

# Effect of solvents on the characteristics of Nafion<sup>®</sup>/PTFE composite membranes for fuel cell applications

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## Abstract

Composite membranes were prepared by impregnation of porous PTFE membrane with 2.5% Nafion<sup>®</sup> solution prepared in various solvents. The solvents chosen were based on their solubility parameters to effectively wet the substrate for obtaining membranes with lower resistances. Earlier studies on composite membrane preparation did not take the solubility parameter of the solvent to wet the substrate into account. Membrane conductivity was dependent on the solvent type and its solubility parameter. Solvents with solubility parameter close to Nafion<sup>®</sup> backbone/PTFE showed lower charge transfer resistance and the solvents with solubility parameter close to ionic groups showed higher conductivity. The effect of other parameters like compaction pressure, humidity and incorporation of Pt particles on the membrane resistance have also been investigated.

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## 1. Introduction

Polymer electrolytes are an important class of polymers with charged group attached to the polymers. The perfluoro-sulphonated ionomer (PFSI) is an important polymer electrolyte due to its wide application in fuel cells, chlor-alkali industries, diffusion dialysis, electro-dialysis, pervaporation, etc. Commercial perfluorinated ionic polymers like Nafion<sup>®</sup>, Aciplex and Flemion have excellent proton conductivity, mechanical strength, thermal and chemical stability [1,2]. However, some disadvantages, such as their high preparation cost, dependence of ionic conductivity on water content and temperatures and their permeability to organic solvents limit their commercial use in fuel cells. Therefore, R&D efforts are focused on developing new membranes based on hydrocarbon [3], modification of the existing polymers [4] and preparation of composite type membranes [5,6].

One method of preparation for composite polymer electrolyte membranes is composed of a neutral porous substrate and polymer electrolyte filling the substrate pores. This process combines the desirable property of the two components like good mechan-

ical strength, chemical inertness and dimensional stability of the porous substrate and the proton conducting property of the polymer electrolyte. The porous support may in addition restrict the in plane swelling during the operation of the membrane thereby reducing the fuel crossover.

The most common materials used in the preparation of composite membranes are expanded porous PTFE films and Nafion<sup>®</sup> ionomer. Cost reduction in these composites can be effected by the reduced amount of polymer electrolyte in these membranes. Penner and Martin reported preparation and ion transport properties of the membranes prepared with Gore Tex porous PTFE membrane and Nafion<sup>®</sup> [6–8]. Verbrugge et al. [9] have studied the effect of ionomer content on the composite membranes. It was found that at high ionomer contents, the membrane properties are similar to that of the ionomer-perfluorosulphonic acid. However, these membranes had reduced water permeability. At intermediate ionomer concentrations when the porosity is highly reduced, they are useful for fuel cells and at low ionomer concentrations the membrane behaves like the hydrophobic PTFE support.

Dutta et al. [10] have cast Nafion<sup>®</sup> solution on to porous Teflon, polypropylene and nylon support. Polypropylene and nylon supports needed annealing at 105 °C for 1 h for improvement in adhesion of Nafion<sup>®</sup> with supports. Koval et al. [11] have reported preparation of composite membranes of Nafion<sup>®</sup> with

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Celgard support by employing Moore and Martin's high boiling point solvent additive procedure [12]. Nouel and Fedkiw [13] have reported the preparation of Nafion<sup>®</sup> based composite membranes with porous Teflon and Celgard films as supports. PTFE composites were found to have higher Nafion<sup>®</sup> uptakes and higher conductivity compared to Celgard based composites.

Nafion<sup>®</sup> composites have also been prepared using porous PTFE supports and sulfonyl fluoride form of Nafion<sup>®</sup> resin [14,15]. The polymer resin film was hot pressed into the porous support due to its melt fabricable property. The composite membrane had comparable performance to Nafion<sup>®</sup> 115. Shim et al. [16] prepared a composite membrane by impregnating Nafion<sup>®</sup> solution into porous PTFE support and characterized the film with respect to single cell performance, gas permeability, water flux and water uptake. The membrane characteristics were dependent on the Nafion<sup>®</sup> loading on substrate and the cell characteristics were comparable to that of Nafion<sup>®</sup> 112. Liu et al. [17] have prepared self-humidifying composite membranes for fuel cells using Nafion<sup>®</sup> solution, porous PTFE supports and Pt/C or Pt. Under dry conditions, the performance of these membranes was good. EIS techniques revealed that self-humidifying composite membranes could minimize conductivity losses under dry conditions. Nafion<sup>®</sup>/PTFE membranes have also been prepared using PTFE having different types of micropores [18]. It was found that fuel cell performance was better with highly porous membranes. Lin et al. [19] have studied the effect of Triton X-100 on the preparation of Nafion<sup>®</sup>/PTFE composite membranes. Better ionic conductivities were achieved with 1–3% of Triton X-100. Yu et al. [20] have shown that Nafion<sup>®</sup>/PTFE composites showed higher thermal stability and better fuel cell performance compared to Nafion<sup>®</sup> 117/115. Nafion<sup>®</sup>/PTFE membranes have also been used for direct methanol fuel cells [21]. It was found that these membranes had lower methanol permeability and gave better performance than Nafion<sup>®</sup> 115/117. Various other preparation procedures and properties of the composite membranes have been discussed in the literature [22–24].

Yeo [25] determined the solubility parameters of Nafion<sup>®</sup> as  $\delta = 9.5$  (cal cm<sup>-3</sup>)<sup>1/2</sup> for backbone and  $\delta = 16.8$  (cal cm<sup>-3</sup>)<sup>1/2</sup> for ionic side chains and found that aggregation of Nafion<sup>®</sup> molecules in solvents is strongly dependent on the solubility parameter of solvents. The properties of the Nafion<sup>®</sup>/PTFE composite is hence, dependent on the method of preparation of the composite. Although reports of preparation of Nafion<sup>®</sup> membrane with various solubility parameters have been reported, the solubility parameter for PTFE (swelling) have not been con-

sidered while preparation of the composite membranes. The interaction between PTFE and Nafion<sup>®</sup> and hence interface formed is dependent upon the solubility parameter of the solvent used. This paper reports the preparation and properties of Nafion<sup>®</sup>/PTFE composite membranes prepared by varying the solubility parameter of the solvents by considering its suitability for both the components. The morphological characteristics of the various films have also been studied. Physical and electrochemical properties of the composite membranes have been analyzed. The main purpose of this paper was to understand the role of solvents in the impregnation of PTFE membranes with Nafion<sup>®</sup> solutions.

## 2. Experimental

### 2.1. Preparation of Nafion<sup>®</sup>/PTFE composites

Porous PTFE membrane (thickness  $0.025 \pm 0.01$  mm) was first washed with alcohol for 3 min at room temperature and dried in the oven. This was mounted on a frame and soaked in acetone for half an hour. Nafion<sup>®</sup> solution obtained from DuPont Co., had an equivalent weight of 1000. The solution had a composition of 5 wt% Nafion<sup>®</sup> and 95 wt% solvent. The solvent mixture was composed of water, propanol, ethanol and unspecified mixed ethers. The solvent of the Nafion<sup>®</sup> solution received was evaporated at 60 °C and the residual Nafion<sup>®</sup> was weighed and mixed with the solvents in a given ratio (Table 1). The solutions prepared contained 2.5% of the polymer in 97.5% solvents to minimize the aggregation of Nafion<sup>®</sup> due to high concentration. The solvents used were of high pure grade and obtained from Ranbaxy Chemicals Ltd. The pre-treated PTFE membranes were then impregnated with these solutions for 24 h. Impregnation was carried out twice to ensure complete blocking of all the pores of PTFE with Nafion<sup>®</sup>.

Membrane post-treatment procedures included pressing the membranes at  $\sim 25$  kg cm<sup>-2</sup> at 120 °C followed by annealing. The membranes were soaked in water for 24 h and then in dilute H<sub>2</sub>SO<sub>4</sub> (0.5 M) for 4 h before use. The average thickness of the Nafion<sup>®</sup> impregnated PTFE membranes were  $35 \pm 5$   $\mu$ m.

### 2.2. Characterization of Nafion<sup>®</sup>/PTFE composites

The morphology of the surface and cross section of composite membranes were studied using scanning electron microscope (SEM). The sample surface was coated with gold before the morphology of the membranes was observed. Dimensional stability of the membranes were obtained by measuring the change in the

Table 1  
Solubility parameters for various solvent mixtures used for impregnation of PTFE with Nafion<sup>®</sup>

Membrane designation	Solvent combination	Ratio	Solubility parameter (cal cm <sup>-3</sup> ) <sup>1/2</sup>	Nafion <sup>®</sup> loading (mg cm <sup>-2</sup> )
1	2-Propanol:water	4:1	14.28	1.1
2	2-Propanol:water:Triton X-100	4:0.7:0.3	13.46	2.2
3	2-Propanol:water:Triton X-100:ethylene glycol	3.5:0.5:0.7:0.3	15.35	2.1
4	2-Propanol:water:Triton X-100:n-hexane	3.9:0.5:0.1:0.5	12.61	1.7

dimensions of the membrane stored at room temperature in the atmosphere and that of the membrane stored in distilled water for 24 h. Water content in the membranes was obtained from the difference in the weight between the dry membrane (dried in vacuum at 80 °C) and the membrane immersed in deionized water for 24 h.

### 2.3. Conductivity measurements

The membranes were fixed in a cell which consisted of two carbon paper electrodes 6 cm × 6 cm and a device to hold the membrane and the electrodes for electrochemical measurement. The resistance of the membranes was obtained by AC impedance techniques using Ecochemie Autolab PGSAT P30 in the frequency range of 100 kHz to 100 Hz. The conductivity of the membranes in the transverse direction is obtained by the equation:

$$\sigma = \frac{l}{RS}$$

where  $\sigma$ ,  $l$ ,  $R$  and  $S$  denote the ionic conductivity, thickness of the membrane, resistance of the membrane and the cross sectional area of the membrane, respectively.

### 2.4. Performance test of PEM fuel cell

The composite membranes prepared as above were used for the preparation of electrode membrane assemblies. The electrode membrane assemblies were made of standard electrodes consisting of gas diffusion layer and catalyst layer prepared by proprietary techniques in the laboratory. The performance data were obtained from a 25 cm<sup>2</sup> active area cell. The fuel used was hydrogen and air was used as the oxidant. The cells were operated at 50 °C under ambient pressure conditions. The gases were humidified to 60 and 50 °C for hydrogen and air, respectively. The stoichiometric ratio (the ratio of the amount of reactant gases added to the fuel cell to the amount required by the electrochemical reaction) of fuel and oxidant were kept at 1.2 and 2, respectively.

## 3. Results and discussion

The solubility parameter is a numerical value that indicates the relative solvency behavior of a specific solvent. It is derived from the cohesive energy density of the solvent that in turn is derived from heat of vaporization. Since polymers would decompose before its heat of vaporization could be measured, swelling behavior values are assigned as solubility parameters. The solubility parameters for 2-propanol, Triton X-100, water, ethylene glycol and *n*-hexane are 11.8, 9.95, 23.5, 16.3 and 7.24 (cal cm<sup>-3</sup>)<sup>1/2</sup>, respectively [20]. The solubility parameters for Nafion<sup>®</sup> are  $\delta = 9.5$  (cal cm<sup>-3</sup>)<sup>1/2</sup> for backbone and  $\delta = 16.8$  (cal cm<sup>-3</sup>)<sup>1/2</sup> for ionic side chains [25]. The solubility parameter for PTFE is 6.2 (cal cm<sup>-3</sup>)<sup>1/2</sup>. When two liquids are physically mixed, the molecules of each liquid are physically separated by the molecules of the other liquid. Solubility of two materials is possible only when their intermolecular attractive

forces are similar, i.e., materials with similar cohesive energy density values would be miscible. As no solvent matches the solubility parameter for the backbone and side chain of Nafion<sup>®</sup>, a mixture of solvents need to be employed to impregnate porous PTFE membranes.

Table 1 lists the solubility parameters for the various solvent combinations employed in this study. The solvents employed for impregnating PTFE with Nafion<sup>®</sup> fall in two groups: solvents which have solubility parameters closer to that of ionic side groups of Nafion<sup>®</sup> and others which have parameters closer to that of PTFE/Nafion<sup>®</sup> backbone. The effects of these solvents on the properties of the impregnated polymer are investigated in this paper.

### 3.1. Impregnation of Nafion<sup>®</sup> solution

PTFE membrane is porous and Nafion<sup>®</sup> gets impregnated into these pores. As the porosity of these membranes is high, vacuum infiltration is not required to impregnate the matrix. The solvent solution should be able to penetrate the interstices and interior volume of the PTFE material. It has been found that by filling >90% of the interior volume of the membrane with the ionomer occlusion of the gases will occur [13]. The ion exchange resin should be securely adhered to both the external and internal membrane surfaces.

The matrix that needs to be impregnated is hydrophobic. Nafion<sup>®</sup> has a backbone which is hydrophobic and pendent chain which is hydrophilic. Surface treatment of the matrix or addition of compounds that would improve impregnation of Nafion<sup>®</sup> into PTFE is crucial in determining the properties of the composite membrane.

Table 1 shows equilibrium impregnated amounts of Nafion<sup>®</sup> solution on to porous PTFE membranes. It can be seen that for the same conditions of impregnation of Nafion<sup>®</sup>, the membranes containing Triton X-100 or combination of solvents containing Triton X-100 give higher impregnation of Nafion<sup>®</sup>. The advantage of using Triton X-100 [19] or solvents whose solubility parameter is close to that of PTFE is that they decrease surface tension of the fluorocarbon polymer thereby making it wettable. This leads to good pore coating and thereby leading to adhesion of the ion exchange resin to the inside surface of the film. These processes lead to increase in the loading of Nafion<sup>®</sup> in the films.

### 3.2. Water uptake and dimensional stability

Table 2 gives water uptake and dimensional stability of the porous PTFE impregnated Nafion<sup>®</sup> membranes (solvent composition 3) and that of Nafion<sup>®</sup> 1135 membrane. The hydropho-

Table 2  
Water uptake and dimensional stability

Membrane type	Water uptake (%)	Dimensional changes (%)		
		Length	Width	Thickness
Nafion <sup>®</sup> 1135	30	11.9	6.2	25
Composite membrane (composition 3)	16	4.5	4.8	16

bic PTFE substrate does not absorb water. However, when the Nafion<sup>®</sup> solution is impregnated into the membrane, the water uptake starts to increase. Water content of Nafion<sup>®</sup> 1135 is higher than that of the composite membrane. PTFE composite membranes were more dimensionally stable compared to Nafion<sup>®</sup> membranes. Nafion<sup>®</sup> 1135 showed anisotropy with respect to dimensional changes while the composite membrane was almost isotropic. Also, the porous PTFE film in the composite membrane suppresses the swelling of Nafion<sup>®</sup> within its pores. For composite membranes hence dimensional change is more likely in the thickness direction.

Water uptake thus depends on the amount of Nafion<sup>®</sup> loaded onto the membranes. The membranes prepared using Triton X-100 and ethylene glycol thus absorb more water (16%) than the one using 2-propanol and water (12%) alone.

### 3.3. SEM study of morphology of Nafion<sup>®</sup>/PTFE composite membranes

Surface morphology of various membranes were studied by SEM. Fig. 1a shows the surface of the PTFE membrane. There are fibres with knots visible on the membrane and enclosed within them are the micropores [20]. Nafion<sup>®</sup> solution penetrates through these micropores and fills them. Fig. 1b and c are the SEM pictures under low and high magnification when PTFE membrane was impregnated with Nafion<sup>®</sup> solution containing 2-propanol, water, Triton X-100 and ethylene glycol. Under low magnification the surface of the films appears to be smooth. At very high magnification fissures on the surface of the membrane are seen. These are formed when the solvents which are used for solubilising the Nafion<sup>®</sup> leaves the surface of the film. When the solvents used are low boiling, then evaporation is faster and the fissures are widely seen. Fig. 1d shows the surface of Nafion<sup>®</sup> film formed using 2-propanol, water, Triton X-100 and hexane. Hexane being low boiling the surface of this film shows wide fissures. The surface of Nafion<sup>®</sup> impregnated PTFE does not show any micropores indicating that all the pores are filled with Nafion<sup>®</sup>. Fig. 1e shows the transverse section of the composite membrane. The surface and the inner pores are completely covered and filled with Nafion<sup>®</sup> resin and no micropore is observed in the micrograph of the composite membrane.

### 3.4. AC impedance studies

Ionic conductivity of the polymer electrolyte is dependent on its water uptake as the diffusion of protons through the electrolyte is directly related to the hydration of the membrane. The performance of PEMFC is also dependent on the membrane resistance. Charge transport processes within Nafion<sup>®</sup>

are dependent on the humidification of the membrane, since membrane resistance changes with water content. Using high frequency and two-electrode methods membrane resistance can be measured. EIS techniques were used to study the effect of solvents on the properties of the membranes preparation of the membranes.

Fig. 2 shows the impedance spectra for the various membranes prepared. The AC impedance spectra exhibit a distinct arc. The equivalent circuit shown in Fig. 3 [26] was used to analyze the spectra. At high frequencies ( $\omega \rightarrow \infty$ )  $Z_{\text{imag}} \rightarrow 0$  and the intercept on the  $X$ -axis gives the membrane resistance  $R_M$ . At low frequencies ( $\omega \rightarrow 0$ ) again  $Z_{\text{imag}} \rightarrow 0$  and the intercept on the right hand side on the  $X$ -axis gives the sum of  $R_M$  and the charge transfer resistance  $R_{CT}$  [27]. Table 3 shows the values of  $R_M$  and  $R_{CT}$  as calculated using the equivalent circuit shown in Fig. 3 and the conductivity of the membranes prepared. It can be clearly seen that  $R_M$  and  $R_{CT}$  are dependent the solvents used for the preparation of the membranes. For the membrane prepared using 2-propanol and water as the solvent the membrane resistance is low. However, the  $R_{CT}$  value is high. Addition of Triton X-100 decreases the  $R_{CT}$  value while the  $R_M$  value is increased. Addition of ethylene glycol increases the  $R_{CT}$  value while lowering the  $R_M$  value. Addition of  $n$ -hexane to composition of membrane 2 decreases both  $R_M$  and  $R_{CT}$  compared to that of composition 3. These results suggest that addition of solvents with solubility parameter closer to Nafion<sup>®</sup> backbone and PTFE results in decrease of the charge transfer resistance of the membrane while addition of solvents that have solubility parameter closer to the ionic side chains decreases the membrane resistance, i.e., improves the conductivity.

The presence of solvents with solubility parameter closer to that of backbone structure of Nafion<sup>®</sup> and PTFE improve the adhesion of PTFE and Nafion<sup>®</sup>. Nafion<sup>®</sup> would hence bond through the backbone exposing the ionic groups. As a result, some of the ionic groups are closer to the walls of the PTFE membrane. The proton hence encounters higher resistance and capacitance to conductivity as it increases the path length for migration of ions [17]. The solvents which have higher solubility parameter on the other hand have no effect on the bonding between PTFE and Nafion<sup>®</sup> and hence lower membrane resistances.

### 3.5. Effect of humidification on EIS

Fig. 4 represents the impedance spectra of the membrane at humidified and dry conditions. Two semicircles are formed one at high frequency and one at low frequency for dry membranes. If the membrane was fully hydrated the high frequency

Table 3  
Membrane resistances as obtained from EIS

Membrane	Thickness ( $\mu\text{m}$ )	$R_M$ ( $\Omega$ )	$R_{CT}$ ( $\Omega$ )	Conductivity ( $\text{S cm}^{-1}$ )
IPA + water	33	0.075	83.5	$1.3 \times 10^{-3}$
IPA + water + Triton X-100	38	0.524	1.63	$2.1 \times 10^{-4}$
IPA + water + Triton X-100 + EG	37	0.0783	2.53	$1.4 \times 10^{-3}$
IPA + water + Triton X-100 + $n$ -hexane	35	0.285	1.08	$4.0 \times 10^{-4}$

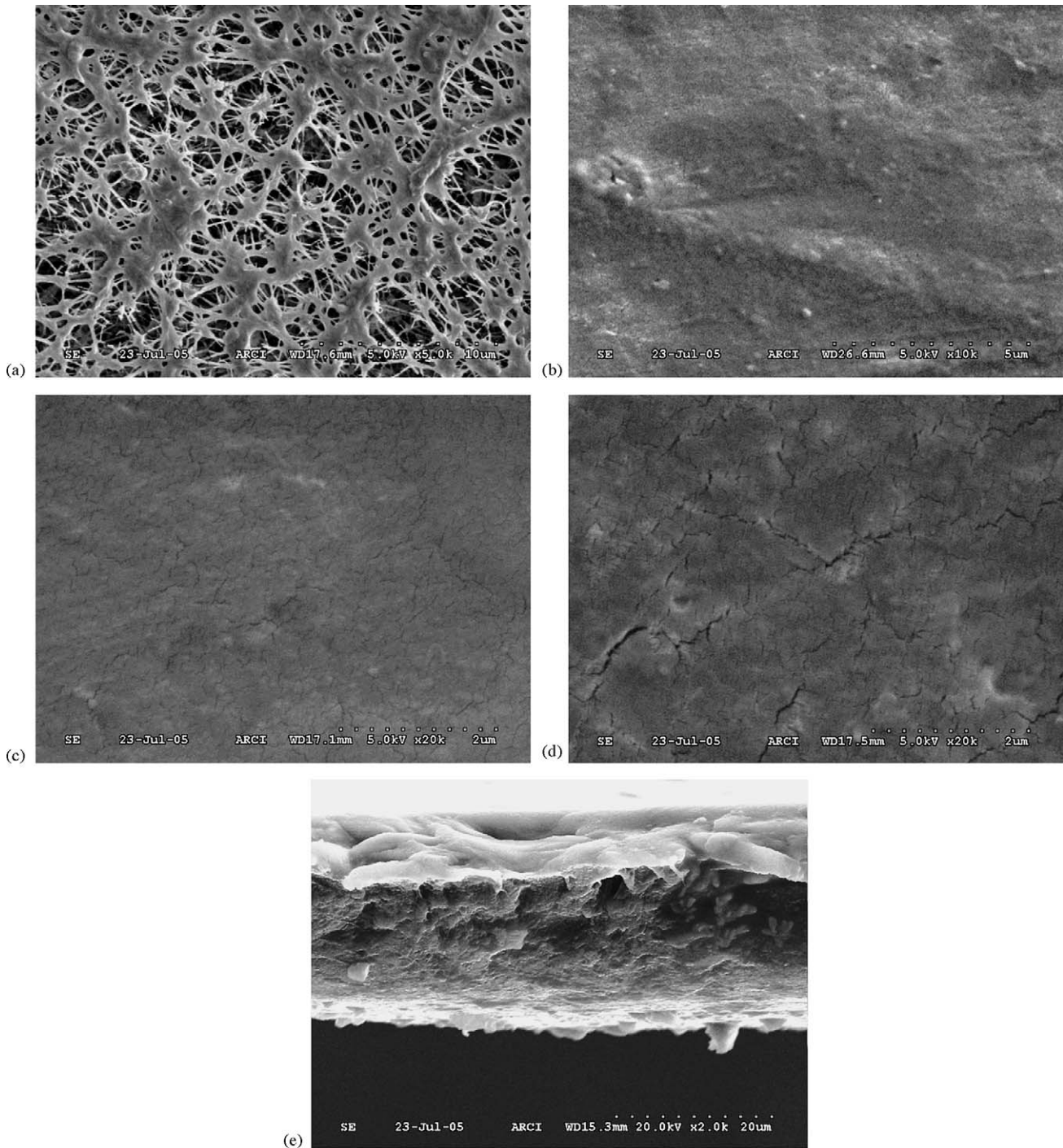


Fig. 1. SEM micrographs of: (a) porous PTFE membrane, (b) Nafion<sup>®</sup> impregnated PTFE at low magnification, (c) Nafion<sup>®</sup> impregnated PTFE at high magnification and (d) Nafion<sup>®</sup> impregnated PTFE with hexane solvent. (e) Transverse section of Nafion<sup>®</sup> impregnated porous PTFE.

arc disappears giving only one semicircle. From humidified to dry conditions, the AC impedance spectra of the membrane  $R_M$  shows significant difference. Assuming that the contact resistance and other component Ohmic resistance are constant during the change from humidified to dry conditions the  $R_M$  changes can be attributed to the change in resistance of the membrane.

In dry conditions or at low humidification conditions the membrane is not sufficiently hydrated and hence the pores contract making the movement of proton difficult. The grain

boundary resistance increases resulting in thinner and longer path for migration of ions [17]. Hence the membrane resistance increases. When the membrane is fully hydrated the water can be divided into two groups [28]:

- (1) Water molecules strongly localized near sulphonic acid group because of strong H-bonding.
- (2) Water molecules attached to the membrane via another water molecule that is held by weak H-bond. It is this type

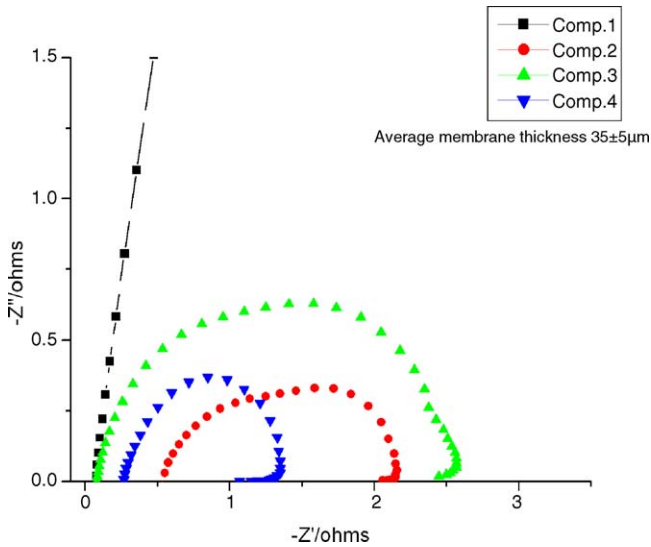


Fig. 2. AC impedance spectra of membranes prepared using solvents of different compositions.

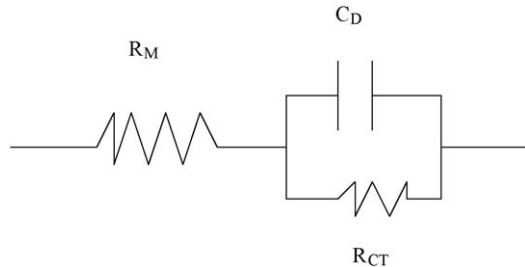


Fig. 3. Equivalent circuit.

of loosely attached water molecules that are required for proton migration. Migration channels are connected to each other and proton conductivity rapidly increases with water content.

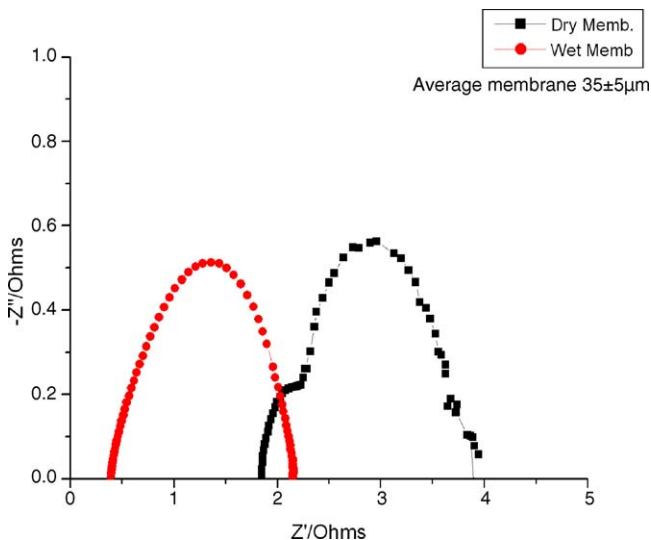


Fig. 4. AC impedance spectra of humidified and dry membrane.

At higher humidification levels, the membrane possesses both the kind of water molecules and hence conductivity under wet conditions is better.

### 3.6. Effect of compaction pressure

When composite polymer electrolyte membranes were prepared by impregnating Nafion<sup>®</sup> ionomer solution into the thin porous expanded PTFE substrates using impregnation methods, the pores on the substrate have to be fully blocked by the Nafion<sup>®</sup> films to prevent the crossover of the reactant gases such as hydrogen and oxygen. However, the possibility of the presence of pinholes or pores that are not filled by Nafion<sup>®</sup> still exists. To reduce this, the composite membranes impregnated with Nafion<sup>®</sup> were hot pressed and their conductivities were measured. Hot pressing would increase the adhesion of Nafion<sup>®</sup> within the substrate and pinholes or pores would decrease when the temperature of hot pressing is above the glass transition temperature and lead to improvement in performance [16]. At very high pressure, the conductivity of the membranes would decrease, as the molecular chains would become too close. As a result, the membrane would not be humidified (water would not easily diffuse into Nafion<sup>®</sup>), resulting in lower ionic conductance. Fig. 5 shows the impedance spectra of the membranes pressed at different pressures. It can be seen that with the increase in pressure the membrane resistance was found to decrease. However, when the membrane is pressed at 10 T the  $R_{CT}$  is found to increase. As membranes with low resistances are required, optimum pressure would be around 5 T.

### 3.7. Effect of incorporation of Pt into the membrane

Performance of fuel cells can be greatly influenced by the thickness and humidification state of the membranes. Good performance can be obtained if thin and fully humidified membranes are used because water molecules can promote pro-

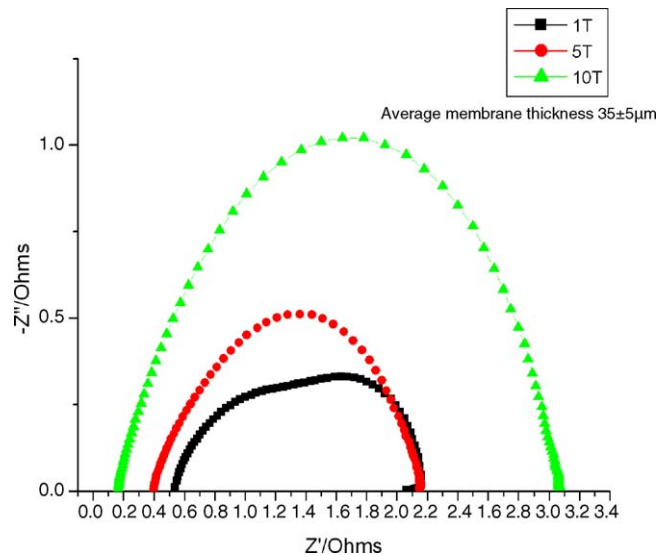


Fig. 5. AC impedance spectra of membranes pressed at various compaction pressures.

ton transport and thin membranes can reduce ionic resistance. But, thin membranes have higher gas permeation rate than the commercial membranes. Hence, OCV is reduced to a mixed potential, resulting from hydrogen oxidation and oxygen reduction at the cathode catalyst surface. This phenomenon not only reduces the cell performance and OCV but also introduces safety considerations. The reaction heat generated by the crossover gases can cause local hot spots, localized membrane drying and higher membrane resistance. Hence membranes containing Pt have advantages as it can effectively suppress gas crossover and can also be used as a self-humidifying membrane by combination of hydrogen and oxygen in the membrane to form water. Watanabe et al. [29] have proposed this method of fabricating self-humidifying membranes. Electroless plating on composite membrane is advantageous, as electron conduction pathway, which may otherwise be formed by network of dispersed Pt particles, will be avoided because of the presence of PTFE membrane in between. The amount of Pt loading in the membrane can be controlled by the concentration of platinum solution used. The Pt present in the membrane surface also helps in reducing the interfacial resistance between the electrode and membrane thereby increasing the conductivity.

Fig. 6 shows the impedance spectra obtained when the membrane containing IPA, water and Triton X-100 were soaked in a solution containing 1% of chloroplatinic acid and reduced with  $\text{NaBH}_4$ . The membranes were then soaked in dilute  $\text{H}_2\text{SO}_4$  to convert them to  $\text{H}^+$  form. The membrane containing platinum owing to its ability to reduce interfacial resistance between electrodes and membrane shows lower membrane resistance and  $R_{\text{CT}}$ .

### 3.8. Fuel cell performance

Performance of electrodes in PEMFC is dependent on the effects of membrane, interfacial kinetics and electrode transport losses [30]. Generally it is assumed that in the ionomeric membrane the charge transference is fixed and does not contribute to any dynamic impedance other than contribution to the high frequency termination of the higher frequency arc on the real axis

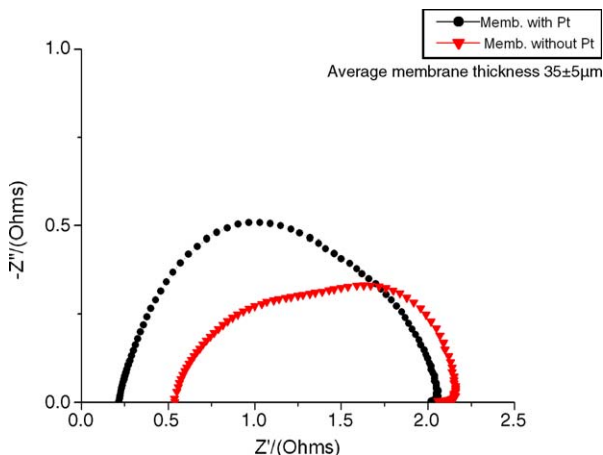


Fig. 6. AC impedance spectra of membranes with and without platinum.

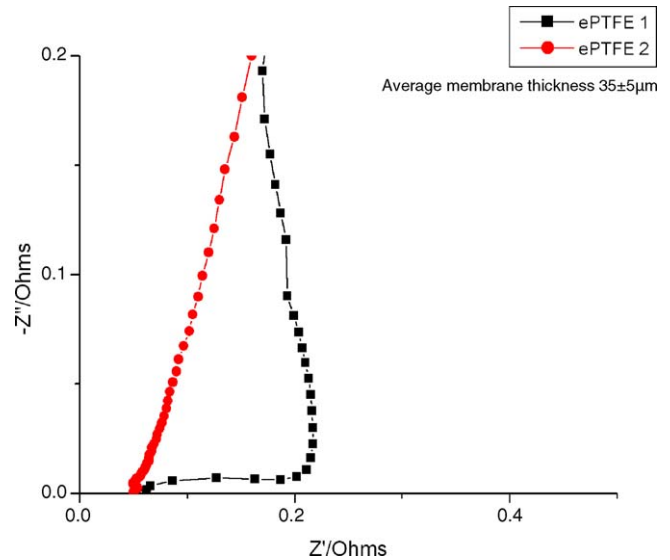


Fig. 7. AC impedance spectra of fuel cell electrodes (ePTFE 1 composition 3 and ePTFE 2 composition 3 Pt incorporated).

of the impedance plot. In the case of experimental membranes, care must be taken to minimize protonic conductivity losses as they contribute significantly to the performance of PEMFC. Figs. 7 and 8 show the impedance spectra and the corresponding fuel cell polarization curves for Nafion<sup>®</sup> impregnated PTFE (composition 3 and Pt incorporated membrane). The electrode ePTFE 1 shows a semicircle at a high frequency followed by a diffusion limited curve. In the electrode ePTFE 2 the semicircle at high frequency is absent as the presence of Pt particles lowers the resistances. It can be clearly seen that a current density of  $300 \text{ mA cm}^{-2}$  can be achieved with a membrane of lower resistance at 584 mV and in the membrane with high resistance the potential is only 510 mV. Based on these results we find that the composite membranes with the lowest resistance results in lower ohmic losses and better performances in fuel cells. These

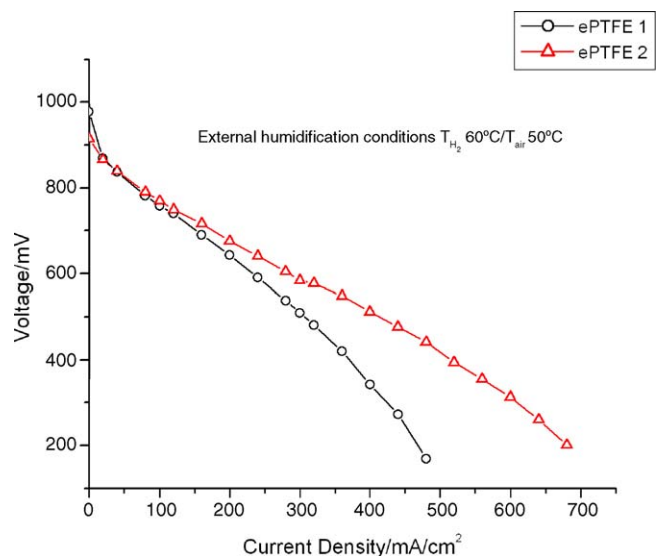


Fig. 8. Polarization curve for PTFE impregnated Nafion<sup>®</sup> based PEMFC ( $\text{H}_2/\text{air}$   $50^\circ\text{C}$  at ambient pressure conditions).

results are comparable to that of commercially obtained Nafion<sup>®</sup> (1135) membranes where a current density of 300 mA cm<sup>-2</sup> was achieved at 570 mV. The better performance of the composite membranes could be attributed to the lower ionic conduction pathway.

#### 4. Conclusions

A study has been conducted on the various preparative procedures for Nafion<sup>®</sup> impregnated PTFE membranes. AC impedance study reveals that the conductivity of the membrane is dependent on the solubility parameter of the solvent. Solvents having solubility parameters closer to ionic side chains improve the conductivity of the membrane. Membrane resistance is also found to depend on compaction pressure and the humidification of the membrane. Optimum compaction pressure for the composite membranes is 5 T. Fuel cell performance is also dependent on the membrane resistance. In general, membranes with low resistances give better performance.

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