



## Short communication

## Preparation and performance of nano silica/Nafion composite membrane for proton exchange membrane fuel cells

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## ABSTRACT

Composite membranes made from Nafion ionomer with nano phosphonic acid-functionalised silica and colloidal silica were prepared and evaluated for proton exchange membrane fuel cells (PEMFCs) operating at elevated temperature and low relative humidity (RH). The phosphonic acid-functionalised silica additive obtained from a sol-gel process was well incorporated into Nafion membrane. The particle size determined using transmission electron microscope (TEM) had a narrow distribution with an average value of approximately 11 nm and a standard deviation of  $\pm 4$  nm. The phosphonic acid-functionalised silica additive enhanced proton conductivity and water retention by introducing both acidic groups and porous silica. The proton conductivity of the composite membrane with the acid-functionalised silica was  $0.026 \text{ S cm}^{-1}$ , 24% higher than that of the unmodified Nafion membrane at  $85^\circ\text{C}$  and 50% RH. Compared with the Nafion membrane, the phosphonic acid-functionalised silica (10% loading level) composite membrane exhibited 60 mV higher fuel cell performance at  $1 \text{ A cm}^{-2}$ ,  $95^\circ\text{C}$  and 35% RH, and 80 mV higher at  $0.8 \text{ A cm}^{-2}$ ,  $120^\circ\text{C}$  and 35% RH. The fuel cell performance of composite membrane made with 6% colloidal silica without acidic group was also higher than unmodified Nafion membrane, however, its performance was lower than the acid-functionalised silica additive composite membrane.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are currently one of the most promising technologies to displace incumbent power generation technologies in several markets including back up power, materials handling, automotive and bus. PEMFCs are environmentally friendly (with zero or near zero emissions) and are highly fuel-efficient compared to other technologies including internal combustion engines. However, the high cost of fuel cells is still a barrier to successful commercialization. The DOE target is to develop a direct hydrogen fuel cell stack suitable for transportation with 60% peak-efficiency,  $650 \text{ W L}^{-1}$  power density, 5000 h durability with cycling, at a cost of  $\$ 45 \text{ kW}^{-1}$  by 2010 and a cost of  $\text{US } \$ 30 \text{ kW}_{\text{net}}^{-1}$  by 2015. To achieve the ultimate cost goal of  $\text{US } \$ 30 \text{ kW}_{\text{net}}^{-1}$  for the fuel cell stack, the cost of all components and materials used in the fuel cell has to be significantly reduced and the performance of the fuel cell stack has to be increased in order to bring the system cost down.

The proton exchange membrane is a critical component in PEMFCs. Perfluorosulfonic acid (PFSA) ionomers, such as Nafion are the current state of the art for fuel cell membranes. PFSA provide excellent chemical stability due to their perfluorinated backbone while exhibiting good proton conductivity at moderate water content. Up to this point of time, PFSA ionomer membranes have been the most effective membranes for PEMFC use. However, they cannot meet the current requirements of PEMFCs for automotive applications which call for an increase in operation temperature from current  $70\text{--}80^\circ\text{C}$  to over  $95^\circ\text{C}$  and drier inlet gases without gas humidification. The operation of PEMFCs at high temperature and low relative humidity can improve CO tolerance of platinum catalyst, improve mass transportation, increase reaction kinetics and simplify the system for water management and gas humidification. These improvements may lead to a reduction in system requirements that can effectively lower the cost.

The development of practical, low-cost, high temperature-capable membrane materials has the potential to solve many of the existing issues for present PEMFC operation at low temperature and high inlet gas RH. Considerable efforts have been made in recent years in the development of proton exchange membranes that have high proton conductivity and good thermal stability at high temper-

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ature and low relative humidity [1–5]. A useful approach to develop this type of membranes is to modify Nafion membranes with micron or submicron inorganic/organic additives such as metal oxides, acid functionalised metal oxides, silica and heteropolyacids (HPA) [6–21]. Such composite membranes have exhibited improvements in water retention and fuel cell performance at elevated temperatures. Wang et al. [17] incorporated bifunctionalised silica (sulfonated phenylethylsilica) into Nafion to form a composite membrane that showed improved water uptake capacity and proton conductivity. However, no fuel cell performance data has been reported. In the modification of Nafion with additives, the particle size of additive could affect composite membrane properties. It was reported [14] that the composite membranes with 30 nm size phosphotungstic acid additive displayed 35% higher proton conductivity compared with the composite membrane with micron sized particles.

The aim of this study was to develop a Nafion composite membrane using nano-scale phosphonic acid-functionalised silica as an additive in order to increase proton conductivity and water retention for PEMFC operation at high temperature and low relative humidity. In the present study, nano-scale phosphonic acid-functionalised silica was synthesized and incorporated into Nafion ionomer to make composite membranes. The acid-functionalised silica additive provides extra proton donors from phosphonic acid to improve proton conductivity and enhanced membrane water retention with high surface area porous silica. The proton conductivity and in-situ fuel cell performance at various conditions, particularly at high temperature and low relative humidity were investigated. Silica–Nafion composite membrane without acidic functional group was also prepared and evaluated for the purpose of comparison.

## 2. Experimental

### 2.1. Materials

Diethoxyphosphorylethyltriethoxysilane (PETES), Tetraethylorthosilicate (TEOS), 37% hydrochloric acid and methanol were purchased from Aldrich Chemical. 22% (w/w) Nafion in *n*-propanol/water was obtained from E.I. Du Pont de Nemours Company. Colloidal silica suspension was obtained from Nalco Nano Technologies.

### 2.2. Additive synthesis

PETES was dissolved in 37% hydrochloric acid with N<sub>2</sub> bubbled into the solution. The solution was heated to 85 °C with constant stirring and maintained for 24 h. The product was then cooled to 40 °C for the removal of HCl under reduced pressure. Light yellow, viscous hydrolyzed PETES was obtained with a yield of 95%. The hydrolyzed PETES was then dissolved in methanol to form a 20% (w/w) solution for additive synthesis. TEOS was also hydrolyzed in a methanol solution containing water and catalytic hydrochloric acid at room temperature for 24 h. The phosphonic-silicate additive was prepared by co-condensation of hydrolyzed PETES and TEOS in methanol with a molar ratio of 6:4 at room temperature for 5 days. The synthesis process is summarized in Fig. 1.

### 2.3. Composite membrane preparation and membrane electrode assembly (MEA)

Various levels of additive solutions were incorporated into Nafion ionomer dispersion by mixing under ultrasonication. The blended solutions were degassed and then cast on either a glass

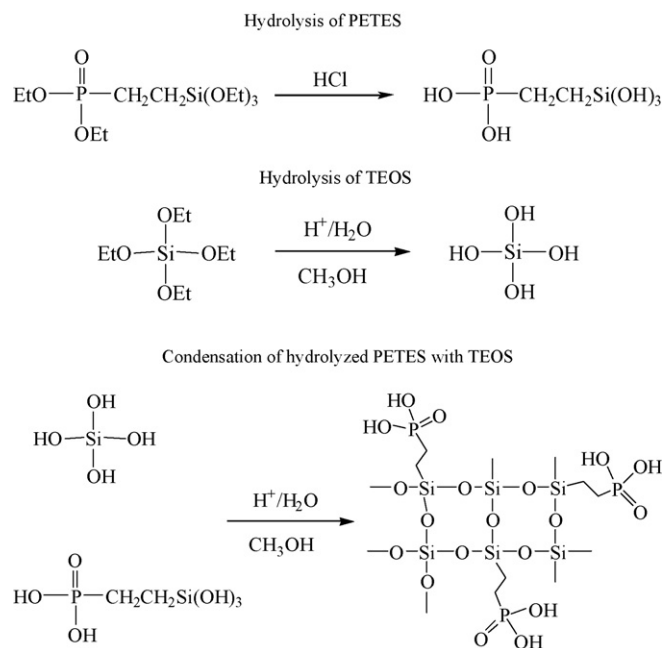


Fig. 1. Synthesis process of phosphonic acid-functionalised silica.

plate for a small scale use or on a carrier film for a continuous processing on a 30 cm wide roll. The composite membranes were dried at room temperature for 18 h, and then annealed at 100 °C for 1 h and 150 °C for another 1 h.

Ballard standard MK9 anodes and cathodes were used to make MEAs. Pt loading levels were 0.7 mg cm<sup>-2</sup> in the cathode and 0.3 mg cm<sup>-2</sup> in the anode. The electrodes and membrane were bonded at 150 °C under pressure.

### 2.4. Membrane characterization

#### 2.4.1. Additive particle size measurements

The phosphonic acid-functionalised silica additive particle size in the sol was monitored by a Mettler Nano-Sizer and was controlled in the range of 20–30 nm by hydrolysis time and temperature. The particle size in the membrane was characterized using a transmission electron microscope (TEM). A strip of the modified membrane was embedded into epoxy, and then cut into thin slices using a Leica Ultracut UCT ultramicrotome at room temperature. The thickness of each slice was 30–50 nm depending on the particle size in the membrane. The slices were examined in a FEI Tecnai Scanning TEM with 200 kV electron beam. The TEM image was analyzed using Image-Pro software for particle size measurement. BET surface area and pore size distributions were analyzed by Micromeritics Analytical Systems.

#### 2.4.2. Equivalent weight (EW) and ion-exchange capacity (IEC) measurements

EW was determined by titration. The membrane was washed with distilled water, and dried at 60 °C under vacuum for 24 h. The membrane was then soaked in a large excess of 2 M NaCl solution at the room temperature for 24 h in order to exchange protons. The supernatant solution was then titrated with 0.01 M NaOH standard solution to the end point of pH 7. The EW of the membrane was calculated via the following equation:

$$\text{EW (g mol}^{-1}\text{)} = \frac{m}{M_{\text{NaOH}}V_{\text{NaOH}}} \times 1000$$

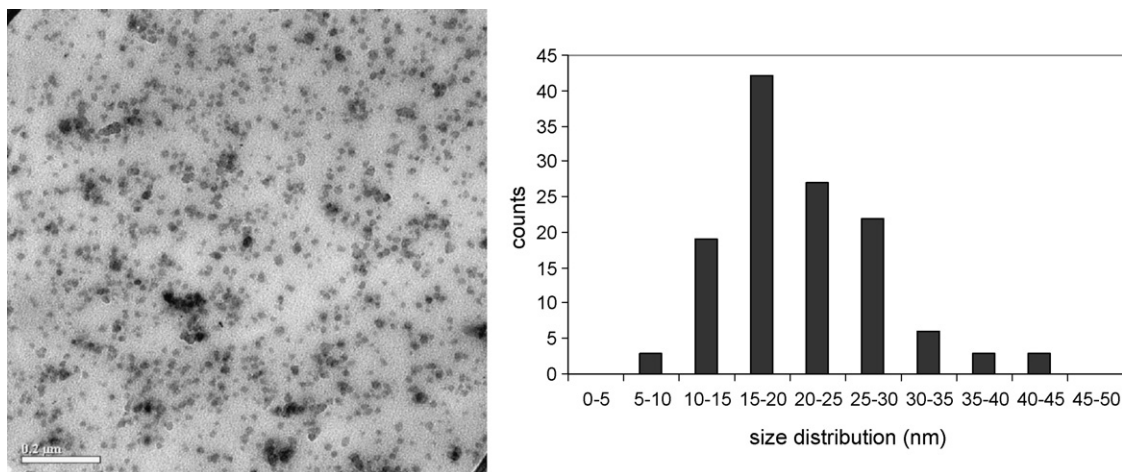


Fig. 2. A typical TEM image of silica/Nafion composite membrane and particle size distribution.

where  $M_{\text{NaOH}}$  was the NaOH molar concentration ( $\text{mol L}^{-1}$ ),  $V_{\text{NaOH}}$  the volume of NaOH (ml) and  $m$  the dry membrane mass (g).

Ion exchange capacity (IEC) was obtained from EW as follows:

$$\text{IEC (mmol g}^{-1}\text{)} = \frac{1000}{\text{EW}}$$

#### 2.4.3. Proton conductivity measurements

Membrane in-plane proton conductivity was measured at  $85^\circ\text{C}$  and 50% RH by a four-probe ac impedance and a Solartron FRA1260 frequency response analyzer. The scanning frequencies ranged from 10 MHz to 100 Hz. The sample was held at the test conditions for 6 h to reach equilibrium prior to measurement.

#### 2.4.4. Evaluation of MEA performance in PEMFC

MEA performance evaluation was carried out using Ballard electrodes in  $50\text{ cm}^2$  single cell hardware designed specifically for membrane evaluation. Polarization curve was obtained at different relative humidities (35–95% RH) and temperatures ( $95\text{--}120^\circ\text{C}$ ). Hydrogen was used for anode and air for cathode. The gas stoichiometric ratio was set at 12/9 (cathode/anode) for all tests. All data was obtained at 30 psi back-pressure.

### 3. Results and discussion

#### 3.1. Additive morphology

Fig. 2 shows a typical TEM image of the silica composite membrane and a histogram analysis of the particle size distribution. The additive particles were uniformly distributed in the membrane, although a few agglomerates with dimension of 100–200 nm were observed. The mean particle size of the colloidal silica without acidic functional group in the membrane was approximately 20 nm with a standard deviation of  $\pm 7$  nm. The mean particle size of the phosphonic acid-functionalised silica in the membrane was approximately 11 nm with a standard deviation of  $\pm 4$  nm. A few of agglomerates ranging in size from 200 nm to 300 nm were observed in the membranes. Energy dispersive X-ray spectrum (EDX) analysis of the phosphonic acid-functionalised silica/Nafion composite membrane showed clear spectral peaks for P and Si (Fig. 3). It indicated that phosphonic functional groups were linked to silica and that the additive was well incorporated into Nafion ionomer. The BET surface areas of the porous phosphonic acid-functionalised silica were in the range of  $680\text{--}715\text{ m}^2\text{ g}^{-1}$  and the adsorption average pore size in the range of 2–3 nm. It is believed that these nanopores

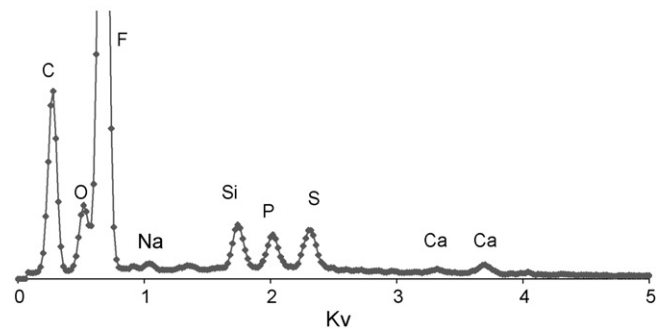


Fig. 3. EDX analysis for 10% phosphonic acid-functionalised silica/Nafion composite membrane.

can hold water, improving membrane water retention during fuel cell operating under dry conditions.

#### 3.2. Composite membrane proton conductivity

The proton conductivity of the phosphonic acid-functionalised silica/Nafion composite membranes increased with the increase in additive loading level at low addition contents from 5% to 10%, as shown in Fig. 4. However, further increase of additive content from 10% to 15% caused a decrease in proton conductivity despite an increase in membrane IEC (Fig. 5). It should be noted that the proton conductivity of acid-functionalised silica composite membranes at all loading levels was still higher than that of unmodified Nafion membrane. It is not clear why the proton conductivity decreased at 15% loading level. It may be due to changes

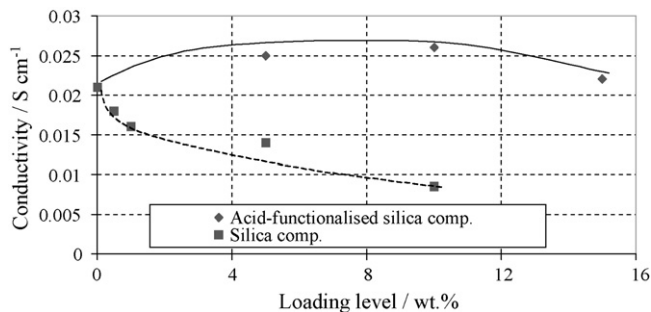


Fig. 4. Proton conductivity of composite membrane vs additive loading level.

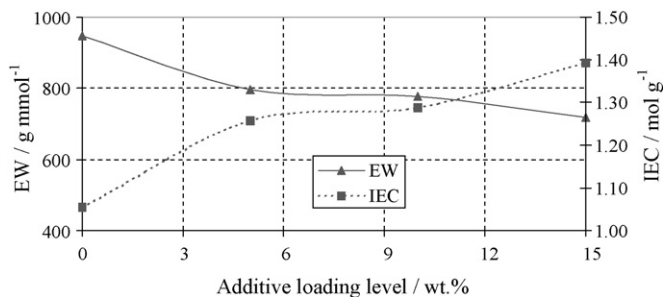


Fig. 5. EW/IEC of phosphonic acid-functionalised silica/Nafion composite membrane vs additive loading level.

in membrane hydrophilic/hydrophobic domain, affecting proton transport in the membrane. The addition of colloidal silica into Nafion decreased membrane proton conductivity (dash line) via possible dilution of Nafion<sup>®</sup> sulfonic acid groups, as shown in Fig. 4.

Wang et al. [17] reported that the proton conductivity of the bifunctional sulfonated phenethylsilica Nafion composite membranes increased with loading level from 2.5% to 5% over the whole RH range at 80 °C, compared to the host polymer Nafion 117. As there were only two additive loadings reported in their study, the conductivity maximum may not have been reached. Similar to our results, Jung et al. [18] reported that the conductivity of Nafion 115 composite membrane with silica significantly decreased by 29% when silica loading level was increased from 3% to 10% at room temperature. Similar trends were also observed in other types of composite membranes, such as titanium phosphate sulfophenylphosphonate/Nafion (TiPSP/Nafion) [12] and ZrO<sub>2</sub>/Nafion composite membranes [11]. The proton conductivity of the ZrO<sub>2</sub>/Nafion composite membrane was 4–5% higher than that of the Nafion 112 at 40% RH and 90 °C. The highest conductivity was observed at 10% additive loading level, while the conductivity dramatically declined with a 20% additive loading level.

### 3.3. In-situ fuel cell performance

Polarization curves of MEAs with 10% phosphonic acid-functionalised silica composite membrane at different relative humidities and temperatures are shown in Figs. 6 and 7. The composite membrane with phosphonic acid-functionalised silica exhibited better performance than the unmodified Nafion membrane under dry conditions. A 20 mV performance improvement at 50% RH and a 60 mV improvement at 35% RH were observed for the MEA with the phosphonic acid-functionalised silica composite membrane compared with the Nafion membrane MEA operating under 95 °C and 1.0 A cm<sup>-2</sup> (Fig. 6). The performance gain was more significant at higher operating temperature because the compos-

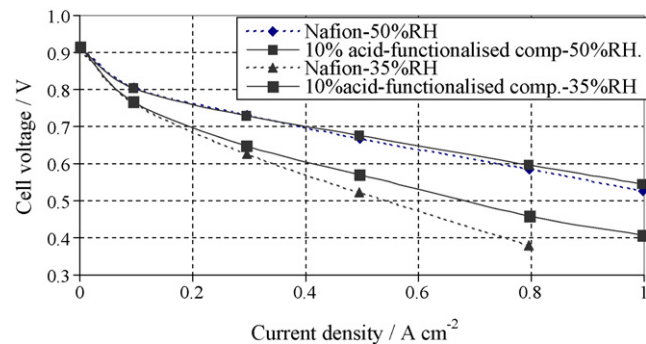


Fig. 7. Fuel cell performance of MEAs with 10% phosphonic acid-functionalised silica/Nafion and Nafion membranes with various RH at 120 °C.

ite membrane dehydration was much slower than that of Nafion membrane, as shown in Fig. 7. At 120 °C and 35% RH, the MEA performance was improved by 80 mV at 0.8 A cm<sup>-2</sup>. The stack with Nafion membrane was unable to operate at 120 °C and 35% RH when the current density was over 0.8 A cm<sup>-2</sup>. However, the performance of the composite membrane MEA was slightly lower than the Nafion membrane under wet conditions (95% RH in Fig. 6). This trend maybe due to increased mass transport loss in the stack as flooding was observed with the composite membrane MEA during operation under wet conditions.

Fig. 8 shows the effect of additive loading of the acid-functionalised silica and the colloidal silica composite membranes on the MEA performance at 0.8 A cm<sup>-2</sup>, 120 °C and 35% RH. The performance of the phosphonic acid-functionalised silica composite membrane MEA was higher at all loading levels from 5% to 15% compared with the Nafion membrane MEA. The best performance was obtained with 10% loading. A similar correlation between MEA performance and additive loading of pure silica composite membrane was also observed, as shown in Fig. 8. Maximum MEA performance was obtained at 6% loading. Further increasing the loading to 9% decreased performance to lower than that of the Nafion membrane MEA. It is worth noting that the acid-functionalised silica composite membrane MEA showed higher performance than the colloidal silica composite membrane at all loading levels. This may be due to the bi-functions of the phosphonic acid-functionalised silica increased both membrane water retention and proton conductivity. Without acid functionality, the silica additive functioned only as a water retention agent, not the proton donor. Subsequently, the performance gain for the silica membrane occurred only at low loading and at low RH.

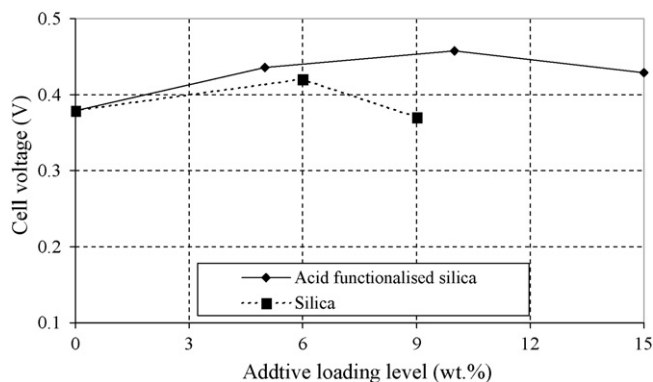


Fig. 8. Fuel cell performances of MEA with phosphonic acid-functionalised silica/Nafion (solid line) composite membrane and MEA with silica/Nafion composite membrane at 0.8 A cm<sup>-2</sup> and 120 °C/35% RH.

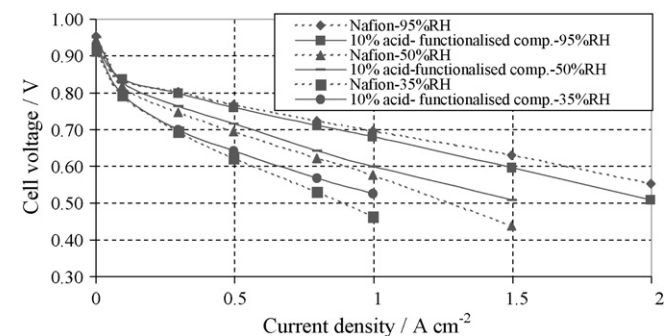


Fig. 6. Fuel cell performance of MEAs with 10% phosphonic acid-functionalised silica/Nafion and Nafion membranes with various RH at 95 °C.

**Table 1**

Cell performance and resistance for 10% functionalised silica composite membrane (under  $1 \text{ A cm}^{-2}$ ) at different temperature and relative humidity

Test conditions	Cell voltage at $1 \text{ A cm}^{-2}$ (V)	Cell resistance ( $\text{m}\Omega$ )
95 °C 95% RH	0.68	2.40
95 °C 50% RH	0.60	2.98
95 °C 35% RH	0.52	3.73
120 °C 50% RH	0.54	3.44
120 °C 35% RH	0.41	5.06

It should be noticed that the cell performances for all membranes decreased when operating conditions went from low temperature and high humidity (95 °C and 95% RH) to high temperature and low humidity (120 °C and 35% RH). When the temperature increased from 95 °C to 120 °C at 35% RH, the cell performance of 10% acid functionalised composite membrane decreased approximately 110 mV at  $1 \text{ A cm}^{-2}$ , as shown in Table 1. The performance drop with increased temperature maybe explained by an increase in the change of Gibbs free energy involving the reaction of hydrogen with oxygen. Another likely reason was the increase in the stack resistance due to rapid water loss in the membrane and ionomer in the catalyst layer at the volatile temperature. The stack resistance increased from 3.73  $\text{m}\Omega$  to 5.06  $\text{m}\Omega$  when temperature was increased from 95 °C to 120 °C at 35% RH. A similar trend was also observed at 50% RH. At elevated temperature (>100 °C), water vapour transporting from cathode through GDL to outlet was much fast than the migration of liquid water, resulting in significant membrane and catalyst layer ionomer water loss. Although the cell performance for the functionalised silica composite membrane displayed an increase of 21% compared with the Nafion membrane at 120 °C and 35% RH at  $0.8 \text{ A cm}^{-2}$ , it still cannot meet the requirements for the automotive fuel cell applications. Further improvement in cell performance of the composite membrane is needed for practical fuel cell applications operating under high temperature and dry conditions.

It should be also mentioned that the purpose of this study is to develop membrane capable of improving fuel cell performance at high temperature and dry conditions. The cell performance is significantly affected by many factors including cell designs, other components such as catalyst layer, gas diffusion layer (GDL), flow field of bi-polar plates and the operation conditions. Optimization of fuel cell performance will require to improve all components, not only the membrane. The important aspects of membrane stability and durability are not within the scope of this study. Further investigation is required to address these issues.

## 4. Conclusions

The phosphonic acid-functionalised silica additive was well incorporated into Nafion membrane with particle sizes around 11 nm with a standard deviation of  $\pm 4$  nm. The highest proton conductivity of the acid-functionalised silica composite membrane was  $0.026 \text{ S cm}^{-1}$ , 24% higher than that of the unmodified Nafion membrane at 85 °C and 50% RH. Compared with the Nafion membrane, the phosphonic acid-functionalised silica (10% loading level) composite membrane exhibited 60 mV higher fuel cell performance at  $1 \text{ A cm}^{-2}$ , 95 °C and 35% RH, and 80 mV higher at  $0.8 \text{ A cm}^{-2}$ , 120 °C and 35% RH. The fuel cell performance with 6% colloidal silica composite membrane was also higher than the unmodified Nafion, however, the colloidal silica additive was much less effective than the acid-functionalised silica additive in the improvement of fuel cell performance.

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