

Chitosan-Poly (Vinyl Alcohol) and Calcium Oxide Composite Membrane for Direct Methanol Fuel Cell Applications

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Abstract—Direct methanol fuel cell (DMFC) has been reported as a promising power source especially polymer electrolytes membrane (PEM) using perfluorosulfonic acid membrane or Nafion® (Du Pont). However the large-scale utilization of Nafion® in DMFC causes some issues such as low power density which is due to methanol crossover and dehydration at high temperature. In this work, new PEM composite membrane comprises of chitosan, polyvinyl alcohol (PVA) and calcium oxide (CaO) were fabricated. Our focus was to study the effect of CaO particle addition into chitosan-PVA conductivity and the feasibility of these membranes for DMFC application also was carried out. CaO particles have the profound effect on the chitosan-PVA conductivity. Fabricated membranes have moderate conductivity and lower methanol permeability compare to Nafion115®. These results indicate that chitosan-PVA-CaO composite membrane have excellent methanol barrier properties therefore feasible for DMFC applications.

Keywords-chitosan,direct methanol fuel cell, methanol permeability, hygroscopic-oxides

1. INTRODUCTION

The direct methanol fuel cell (DMFC) has been highlighted as a possible energy converter for portable, transportation and stationary power application. The polymer electrolyte membrane (PEM) technology plays an important role in the DMFC [1]. A perfluorosulfonic acid membrane or Nafion® (Du Pont) is widely used as proton conducting electrolyte membrane due to its excellence in the proton conductivity, good chemical resistance and high mechanical properties. However, large-scale utilization of Nafion® in DMFC is still constrained by high cost and dehydration at the high temperature operation. Furthermore, most Nafion® currently used in fuel cell modules are quite permeable to methanol and that leads to methanol crossovers to the oxygen/air cathode which eventually reduce the overall fuel efficiency of the system [2]. Therefore, the development of more cost-effective PEM with methanol permeability and suitable proton conductivity especially at high temperature is crucial. Poly-vinyl alcohol (PVA) has a low methanol permeability since PVA has been reported to have a low selectivity of water to alcohol [3]. The water retention of PEM at the

elevated temperature can be improved by incorporating hygroscopic particles such as Calcium oxide (CaO) [4]. Calcium oxide (CaO) is a hygroscopic oxide and proton conducting materials that has been used in construction industries, glass manufacturing as well as in a number of significant because they constitute a widely available and inexpensive solid sources of protons. In addition, CaO can be added to the Zirconia oxide (ZrO₂) to aid the oxygen ions conduction for high temperature operation of solid oxide fuel cell (SOFC) application [5]. On the other hand, natural polymers such as starch, cellulose and chitosan have been reported to have superior mechanical and electrical properties [6]. Several authors have reported that the plasticized starches have been developed as new material for solid polymer electrolyte (SPE). In this work, newer PEM materials comprised of PVA, chitosan and various weight ratios of CaO were fabricated. The feasibility study for DMFC application was also conducted.

2. EXPERIMENTAL AND MATERIALS

Membrane preparation

The membrane films were prepared by conventional casting method. Chitosan were dissolved in acetic acid and stirred for 6 hours at room temperature. Chitosan solution was then filtered to remove undissolved material. PVA and phosphotungstic acid were dissolved in hot 100 ml distilled water with constant stirring. The various weight ratio of CaO particles (0, 10, 15 and 20 wt%) were directly added into PVA,phosphotungstic acid and chitosan mixture; and the relative film was named as CPV0, CPV1, CPVS2, & CPV3). The mixture was heat at 70°C with constant stirring for 12 hours. Then the mixture was soaked in NaOH solution before it was washed with distilled water in order to eliminate any free ions from membranes. Lastly, fabricated membranes were then immersed in 0.05M phosphotungstic acid solution for 12 hours. The mixtures was casted into petri dishes and placed in air-convection oven at 60°C until dry (12 hours).. The average thickness of dry films was about 1.50mm. All samples were stored airtight under room temperature immediately

Morphological characterization using Scanning Electron Microscope (SEM)

All the fabricated membranes were dried and scanned by using SEM (JEOL Co.Ltd, Japan) with a magnification of 300X. All samples were coated with platinum before the scanning process.

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Water/methanol uptake

Water and methanol uptake of membranes were performed by drying the samples of known weight at 100°C for 24 hours, immersing them in deionized water and pure methanol and equilibrating it for 2 days. The weight of swollen membranes

(W_w) was measured carefully after carefully removing the liquid from both surfaces with filter paper. Weight of dry membrane (W_d) was determined after being completely dried after 60°C for 12 hours. The water uptake tests were calculated using Eq (1):

$$W U (\%) = \frac{(W_w - W_d)}{W_d} \times 100 \quad (1)$$

Methanol permeability

The methanol uptake was carried out in diffusion cell. Membranes (with effective area of 7.5 cm²) were clamped between chambers A and B (volume V of each chamber was 10 mL). Chamber A was filled with 1.5 M methanol, while chamber B filled with deionized water. The membrane was kept under stirring. The methanol concentration in the receptor chamber was measured using time using gas chromatography. The methanol permeability was calculated using Eq (2):

$$C_B(t) = \frac{A P}{V_B L} C_A (t - t_0) \quad (2)$$

where $C_B(t)$ is the concentration of methanol measured in the receptor compartment as a function of time, V_B the volume of the receptor compartment, L is the membrane thickness, A is the membrane area and P is the membrane permeability. Membrane permeability P was determined from the slope of the plot methanol concentration in the receptor compartment versus time.

Proton conductivity

The proton conductivity of each membrane was determined by AC impedance method. Membrane sample was equilibrated in deionized water for 24 h at room temperature before testing. The proton conductivity ($\sigma, S\text{cm}^{-1}$) of membrane was calculated using Eq.(3):

$$\sigma = \frac{L}{A R} \quad (3)$$

Where L (cm) and A (cm²) is are the thickness and area of the membrane samples respectively, and R is the membrane resistance derived from impedance data.

3. RESULTS AND DISCUSSIONS

Scanning Electron Microscope (SEM)

Fig.1 shows the surface area SEM images of chitosan-PVA and chitosan-PVA/CaO membranes. No obvious agglomeration of CaO particles was observed in CPV1 and CPV2, thus suggesting that CaO particle can be well dispersed in chitosan-PVA matrix and the fabricated membrane can be considered as homogenous and dense with no obvious phase separation. However, in case of CPV3, the agglomeration of various sizes of CaO particles which randomly dispersed within the chitosan-PVA matrix are observed. Due to the randomness of particle distribution, CPV3 can be regarded as quasi homogenous.

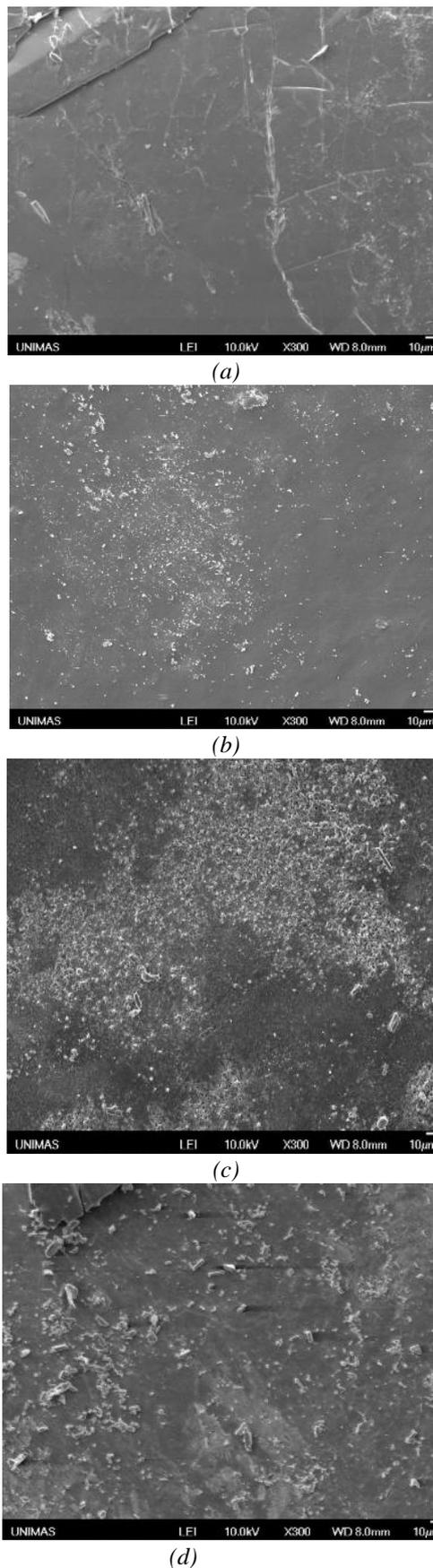


Fig. 1: SEMs of the surface of various membranes samples (a) CPV0 (b) CPV1 (c) CPV2 (d) CPV3

Water/Methanol Uptake

The effect CaO addition to the water and methanol uptake of the fabricated membrane is presented in **Fig.2**. The water uptakes are much higher than the methanol uptake. This is attributed to the higher water selectivity of chitosan-PVA matrix. On the other hand, the incorporation of CaO particles decreased the water and methanol uptake of the Chitosan-PVA membrane. This result suggests that CaO particles had priority to absorb methanol and water molecules therefore suppress the methanol transport in CaO particles..

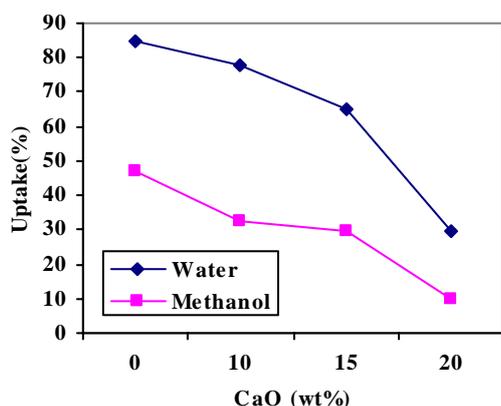


Fig.2: Water and methanol uptake of chitosan-PVA composite membrane as function of CaO (at room temperature)

Methanol Permeability

Fig.3 shows the methanol permeability data of the fabricated membrane. Methanol permeability (P) was determined from the slope of this graph using Eq. (2). The methanol permeability decreases with the increasing CaO content. Since the permeability coefficient is proportional to the product of diffusivity (D) and solubility (K), methanol diffusion coefficient (D) was also determined from the **Fig.3**, and the results shown in **Table 1**. In comparison with Nafion[®] 115, both methanol permeability (P) and diffusion of CPV membrane are much lower. This result also correlated with the lower methanol uptake result. Therefore, it can be suggested that CaO can act as methanol barrier which is likely to be from the high water and methanol sorption characteristic of CaO.

Proton conductivity

Fig.4 shows the proton conductivity of the CPV membrane as a function of CaO content at room temperature. The obtained proton conductivity values of CPV membranes were much lower than Nafion[®] 115 (1.4×10^{-2} S/cm) [6]. The proton conductivity of CPV membranes decrease with the CaO content. The reason for this result could relate to the low water sorption properties of the Chitosan-PVA- CaO matrix as proton conductivity of polyelectrolyte membrane governed by the water content [7]. In addition, at higher CaO weight ratio, CaO were agglomerate rather than penetrating into chitosan-PVA matrix. As a result, these CaO agglomeration disrupt the proton conduction, thus increased the proton transport resistance.

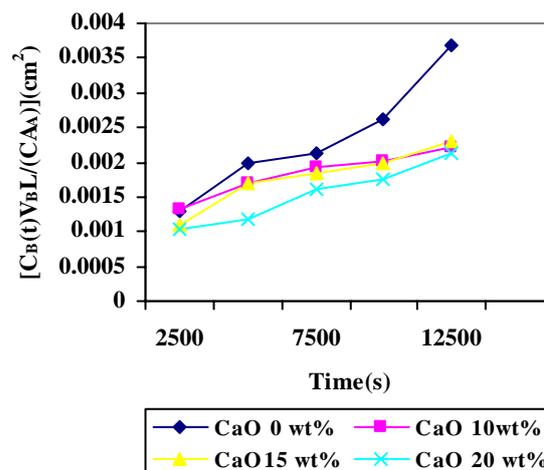


Fig 3: Methanol permeability of chitosan-PVA composite membrane as a function of CaO (at room temperature)

Table 1: The water and methanol permeability and diffusion coefficients of various CPV and Nafion[®] 115 membranes

Membrane	$P(\text{cm}^2\text{s}^{-1})$	$D(\text{cm}^2\text{s}^{-1})$
CPV0	3.19×10^{-8}	5.19×10^{-7}
CPVS1	1.62×10^{-8}	7.45×10^{-7}
CPVS2	1.59×10^{-8}	8.21×10^{-7}
CPVS3	1.03×10^{-8}	8.49×10^{-7}
Nafion [®] 115 ^a	1.8×10^{-6}	9.01×10^{-6}

^a Obtained from Ref.[6]

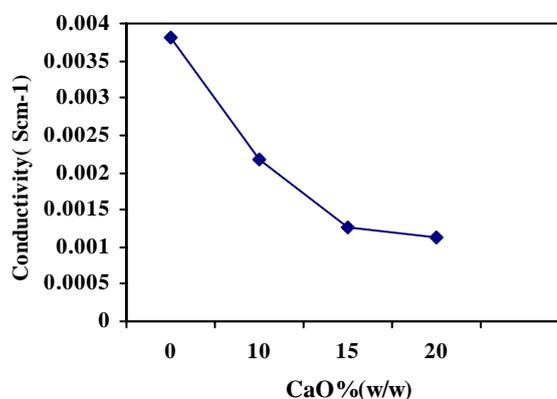


Fig.4 Proton conductivity of CPV membranes as a function of CaO content (at room temperature)

4. CONCLUSION

PVA-chitosan were fabricated and the effect of CaO particles addition were carried out. The following conclusions can be drawn from the experimental results:

- CaO particles decrease the water and methanol uptake of PVA-chitosan polymeric matrix due to the high water and methanol sorption properties of CaO.
- Methanol permeability in fabricated membrane is lower than Nafion[®]115, thus suggested that CaO could act as methanol barrier for direct methanol fuel cell.
- Incorporating CaO into PVA-chitosan matrix increases the proton transport resistance therefore resulting in a lower conductivity compare to Nafion[®]115

ACKNOWLEDGEMENT

The authors would like to acknowledge University Malaysia Sarawak (UNIMAS) for the generous financial support.

REFERENCES

- [1] H.Dohle, J.Divisek.,and ,R. Jung, (2000), "Process engineering of the direct methanol fuel cell", *Journal of Power Sources*, Volume86, pp469-477.
- [2] A.Heinzel, V.M.Barragan, (1999), "A review of the state-of-the-art methanol crossover in direct methanol fuel cells", *Journal of Power Sources*, Volume 84, pp 70-74.
- [3] A. Svang-Ariyaskul, and R.Y.M. Huang, (2006), "Blended chitosan and polyvinyl alcohol membranes for the pervaporation dehydration of isopropanol", *Journal of Membrane Science*, Volume 280, pp 815-823.
- [4] Y. Daiko., T., Kasuga, and M .Nogami., (2006), "Hygroscopic-oxides Nafion hybrid electrolyte for direct methanol fuel cells", *Journal of Membrane Science*, Volume 281, pp 619-625
- [5] Breeze,P.A., (2000), "Solid Oxide Fuel Cell", *Power Generation Technologies*, pp 99-100
- [6] L.V.S. Lopes, D.C. Dragunsk, and.A. Pawlicka,(2003), "Nuclear magnetic resonance and conductivity study of starch based polymer electrolyte", *Electrochimica Acta*, Volume 48, pp 2021-2027
- [7] Y.Wang, D.Yang, X.Zheng, Z.Jiang and J.Li, (2008), "Zeolite beta-filled chitosan membrane with low methanol permeability for direct methanol fuel cell,"*Journal of Power Sources*,Volume 183, pp 452-463
- [8] Y.F.Huang, L.C.Chuang,A.M.Kannan and C.W.Lin, (2009), "Proton-conducting membranes with high selectivity from cross-linked poly(vinyl alcohol) and poly(vinyl pyrrolidone) for direct methanol fuel cell applications",*Journal of Power Sources*,Volume 186, pp 22-28
- [9] B.Smitha, S.Sridhar and A.A.Khan,(2005), "Synthesis and Characterization of Poly(vinyl alcohol)-based membranes for direct methanol fuel cell", *Journal of Applied Polymer Science*, Vol 95,pp1154-1163