



## Performance of carbon dioxide vent for direct methanol fuel cells

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### ABSTRACT

Direct methanol fuel cells have potentially high energy density if the balance of plant and fuel losses can be kept to a minimum. CO<sub>2</sub> accumulation in the fuel tank can lower the efficiency and performance of closed-tank methanol fuel cells. This report discusses the implementation of a passive CO<sub>2</sub> vent fabricated with poly(1-trimethyl silyl propyne) and 1,6-divinylperfluorohexane. The performance of the membrane as a selective vent for carbon dioxide in the presence of methanol has been studied at various operating conditions. First, the selectivity of the vent membrane improved with temperature. Second, the activation energy for permeation through the polymer membrane corresponded to diffusion controlled transport of CO<sub>2</sub> and sorption controlled transport for methanol vapor. The activation energy for CO<sub>2</sub> transport through the poly(1-trimethyl silyl propyne) and 1,6-divinylperfluorohexane membrane was less than that for a pure poly(1-trimethyl silyl propyne) membrane. Finally, the polymer had a high selectivity for carbon dioxide compared to both liquid and vapor phase methanol.

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### 1. Introduction

Fuel cells are a promising source of alternative energy with minimal harmful byproducts [1,2]. Direct methanol fuel cells (DMFCs) are an attractive choice as a power source for stationary and small portable electronics due to their high energy density and the use of renewable fuel [3]. They may be appropriate for small, portable devices (e.g. microWatts to milliWatts), where size and weight are a premium. Such portable DMFCs must have a minimum of components, including pumps and pressure relief systems, to achieve the highest energy density.

In a DMFC, methanol is oxidized at the anode forming CO<sub>2</sub> [4,5]. Traditional DMFCs with an active fuel delivery system remove CO<sub>2</sub> through the re-circulating fuel channels, as shown by Yang et al. [6,7]. CO<sub>2</sub> bubbles formed in the anode field coalesce to form a CO<sub>2</sub> slug and are transported through the channel with methanol. However, in small, low-power DMFCs, the restricted volume prohibits the use of an active fuel delivery system or pump. Thus, it is desirable to passively deliver the fuel from a closed tank, such as by wicking, and discharge the CO<sub>2</sub> produced by venting without discharge of appreciable amounts of methanol.

The accumulation of CO<sub>2</sub> inside the closed fuel tank can lead to device failure. It is known that CO<sub>2</sub> adheres to the catalyst layer and blocks the catalyst from being electrochemically useful [5]. The pressure build-up within the tank can rupture the seal and accelerate methanol crossover through the membrane due to

pressure-driven flow. Thus, it is essential to design a CO<sub>2</sub> release mechanism that allows venting of CO<sub>2</sub> without the loss of substantial amounts of methanol.

One way to deal with CO<sub>2</sub> accumulation in portable DMFCs is the use of mechanical pressure relief micro-valve which periodically opens to relieve the excess pressure in the fuel tank's head-space. However, the complexity of this design, non-steady state operation, and venting of all gases in the head-space (not the selective venting of CO<sub>2</sub>) make this approach less desirable. Membrane technology on the other hand is a non-intrusive approach for separation processes. Polymeric or ceramic membranes are widely used for industrial grade gas separation processes and can achieve efficient separations [8].

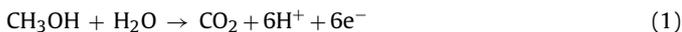
The transport mechanism of a gas or vapor molecule through a polymer layer is a function of the intrinsic interaction among transporting species, polymer matrix and the polymer structure. The overall polymer transport process is broadly dependent on two factors: polymer chain segmental mobility and the presence of defects in the form of voids and pores that influences the diffusion and sorption of a transporting moiety through the polymer [9]. Thus, it is important that the polymer membrane used for gas separation exhibit certain intrinsic properties that facilitate separation. According to Nakagawa et al., these intrinsic properties include high gas permeability coefficient, high separation factor between transporting molecules, the ability to form non-porous thin layers, and chemical and mechanical durability [10].

The polymer matrix must be paired with a fast moving permeate to achieve high gas permeabilities. Additionally, the individual components in a mixture must exhibit a difference in their interaction with the polymer backbone for high separation. As an example,

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the volatile and non-volatile species in a permeating mixture can interrelate uniquely with the voids and pores in a polymer structure and affect the chain mobility of the polymer backbone. While the non-volatile molecules diffuse through the porous interface of the membrane due to their unique interaction with the polymer backbone, the transport of volatile organic compounds (VOC) entails complex sorption and desorption process. The transport mechanism of VOC across a membrane layer involves three distinct steps: (1) adsorption on the upstream surface of the membrane, (2) diffusion through the bulk of the membrane matrix, and (3) desorption at the downstream interface of the membrane [11].

In this work, the transport of CO<sub>2</sub> and methanol through a polymer membrane are examined. The relative permeability of carbon dioxide and methanol are of interest here because both are present in the fuel tank, Eq. (1), however, the loss of methanol through a vent would not be desirable.



In an operating DMFC, methanol will be present in the headspace at its saturated vapor pressure while the CO<sub>2</sub> will achieve an equilibrium pressure based on the properties (i.e. rate of discharge) of the membrane vent and current (i.e. rate of production).

We have previously described the performance of two polymer membranes, poly(dimethyl siloxane) (PDMS) and poly(1-trimethyl silyl propyne) (PTMSP), for use as a CO<sub>2</sub> vent [12]. Both PDMS and PTMSP membranes are hydrophobic in nature and have high gas permeabilities [13,14]. Moreover, because the hydrophobic nature of the membrane suppresses the transport of hydrophilic methanol, these membranes are more permeable to CO<sub>2</sub> than to methanol [12,15]. The permeation rate of methanol and CO<sub>2</sub> through PDMS and PTMSP membranes were measured and the permeability coefficient,  $P_i$  was estimated from Eq. (2).

$$P_i = \frac{N_i l}{\Delta p A} \quad (2)$$

where  $N_i$  is the steady state rate of mass transfer of species  $i$  through the polymer matrix,  $l$  is the thickness of the polymer membrane,  $A$  is the area, and  $\Delta p$  is the pressure gradient of species  $i$  between the membrane interface. Since the permeability coefficient is an intrinsic property of the permeating molecule and the polymer membrane, it can be used to compare the performance of different permeates through the polymeric membrane. The performance of a membrane to act as a selective vent is expressed by considering the ratio of the permeation of CO<sub>2</sub> (the desired venting product) to the permeation of methanol (the undesired venting product) in Eq. (3) [12].

$$\alpha = \frac{P_{\text{CO}_2}}{P_{\text{MeOH}}} \quad (3)$$

where the figure of merit,  $\alpha$  is the ratio of the permeability coefficient of CO<sub>2</sub> ( $P_{\text{CO}_2}$ ) to methanol ( $P_{\text{MeOH}}$ ). It should be noted that at room temperature, the pressure of carbon dioxide within the tank can exceed the partial pressure of methanol, making the permeation rate of carbon dioxide much higher than methanol, Eq. (2). The results from our previous study show that PTMSP membranes exhibit higher values of  $\alpha$  than PDMS membranes. The permeability coefficient for CO<sub>2</sub> and methanol through the PDMS membrane are  $1.6 \times 10^{-9}$  and  $9.05 \times 10^{-10}$  mol cm cm<sup>-2</sup> day<sup>-1</sup> Pa<sup>-1</sup>, respectively, yielding an  $\alpha$  of 1.8. The corresponding values through a PTMSP membrane are  $1.7 \times 10^{-9}$  and  $8 \times 10^{-10}$  mol cm cm<sup>-2</sup> day<sup>-1</sup> Pa<sup>-1</sup>, respectively, giving an  $\alpha$  of 2.12. The presence of four hydrophobic methyl groups per monomer unit of the polymer on PTMSP helps increase the rate of transport of CO<sub>2</sub> with respect to methanol. Furthermore, the presence of a molecular sieve like matrix in the PTMSP network improves the permeability of the transporting molecules resulting in a less tortuous path for transport through the

membrane [16]. Lastly, the addition of hydrophobic additives like 1,6-divinylperfluorohexane and 1,9-decadiene to PDMS and PTMSP membranes enhances the selectivity resulting in values of  $\alpha$  as high as 9.2 [12].

In this work, the performance of the CO<sub>2</sub> vent membrane as function of temperature is investigated along with other performance parameters including a comparison of liquid and gaseous methanol.

## 2. Theory

The permeability coefficient of a permeate through a polymer matrix can be estimated using Nernst distribution function, Eq. (4) [17–19].

$$P_i = D_i \cdot S_i \quad (4)$$

where  $D_i$  is the diffusion coefficient and  $S_i$  is the sorption (solubility) coefficient of species  $i$ . The mode of transport of a molecule through a glassy polymer matrix is a function of the intersegmental attraction between the permeating species and the polymer matrix. The permeation of gases is generally diffusion controlled, while the permeation of a condensable vapor is sorption controlled. Often the mechanism of permeation and its dependence on diffusion and sorption is explained through the solution–diffusion model, as shown in Eq. (5) [10,20].

$$E_p = E_D + \Delta H_S \quad (5)$$

where  $E_p$  is the activation energy of permeation,  $E_D$  is the activation energy for diffusion, and  $\Delta H_S$  is the change in enthalpy of sorption. The value of  $E_p$  can be estimated using an Arrhenius relationship between  $P_i$  and temperature,  $T$ , as given in Eq. (6) [20].

$$P = P_A \exp\left(\frac{-E_p}{RT}\right) \quad (6)$$

where  $P_A$  is the pre-exponential constant and  $R$  is the gas constant.

The amount of CO<sub>2</sub> generated inside a DMFC tank is directly proportional to the methanol oxidation rate assuming six equivalents per mole. At steady state, if it is assumed that the rate of CO<sub>2</sub> generation is the same as its release rate through the vent ( $N_{\text{CO}_2}$ ), then the flux of CO<sub>2</sub> can be defined in terms of current ( $i$ ) as shown in Eq. (7).

$$N_{\text{CO}_2} = \frac{i}{nF} \quad (7)$$

where  $n$  is number of equivalents per mole and  $F$  is Faraday's constant. Eq. (2) and (7) can be used to define the theoretical vent efficiency, Eq. (8).

$$\gamma_{\text{theoretical}} = \frac{i/nF}{(i/nF) + (P_{\text{MeOH}} \Delta p A)/L} \quad (8)$$

where  $\Delta p$  is the saturated vapor pressure of methanol (assuming the partial pressure of methanol outside the tank is zero),  $A$  is the cross-sectional area of the membrane, and  $L$  is the thickness of the membrane. Additionally, the efficiency of the vent can be defined as the ratio of the measured CO<sub>2</sub> flux ( $N_{\text{CO}_2}$ ) to that of the total flux through the vent membrane, Eq. (9).

$$\gamma_{\text{experimental}} = \frac{N_{\text{CO}_2}}{N_{\text{CO}_2} + N_{\text{MeOH}}} \quad (9)$$

## 3. Experimental

PTMSP was obtained from Gelest Corporation and was dissolved in toluene at room temperature. The amount of solvent in the polymer was adjusted to obtain a desired viscosity of the polymer mixture so as to facilitate spin coating. Thin films of the membrane were spin coated on a Teflon substrate. Slow evaporation of the solvent was achieved by placing the cast membrane

in a pressure vessel at 90 psia (600 kPa absolute) and 60 °C for 3 h. The resulting membranes were peeled from the substrate. In this study, hydrophobic additive, 1,6-divinylperfluorohexane (97%) (Matrix Scientific), was mixed with PTMSP membranes. A single layer membrane was cast from a liquid mixture of the two components. The amount of additive in the mixture was 10% of the total weight.

Small 0.5 mm × 0.5 mm membrane samples were prepared for thermogravimetric analysis (TGA) using a TA Instruments TGA Q500. The temperature was ramped at 10 °C min<sup>-1</sup> in a nitrogen atmosphere.

The permeability coefficient of CO<sub>2</sub> and methanol were measured using a quadrupole mass spectrometer QMS 100 Series Gas Analyzer by Stanford Research Systems. The QMS was paired with a pressure vessel and a 4836 Parr temperature controller. The details of the system schematic has been described in our previous work [12].

The theoretical and experimental efficiencies of the CO<sub>2</sub> vent was evaluated as a function of current by designing in situ experiment. For this setup, known flow rates of CO<sub>2</sub> were used to calculate the current flow in DMFC systems, using Eq. (7). The design limitation on micro-DMFCs for portable applications requires the volume of the system in the range of 1–5 cm<sup>3</sup>, with a current demand of 100–500 μA. As a result, the current to volume ratio is approximately 10<sup>-3</sup> A cm<sup>-3</sup>. The fuel cell operating condition was replicated by changing the CO<sub>2</sub> flow rate such that the current to volume ratio was kept constant in the 10<sup>-3</sup> A cm<sup>-3</sup> range. For estimating experimental efficiency, CO<sub>2</sub> was allowed to enter the methanol tank at a known flow rate such that the current to volume ratio remained constant at 10<sup>-3</sup> A cm<sup>-3</sup>. The exit stream from the methanol tank via the CO<sub>2</sub> vent window was sampled by the quadrupole mass spectrometer, till steady state conditions were achieved. At steady state, the flux of methanol and CO<sub>2</sub> in the exhaust stream was measured by the spectrometer. The experimental efficiency was estimated at each CO<sub>2</sub> flow rate (and therefore at the corresponding current) using the measured steady state flux in conjunction with Eq. (9) above.

The theoretical flux of CO<sub>2</sub> and methanol through the vent was calculated from Eq. (2). The permeability coefficients used for theoretical flux estimation are 7.56 × 10<sup>-9</sup> and 2.16 × 10<sup>-9</sup> mol cm cm<sup>-2</sup> day<sup>-1</sup> Pa<sup>-1</sup>, for CO<sub>2</sub> and methanol respectively. The theoretical efficiency of the vent was estimated using the calculated theoretical fluxes in conjunction with Eq. (8).

#### 4. Results

Thermogravimetric analysis was used to test the thermal stability of the vent material. Membrane samples were prepared by mixing PTMSP with 1,6-divinylperfluorohexane at a 1:0.1 weight ratio. Previous experiments for permeation for this polymer ratio resulted in an  $\alpha$  of 4.5 [12]. Fig. 1 shows the thermogravimetric degradation profile of a PTMSP and 1,6-divinylperfluorohexane blend. The polymer film shows no sign of weight loss or thermal degradation from 20 to 90 °C. The weight loss starts at about 90–100 °C and continues at the rate of 0.03% per degree to about 210 °C. Between 210 and 350 °C, the polymer film shows a negligible weight loss. Beyond 350 °C, the polymer film's weight drops sharply, indicating bulk polymer degradation.

The experimental procedure for estimating the permeability coefficient was similar to that previously reported [12]. Fig. 2 shows the permeability coefficient of CO<sub>2</sub> and methanol as a function of temperature from 20 to 50 °C for the individual-component and mixture experimental setups. The flux of methanol and CO<sub>2</sub> through a PTMSP and 1,6-divinylperfluorohexane blend were measured at 22, 30, 40, 45, and 50 °C. The permeabil-

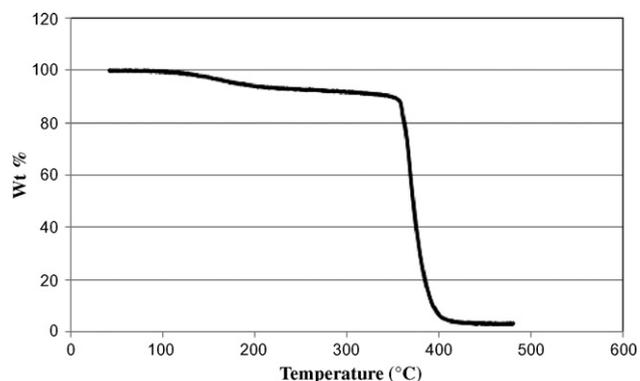


Fig. 1. TGA of PTMSP with 1,6-divinylperfluorohexane at 1:1 weight ratio.

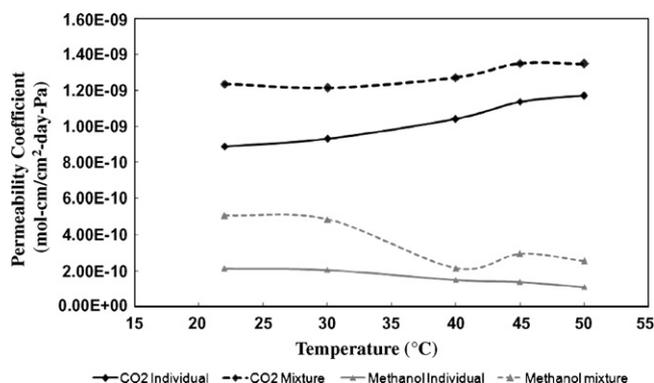


Fig. 2. Permeability coefficients of CO<sub>2</sub> and methanol through PTMSP and 1,6-divinylperfluorohexane.

ity coefficients were not measured at temperatures above 50 °C to avoid methanol boiling. Using Eq. (2), the measured fluxes were translated into the corresponding permeability coefficients. For consistent results, the same membrane (2.85 cm<sup>2</sup> area and 150 μm thick) was used in both experimental setups. The permeability coefficient of methanol decreased with increase in temperature, and the permeability coefficient of CO<sub>2</sub> increased. This trend was observed in both individual-component and mixture setups. At ambient temperature, the permeability coefficient of CO<sub>2</sub> was 9 × 10<sup>-10</sup> and 1.2 × 10<sup>-9</sup> mol cm cm<sup>-2</sup> day<sup>-1</sup> Pa<sup>-1</sup> for the individual and the mixture setup, respectively. The CO<sub>2</sub> permeability coefficient at 50 °C was estimated to be 1.21 × 10<sup>-9</sup> moles cm cm<sup>-1</sup> day<sup>-1</sup> Pa<sup>-1</sup> for individual-component experiment. In the presence of methanol, the CO<sub>2</sub> permeability was essentially the same: 1.35 × 10<sup>-9</sup> mole cm cm<sup>-2</sup> day<sup>-1</sup> Pa<sup>-1</sup>.

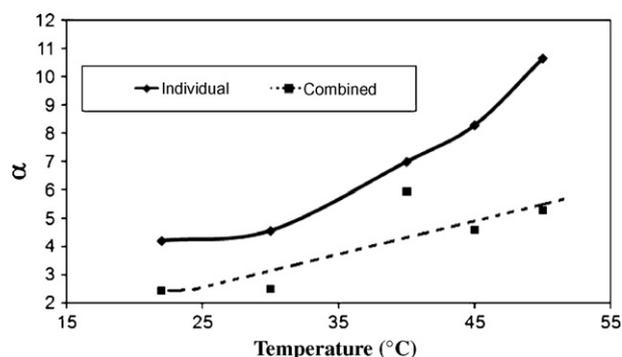


Fig. 3. Values of  $\alpha$  as measured through PTMSP and 1,6-divinylperfluorohexane membrane.

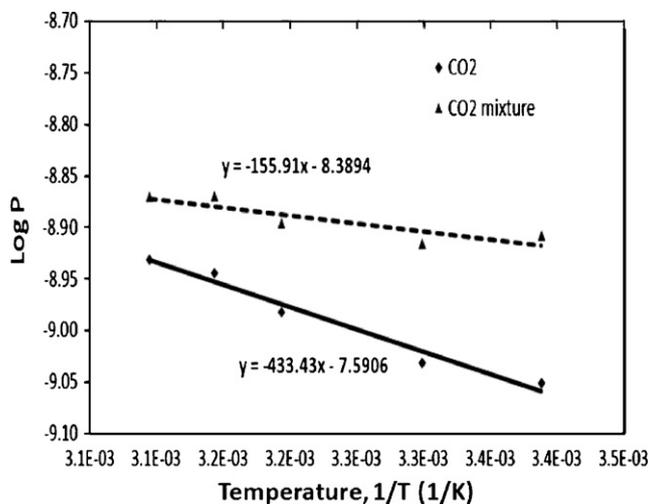


Fig. 4. Arrhenius plot of CO<sub>2</sub> permeability coefficient through PTMSP and 1,6-divinylperfluorohexane.

Fig. 3 shows the value of  $\alpha$  for both the individual-component and mixture experiments. The value of  $\alpha$  was determined from the permeability coefficients of CO<sub>2</sub> and methanol using Eq. (3). The values of  $\alpha$  increased as the temperature increased from 20 to 50 °C. While it increased from 4.2 to 10.6 for the individual-component experiment, the increase for the mixture experiment was comparatively lower (2.8–5.3).

Figs. 4 and 5 show the Arrhenius relationship for CO<sub>2</sub> and methanol permeability coefficient. The activation energy of permeation ( $E_p$ ) through PTMSP and 1,6-divinylperfluorohexane was estimated from the slope of the curve in Figs. 4 and 5, using Eq. (6). The  $E_p$  of pure CO<sub>2</sub> through the vent membrane was 3.603 kJ mole<sup>-1</sup>. However, in the presence of methanol,  $E_p$  for CO<sub>2</sub> was comparatively lower at 1.296 kJ mole<sup>-1</sup>. While the  $E_p$  for pure methanol was -9.03 kJ mole<sup>-1</sup>, the  $E_p$  for methanol in mixture was -8.08 kJ mole<sup>-1</sup>.

Fig. 6 shows the theoretical and experimental efficiency of the CO<sub>2</sub> vent as a function of the operating current. At each operating current, the theoretical and experimental efficiencies were estimated from Eq. (8) and (9) in conjunction with the calculated and the measured fluxes. The permeability coeffi-

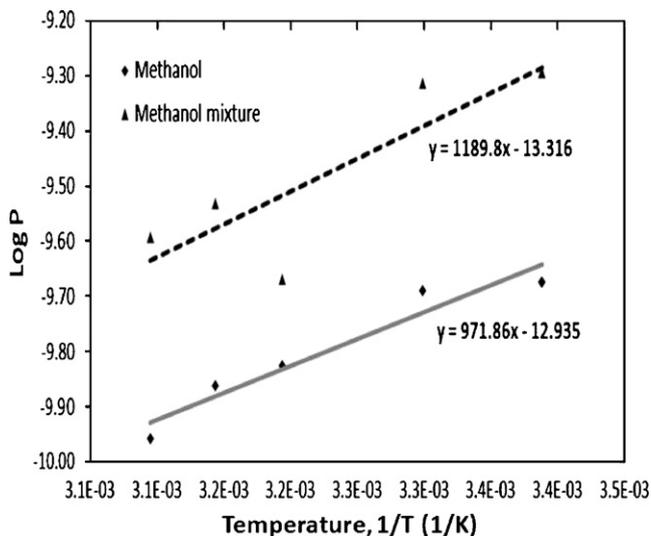


Fig. 5. Arrhenius plot of methanol permeability coefficient through PTMSP and 1,6-divinylperfluorohexane.

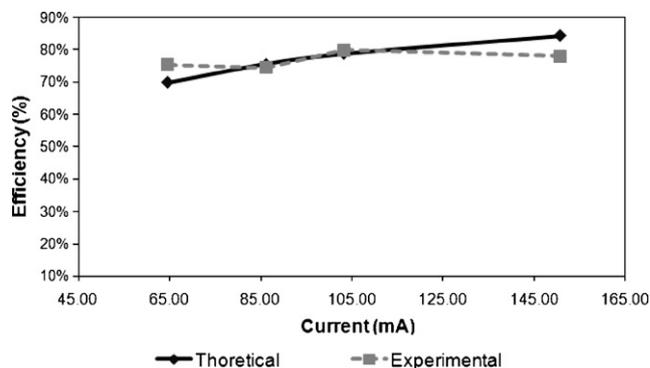


Fig. 6. Theoretical and experimental efficiency of CO<sub>2</sub> vent membrane as a function of operating current.

cients used for theoretical flux estimation are  $7.56 \times 10^{-9}$  and  $2.16 \times 10^{-9}$  mol cm cm<sup>-2</sup> day<sup>-1</sup> Pa<sup>-1</sup>, for CO<sub>2</sub> and methanol, respectively. The steady state flux of CO<sub>2</sub> and methanol was measured using the response from the quadruple mass spectrometer at each operating current, which corresponded to a unique CO<sub>2</sub> flow rate. The theoretical and experimental efficiencies are very close to each other. The overall efficiency for a 10-to-1 PTMSP-to-1,6-divinylperfluorohexane membrane is approximately 80%.

When a DMFC is operating in an upright condition, the CO<sub>2</sub> vent is in contact with methanol vapor and CO<sub>2</sub> gas. However, if the orientation is changed (or the tank is full), it is likely that the vent will be in direct contact with liquid methanol (wet condition). A permeation experiment, with the vent window below the liquid level, was designed to evaluate the performance of the CO<sub>2</sub> vent in contact with liquid methanol. The total driving force for liquid methanol transport is due to the saturated vapor pressure of methanol and the pressure due to the liquid column of methanol. The driving force for CO<sub>2</sub> transport in wet condition is a function of Henry's Law for CO<sub>2</sub> solubility in methanol and its partial pressure in gas phase. Table 1 shows the permeability coefficient of methanol and CO<sub>2</sub> under wet (liquid methanol) and dry (methanol vapor) conditions. The permeability coefficient of CO<sub>2</sub> under liquid methanol conditions is lower than that under methanol vapor conditions. The permeability coefficient of methanol in liquid and vapor conditions is approximately the same ( $1.9 \times 10^{-9}$  mol cm cm<sup>-1</sup> day<sup>-1</sup> Pa<sup>-1</sup> vs.  $2.1 \times 10^{-9}$  mol cm cm<sup>-1</sup> day<sup>-1</sup> Pa<sup>-1</sup>). As a result, the value of  $\alpha$  is higher in vapor conditions than in liquid conditions.

## 5. Discussion

CO<sub>2</sub> accumulation in a "stand alone DMFCs" has been addressed in our previous study. It was reported that a CO<sub>2</sub> vent fabricated with polymer blends of PTMSP and PDMS membranes have high selectivity for CO<sub>2</sub> over methanol [12]. The results generated from models for the CO<sub>2</sub> vent show high selectivity, controlled methanol loss, and negligible sensitivity to abrupt changes in operating current of the DMFC. It was also observed that a combination of PTMSP and 1,6-divinylperfluorohexane has the highest values of  $\alpha$  [12]. The current study addresses the performance of the CO<sub>2</sub> vent as a function of temperature and provides experimental validation for carbon dioxide and methanol mixtures.

Table 1

Permeability coefficients of CO<sub>2</sub> and methanol (mol cm cm<sup>-2</sup> day<sup>-1</sup> Pa<sup>-1</sup>) in wet and dry conditions.

	CO <sub>2</sub>	Methanol	$\alpha$
Dry conditions	$7.56 \times 10^{-9}$	$2.1 \times 10^{-9}$	3.6
Wet conditions	$2.8 \times 10^{-9}$	$1.9 \times 10^{-9}$	1.5

Fig. 1 shows the thermogravimetric analysis of PTMSP with 1,6-divinylperfluorohexane (9:1, wt%) membrane. The negligible weight loss from 20 to 90 °C shows that the vent membrane is thermally stable at the normal DMFC operating temperatures. The onset of first weight loss at 90–100 °C corresponds to the removal of 1,6-divinylperfluorohexane, according to the manufacturer's data. The accumulated weight loss at 210 °C corresponds to the volatilization of the 10% of 1,6-divinylperfluorohexane contained in the mixture. The sharp decline observed at about 350 °C corresponds to the weight loss due to the PTMSP backbone. The high decomposition temperature suggests that the polymer blend formed by the mixture of PTMSP and 1,6-divinylperfluorohexane is glassy in nature, and exhibits behavior similar to that observed by Nakagawa et al. for pure PTMSP with a  $T_g$  above 300 °C [10].

The temperature dependence of the CO<sub>2</sub> and methanol permeability coefficients (Fig. 2) shows that while the overall permeability coefficient of CO<sub>2</sub> through PTMSP and 1,6-divinylperfluorohexane increased with temperature, the permeability of methanol decreased with temperature. At high temperature, CO<sub>2</sub> molecules acquire sufficient kinetic energy to increase their diffusivity and flux through the membrane. The flux of hydrophobic CO<sub>2</sub> molecules through the pores of the PTMSP matrix is governed by molecular and Knudsen diffusion. This observation is supported by Koros and Fleming who describe diffusion-dominated transport through the permeating polymer [21]. Furthermore, Wijmans and Baker found that the large free volume available in a glassy matrix facilitates diffusion of non-condensable molecules and allows for a pore-flow mechanism [22]. Thus, at higher temperature, the diffusion of CO<sub>2</sub> molecules through the pores increases, leading to an increase in their permeability coefficient.

On the other hand, the transport of methanol through a hydrophobic polymer is a sorption-dominated process. The phenomenon is similar to the behavior observed by Morlière et al. where the decrease in permeability coefficient of the permeate vapors with temperature is due to the decrease in their sorption properties [23]. Chandak et al. have also shown a sorption-based transport mechanism for volatile organic compounds (VOCs) [11]. The transport mechanism involves sorption of VOC at the membrane interface, followed by diffusion through the polymer bulk, and desorption at the downstream interface of the polymer membrane [11].

During pervaporation, the VOC molecules come in contact with the upstream interface of the glassy membrane and undergo a phase change resulting in condensation on the porous surface [24]. Barer et al. have found that the presence of a fine-mesh supported micro-porous structure of PTMSP matrix facilitates the adsorption of condensed vapors [25]. As a result, the pores fill with VOC molecules producing capillary condensation, which blocks the open face of the pores and prevents further adsorption [25,26]. Prabhakar et al. have also reported a similar observation where the entrapped methanol in the pores of the polymer create bottlenecks in the free volume network [27]. These bottlenecks restrict the flow of methanol through the bulk of the polymer matrix. As temperature increases, more energy is spent in overcoming the barriers to transport, compared to the actual transport mechanism. Consequently, the adsorption of methanol into the porous microstructure of PTMSP and 1,6-divinylperfluorohexane becomes a relatively slow process. Thus, as the temperature increases, sluggish transport of methanol is observed through the polymer matrix resulting in a decrease in the permeability coefficient.

Fig. 2 also shows that the overall permeability coefficient of methanol is higher in the presence of CO<sub>2</sub> (mixture experiment) than in the individual-component experiment. In the absence of a second species (i.e. CO<sub>2</sub>), the bottlenecks for transport formed within the free volume network of the polymer impedes the transport of methanol. However, in a binary system (i.e. combined carbon

dioxide and methanol experiments), some of the trapped methanol within the polymer free volume network is flushed out with CO<sub>2</sub>. As a result, the permeability coefficient of methanol is higher in the mixture experiment than in individual-component experiment. As a consequence, the figure of merit  $\alpha$ , as shown in Fig. 3, is higher for the individual-component experiment than for the mixture experiment. In both cases, the values of  $\alpha$  increase with temperature, indicating a more favorable CO<sub>2</sub> transport mechanism through the polymer matrix.

The Arrhenius relationship, as shown in Eq. (6), can be used to describe the transport pathway of a molecule through a polymer matrix and understand the transport mechanism. From Fig. 4, the activation energy of permeation ( $E_p$ ) of CO<sub>2</sub> was 3.6 and 1.3 kJ mole<sup>-1</sup> for the individual-component experiment and mixture experiment, respectively. A positive  $E_p$  value indicates a diffusion controlled mechanism for CO<sub>2</sub> transport. The lower  $E_p$  value for CO<sub>2</sub> in the mixture experiment indicates a lower barrier for CO<sub>2</sub> permeation through the polymer matrix in the presence of methanol vapor. The lower value of  $E_p$ , and thus better permeability for the mixture experiment is a consequence of the synergistic nature of the combined CO<sub>2</sub>–methanol transport.

In a previous study, Merkel et al. reported that the CO<sub>2</sub> permeation activation energy through pure PTMSP is –6.8 kJ mole<sup>-1</sup> [16]. The difference between this activation energy for pure PTMSP and the value here for the PTMSP and 1,6-divinylperfluorohexane blend, can be attributed to the difference in the polymer properties. Since the polymer blend studied here is more hydrophobic than pure PTMSP [12], CO<sub>2</sub> experiences a smaller barrier to transport. As a result, the hydrophobic CO<sub>2</sub> can more easily diffuse through the polymer blend (lower magnitude of activation energy) in comparison to pure PTMSP.

The activation energy for permeation is a negative quantity (–9 and –8 kJ mole<sup>-1</sup>) for methanol transport through the polymer blend, Fig. 5. The negative value supports the sorption-dominated transport model for methanol and can be explained by the solution–diffusion theory, Eq. (5) [10]. The activation energy of permeation is the sum of the activation energy of diffusion ( $E_D$ ) and the change in enthalpy of sorption ( $\Delta H_S$ ). The enthalpy of sorption of methanol decreases as the methanol vapors condense (compared to methanol in the vapor phase) within the polymer matrix. Thus,  $\Delta H_S$  for methanol in the polymer blend is a large negative value for vapor at elevated temperature. This causes the value of  $E_p$  for methanol to be dominated by the more negative  $\Delta H_S$  at high temperature. It is not compensated by the small positive value of  $E_D$ . As a result, the activation energy for permeation for methanol through the PTMSP and 1,6-divinylperfluorohexane membrane is a negative value.

Fig. 6 shows the theoretical and experimental efficiency of the CO<sub>2</sub> vent as a function of the operating current. At 9:1 ratio of PTMSP-to-1,6-divinylperfluorohexane, the efficiency of the vent is approximately 80%, for both theoretical and experimental cases regardless of the operating current. That is, if the DMFC were to operate with this vent, only 20% of the available fuel would be lost through the CO<sub>2</sub> vent. If a higher PTMSP-to-1,6-divinylperfluorohexane ratio were used, the efficiency would be higher, reaching to 95% at 1:1 weight ratio of PTMSP-to-1,6-divinylperfluorohexane.

The comparison between the liquid and vapor permeation of methanol (Table 1) shows a slight decrease in the permeability coefficient for CO<sub>2</sub> when in the liquid condition, which is due to the low solubility of CO<sub>2</sub> in methanol (Henry's law constant of 0.489 MPa) at room temperature [28]. The permeability coefficient for liquid and vapor methanol are about the same. Methanol vapor forms a thin layer of condensed liquid when it comes in contact with the polymer surface. Thus, the permeability coefficient for methanol liquid and vapor are similar.

## 6. Conclusion

The performance of PTMSP and 1,6-divinylperfluorohexane membranes as a selective CO<sub>2</sub> vent was studied. It was observed that the permeability coefficient for CO<sub>2</sub> increased with temperature while that for methanol decreased. The observed behavior was due to a difference in the transport mechanism of CO<sub>2</sub> and methanol through the polymer membrane. The transport process of small, hydrophobic CO<sub>2</sub> molecules through the hydrophobic membrane is diffusion controlled. As a result, their permeability coefficient increased with temperature. Methanol, on the other hand, was transported by a sorption controlled mechanism and required condensation of the vapor within the membrane resulting in a permeability coefficient which decreased with temperature. Furthermore, the solution–diffusion model and the measured activation energies of permeation ( $E_p$ ) also support the transport process of CO<sub>2</sub> and methanol. The positive  $E_p$  for CO<sub>2</sub> corresponds to a high diffusivity while the negative  $E_p$  for methanol vapor corresponds to a large negative change in enthalpy of sorption.

The theoretical model for the CO<sub>2</sub> vent was validated with experimental results. A membrane with a 9:1 ratio of PTMSP-to-1,6-divinylperfluorohexane had an 80% vent efficiency regardless of the operating current. Based on the above results, higher efficiencies could be achieved at higher concentrations of 1,6-divinylperfluorohexane in the polymer blend. It was observed that on contact with liquid methanol, the vent membrane showed a small decrease in CO<sub>2</sub> permeability due to low solubility of CO<sub>2</sub> in methanol. Nonetheless, the vent membrane was more selective to CO<sub>2</sub> than methanol.

This study shows that the CO<sub>2</sub> vent is a feasible method of discharging CO<sub>2</sub> from a closed methanol fuel tank. Its selectivity towards CO<sub>2</sub> over methanol remained unaltered at high temperature and when in contact with liquid methanol. Finally, the vent can be customized using the model to achieve a desired efficiency and performance.

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