Plasma modification on a Nafion membrane for direct methanol fuel cell applications

Shingjiang Jessie Lue[†], Te-Shun Shih and Ta-Chin Wei*

Department of Chemical and Materials Engineering, Chang Gung University, Taoyuan, Taiwan
*Department of Chemical Engineering, Chung Yuan University, Taoyuan, Taiwan
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Abstract–This research focuses on Nafion modification using plasma techniques for direct methanol fuel cell applications. The results indicated the both argon (Ar) and carbon tetrafluoride (CF_4) plasma treatments modified the Nafion surface substantially without altering the bulk properties. The Nafion surface exposed to CF_4 plasma resulted in a more hydrophobic layer and an even lower MeOH permeability than the Ar-treated membrane. The plasma operating conditions using CF_4 were optimized by utilizing an experimental design. The minimum MeOH permeability was reduced by 74%. The conductivity was $1\text{-}2 \times 10^{-3}$ S/cm throughout the entire experimental range. Suppressed MeOH permeability can be achieved while maintaining the proton conductivity at a satisfactory level by adjusting the plasma operating conditions.

Key words: Plasma Modification, Nafion, Methanol Permeability, Optimization, Fuel Cell

INTRODUCTION

Searching for alternative power and energy sources has gained much attention due to the high cost and dwindling crude petroleum oil supply. Among the alternative sources, fuel cells are a popular topic because of environmentally friendly advantages. Among several types of fuel cells, proton exchange membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC) use proton conducting polymer membranes [Kim et al., 2002]. The DMFC has many advantages over the PEMFC, including higher energy density, simpler system, long life-time, low poisonous emission, and possibility of ambient temperature start-up [Kim et al., 2002; Lee et al., 2005].

The proton exchange membrane based on sulfonated fluorocarbon polymer, Nafion® for example, is widely used for PEMFC applications. Nafion has high proton conductivity and good thermal, chemical, and mechanical properties [Scott et al., 2000]. However, the high methanol (MeOH) permeability through Nafion from anode to cathode is too high to use in DMFC devices. This MeOH crossover causes MeOH poisoning at the cathode and low efficiency of fuel consumption due to reactant (MeOH) losses [Heinzel and Barragan, 1999; Pak et al., 2005]. Therefore, research aimed at the development of new proton conductive membranes with suppressed MeOH permeability is actively underway.

Many approaches have been employed for membrane renovation. One method involves synthesizing new materials with decreased MeOH permeability and sufficient proton conductivity. These attempts include sulfonated hydrocarbon polymers and copolymer preparation [Carretta et al., 2000; Kim et al., 2002; Elabd et al., 2003; Manea and Mulder, 2002; Li et al., 2003; Sauk et al., 2005; Yin et al., 2003]. Another approach modifies the existent Nafion or other perfluorosulfonate polymers and creates a thin barrier on the membrane surface to retard MeOH permeability using metal alloy deposition [Ma et al., 2003], electron beam irradiation [Hobson et al., 2001], radiation-grafting [Scott et al., 2000], microwave exciting

with hexane/hydrogen gases [Walker et al., 1999], plasma polymerization with ethylene/ammonia [Zeng et al., 2000], and plasma etching followed by palladium sputtering [Choi et al., 2001].

This research investigates plasma-modified Nafion in a fuel cell application. The extent of surface modification is discussed in a separate paper [Lue et al., 2006]. In this paper, the modified films are characterized with parameters for the DMFC applications. Two plasma modification methods were investigated: a plasma treatment using argon (Ar) and plasma polymerization using a reactive gas, carbon tetrafluoride (CF_4). Then plasma operating conditions using CF_4 were optimized utilizing a response surface methodology.

EXPERIMENTAL

1. Membrane Preparation

The Nafion 117 membrane (from DuPont Co., Fayetteville, North Carolina, USA) was first boiled with hydrogen peroxide (3 wt%) to remove organic matters. It was then rinsed in pure water, boiled in H_2SO_4 (1 M, Riedel-de Haen, Seelze, Germany) for 1 hour, and then rinsed again with pure water. The radio frequency (RF) plasma treatment of Nafion was performed in a parallel plate reactor (PECVD). To compare the effect of Ar and CF_4 plasma modifications, the Nafion underwent a 100-W plasma treatment with either Ar or CF_4 for 5 minutes at a pressure of 0.35 Torr. The temperature was kept at 100 °C, gas flow rate at 10 cm^3/min (STD), and frequency at 13.56 MHz. After plasma modification the membrane was boiled again in H_2SO_4 (1M) and rinsed with pure water. Argon of 99.999% purity and CF_4 gas (99.998%) were obtained from San-Fu Gas Co. Ltd. (Taipei, Taiwan) and Ming-Yang Co. (Taipei, Taiwan), respectively. All chemicals used were reagent grade (from Acros Organics, Geel, Belgium, unless otherwise stated). The pure water was produced by using a Millipore water purifier (RiOs-5 and Millipore-Q Gradient, Millipore Corp., Bedford, Massachusetts, USA).

2. Membrane Characterization

Treated and control membranes were analyzed by the following methods. The ion exchange capacity was measured by titrating 0.005

[†]To whom correspondence should be addressed.
E-mail: jessie@mail.cgu.edu.tw

N NaOH solution into the 25 mL 1M NaCl solution already soaking the tested membrane. The water content was determined after boiling of the membrane in water for 1 hour followed with cooling and drying in a vacuum oven at 80 °C for 48 hours. The water content was calculated as the ratio of weight loss before and after drying to the dry weight. The above tests were carried on triplicate samples and the averages were reported. The conductivity was measured by using an AC impedance (Parstat 2263, Princeton Applied Research, Oak Ridge, Tennessee, USA) by applying 10 mV at frequency 100-700 kHz. The Nyquist method was employed and the membrane resistance was obtained by extrapolating the data to infinite frequency. The conductivity was calculated from the membrane thickness and the cell electrode area [Woo et al., 2003].

The membrane thermal stability was evaluated with a thermogravimetric analyzer (TGA 2050, TA Instrument, New Castle, Delaware, USA). The stability temperature was defined as the temperature at 10% weight loss. The dried membrane was recorded for the weight changes in nitrogen gas flow under a heating rate of 10 °C/min until 650 °C was reached. The membrane thickness was measured by using a dial thickness gauge (model 7331, Mitutoyo Corp., Kawasaki, Japan). Ten data points were collected and the mean was reported. The tensile strength was measured with a dynamic testing machine (Sintech 5/G, MTS Systems Co., Ltd., Eden Prairie, Minnesota, USA) at a rate of 10 mm/min according to the standard procedure [ASTM, 1994].

3. Methanol Permeability

The MeOH permeability was determined by using two stirred double-jacked glass reservoirs (35 cm^3 each) separated by the membrane material under test conditions [Lue et al., 2002]. The effective membrane area was 5.3 cm^2. One reservoir was filled with 5 M MeOH (referred as the donor reservoir) and the other with de-ionized water (referred as the receiving reservoir). The permeation temperature was maintained at 25 °C throughout the experiments. At predetermined time intervals small aliquots (1 μL) of solution were withdrawn from the receiving reservoir and the concentrations were analyzed with a gas chromatograph (Varian 3400, Varian Associates, Inc., Walnut Creek, California, USA) equipped with a flame ionization detector (FID).

Several assumptions were made in calculating the MeOH permeability. First, the MeOH flux was established across the membrane as a result of the concentration gradient between the two interfaces at adjacent reservoirs. Second, the solution volumes inside the two reservoirs did not change during the experimental period. Third, the amount of MeOH dissolved in the membrane was negligible compared with that in the two reservoirs. Fourth, the solutions were mixed thoroughly and the concentration polarization phenomenon was ignored. It was assumed that the equilibrium sorption between the solution and the membrane interface would be established faster than the diffusion step. Finally, the permeability (defined as the product of the MeOH diffusion coefficient and the partition constant between the solution and the membrane) was concentration independent.

According to the Fick's law Eq. (1) holds true for a diffusion process:

$$\text{flux} = -D\frac{dC^m}{dx} = D\frac{(C_A^m - C_B^m)}{L} \tag{1}$$

where D is MeOH diffusion coefficient, C^m is MeOH concentration inside the membrane, x is the distance along transmembrane direction, L the membrane thickness, and subscripts A and B represent the interface at the donor and receiving reservoirs, respectively.

The following equation is also true for MeOH mass conservation:

$$\text{flux} = \frac{V_B}{A}\frac{dC_B}{dt} = -\frac{V_A}{A}\frac{dC_A}{dt} \tag{2}$$

which V is solution volume in reservoir, C the MeOH concentration in solution, A the effective membrane area, and t the time elapsed.

The relationship between MeOH concentration in solution and that in membrane can be expressed by introducing the partition constant K:

$$C^m = KC$$

Taking mass balance on MeOH by assuming insignificant volume changes in both reservoirs and negligible MeOH sorbed inside the membrane yields Eq. (3).

$$C_{A,o} = C_A + C_B \tag{3}$$

which $C_{A,o}$ is the initial MeOH concentration in the donor reservoir.

Eq. (4) is obtained by combining Eqs. (1)-(3):

$$\frac{dC_B}{dt} = \frac{ADK}{LV}(C_{A,o} - 2C_B) \tag{4}$$

Integrating Eq. (4) results in Eq. (5).

$$\ln\frac{C_{A,o}}{C_{A,o} - 2C_B} = \frac{2ADKt}{LV} = \frac{2At}{LV}P \tag{5}$$

where permeability P equals to DK and can be obtained as the slope by plotting $\ln(C_{A,o}/C_{A,o} - 2C_B)$ versus 2At/LV.

4. Experimental Design for Optimization

A face-centered cubic experimental design [Montgomery, 2001] was used to find the optimal plasma operating conditions. The tested factors were plasma power (100-200 W), temperature (60-100 °C), and reaction time (5-9 minutes). Three levels for each factor were chosen (Table 1).

RESULTS AND DISCUSSION

1. Physio-chemical Properties

Table 2 summarizes the physical properties of the untreated and plasma modified Nafion membranes. It has been pointed out that the plasma treatments have pronounced effects on the chemical composition and topology of the treated surface. The Ar plasma caused oxygen incorporation and increased wettability of the exposed area. In contrast, the CF$_4$ plasma resulted in a highly fluorinated, hydrophobic surface. Such modifications, however, were limited only to a very thin top layer [Lue et al., 2006].

The ion exchange capacity (IEC) of untreated Nafion was 0.877 mmol/g. That value was slightly decreased to 0.851 and 0.842 for Ar- and CF$_4$ plasma-treated samples, respectively. The standard deviation of IEC result for the untreated membrane was 0.008 mmol/g. After the plasma treatments the data varied more significantly, as revealed in the higher standard deviations of the IEC results of the modified samples. The data fluctuation implies the heterogene-

Table 1. Experimental design (face-centered cubic design) and results of plasma polymerization with CF₄

Run #	Factor[a]			MeOH permeability $(10^{-6}$ cm^2/s)	Conductivity $(10^{-3}$ S/cm)
	Temperature (°C), X_1	Power (W), X_2	Time (min), X_3		
1	60 (−1)	100 (−1)	5 (−1)	0.882	1.84
2	100 (1)	100 (−1)	5 (−1)	0.985	1.58
3	60 (−1)	200 (1)	5 (−1)	0.609	1.36
4	100 (1)	200 (1)	5 (−1)	0.680	1.26
5	60 (−1)	100 (−1)	9 (1)	0.563	0.949
6	100 (1)	100 (−1)	9 (1)	0.846	1.57
7	60 (−1)	200 (1)	9 (1)	0.458	1.15
8	100 (1)	200 (1)	9 (1)	0.590	1.06
9	60 (−1)	150 (0)	7 (0)	0.583	1.19
10	100 (1)	150 (0)	7 (0)	0.900	1.86
11	80 (0)	100 (−1)	7 (0)	1.062	2.05
12	80 (0)	200 (1)	7 (0)	0.662	1.42
13	80 (0)	150 (0)	5 (−1)	0.609	1.67
14	80 (0)	150 (0)	9 (1)	0.560	1.54
15	80 (0)	150 (0)	7 (0)	0.665	1.00
16	80 (0)	150 (0)	7 (0)	0.614	1.08
17	80 (0)	150 (0)	7 (0)	0.661	1.15

[a]Numbers in parentheses are coded values

Table 2. Characteristics of Ar- and CF₄-treated Nafion membranes (mean±standard deviation)

Property	Ar plasma treated	CF₄ polymerization	Untreated
IEC (mmol/g)	0.851±0.024	0.842±0.016	0.877±0.008
Water content (wt %)	25.5±1.84	24.7±1.23	25.7±1.29
Contact angle (°)	73.4±1.69	87.6±1.28	80.1±2.61
Micro-roughness (nm)	77.0	70.2	70.5
Thermal stability (°C)	339	332	325
Tensile strength (MPa)	16.6	16.1	17.3
MeOH permeability (10^{-6} cm^2/s)	1.47±0.024	0.985±0.022	1.73±0.045
Conductivity (10^{-3} S/cm)	2.88	1.58	8.20

ity ion exchange characteristics resulted from the plasma treatments. This might be attributed to the inconsistent etching and polymerization reactions exerted from one spot to another on the surface during plasma modification. As shown in a separate paper [Lue et al., 2006], the Ar plasma caused surface roughening on the top layer due to the etching effect. The extent on sulfonate breaking might not be uniform throughout the surface and could lead to deviated IEC results. For CF₄ plasma, the polymerization reaction was more pronounced than the etching effect. The polymer deposition might have covered the bumpy regions etched by the plasma action. Therefore, the micro-roughness of this CF₄ modified sample was similar to that of virgin Nafion film (Table 2).

The etched top layer of the Ar-treated membranes might have fewer sulfonic groups, resulting in lower water content because the sulfonate regions are responsible for hydrophilicity and water sorption. This top layer also contained more oxygen atoms due to an oxidation reaction [Lue et al., 2006] and became wettable. The overall effects were balanced out and the resulting water content of the Ar-modified sample was similar to that of the untreated membrane (P>0.90). The CF₄ plasma exhibited a polymer deposition effect

and the top layer resembled a hydrophobic, Teflon-like structure. Such hydrophobic surface (as shown in the higher contact angle reading) had limited water sorption. However, this layer was very thin and the water was readily sorbed through the back side of membrane; the resulting water content was only slightly decreased from 25.7 to 24.7%.

The etching and polymer deposition effects of Ar and CF₄ plasmas rendered a heterogeneous chemical structure on the top thin layer. The mechanical strength was slightly decreased and thermal stability slightly improved by the plasma actions. However, the differences were not significant between the modified and the virgin membrane. The bulk properties such as mechanical and thermal resistances were barely changed by the Ar or CF₄ plasma treatment.

2. MeOH Permeability

The MeOH permeability of the Ar plasma-treated sample was decreased by 15% compared with the untreated sample. This was probably due to the crushed sulfonic groups at the treated surface, which serve as the channel networks for MeOH permeation. Choi et al. [2001] also reported a 12% decrease in MeOH permeability on an Ar plasma-modified Nafion sample.

The MeOH permeability of the CF_4 plasma-treated sample was decreased significantly by 43%. The lack of the sulfonic groups at the treated surface could have played a role for that decrease. Furthermore, the Teflon-like backbone with hydrophobic surface using CF_4 plasma suppressed the MeOH sorption and permeation even more remarkably.

3. Proton Conductivity

Our result showed that the proton conductivity of the pristine Nafion was 8.20 mS/cm. This value was lower than the data published by the manufacturer [DuPont, 2004] and Sauk et al. [2005]. They reported values of 0.083 and 0.04 S/cm, respectively, for untreated Nafion. The lower conductivity in this research might be ascribed to the differences in the sample conditioning method and operating conditions during measurement - especially temperature, humidity [Damay and Klein, 2003], and the pressure exerted between the tested membrane and electrodes. Therefore, the extent of the changes in conductivity in modified membranes from the untreated Nafion would serve as a better basis for comparison.

The proton conductivity of the Ar- and CF_4-modified membrane was decreased to 2.88 and 1.58 mS/cm, respectively. Those corresponded to decreased extents of 65% (Ar treatment) and 81% (CF_4 treatment). This was due to the introduction of a non-conductive layer and the resistance was inevitably increased compared with the untreated Nafion.

Many researches on the DMFC applications strived to suppress the MeOH permeability while maintaining sufficient proton conductivity although these two parameters have always showed a trade-off relationship. Feichtinger et al. [2001] and Walker et al. [1999] demonstrated that forming a polymerized barrier using hexane or hexane/hydrogen plasmas could greatly suppress MeOH permeation by a factor of 15 or 13. However, the electrical resistance increased 55 times. Sputtering a palladium layer on Nafion surface may help sustain the conductivity. However, the MeOH permeability was reduced only by 29% [Choi et al., 2001]. Zeng et al. [2000] deposited a thin anionic layer on Nafion surface using ethylene/ammonia plasmas and found little improvement in conductivity. The resistance data either remained unchanged or increased up to 4.7 times. Furthermore, the hydrophilic nature of the anionic layer facilitates MeOH transport and worsens MeOH crossover. Considering the reduction of MeOH permeability at the expense of conductivity decrease, CF_4 plasma may have higher potentials in the DMFC application.

4. Process Optimization

A response surface methodology was employed to find the optimal plasma polymerization operating conditions with CF_4. A face-centered cubic design on three factors (temperature, power, and time) was chosen, as shown in Table 1. The statistical analysis on the MeOH permeability indicated that a linear quadratic model was adequate with an R-square of 0.9456 and non-significance in the lack-of-fit test. Among these three factors, power was the most influential, followed by time. The response plots are shown in Fig. 1. The optimal operating conditions were power at 161 W, temperature at 70.8 °C, and a treatment time of 8.71 minutes. The minimum MeOH permeability of 4.51×10^{-7} cm^2/s was achieved at these optimal conditions, equivalent to a 74% decrease compared with the untreated Nafion sample.

Fig. 1(a) indicates that increasing the RF power or plasma treatment time would decrease the MeOH permeability. RF power input
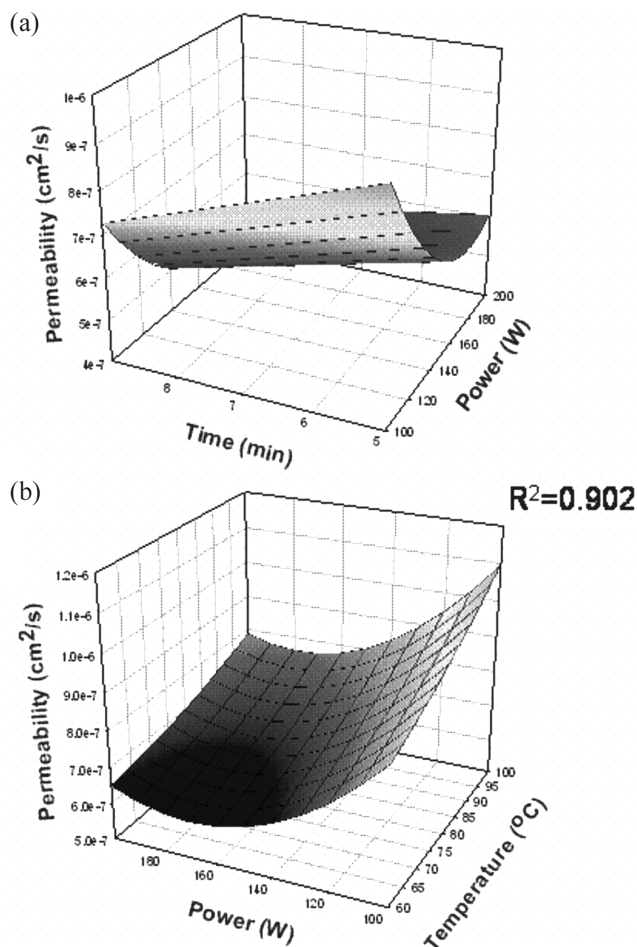

Fig. 1. Methanol permeability response as a function of power, time, and temperature.

directly enhances the density of all active species: atoms, radicals, ions, and electrons. The consequences include more vigorous bombardments and polymer formation. The CF_4 plasma is full of CF and CF_2 radicals, known for involvement in polymerization reaction on the exposed surface [Kim et al., 2003]. A higher power was shown to associate with the formation of a more hydrophobic layer using C_2F_6-H_2 mixture [d'Agostino et al., 1986]. This barrier layer would reduce the MeOH sorption on the Nafion membrane. Increasing treatment time has a tendency to thicken the deposited Teflon-like layer, resulting in a higher resistance toward MeOH permeation.

The substrate temperature is a complicated factor. d'Agostino et al. [1986] proposed that the plasma polymerization using C_2F_6-H_2 mixture involves a two-step mechanism: a reversible sorption of reactive CF_x species on the substrate surface (physical contribution), and a chemical reaction to form a polymer from the sorbed species and surface sites. They also found that the physical sorption reaction exhibited a negative enthalpy. In this study, a lower substrate temperature may have slowed down the polymerization reaction rates (e.g., a kinetic nature). However, it also promotes polymer deposition as the condensation tendency of reactive species was enhanced (e.g., a thermodynamic nature). Our results showed that the latter scenario played a dominant role. Fig. 1(b) implies that the lower temperature favored the barrier formation and thus retarded the MeOH

permeation.

A statistical analysis on the conductivity indicated that none of the factors had a significant effect on the response. The proton conductivity was in the range of $1\text{-}2\times10^{-3}$ S/cm throughout the experiments. As a matter of fact, an F-test showed that the variation caused by operating parameters was within the experimental error.

CONCLUSION

The water uptake, mechanical strength and thermal stability were not significantly influenced by the Ar and CF_4 plasma modification. The ion exchange capacity (IEC) was slightly decreased. The methanol (MeOH) permeability of the Ar- and CF_4 plasma-treated samples was decreased by 15 and 43% compared with the original Nafion. The corresponding conductivities of the plasma-treated samples were reduced by 65 and 81%, respectively.

The optimal plasma operating conditions were searched by using the response surface methodology. The radio frequency power was the most influential factor in reducing MeOH permeability, followed by time. The conductivity, however, was not affected by the operating factors and maintained $1\text{-}2\times10^{-3}$ S/cm throughout the experiments. This finding implies that suppressed MeOH permeability can be achieved and the proton conductivity may be maintained at a satisfactory level by adjusting the plasma operating conditions.

The results along with the data published in previous papers indicate that employing aliphatic plasma modification on Nafion often suppresses the methanol permeability at the expense of decreasing conductivity. Other ways of modification need to be explored in order to enhance the DMFC performance. One modification method would be the use of aromatic plasma gas to produce a thin conducting layer, which will retard the MeOH permeability but will not hamper the conductivity. Another approach would be controlling the morphology of the modified top layer. Instead of forming a covering uppermost layer, one could create a mosaic or porous structure with specific features that will help break the trade-off relationship. This type of membrane will have micro- or nano-scale channels which permit proton conductivity but prohibit the larger MeOH transport. These modifications are underway in our research lab.

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