design. Finally, fuel cells have multiple choices of potential fuel feedstock from renewable ethanol to biomass hydrogen production and a nearly instantaneous recharge capacity compared to batteries [7-8]. Fuel cell could be used in many applications. Therefore, there are several types of fuel cell technologies being developed for different applications, each using a different chemistry, electrolyte used and

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their operating temperature. One of the promising types for small appliances and vehicle application is the proton exchange membrane fuel cell.

Proton exchange membrane fuel cells (PEMFC) are one of the most promising clean energy technologies under development. It has becoming increasingly important as alternative energy sources for stationary, automobile and portable power [9-12]. The major advantages include: current prototype efficiency of up to 64%, high energy densities (relative to batteries) and the ability to operate on clean fuels while emitting no pollutants. This fuel cell type operates at relatively low temperature (30-150 °C) but generate more power for a given volume or weight of a hydrogen-air fuel than any other type of fuel cell. In addition, proton exchange membrane fuel cells have drawn a lot of attentions because of the high efficiency, quiet operation, use of fuel from totally renewable resources and environmentally friendly processes.

Despite these benefits, diffusion of PEMFC technology into the market place is being limited by cost and reliability issues. Recent research has attempted to tackle these problems with moderate success. As a result, it is widely acknowledged that the goal of large scale fuel cell market penetration in areas including transport have moved from 2010 to 2015 and that there are still many technical and social issues to overcome [13]. These challenges include: choosing the appropriate fuel (basically hydrogen) source and infrastructure, industry regulation, safety and public acceptance and hydrogen handling problem. Therefore, research into fuel cells has grown exponentially over the last 15 years. In case of polymer fuel cell, Direct Methanol Fuel Cell (DMFC) which does not use hydrogen as fuel is gaining more attention nowadays.

Direct methanol fuel cell (DMFC) is a type of PEMFC that uses direct aqueous methanol solution as fuel. The methanol is fed at anode and oxygen at cathode, separated by a polymer electrolyte membrane. As the methanol fuel is directly fed to the anode, reaction occurs in the oxidation of the methanol into carbon dioxide (CO_2), proton and electron. The released electron will travel through an external circuit where electrical energy can be harnessed. Protons move from anode to the cathode via the polymer electrolyte membrane and combine with the oxygen and electron to form water [4-8]. Direct use of methanol in DFMC is a topic of considerable interest. Yet there are still a lot of obstacles that DMFC have to overcome in order to penetrate the commercialization.

The most influential factor is its high cost and low power density. Its high cost is contributed mainly by its catalyst and the MEA parts which contain the high cost membrane however will not be discussed into greater detail. The relatively low power density or lower cell performance compared to PEMFC is caused mainly by the poor kinetics of the anode electro-oxidation of methanol, low membrane proton conductivity and by the crossover of methanol through the polymer electrolyte membrane. The slow oxidation kinetic of methanol to carbon dioxide is due to the formation of carbon monoxide as an intermediate which strongly adsorbs on the catalyst surface is however out of the scope of this study.

A primary criterion for choosing proton exchange membrane in DMFC is high in proton conductivity as well as low in methanol permeability. High proton conductivity is desired to transport as much proton as possible from anode to cathode in order to enhance its performance. Methanol crossover from the anode to the cathode is also detrimental for the DMFC performance as it reduces the coulombic efficiency and cell voltage, leading to an efficiency reduction down to 35% [9]. The key to resolving proton conductivity and methanol crossover lies mainly in the polymer electrolyte membrane which must be able to filter methanol but pass the proton through to the cathode.

Nowadays, the most widely use commercial polymer electrolyte membrane is Nafion produced by Du Pont since 1992. Nafion is a plain perfluorosulfonic membrane that is thermally stable and is excellent for PEMFC because of its high conductivity. However Nafion is not suitable for DMFC applications, part from being costly, this type of membrane has high permeability towards methanol even at low temperatures, which drastically reduces the DMFC performance [2]. This is worsening by high water permeability in perfluorinated membranes that can cause cathode flooding and, thus, lower cathode performance which also contributed to lower DMFC performance. Moreover, Nafion will loss its mechanical properties at elevated temperatures.

Many promising non-flourinated polymers are based on aromatic thermoplastics, such as poly (ether ether ketone), PEEK; poly (ether sulfone), PES; polybenzimidazole, PBI; and other poly (aryl ether ketone), PAEK. The aromatic polymers possess excellent chemical resistance, high thermo-oxidative stability, good mechanical properties and low cost [2-3]. Among these aromatic membranes, particularly PEEK has been extensively studied by many researchers for instance on

crosslinking, composite membrane with inorganic, blend membranes with other polymer and surface modification such as plasma treatment and grafting reaction, surface coating or combining the said methods [9-12].

Another technique of surface modifying is by blending method. The blending methods of surface modifications have great advantages in membrane applications especially in pharmaceutical and separation area [13-18]. Even though the technology was widely reported, there is yet any study on PEM, in particular SPEEK, incorporating surface modifying macromolecule approach. Recently [19], reported on hydrophilic surface modifying macromolecule (SMM) for polymeric membrane, which could suite the application for PEM applications.

SMM is a simple blending method which uses the concept of surface segregation in polymer science. SMM when introduced as an additive in a base polymer will migrate to the surface and change the chemistry of the surface while maintaining its bulk properties. The migration of the hydrophilic or hydrophobic SMM segment is according to the thermodynamic principles of the tendency to minimize the interfacial energy. Due to this fact, when a membrane of blended polymer with SMM is cast, the polymer with the lowest surface energy of hydrophilic or hydrophobic will migrate and concentrate at the top or air interface. The bulk properties relatively remained unchanged due to very small amount of SMM, usually less than 5%, is added to the dope solution. This research focuses on the development of SPEEK/cSMM blend as polymer electrolyte membrane, characterization of blended SPEEK/cSMMs membranes and performance evaluation of blended SPEEK/cSMMs membranes for DMFC.

Experimental: Deuterated dimethyl sulfoxide (DMSO-d_6 99.96 atom% D) was purchased from CDN Isotopes, Point-Claire, PQ, Canada. N,N-Dimethylacetamide (DMAc, anhydrous 99.8%) and 1-Methyl-2-pyrrolidinone (NMP, anhydrous 99.5%) was purchased from Aldrich Chemical Company, Inc., Milwaukee, WI, USA. 4,4'-Methylene bis(phenyl isocyanate) (MDI, 98%), 4-Hydroxybenzenesulfonic acid, sodium salt dehydrate (HBS) and Di(ethylene glycol) Reagent-Plus (DEG, 99%) was supplied by Sigma-Aldrich, Inc., St. Louis, MO, USA. Poly(ether ether ketone) (PEEK), powder form (< 80 mm) was supplied by Victrex Inc., Westchester, PA, USA. Methanol, 99.9% and Sulfuric acid, 95-99% was purchased from Merck KGaA, Damstadt, Germany. Nafion 112 and Nafion 117 were supplied by DuPont.

Synthesis of SPEEK: PEEK was sulfonated following the technique described [9, 20-22]. A 5g of PEEK was dried in a vacuum oven at 100°C for 24 hrs and then dissolved in 95ml of concentrated (95-98%) sulfuric acid (H_2SO_4) at room temperature to suppress the heterogeneous sulfonation. After completing the dissolution of PEEK (about 1 h), the polymer solution was brought to the desired temperature of 55°C and held for 3 hrs to obtain the desired degree of sulfonation (DS). In order to terminate the reaction, the polymer solution was poured into excess ice-cold deionized water under continuous stirring for one night to remove the residual acid. The polymer was washed repeatedly with deionized water until a neutral pH was reached. Then it was dried in air circulation oven at 60°C overnight. The formation of SPEEK from PEEK is shown in Figure 1. The sulfonated poly(ether ether ketone), SPEEK, is basically a copolymer, consisting of sulfonated PEEK structural unit and original PEEK structural unit.
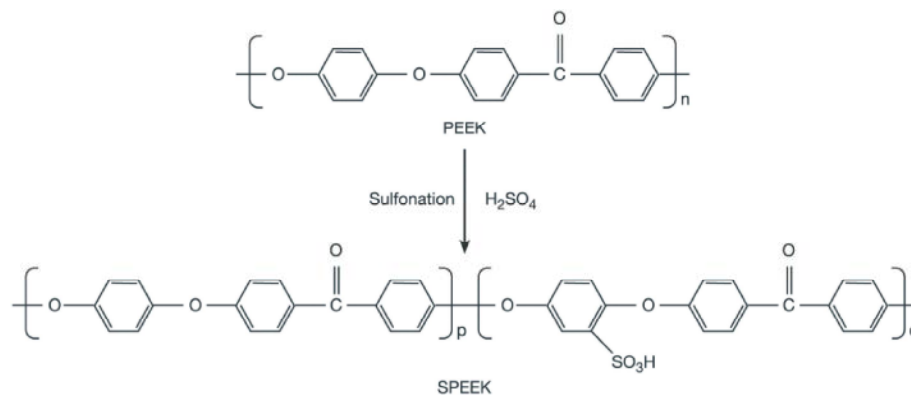

Fig. 1: Sulfonation of PEEK

Synthesis of Charged SMM: The charged surface modifying macromolecule, cSMM, end-capped with hydroxyl benzene sulfonate, was synthesized using a two-step solution polymerization method. The initial step involved the reaction of MDI with DEG in a common solvent of DMAc. This mixture formed a urethane prepolymer solution. The prepolymer is a segment-blocked urethane oligomer, poly (4,4'-diphenylenemethylene methoxymethylene urethane) having both ends capped with isocyanate. The reaction was then terminated by the addition of HBS resulting in a solution of charged or sulfonated surface modifying macromolecules (cSMM).

Membranes Preparation: Ten (10) gram of SPEEK was dissolved in 90 g NMP to make a 10 wt% of original SPEEK solution. The blend solution was prepared by adding 0.4 g of cSMM, 9.6 g of SPEEK and 90 g of the NMP solvent. Both mixtures were stirred for 24 hrs, before the mixtures were cast onto a glass plate using a pneumatic casting machine to a thickness of 1×10^{-4} m. The membrane was dried at 120°C for 24 hrs in a vacuum oven. After cooling to room temperature, the membrane was peeled off from the glass in deionized water. Finally, the membrane was converted into the H^+-form by immersing it into a 1 M sulfuric acid solution for 24 hrs at the room temperature and blotted dry with absorbent paper before it was air dried.

Contact Angle of Membranes: The contact angle, CA, of the membrane surface was measured using a VCA Optima Surface Analysis System (AST Products, Inc., Billerica, MA). Sample coupons with an area of about 5 cm×1.5 cm were prepared by cutting pieces at random locations within the membrane sheet. The sample was placed on a glass plate and fixed with a tape. Then, a drop of distilled water (2 μL) was placed on the sample surface using a micro syringe (Hamilton Company, Reno, NV). The CA was measured within a 30 sec period after the water drop was placed The CAs were measured at ten different spots on each membrane sample coupon and the values averaged.

Water Uptake of Membranes: Water uptake, which is used to determine the water content of the membrane in its wet state, is one of the fundamental measurements for DMFC electrolyte. The membrane was dried in an oven at 60°C for 48 hrs, weighed, soaked in deionized water overnight at room temperature, blotted dry with absorbent paper to remove any surface moisture and re-weighed. Then,% of water uptake was calculated from the equation below,

$$Water\ uptake\% = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{1}$$

where W_{wet} and W_{dry} are the weight of the wet and the dry membrane respectively. The accuracy of the measurement is within ± 3%.

Membrane Morphology: The morphology of the blend membrane was investigated using scanning electron microscopy (SEM). Specimen for the SEM was prepared by freezing the dry membrane sample in liquid nitrogen up to 10 min and breaking it to produce a cross-section. Fresh cross-sectional cryogenic fractures of the membrane was vacuum sputtered with a thin layer of gold by using an ion sputtering (Biorad Polaron Division, Hertfordshire, UK) before viewing on the scanning electron microscope (SEMEDAX; XL 40; PW6822/10, Phillips, UK) with a potential of 10 kV.

Thermal Stability of Membranes: The glass transition temperature (T_g) was examined by differential scanning calorimeter (DSC) equipped with universal analysis 2000 program (DSC Q1000-0760, TA Instruments, New Castle, DE). Indium was used for the calibration of the temperature. About 10 mg of polymer was crimped into aluminum pan. The polymers were annealed at about T_g+50°C for 10 min under nitrogen atmosphere and then quenched and scanned at a heating rate of 10°C min^{-1}. The T_g value was recorded at the midpoint of the corresponding heat capacity transition. The sample weight loss was measured by thermogravimetric analysis (TGA) using thermogravimetric analyzer (Mettler, Toledo, OH). A pre-oven dried sample of 10 mg was heated under room temperature to 800°C at 10°C min^{-1} in air.

Performance of Membrane as DMFC Electrolyte
Methanol Permeability of Membrane: A diaphragm diffusion cell, as described in detail elsewhere [21, 23] was used to determine the methanol permeability of the membrane. The apparatus consists of plastic compartments (A and B), separated by the test membrane with an effective area of 2.5447×10^{-4} m^2. The compartment A ($V = 5 \times 10^{-5}$ m^3) was filled with 1M methanol and the compartment B was filled with distilled water. The methanol molecules diffuse along the

oncentration gradient through the membrane into the opposite compartment of the diffusion cell. Magnetic stirrer was used in each reservoir to ensure uniformity during the diffusion experiment. To determine the methanol permeability of each membrane, liquid samples of 500 μL were taken every 30 min from the permeate compartment using a syringe and the samples were then analyzed with a digital differential refractometer (Perkin Elmer, USA). Prior to testing, all membranes were hydrated in de-ionized water for at least 24 hrs. Methanol diffusion is induced by a concentration gradient across the membrane. Hence, from the change of methanol concentration in the diffusion reservoir the diffusion coefficient is obtained by equation (2) [21, 23].

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_o) \tag{2}$$

where A is effective area of membrane (m^2), L is thickness of membrane (m), V_B is volume of diffusion reservoir (m^3), C_A is methanol concentration in feed (mol L^{-1}), C_B is methanol concentration in diffusion reservoir (mol L^{-1}), D is methanol diffusivity ($m^2 sec^{-1}$), K is partition coefficient and t_0 is time lag (sec).

The time lag is explicitly related to the diffusitivity ($t_0 = L^2/6D$). Methanol permeability (τ) is defined as the product of the diffusivity of methanol (D) and the partition coefficient (K); $\tau = DK$. The methanol concentration in diffusion reservoir (C_B) at t was calculated from the linear interpolation of C_B versus t and the slope (m) of the graph can be written as follows:

$$\frac{C_B(t)}{t - t_0} = m \tag{3}$$

Therefore, equation (3) can be rearranged to calculate the methanol permeability as expressed below:

$$\tau = m \frac{V_B}{A} \frac{L}{C_A} \tag{4}$$

Proton Conductivity of Membranes: The proton conductivity of the membrane was measured by AC impedance technique using a Solartron impedance-gain phase analyzer. The detail of the conductivity measurement is given in the earlier report [23]. The impedance spectra were recorded over the frequency range of 10 MHz to 10 Hz with 50 to 500 mV oscillating voltage. Membrane sample was equilibrated in deionized water for 24 hrs at room temperature prior to testing.

Then, the surface water was removed and the swollen membrane was rapidly placed between two stainless-steel electrodes in a conductivity cell (this cell is used to host the sample). The water content of the membrane was assumed to remain constant during the short period of time required for the measurement. All impedance measurements were performed at room temperature and 100% relative humidity (RH). The membrane resistance (Ω) was obtained from the intercept of the impedance curve with the real-axis at the high-frequency end. Then, proton conductivity of membrane, σ (S m^{-1}), was calculated according to equation (5).

$$\sigma = L / \Omega S \tag{5}$$

where L and S are the thickness and area of the membrane, respectively.

Preparation of MEA: MEA were prepared by doctor blade technique. The same Pt loading (1 mg/cm^2 and 5 mg/cm^2) in the catalytic layer was used for both anodes and cathodes and a 40% Pt/C was used as an electro catalyst. MEAs were prepared by hot pressing the membranes at 150°C for 60 minutes on the prepared electrodes.

Electrochemical Measurements: DMFC tests were carried out in a 5 cm^2 single cell using a H-Tech Inc. fuel cell test station. The fuel cell tests were carried out at room temperature. The polarization curves were recorded using a high power potentiostat (Wenking model HP 88) interfaced with a PC to apply the current sequences and to store the data and a variable resistance in order to fix the applied current to the cell.

RESULT AND DISCUSSION

Mixing SPEEK and cSMM (MDI-DEG-HBS) in NMP formed homogeneous and transparent solution; however, after casting on a glass plate, the blended membrane was more yellowish than the original SPEEK, cSMM and SPEEK, due to the similar chemical structure of sulfonic group, are thermodynamically miscible. Therefore, the cSMM has dispersed homogeneously into SPEEK. The homogeneity of dispersions of cSMM in SPEEK was examined with SEM.

Figures 2a and b show the SEM pictures of low magnification of the SPEEK and SPEEK/cSMM blend membrane, respectively. Both membranes look similar with dense structures. Figures 2c and d, on the other hand, are SEM pictures of high magnification. In both, nodular
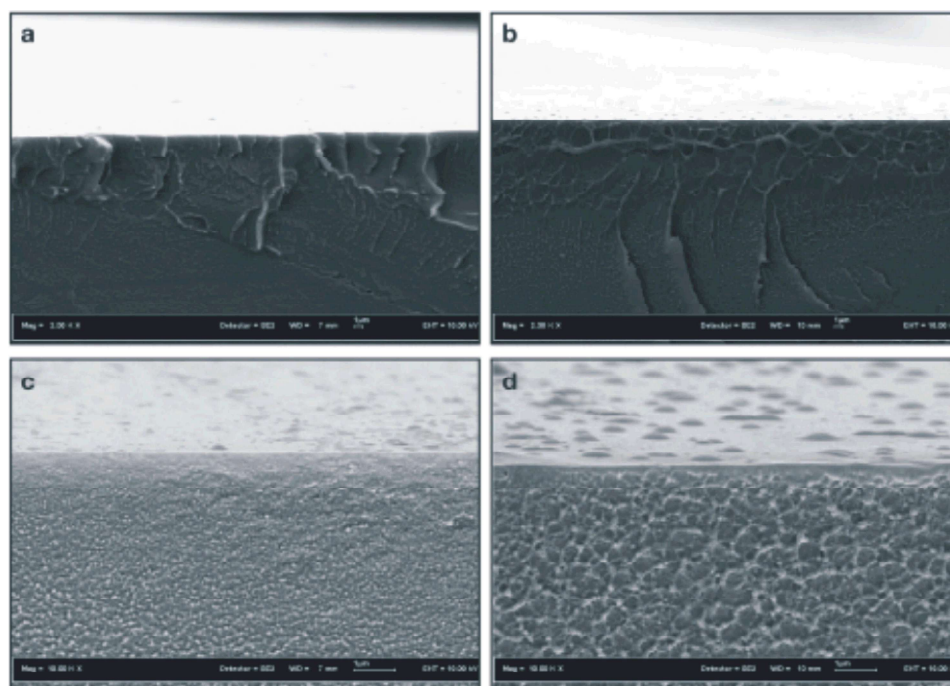
Fig. 2: Cross-sectional pictures of low magnification (a) SPEEK; (b) SPEEK/cSMM; and of high magnification (c) SPEEK; (d) SPEEK/cSMM

Table 1: Characterization of Nafion 112, SPEEK and SPEEK/cSMM films

Membran	Water uptake	CA	Tg (°C)	Methanol permeability (τ, cm2 sec-1)	Proton conductivity σ S cm-1
Nafion 112	20	80	143.24	6,21 x 10-6	$1,2 \times 10^{-2}$
SPEEK DS58	32	84.24	151.25	4.15 x 10-7	$1,01 \times 10^{-2}$
SPEEK DS58+ cSMM	38	67.23	209.17	5.17 x 10-7	$2,67 \times 10^{-2}$

structures are observed. Judging from the size of each spherical unit, it represents the super nodular aggregates. There is a notable increase in the size of the sphere from the SPEEK to the SPEEK/cSMM blend membrane.

Water uptake is used to determine the water content of the membrane in its wet state. Water uptake is related with conductivity of membrane. Table 1 shows the result of water uptake measurements. It shows that water uptake increased significantly from SPEEK to SPEEK/cSMM blend. In SPEEK the sulfonate ions in the ion cluster domain are hydrated with absorbed water molecules [24]. The increase in water uptake means, therefore, the increase in the sulfonate ion density in the cluster. It is likely that the excess sulfonate ions are provided by the added cSMM.

Moreover, as reported in [25, 26], the water sorbed in the membrane can be categorized into two different groups; bound water and free water. The former is the state of water associated with the ionic site whereas the latter is present in the space between the sulfonic groups. In view of the dense structure of the membrane, the space between the sulfonic groups must be very small. Hence, water in the membrane is present most likely as the water bound to the ionic site. The increase in the amount of the sorbed water upon addition of cMMS is then due to the increase in the amount of the bound water. The membranes characterizations were shown in Table 1.

Table 1 also shows the results of the CA measurement.The hydro-philicity/-phobicity of the membrane surface can be evaluated by measuring the CA. SPEEK is higher than SPEEK/cSMM blend. At the top surface, the side was in contact with air when the membrane was cast. At the bottom surface, it was in contact with the glass plate when the membrane was cast, but the difference is not significant considering the experimental errors. Inside of that, this difference is most likely due to the migration of cSMM to the top surface, covering the surface with the sulfonic acid end groups that are protruded vertical to the surface while the urethane prepolymer part of cSMM is anchored to the host SPEEK.
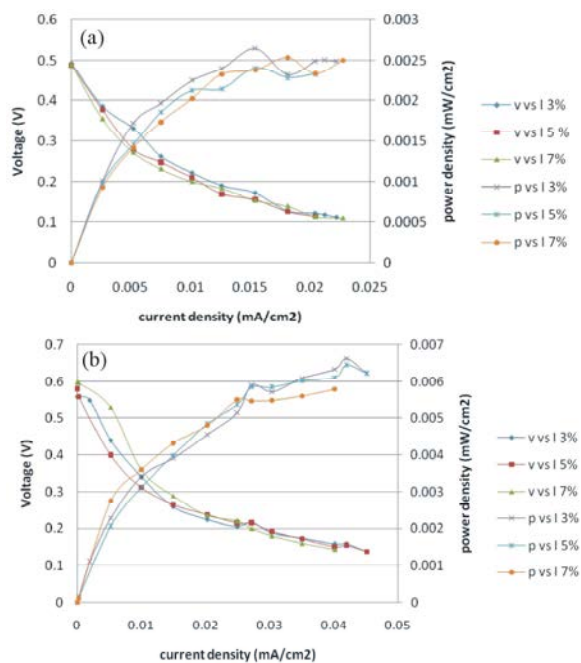
Fig. 3: Polarization Curve of DMFC using SPEEK DS 58 with (a) 1 mg/cm^2; (b) 5 mg/cm^2 catalyst loading

Thermal stability of Nafion 112, SPEEK, SPEEK/cSMM blend as well as cSMM was determined by TGA. The T_g of polymer samples are also shown in Table 1. The T_g of cSMM and SPEEK/cSMM blend are 143.24°C and 209.17°C, respectively. SPEEK+cSMM that has higher Tg than SPEEK without modification will give higher stability at higher operating temperature [27]. Increasing in T_g of the blend is most probably because the presence if cSMM reduced the rigidity of the SPEEK structure. It also suggests that no cross-linking is formed [28, 29].

Methanol permeability measurement is one of the fundamental tests of the membrane for DMFC application. Table 1 was also presented the methanol permeability of Nafion 112, SPEEK and SPEEK/cSMM blend membranes. It can be observed from the table that the methanol permeability of the SPEEK membrane, 4.15×10^{-7} m^2 sec^{-1}, is far less than the Nafion 112 membrane, 6.21×10^{-6} m^2 sec^{-1}. Both values are considered acceptable as compared to other reported values [23, 30]. Interestingly, the methanol permeability of the SPEEK/cSMM blend membrane, 5.17×10^{-11} m^2 sec^{-1}, is even higher than the SPEEK membrane. The increase in methanol permeability is expected since the water uptake increased by blending cSMM. However, both methanol permeability and water uptake are determined by a delicate interplay of the porosity, the size of the hydrophilic/hydrophobic domain

and tortuosity. The hydrophilic/hydrophobic domain behavior is noticed by other researches in nano-composite fuel cell membrane [27, 31]. As shown in Table 1, the highest proton conductivity was Nafion membrane. Proton conductivity value is related to its water uptake. Addition of SPPEK will increase water uptake and its proton conductivity. Ionic conductivity for SPEEK and SPEEK/cSMM are $1,01 \times 10^{-2}$ and $2,67 \times 10^{-2}$ S/cm, respectively. It shows high conductivity's values for polymer hydrocarbon.

Effect of methanol Concentration and Catalyst Loading on SPEEK DS 58 Polarization Curves: The current density/power density plots of MEAs made with the investigated SPEEK DS 58 are shown in Figure 3; (a) for catalyst loading of 1 mg/cm2 and (b) for catalyst loading of 5 mg/cm^2.

From the Figures 3a-b, it can be observed that there are difference polarization result between MEA with catalyst loading 1 mg/cm^2(a) and 5 mg/cm^2(b). MEA (a) can achieved power density value of 0.0058968 mW/cm^2 for 0.0451 mA/cm^2 (3% methanol concentration) and MEA (b) only achieved power density value of 0.002649 mW/cm^2 for 0.0227 mA/cm^2 (3% methanol concentration). MEA (a) gave a better stability than MEA (b) at the same methanol concentration. Increasing of catalyst loading causes proton transfer via membrane is higher. Therefore power density of MEA (a) is higher than MEA (b). However, 3% methanol concentration is the best concentration than other. Stability of membrane by time for DMFC application observed for 10 hours. The loading is fan that integrated to DMFC kit. Result is displayed in Figure 4(a) for catalyst loading of 1 mg/cm2 and (b) for catalyst loading of 5 mg/cm^2.

Based on Figure 4, it can be concluded that the achieving voltage of DMFC and its stability was 10 hours. SPEEK with 1 mg/cm2 catalyst loading gave the best stability at 5% methanol concentration. Based on its polarization curves, it was gave the same result since polarization curves shows 5% methanol concentration achieved highest power density. Then, SPEEK with 5 mg/cm2 catalyst loading gave the best stability at 7% methanol concentration. This phenomenon can be explained by this way. Oxidation of methanol at anode caused decreasing of methanol concentration that crossing over from anode to catode. It means that methanol crossover will increase according to increasing of loading. When we used fan as loading, it means that we are using constant loading. SPEEK membrane will operate maximum at 7% methanol concentration for constant
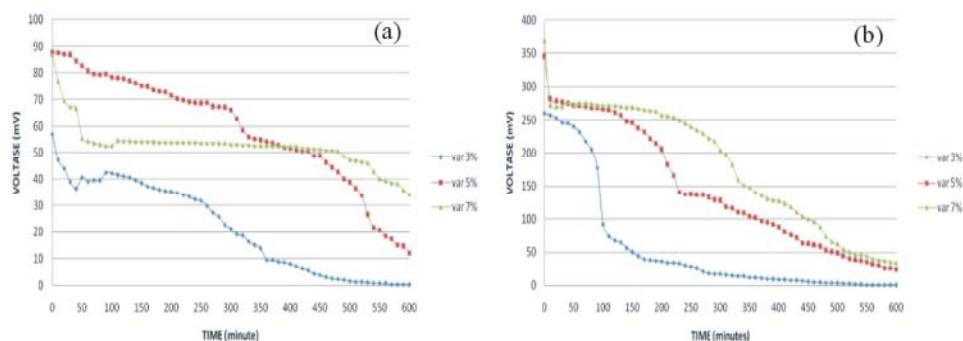
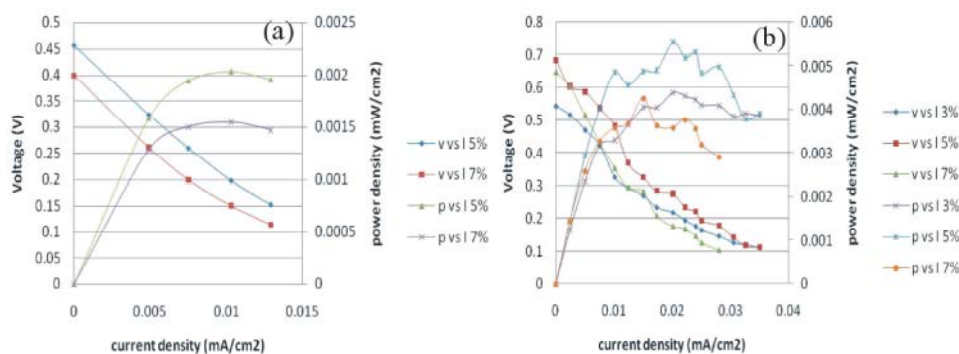Fig. 4: Voltage vs Time Curve for SPEEK DS 58 Membrane with (a) 1 mg/cm^2 and (b) 5 mg/cm^2 catalyst loading

Fig. 5: Polarization Curve of DMFC using SPEEK DS 58+cSMM with (a) 1 mg/cm^2; (b) 5 mg/cm^2 catalyst loading
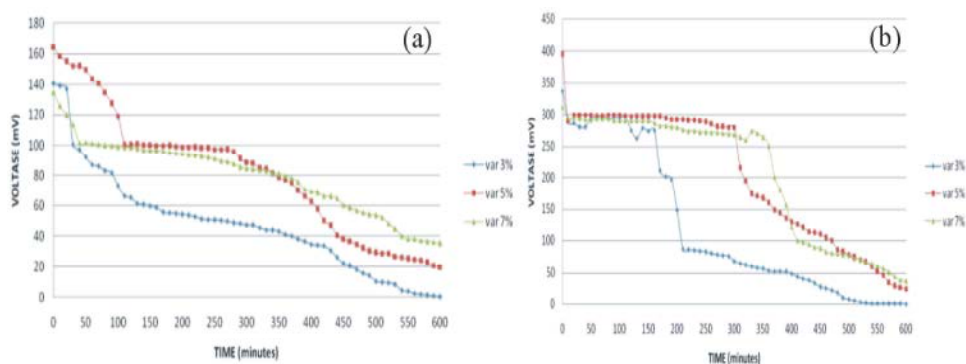

Fig. 6: Voltage vs Time Curve for SPEEK DS 58+cSMM Membrane with (a) 1 mg/cm^2 and (b) 5 mg/cm^2 catalyst loading

loading. For continuity addition of loading, methanol crossover will increase that effect to drop its voltage and power density.

Effect of methanol Concentration and Catalyst Loading on SPEEK DS 58+cSMM Polarization Curves: The current density/power density plots of MEAs made with the investigated SPEEK DS 58+cSMM are depicted in Figure 5(a) for catalyst loading of 1 mg/cm^2 and (b) for catalyst loading of 5 mg/cm^2, respectively. Figure 5(a) and (b) shows the same result where the best methanol concentration were 5%. Maksimum power density for 1 mg/cm^2 and 5 mg/cm^2 cataliyst loading is 0.002039

mW/cm^2 for 0.0129 mA/cm^2 and 0.0055476 mW/cm2 for 0.035 mA/cm^2, respectively. It shows that 5 mg/cm^2 catalyst loading gave higher power density and voltage than 1 mg/cm^2 catalyst loading. The same reason with SPEEK DS 58 curves polarization result, increasing of loading effect to oxidation of methanol. This reaction will run faster and perfect, then it result more electrons that give high power density.

Stability of membrane by time for DMFC application and methanol crossover observed for 10 hours. The loading is fan that integrated to DMFC kit. Result is showed Figure 6(a) for catalyst loading of 1 mg/cm2 and (b) for catalyst loading of 5 mg/cm^2 below.
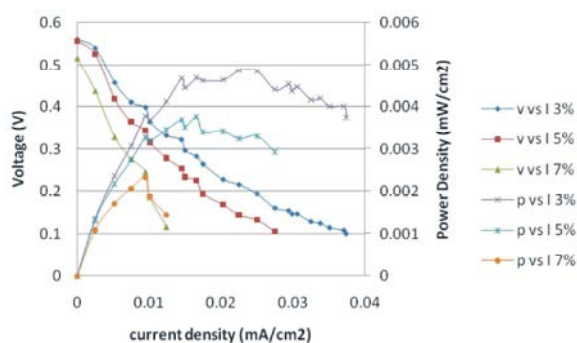
Fig. 7: Polarization Curve of DMFC using Nafion 112 with 5 mg/cm^2 catalyst loading
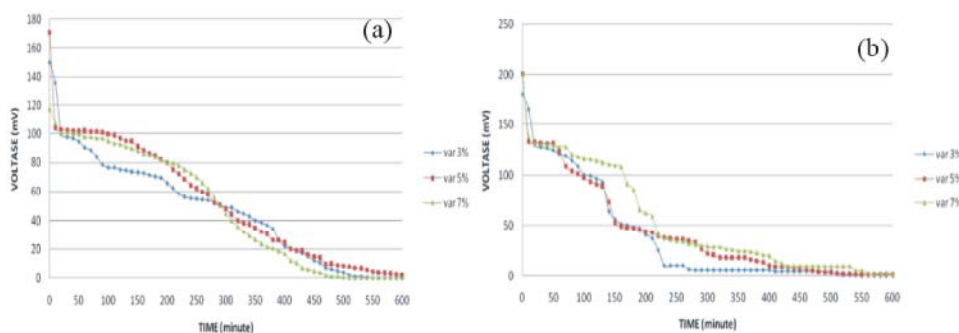

Fig. 8: Voltage vs Time Curve for Nafion 112 Membrane with (a) 1 mg/cm^2 and (b) 5 mg/cm^2 catalyst loading

According to polarization curves, this 10 hours observation showed optimum methanol concentration for DMFC application with loading catalyst of 1 mg/cm2 and 5 mg/cm2 is 5%. Methanol concentration of 7% is easier to crossover from anode to catode so its voltage is easier to drop. Increasing of methanol concentration will raise solubility of methanol in water, higher solubility will increase methanol crossover to catode side.

Effect of methanol Concentration and Catalyst Loading on Nafion 112 Polarization Curves: Nafion 112 is used as comparison membrane for this research. The effect of methanol concentration at Nafion 112 for polarization curve was shown in Figure 7 for loading catalyst of 5 mg/cm^2, respectively. Nafion 112 with 1 mg/cm^2 loading catalyst cannot be characterized and result polarization curve due to its instability.

From the plots above, it seems that stability of DMFC using Nafion 112 with loading catalyst of 5 mg/cm^2 will decrease because of increasing of methanol concentration. Methanol concentration of 3% and 7% become stable until current density of 0.0275 mA/cm^2 and 0.0124 mA/cm^2, respectively. Decreasing of stability by increasing of methanol concentration effect to decrease the peak of power density indicated that the maximum power of DMFC. Methanol concentration of 7% only

result power density of 0.002337 mW/cm^2. Methanol concentration of 7% is easier to crossover from anode to catode so its voltage is easier to drop. Increasing of methanol concentration will raise solubility of methanol in water, higher solubility will increase methanol crossover to catode side. Methanol crossover will decrease efficiency of DMFC and decrease power density. Stability of membrane by time for DMFC application and methanol crossover observed for 10 hours. The loading is fan that integrated to DMFC kit. Result is showed Figure 8(a) for catalyst loading of 1 mg/cm^2 and (b) for catalyst loading of 5 mg/cm^2 below.

Based on Figure 8, the best condition to operate Nafion 112 for DMFC is using 5% methanol concentration. Therefore, it can be concluded that SPEEK +cSMM gave better performance for DMFC application compare to Nafion 112. It shows by higher power density from polarization curves and higher voltage stability from 10 hours observation. Meanwhile, the Nafion 112 is easier to drop than other two membranes.

Effect of methanol Concentration and Catalyst Loading on Nafion 117 Polarization Curves: Beside of Nafion 112, Nafion 117 was also used as comparison membrane. Effect of methanol concentration is showed at Nafion 117 polarization curve on Figure 9 for loading catalyst of (a) 1 mg/cm^2 and (b) 5 mg/cm^2.
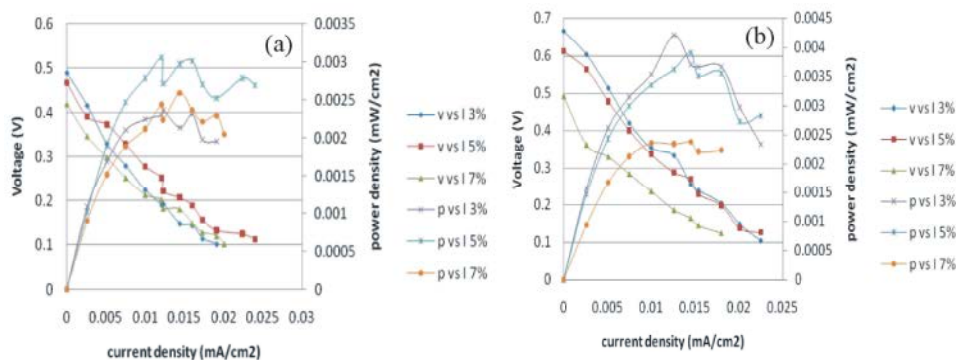
Fig. 9: Polarization Curve of DMFC using Nafion 117 with (a) 1 mg/cm^2; (b) 5 mg/cm^2 catalyst loading
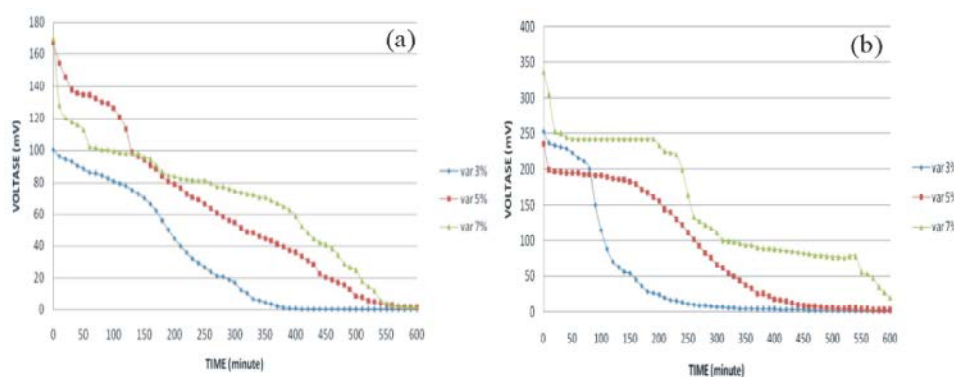

Fig. 10: Voltage vs Time Curve for Nafion 117 Membrane with (a) 1 mg/cm^2 and (b) 5 mg/cm^2 catalyst loading

Nafion 117 with catalyst loading of 1 mg/cm^2 was resulted the maximum power density when it used 5% methanol concentration. Meanwhile, Nafion 117 with loading catalyst 5 mg/cm^2, maximum power density was resulted by 3% methanol concentration. It shows difference ability of polarization at difference catalyst loading. Higher catalyst loading will be affected rate of reaction. Reaction will run faster and the used of low methanol concentration will result higher power density than used of lower concentration. The power density value of MEA with 5 mg/cm2 catalyst loading and 1 mg/cm^2 are 0.004208 mW/cm^2 and 0.003049 mW/cm^2, respectively. But the same phenomenon seems at 7% methanol concentration that power density will decrease. This phenemenon might be caused by methanol crossover. Methanol concentration of 7% is easier to crossover from anode to catode so its voltage is easier to drop. Increasing of methanol concentration will raise solubility of methanol in water, higher solubility will increase methanol crossover to catode side. Stability of membrane by time for DMFC application and methanol crossover observed for 10 hours. The loading is fan that integrated to DMFC kit. The effect of catalyst loading on the voltage is showed in Figure 10.

As shown in Figure 10, the methanol with 5% concentration gave the best result in voltage and stability for Nafion 117 with catalyst loading of 1 mg/cm^2. It was according to its polarization curves where 5% methanol concentration result the higher power density. Nafion 117 with catalyst loading of 5 mg/cm^2 result highest stability and voltage at methanol concentration of 7%. The phenomenon could be explained that the oxidation of methanol at anode caused decreasing of methanol concentration that crossing over from anode to catode. It means that methanol crossover will increase according to increasing of loading.

Comparison the Membranes Performance: Observation should be done in the same condition to compare membrane performance accurately. These conditions are including methanol concentration and catalyst loading. Result of membrane performance comparison is showed in Figure 11 a for 3% methanol concentration, Figure 11 b for 5% methanol concentration and Figure 11 c for 7% methanol concentration. We only used loading catalyst of 5 mg/cm^2 because it is assumed as the most effective loading than 1 mg/cm^2 catalyst loading.
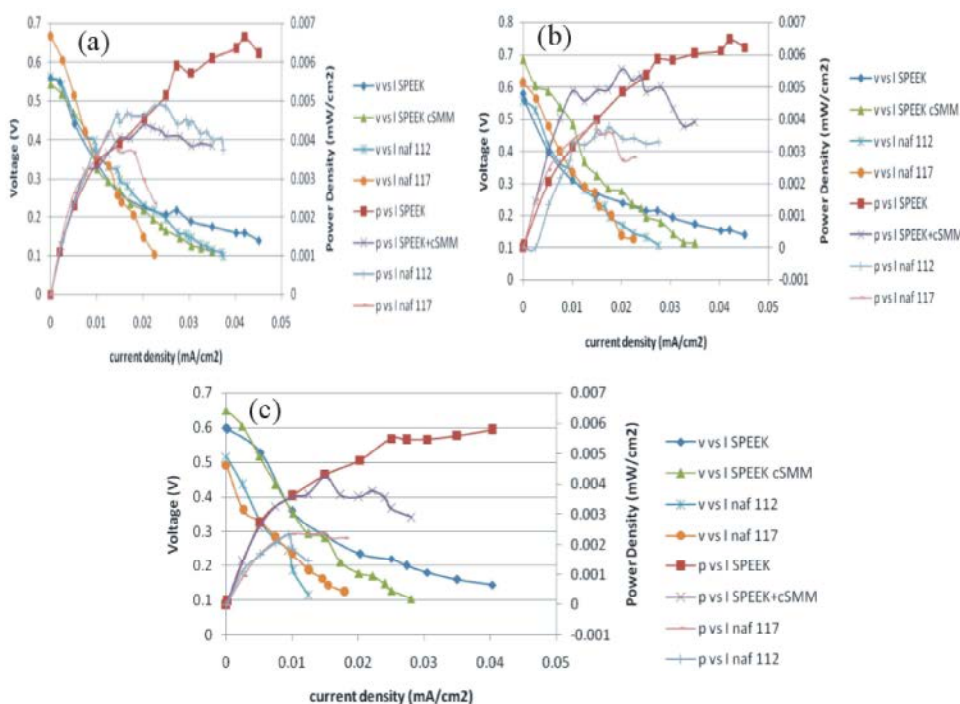
Fig. 11: Polarization Curves of DMFC using SPPEK, SPEEK+cSMM, Nafion 112 and Nafion 117 for Catalyst Loading of 5 mg/cm^2 and Methanol Concentration of (a) 3%, (b) 5% and (c) 7%

Based on Figure 11, it seems that the best membrane is SPEEK. It is showed by maximum power density for every methanol concentration. SPEEK was resulted the highest power density. Instead of that, stability of SPEEK is higher than other. SPEEK membrane is still stable at high current density when other membrane has already dropped. But, if we see from maximum voltage that achieved, SPEEK+cSMM gave the best result. SPEEK+cSMM gave the maximum voltage especially for methanol concentration of 5% and 7%. But its stability is still lower than SPEEK. Superiority of SPEEK membrane is suitable with its characterization. SPEEK methanol permeability 4.15×10^{-7} is lower than SPEEK+cSMM's, 5.17×10^{-7}. It means that SPEEK membrane has better performance if it is applied to DMFC. Methanol crossover on SPEEK is lower than SPEEK+cSMM because of its lower methanol permeability. Lower methanol crossover means higher efficiency and high performance of DMFC.

Proton conductivity of SPEEK+cSMM, 2.67×10^{-2}, is higher than proton conductivity of SPEEK, 1.0×10^{-2}. It was showed proton transfer ability for SPEEK+cSMM is higher than SPEEK. When it is applied to DMFC, SPEEK+cSMM showed higher voltage that caused by high proton transfer. But its performance limited by

high methanol permeability that effect to its stability that still lower than SPEEK without modification. These experimental results are the increase in methanol permeability and an increase in proton conductivity upon addition of cSMM to SPEEK can be interpreted in the following way. The membrane with ionic charges consists of ionic cluster domains surrounded by a continuous non-ionic domain of polymer matrix. Each isolated ionic cluster domain is connected by a narrow ionic cluster channel. The transfer of protons, water molecules and methanol molecules takes place primarily through the ionic cluster domains and ionic cluster channels and the rate of transport is controlled by the ionic cluster channel. The wall of the ionic cluster channel is covered by ionic sites and in the channel center there is a space that is free from the influence of ionic sites.

The sorbed water molecules are present mostly in the ionic cluster domains and ionic cluster channels. In particular, in the ionic cluster channels, the water molecules exist in two different forms. One is the hydrated water (mostly non-freezing bound water) that is bound strongly to the ionic site. The other is (freezing) free water that occupies the central space free from the influence of the ionic sites. The proton transfer through the ionic cluster channel occurs by two different mechanisms.

One is near the channel wall via the bound water. Proton is transported by the Grotthuss mechanism [32, 33], hopping from one ionic site to the other, creating continuous-like pathways. The other is via free water by vehicle mechanism, which means proton is carried by the water molecules moving through the interconnected central channel space.

Upon adding cSMM into SPEEK, it is postulated that the ionic charge concentration in the channel increases. The increase in the charge concentration is understandable considering that additional sulfonic groups are provided from the end group of the cSMM. Since proton transport occurs mainly via bound water by Grottuss mechanism, proton permeability increases upon addition of cSMM. On the other hand, water and methanol molecules are transported mainly via the central space occupied by free water. In this research, methanol permeability increase after addition of SPEEK. The results can be concluded that increasing of methanol permeability will be increased methanol crossover.

CONCLUSION

In this study, SPEEK were successfully modified by cSMM method. The synthesized of cSMM carries charged sulfonic groups. Surface migration of cSMM occurs when blended into SPEEK membrane. Blending cSMM into the SPEEK membrane decreases T_g and tensile strength and increases proton conductivity. But an unexpected result that blending cSMM into the SPEEK membrane increases methanol permeability. As a result, blending cSMM into the SPEEK membrane increases the PEM performance at voltage and power density. But cSMM cannot increases SPEEK stability because of its high methanol permeability. Addition of cSMM into SPEEK indicating the SPEEK/cSMM blend membrane is good to the other studied fuel cell that does not use methanol as its fuel.

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