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SYNTHESIS AND CHARACTERIZATION OF NANOCOMPOSITE ELECTROLYTE MEMBRANE USING SOL-GEL METHOD FOR PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC) APPLICATION

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Abstract

Organic-inorganic composite membrane from Nafion – silica and phosphotungstic acid (PWA) have been synthesized. A series of composite membrane with varying amounts of silicone dioxide (SiO_2) and PWA were prepared by solution phase sol-gel method. The ratio of (Nafion:SiO_2:PWA) was varied in the range of (100:2.88:1.15), (100:4.33:1.73) and (100:5.76:2.30). These composite membranes were designated as NS10W, NS15W and NS20W, respectively. Composite membrane was composed by mixing the Nafion in dimethyl formamide solution and tetraethoxyorthosilicate and PWA solution and casted the preform composite solution at 80°C for 2 hour to remove the solvent. It was continuosly heated to strenghten the structure of the composite at temperature 140°C until the membran appearance became transparent. The incorporation of PWA and SiO_2 was confirmed by FTIR analysis. TEM and SEM analysis showed the homogeneous structures of composite membrane with the inorganic particle size in the composite of each membrane to be 6.9 nm, 7.8 nm and 12 nm for NS10W, NS15W and NS20W, respectively. When appropriately embeded in the Nafion cluster, the hydrated PWA and SiO_2 are expected to endow the composite membrane with their high proton conductivity, while retaining the desirable mechanical properties of the polymer film. These composite membrane were evaluated for thermal stability, water uptake rate and proton conductivity. Water uptake rate and the conductivity of the composite membranes increased with the increase in SiO_2 and PWA weight content after which it is reduced when the ratio of Nafion:SiO_2:PWA became 100:4.33:1.73. However, the conductivity of all the composite membranes were higher compare to the Nafion membrane at cell operation condition of 80-90 °C and 40% humidity. This study shows that Nafion-SiO_2-PWA composite membrane can be viable substitute for Nafion for PEMFC which showed good conductivity comparable to Nafion 112 at temperature nearing 100°C, keeping in mind that Nafion-SiO_2-PWA composite membranes have good thermal stability.

1.INTRODUCTION

Nafion membrane and series such as aciplek and Dow membranes are still used as electrolyte of PEMFC due to their high conductivity in the saturated condition, stable to chemical attack and high resistance to the mechanical force [1,2,3,4]. The weakness of Nafion is the conductivity will be reduced drastically in the low relative humidity due to membrane shrinkage. During cell operation especially at high temperature and current density, water is produced excessively at cathode surface and its become membrane swelling. Shrinkage and swelling may cause damage in surface linking structure between electrode-membrane cause performance reduction [3,4]. To keep membrane in the saturated condition, external humidifier is needed to supply water to the hydrogen and air stream before enter to the cell system. During cell operation, electrical resistance will be change to heat. Therefore cell temperature will be increase and its effect to the dehydration of the membrane. Cooling system usually use to keep cell temperature below 80^{o}C. External humidifier and cooling system make the cell system not simple. This problem is one of the obstacle of PEMFC commercialization.

On account of this reason, modification of the Nafion membrane is crucial in order to enhance membrane stability at high temperature and low relative humidity so that could to eliminate the external humidifier and cooling system. In other side the cell operation at high temperature is needed to easier and more efficiency water management, higher reaction rate, improve CO tolerance by anode electro catalyst, faster heat rejection and better system integration [4,5,6]. Therefore, a need exists to develop proton exchange membrane (PEMs) that are functional at low operating RHs.

For this purpose, approach have been develop with modifying PFSA membrane to improve their water retention properties at high temperature [4,7] In this study, phosphotungstic acid (PWA) is selected as inorganic filler to enhance conductivity of the Nafion membrane at high temperature and low relative humidity, PWA is solid acid with high proton conductivity at room temperature (0.2 S/cm) and high thermal resistance [8]. The problem is encountered with the particle size and high solubility of PWA in the polar solvent like water and alcohol cause PWA leach out from the membrane during this membrane applied as electrolyte in the cell [6]. To solve this problem, silica porous particle is used as adsorbent to immobilized PWA and produce Nafion-SiO_2-PWA composite membrane using sol-gel method. Sol-gel methods has been used by many researches previously in the field of new material and catalyst synthesis to improve from micro to nanostructure [5,8,9,10,11,12].

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. So far in this case, 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 saturated favor pressure. So the membrane is not dry at low relative humidity [13,14]

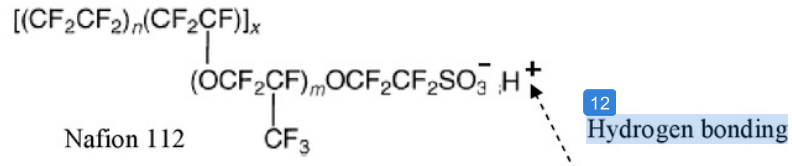
The key parameters that affect the conductivity of the Nafion-SiO_2-PWA composite membrane are the particle size of PWA and stability of this particle in the Nafion polymer matrix. The particle size of the additive must be the same or less than the ionic cluster

size in the Nafion polymer.. This particles function as proton hopping bridge at the critical condition (low level hydration) of the membrane [6].

The main objective of this study to enhance conductivity of Nafion membrane at moderate temperature (80-90)^{o}C and low relative humidity by incorporation of hygroscopic and high conductivity compound (PWA) in to Nafion cluster network using sol-gel method The solution phase sol-gel method is the most common method used in the synthesis of nanocomposite material with a given structure and property [3,4,9,15].

In this study, the composite membranes of Nafion-SiO_2-PWA is fabricated by mixing Nafion solution in DMF solvent and TEOS-PWA solution. The mixture is then poured and cast to remove solvent. To strengthen the composite network, the membrane is then heated under higher temperature until forming homogeneity and transparent thin layer of membrane. The transparency appearance can be used as indicator that the particles size in the membrane is already in the nanometer dimension [16,17,18].

The mechanism of sol-gel reaction between Nafion-SiOH and PWA is shown as equation (1) and (2) as follows [19,20].



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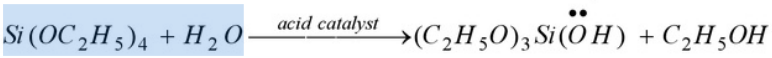
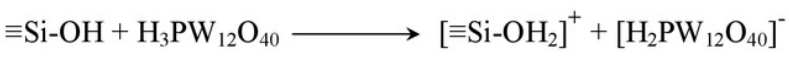


TEOS Water



2

Electrostatic force interaction
between silanol and PWA ions

Equation (1) and (2) suggest that nanostructure of Nafion-SiO_2-PWA has strong interaction of hydrogen bonding between SiOH and sulfonic acid group from Nafion polymer and electrostatic force interaction between SiOH and $[H_2PW_{12}O_{40}]^{-1}$ ions. The strong interaction among these component prevent formation of particles aggregate because the bonding among the component takes place at nanoscale or molecular size. Nanostructure of inorganic particles in the cluster is very important in this case, cause increasing role of PWA and SiO_2 as bridge material to fasicilitated proton hopping at low level hydration condition.

2.EXPERIMENTAL

2.1 Membrane preparation

Appropriately 5% wt Nafion solution was evaporated at room temperature to obtain solid Nafion. Solid Nafion was dissolved in DMF solvent to obtain 5% wt Nafion solution in DMF. PWA was also dissolved in deionized water and then mixed with TEOS at weight ratio of PWA:SiO_2 = 4:10. Subsequently, it was stirred in an ultrasonic bath for 30 min,

and added to the Nafion-DMF solution and further stirred in an ultrasonic bath for 6 hours. The mixture was allowed to stand at room condition to release trapped air bubbles for another 24 hours without mixing. This solution was casted in a Petri dish and heated at 80^{0}C for 2 hours to remove the solvent. In order to enhance the mechanical properties of the composite matrix, heating was continuously applied at 140^{0}C at different periods of 2, 4, 6 and 10 hours until transparent membrane was obtained. Then, the recast composite membrane was made to detach from the Petri dish by boiling it in the de-ionized water. Finally, the membrane was cleaned by heating at 80^{0}C in the solution of 3 wt. % H_2O_2, de-ionized water, 0.5M H_2SO_4 and again in de-ionized water until the pH of the washing water becomes almost neutral. These composite membranes are designated NS10W, 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 (Table.1)

Table 1. The composition of the composite membrane in the weight ratio.

Composite Membrane	Composition (part) Nafion	TEOS	SiO_2	PWA	Total weight of Nafion-SiO_2-PWA
NS10W	100	10	2.884	1.1538	104.0378
NS15W	100	15	4.326	1.7303	106.0563
NS20W	100	20	5.768	2.3072	108.0752

Table 1. Show that the ratio of PWA/TEOS and the ratio of PWA/SiO_2 are constant and the ratio of TEOS/Nafion and the ratio of PWA/Nafion is varied. Schematic diagram synthesis of Nafion-SiO_2-PWA composite membrane using sol-gel method is depict in Fig.1

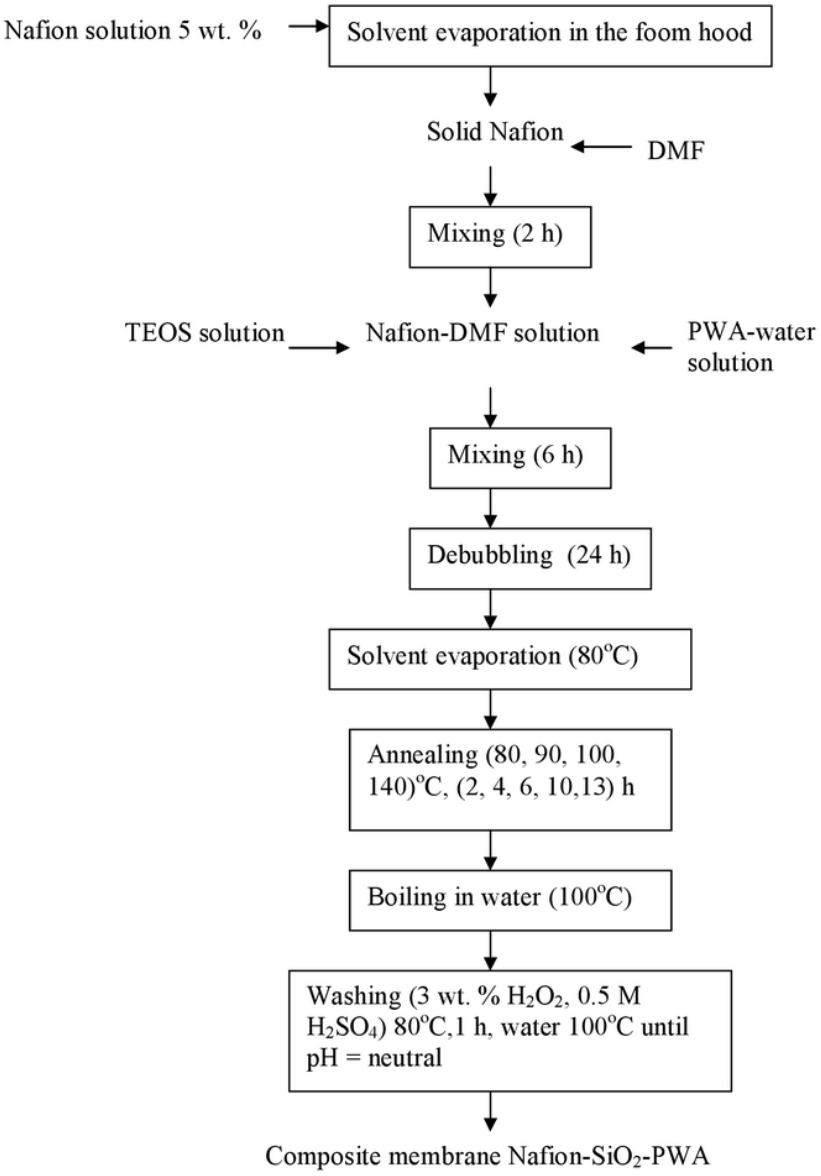


Fig.1. Schematic diagram synthesis of Nafion-SiO_2-PWA composite membrane using sol-gel method

2.2. *Membrane-electrode assembly*

Gas diffusion electrodes were fabricated with 20 wt. % Pt on carbon and 0.4 mg Pt cm^{-2}. The membrane was sandwiched between the two electrodes and then hot pressed at 130^{0}C and 70 atm for 90 s to obtain membrane electrode assembly (MEA).

2.3. *Physico-chemical characterization*

The morphology of the composite polymer membranes was investigated using the scanning electron microscope (SEM: JEOL-6300F). Before analysis, the membrane was cracked in liquid nitrogen and then sputter coated with fine gold layer after which the micrograph was taken. Transmission electron microscopy (TEM:JEM-1010 JEOL Electron Microscope). Microtom: *REICHERT ULTRACUTS* Leica was used to determine real particle size of PWA and SiO_2 in the composite membranes. Infrared (IR) attenuated total reflection (ATR) spectra of the composite membranes were measured with Fourier transform infrared (FTIR) spectroscopy (Bio-Rad FTS 6000).. TGA was carried out on (TGA, TA 951). The rate of heating was 10^{o}C/min with sample weight about 10-15 mg.

An important characteristic of the membrane is the water uptake rate (WUR), which provides information on the water retention ability of the membrane. This is calculated from the difference in weight between the wet and dry samples. The wet weight (m_{wet}) was determined after immersion of the samples in water at room temperature for 48 h. As for the dry weight (m_{dry}), the samples were heated in the oven at 120^{0}C for 2 h. The percentage of water uptake rate is thus given as; [7]

$$WUR = \left(\frac{m_{wet} - m_{dry}}{m_{dry}} \right) x\ 100\% \qquad (3)$$

Infrared (IR) attenuated total reflection (ATR) spectra of the composite membranes were measured with Fourier transform infrared (FTIR) spectroscopy (Bio-Rad FTS 6000).

2.4 Internal resistance and conductivity determination of the composite membrane and cell performance testing

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_2/O_2 was fixed at the stoichiometric (H_2 + ½ O_2 ↔ H_2O) 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^{0}C. 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 100 and 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 4 [21].

$$E = E_o - b\ log(i) - R(i) - \gamma\ exp\ (\omega i) \quad (4)$$

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 5 was be used to calculate the membrane conductivity as; [6]

$$\sigma = \left(\frac{1}{R}\right)\left(\frac{l}{S}\right) \quad (5)$$

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)

3. RESULT AND DISCUSSION

3.1 SEM and TEM

The time required to produce transparent membrane is 10 hours at annealing temperature of 140^{o}C for each of the composite membrane (NS10W, NS15W and NS20W). After post treatment of washing and drying, the membrane was analyzed using SEM and TEM. SEM photograph shows the membrane was completely transparent, homogeneous, isotropic materials. A plate membrane of 11 cm diameter and a thickness of 70 μm can

be obtained, as shown in Fig. 2. The mechanical stability was very good for Nafion-SiO_2-PWA composite materials in particular, for example, it can be rolled up by easily without breaking the membrane for all membrane produce.

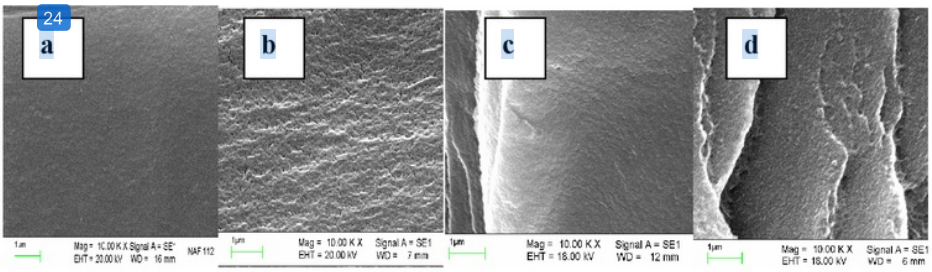


Fig. 2. SEM images of the N112 (a), NS10W (b), NS15W and (c) NS20W membrane

TEM images of NS10W, NS15W and NS20W composite membrane are shown in Fig. 3. It could be seen that the particles size of the composite membrane strongly depend to the ratio between Nafion:SiO_2:PWA. The particles size of NS10W, NS15W and NS20W composite membrane are (6.9, 7.8 and 12) *nm*. It was large then the particles size of NS10W, NS15W and NS20W composite membrane measured by UV analysis that are (4.72, 5.13, 5.32) *nm* for NS10W, NS15W and NS20W composite membrane (the formulation to determine particles size using transmitance data from UV analysis is not show in this paper) The diffrent particles size between TEM and UV analysis prove that PWA nanoparticles were covered by silica [11]. It was also showed by TEM images, that a few particles sizes were about 3-6 *nm* which should be the PWA nanoparticles. These TEM and UV data evidebt that the particles size lesser than the Nafion cluster size and these particles can be suggest embeded in the cluster.

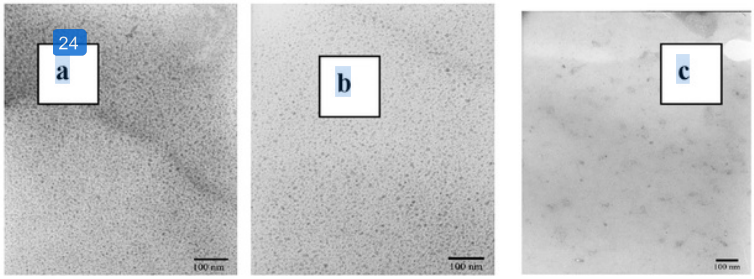
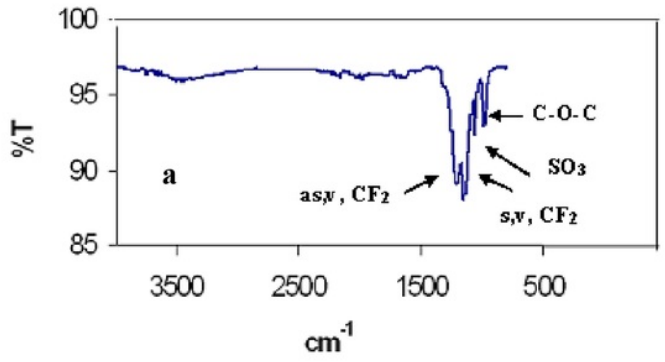


Fig. 3. TEM images of NS10W (a), NS15W (b), NS20W (c) with magnification 80.000x.

3.4 FTIR

Fig. 4 (a) shows the FT-IR spectrum of Nafion (N112) and NS20W membranes was measured in the wave number between (600-4000) cm^{-1}. The absorption peaks at 967, 1054, 1134 and 1194 were attributed to C-O-C, SO_3, $_{s,v}(CF_2)$ and $_{as,v}(CF_2)$ groups respectively Additionally, the band at 3500 cm^{-1} was assigned to OH group of water [6, 3, 7]. The $_{s,v}(CF_2)$ and $_{as,v}(CF_2)$ could be attributed to the organic back bond of Nafion polymer. The C-O-C could be attributed to the side chain of Nafion. FT-IR spectrum of Nafion-SiO_2-PWA composite membrane was show in Fig 4 (b). Fig. 4 (b) show a new peak in the wave number of 624, 765, 800, 981 and 3415 cm^{-1} attributed to Si-O-C, W-Oc-W (corner shared octahedral of Kegin unit) [12], $_{s,v}$(Si-O-Si) [10], $W=O_d$ (terminal oxygen) [6] and Si-OH [11] respectively. The new peak in the Fig. 4 (b) prove that Si and PWA compounds was incorporated in the Nafion structure. The whole peak of Nafion and NS20W composite membrane was show in table 2. FT-IR for NS10W and NS15W is not shown.



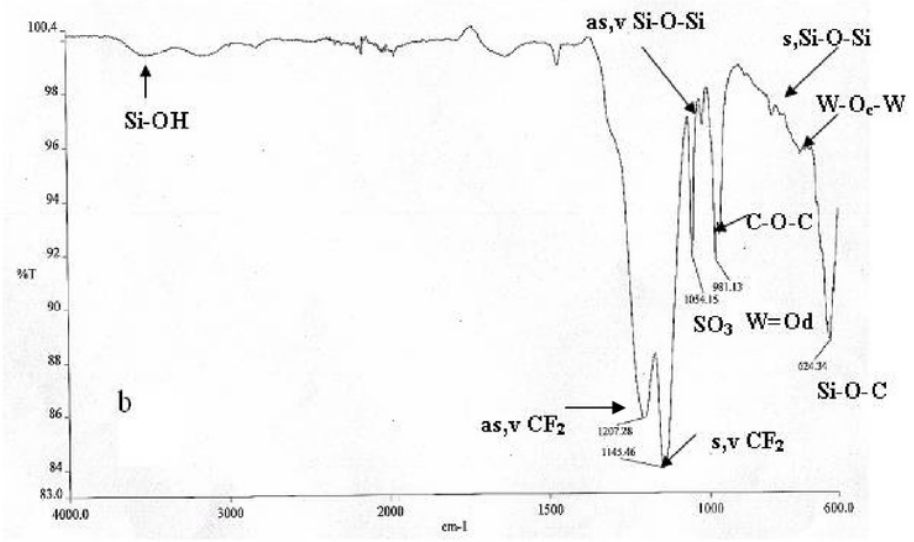


Fig.4. FTIR spectra for (a) N112 and (b) NS20W membrane, NS10W and NS15W is not shown

Table 2. Bonding structure of Nafion-SiO_2-PWA composite membrane and wave number resulted from FTIR analysis from wave number (600-4000) cm^{-1}. For FT-IR spectrum of NS10W and NS15W are not shown.

N112		NS20W	
Wave number (cm^{-1})	Bonding structure	Wave number (cm^{-1})	Bonding structure
967	C-O-C	964	C-O-C
1054	SO_3	1054	SO_3
1134	$_{s,v}(CF_2)$	1145	$_{s,v}(CF_2)$
1194	$_{as,v}(CF_2)$	1202	$_{as,v}(CF_2)$
		624	Si-O-C
		765	W-O_c-W (corner shared octahedral of Kegin unit)
		800	$_{s,v}$(Si-O-Si)
		981	W=O_d (terminal oxygen)
		3415	Si-OH

Table 2 shows the incorporation of SiO_2 and PWA into Nafion polymer matrix by a shift in spectrum peak of C-O-C bonding (side chain of Nafion). In the Nafion membrane C-O-C peak at wave number of 967 cm^{-1}, while for Nafion-SiO_2-PWA membrane the peak attributed to the C-O-C structure shift to 964 cm^{-1}. Peak shifting is also occurred for the bonding of s,v(CF_2) and as, v(CF_2) at wave number 1134 and 1194 cm^{-1} are shift to 1145 and 1202 cm^{-1} in the composite membrane respectively. The shift to higher wave number indicates weaker bonding of the backbone structure of polymer. This because by happening of interaction of side chain of polymer that is SO_3 group with SiOH via hydrogen bonding yielding weaker bonding to the backbond structure.. The spectrum of P-O bonding is not appeared in FTIR spectrum of the composite membrane that it should appear at wave number between 1079-1278 cm^{-1} [22,23]. The invisible P-O spectrum is caused by overlapping with s,v (CF_2) and as,v(CF_2) spectrum. The spectrum of W=Od appear at wave number of 981 cm^{-1} Silanol is appear at wave number 3415 cm^{-1} . It means the condensation of silanol is not complete so the spectrum attributed to the silanol group still appear.

It should be noted, FTIR spectrum of Nafion-SiO_2-PWA composite membrane is different with the spectrum of Nafion membrane. A new peak appear at certain wave number attributed with presented the structure of Si-O-Si at wave number 800 cm^{-1}. Si-O-C at 624 cm^{-1} and W-O_c-W (corner shared octahedral of Kegin unit) at 765 cm^{-1}. The new peak indicate that inorganic compound added to the Nafion polymer have been embedded in the structure of Nafion polymer [6, 22, 23].

3.4. Water Uptake Rate (WUR)

The variation of water uptake rate of the inorganically modified membranes with that of the commercial Nafion 112 have been shown in table 3. It is observed that the composite membranes have a tendency to absorb more water than the commercial membrane sample, which is consistent with the work of []. The water uptake characteristics 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 membranes is also increased when the HPA is increased. This result 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 membranes. Table 3 show for Nafion 112, NS10W, NS15W and NS20W membranes are 26.52, 30.25, 33.43 and 32.72 (wt.water/wt. membrane), respectively.

Table 3. Water uptake rate of the N112, NS10W, NS15W and NS20W membranes

Membrane	Ratio (w/w) PWA/SiO_2	Ratio (w/w) SiO_2/Nafion	Water uptake rate gr water/gr membrane
N112	0	0	26.52
NS10W	0.4	0.02884	30.25
NS15W	0.4	0.04326	33.43
NS20W	0.4	0.05768	32.72

Table 3 showed that the water uptake increased from 30.25 (NS10W) to 33.43 % (NS15W) and then dropped to 32.72 as the PWA/Nafion ratio increased from 1.73/100 to 2.3/100. This might be due to the decrease in the water affinity of composite membrane at the PWA/Nafion ratio greater then 1.73/100. At the ratio of PWA/Nafion ratio 2.3/100, the composite has large particle size such that it could not get into the ionic cluster of the Nafion membrane. In accordance with the proton hopping model, the effective additional of PWA is related to its role in increasing the conductivity of the Nafion membrane at high temperature and low relative humidity. The conductivity increase if the particles is incorporated into the cluster of Nafion membrane because in the ionic cluster the particle act as proton hopping bridge of the proton transfer [6]. For NS10W and NS15W the particle size are small enough to be occupied within the ionic cluster and its role as proton hopping bridge of the proton trnafer at dry condition at dry condition can be reached. This is appropriate with the nature of PWA and SiO_2 as hygroscopic material that can induce water crystal into the ionic cluster. For NS20W with diameter particle size larger then the cluster size, the PWA can be assumed to be adsorbed on the outside of the cluster. Such water molecules outside the cluster have physical bonding, which is easily released during heat treatment of the membrane. So the contribution of the particle to water uptake in this composite membrane is not apparent if the PWA particle on the ionic cluster cannot be used as proton hopping bridge at low level of hydration of the membrane. Under this condition, the water will be released from the membrane during heat treatment thus resulting into a dry membrane. [24, 25, 26]

3.5 TGA analysis

The thermal stability of the membrane is usually evaluated by means of TGA. As shown in Fig 5. The TGA of composite membrane indicated that there was a gradual weight loss up to about 290°C. This was due to the evaporation of a little water absorbed, volatile molecule and solvent molecule into the composite membrane during the course of preparation. Upon further heating the composite membrane exhibited a rapid weight loss from 290°C to 360°C, corresponding to the decomposition of sulfonic acid groups. It was also show that sulfonic acid groups in the pure Nafion membrane began to decompose at 280°C. The temperature has been reported by [7]. From 360-420°C the weight loss was resulted from the decomposition of polar perfluorosulfonic vinyl ether segments and after which, occur the decomposition of backbone of the Nafion polymer (CF_2-CF_2). The last remainder should be the inorganic phase-SiO_2 and PWA. For comparison, the TGA curve of Nafion 112 was also obtained under the less temperature that the start of the decomposition of sulfonic acid group at 280°C. And the decomposition of polar perfluorosulfonic vinyl ether occure at 340-395°C. While the decomposition of backbone polymer (CF_2-CF_2) occur at temperature less then temperature decomposition of the composite membrane. Due to insertion inorganic compound in the Nafion cluster increase stability of polymer matrix. At temperature 657°C the weight of Nafion membrane is zero (no residue). And at te,perature 787°C the weight of Nafion-SiO_2-PWA composite membrane is 2.61 %. The residue is assumed consist of the inorganic nonvolatile (SiO_2, P, W) compound. From this explanation the composite membrane show higher temperature decomposition compare with Nafion membrane. This reason prove that thermal stability of composite membrane a better then Nafion membrane. As has been reported by many researches before, incorporated inorganic component to the organic matrix polymer increase stability of the polymer.

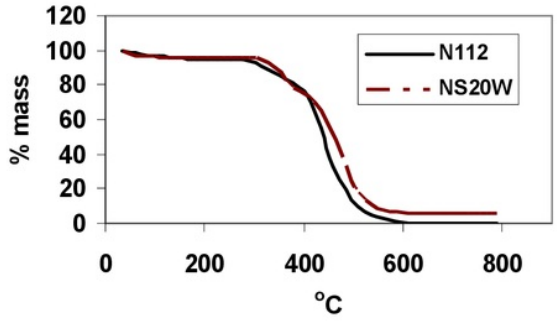


Fig. 5 TGA thermo gram of N112 and NS20W composite membrane, NS10W and NS15W is not shows.

3.6 Single cell performance

Performance of the single cell membrane electrode assemblies (MEA) using all the membranes (N112, NS10W, NS15W and NS20W), was obtained for the cell voltage versus current density measurement. The results of the test at temperature of 80°C and at temperature 90°C, 40% RH are presented in Fig 6 a-b. All the experimental data are presented together with mathematical correlation based on Eq 4 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 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 4) with the experiments for all membranes are presented in Table 4

The proton conductivity is decisive property of fuel cell membranes as the efficiency of the fuel cell depends on the proton conductivity. Generally conductivity directly depends on the water uptake rate and ion exchange capacity (IEC) of the polymer membrane. The conductivity data of Nafion-SiO_2-PWA membrane with increase in temperature were measured and are given in Table 4 and Table 5. The conductivity of the synthesized composite membranes were compared with that of the commercial Nafion 112 (N112) to ascertain its usefulness. The conductivity of the membrane increase with increase in temperature. The NS10W, NS15W and NS20W composite membranes exhibited higher proton conductivity than Nafion 112 at low relative humidity (e.g. 40% RH) in the two different temperature. At high temperature and low relative humidity, the cluster

shrinkage and increase to the proton hopping resistance and reduced proton conductivity. Mean while the conductivity of composite membrane of NS10W, NS15W and NS20W the conductivity are higher than Nafion 112. This attributed to the retention of trapped water even at high temperature and low relative humidity because capillary condensation effect by the presence of filler PWA particles in the Nafion cluster. The role of the filler when appropiately embeded in the Nafion cluster (hydrophilic Nafion polymer matrix), the hydrated PWA and SiO_2 are expected to endow the composite membrane with their high proton conductivity, while retaining the desirable mechanical properties of the polymer film.

Table 4. Open circuit voltage, Tafel slope, internal resistence, flooding constant and fitting constant for N112, NS10W, NS15W and NS20W membranes, with thickness 70 μm and surface area 50 cm^2 at temperature 90°C and 40% RH.

Membran	*Eo* *(mV)*	*b* *(mV)*	*R* *(Ω cm^2)*	*γ (mV)* *(ϖ=0.01)*	i_{maks} *(mA cm^2)*	*V* *(V)*	P_{maks} *(wat)*	*Konduktiviti* *(S cm^{-1})10^3*
N112	895.40	43.40	6.01	150.59	31.4	0.32	0.50	1.16
NS10W	890.91	35.58	2.78	135.56	42.7	0.40	0.86	2.51
NS15W	935.87	18.40	2.45	20.00	88.6	0.60	2.66	2.85
NS20W	912.48	16.55	3.01	49.65	69.5	0.52	1.81	2.32

Tabel 5.

Open circuit voltage, Tafel slope, internal resistence, flooding constant and fitting constant for N112, NS10W, NS15W and NS20W membranes, with thickness 70 μm and surface area 50 cm^2 at temperature 80°C and 40% RH.

Membran	*Eo* *(mV)*	*b* *(mV)*	*R* *(Ω cm^2)*	*γ (mV)* *(ϖ=0.01)*	i_{maks}) *(mA cm^{-2})*	*V* *(V)*	P_{maks} *(wat)*	*Konduktiviti* *(S cm^{-1}) 10^3*
N112	800.42	44.61	4.56	100.51	33.90	0. 32	0.55	1.53
NS10W	803.85	40.99	2.90	107.10	39.80	0.36	0.73	2.41
NS15W	815.86	30.99	2.85	55.10	59.15	0.42	1.27	2.45
NS20W	800.97	37.43	3.31	125.00	42.24	0.36	0.77	2.12

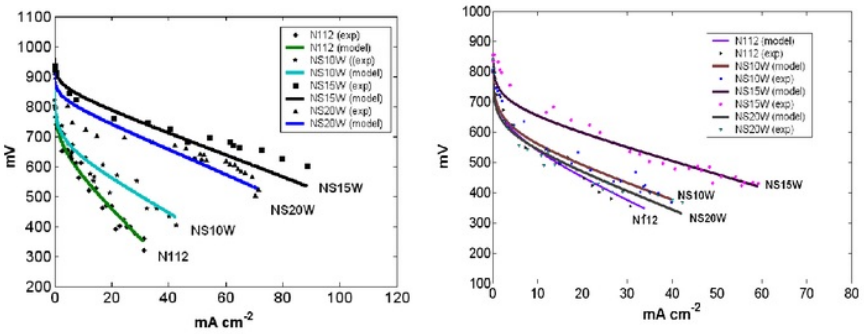


Fig.6. I-V characteristics of the PEMFC made from the Nafion-SiO_2-PWA composite membranes at (a) 90°C, 40% RH and (b) 80°C, 40% RH.

Fig. 6 shows the I-V characteristic of the PEMFC at different operational temperatures. As shows in table.4 and table 5 the open circuit potential of approximately >800 mV is a conventional potential for hydrogen/air cell and indicates there is negligible gas permeability through the membrane [27].

4. CONCLUSION

Throughout this paper, we have describe the preparation and the structural and electrochemical characterization by vibrational spectroscopy of three [Nafion-SiO_2-PWA] membranes with the ratio of Nafion:SiO_2-PWA are (100:2.88:1.152), (100:4.33:1.728) and (100:5.76:2.304). This composite membrane are designated NS10W, NS15W and NS20W respectively. By solvent solution phase sol-gel method transparent and homogeneous and smooth surface film with thickness 70 *αm* were obtained. SEM and TEM measurement disclosed that morphology of the membranes in typicall of homogeneous material with flexible and very smooth surface and the SiO_2 and PWA particles size of NS10W, NS15W and NS20W are (6.9, 7.8 and 12) nm respectively. It was large then the particles size of NS10W, NS15W and NS20W composite membrane measured by UV analysis that are (4.72, 5.13, 5.32) *nm*. The diffrent particles size between TEM and UV analysis prove that PWA nanoparticles were covered by silica [11]. It was also showed by TEM images, that a few particles sizes were about 3-6 *nm* which should be the PWA nanoparticles. The water uptake rate increase with increasing of the ammount of added SiO_2 and PWA and the water uptake rate reaches to maximum when the ratio of Nafion:SiO_2-PWA is (100:4.33:1.728) (wt:wt). The singgle cell

performance test and internal resistance measurement show that the Nafion-SiO_2-PWA composite membrane gives better performance at medium temperature (80-90)°C and 40% RH, especially when the ratio of Nafion:SiO_2-PWA is (100:4.33:1.728) (wt:wt) (NS15W). Therefore, the composite membrane is very promising membrane material for PEMFC opeartion at medium temperature and lower humidity.

REFFERENCE

1. Smita B. Brijmohan, M.T. Shaw. Proton exchange membranes based on sulfonated crosslinked polystyrene micro particles dispersed in poly (dimethyl siloxane). Journal of Polymer 47 (2006) 2856-2854
2. Homgwei Jang, Baoku Zhu, Youyi Xu. Composite membranes of sulfonated poly(phtalazinone ether ketone) doped with 12-phosphotungstic acid ($H_3PW_{12}O_{40}$) for proton exchange membranes. Journal of solid state ionics 177 (2006) 1123-1128.
3. Vito Di Noto & Michele Vittadello.. Two new siloxanic proton-conducting membranes Part I. Synthesis and structural characterization. Journal of electrochimica acta 50 (2005) 3998-2006
4. Sacca., A.C, Pedicini, R., Portale, G., Ilario L.D., Longo, A., Mortorana, A. & Passalacqua E. Structural and electrochemical investigation on re-cast Nafion membranes for polymer electrolyte fuel cells (PEFCs) application 1. Journal of Membrane science 278 (2005). 105-113.
5. Klein L.C, Y. Daiko, M. Aparicio, F. Damay. Methods for modifying proton exchange membranes using the sol-gel process. Journal of polymer 46 (2005) 4505-4509.
6. V. Ramani, H.R. Kunz and F.M. Fenton, Investigation of Nafion/HPA composite membranes for high temperature/low relative humidity PEMFC operation, Journal of Membrane Sci., 232 (2004) 31.
7. Yunfeng Zhai, Huanming Zhang, Jingwei HU, Baolian Yi. Preparation and characterization of sulfated zirconia (SO_4^{2-}/ZrO_2)/ Nafion composite membranes for PEMFC operation. Journal of membrane science 280 (2006).148-155

8. Ramani, V, H.R. Kunz, J.M. Fenton. Stabilized heteropolyacid/Nafion composite membranes for elevated temperature/low relative humidity PEFC operation. Journal of electrochimica acta 50(2005) 1181-1187.
9. A. Kukovecz, Zs Balogi, Z. Konya, M, Toba, P. Lentz, S.-I. Niwa, F. Mizukami, A. Molnar, J.B. Nagy, I. Kiricsi. Synthesis, characterization and catalytic application of sol-gel derived silica-phosphotungstic acid composites. Journal of applied catalysis A: General 228 (2002) 83-94
10. Adjemian K.T, S. Srinivasan, J. Benziger, A.B. Bocarsly. Investigation on PEMFC operation above 100°C employing perfluorosulfonic acid silicon oxide composite membranes. Journal of power sources 109 (2002) 356-364.
11. Zhijie Li, Wenzhong Shen, Limei Fang, Xiaotao Zu. Synthesis and characteristics of silica-modified ZnS nanoparticles by sol-gel hydrothermal method. Journal of alloys and compounds 463 (2008).129-133.
12. W. Jang, S. Choi, S. Lee, Y. Shul and H. Han, Characterizations and stability of polyimideephosphotungstic acid composite electrolyte membranes for fuel cell, Polymer Degradation and Stability, 92 (2007) 1289-1296.
13. P. Uchytil, R. Petrickovic, S. Thomas, A. Seidel-Morgenstern. Influence of capillary condensation effects on mass transport through porous membranes. Journal of separation purification technology 33 (2003) 273-281
14. F. Celistini. Capillary condensation within nanopores of various geometries. Journal of physics Letters. A 228 (1997). 84-.
15. Kamal M.S. Khalil, Salah A. makhlouf. High surface thermally stabilized porous iron oxide/silica nanocomposite via a formamide modified sol-gel process. Journal of applied surface science 254 (2008) 3767-3773.
16. B. Farkas, J. Budai, I. kabalci, P. Heszler, Zs Geretovszky. Optical characterization of PLD grown nitrogen-doped TiO_2 thin films. Journal of surface applied science 254 (2008) 3484-3488.
17. P.K. Khanna, N. Singh, S. Hasan and A.K. Viswanath, Synthesis of Ag/polyaniline nanocomposite via in-situ photo redox mechanism, Materials Chemistry & Physics, 92 (2005) 214.
18. H.M. Wang, P. Fang, Z. Chen and S. Wang, Synthesis and characterization of CdS/PVA nanocomposite films, J. Surface Sci., 253 (2007) 8495.
19. H.G. Haobold, T.H. Vad, H. Jungbluth and P. Hiller, Nano structure of Nafion a SAXS study, Electrochim Acta, 46 (2001) 1559.

20. M.H. Bhure, I. Kumar, A.D. Natu, R.C. Chikate and C.V. Rode, Silica with modified acid sites as a solid catalyst for selective cleavage of tert-butyldimethylsilyl ethers, Catal. Commun. (2008 impress).
21. J.J. Baschuk and X. Li, Modelling of polymer electrolyte membrane fuel cells with variable degree of water flooding, J. Power Sources, 86 (2000) 181.
22. Lin, C.W, Thanganuthu, R, Chang, P.H. 2005. PWA-doped PEG/SiO_2 proton conducting hybrid membrane fuel cell application. Journal of Membrane science 253 : 23-31.
23. J.D. Kim and I. Honma, Synthesis and proton conducting properties of Zirconia bridge hydrocarbon/phospotungstic acid hybrid materials, Electrochim Acta, 49 (2004) 3179.
24. Staiti, P, Arico, A.S, Baglio, V, Lufrano, Passalcqua F. E. &V Antonucci,. Hybrid Nafion-Silica membranes doped with heteropolyacids for application in DMFC. Journal of solid state ionic 145 (2001) 101-107.
25. Joongpyo Shim, Heung Yong Ha, Seong-Ahn Hong, In Hwan Oh. Characteristic of the Nafion ionomer-impregnated composite membrane for polymer electrolyte fuel cells. Journal of Power Sources 109 (2002) 412-417.
26. Z.G. Shao, P. Joghee, I.M. Hsing. Preparation and characterization of Hybrid Nafion-silica membrane doped with phosphotungstic acid for high temperature operation of proton exchange membrane fuel cells, J. Membrane Sci., 229 (2003) 43.
27. Itaru Honma, Hitoshi Naajima, Shigeki Nomura. High temperature proton conducting hybrid polymer electrolyte membranes. Journal of Solid State Ionic, 154-155 (2002) 707-712.

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