

Polyvinyl Alcohol Incorporated with Mesoporous Phosphotungstic Acid for Direct Methanol Fuel Cell Application

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ABSTRACT

The development of potential and novel proton exchange membrane (PEMs) is imperative for further commercialization of Direct Methanol Fuel Cell (DMFC). In this study, flat sheet hybrid membrane as an alternative PEM made up of polyvinyl alcohol (PVA) and mesoporous phosphotungstic acid-Silica (mPTA-Si) at various loadings of 0.5, 1.0, 1.5 and 2.0 wt% was prepared to examine the desirable properties for DMFC application. The characteristic test such as water uptake and proton conductivity were conducted. As the mPTA-Si loading increases, the proton conductivity of PVA/mPTA-Si membrane increased up to $1.81 \times 10^{-3} \text{ Scm}^{-1}$ with 68% of water uptakes. The obtained results could reflect the enhance performance of mPTA-Si membrane and high potential alternative membrane for DMFC. Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) results proved a good dispersion and the existence of Keggin anion from mPTA-Si particles formed a strong interfacial bonding between fillers and PVA matrix. Owing to these superior characteristics of the mPTA-Si, PVA/ mPTA-Si membrane is considerably promising materials as PEM for DMFC application.

Keywords: Direct methanol fuel cell (DMFC), polymer electrolyte membrane (PEM), polyvinyl alcohol (PVA), mesoporous phosphotungstic acid – Silica (mPTA-Si), composite PEM

1.0 INTRODUCTION

The direct methanol fuel cell (DMFC) is a promising candidate system for portable electric devices as the uses of methanol in the system as an energy carrier offers many advantages such as significant electroactivity and being easily oxidized directly to water and carbon dioxide in catalyst alloys without the need for a reformer. Besides, as a viable energy sources, it also easy in fuel delivery, low-cost methanol, low design complexity and high-power density. Nevertheless, only acidic electrolytes can be used in DMFC because the efficiency of the fuel cell and its' power density strongly

depend on the electrolyte conductance which also could facilitate in carbon dioxide rejection

A well-known ionomer membrane in the market, Nafion often used in electrochemical technology as a proton conductive electrolyte. Nafion is perfluorinated ion-exchange membrane that has an architecture of copolymer molecular consisting of perfluoroether side chains terminated with sulfonic acid groups distributed randomly along the backbone of semicrystalline polymer (perfluoroethylene) [1-2]. Nafion has been widely used in DMFC as electrolyte membrane as it has high conductivity of protons and chemical stability.

Though Nafion has been industrially used for fuel cell applications for decades, its high manufacturing costs, water control for operation at high temperatures, poor conductivity at low humidity and high temperatures, low tolerance for fuel impurities such as carbon monoxide, CO and sulphur, S remain as major drawbacks [3]. Moreover, it also suffers of high methanol permeability which leads to an oxygen cathode crossover in DMFC [4]. Thus, it is highly desirable to develop new PEM with greater stability and conductivity for application under anhydrous conditions.

Many efforts have been made to develop alternative proton exchange membranes (PEMs) for DMFCs with improved functionality and low cost. An effective approach to decrease the extent of methanol crossover is to replace the commercial membrane, Nafion with low cost polymeric materials such as PEEK [5], poly(vinyl alcohol) (PVA) [6], polybenzimidazole [7] and chitosan [8]. PVA is found as one of the best methanol-blocking polymers because it can selectively transport water over methanol, however, PVA membranes suffer from poor proton. Therefore, a proper functionalization on PVA membrane is necessary to improve its' proton conductivity, and one of the approach is by incorporating of inorganic materials such as heteropoly acids (HPAs), such as phosphotungstic acid (PTA) [8]. The composite materials able to extend or provide novel capabilities that are difficult to obtain by using each component individually.

PTA is the most widely studied heteropolyanion because of its high acid resistance with its chemical formula $H_3PW_{12}O_{40}$ [9]. PTA soluble in polar solvents, and appear as solid crystalline materials that are highly conductive and thermally stable. Besides, they exhibit well-defined

molecular structures, surface charge densities and chemical and electrochemical properties [10]. PTA is primarily used as a homogeneous catalyst for acid and oxidation, due to its high acidity and good oxidizing ability. Because the high oxidation level of 6 tungsten in PTA, reducing W^{6+} to W^{3+} in PTA may produce high energy and power densities for energy cells [11]. In addition, PTA also have been used in fuel cell applications to improve proton conductivity. It exhibits strong proton conductivities that could reach as high as $1.9 \times 10^{-1} S cm^{-1}$ [12]. It also can improve membrane performance even under low-humidity and high-temperature experimental conditions [13-14]. At low temperature, the proton conductivity for reduction of oxygen on platinum and oxygen affinity properties of PTA are considerable and comparable with the same characteristics that exhibits from perfluorosulfonic acid electrolyte due to the 29 water molecules in the PTA ($H_3PW_{12}O_{40} 29H_2O$) [15].

In this study, the PVA membranes with different mPTA-Si loadings were prepared using simple solution casting method. The morphological structure analysis, chemical bonding determination, water uptake and proton conductivity were studied in details for potential application in DMFCs.

2.0 METHODS

2.1 Materials

Dimethyl sulfoxide (DMSO) with purity (GC) $\geq 99.9\%$, provided by Merck Co., Germany, modified phosphotungstic acid-Silica (mPTA-Si) was synthesized and supplied by this project collaboration team member from the University of South Australia. Meanwhile, polyvinyl alcohol (PVA) and methanol were obtained from Sigma Aldrich.

2.2 Fabrication of Flat Sheet PVA/mPTA-Si Membrane

5 wt. % of Polyvinyl alcohol (PVA) was prepared by gradually added it into Dimethyl sulfoxide (DMSO) solution (95 wt.%) at 90°C with continuously stirred for 2 hours. The desired loading of mPTA-Si (0.5, 1.0, 1.5 and 2.0 wt%) was slowly added into the mixture and stirred for about 3 hours at 60°C until the homogenous solution was obtained. Next, the homogenous solution was poured into a petri dish to allow the solvents to be evaporated at temperature of 60°C for 6 hours before the membrane was peeled off and annealed for 1 hour at 120°C. The thickness of the membranes was around 100 μm.

2.3 Membrane Characterization

The surface morphology analysis of the composite membrane was observed using a scanning electron microscopy (SEM-TM 3000) at an accelerating voltage of 15 kV. The membrane samples were prepared by submerged it into liquid nitrogen for a few seconds before passed through for gold sputtering. The fourier transform infrared (FTIR) spectroscopy was used to obtain some information on the functional groups present in the membranes and inorganic filler (mPTA-Si powder).

2.4 Water Uptake

To study the hydrophilicity of the membrane, the water uptake (WU) of the membranes were carried out through measuring the changes in the weight of the samples in the dry and wet conditions. After weighing the weight (W_{dry}), the dry membrane was soaked in deionized water for 24 h at room temperature and then recorded the weight (W_{wet}) of the wet sample. WU of

the membrane are calculated according to the following equation:

$$\text{Water uptake} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad (1)$$

2.5 Proton Conductivity

Proton conductivity of the fabricated membrane samples were obtained by electrochemical impedance spectroscopy (EIS) (model of Solartron 1260 Gain phase Analyzer, AMETEK, Inc., UK) over a frequency range of 1 to 107 Hz with 50 to 500 mV. Initially, all the membranes were fully hydrated by immersing in deionized water for 24 h, and then put onto a home-made two-stainless steel electrode. After that, the measurements of the proton conductivity were calculated using equation 2:

$$\sigma = \frac{L}{RA} \quad (2)$$

where, σ is the membrane conductivity, L is the thickness of the membrane, R is derived from the low intersection of the high frequency semi-circle on a complex impedance plane with the $\text{Re}(Z)$ axis and A is the cross-sectional area of membrane.

3.0 RESULTS AND DISCUSSION

3.1 Surface Morphology of PVA/mPTA-Si membranes

A good dispersion of particles in the polymer matrix is critical for obtaining high-performance of composite membrane for DMFC application as it contribute to form new channel-like pathways for proton transport. Besides, the amount of filler mPTA-Si also influence its distribution in the PVA matrix, thus affected the morphologies of the membrane. Different amounts of mPTA-Si loading have led to different

membrane structures and morphologies. Figure 1 and 2 represent the SEM images of surface and cross-section of pure PVA and fabricated composite membranes at different mPTA-Si loading content. As can be seen, the surface of pure PVA membrane was plane (Figure 1a). However, after the addition of mPTA-Si, the even distribution of mPTA-Si on PVA was seen on the surface of membranes. Moreover, the compactness and the distribution of mPTA-Si in the PVA matrix increases and more uniform (white dots are the mPTA-Si particles) with the increases of loading content (Figure 1b-e). It is suggested that the structural order of mPTA in PEM matrix was improved with the increases amount of mPTA [11], owing to the higher particles number (red circle) of fillers. In addition, the surface of the membranes also was found in smooth and no

aggregation formed in the structure. It is suggested that these fillers particles do not enter the matrix of membrane [12] due to the huge particles average size of mPTA-Si, however they are available at the pore edges. The cross-sectional surface of pure PVA and PVA composite membranes were also examined (Figure 2a-e). This examination was important to determine the distribution and interaction of mPTA-Si within PVA matrix. As can be seen, mPTA-Si were uniformly distributed in PVA matrix, even at the highest loading of mPTA-Si (2%). The mechanical properties of nanocomposite membranes highly depend on the distribution of the mPTA-Si in the PVA matrix. The thickness of the nanocomposite membranes varied due to the evaporation rate of DMSO solvent during the drying process.

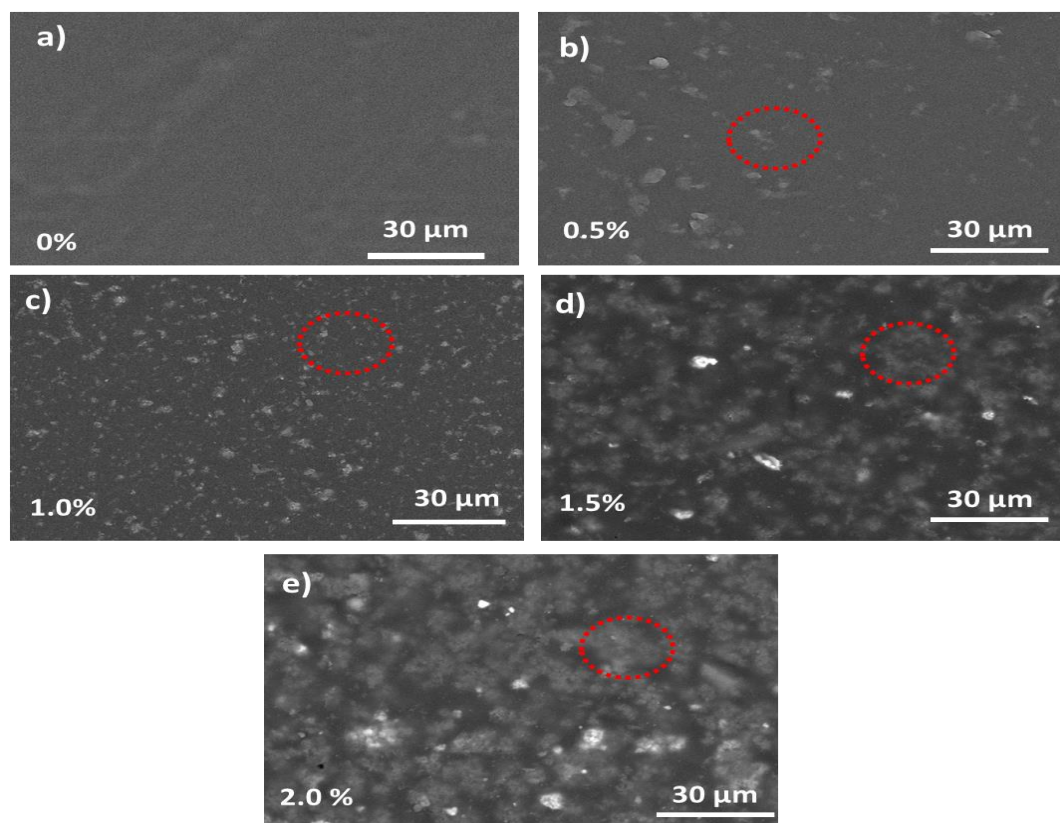


Figure 1 Surface images of membrane (a) blank PVA; (b) 0.5 wt%; (c) 1.0 wt%; (d) 1.5 wt%; (e) 2.0 wt%

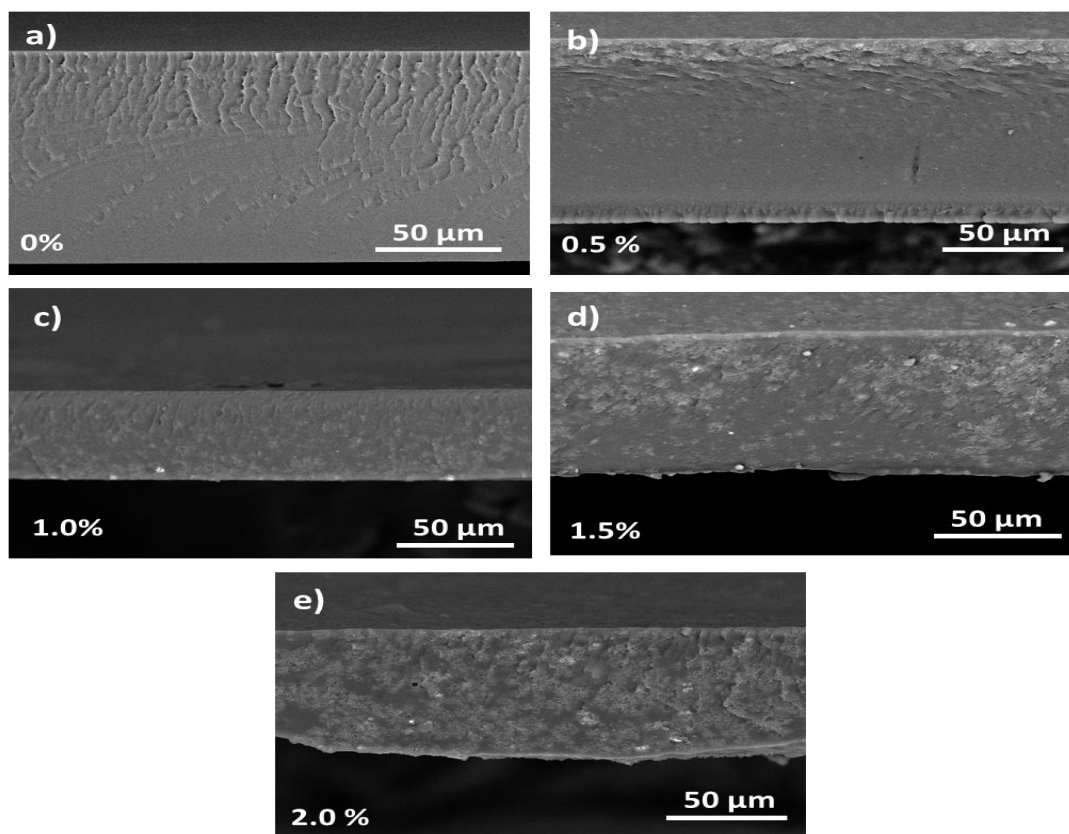


Figure 2 Cross-sectional images of membrane (a) blank PVA (b) hybrid 0.5 wt%;(c) hybrid 1.0 wt; (d) hybrid 1.5 wt%; (e) hybrid 2.0 wt%

3.2 Elements of mPTA-Si in Membrane

The FTIR spectra of PVA/ mpTA-Si nanocomposite membranes with varying concentration of mpTA-Si are depicted in Figure 3. As can be seen in Figure 3 (a), the presence of a Keggin anion ($PW_{12}O_{40}^{3-}$) in the mPTA-Si powder resulted in distinct characteristic bands at around 1045.1 cm^{-1} , 947.02 cm^{-1} , 919.45 cm^{-1} and 727.21 cm^{-1} , which are assigned to heteroatom-oxygen ($P-O_a$), tungsten-terminal oxygen ($W=O_t$), tungsten-corner-shared oxygen ($W-O_c-W$) and tungsten-edge-shared oxygen ($W-O_e-W$) stretching vibration, respectively [12,16-17]. However, after the addition of mPTA-Si powder into the PVA matrix, the presence of mPTA-Si characteristic did not affect the FTIR signal of PVA which indicating the

membrane characteristic remains unchanged (Figure 3b). This shows that the mPTA-Si doesn't interfere with the chemical structure of the PVA. Meanwhile, the Si – O – Si stretching bond and bending of OH bond in O_3Si-H caused the overlapping in the peaks range of between $800\text{ to }1000\text{ cm}^{-1}$ [16], and the transmission peak found at around 3257 cm^{-1} and 2933 cm^{-1} were ascribed for O – H stretching bond and C – H asymmetric stretching bond in PVA [12]. A band around 3275 cm^{-1} is observed in all spectra is assigned to the free O-H stretching vibration of the -OH groups. O-H stretching vibration from the intramolecular hydrogen bonds within the PVA and intermolecular hydrogen bonding between hydroxyl groups of PVA and the mPTA-Si are responsible for this band. The addition of mPTA-Si causes a shift toward higher wavenumber. The

peak for C-H stretching vibrations from alkyl groups is present at 2919 cm^{-1} in all formulations. In addition, there is also red-shift in $\text{W}-\text{O}_c-\text{W}$ signal and it's intensity increases with higher loading indicating that the strong interaction of mPTA-Si particles in the

PVA matrix (as highlighted in Figure 3b), resulted in high degree of mPTA-Si particles dispersion in PVA matrix, which could improve the thermal and mechanical properties of nanocomposite membrane.

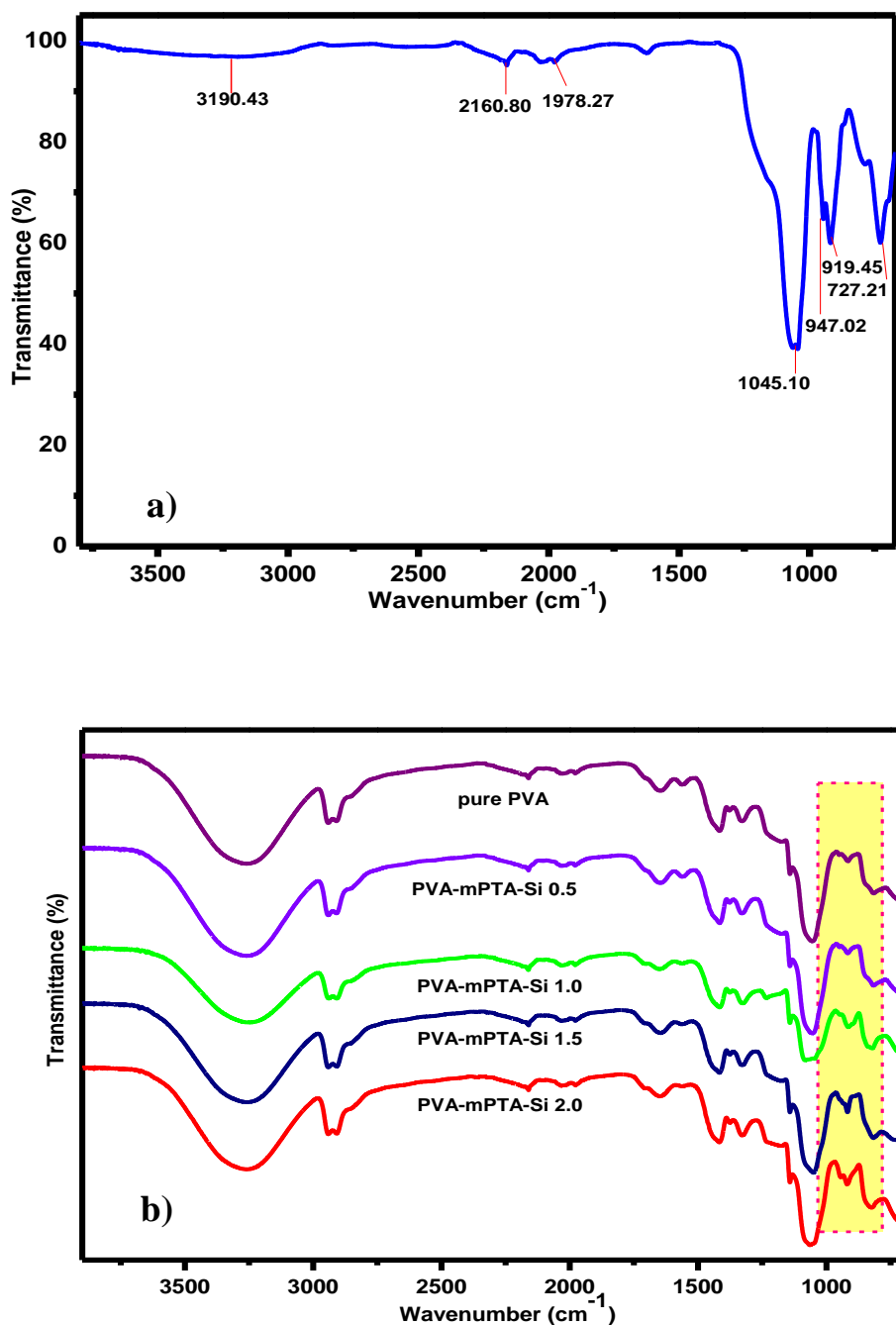


Figure 3 (a) FTIR spectra of mPTA-Si powder; (b) pure and composite membranes with various loadings of mPTA-Si

3.4 Relationship of Water Uptake and Proton Conductivity

The term water uptake describes the ability of a membrane to absorb and retain water desirable for conductivity to the proton. Appropriate amount of water uptake between 75 to 35% is essential for proton transportation in the membrane as water molecules able to form the hydrogen bond networks by supplying proton carriers [18-19]. However, high water content always decreases the mechanical property and

dimensional stability of the membranes. Figure 4 shows that the pure PVA exhibited the highest water uptakes compared to the hybrid membranes, however it is significantly decreases after the addition of mPTA-Si, due to the interaction of mPTA-Si with unconsumed hydroxyl groups in PVA; creating a more compact inner structure and reduces the number of free voids containing water molecules. Besides, the excess and expended volume of water channels also decreased with the increase of mPTA-Si contents.

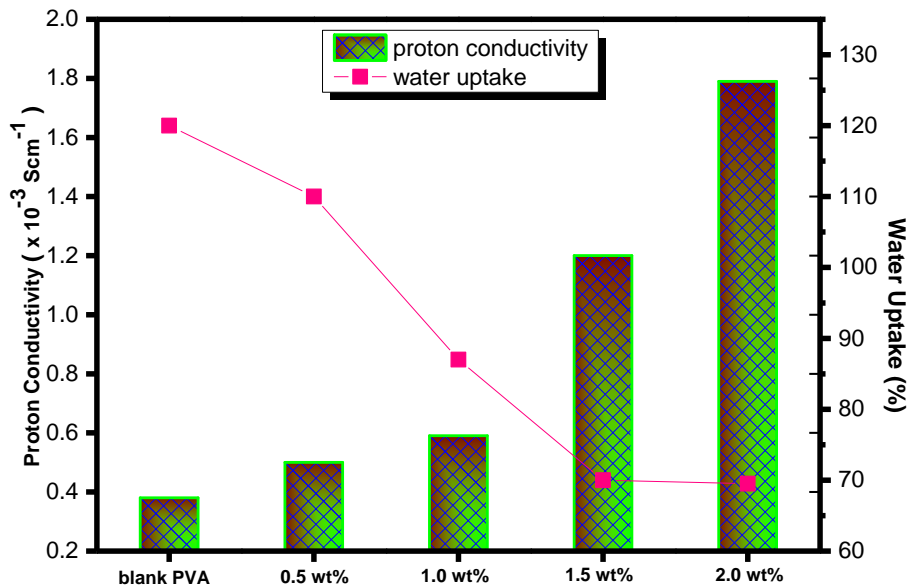


Figure 4 Water uptake and Proton Conductivity at different amount of mPTA-Si content in membrane

The hybrid membranes showed a good balance between the hydrophilicity and the mechanical stability, being water insoluble. As further increase of the filler content, the water uptake in polymer matrix began to decrease due to the blocking effect of mPTA. This indicates that the higher loading content of mPTA-Si significantly produced a strong molecular interaction between PVA matrix and mPTA-Si, which resulted in

membrane compactness and thus reduced the available channels for water transport [20]. Moreover, this phenomenon also can be attributed to the uniform dispersion of mPTA-Si in the membrane at higher loading content (2.0%). This value (68%) is still comparable with the water uptake value reported for good proton conductivity [18-19]. For PEM performance in fuel cell applications, H^+ conductivity is one of the imperative indicators because a

high proton conductivity value ($\sim 0.082 \text{ Scm}^{-1}$) always indicates good proton exchange properties [21]. As shown in Figure 4, the proton conductivities of pure PVA and hybrid PVA membranes were investigated. As can be seen the proton conductivity value increased drastically after 1.0 wt% while there is only a mild response observed from 0.5 wt% to 1.0 wt%. The similar trends also had been reported in the previous study [13]. The hybrid membrane with 2.0 wt% showed the highest proton conductivity value compared others due to the uniform distribution of mPTA-Si in the PVA matrix which resulted in to the formation of hydrated area around its position. Owing to this, it therefore significantly facilitates the proton transfer and yielding maximum proton conductivities for PEM.

4.0 CONCLUSION

PVA/mPTA-Si membranes were successfully fabricated by solution casting method. The fabricated PVA/mPTA-Si membranes displayed desired properties of ideal PEM for DMFC application such as high water uptake and proton conductivity. This positive attributes are mainly due to the formation of strong hydrogen bonding between the PVA and mPTA-Si. In particular, the interconnection of ionic regions between mPTA and PVA matrix and water channels may create a continuous pathway for the transfer of protons hence improving the composite membrane's proton conductivity. Moreover, the surface morphologies analysis also showed that the mPTA-Si particles were uniformly scattering in PVA matrix resulted in the ideal water uptake and high proton conductivity, therefore, a high current and power densities was expected to be achieved. In conclusion, PVA incorporated mPTA-Si membranes at 2.0 wt%

possessed as an ideal PEM to enhance overall efficiency in DMFCs.

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