

RSCE-SOMCHE 2008
Edited by Daud et al.

473

PERFORMANCE OF NANO COMPOSITE MEMBRANES AS ELECTROLYTE FOR PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC) APPLICATION

A. Mahreni, A.B. Mohamad, A. A. H. Kadhum, W.R. W. Daud
Department of chemical and Process Engineering,
Faculty of Engineering,
Universiti Kebangsaan Malaysia (UKM)
Bangi-Selangor DE- Malaysia 43600

Keywords: Nafion-SiO₂-PWA; Performance; Proton conductivity;

ABSTRACT

Investigation of the single cell Proton Exchange Membrane Fuel Cell (SCPEMFC) using a series of Nafion-SiO₂-PWA composite membranes as electrolyte have been carried out using the Arbin Fuel Cell Test System (FCTS). PEMFC performance and proton conductivity of the composite membrane have been determined over a temperature range of 30-90°C at pressure 1-1.7 atm at 40% RH. Analysis with FCTS showed that higher current density was yielded by composite membrane (82 mAcm⁻² at 0.6 V for NS15W) than with the Nafion membrane (30 mAcm⁻² at 0.2 V) at 90 °C. Hence the composite is potentially a good candidate to substitute Nafion membrane especially for the electrolyte of PEMFC operating at higher temperature range and lower RH.

INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) are well suited for a variety of applications by virtue of their efficiency, environment friendly nature and high power density. For automotive or stationary power application, several advantages could result operating a PEMFC at elevated temperature (above 100°C), such as easier and more efficiency water management, higher reaction rate, improved CO tolerance by anode electro catalyst, faster heat rejection and better system integration [Ramani, V. et al. 2006]. However, operating a fuel cell above the boiling point of water necessitates neither pressurized operation at high relative humidity or lower relative humidity operation at atmospheric pressure

The synthesis and physical-chemical characterizations of Nafion-SiO₂-PWA composite membrane have been given elsewhere (Mahreni, A et al. 2008). The aim of this experiment is to investigate the prepared Nafion-SiO₂- SCPEMFC)

operating at low RH. Membrane performance was analyzed using a single cell fuel cell test system (FCTS). The polarization data were recorded between 60-90°C at 40 % RH for H₂/air operation at pressure of 1-1.7 atm.

MATERIALS AND METHOD

Materials

The materials that have been used is a series of prepared Nafion-SiO₂-PWA composite membrane and signified as NS0W, NS15W and NS20W whose specifications in ratio of Nafion/TEOS/PWA are 100:10:1.1538; 100:15:1.7303 and 100:20:2.3072 (wt./wt./wt.), respectively.

METHOD

Membrane-Electrode Assembly (MEA)

Gas diffusion electrodes were fabricated with 20 wt. % Pt on carbon and 0.4 mg Ptcm⁻². The membrane was sandwiched between the two electrodes and then hot pressed at 130°C and 70 atm for 90 s to obtain (MEA).

Internal resistance and conductivity determinations of composite membrane and cell performance testing

The cell polarization test and determination of the internal resistance of the membrane were performed using the Fuel cell test (FCT) station (FCT-2000 Electro Chem, USA). The gas flow of H₂/O₂ was fixed at the stoichiometric (H₂ + ½ O₂ ↔ H₂O) 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 H₂ and O₂ gas humidifiers. During the Voltage and current 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 mathematical model for polarization curve was used to correlate V-I at 40 % RH using least square method. In the (V-I) model, all resistance parameters were used based on a single fuel cell test system, which include the flooding parameter as given in Eq 1 [Baschuk J.J. and Li, X. 2000].

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

where E, E_o, b, R, γ and ω 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 has been used to calculate the membrane conductivity [Sacca, A.C. et al. 2005].

$$\sigma = \left(\frac{1}{R}\right) \left(\frac{l}{S}\right) \quad (2)$$

where σ is the conductivity of the composite membrane (Scm^{-1}), R is the resistance (ohm), l is thickness of the membrane (cm) and S is contact surface area of the electrode (cm^2) [Sancho, T. et al. 2007].

RESULTS AND DISCUSSION

Single cell performance

The performances of the single cell MEA using the Nafion membrane (N112), all the prepared membranes NS10W, NS15, NS15W and NS20W, were obtained for the cell voltage versus current density measurement. The results of the test at temperature of 60-90°C and 40% RH are presented in Fig 1. All the experimental data are presented together with mathematical correlation based on Eq 1 above with volumetric velocity of air at 4.15 L/min, volumetric velocity of H_2 at 1.15 L/min and total pressure of 1-1.7 atm. Interestingly, the model shows good fitting correlation with the experimental data for all the membranes under study. The optimized parameters used in fitting the model (Eq 1) with the experiments for all membranes are presented in Table 1-3.

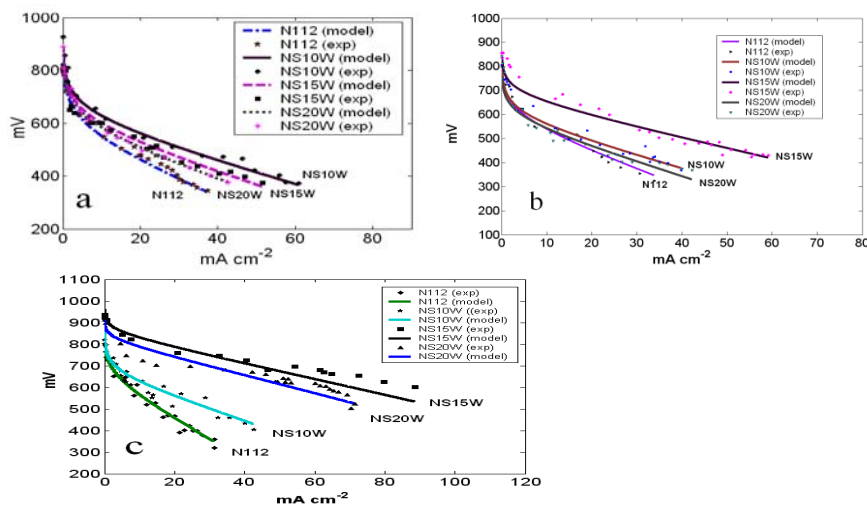


Figure 1.

Polarization Curves of N112, NS10W, NS15W and NS20W Membranes at Cell Temperature (a) 60°C, (b) 80°C and (c) 90°C at 40% RH.

Table 1.
Optimization Parameters of Polarization V-I of PEMFC Using N112, NS10W,
NS15W and NS20W Membranes at Temperature 60°C and 40% RH.

Membrane type	E_o (mV)	b (mV)	R (Ω cm ²)	γ (mV) ($\varpi=0.01$)	i_{max} mA cm ⁻²	P_{max} (wat)	Conductivity (S cm ⁻¹) 10^3
N112	800.4	55.03	4.21	70.99	37.5	0.65	1.66
NS10W	805.7	48.40	3.01	40.98	60.9	1.13	2.32
NS15W	806.0	49.74	3.15	45.10	51.6	1.02	2.22
NS20W	802.6	51.34	3.35	48.90	42.7	0.73	2.09

Table 2.
Optimization Parameter of Polarization V-I of PEMFC using N112, NS10W,
NS15W and NS20W) Membranes at Temperature 80°C and 40% RH.

Membrane type	E_o (mV)	b (mV)	R (Ω cm ²)	γ (mV) ($\varpi=0.01$)	i_{max} (mA cm ⁻²)	P_{max} (wat)	Conductivity (S cm ⁻¹) 10^3
N112	800.4	44.61	4.56	100.51	33.90	0.55	1.53
NS10W	803.8	40.99	2.90	107.10	39.80	0.73	2.41
NS15W	815.8	30.99	2.85	55.10	59.15	1.266	2.37
NS20W	800.9	37.43	3.31	125.00	42.24	0.77	2.12

Table 3.
Optimization Parameters of Polarization V-I of PEMFC Using N112, NS10W,
NS15W and NS20W Membranes at Temperature 90°C and 40% RH.

Membrane type	E_o (mV)	b (mV)	R (Ω cm ²)	γ (mV) ($\varpi=0.01$)	i_{max} (mA cm ²)	P_{max} (wat)	Conductivity (S cm ⁻¹) 10^3
N112	895.4	43.40	6.01	150.59	31.4	0.50	1.16
NS10W	890.9	35.58	2.78	135.56	42.7	0.86	2.51
NS15W	935.8	18.40	2.45	20.00	88.6	2.66	2.85
NS20W	912.4	16.55	3.01	49.65	69.5	1.81	2.32

In comparing the current density and resistivity of the cell, the order of performance of the composite membranes at temperature range of 80-90°C, 40% RH starting from the best to worst is as follows: NS15W, NS20W, NS10W and N112. While at temperature of 60°C and 40% RH. the order of performance of the composite membranes from the best to worst follows: NS10W, NS15W, NS20W and N112. This trend can clearly be rationalized by considering the physico-chemical and electrochemical properties of the membrane as indicated in the SEM, TEM, WUR and UV-VIS analyses [Mahreni, A. et al. 2008].

The low water uptake rate observed with NS20W when compared to that of NS15W is perhaps due to the fact that the particle sizes of SiO₂ and PWA are bigger than that of the ionic cluster, such that the inorganic particles were adsorbed on the outer surface of the cluster [Hiroki Takata, Masabumi Nishikawa, 2005].

Fig 1.c shows the performance of single cell using N112, NS10W, NS15, and NS20W as the solid electrolyte operated at 90°C and 40% RH. The best performance under these conditions was obtained for NS15W, which produced current density of 82 mA cm⁻² at 0.6 V as compared to the Nafion membrane of 30 mA cm⁻² at 0.2 V. All other composite membranes (NS20W, NS10W and NS15) showed better performances than the Nafion membrane under these conditions possibly due to the incorporation of the inorganic hygroscopic materials to the Nafion polymer matrix.

Incorporated inorganic compound like PWA that have hygroscopic and high proton conductivity properties in the Nafion cluster strongly increase the amount of structural water in the film. It maybe seen that the role of inorganic compound in the Nafion cluster is to create capillary condensation phenomena in the polymer matrix. Capillary condensation could condense water molecules in the pore network at pressure less then the saturated vapor pressure [Celistini. F. 1997]. Hence the membrane is not dry at low relative humidity and conductivity is not reduced dramatically under similar low relative humidity condition as shown in see Tables (1-3).

CONCLUSION

Single cell Fuel cell system performance was shown to be improved for all of the SiO₂ and PWA loaded composite membranes as compared to the pure Nafion membrane. This enhanced performance can be attributed to the marked increased in conductivity found in these nanocomposite membranes. The nanocomposite membrane NS15W (TEOS/Nafion is 15/100) showed the best fuel cell performance at the cell operational temperature of 90 °C and 40% relative humidity, compare to the rest of the prepared composite membranes and Nafion membrane.

Acknowledgement

The financial support from the Malaysian Ministry of Science, Technology and Environment, through IRPA Project 02-02-02-0003PR0023/11-08 is much appreciated.

REFERENCE

- Baschuk J.J., and Li, X. 2000. Modeling of polymer electrolyte membrane fuel cells with variable degree of water flooding, *J. Power Sources*. 86: 181-196.
- Celistini, F. 1997. Capillary condensation within nanopores of various geometries. *Physics Letters. A*. 228: 84-90.
- Hiroki Takata, Masabumi Nishikawa, 2005. Yusaku Arimura, Takayuki Egawa, Sathoshi Fukada, Masaru Yoshitake. Study on water uptake of proton exchange membrane by using tritiated water sorption method. *Int. J. Hydrogen Energy*. 30: 1017-1025.
- Mahreni, A., A.B. Mohamad, A. A. H. Kadhum, W.R. W. Daud and Iyuke, S.E. 2008. Nafion/silicon oxide/phosphotungstic acid nanocomposite membrane with enhanced proton conductivity. Submission paper in *J. Membrane Science*.
- Ramani, V., H.R. Kunz and J.M. Fenton, 2006. Metal dioxide supported heteropolyacid/Nafion® composite membranes for elevated temperature/low relative humidity PEMFC operation Membrane. *J. Membrane Science*. 266: 506-512.
- Sacca, A.C., Pedicini, R., Portale, G., Ilario, L.D., Longo, A., Mortorana A., and Passalacqua, E. 2005. Structural and electrochemical investigation on re-cast Nafion membranes for polymer electrolyte fuel cells (PEFCs) application I. *J. Membrane Science*. 278:105-113.
- Sancho, T., Soler, J. and Pina, M.P. 2007. Conductivity in zeolite-polymer composite membranes for PEMFCs, *J. of Power Sources*. 169: 92-97.
- Shao, Z.G., Joghee, P., Hsing, I.M. 2003. Preparation and characterization of Hybrid Nafion-silica membrane doped with phosphotungstic acid for high temperature operation of proton exchange membrane fuel cells, *J. Membrane Science*. 229: 43-51.
- Zhai, Y., Zhang, H., Hu J. and Yi, B. 2006. Preparation and characterization of sulfated zirconia (SO₄⁻²/ZrO₂/Nafion composite membrane for PEMFC operation at high temperature /low humidity. *J. Membrane Science*. 280: 148-155.