

An experimental and modeling based investigation into the high stoichiometric flow rates required in direct methanol fuel cells

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Abstract

Direct methanol fuel cells (DMFCs) characteristically require high stoichiometric flow rates in order to optimize their performance. Experiments and modeling were performed in order to provide an improved understanding of the physical basis of this requirement. Anode side modeling suggests that high stoichiometry is necessary to keep the carbon dioxide (CO₂) gaseous volumetric generation rate to a fraction of the overall anode flow rate such that CO₂ gaseous clogging may not result. This requires anode stoichiometries generally greater than 20, and higher with increasing molarity. Cathode side modeling and measurements show that saturated exit air is directly related to poor cell performance. The modeling suggests that the cathode side mass transfer effect is quite strong despite the laminar flow conditions. Stoichiometries greater than 5 are seen to reduce the cell's exit relative humidity (RH) and improve cell performance. Published by Elsevier B.V.

Keywords: Direct methanol; Fuel cell; Stoichiometry; Operating conditions; Engineering; Polymer electrolyte

1. Introduction

Direct methanol fuel cells (DMFCs) are being considered as portable power sources in both military and commercial applications due to their attractive power to weight ratio coupled with the high energy density of methanol fuel. Unfortunately, in order to increase DMFC power output, both the anode and cathode reactant streams need to be forced often via pumps. This situation is made additionally less attractive when coupled with the high stoichiometric fuel and air requirements associated with DMFCs. It is characteristic to see flow rates into DMFCs at 10–100 times the basic stoichiometric requirement in order to optimize performance. Thus, large pumps are required to provide these high flow rates with their associated significant parasitic losses. Thus, the balance of plant (BOP) can become quite large for DMFC systems.

With the future hope of reducing these BOP requirements, this study looks into the physical reasons required for high

flow rates in DMFCs. On the anode side, carbon dioxide (CO₂) gas clogging is a practical reason often provided for why DMFCs require high methanol–water flow rates. Excessive cathode side humidity effects are believed to lead to gas diffusion layer (GDL) flooding at low air flow rates near stoichiometric. Both these effects have the potential to reduce fuel cell electrical output. This study seeks to quantify and measure these effects that may be leading to high flow rate requirements in DMFCs. Where measurements are not possible, physically based modeling is employed to provide additional insights and interpret the experimental results.

Much excellent research has gone into DMFC anode side behavior. Yang et al. [1] have observed gaseous CO₂ behavior in a transparent cell. They saw increased CO₂ vapor slugs with increasing current densities, which could be reduced in length with higher anode flow rates, but leading to higher crossover. Cell orientation was also important for managing CO₂ behavior. Scott et al. [2] looked at the combined effect of CO₂ and gaseous methanol from the anode stream, discovering that a significant amount of fuel-methanol can leave the fuel cell unreacted at higher operating tempera-

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Nomenclature

BOP	balance of plant
<i>C</i>	concentration
CO ₂	carbon dioxide
DMFC	direct methanol fuel cell
<i>F</i>	Faraday's constant
GDL	gas diffusion layer
<i>I</i>	current (A)
<i>m</i>	mass flow rate
<i>M</i>	molarity
MEA	membrane electrode assembly
MW	molecular weight
<i>P</i>	pressure
Pt	platinum
<i>Re</i>	Reynolds number
RH	relative humidity
Ru	ruthenium
<i>Sh</i>	Sherwood number
<i>V–I</i>	voltage–current polarization curve

Greek letter

λ	stoichiometry (actual flow rate/required flow rate)
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Subscripts

airin	air into fuel cell cathode
airout	air out of fuel cell cathode
<i>c</i>	concentration
CO ₂	carbon dioxide
H ₂ O	water
<i>m</i>	methanol
O ₂	oxygen
sat	saturated
vap	vapor

tures. Operational methanol–water molarity would also like to be increased to improve DMFC power density, however methanol crossover is a significant issue [3–5]. On the cathode side, studies have characterized that high flow rates of air are necessary to maximize DMFC electrical power output [6,7]. When high air flow rates are coupled within the system's design, the size and effectiveness of a cathode side condenser is significant in order to maintain a neutral water balance [8]. In the following, further experimental and modeling insights are provided into the high flow rates characteristic of DMFCs.

2. Experimental apparatus and method

Two different commercially available direct methanol single cell fuel cells (Giner and Lynntech) were used in this

study. They were connected to a Lynntech Methanol test stand in the following experiments. The test stand managed the cathode-side (air) flow rate as well as the anode side (methanol–water) flow rate and temperature. Cell temperature was controlled by the anode flow stream using a dilute methanol–water mixture in the range of 0.25–2 M (molar methanol). Fuel cell load (either desired current, voltage or power) could be automatically or manually controlled by the test stand. An external Agilent milliohm ($m\Omega$) meter measured the cell's resistance. For all testing, the fuel cell was oriented vertically with the anode stream flowing from the cell's lower side to upper side to aid in CO₂ transfer out of the cell, and the cathode stream flowing from the cell's upper side to lower side to aid in liquid water transport out of the cell. A Vaisala high humidity detector (HMP 240) as well as a moist environment CO₂ (Vaisala GMT 220) detector were attached at the fuel cells' cathode side outlet.

The Lynntech DMFC MEA (membrane electrode assembly) contained 4 mg cm⁻² of Pt–Ru catalyst on the anode electrode, with a 4 mg cm⁻² Pt cathode side loading. The base membrane was Nafion 117. ELAT (Teflon impregnated carbon paper) was used for the cathode GDL (gas diffusion layer) while carbon cloth was used for the anode GDL. The flow channels (0.8 mm wide with 0.8 mm spacing), which also functioned as the current collector plates, were cut in stainless steel end plates (built in-house) and were gold plated. Both the anode and cathode side flow channels were of parallel flow. The cells' active area was 50 cm². The overall cell resistance was 7.5 m Ω .

The Giner single cell DMFC contained an 80 cm² active area MEA with catalyst loadings of 4 mg cm⁻² Pt–Ru on the anode and 4 mg cm⁻² Pt on the cathode. A Nafion-117 membrane was at the center of the MEA and carbon paper provided the cells' GDLs with the cathode GDL having an additional Teflon coating for water management. Fiberglass end plates held the copper current collector plates which were in direct contact with the carbon based flow channel plates. The overall Giner single cell's resistance was 4.5 m Ω as measured at the current collector plates. The anode and cathode flow channels (machined into the carbon flow channel plates) were parallel flow, with the cathode carbon plate pattern using pins instead of channels to contact both the GDL and carbon flow channel plate.

The fuel cells were operated with fuel molarities from 0.25 to 2.0 M with de-ionized water–methanol temperatures (and fuel cell temperatures) from 45 to 75 °C across a range of stoichiometries (λ = actual reactant flow rate/flow rate required for complete reactant consumption, where the anode reactant was a methanol–water mixture, and the cathode reactant was air, in this study). Laboratory ambient bottled air was used for the cathode reactant stream. Voltage–current (*V–I*) sweeps were performed at the various experimental conditions, as well as manual testing at higher current loadings. Back pressure was not used in this study, thus the reactant streams operated just slightly above atmospheric pressure.

Methanol crossover measurements were performed on both DMFCs tested using the procedure outlined in Ref. [5]. The Giner cell's crossover current was approximately constant with load at 25 mA cm^{-2} . The Lynntech MEA had a higher methanol crossover increasing from 30 to 70 mA cm^{-2} with increasing load. These data were used in the DMFC model below.

3. Model description

It was desired in this study to quantify physical effects that may lead to high stoichiometric flow requirements in DMFCs. Thus on the anode side, gaseous CO_2 behavior is characterized, as CO_2 clogging is believed to be a performance inhibitor. On the cathode side, GDL flooding from excessively humid cathode air flow is characterized and measured.

A basic physically based DMFC model was developed and then coded in FORTRAN. The main physical principal of this code revolves around Faraday's electrochemical law: the number of moles of a substance produced at an electrode is proportional to the number of moles of electrons transferred at that electrode.

The following two equations show Faraday's law as applied to the anode (methanol–water) consumption and the cathode (air–oxygen) consumption, respectively:

$$\begin{aligned} \dot{m}_{\text{m,consumed}} (\text{g}_\text{m}/\text{s}) \\ = \frac{\text{MW}_\text{m} (32 \text{ g}_\text{m}/\text{mol}_\text{m}) I (A = C/\text{s})}{(6\text{e}^-/\text{molec}_\text{m})(6.023\text{e} + 23\text{molec}_\text{m}/\text{mol}_\text{m})} \\ (1.602\text{e} - 19C/\text{e}^-) \end{aligned} \quad (1)$$

$$\begin{aligned} \dot{m}_{\text{O}_2,\text{consumed}} (\text{g}_{\text{O}_2}/\text{s}) \\ = \frac{\text{MW}_{\text{O}_2} (32 \text{ g}_{\text{O}_2}/\text{mol}_{\text{O}_2}) I (A = C/\text{s})}{(6\text{e}^-/1.5\text{molec}_{\text{O}_2})(6.023\text{e} + 23\text{molec}_{\text{O}_2}/\text{mol}_{\text{O}_2})} \\ (1.602\text{e} - 19C/\text{e}^-) \end{aligned} \quad (2)$$

It can be seen that fuel cell current (I) is an input to these equations. MW is the molecular weight of the sub-scripted specie (m: methanol, O_2 : oxygen, H_2O : water). Equations similar to these are used for water consumption and carbon dioxide formation of the anode side, and water formation on the cathode side. Fuel crossover is a model calibration item that was measured from experimental results, and is modeled in conjunction with Faraday's Law to provide additional water plus CO_2 formed on the cathode side as a result of crossover. Mass conservation is then performed on each species tracked on each side of the modeled MEA.

As discussed earlier, cathode side humidity behavior is believed critical to DMFC operation. The MEA needs to be moist but not too wet. A water accounting is performed to determine the cell's exit relative humidity (RH), and if saturated, then how much liquid water is expected to exit the cell. Eqs. (3)–(5) [9], reflect the maximum amount of water

that the cathode air stream can hold (e.g. 100% RH – saturated air). This maximum amount of water vapor in air is compared against the results from the mass conservation of water in the cathode side. Water comes into the cathode as a function of the inlet relative humidity, which was zero in this study due to the bottled air. Water is formed from the normal fuel cell reaction and the fuel crossover reaction. These are added together to provide the net water out of the cathode side. $P_{\text{vap,sat}}$ is the saturated water vapor pressure at the specified cell exit temperature and P_{cathode} (equal to 1 atm for this study) is the cathode air pressure:

$$\begin{aligned} \dot{m}_{\text{H}_2\text{O-vap,airout}} \\ = \dot{m}_{\text{airout}} \frac{\text{MW}_{\text{H}_2\text{O}}}{\text{MW}_{\text{air}}} \frac{P_{\text{vap,sat}}(T_{\text{out,cathode}})}{P_{\text{cathode}} - P_{\text{vap,sat}}(T_{\text{out,cathode}})} \end{aligned} \quad (3)$$

Additionally, oxygen is consumed so the air out of the cathode side of the fuel cell is reduced in oxygen concentration. This factor must also be taken into account, and is shown in the equation below where λ_{air} and CO_2 are the cathode air stoichiometry and ambient concentration of oxygen in air (21%), respectively. F is the Faraday's constant:

$$\begin{aligned} \dot{m}_{\text{airout}} &= \dot{m}_{\text{airin}} - \dot{m}_{\text{O}_2\text{-consumed}} \\ &= \left(\frac{\lambda_{\text{air}}}{\text{CO}_2} \text{MW}_{\text{air}} - \text{MW}_{\text{O}_2} \right) \frac{I}{4F} \end{aligned} \quad (4)$$

Thus, the maximum amount of water vapor that the exit air stream can hold is shown in

$$\begin{aligned} \dot{m}_{\text{H}_2\text{O-vap,airout}} \\ = \left(\frac{\lambda_{\text{air}}}{\text{CO}_2} - 1 \right) \text{MW}_{\text{H}_2\text{O}} \frac{P_{\text{vap,sat}}(T_{\text{out,cathode}})}{P_{\text{cathode}} - P_{\text{vap,sat}}(T_{\text{out,cathode}})} \frac{I}{4F} \end{aligned} \quad (5)$$

Eq. (5). The model determined actual water out of the cathode is then compared to this. If the water mass is greater, then the amount of liquid precipitate in the cathode cell is determined. If the actual water is less, then the exit relative humidity can be determined.

Conventional heat transfer channel flow correlations [10] are used for both the liquid-anode side behavior as well as the gaseous-cathode airside of the fuel cell. This heat transfer sub-model was calibrated to the actual cell exit temperatures. The heat transfer sub-model assumes pure water on the anode side and pure air on the cathode side since both streams are very dilute mixtures in practice. It is interesting to note that due to the small channel sizes, the flow through the fuel cell plate channels is laminar.

4. Results

4.1. Anode stream

Very high stoichiometries are frequently used for the methanol–water flow stream. Often from 10 up to 100 times

the base stoichiometric requirement is used to maximize cell performance. Direct measurement is very difficult on the anode stream due to its two phase nature, especially at high loads. At higher current densities, substantial volumes in the form of vapor slugs of CO₂ (including possibly some methanol vapor as well [2]) are observed emanating from the anode exit via clear tubing that returns the anode stream to the test stand. In between these vapor slugs are the slugs of liquid methanol–water that are not consumed by the reacting fuel cell. While this behavior appears mostly random, it is clear to the experimental observer that as current densities are increased, the frequency and volume of these CO₂ vapor slugs increases. Due to the complexities of measuring this two phase behavior, the above DMFC model is used to interpret this anode reactant stream behavior, and then is compared to some empirical results.

Fig. 1 shows the model predicted gaseous CO₂ volume flow rate due to anode CO₂ generation divided by the liquid anode flow rate for different water–methanol molarities at a cell temperature of 60 °C. A reference line is also shown at which point the volumetric flow rate of CO₂ is equal to the anode stream volumetric flow rate (1 on the ordinate). When the CO₂ generation rate is larger than the anode flow rate (ordinate > 1) it can be expected that gaseous CO₂ clogging will result in the anode flow channels due to the dominance of volumetric CO₂ relative to the base liquid methanol–water reactant. In order to have CO₂ generation rates relative to the anode flow rate that are much less than 1, and thus reduce this gaseous CO₂ vapor dominance, Fig. 1 predicts that high stoichiometries are required, roughly greater than 20. As methanol molarities increase, the associated stoichiometry necessary to keep the CO₂ generation rate much below the base flow rate increases significantly. This effect is due to the higher reactivity with higher methanol concentrations and the associated increased generation of CO₂ gas.

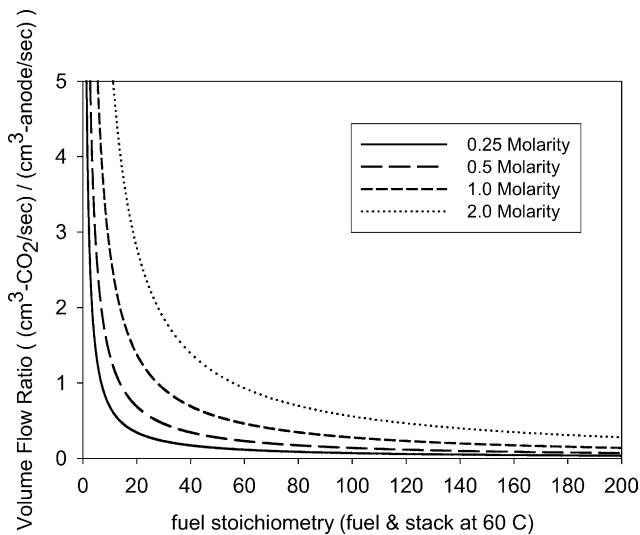


Fig. 1. Model predicted gaseous CO₂ volumetric flow rate normalized to anode volumetric flow rate as a function of anode stoichiometry for different molarities.

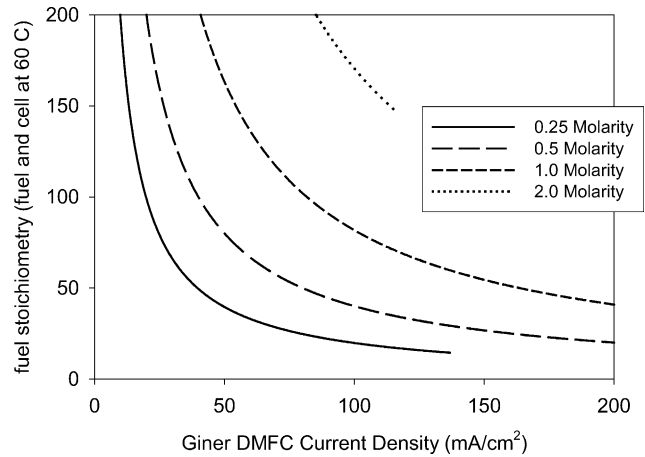


Fig. 2. Giner single cell data (60 °C): fuel stoichiometry as a function of current density at various molarities.

Experimental Giner single cell results are shown in Fig. 2 for cell operation on different fuel molarities. *V–I* sweeps were performed using the test stand, and the resulting fuel stoichiometry versus current density is shown in the figure. The anode stream flow rate was set to be constant during the sweep and for all the molarities tested, thus the experimental results show decreasing stoichiometry with increasing current draw from the cell. It is seen that for a given cell current density (e.g. constant CO₂ formation rate), the associated stoichiometry increases with increasing methanol molarity. For example, with a cell current draw of 100 mA cm⁻², the 0.25 M anode stream is operating at a stoichiometry of 20, whereas the 2 M anode stream is operating with a stoichiometry of approximately 160, where the eight-fold increase is due to the eight-fold methanol concentration increase. For a specified CO₂ generation rate and fixed anode stream flow, the anode side model behavior is in agreement with these experimental data, requiring larger stoichiometries for higher molarity fuels.

Fig. 3 shows *V–I* curves for the Giner single cell at different anode flow rates using a 0.5 M anode stream at 60 °C. It is seen that for an anode stream flow of 32 cm³ min⁻¹ (and to

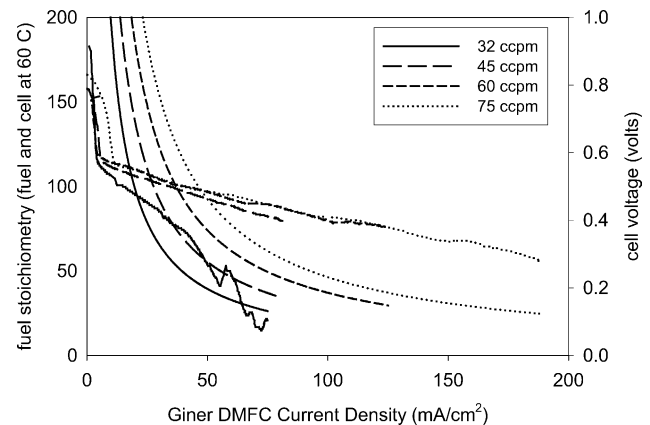


Fig. 3. Giner single cell data (60 °C): fuel stoichiometry as a function of current density for various anode flow rates.

a lesser extent at $45 \text{ cm}^3 \text{ min}^{-1}$) at all cell currents, the cell voltage is poorer than with higher anode flow rates and stoichiometries. For example at a given operating stoichiometry, cell current density performance increases tremendously due to the higher flow rates. Alternatively, at a given cell current density output, for example 50 mA cm^{-2} , cell voltage performance is very poor until higher anode flow rates are used ($60 \text{ cm}^3 \text{ min}^{-1}$ and above). This corresponds to anode stoichiometries greater than 50. From the above anode side modeling results this requires that the CO_2 generation rate is less than $1/4$ of the anode flow rate.

Anode side CO_2 model predicted behavior at different cell and anode stream temperatures shows very little change in the predicted performance of Fig. 1 due to the very small fluid density changes in moving the cell temperature from 45 to 75°C . However, cell performance drops significantly with decreasing temperature most likely due to kinetic effects.

4.2. Cathode stream

Model predicted cathode exit humidity is shown in Fig. 4 for four different cell operating temperatures. As expected, with higher operating temperatures the cathode air stream will be able to hold more water in the vapor form, and thus have a lower relative humidity for a given air flow. Ref. [11] details the desired operating RH to be between 85 and 95% for polymer electrolyte membrane (PEM) fuel cells. It is interesting to note that the minimum predicted stoichiometry to achieve this desired range decreases rapidly with increased operating temperature from $\lambda_{\text{air}} = 9$ at 45°C to $\lambda_{\text{air}} = 2$ for 75°C . At an operating temperature of 90°C , the model predicts that excessive drying may result.

RH measurements from the Lynntech DMFC single cell are shown in Fig. 5 as a function of operating temperature and air stoichiometry. As a general trend, and predicted by the model, cell exit RH decreases with increased operating temperature. At low air stoichiometries ($\lambda_{\text{air}} < 5$) the exit cathode

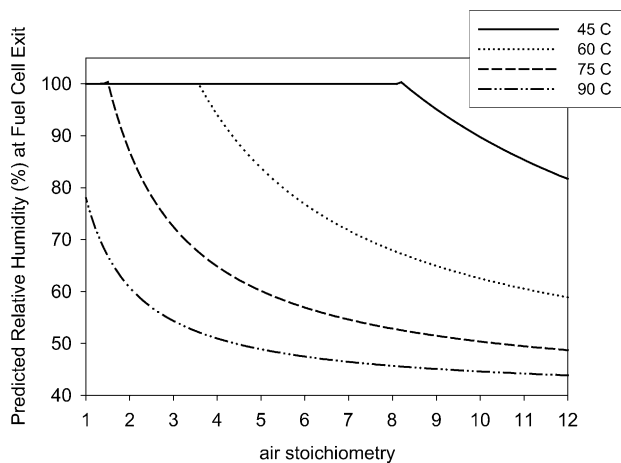


Fig. 4. Model predicted cathode side exit RH as a function of air stoichiometry at various operating temperatures.

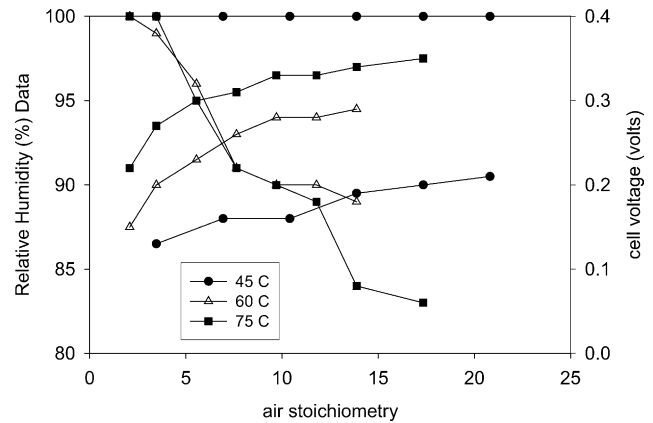


Fig. 5. Lynntech single cell data: RH and cell voltage vs. air stoichiometry at various operating temperatures.

stream is saturated at 100% RH, and the cell voltage drops to very poor levels for all three operating temperatures. As expected, it can be seen that at 45°C , the air is able to hold less water in the vapor form as compared to 60°C and thus is saturated for all the air stoichiometries tested. Alternatively, at 75°C , the cathode air stream can hold significantly more water in the vapor form, and thus it tends to have lower RH at its exit as compared to other operating temperatures for the same stoichiometry. The data clearly shows decreased cell performance with saturated or near saturated exit cathode air.

Further experiments were performed using the Giner DMFC while measuring the cathode's exit stream with a high humidity detector. Fig. 6 shows the results from the Giner single cell operating at 60°C with current densities of 50 and 80 mA cm^{-2} . Air stoichiometry is varied with all other experimental parameters held constant. It can be seen that as the air flow rate is increased the cell's cathode exit stream decreases modestly from water saturated air (100% relative humidity, RH) to approximately 95% RH at stoichiometries approaching 20. Thus higher airflows do prevent full saturation of the water in the airflow from occurring. At the low

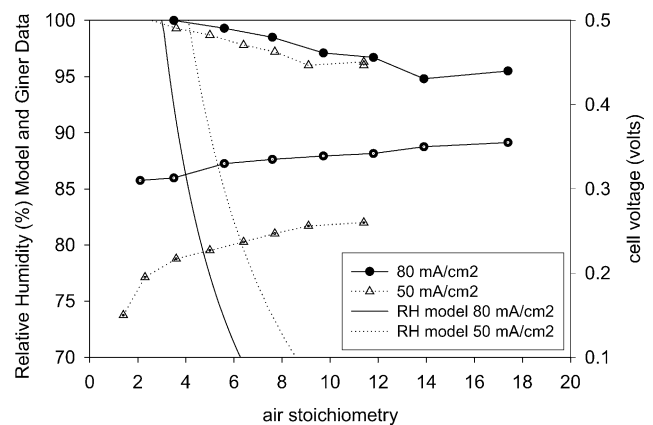


Fig. 6. Giner single cell data (60°C): RH and cell voltage vs. air stoichiometry at various current densities. Model predicted RH is also shown.

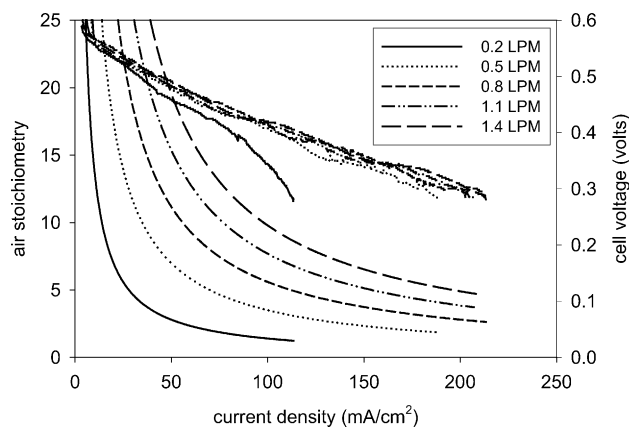


Fig. 7. Giner single cell data (60°C): air stoichiometry as a function of current density for various cathode air flow rates.

air stoichiometries with the fully saturated airflow at 100% RH, it can be seen that cell voltage is falling, especially at the lower current density. This effect is believed to be the cathode GDL flooding, in which liquid water is coating the GDL and prevents the reactant oxygen from diffusing to the cathode catalyst surface.

Also shown in Fig. 6 is the model predicted RH for both current densities. The water sources that contribute to this model predicted RH come from the cathode water formation mechanisms due to the cell reaction as well as crossover effects. It is evident that the model significantly under predicts the exit streams' RH. This suggests that significant water mass transfer is occurring from the moist GDL to the cathode air stream. Using Reynolds' analogy between heat and mass transfer, heat transfer correlations converted to mass transfer Sherwood numbers (Sh) were analyzed for pipe and channel flows, however, they too significantly under predicted the exit stream's RH. Correlations in which $Sh \sim Re^n$, where n was 1.5–2.0 showed success in matching the model predictions to the experimental results, however the correlations were sensitive to the specific fuel cell and operating conditions. It is interesting that such a strong Reynolds number mass transfer effect is likely active in this laminar flow situation. In order to achieve this measured high level of RH from the fuel cell at high air stoichiometries, the mass transfer must be a strong effect with increasing Reynolds number.

Finally, Fig. 7 shows the experimental results from the Giner DMFC in which $V-I$ sweeps were performed at different air flows. Both stoichiometry and cell voltage are plotted against the cell's output current density. At the lowest air flow, 0.2 L min^{-1} , the cell voltage is quite poor, especially at higher current densities. This corresponds to $\lambda_{\text{air}} < 5$. Air stoichiometries greater than 5 are seen to provide more consistent performance.

5. Conclusions

Anode side model predictions suggest that in order to keep the CO_2 volumetric generation rate significantly below the anode volumetric flow rate, stoichiometries greater than 20 are required. For a given CO_2 formation rate the model predicts that even higher fuel stoichiometries are necessary with increasing water–methanol molarities. These results are corroborated by the empirical testing which showed that low anode stream flow rates with all other variables held constant can result in poor cell output. Very high stoichiometries (>20) were necessary to achieve optimized performance.

Direct measurement of the cathode's exit stream revealed that water saturated air exit streams result in poor fuel cell performance. These saturated exit streams result from low air stoichiometries ($\lambda_{\text{air}} < 5$). Model predictions showed similar trends with air stoichiometries and operating temperature, however, significant water mass transfer effects are believed to be occurring in order for the model RH predictions to approach the relative humidity measurements.

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