



Dramatic Reduction of Water Crossover in Direct Methanol Fuel Cells by Cathode Humidification

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As a key parameter in enabling the operation of high concentration methanol fuel cells, the water transport coefficient through the membrane must be reduced to between 0 and $-1/6$. We show that this coefficient can be lowered to -0.7 at 60°C and under common cathode flow conditions using fully humidified air. A previously developed membrane electrode assembly based on a Nafion 112 membrane was used. The present result gives rise to the possibility of achieving a water-neutral state for use of pure methanol, i.e., with the water crossover coefficient of $-1/6$, under temperatures much higher than 60°C and in active air-flowing direct methanol fuel cell systems with high power density.

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Direct methanol fuel cells (DMFCs) are attractive power sources for mobile and wireless devices principally because of their high energy density and easy storage of liquid fuel.¹ Work in our laboratory has demonstrated the paramount importance of water crossover through the membrane in the development of high concentration methanol fuel cells (HC-MFCs) with high performance and alleviated cathode flooding.²⁻⁴ We first revealed the direct link between the water transport coefficient (α) through the membrane and the maximum possible methanol concentration used in the anode feed, and thus proposed the development of a low- α membrane electrode assembly (MEA).²⁻⁴ Here α is defined as the ratio of the net water flux through the membrane to the protonic flux. The α value for the conventional DMFCs based on Nafion 117 is roughly 2.5,⁵ which corresponds to a theoretical maximum methanol concentration of ~ 3 M, thus dramatically limiting the energy density of a DMFC system. A 10 M methanol operation requires an MEA to have α equal to or smaller than 0.6. To enable the direct use of pure methanol, α must be reduced to $-1/6$.³ Over the past few years, much effort has been expended on reducing α ,^{2-4,6-8} but the lowest α value that can be experimentally achieved is ~ 0.6 at 60°C , atmospheric pressure, and under active cathode flow, due to Wang and co-workers.²⁻⁴ Such low α value was realized by using an MEA developed by Lim and Wang⁹ based on Nafion 112 membranes. To enable the use of concentrated methanol solutions higher than 10 M, there is a clear need to dramatically reduce α to below zero.

Previous research has identified several key factors influencing α , which are listed in the following order of significance: (i) the presence of a hydrophobic anode microporous layer (MPL), (ii) cell temperature, (iii) cathode airflow stoichiometry, and (iv) the presence of a cathode MPL. The present communication reports that by using cathode humidification such as humidified air, we achieve ultralow and even negative water crossover from the anode to the cathode using the same MEA we developed previously. Moreover, we show how to control α over a wide range by varying the relative humidity (RH) of air, thus providing an excellent laboratory tool to study the impact of water crossover through the membrane on various cell designs and operations of HC-MFCs.

Experimental

Both MEA fabrication and experimental hardware have been detailed in previous publications^{2,3} and thus were not repeated here. The cathode gas diffusion layer (GDL) was a carbon cloth with a precoated hydrophobic MPL containing carbon black and poly(tetrafluoroethylene) (PTFE). Carbon papers with 10% wet proofing (Toray TGPH 090) were used as the anode GDL. A mixture of

Vulcan XC72R carbon black and 40 wt % PTFE (TFE 30, DuPont) was coated on the carbon paper using a gap-adjustable blade to fabricate a hydrophobic MPL with the loading of 2 mg/cm^2 (carbon and binder). An MEA of 12 cm^2 based on Nafion 112 membrane was prepared by the decal method. The catalyst loadings in the anode and cathode catalyst layer were 5.3 mg PtRu/cm^2 and 1.2 mg Pt/cm^2 , respectively. The MEA was mounted between two identical graphite flow plates with two-pass serpentine channels. The cell was operated at 60°C and ambient pressure on both sides. A 2 M methanol solution (0.19 mL/min) and air (97.3 mL/min) were fed to the anode and cathode, corresponding to stoichiometries of 2 and 3, respectively, at 150 mA/cm^2 . The total water collected from the cathode exit at constant-current discharge, including the water produced from the oxidation of the crossover methanol, was used to calculate the net water transport coefficient α as detailed in Ref. 2 and 3.

Results and Discussion

The constant-current discharge of the cell was performed at 60°C and ambient pressure on both sides. DMFC voltage variations over discharge time at 150 mA/cm^2 are recorded in Fig. 1 for various RHs of cathode air. It is seen that as the air RH increases, the cell performance improves. There is almost a 30 mV gain between the dry and fully humidified air cases. During constant-current discharge at 150 mA/cm^2 , the water collected from the cathode outlet stream was used to calculate α values, which are displayed in Fig. 2 as a function of the air RH. It is noticed that α is approximately 0.7 in the case of dry air, in good agreement with previous measurements.^{2,3} However, as the air RH increases, α is dramatically reduced, reaching zero at about 65% RH and -0.7 at 100% RH. This low α is a key requirement for the successful demonstration of the direct use of highly concentrated methanol in the anode of an HC-MFC.¹⁰ Physically, $\alpha = 0$ means that there is no water crossing through the membrane and the cathode contains only the product water from the oxygen reduction reaction (ORR). When α approaches -0.7 , it implies that not only all the product water generated from ORR on the cathode flows back to the anode, which is equivalent to $\alpha = -0.5$, but that some water contained in the fully humidified air stream also moves from the cathode to the anode side. This brings about dual benefits: cathode flooding is alleviated despite the fully humidified air entering the inlet, and there is significant dilution of the methanol solution in the anode by water coming from the cathode. The former effect is demonstrated by a stable cell performance, as shown in Fig. 1, and the latter effect is clearly illustrated in Fig. 3, where the methanol concentration in the anode effluent is measured by using an ice trap and densitometer and plotted as a direct function of the dimensionless water crossover rate through the membrane. The feed concentration and flow stoichiometric ratio at the anode inlet were fixed at 2 M and 2, respectively, at 150 mA/cm^2 in all experiments. The cell was discharged at

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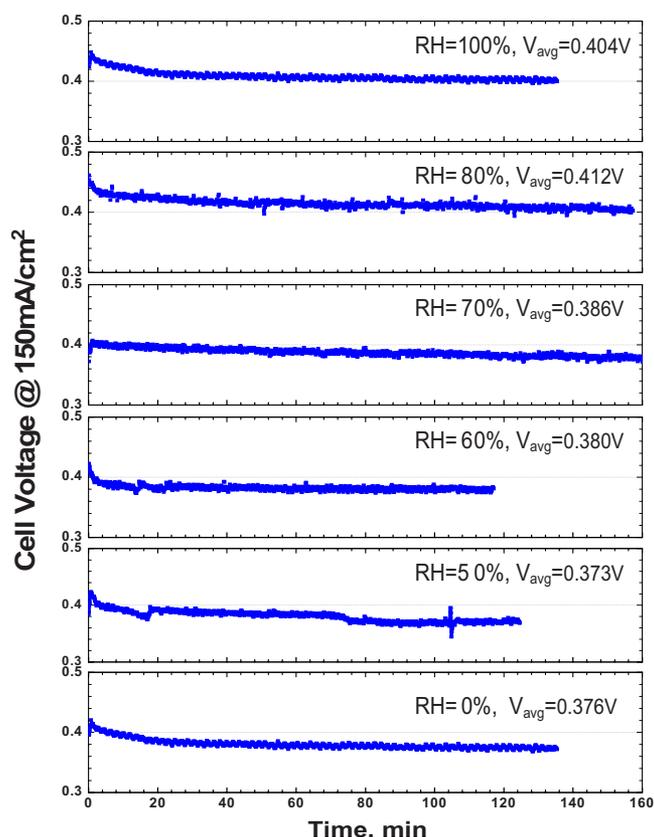


Figure 1. (Color online) DMFC voltage variations with time at constant-current discharge (150 mA/cm^2) for various air RHs. The average voltages shown in the plots are calculated after 1 h of operation. The cells were operated at 60°C and ambient pressure on both sides. The stoichiometries at the anode (2 M methanol) and cathode (air) are 2 and 3 at 150 mA/cm^2 .

150 mA/cm^2 . Indeed, it is seen that the anode outlet concentration of methanol drastically decreases, with the water crossover decreasing and turning negative. There is a significant drop at around $\alpha = 0.45$. When α approaches $-1/6$ or -0.167 , the one stoichiometric molecule of water necessary to oxidize each CH_3OH molecule then comes from the cathode side, indicating no consumption or loss of

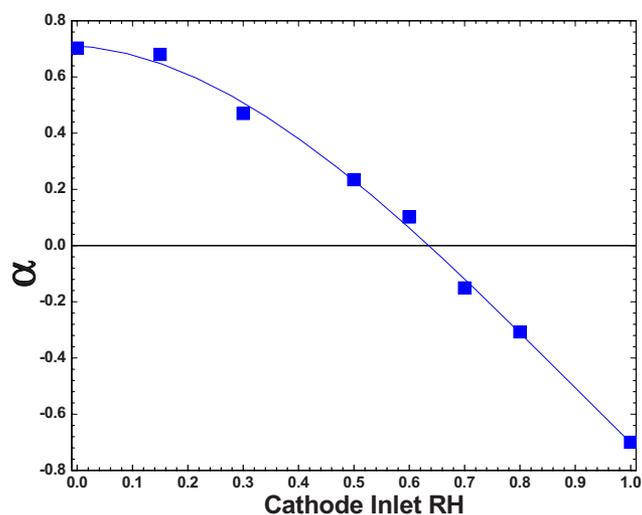


Figure 2. (Color online) Net water transport coefficient (α) at different cathode inlet RHs. Note that the α values reported here include the water from the oxidation of crossover methanol.

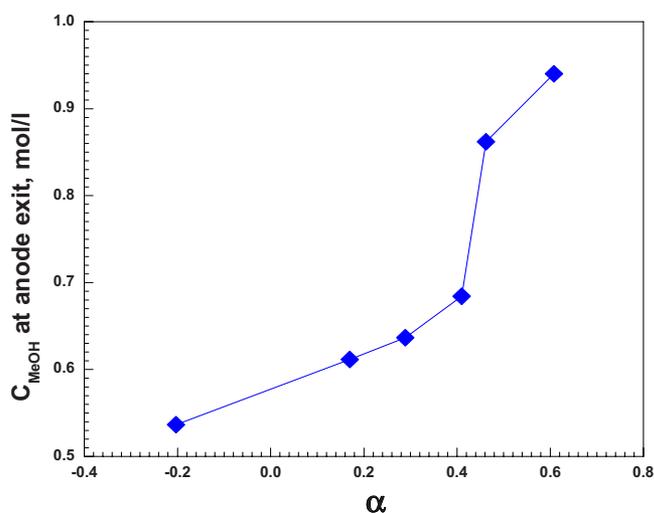


Figure 3. (Color online) Methanol concentration in the anode effluent as a function of the net water transport coefficient (α). Methanol solution was collected from the anode exit by an ice trap during constant-current discharge at 150 mA/cm^2 , and the density was measured to determine the concentration.

water from the methanol solution supplied into the anode. Thus, the methanol water solution at the anode outlet loses only methanol by methanol electro-oxidation, resulting in a concentration substantially lower than the inlet value of 2 M.

Figure 2 clearly shows a large range of α effected by controlling the cathode air RH. This large variation provides a great tool to design and test innovative ideas of HC-MFCs, where a highly concentrated methanol solution, greater than 10 M, can be directly fed into the anode without causing excessive methanol crossover or loss of cell performance, and where controlling water crossover through the membrane is a must to maintain mass balance and, hence, steady operation.

While using externally humidified air may prove impractical for portable DMFC systems, there are ways to induce internal humidification within the cathode structure, e.g., using porous plates. This idea and other practical methods to achieve cathode humidification and, hence, significantly promote water back-flow from the cathode to anode have been disclosed by Wang et al.¹¹

Conclusion

Cathode air humidification is found to dramatically promote water back-flow from the cathode to anode in DMFCs, thus leading to an unprecedented level of water crossover through the membrane required for HC-MFC operation. In this work we have shown α values as low as -0.7 .

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