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Organic-Inorganic Nanocomposite Membranes as High Temperature Proton Exchange Membranes for a Direct Dimethyl Ether Fuel Cell Application

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Abstract: Nafion/poly(phenylmethyl silsequioxane) (PPSQ)/calcium hydroxyphosphate (CHP) and Nafion/PPSQ composite membranes are fabricated using homogeneous dispersive mixing and a solvent casting method for direct dimethyl ether fuel cell (DDMEFC) applications for use above 100°C. The recast composite membranes were characterized by means of scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis, and thermogravimetry (TGA). The results showed that PPSQ and CHP are compatible with the Nafion membrane and improve the initial degradation temperature of the Nafion membrane. In addition, the crystallinity calculated by a Gaussian peak deconvolution technique increases as the PPSQ and CHP increase in composite membranes. This composite membrane showed less fuel crossover compared to both the recast Nafion membrane and Nafion 115. This is likely to be due to the high crystallinity and low water uptake content in the composite membranes. On the other hand, the fuel crossover of the composite

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membrane impregnating CHP increased as the CHP content increased. This is related to the hydrophilic character of CHP. In addition, the proton conductivity of the composite membranes containing PPSQ and CHP appeared to be higher that of the Nafion membrane at a high temperature. Nafion/PPSQ/CHP and Nafion/PPSQ composite membranes showed better cell performances compared to Nafion 115 at temperatures ranging from 100°C to 120°C and at pressures from 1 atm to 2 atm.

Keywords: Direct dimethyl ether fuel cell, composite membrane, proton conductivity, nafion, poly phenylmethyl silsequioxane

INTRODUCTION

Fuel cells have received considerable attention as an alternative power source to the conventional fossil fuels, as conventional fossil fuels contribute to environmental pollution and decrease the overall oil supply. In particular, direct fuel cells are attractive for applications involving portable power sources and electric vehicular transportation units in view of their lower weight and volume as they require no fuel reforming system. Methanol (1), ethanol (2), formic acid (3), and others have been considered as a candidate fuel for direct fuel cells. There are considerable problems inherent with the commercialization of these fuels due to excessive fuel crossover issues, the low activity of electro oxidation, and the toxicity of the fuel. DME is an additional candidate fuel for portable power sources. Compared to other fuels, DME has low toxicity, a pumpless fuel delivery, and a high energy density. In addition, DME has a less flammability limit due to its higher ignition temperature point (235°C). Its physical properties are similar to those of LPG, implying that it can be handled and stored in the same way LPG can be. As DME is an environmentally friendly material, it is widely used as an aerosol propellant compared to ozone-depleting Freons (4).

Recently, several studies have been performed on the performance of the direct dimethyl ether fuel cell (DDMEFC). Müller et al. found that the performance of a DDMEFC was nearly identical to that of a DMFC under 5 atm at 130°C (5). Mench et al. reported that the electrolyte polarization data showed very different behavior depending on electrolyte thickness, and suggested that the cathode displayed a high relative performance loss for thinner Nafion 115, and that performance with a thicker electrolyte was hindered due to anode dryout issues (4).

The main drawback of DDMEFCs is related to the slow DME oxidation kinetics. Increasing the operating temperature will improve the electrode kinetics of the oxidation reaction. For this reason, an increase in the operation temperature of the DDMEFC from 100 to 130°C is highly desirable. This implement to the development of the fuel cell concerns limitations associated with the typically employed proton exchange membranes. It is obvious that the operation of the DDMEFC above 100°C posses technical challenges in terms of maintaining a proper level of hydration for these membranes. Additionally, the operation involving higher temperatures than the glass transition temperature of polymer electrolyte can lead to structural changes in the membrane and thus reduce the stability, performance, and the life-time of the membrane.

The important factors for a proton exchange membrane that affect the fuel cell performance are the fuel crossover and proton conductivity. A lower fuel crossover of the membrane can offer much higher fuel utilization and thus higher performance. In order to suppress fuel crossover, considerable research has been performed. Hybrid composite membranes using organic materials (6) and inorganic materials (7–10), nanoporous membranes (11), and multi-layered membranes (12, 13) have been fabricated. Higher conductivity is also being required to retain high cell performance and to reduce the size of cell.

Perfluorinated membranes such as Nafion have been used as a proton exchange membrane in direct fuel cells, owing to their excellent electrochemical and mechanical stabilities and high ionic conductivity. However, the use of this type of membrane is restricted according to the fuel crossover and dehydration phenomena for the application. The membrane performs very well in a saturated state, and its proton conductivity depends strongly on the water content. The upper limit of the temperature results from the difficulty in maintaining the water content of the membrane at temperatures at or above 100°C. Consequently, the proton conductivity of Nafion at high temperatures due to the dehydration phenomena and low thermal stability in the main backbone decreases considerably at low relative humidity levels, leading to large resistive losses and a reduction in the cell voltages (7, 12). The dehydration also results in membrane shrinkage and resulting poor contact and proton conduction between the membrane and the electrode. Therefore, Nafion/Inorganic membranes with good water retention properties at high temperatures have been studied (14, 15). The addition of an inorganic material to a polymer electrolyte membrane can improve physical and chemical properties such as the modulus, fuel permeation rate, tensile strength, and glass transition temperature.

Several researchers have attempted to prevent the loss of water from the ionic pores of the perfluorosulfonic acid by way of modifying membranes (7–9). One such approach was by incorporating hydrophilic inorganic particles such as SiO_2 in an effort to enhance the water retention property and resulting proton conductivity under high temperature operating conditions (7, 8). Another approach was impregnation with heteropolyacids such as phosphotungstic acid (PWA), which have high proton conductivity, into the perfluorosulfonic acid membranes (9). However, PWA tends to dissolve in water that can be present in the membrane due to its high solubility characteristic in water. To avoid this problem, Tatsumisago et al. reported that PWA can be immobilized in silica gel (11).

In an attempt to improve the performance of the perfluorosulfonic acid membrane for a high temperature operation, composite membranes was preprared by incorporating poly(phenylmethyl silsequioxane) (PPSQ) and poly(phenylmethyl silsequioxane) (PPSQ)/calcium hydroxyphosphate (CHP) into the perfluorosulfonic acid membrane. In this study, a hybrid Nafion membrane using inorganic additives, PPSQ and CHP, is tested as a suppressant of the fuel crossover and as a conducting promoter. Additionally, the inorganic materials used, PPSQ and CHP, were chosen due to their high heat stability, high crystallinity, and fuel suppressant. Furthermore, these inorganic materials are compatible with various polymers and have easy solution processing. They also possess ion exchange properties through a hydroxyl ion channel that may allow various proton paths in the composite membrane (16), and they have good compatibility with a number of polymers (17). The performances of organic-inorganic nanocomposite membranes were tested at elevated temperatures in altering the membrane performance in DDMEFC.

EXPERIMENTAL

Membrane Preparation

Nafion/PPSQ and Nafion/PPSQ/CHP composite membranes were prepared using 5 wt% Nafion solution (DuPont, EW 1100), PPSQ (Gelest), and CHP (Aldrich) in a powder form. The composite membranes were prepared from a 5 wt% Nafion solution (DuPont, EW1100) according to the following processes: First, the Nafion solution was evaporated under 50°C for 24 h untill the Nafion solution become solid resin. Second, the Nafion was redissolved with a desired volume of dimethylformamide (DMF, Aldrich) used as the solvent. Following this, measured amounts of PPSQ were mixed with CHP in a DMF solution and then stirred in an ultrasonic bath for 30 min. Next, appropriate amounts of the Nafion/DMF solution were mixed with PPSQ and PPSQ/CHP in an ultrasonic bath for 30 min to ensure complete mixing. The mixing solution was then cast into a glass plate and heated at 80°C for 12 h until most of the solution was evaporated and the composite membrane obtained was then placed in a vacuum oven at 140°C for at least 3 h to remove the last traces of solvent. Finally, the membrane was pretreated in a solution of 3 wt% H_2O_2, deionized water, 0.5M H_2SO_4, and in de-ionized water subsequently. Each step was carried out at 80°C for 2 h.

Conductivity Measurement

The proton conductivity of the sample was measured using the two electrodes and an apparatus that was designed in our laboratory. The proton conductivity cell is shown in Figure 1.

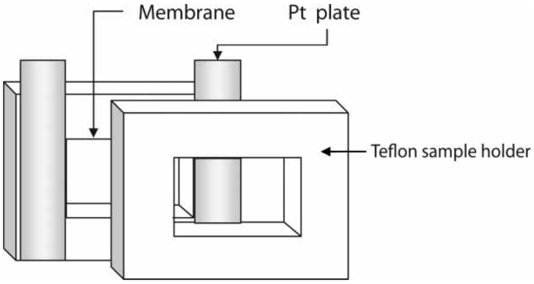


Figure 1. Schematic diagram of cell for proton conductivity measurement.

All of the membrane samples were in their protonated state, and the condition of measurement was 100% humidified. The proton conductivity, σ, was calculated from the impedance data, using the relationship

$$\sigma = l/RS$$

where l and S are the thickness and area of the membrane, respectively. R was derived from the low intercept of the high frequency semicircle on a complex impedance plane with the Re(x) axis.

DME Permeability

The equipment used for measuring the DME permeation is shown schematically in Figure 2. The system consists of a mass flow meter (MKS Co.), a pressure read-out unit (SENSOTEC, Model60-3152-05), a pressure transducer, a membrane cell, a humidifier, and a temperature controlling cabinet. The effective area of the membrane was 3.14 cm^2. DME gas with saturated water vapor in the upstream was controlled by using a needle valve and a backpressure controller. Water vapor on the permeation side was collected in a cold trap jar. The flux of DME gas rejecting the water vapor was measured using the mass flow meter and the permeability of DME was calculated using the following equation:

$$P = Ql/(p_1 - p_2)A \tag{1}$$

Here, P is the permeability($cm^3 \cdot cm/cm^2 \cdot$ cmHg $\cdot$ s), Q is the permeation volume per time (cm^3(STP)/s), p_1 and p_2 are the feed side and permeate side pressure (cmHg), respectively, and l and A are the thickness (cm), and the area of the membrane (cm^2), respectively. The permeation of DME was carried out at temperature of 80°C and a pressure difference of 1 atm. The permeate pressure in all runs was kept constant at 1 atm.

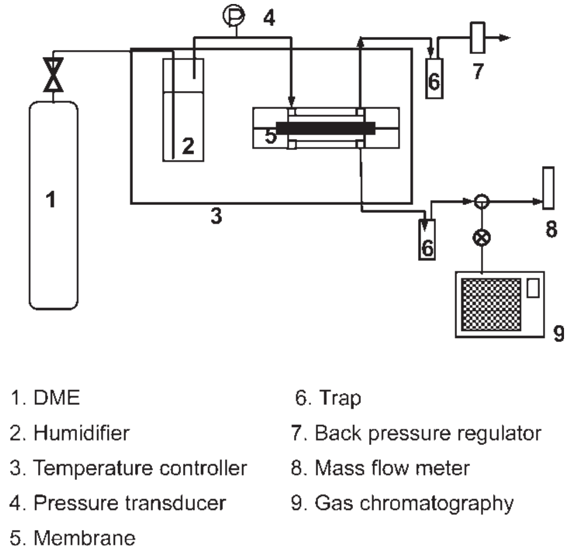


Figure 2. Schematic diagram of DME permeability apparatus.

Membrane Swelling Ratio (SR)

Dry membranes were immersed in deionized water overnight at room temperature to reach equilibrium sorption. After measuring the wet weight of a membrane at equilibrium sorption, the film was dried in a vacuum oven at 100°C for 24 h, and the weight of the dry membrane was measured. The water uptake of the membrane was determined using the following equation:

$$S_W = (W_w - W_d)/W_d \times 100\ (\%) \tag{2}$$

In the equation, W_w is the weight of the wet membranes and W_d is the weight of the dry membranes.

Characterization

The morphologies of the composite membranes and membrane electrode assemblies (MEAs) were observed using a scanning electron microscope (SEM, PHILIPS, XL30S FEG) and by transmission electron microscopy. The phase structures of the composite membranes were determined by X-ray diffraction (Rigaku Dmax 2200V). A thermogravimetry (TGA, DuPont) analysis of the composite membrane was performed in a temperature range of 25 to 650°C with a heating rate of 10°C/min in a N_2 atmosphere.

Membrane-Electrode Assembly (MEA)

The membrane electrode assembly (MEA) for a single test for the DDMEFCs consists of the membrane, catalysts, and gas diffusion layers. Unsupported Pt-Ru black (50 wt% Pt, 50 wt% Ru, Hispec 6000) and Pt black (Hispec 1000) used as the anode and cathode catalyst, respectively, was purchase from the Johnson Matthey Corporation. The loading of both Pt-Ru at the anode and Pt at the cathode were 4.0 mg $\pm$ 0.3/cm^2 in the experiments. The MEA was prepared by a decal transfer method and then hot-pressed at 125°C and 2300 psi for 3 min. The geometrical area of the electrode was 4 cm^2.

DDMEFC Single Cell Performance

Single cell performance was tested at different temperatures and pressures with an in-house electrochemical test station and a Fuel Cell Test System (P&P Energytech). The MEA was installed into a homemade graphite cell with an active area of 4 cm^2 and a serpentine flow field with one channel of 2 mm × 2 mm. The gas diffusion layers were used teflonized carbon papers. Prior to the DDMEFC performance test, the MEA was activated with a methanol solution to be fully moistured at 25°C overnight. The MEA had to be humidified enough to have high ionic conductivity. DME and oxygen gases were to the single cell at a flow rate of 200 SCCM and 500 SCCM, respectively and were bubbled through water in temperature-controlled stainless steel bottles to humidify the feeds prior to entry to the fuel cell. Humidified DME and humidified oxygen were preheated in same temperatures of the cell and fed to the cell. The operating temperature of the cell was maintained at ranging from 100 to 120°C. The anode and cathode back-pressure were varied at 1 bar and 2 bar as the temperature was increased from 100 to 120°C. The equipment used to measure the performance of the DDMEFC is shown schematically in Figure 3.

RESULTS AND DISCUSSION

Figure 4 (a) and (b) shows SEM pictures of the PPSQ and CHP powders, showing several agglomerates of the PPSQ powders in the range of 10∼200 μm and the CHP powders in the range of 5∼20 μm. It is important to make the nano-sized composite membrane and to modify the original Nafion structure. Hybrid materials with a nano-sized interface between the organic and inorganic domains offer exceptional opportunities to create materials with unique properties. It is shown that these inorganic particles are well-distributed in the form of several small fragments as shown in the TEM picture of Nafion/PPSQ10%/CHP2.5% composite membrane (Figure 4 (c)). The TEM picture shows that the two-phases are separated at

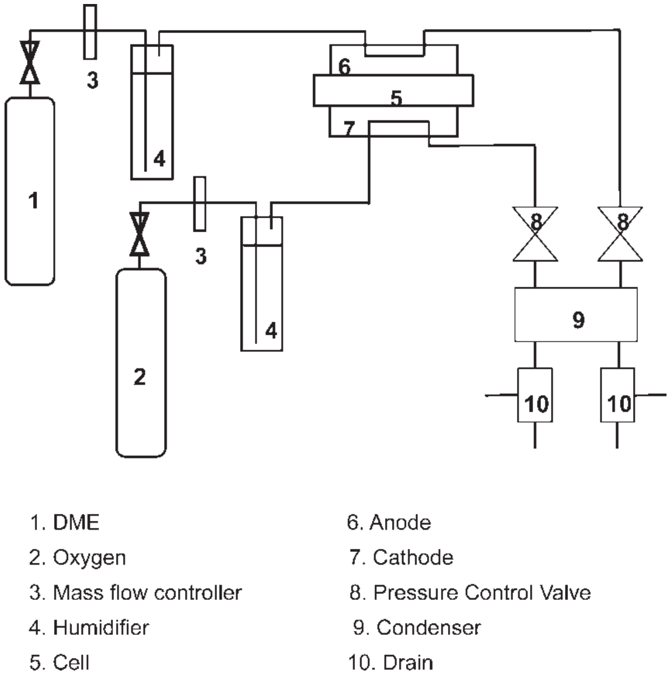


Figure 3. Schematic diagram of direct dimethyl ether fuel cell.

a nano-scale of 10 to 50 nm, where the dark regions represents the inorganic-rich phase, and the bright region represents the organic rich phase. The original aggregate was smashed into fine fragments during the homogenizing step. Calcium hydroxyphosphate is considered to be a bound inorganic silsequioxane-based moiety by strong interaction; these acidic clusters might be assembled within the continuous nano-sized channels of the hybrid materials. This continuous structure should facilitate ionic transport through the membranes.

The SEM pictures of the surface and cross-section for Nafion, Nafion/PPSQ, and the Nafion/PPSQ/CHP composite membranes are shown in Figure 5. It can be seen that solid PPSQ and PPSQ/CHP are uniformly and well-distributed over the membrane and do not form any agglomerated structures. Microphase separation at the interface between the inorganic filler and Nafion was not observed, implying good compatibility and strong interfacial adhesion between the two materials. On the other hand, by adding CHP, the channels seem to be well-arranged perpendicularly. Park et al. suggest the formation of these channels may contribute to the high proton conductivity for composite membrane (18).

Figure 6 shows SEM pictures of the surface and cross-section of MEA with the Nafion/PPSQ/CHP recast membrane. From the SEM picture of

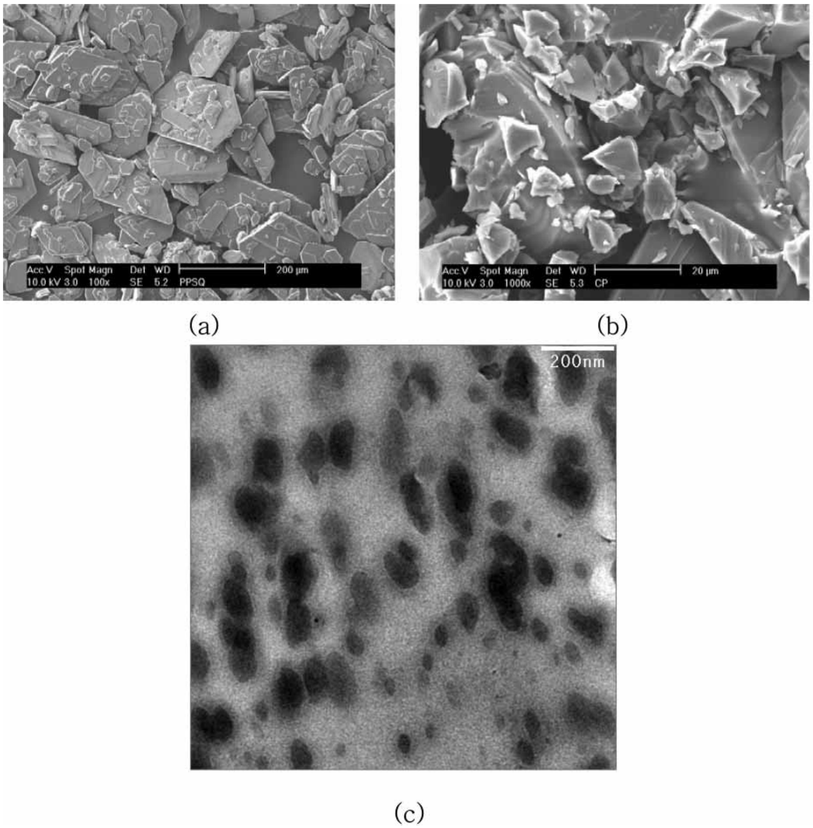
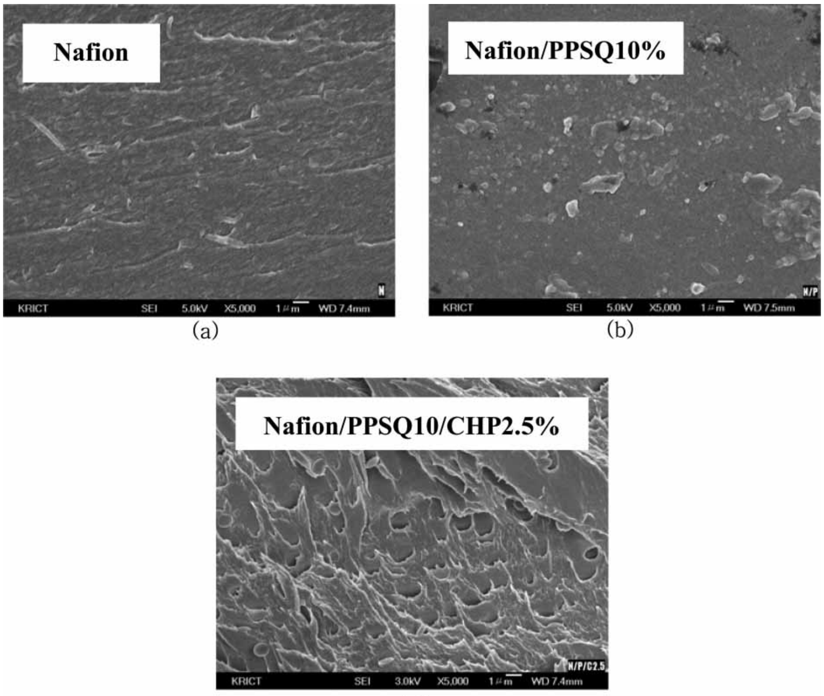


Figure 4. Microstructures of (a) PPSQ powder, (b) CHP powder (SEM), and (c) the distribution of inorganic filler in the Nafion/PPSQ10%/CHP2.5% composite membrane (TEM).

the MEA cross-section, the thicknesses of catalyst layers for the anode and cathode are observed to be 10 μm and 7 μm, respectively. Additionally, the thickness of the composite membrane was measured to be 100 μm after it was hot pressed. The impregnation of PPSQ/CHP into the Nafion membrane did not affect the nature of the membrane or the MEA.

Figure 7 shows diffractograms of the recast Nafion membranes. The entire membrane display a board diffraction peak at $2\theta = 10{-}22^\circ$. According to the literature (19), this broad peak can be deconvoluted into two peaks, assigned as amorphous ($2\theta = 15.9^\circ$) and crystalline ($2\theta = 17.4^\circ$) scattering from the polyflurocarbon chains of Nafion. From the areas of these two peaks, the crystallinity of the membranes can be calculated. These values are given in Table 1. It can be seen that the crystallinity of the composite membrane increases by 16% when 10 wt% PPSQ is incorporated into it. In addition, the crystallinity of the



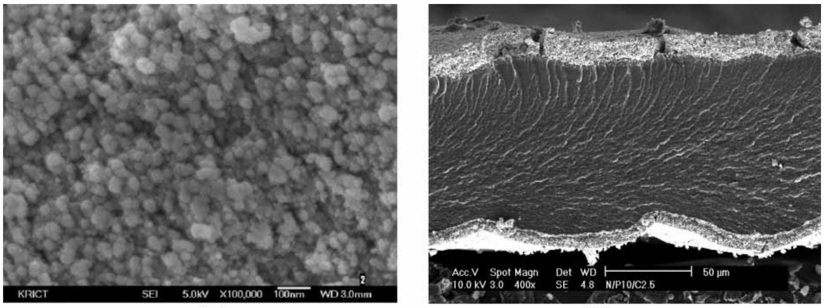
(a) (b)

(c)

Figure 5. SEM pictures of the cross-section of (a) recast Nafion, (b) Nafion/PPSQ 10% and (c) Nafion/PPSQ10%/CHP2.5% composite membrane.

Nafion/PPSQ/CHP composite membrane was found to have increased. It has high crystallinity that may allow a low level of fuel crossover and high thermal stability in the composite membrane. In addition, the increase in crystallinity suggests that the interface adhesion is strong between inorganic additives and organic Nafion structure due to the structural modification. High crystalline composite membranes exhibit lower fuel permeabilities if water and fuel cannot infiltrate into hydrophobic crystalline region due to the close packing of the main chain; thus, the high impermeability explains the low fuel crossover and low water uptake content.

Figure 8 shows TGA thermograms of the recast Nafion and recast composite membranes. It is seen that all of the membranes retain more than 95% of their weight up to a temperature of nearly 300°C, at which point the membranes start to decompose rapidly. This decomposition accounts for the loosening of the sulfonic acid group present in the Nafion membrane. However, the incorporation of the PPSQ and CHP into the Nafion membrane improved the initial degradation temperature of the Nafion membrane. The temperature at which these decomposition events occur shifts depending on the nature of inorganic content.



(a) (b)

Figure 6. SEM pictures of the surface and cross-section of MEA employing the composite membrane.

Figure 9(a) shows the DME permeability for the recast Nafion, along with the composite membranes incorporating PPSQ. It was found that the composite membranes have lower DME permeabilities relative to the recast Nafion. Also found was that the presence of PPSQ in the composite causes a significant reduction in the fuel crossover characteristic. There was a difference in the microstructure in terms of the thermal stability, the free volume in the amorphous phase, and the chain arrangement in the amorphous and crystalline volume with the incorporation of PPSQ into the Nafion structure.

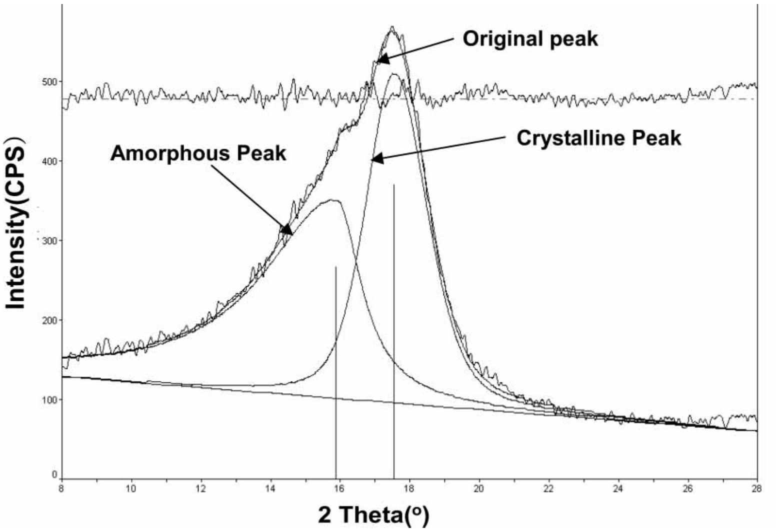


Figure 7. X-ray diffractogram for the characteristic crystalline peak of recast nafion, showing peak deconvolution process into the crystalline and amorphous regions by means of Gaussian function to obtain crystallinity.

Table 1. Comparison of crystallinity of recast Nafion and the composite membranes

Membrane	Crystallinity (%)
Recast Nafion	45.82
Nafion/PPSQ5	46.11
Nafion/PPSQ10	61.58
Nafion/PPSQ10/CHP2.5	74.85
Nafion/PPSQ10/CHP3.75	88.62

Figure 9(b) shows the DME permeability of the composite membranes after incorporating CHP. With an adding CHP content, the DME permeability of the composite membrane decreased and then increased as the CHP content increased. The behavior of the fuel crossover properties of the composite membranes as the increasing of the CHP content was parallel to the water uptake behavior of the composite membrane. On the other hand, as the CHP content increased, in spite of the increase in the crystallinity as shown in Table 1, the water uptake increased. These results can be explained that the DME gas mainly passed through the free volume micropore of the composite membrane, which was filled by the water. Usually, for a composite membrane swollen by water, the absorbed water functions as a plasticizer and increases the intermolecular distance of the polymer molecules and increases its free volume, and eventually increases the fuel crossover.

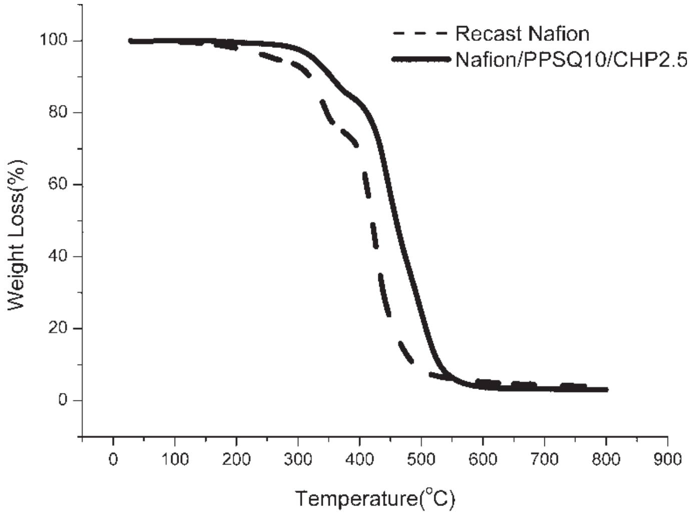


Figure 8. TGA thermograms of recast Nafion and Nafion/PPSQ10%/CHP2.5% composite membrane.

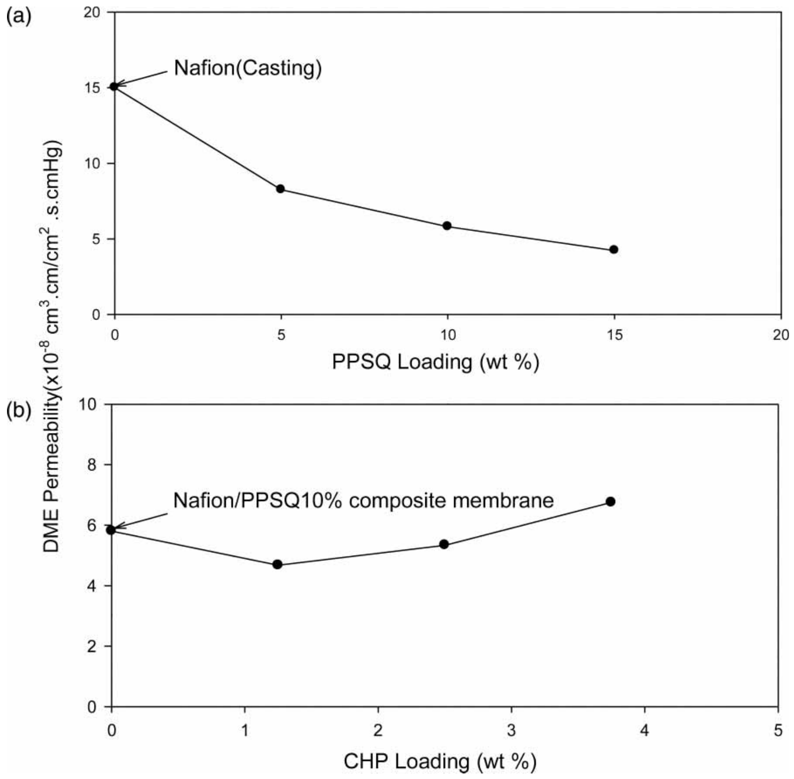


Figure 9. DME permeability of the composite membrane with (a) PPSQ loading and (b) CHP loading.

Thermally stable PPSQ and CHP embedded may increase the thermal stability in the composite membrane by fastening the fluorocarbon main backbone and vinyl-ether side chain of Nafion, alleviating heat swelling at high temperatures even in the hydrate state. Additionally, micro-dispersed inorganic fillers possibly occupy the amorphous region that was originally occupied by water molecules in the cast Nafion and Nafion 115, resulting in a decrease in the free volume, cluster size, the sorption capacity of the fuel, and finally resulting in a decrease fuel crossover.

Figure 10 shows the proton conductivity of Nafion 115, the recast Nafion with PPSQ, and the PPSQ/CHP impregnated Nafion composite membrane at temperatures ranging from 30 to 120°C under a 100% RH environment. The proton conductivity of the Nafion/PPSQ10%/CHP2.5% composite membranes appeared to be higher that of the Nafion cast membrane. Moreover, the conductivity of recast Nafion increases from 40 to 110°C, but starts to decline past this range. And the conductivity of Nafion 115 decreases slightly above 110°C. This phenomenon can be explained by the

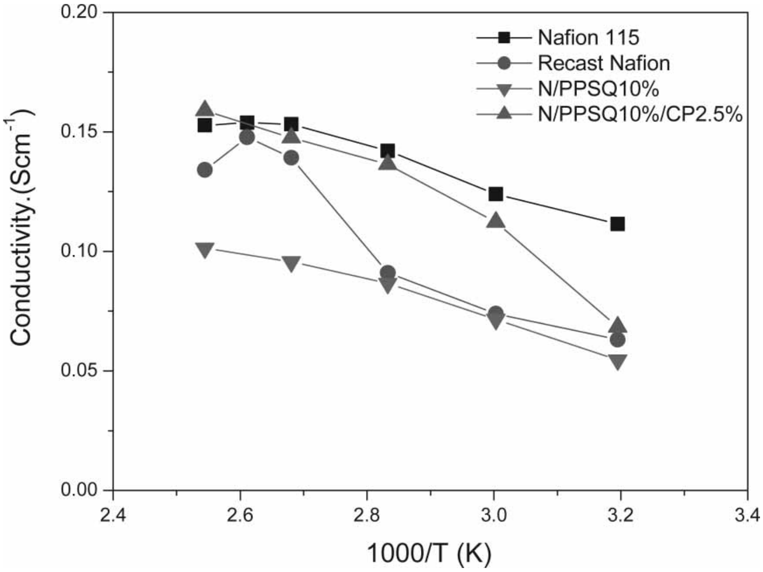


Figure 10. Temperature dependence of proton conductivity of Nafion115, recast nafion, Nafion/PPSQ, and Nafion/PPSQ/CHP composite membranes.

membrane dehydration at high temperatures and by the decrease of unassociated sulfonic groups due to the fluoro-backbone deformation (20, 21). On the contrary, the conductivity increases even at a high temperature in the Nafion/PPSQ and Nafion/PPSQ/CHP composite membranes. The Nafion/PPSQ10%/CHP2.5% composite membranes have higher proton conductivity relative to Nafion 115 in a higher temperature range above 110°C.

The water uptake characteristics are very important factors that directly affect proton transport through the membrane. Generally, it is accepted that protons can be transported along with hydrogen-bonded ionic channels and cationic mixtures such as H_3O^+ in a water medium (22). The hydration of the membrane is closely related to the conductivity. A proper water content level should be maintained in order to guarantee high proton conductivity.

Variation of the water uptake of the recast Nafion and the composite membranes are given in Table 2. From Table 2, it is observed that the water uptake of the composite membrane decreases with the incorporation of PPSQ. On the other hand, the water uptake of the composite membrane increases as the CHP content increases. These results can be explained by factors such as the hydrophilic character of CHP, the stronger interactions between the absorbing of a higher amount of water, and the number of exchange sites available per cluster increase, indicating that the proton conductivity of the membrane increases. Zawodzinski et al. (12) reported that

Table 2. Water uptakes of recast Nafion and the composite membranes (measured value at 25°C)

Membrane	Water uptake (%)
Recast Nafion	35.08
Nafion/PPSQ10	20.25
Nafion/PPSQ15	17.86
Nafion/PPSQ10/CHP2.5	21.5
Nafion/PPSQ10/CHP3.75	25.27

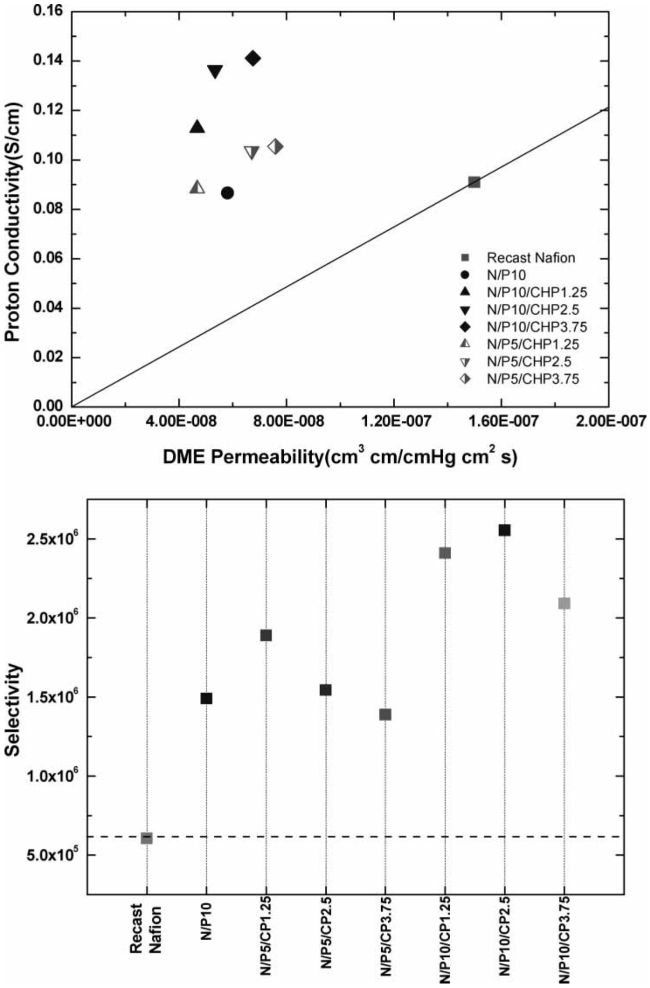


Figure 11. Relationship between DME permeability and proton conductivity of Nafion and composite membranes.

the proton conductivity of the Nafion membrane increases in a roughly linear manner with the increase of water uptake in the membrane. With the increasing of the CHP content, a higher water uptake is expected to lead to higher proton conductivity.

Therefore, the hybrid of Nafion-based membrane exhibits higher ionic conductivity and low fuel permeability at a high temperature compared to the Nafion membrane. It was also found to be thermally stable due to the cross-linking with temperature-tolerant frameworks in the hybrid. The observed characteristics of these composite membranes allow them to be candidate electrolytes in high temperature operations involving DDMEFCs.

Figure 11 shows the relationship between DME permeability and proton conductivity in addition to the ratio of proton conductivity to fuel permeability, selectivity, of the recast Nafion and composite membranes at 80°C. Most of the composite membranes showed lower fuel permeability and higher proton conductivity than the Nafion membrane. The selectivity indicates the characteristic factor in the evaluation of the membrane performances considering both the proton conductivity and fuel permeability. It must be employed in comparison with a membrane with the same order of magnitude in proton conductivity. In this case, the selectivity can be used as a barometer to develop the best proton conductive membrane with reduced fuel permeability. Among the composite membranes, the Nafion/PPSQ10%/CHP2.5% composite membrane showed the highest selectivity due to the high proton conductivity and low fuel permeability.

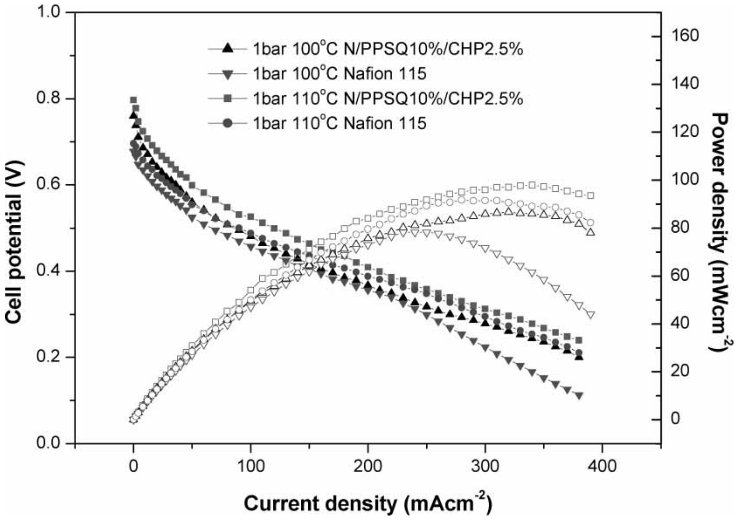


Figure 12. Polarization curve and power density of DDMEFC using Nafion115, and Nafion/PPSQ10%/CHP2.5% composite membrane.

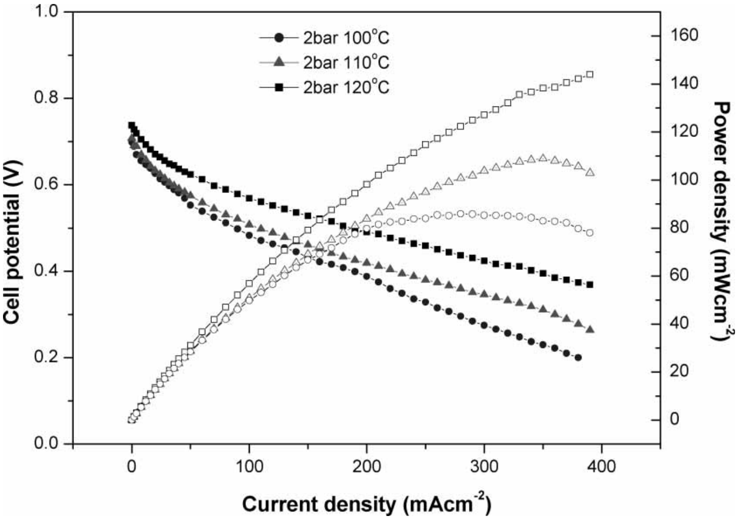


Figure 13. Temperature dependence of DDMEFC performance using Nafion/PPSQ10%/CHP2.5% composite membrane.

The single cell performances of the Nafion composite membrane incorporating PPSQ/CHP operated at temperatures ranging from 100 to 120°C and at pressures ranging from 1 to 2 atm are compared with that of Nafion 115 in Figure 12. The recast Nafion/PPSQ/CHP composite membrane is superior compared to the Nafion115 membrane. The experimentally measured maximum power densities for Nafion115 and the recast Nafion/PPSQ/CHP composite membrane were 91 and 98 mW/cm^2, respectively, at a temperature of 110°C and a pressure of 1 bar. This lower performance of the cell with the Nafion 115 membrane is attributed to the higher membrane resistance caused by the lower water vapor pressure and the proton conductivity in the cell.

Figure 13 shows the dependence of the polarization curves and maximum power density on the temperature for Nafion/PPSQ10/CHP2.5 operated at temperatures ranging from 100 to 120°C and a pressure of 1 bar. The single cell performance with the composite membrane was increased as the operating temperature increased, owing to the improvement of the oxidation reaction kinetics.

CONCLUSIONS

The use of Nafion for a proton exchange membrane at high temperatures above 100°C is restricted, in spite of many advantages such as the prevention of catalyst poisoning by CO, the higher system efficiency, and the superior water management capabilities.

Nafion/PPSQ and Nafion/PPSQ/CHP composite membranes were prepared through a recasting procedure using a Nafion solution mixed with PPSQ or PPSQ/CHP mixtures for DDMEFC applications. The incorporation of the inorganic additives of PPSQ and CHP into the Nafion has resulted in a lower fuel permeability, higher proton conductivity, enhanced thermal stability, and higher single cell performance compared to only Nafion. The proton conductivity for the Nafion/PPSQ/CHP composite membrane is higher than that of the Nafion membrane at high temperatures and at 100% RH. By adding of the PPSQ and CHP, the composite membranes showed less fuel crossover compared to Nafion due to the high crystallinity and path interruptions by nanoparticles. A single DDMEFC employed with the composite membranes was able to deliver higher current density values than that of the Nafion 115 membrane in operating conditions above 100°C. Therefore, these composite membranes are shown as promising candidate electrolytes for high-temperature operations of the PEMFCs and DDMEFCs.

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