

Effect of Calcium Hydroxy Phosphate as a Crystallinity Enhancer in Nafion Membrane for Direct Methanol Fuel Cell

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Nafion is a widely used membrane in direct methanol fuel cell (DMFC). Many advantages of Nafion including good chemical stability, good thermal resistance, and high proton conductivity. However, Nafion has high methanol crossover which remarkably reduces the performance of DMFC and results in waste of fuel. Therefore, in this work, calcium hydroxy phosphate (CHP) was incorporated into Nafion to increase its crystallinity. The properties of Nafion/CHP such as crystallinity, water uptake, ion exchange capacity, methanol crossover, and solubility were studied. SEM/EDS with elemental mapping was used to observe the dispersion of CHP within the membrane. It was clearly shown that by incorporating 1.0 wt% and 2.5 wt% of CHP into the membrane, methanol crossover at 30 °C was reduced from $125.6 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ to $2.58 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ and $65.58 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$. The reduction of methanol crossover of CHP/Nafion composite membrane at higher weight was lesser than that of the composite at lower weight due to the agglomeration of CHP.

1. Introduction

Sustainable energy development is more challenging each year because of higher population. This results in higher energy consumption (Holdren,1991). Fuel cell technologies have been developed to satisfy this demand. Direct methanol fuel cell (DMFC) is used as power source of portable electronic device and energy storage (Palma et al., 2018) due to its high energy density, low carbon emission, and relatively high efficiency (Yoonoo et al., 2011). Using methanol as a fuel offered many advantages such as low cost of fuel, convenient transportation and storage of fuel (Prapainainar et al., 2017). Moreover, methanol is sustainable fuel which can be produced from synthesis gas by gasified bio-feed stock to synthesis gas (Speight, 2011) or converting carbon dioxide and methane using photocatalytic to produce synthesis gas (Tahir et al., 2019) followed by conventional methanol synthesis. Nafion was used as a membrane due to its good chemical stability and high proton conductivity when it was fully hydrated (Rodríguez et al., 2016). However, high amount of methanol can diffuse through the membrane causing high methanol crossover and reducing the performance of DMFC. Many attempts have been carried out on Nafion membrane by incorporating organic/inorganic material into Nafion to reduce methanol crossover and improve proton conductivity of membrane. Mordenite was one of inorganic material widely used to eliminate high methanol crossover within DMFC because its ability to block methanol in water channel (Prapainainar et al., 2017). However, it has poor interfacial interaction with Nafion. Therefore, it tends to precipitate at bottom side of membrane (Prapainainar et al., 2019). Alternative to mordenite, calcium hydroxy phosphate (CHP) was incorporated into 5 wt% Nafion solution then using solution casting method resulted in lower methanol crossover (Park and Yamazaki, 2006) and higher proton conductivity (Park et al., 2004) compared to pure cast Nafion. Their work studied the effect of CHP without adding any chemicals during membrane casting process which might affected the uniformity of solution. The objective of this work was to study the crystallinity of CHP/Nafion membrane at different content of CHP and the different casting procedures from the previous published works (Park et al., 2004) was done by adding

DMF and alcohol to ensure the homogeneous of solution. The membranes were characterized by WAXS and SEM/EDS mapping of fluoride and calcium elements, solubility, ion exchange capacity, water uptake, and methanol permeability.

2. Materials and method

2.1 Materials

Nafion® D2021 20 wt% solution was purchased from Ion Power. Calcium Hydroxy Phosphate (CHP) was purchased from Sigma-Aldish. Methanol 99.99 % purity and ethanol 99.99 % purity were purchased from ACI Labscan. Dimethylformamide (DMF) 99.8 % purity was purchased from Riedel-de Haen. Hydrogen peroxide 35 wt% was purchased from Chem-supply. Sulfuric acid (H₂SO₄) 98 wt% from QReC. Toluene 99.99 wt% was purchased from Fisher Scientific. Sodium hydroxide (NaOH) 97.0 wt% was purchased from Ajax Finechem.

2.2 Incorporating CHP into Nafion solution

First, 0.01559 g (1.0 wt%) and 0.0388 g (2.5 wt%) of CHP were mixed in 7.5 mL of 20 wt% Nafion solution and vigorously homogenized by switching between ultrasonic bath and magnetic stirrer with an interval of 15 min for 1 h. At this point, CHP powder was hard to be observed.

2.3 Fabrication of membrane

First, 7.5 mL of Nafion solution was mixed with 28.9 mL of ethanol, 5.1 mL of methanol, and 20.5 mL of DMF. Then, the solution was placed in 88 mm glass Petri dish and put in a vacuum oven at 100 °C/-0.9 bar for 20 h. After that, it was heated up to 150 °C for 4 h and then the membrane was removed from the dish following (i) a few drops of deionized water were added at the edge of the membrane; (ii) the membrane was cut along the edge of the membrane; (iii) the edge of the membrane was gently and slowly lifted; (iv) several drops of deionized water was added at the contact between the membrane and the glass to assist the removing of the membrane.

2.4 Membrane pretreatment

Membranes were treated by boiling in deionized water for 10 min to make sure that it was fully hydrated. The membranes were soaked in a 5 wt% H₂O₂ and heated at 80 °C for 30 min in order to remove organic residues. Then, they were washed by deionized water and removed. Then it was boiled in 1 M H₂SO₄ acid solution for 30 min. Finally, boiling water was used to wash the membrane for 3 times.

3. Experimental

3.1 Wide angle x-ray scattering (WAXS)

Membrane was tested by SAXS Point 2.0 using WAXS mode of operation equipping microfocus X-ray source with Cu 50kV 1 mA, detector: 2D EIGER R 1M CMOS, 75 um x 75 um, 1030 x 1065 pixel, scattering angle at 0-10°, and wavelength of x-ray at 0.15 nm. The crystallinity can be calculated by integrating crystalline intensity (I_c) and total intensity (I_T) shown in Eq(1) (Alonso et al., 2009).

$$X_c = \frac{\int q^2 I_c(q) dq}{\int q^2 I_T(q) dq} \times 100\% \quad (1)$$

3.2 Scanning electron microscope with Energy Dispersive Spectroscopy (SEM/EDS)

The membrane was cut to observe the cross-section by FEI QUANTA450 equipped with Oxford X-Max EDX detector at scope of 600, 900, and 10,000. CHP composite membranes were characterized using the same equipment but at scope of 1,500, 10,000, and 20,000.

3.3 Solubility testing

First, 50 mg of membrane was added into 10 mL of 50:50 ethanol-water mixture and sonicated in ultrasonic cleaner for 1 h. The mixture was then filtered through Whatman No1 filter paper. Finally, the filtered solid was dried at 100 °C and weighted to calculate % soluble as shown in Eq(2).

$$\% \text{ soluble} = \frac{\text{weight of residue}}{\text{weight of membrane}} \times 100\% \quad (2)$$

3.4 Water uptake (WU) Testing

Membrane sample was dried at 80 °C in vacuum oven for 24 h. The dried membrane was weighted to determine its dry weight. The membrane was then soaked in deionized water at room temperature for 24 h. The membrane was weighted again. The value was recorded as wet weight and % water up take was calculated using Eq(3)(Prapainainar et al., 2017).

$$\% \text{ water uptake} = \frac{\text{wet weight} - \text{dryweight}}{\text{dry weight}} \times 100\% \quad (3)$$

3.5 Ion exchange capacity (IEC)

First, 50 mg samples of treated membranes were immersed in 10 mL of 1M NaCl for 24 h. The mixture was then titrated with NaOH 0.01M using phenolphthalein as an indicator. Finally, the ion capacity was calculated by Eq(4) (Prapainainar et al., 2017).

$$\text{IEC} = \frac{(\text{concentration of NaOH}) \times (\text{volumn of NaOH})}{\text{dry weight of membrane}} \quad (4)$$

3.6 Methanol permeability

The treated membrane was placed in a diffusion cell and sealed with gasket to prevent the leak. The cell was connected to 1M methanol feed solution tank (2000 mL) and deionized water tanks (250 mL). The pump was started at the feed side to saturate the system for 25 min. The pump at the permeate side was then started and 1 mL of liquid sample was collected at 5, 30, 60, and 90 min. Methanol permeability test was performed at 30°C and 70 °C. Permeability of methanol can be calculated by Eq(5) (Prapainainar et al., 2017).

$$P = \frac{kVL}{SC_{A_0}} \quad (5)$$

where k is the slope of the curve plotted between concentration and time ($\text{mol cm}^{-3}\text{s}^{-1}$), V is the volume on the permeate side (cm^3), S is the area of the membrane (cm^2), L is the thickness of the membrane (cm), and C_{A_0} is the initial methanol concentration on the feed side (mol cm^{-3}).

4. Results and discussion

4.1 Membrane characterization

Figure 1 showed SEM/EDS images of each membrane. From surface and cross-sectional images of the membrane, it clearly showed that CHP and Nafion had good interfacial interaction with each other which was confirmed by EDS mapping of calcium. CHP was well dispersed throughout the membrane which was indicated by the red mapping color (see Figure 1 right images)). However, at 2.5 wt% of CHP, there were groups of agglomerated CHP within the membrane which may cause by either insufficient free volume of Nafion membrane or inadequate time of homogenizing resulted in CHP particles reassemble themselves. This was affected other parameters including methanol crossover which was discussed in section 4.5. Figure 2 showed WAXS image of each membrane. It was found that adding more CHP content, the crystalline region area of Nafion was increased and the amorphous region area was decreased which may cause by CHP particles enhanced the nucleation rate of Nafion (Park and Yamazaki, 2006) which increased the crystallization of the polymer (Sullivan et al., 2014) by reducing interfacial free energy of nucleation (Mileva et al., 2018) resulted in higher crystalline region. The crystallinity was calculated using eq. (1) and showed in Table 1 which could be seen that the crystallinity of Nafion composite membrane was increased from 44.46 % (0.0 wt% CHP) to 50.13 % (2.5 wt% CHP) the crystallinity values of this work were all higher than the previous work of (Park and Yamazaki, 2006) and (Park et al., 2004) because differences in method of membrane casting which we use DMF and higher temperature(100°C) to cast the membrane and ensure good dispersion of the filler (Lin et al., 2005). The crystallinity increased from the work from (Park and Yamazaki, 2006) which was concluded that adding higher CHP content yielded higher crystallinity.

4.2 Solubility

Solubility was used to evaluate the chemical resistance of the membrane which should be lower than 5 % for proton exchange membrane (Moore and Martin, 1988). It was calculated from Eq(2). Table 2 shows the solubility of each membrane. The solubility was increased as the content of CHP became higher. It was seen that adding more CHP resulted in lower chemical resistance of the membrane compared to that of the pure recast Nafion (0.0 wt% CHP). Nafion composite with higher CHP content likely to dissolve in an organic

solvent more than plain recast Nafion alone (Moore and Martin, 1988). However, the solubility of composite membranes fell within an acceptable range (lower than 5 %) which could still be considered as high chemical stability because the membrane will not easily be disintegrated in organic solvent and satisfy all of the requirements including has both dry and wet mechanical strength (Moore and Martin, 1988).

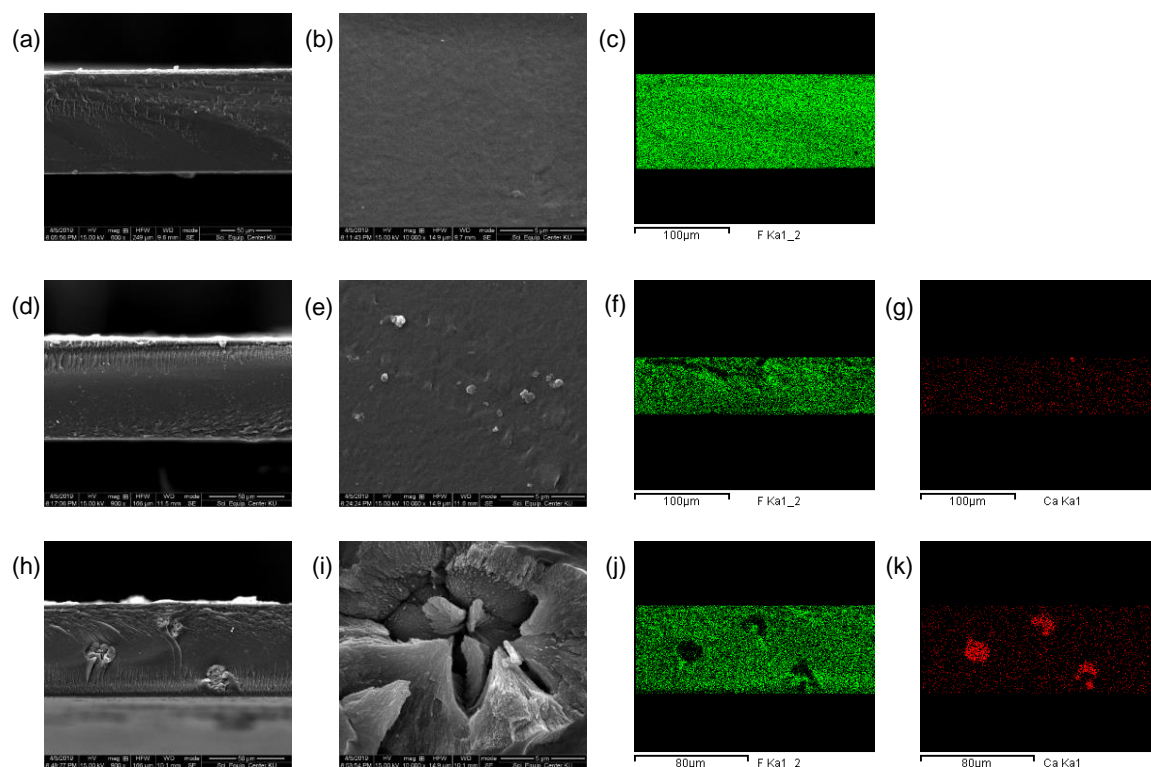


Figure 1: SEM/EDS images (a) to (c) 0.0 wt% CHP/Nafion, (d) to (g) 1.0 wt% CHP/Nafion, (h) to (k) 2.5 wt% CHP/Nafion. SEM images of cross-section (left); SEM images of surface (middle); EDS images of fluoride mapping images (right/green); and EDS images of calcium mapping images (right/red).

Table 1: Crystallinity and Methanol permeability at 30 °C and 70°C of 0.0 wt% CHP/Nafion membrane, 1.0 wt% CHP/Nafion membrane, and 2.5 wt% CHP/Nafion membrane.

Membrane	CHP content wt%	Crystallinity (%)	Methanol Permeability ($10^{-6} \text{ cm}^2 \text{ s}^{-1}$)	
			30 °C	70°C
0.0 wt% CHP/Nafion	0.0	44.46	125.6	373.2
1.0 wt% CHP/Nafion	1.0	47.44	2.6	3.1
2.5 wt% CHP/Nafion	2.5	50.13	67.6	274.2

4.3 Water uptake

Table 2 shows water uptake of all membranes. It is an important parameters of proton exchange membrane when transporting proton by Grotthuss and Vehicle mechanisms (Prapainainar et al., 2019) which should not be too great to give excess water within the membrane that may lead to unexpected mechanical properties (Xu et al., 2015). The water uptake was evaluated using Eq(3) and it was found that water uptake was decreased from 49.21 % to 11.01 % as CHP content increased from 0.0 wt% to 2.5 wt% which indicated that CHP/Nafion composite membrane absorbed lower water molecule than that of the plain Nafion membrane. This was attributed to free volumes within the membrane occupied by the CHP preventing water molecules to penetrate into the membrane which led to lower proton conductivity (Awang et al., 2018).

4.4 Ion exchange capacity (IEC)

IEC was used as indirect approximation of proton conductivity (Wu et al., 2007) and has related relationship with water uptake. Table 2 showed IEC of all membranes. From Table 2, it was found that adding more CHP content resulted in lowering the IEC of membrane from $0.010225 \text{ molg}^{-1}$ to $0.003378 \text{ molg}^{-1}$. The reduction of

IEC was mainly due to the addition of CHP particle which maybe similar to the addition of CeO₂ which had no proton dissociation and undesirable packing of ionic particle (Velayutham et al., 2017).

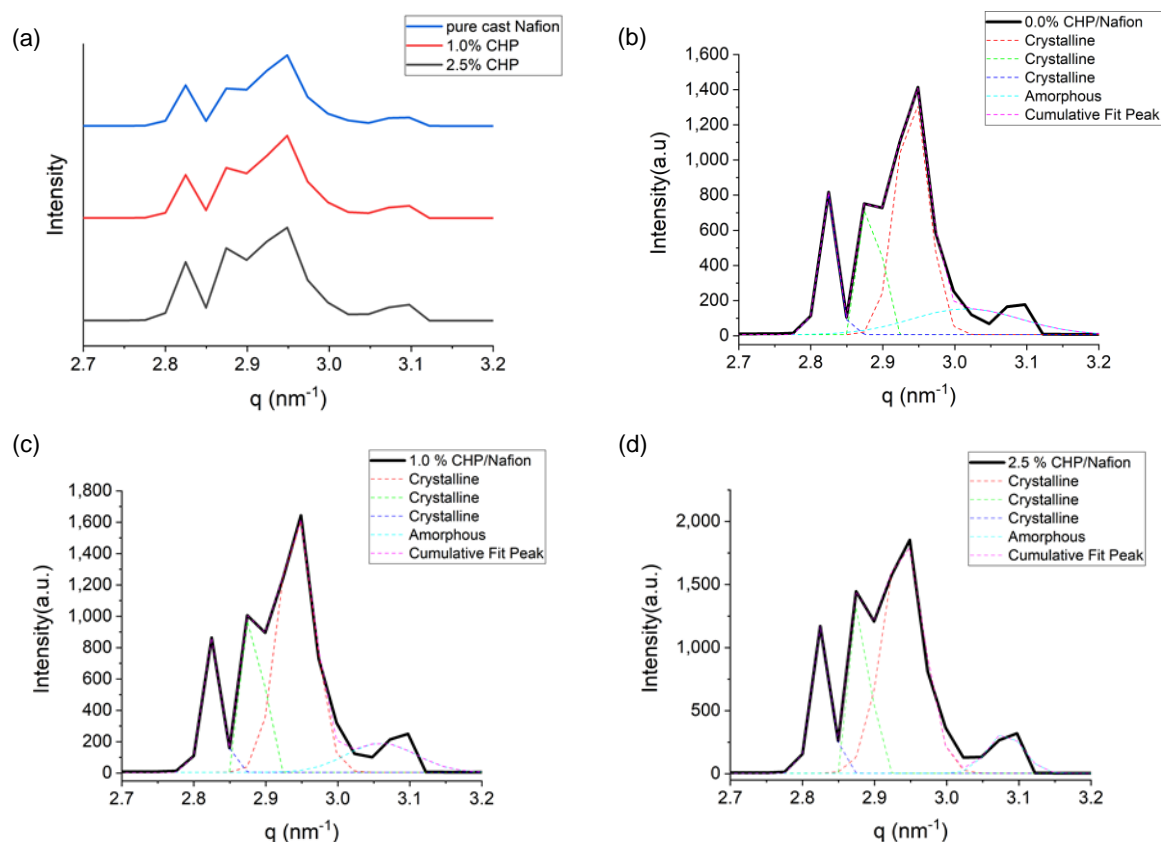


Figure 2: WAXS images (a) WAXS image of 0.0 wt% CHP/Nafion, 1.0 wt% CHP/Nafion, and 2.5 wt% CHP/Nafion (b) WAXS image of 0.0 wt% CHP/Nafion, (c) 1.0 wt% CHP/Nafion, and (d) 2.5 wt% CHP/Nafion.

4.5 Methanol permeability

At 30°C and 70°C, the permeability of Nafion membrane was reduced from $132.3 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ to $2.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $373.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ to $3.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ after added 1.0 wt% of CHP to the membrane (Table 1). It was clearly seen that incorporating of small amount of CHP into Nafion remarkably reduced the methanol crossover of membrane. This might be due to CHP occupied the former free volume of Nafion membrane in amorphous region preventing water molecule and methanol molecule to penetrate into the membrane and crossover to the other side (Park and Yamazaki, 2006). Adding more CHP into Nafion could not further decrease the methanol permeability compared to the previous work of (Park and Yamazaki, 2006) because of the glomeration of CHP particles resulting in lowering the ability to block methanol in water channel. The permeability rather depended on the dispersion of CHP within the free volume and ability of filler to block water and methanol molecule (Prapainainar et al., 2019).

Table 2: Water uptake, solubility and Ion exchange capacity of 0.0 wt% CHP/Nafion membrane, 1.0 wt% CHP/Nafion membrane, and 2.5 wt% CHP/Nafion membrane.

Membrane	CHP content (wt%)	Water Uptake (%)	Solubility (%)	Ion exchange capacity (mol/g)
0.0 wt% CHP/Nafion	0.0	49.24	0.7050	0.01023
1.0 wt% CHP/Nafion	1.0	21.03	0.9270	0.008490
2.5 wt% CHP/Nafion	2.5	11.05	1.698	0.003378

5. Conclusions

CHP/Nafion composite membrane was fabricated by solution casting method. The membrane was tested and characterized for DMFC. It was found that CHP had good compatibility with Nafion by showing well dispersion

throughout the Nafion membrane. Adding CHP into the Nafion resulted in an increase of crystallinity of the membranes, and lower methanol crossover. However, ion exchange capacity and water uptake were reduced which could potentially reduce the performance of DMFC base on Grotthuss and Vehicle mechanisms of proton transportation. Therefore, using 1.0 wt% of CHP as a filler to eliminate methanol crossover was suggested.

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