

## NANOCOMPOSITE ELECTROLYTE MEMBRANE FOR MODERATE TEMPERATURE AND LOW RELATIVE HUMIDITY HYDROGEN PROTON EXCHANGE MEMBRANE FUEL CELL (HPEMFC) APPLICATION

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Nowadays PEMFC with hydrogen fuel has developed to commercialize to replace the conventional machine. Several limitations in PEMFC commercialization are its low efficiency, viability of hydrogen fuel supply and problem of controlling fuel and water as reaction products. Effective effort to increase efficiency and water management include elevating temperature of PEMFC operation near water boiling point to increase energy produced, prevent water flooding, enhanced cooling efficiency and also the possibility to use hydrogen and air under lower humidity in order to make simple PEMFC design. But at elevated temperature and low relative humidity, Nafion membrane that during the time still used as electrolyte will shrink and at high humidity and high temperature above 80°C membrane will swell and irreversibility decay occur. Membrane shrinking and swelling will reduce PEMFC performance. The objective of this study is to investigate the usage of Nafion-SiO<sub>2</sub>-PWA nanocomposite membrane NS10W, NS15W and NS20W with the ratio of Nafion:SiO<sub>2</sub>-PWA = (1:0.0288:0.0154), (1:0.0432:0.0173) and (1:0.05768:0.023) respectively as PEMFC electrolyte to improve PEMFC performance at moderate temperature and low relative humidity. The Fuel cell test (FCT) station (FCT-2000 ElectroChem, USA) was used for the cell polarization test and determination of the internal resistance of the membrane. The gas flow of H<sub>2</sub>/O<sub>2</sub> was fixed at the stoichiometric (H<sub>2</sub> + ½ O<sub>2</sub> ↔ H<sub>2</sub>O) mole ratio 0.5/0.38 while the hydrogen and oxygen pressures were fixed at 1 atm. The operating temperature of the cell was varied between 30–90°C. The relative humidity (RH) was controlled by using the water temperature of the H<sub>2</sub> and O<sub>2</sub> gas humidifiers. During the (V-I) measurement, the testing system was stabilized for about 1 h in order to obtain constant value for all the parameters of interest and the resistance of the membranes was measured by optimizing the (V-I) experiments. The electrochemical performance of the composite membrane with dry and humidified reactants are compared with those of the native Nafion membrane to identify the operating condition with low relative humidity condition. The results show that at temperature of 30–90°C and 100% RH humidity, the Nafion membrane performance is higher compare to composite membrane under same temperature value. But at 40% RH and same temperature, the composite membrane performance is higher compared to Nafion membrane. The result of data analysis and optimized polarization curve model shows that the mechanism of proton transfer in the Nafion membrane followed the vehicular model, which is as in the composite membrane is close to the proton hopping model. The performance of the Nafion-SiO<sub>2</sub>-PWA composite membrane is stable at low relative humidity operating at 30–90°C temperature. Since the humidity is low and operating temperature are high, the PEMFC using the nanocomposite membrane can run with lower humidity and with higher power compared to a PEMFC using the pure Nafion membrane.

### 1. Introduction

Operation of proton exchange membrane fuel cells (PEMFC) at elevated temperatures can alleviate the anode electro catalyst poisoning and accelerate the oxygen reduction reaction (ORR) kinetics of the fuel cells. Common perfluorosulfonic acid (PFSA) membrane, such as Nafion, is widely used as

the polymer electrolyte membrane under low-temperature because of its excellent chemical, mechanical and thermal stability. However, the proton conductivity of the Nafion membrane depends strongly upon the water content in the membrane. Thus, development of proton-conducting membranes with high water-retention ability is crucial for elevated temperature PEMFCs and high power output [1].

Much work has been conducted to modify the Nafion membrane with incorporated hygroscopic and high conductivity material such as Silicon oxide and heteropolyacid in the Nafion matrix [2], to increase water absorption of the membrane and conductivity. Many reports have evident the Nafion-inorganic composite membrane more stable than pure Nafion membrane at low relative humidity condition [3, 4, 2, 5]. But in those reported papers, phenomenon behind the conductivity improvement not fully described in detail.

This research was conducted to investigate the role of inorganic component in the Nafion membrane to the electro-chemical properties. To know the effect on addition of inorganic component to the electro-chemical property, the Nafion-SiO<sub>2</sub>-PWA membrane was synthesized with varies the ratio of Nafion: SiO<sub>2</sub>: PWA in the range of (1:0.0288:0.0154), (1:0.0432:0.0173) and (1:0.05768:0.023) respectively. Hopefully, incorporated inorganic compound like PWA that is hygroscopic and has high proton conductivity properties in the Nafion cluster strongly increase the amount of structural water in the film, improve the conductivity of the membrane and PEMFC performance especially at higher temperature and low relative humidity condition [5].

## 2. Experiment

### 2.1 Membrane preparation and membrane electrode assemblies

Material and method of the Nafion-SiO<sub>2</sub>-PWA composite membrane and membrane electrode assemblies (MEA) have been reported in the previous paper [5] and a brief description described in Fig.1

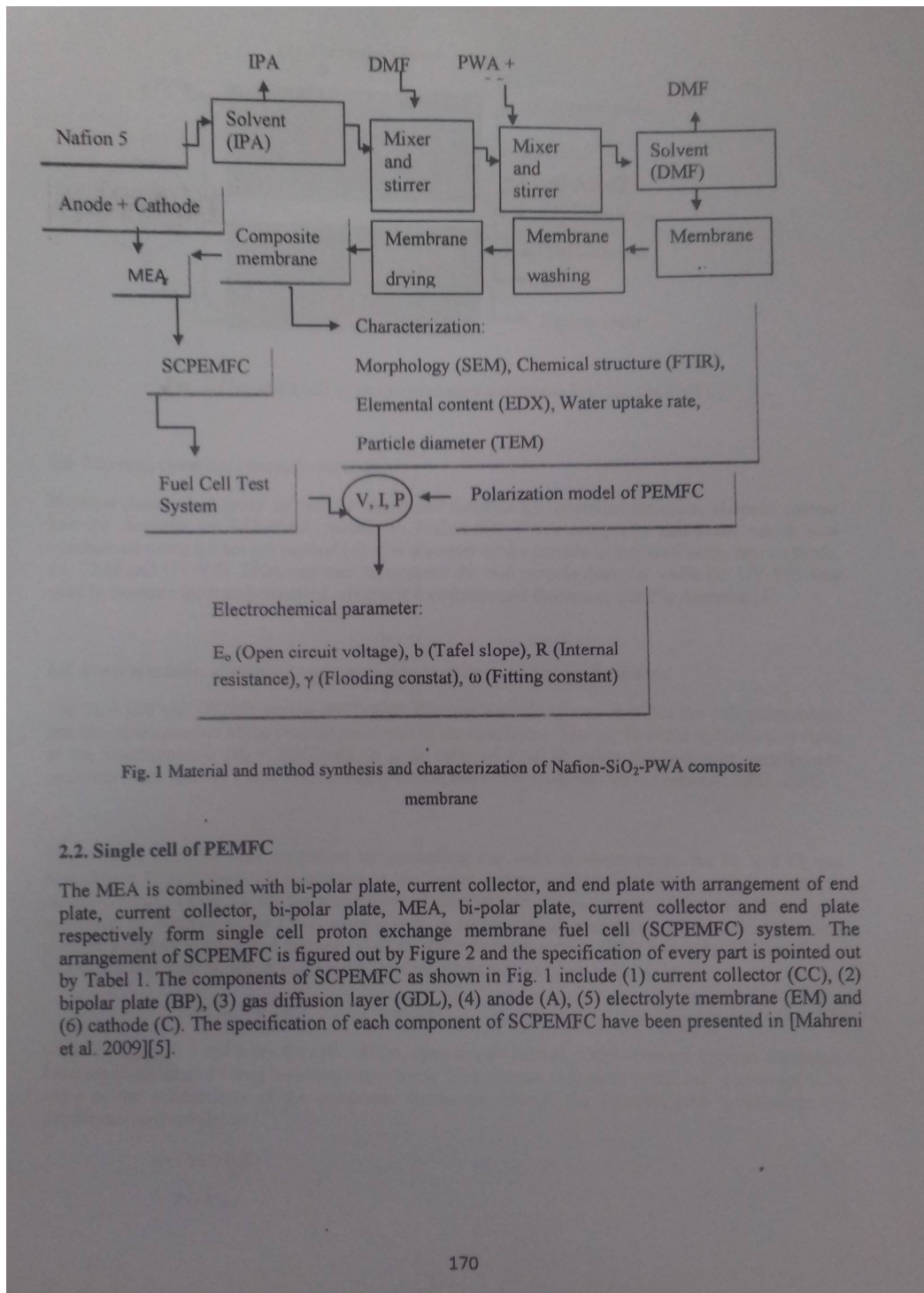


Fig. 1 Material and method synthesis and characterization of Nafion-SiO<sub>2</sub>-PWA composite membrane

## 2.2. Single cell of PEMFC

The MEA is combined with bi-polar plate, current collector, and end plate with arrangement of end plate, current collector, bi-polar plate, current collector and end plate respectively form single cell proton exchange membrane fuel cell (SCPEMFC) system. The arrangement of SCPEMFC is figured out by Figure 2 and the specification of every part is pointed out by Tabel 1. The components of SCPEMFC as shown in Fig. 1 include (1) current collector (CC), (2) bipolar plate (BP), (3) gas diffusion layer (GDL), (4) anode (A), (5) electrolyte membrane (EM) and (6) cathode (C). The specification of each component of SCPEMFC have been presented in [Mahreni et al. 2009][5].



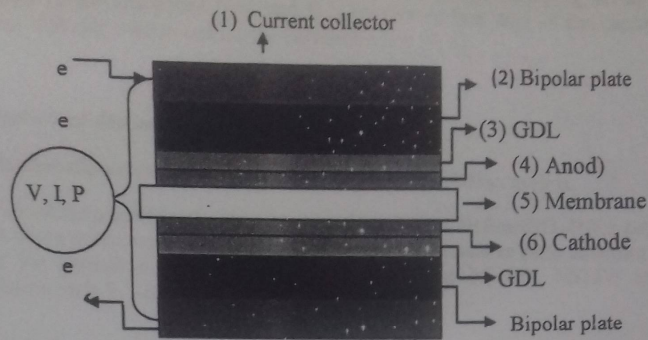


Fig. 2 The single cell of proton exchange membrane fuel cell (SCPMFC)

### 2.3 Physical-chemical characterization

Physical-chemical property as well as membrane morphology, chemical structure, element content and the diameter of  $\text{SiO}_2$ -PWA particle in Nafion- $\text{SiO}_2$ -PWA composite membrane which was synthesized using the sol-gel method [5]. The diameter of the particle is analyzed using two methods, i.e. TEM and UV-VIS. TEM was used to measure the real particle diameter while the UV-VIS was used to measure the transparency of composite membrane and theoretical particle diameter [5].

### 2.4 Determination of internal resistance, conductivity and cell performance

The Fuel cell test (FCTS) station (FCT-2000 ElectroChem, USA) was used for the cell polarization test and determination of the internal resistance of the membrane. The gas flowrate of  $\text{H}_2/\text{O}_2$  was fixed at the stoichiometric ( $\text{H}_2 + 1/2\text{O}_2 \leftrightarrow \text{H}_2\text{O}$ ) mole ratio of 0.5/0.38 while the hydrogen and oxygen pressures were fixed at 1 atm. The operating temperature of the cell was varied between  $30^\circ\text{C} - 90^\circ\text{C}$ .

The relative humidity was controlled by controlling the water temperature in the  $\text{H}_2$  and  $\text{O}_2$  gas humidifiers. During the (V-I) measurement, the testing system was stabilized for about 1 h in order to obtain constant value for all the parameters of interest and the resistance of the membranes was measured by optimizing the (V-I) experiments. A mathematical model for polarization curve was used to correlate voltage and current (V-I) at 100% relative humidity (RH) and 40% RH based in a single fuel cell system, which include the flooding parameter as given in Eq. (1) [6].

$$E = E_o - b \log(i) - R(i) - \exp(\omega i) \quad (1)$$

where  $E$ ,  $E_o$ ,  $b$ ,  $R$ ,  $\gamma$  and  $\omega$  are the cell voltage, open circuit voltage, Tafel constant, internal resistance, flooding constant and fitting constant, respectively. The internal resistance of the cell is assumed to be same as the conductivity of the composite membrane. Hence, Eq. (2) was used to calculate the membrane conductivity as [7]

$$\sigma = (1/R) (l/S) \quad (2)$$

$$P = V \times I \quad (3)$$

where  $\sigma$  is the conductivity of the composite membrane ( $S\ cm^{-1}$ ),  $R$  the resistance (ohm),  $l$  is thickness of the membrane (cm) and  $S$  is contact surface area of the electrode ( $cm^2$ ),  $P$  is power density,  $V$  is cell voltage and  $I$  is the current density [7, 8]

### 3. Results and discussion

#### 3.1 Particle diameter of inorganic component in the Nafion matrix.

Solution phase sol-gel method had been used to produce Nafion-SiO<sub>2</sub>-PWA composite membrane and could improve the membrane structure from micro structure to nano structure. Analysis using TEM found the particle diameter of SiO<sub>2</sub> and PWA in the NS10W, NS15W and NS20W composite membrane are 9, 7.86 and 12.64 nm respectively.

The particle size of SiO<sub>2</sub> and PWA in the NS10W, NS15W composite membranes found less than the size of the Nafion cluster. Therefore, it can be concluded that SiO<sub>2</sub> and PWA particles are in the Nafion cluster. The presence of inorganic particles in the Nafion cluster increase water uptake rate of the membrane. The water uptake rate of N112 (pure Nafion) membrane is 26.52 % weight, meanwhile of NS10W, NS15W are 30.25 g %, 33.43 g %, respectively. The increase of water uptake rate is identical to the increase in the membrane conductivity. At 90°C of temperature and at 40% RH, the conductivity of NS15W membrane is  $2.85 \times 10^{-3}\ S\ cm^{-1}$  while compared to Nafion membrane under the same condition to be only at  $1.16 \times 10^{-3}\ S\ cm^{-1}$ .

#### 3.2 Performance of PEMFC

The performance of the single cell MEA using N112, NS10W, NS15W and NS20W membranes were obtained from the cell voltage versus current density measurement. The results of the test at temperature range of 30 – 90°C of two different relative humidity, namely those are 40% RH and 100% RH, were recorded and presented as power density ( $mW\ cm^{-2}$ ) vs current density ( $mA\ cm^{-2}$ ) as shown in Fig. 3 (from a to g). All of the data are presented with the mathematical model of polarization curves. The electrochemical parameters was found from the optimization and experimental data in fitting with mathematical model to measure internal resistance ( $R$ ), open circuit voltage ( $E_c$ ), Tafel slope ( $b$ ) and flooding constant ( $\gamma$ ) as presented elsewhere [5]. Conductivity values were calculated from electrochemical parameters in which obtain from graphs in Fig.3 and the data is listed in table 1. The best cell performance was recorded 90°C, 1.7 atm at 40% RH with using NS15W membrane.



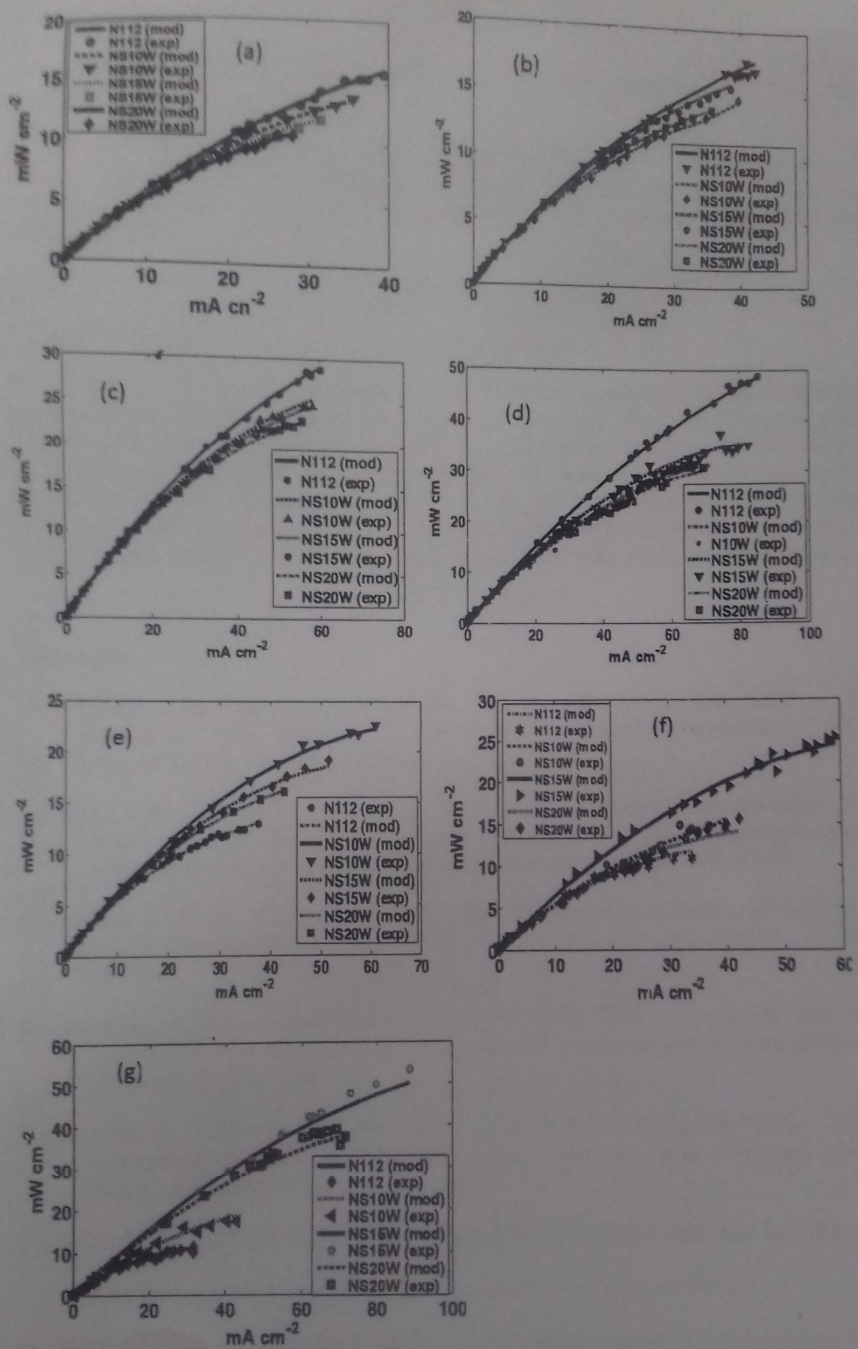


Fig. 3. Power output of single cell PEMFC using N112, NS10W, NS15W and NS20W membranes as electrolyte at temperature of: (a) 30° at 100% RH; (b) 60°C, 100%RH; 80°C, 100% RH; (d) 90°C, 100% RH; (e) 60°C, 40% RH; (f) 80°C, 40% RH and (g) 90°C, 40% RH.



Table 1. Values of conductivity ( $\sigma$ ) and maximal power ( $P_{max}$ ) for N112, NS10W, NS15W and NS20W membranes, with membrane thickness 70  $\mu\text{m}$  and surface area 50  $\text{cm}^2$ .

Membrane	30°C, 100% RH		60°C, 100% RH	
	$\sigma$ ( $\text{S cm}^{-1}$ ) $10^3$	P (watt)	$\sigma$ ( $\text{S cm}^{-1}$ ) $10^3$	$P_{max}$ (watt)
N112	2.69	0.79	2.79	0.83
NS10W	2.40	0.68	2.49	0.75
NS15W	2.19	0.58	2.31	0.82
NS20W	2.12	0.50	2.19	0.66
80°C, 100% RH		90°C, 100% RH		
N112	3.03	1.42	3.33	2.04
NS10W	2.64	1.20	3.04	1.53
NS15W	2.97	1.24	3.29	1.75
NS20W	2.64	1.13	3.02	1.47
60°C, 40% RH		80°C, 40% RH		
N112	1.66	0.65	1.53	0.55
NS10W	2.32	1.13	2.41	0.73
NS15W	2.22	1.02	2.37	1.26
NS20W	2.00	0.73	2.12	0.77
90°C, 40% RH				
N112	1.16	0.55		
NS10W	2.51	0.86		
NS15W	2.85	2.66		
NS20W	2.32	1.81		



The performance of N112 Nafion membrane was exhibited best performance at saturation humidity at all temperature range in this study. While composite membrane was performing better than Nafion membrane at 40% relative humidity. The best performance among all these membrane was a composite NS15W.

It was observable that the presence of inorganic compounds in the Nafion cluster may create a capillary condensation that making the composite membrane has more hygroscopic properties in compare with Nafion membrane. The conductivity of the composite membrane stable at reduced relative humidity.

#### 4. Conclusion

Nafion-PWA-SiO<sub>2</sub> composite membrane was fabricated to improve the water-retention ability of the membrane with the assistance of the hydrophilic capillary. The PWA-SiO<sub>2</sub> was characterized to be ordered meso-structure with pores size of 3.5 nm. The proton conductivity through the Nafion-PWA-SiO<sub>2</sub> composite membrane has little change under elevated temperature and low humidity. As a result, the Nafion-PWA-SiO<sub>2</sub> composite membrane (NS15W), presented a steady performance under 90°C, 40 % RH. The power of the cell assembled with Nafion-PWA-SiO<sub>2</sub> composite membrane reached a peak value of 2.66 Watt, which is much higher than pure Nafion membrane.

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