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## **SYNTHESIS AND CHARACTERIZATION THE COMPOSITE ORGANIC-INORGANIC MEMBRANE USING SOL-GEL PROCESS FOR PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC)**

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### **ABSTRACT**

Nafion-silicon oxide (SiO<sub>2</sub>)-phosphotungstic acid (PWA) composite membrane has been synthesized for medium temperature Proton Exchange Membrane Fuel Cell (PEMFC) application using sol-gel method. X-ray diffraction (XRD) was used to determine saturated absorption of PWA in the silica matrix. A transparent film was achieved at annealing temperature of 140°C over 10 hours duration. The film than was characterized by Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Fourier Transform Infrared Spectroscopy (FTIR). The SEM and TEM results indicated homogenous structure of the Nafion-SiO<sub>2</sub>-PWA composite membrane with SiO<sub>2</sub> and PWA particles size less than 10 nm. X-Ray Diffraction (XRD) result showed that the maximum loading of PWA in the SiO<sub>2</sub> matrix is in the ratio of PWA/SiO<sub>2</sub> equal to 0.45 (wt./wt.). The vibration absorption peak of Si-O-Si bond at 800 cm<sup>-1</sup> and W-O-W at 755 cm<sup>-1</sup> were observed thus indicated the inorganic compound was embedded in the Nafion matrix and did not leach out after washing treatment using acid and base solutions.

### **INTRODUCTION**

Perfluorosulfonic acid (PFSA) membrane (e.g. Nafion) is not suitable for low relative humidity PEMFC application because the conductivity of PFSA membrane was dramatically reduced at low relative humidity (RH). Therefore, a need exists to develop membrane for PEMs application that are functional at low operating RHs.

Nafion based organic/inorganic composite membrane with heteropolyacid (phosphotungstic acid, PWA) additive using tetraethoxyorthosilicate (TEOS) as immobilizer to the PWA have been investigated as alternative material for low humidity PEMFC operation.

The aim of this experiment is to prepare the Nafion-SiO<sub>2</sub>-PWA composite membrane using solution phase sol-gel method with incorporation of silica and PWA in the Nafion cluster to produce Nafion-SiO<sub>2</sub>-PWA nanocomposite membrane. XRD was utilized to determine the maximum PWA loading in the silica matrix. The parameters that have been studied are: (i) annealing time and (ii) ratio of SiO<sub>2</sub>/Nafion to the physic-chemical properties of the composite membrane.

## MATERIALS AND METHOD

### Materials

Nafion solution of 5 wt% (EW 1100 Dupont), TEOS (Si(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) 98%, PWA (H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>) 96%, Dimethylformamide (DMF), Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) 98%, Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>) 30% were all purchased from Aldrich. Deionized water was used as solvent in all the experiments.

### Method

#### 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<sub>2</sub> = 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°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°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°C in the solution of 3 wt. % H<sub>2</sub>O<sub>2</sub>, de-ionized water, 0.5M H<sub>2</sub>SO<sub>4</sub> 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.

## RESULTS AND DISCUSSION

### Saturated Loading of PWA Particle in the SiO<sub>2</sub> Matrix

The XRD pattern of pure silica, pure PWA and the mixture of Silica-PWA are as show in Fig 1. The amount of heteropolyacid (PWA) loaded on silica was limited

by the uptake characteristics of silica. Fig 1(a-b) show consecutively the XRD pattern of PWA crystalline and silica amorphous phase. While Fig 1(c-e) show the XRD pattern of the PWA entrapped on silica with the ratio of PWA/SiO<sub>2</sub> is 0.45, 0.6 and 0.15 (wt/wt.), respectively. The selected of PWA loaded amount correspond to uniform distribution of the PWA on the silica pore shows overlapping between the typical crystalline structure of PWA and the amorphous structure of silica at ratio of PWA/SiO<sub>2</sub> is (0.15) and (0.45) (wt/wt.).

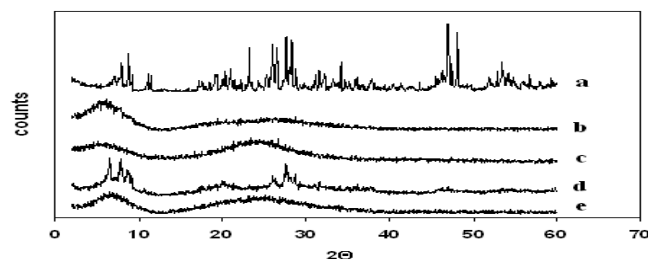


Figure 1.

XRD Pattern of (a) Pure PWA, (b) Pure SiO<sub>2</sub>, (c) Ratio of PWA/SiO<sub>2</sub> (0.45), (d) Ratio PWA/SiO<sub>2</sub> (0.6) and (e) Ratio PWA/SiO<sub>2</sub> (0.15).

Fig 1(c) and Fig 1(e). revealed an overlapping between the typical crystalline structure of PWA and the amorphous structure of silica. The results indicated that at the ratio of PWA/SiO<sub>2</sub> (0.15) until 0.45 all of the PWA particles have inserted in the silica pores and the peak assign to the PWA particle has disappeared. If the ratio of PWA/SiO<sub>2</sub> increase to 0.6, a different spectral pattern is obtained that the sharp spectral peak attributed to the presence of PWA crystalline in the SiO<sub>2</sub>-PWA mixture appear. It means that a part of PWA particle is not insert in the silica pores cause the silica pore has been full filled by PWA particles and saturated loading has been reached. Therefore it can be conclude that the saturated PWA loading on the silica pore is best at the ratio of 0.45 (wt./wt.) as show by Fig 1 (c). This ratio will be used for the designed of the composition of NS10W, NS15W and NS20W composite membrane prepared using sol-gel method.

Clarity analysis to optimize annealing time and temperature

The time required to produce transparent membrane is 10 hours at annealing temperature 140°C for all the composite membranes. After the post treatment of

washing and drying, the membrane was analyzed using UV-VIS spectrophotometer, to determine qualitatively the amount of inorganic phase distribution in the organic polymer matrix. The transparency of the composite membrane is a measure of inorganic phase distribution in the range of nanoscale dimension in the organic polymer matrix [Khana, P.K. et al. 2005]. If phase dissociation has taken place, the composite membrane formed is neither transparent nor translucent. Phase separation and homogeneity of the particle distribution also influence the mechanical strength properties of the membrane. Physical visibility of Nafion 112 (commercial) and all the composite membranes are transparent in the UV-VIS spectrum at the annealing time of 10 hours and temperature of 140°C, which indicated the absence of the phase separation of both the inorganic and organic phase (The UV-VIS) result is shown in [Mahreni, A et al. 2008].

The result also showed that there are chemical interactions taking place between the organic and inorganic compounds through the hydrogen bonding between the sulfonate group of Nafion polymer and the hydroxyl (OH) group of the silanol Si(OH) produced via the hydrolysis of TEOS molecules. On the other hand, the electrostatic interactions between the ions of  $H_3PW_{12}O_{40}$  and SiOH took place in the composite membrane material. Therefore, the composite membrane has strong bonding between organic-inorganic compounds, which could have been responsible for the transparency and homogeneous distribution of the inorganic phase in the organic matrix.

#### SEM and TEM analysis

The morphology of the composite Nafion-SiO<sub>2</sub> recasted membrane are shown in Fig 2. It can be seen that the solid SiO<sub>2</sub> and PWA are uniformly distributed within the membrane and do not form any agglomerate structures. The thickness of composite membrane is measured to be  $70 \pm 5 \mu m$ .

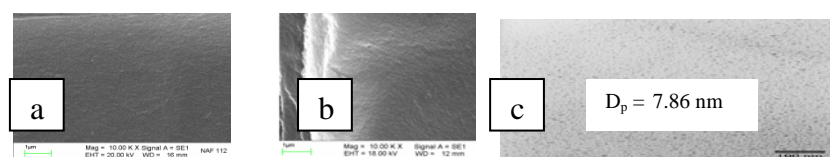


Figure 2.

- (a) SEM Cross Section Image of Nafion 112 (Commercial)  
 (b) NS15W With Magnification 10.000 X, (c) TEM Cross Section Image of NS15W Membrane With Magnification 60.000 X, (NS10W and NS20W are not shown)

#### FTIR analysis

The interactions between SO<sub>3</sub>H and SiOH and PWA were studied by FTIR which were used to monitor the formation of Nafion/SiO<sub>2</sub>/PWA nanocomposite film [Ramani, V. et al. 2005]. The FTIR spectra at 4000-400 cm<sup>-1</sup> were shown in Fig.

3. The major vibration associated with the Nafion membrane (Fig. 3a) were found in N112, NS10W, NS20W nano-composite membranes. The two C–F stretching vibrations of the PTFE backbone can be observed at  $1194\text{ cm}^{-1}$  and  $1134\text{ cm}^{-1}$ . The peaks observed at  $1054\text{ cm}^{-1}$  and  $9670\text{ cm}^{-1}$  were attributed to the stretching vibration moieties of  $\text{SO}_3^-$  and C–O–C, respectively. IR spectra for bonding structure of C–O–C of Nafion membrane at wave number ( $967\text{ cm}^{-1}$ ) shifts to lower wave number of  $967\text{ cm}^{-1}$  for NS15W composite membranes. This phenomenon can be attributed to the strong interactions of  $\text{SiO}_2$  component and sulfonate groups in side chain of the Nafion polymer [Ramani V. et al. 2004] [Shao Z.G. et al. 2004]

The observable peak at  $980\text{ cm}^{-1}$  represents the vibration moiety of the W=O functional group. Therefore, it is evident from these data that the  $\text{SiO}_2$  and PWA are indeed present in the composite membranes even after these membranes had undergone the pretreatment process of washing using 3wt %  $\text{H}_2\text{O}_2$  and 0.5 M  $\text{H}_2\text{SO}_4$  solution at the temperature of  $80^\circ\text{C}$  for 1 hour. It is apparent that the  $\text{SiO}_2$  and PWA are compatible with Nafion membrane and the PWA is able to be immobilized into the  $\text{SiO}_2$  media.

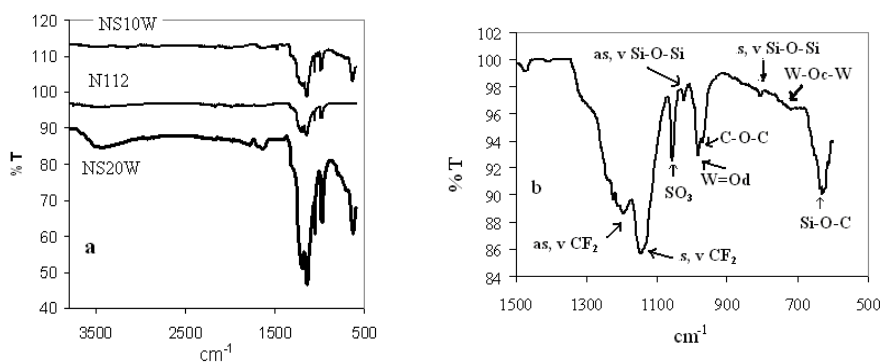


Figure 3  
FTIR Spectra of (a) N112 Commercial Membrane, NS10W and NS20 Composite Membrane for NS15W is not shown (b) NS20W Composite Membrane

## CONCLUSION

Nafion-SiO<sub>2</sub>-PWA composite membrane has been successfully made using sol-gel method at solvent evaporation temperature of 80°C and annealing temperature of 140°C for 10 hours at fixed ratio of PWA/SiO<sub>2</sub> = 0.4 (wt./wt.). All of the composite membrane synthesized at above conditions showed transparent visibility and suggested that the homogeneous distributions of the inorganic particles in the nano dimension of the organic matrix. The SEM and TEM measurements showed homogeneous structure of the composite and the particle size of less than 10 nm is obtained. The observable peak at 980 cm<sup>-1</sup> represents the vibration moiety of the W=O functional group. Therefore, it is evident that the SiO<sub>2</sub> and PWA are indeed present in the composite membranes even after these membranes had undergone the pretreatment process. It is apparent that the SiO<sub>2</sub> and PWA are compatible with Nafion membrane and the PWA is able to be immobilized into the SiO<sub>2</sub> media.

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