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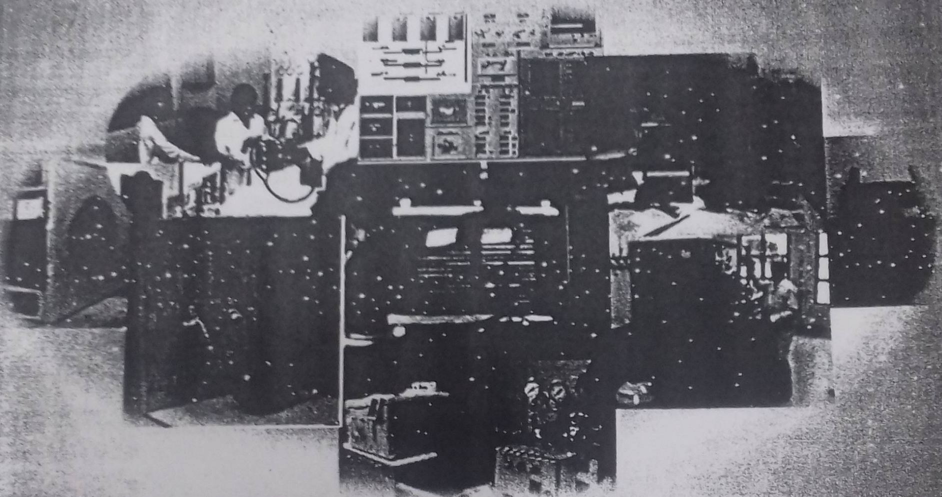

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ELECTROCHEMICAL PROPERTIES OF NANOCOMPOSITE MEMBRANE FOR PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC) APPLICATION

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ABSTRAK

Membran nanokomposit Nafion-silicon oksid (SiO_2)-asid fosfotungstik (PWA) disiapkan menggunakan kaedah sol-gel fase larutan. Membran komposit yang dihasilkan digunakan sebagai elektrolit didalam PEMFC dan sifat-sifat elektrokimia membran dianalisis menggunakan (*Fuel cell test system, FGTS*) pada julat suhu (60-90) °C, kelembapan relatif 40 % dan pada tekanan 1-1,7 atm. Sifat-sifat elektrokimia membran komposit meliputi voltan litar terbuka (OCV), kecerunan tafel (b), ketumpatan arus maksimum (i_{max}), ketumpatan tenaga (P) dan konduktiviti proton telah dikira secara kuantitatif. Hasil analisis menunjukkan konduktiviti proton (σ), ketumpatan tenaga (P) dan ketumpatan arus maksimum (i_{max}) membran komposit lebih tinggi dibandingkan dengan membran Nafion tulen. Sementara kecerunan tafel (b) lebih rendah dibandingkan dengan membran Nafion tulen. Didasarkan kepada hasil analisis tersebut dapat disimpulkan bahawa membran komposit Nafion-SiO_2-PWA boleh dipertimbangkan sebagai elektrolit PEMFC untuk menggantikan membran Nafion tulen pada kondisi sel sampai dengan suhu 90°C dan kelembapan relatif 40 % dengan menghasilkan tenaga yang lebih tinggi dibandingkan dengan membran Nafion tulen.

ABSTRACT

Nanocomposite Nafion-silicon oxide (SiO_2)-phosphotungstic acid (PWA) has been synthesized using sol-gel method. The electrochemical properties of the composite membrane was investigated in the single cell of PEMFC using Fuel Cell Test System (FCTS) at temperature in the range of (60-90) °C and 40 % Relative Humidity (RH) and pressure 1-1.7 atm. Electrochemical properties of the composite membrane as well as (Open Circuit Voltage, OCV), (Tafel slope, b), (Maximum Current Density, i_{max}), (Power Density, P_{max}) and Proton Conductivity have been measured quantitatively. The results show the proton conductivity (σ), P_{max} and I_{imax} of the composite membrane are higher than Nafion 112 membrane under test condition. A while Tafel slope through the composite are lower than Nafion 112. Based on those results, the synthesized composite membrane is considerably could replace Nafion 112 membrane, to use as electrolyte for PEMFC at moderate temperature and low relative humidity condition with the power higher compare with Nafion 112 membrane.

Keyword: PEMFC, proton conductivity, composite membrane, performance.

0.5/0.38 while the hydrogen and oxygen pressures were fixed at 1 atm. The operating temperature of the cell was (60-90^{0}C at 40% RH). The relative humidity (RH) was controlled by using the water temperature of the H_2 and 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. The mathematical model for polarization curve was used to correlate voltage and current (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 system, which include the flooding parameter as in Eq 1 (Baschuk et al. 2000).

$$E = E_o - b\,log(i) - R(i) - \gamma\,exp\,(\omega i)$$
(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 was be used to calculate the membrane conductivity as;

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

where σ is the conductivity of the composite membrane (Scm^{-1}), R the resistance (ohm), l is thickness of the membrane (cm) and S is contact surface area of the electrode (cm^2) (Sacca et al. 2005; Sancho et al. 2007).

RESULT AND DISCUSSION

ELECTROCHEMICAL TESTING

The result of physic-chemical characterization using SEM, TEM and WUR have been presented in previous paper (Mahreni et al. 2008). The result of TEM images of NS10W, NS15W and NS20W composite membranes show that the average particles diameter for inorganic compound (Si and PWA) in the composite are 6.9, 7.86 and 12.64 *nm* for NS10W, NS15W and NS20W respectively and the solid SiO_2 and PWA are uniformly distributed within the membrane and do not form any agglomerate structures. The water uptake characteristic of the Nafion-SiO_2-PWA composite membrane is found to be improved from that of the pure Nafion membrane. The water uptake of the Nafion recast membrane is also increased when the HPA is increased. These results can be supported from the fact that the hydrophilic characters of the SiO_2 and PWA play a dominant role in the increase water uptake rate of the composite membrane. The percentages of water uptake rate for Nafion 112, NS10W, NS15, NS15W and NS20W membranes are 26.52, 30.25, 30.01, 33.43 and 32.72 and 31.96 (wt.water/wt. membrane), respectively.

Performance of the single cell MEA using all the membranes (N112, NS10W, NS15, NS15W and NS20W), was obtained for the cell voltage versus current density measurement. The results of the test at temperature in the range of (60-90) ^{0}C and 40% RH are presented in Figure 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 1.3-1.7 atm. Interestingly, the model shows good fitting correlation with the experimental data for all the membranes under study as shows in Figure 1 (a-c). The optimized parameters used in fitting the model (Eq. 1) with the experiments for all membranes are presented in Table 1-3. The conductivity and power of membrane strongly depend by temperature. Conductivity and power increase with temperature as shows in Table 1-3 and Figure. 2 (a-b) below.

Table 1 Optimization parameter of membrane performance and hydrogen crossover at temperature 90°C and at 40% RH

Membrane	E_o *(mV)*	*b* *(mV)*	*R* *(Ω cm²)*	*γ (mV)* *(ϖ=0.01)*	i_{max} *mA cm-2*	P_{max} *(wat)*	*σ* *S cm⁻¹* *10³*
N112	895.40	43.40	6.01	150.60	31.4	0.5	1.16
NS10W	890.91	35.59	2.79	135.57	42.7	0.86	2.51
NS15W	935.87	18.40	2.45	30.00	88.6	2.66	2.85
NS20W	912.49	16.55	3.01	49.66	69.5	1.81	2.32

Table 2 Optimization parameter of membrane performance and hydrogen crossover at temperature 80°C and at 40% RH

Membrane	*Eo* *(mV)*	*b* *(mV)*	*R* *(Ω cm²)*	*γ (mV)* *(ϖ=0.01)*	i_{maks}) *(mA cm⁻²)*	P_{maks} *(wat)*	*σ* *(S cm⁻¹)* *10³*
N112	800.42	44.61	4.56	100.51	33.90	0.55	1.53
NS10W	803.85	40.99	2.90	107.10	39.80	0.73	2.41
NS15W	815.86	30.99	2.85	55.10	59.15	1.266	2.37
NS20W	800.97	37.43	3.31	125.00	42.24	0.77	2.12

Table 3 Optimization parameter of membrane performance and hydrogen crossover at temperature 60°C and at 40% RH

Membrane	*Eo* *(mV)*	*b* *(mV)*	*R* *(Ω cm²)*	*γ* *(ϖ=0.01)*	i_{maks} *(mA cm⁻²)*	P_{maks} *(wat)*	*σ* *S cm⁻¹* *10³*
N112	800.42	55.03	4.21	70.99	37.5 (0.34)	0.65	1.66
NS10W	805.72	48.40	3.01	40.98	60.9 (0.37)	1.13	2.32
NS!5W	806.05	49.74	3.15	45.10	51.6 (0.39)	1.02	2.22
NS20W	802.61	51.34	3.35	48.90	42.7 (0.34)	0.73	2.09

In comparing the current density, resistivity, Tafel slope, proton conductivity and P_{max} of the cell, the order of performance of the composite membranes at 90 °C and 40% RH, starting from the best to worst is as follows: NS15W, NS20W, NS10W, NS15, 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 analysis (Mahreni 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 SiO_2 and PWA are bigger than that of the ionic cluster, such that the inorganic particles were adsorbed on the outer surface of the cluster.

Figure 1 shows the performance of single cell using N112, NS10W,NS15, NS15W 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 with 30 mA cm^{-2} at 0.2 V. As show by Figure 1 (a-c) and Figure 2 (a-b) all of the composite membranes (NS10W, NS15W and NS20W) showed better performance than the Nafion membrane under these conditions possibly due to the incorporation of the inorganic hygroscopic materials to the Nafion polymer matrix.

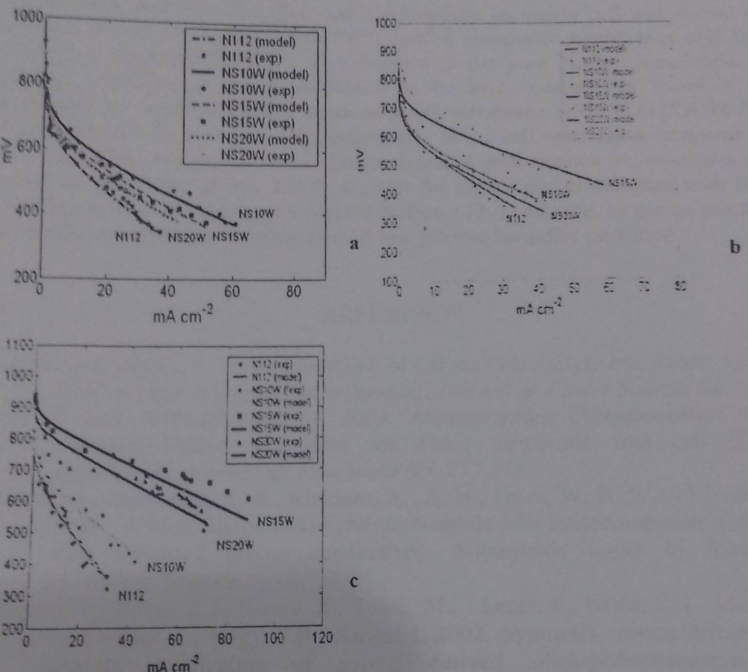

Figure 1 Polarization curves of N112, NS10W, NS15W,NS20W and NS15 membranes at (a) 60°C, (b) 80°C and (c) 90°C and at 40% RH.

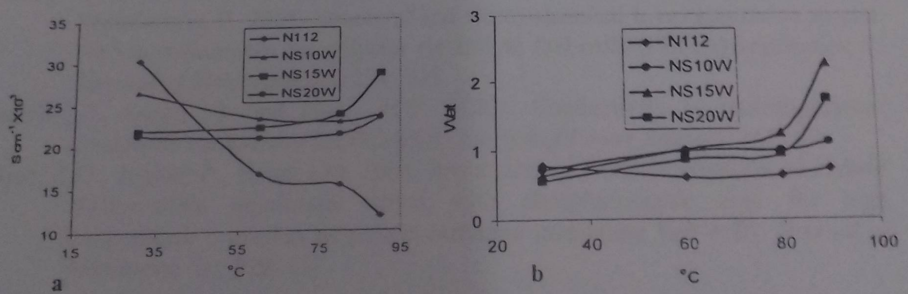

Figure 2 (a) Conductivity, (b) Power of N112, NS10W, NS15W,NS20W and NS15 membranes at temperature (30°C, 100% RH) and (60-90)°C at 40% RH

0.5/0.38 while the hydrogen and oxygen pressures were fixed at 1 atm. The operating temperature of the cell was (60-90°C at 40% RH). The relative humidity (RH) was controlled by using the water temperature of the H_2 and 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. The mathematical model for polarization curve was used to correlate voltage and current (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 system, which include the flooding parameter as in Eq 1 (Baschuk et al. 2000).

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CONCLUSION

A series of the Nafion-SiO_2-PWA composite membranes have been synthesized and used as electrolyte in the Single Cell of Proton Exchange membrane Fuel Cell (SCPEMFC) at moderate temperature and low relative humidity condition.The results show that the proton conductivity is increase with temperature between (60-90)°C at 40% RH where maximum value was achieved at the TEOS/Nafion ratio of 15/100 (w/w) at 90°C and 40% RH. Fuel cell performance on single cell was shown to be improved for all of the SiO_2 and PWA loaded composite membranes and for all temperature between (60-90)°C as compared to the pure Nafion membrane. This enhanced performance can be attributed to the high conductivity found in these nanocomposite membranes. The nanocomposite membrane NS15W (TEOS/Nafion = 15/100) showed the best fuel cell performance at the cell operational temperature of 90 ^{0}C and 40% relative humidity. Electrichemical performance improvement of the composite membrane at low RH in account for higher power compare with Nafion membrane is considerably could replace Nafion 112 membrane, to use as electrolyte for PEMFC at moderate temperature and low relative humidity condition.

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