



Effect of operating parameters and anode diffusion layer on the direct ethanol fuel cell performance

V. Alzate, K. Fatih*, H. Wang

National Research Council Canada - Institute for Fuel Cell Innovation, 4250 Wesbrook Mall, Vancouver, British Columbia, V6T 1W5, Canada

ARTICLE INFO

Article history:

Received 24 May 2011

Received in revised form 19 August 2011

Accepted 20 August 2011

Available online 3 September 2011

Keywords:

Direct ethanol fuel cells

Direct alcohol fuel cells

Ethanol oxidation

Fuel cell operating parameters

Cell performance

ABSTRACT

A parametric study was conducted on the performance of direct ethanol fuel cells. The membrane electrode assemblies employed were composed of a Nafion[®] 117 membrane, a Pt/C cathode and a PtRu/C anode. The effect of cathode backpressure, cell temperature, ethanol solution flow rate, ethanol concentration, and oxygen flow rate were evaluated by measuring the cell voltage as a function of current density for each set of conditions. The effect of the anode diffusion media was also studied. It was found that the cell performance was enhanced by increasing the cell temperature and the cathode backpressure. On the contrary, the cell performance was virtually independent of oxygen and fuel solution flow rates. Performance variations were encountered only at very low flow rates. The effect of the ethanol concentration on the performance was as expected, mass transport losses observed at low concentrations and kinetic losses at high ethanol concentration due to fuel crossover. The open circuit voltage appeared to be independent of most operating parameters and was only significantly affected by the ethanol concentration. It was also established that the anode diffusion media had an important effect on the cell performance.

Crown Copyright © 2011 Published by Elsevier B.V. All rights reserved.

1. Introduction

Direct liquid fuel cells are an attractive technology because of the fuel's high volumetric energy density, which translates in system compactness and simplicity. In the liquid fuel options, ethanol has two main advantages; its low toxicity and its established production infrastructure. The main issue of direct ethanol fuel cells (DEFC) is their low efficiency, mainly due to the difficulty to break the ethanol's carbon-carbon bond at the fuel cell's operating temperature. In addition, the presence of ethanol in the cathode, due to the crossover through the Nafion[®] membrane, reduces the open circuit voltage and poisons the catalyst. Because of the importance of the electrochemical reaction kinetics in this system most of the research work has been focused on the anode catalyst. Platinum-tin based catalysts have shown the best initial performance for the ethanol electro-oxidation reaction (EOR) [1,2], while Pt-Sn containing Ir showed better long term performance [3]. Almost all of the catalysts applied to EOR showed very low CO₂ yields with acetic acid and acetaldehyde being the main oxidation products. Efforts to increase the platinum-tin electrocatalytic activity and CO₂ selectivity include design of its microstructure [4], adding a third [5–9], and fourth catalyst component [3] and modifying the catalyst support [10–12].

Single fuel cell testing is one important tool for fuel cell catalyst design as it reveals the performance of the catalyst in actual operating conditions. Published work has shown that the direct ethanol fuel cell performance is significantly affected by the employed testing conditions, the fabrication processes and materials of the membrane electrode assembly (MEA). The effect of temperature and ethanol concentration on the ethanol crossover rate and its impact on cell performance has been studied by Song et al. [13]. The authors found that ethanol crossover increased with increasing temperature and ethanol concentration. Similarly, using a reference electrode Li and Pickup found that temperature and ethanol concentration have a positive effect on the ethanol oxidation reaction, but the opposite effect was found for the oxygen reduction reaction, demonstrating the significant impact that ethanol crossover has on the oxygen reduction reaction [14]. Praminik et al. [15], studied the effect of the temperature of the anode and the cathode, separately, as well as the effect of the ethanol concentration. The authors found a performance maximum at 90 °C for the anode and 60 °C for the cathode with the testing temperature range of 42–120 °C and 42–88 °C for anode and cathode, respectively. The authors established an optimum ethanol concentration of 2 M. In addition to the testing parameters, the MEA fabrication processes also affect the DEFC performance. This has been demonstrated by Song et al., who compared the performance and stability of a gas diffusion electrode (GDE) based MEA with a catalyst coated membrane (CCM) based MEA [16]. Although the CCM MEA had higher ethanol crossover rate, its performance and stability were superior compared to the GDE MEA, having a peak power degradation

* Corresponding author. Tel.: +1 604 221 3071; fax: +1 604 221 3001.

E-mail address: Khalid.Fatih@nrc.gc.ca (K. Fatih).

Table 1
Properties of the anode diffusion layer.

Anode diffusion layer	Thickness [μm]	Porosity [%]	PTFE loading [wt.%]	Description
CFP Toray-120	370	78	0	Without MPL
CFP-25BC SGL	235	80	5	With MPL (23% PTFE)
CFC E-tek B-1/B (cloth)	445	–	0	Without MPL

of 15% against 34% for the GDE MEA in a 10 h life test, which was attributed to less delamination problems in the case of the CCM MEA. The structure of the catalyst layer has also been investigated for DEFC [17]. In this work, the authors obtained higher cell performance using pore formers in the anode catalyst layer, and by increasing PTFE content in the catalyst layer from 10 to 20 wt%. These two parameters were said to improve the flow system network for the removal of ethanol electro-oxidation product species and therefore having more catalyst sites available for the reaction.

The objective of this work is to create a clearer and broader picture of the effect of the main parameters used during direct ethanol fuel cell testing. Specifically, the effect of cathode backpressure, cell temperature, ethanol solution flow rate, ethanol concentration, and oxygen flow rate will be presented. Furthermore, three different anode diffusion media were tested. The effect of using carbon fibre cloth (CFC) and carbon fibre paper (CFP) is examined, as well as the presence of a microporous layer (MPL). The cell performance was evaluated measuring the fuel cell voltage as a function of current density and calculating the power density from these measurements. The results are presented as polarization and power curves.

2. Experimental

2.1. Materials

Nafion[®] N117 membranes (DuPont) were pre-treated at 80 °C with 3 wt% H₂O₂ and 0.5 M H₂SO₄ solutions for 1 h and, rinsed and stored in de-ionised water. HiSPEC (Johnson Matthey) 4000 (Pt/C) and 5000 (Pt₁Ru₁/C) were used as the cathode and the anode catalyst, respectively. The cathode diffusion media was Sigracet[®] GDL 25DC (SGL Group), which has 20% PTFE content. For the anode, three types of diffusion layers were used: (i) Sigracet[®] GDL 25BC (SGL Group), which is a CFP with a 5% PTFE content and a microporous layer (MPL) (23% PTFE), (ii) TGP-H-120 CFP (Toray) and (iii) CFC (E-TEK). Table 1 summarizes the properties of the three different diffusion media used.

2.2. Electrode and MEA preparation

Electrodes were prepared by spraying the catalyst on the diffusion media. The catalyst ink was composed of the catalyst, Nafion[®] ionomer solution (5 wt% in alcohols/water, Alfa Aesar), and alcohol/water solution. This mixture was treated with an ultrasonic processor (Cole-Palmer) in pulse mode for 1 h. The ink was sprayed using an auto-spray (nozzle-XY table) system. The catalyst metal loading was 2 mg cm⁻² for both anode and cathode, while the Nafion[®] ionomer content in the catalyst layer was 20 wt%. The MEAs were fabricated by hot-pressing the Pt/C and PtRu/C electrodes (5 cm²) onto each side of the Nafion[®] membrane at 90 kg cm⁻² and 140 °C for 4 min.

2.3. Fuel cell measurements

DEFC performance tests were conducted in a 5 cm² single fuel cell hardware (Fig. 1). Serpentine flow field graphite plates were used for both cathode and anode. Tests were performed with a commercial test station (Fideris). Prior to polarization curve

measurements, the break-in of the MEA was performed by setting the cell at a constant voltage of 0.2 V for 2–4 h until the current was stable using 1 M methanol solution as fuel. For the actual measurements ethanol solutions and un-humidified oxygen were used as reactants. The variables and testing conditions are summarized in Table 2. Polarization curves were performed galvanostatically, each point was measured for 2 min, which was enough time to get a stable potential response. After each polarization curve deionised water was flown through the anode compartment to avoid cell degradation. Before measuring each polarization curve, the cell was kept at open circuit voltage (OCV) under the testing conditions for 30 min for stabilization.

3. Results and discussion

3.1. Effect of anode diffusion layer

The effect of the anode diffusion layer was studied using three types of substrates, CFP with MPL, CFP, and CFC. In hydrogen PEM fuel cells the MPL is known to improve the cell performance affecting the water transport properties, the catalyst layer structure and electrical contact; in the case of methanol fuel cells, the MPL can also affect the fuel crossover and CO₂ transport [18]. Fig. 2 shows the SEM images of the uncoated and coated surfaces of the diffusion layers. The CFP with MPL has a very homogeneous surface with pore sizes less than 1 μm in size (Fig. 2a), while CFP (Fig. 2b) and CFC (Fig. 2c) have greater and broader pore size distribution. After the catalyst layer is sprayed on these substrates a clear difference in the structure is observed between the CFC (Fig. 2f) and the CFP based samples (Figs. 2d and e). The catalyst layer deposited on the CFC has a more open structure that follows the direction of the woven fibres compared to a more flat surface in the CFP samples. On the other hand, there is no visible difference in the catalyst layer surface between the samples with and without MPL (Figs. 2b and d).

Fig. 3 shows the polarization and power curves for the three types of anode diffusion layers. The type of diffusion layer does not affect the OCV, as well as the performance in the kinetic controlled region; the three curves show the same behaviour up to a current density of 0.020 A cm⁻². At higher current density, the anode with the CFP and MPL showed a lower performance, reaching a maximum power density of 0.017 W cm⁻² compared to 0.028 W cm⁻² obtained with both CFP and CFC based anodes. Furthermore, the

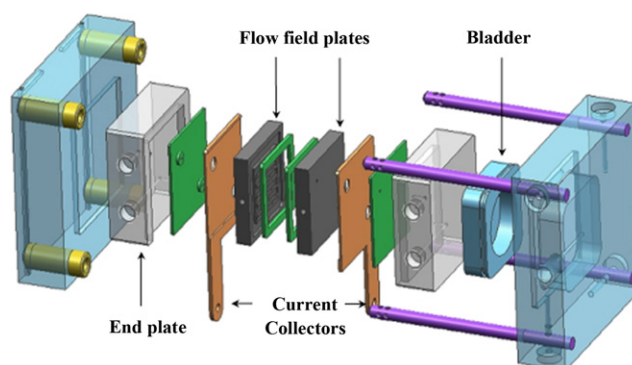


Fig. 1. Expanded view of the direct ethanol fuel cell hardware.

Table 2
Experimental conditions used for each set of test.

Exp. series	Variables					
	Anode diffusion layer	O ₂ flow rate (mL min ⁻¹)	Ethanol flow rate (mL min ⁻¹)	[Ethanol] (M)	Temp. (°C)	Cathode back-pressure (psig)
1	CFP CFP-MPL CFC	300	2	1	90	30
2	CFP	300	2	1	90	0–10–20–30
3	CFP	300	2	1	60–70–80–90	0–30
4	CFP	300	0.6–1–2–5	1	90	30
5	CFP	300	2	0.1–0.5–1–2–5	90	30
6	CFP	50–100–300–500	2	1	90	0–30

cell with the CFC based anode achieved the highest current density. There are two differences between the CFP with MPL and the other two samples. The first one is the PTFE content in CFP (5 wt.%). The hydrophobicity of the CFP can reduce the transport of water but in a lesser degree the transport of an ethanol/water solution, which has a lower surface energy. In addition, the PTFE can reduce the electrical conductivity of the CFP. The second difference is the presence of the MPL, which might act similar to a barrier preventing the flow of liquid to and from the catalyst layer due to the high PTFE content (23 wt.%) as well as the very small pores and lower porosity. Considering the low content of PTFE in the CFP, the pore size of

the MPL and its hydrophobicity seem to be complementary factors in the reduction of the cell performance. This postulate goes in the same direction as the modelling work done by Andreadis et al. [19] in which was reported that the porosity of the diffusion layer has an important effect on the performance. For example a 22% increase in performance was calculated when the diffusion layer's porosity is changed from 0.4 to 0.8. In fact their simulated polarization curves have a very similar behaviour as to Fig. 3, i.e., the kinetic region is not affected by changing the diffusion layer porosity while at higher currents the slope of the curve increases with decreasing porosity. Furthermore, Biswas et al. [17] found better performance

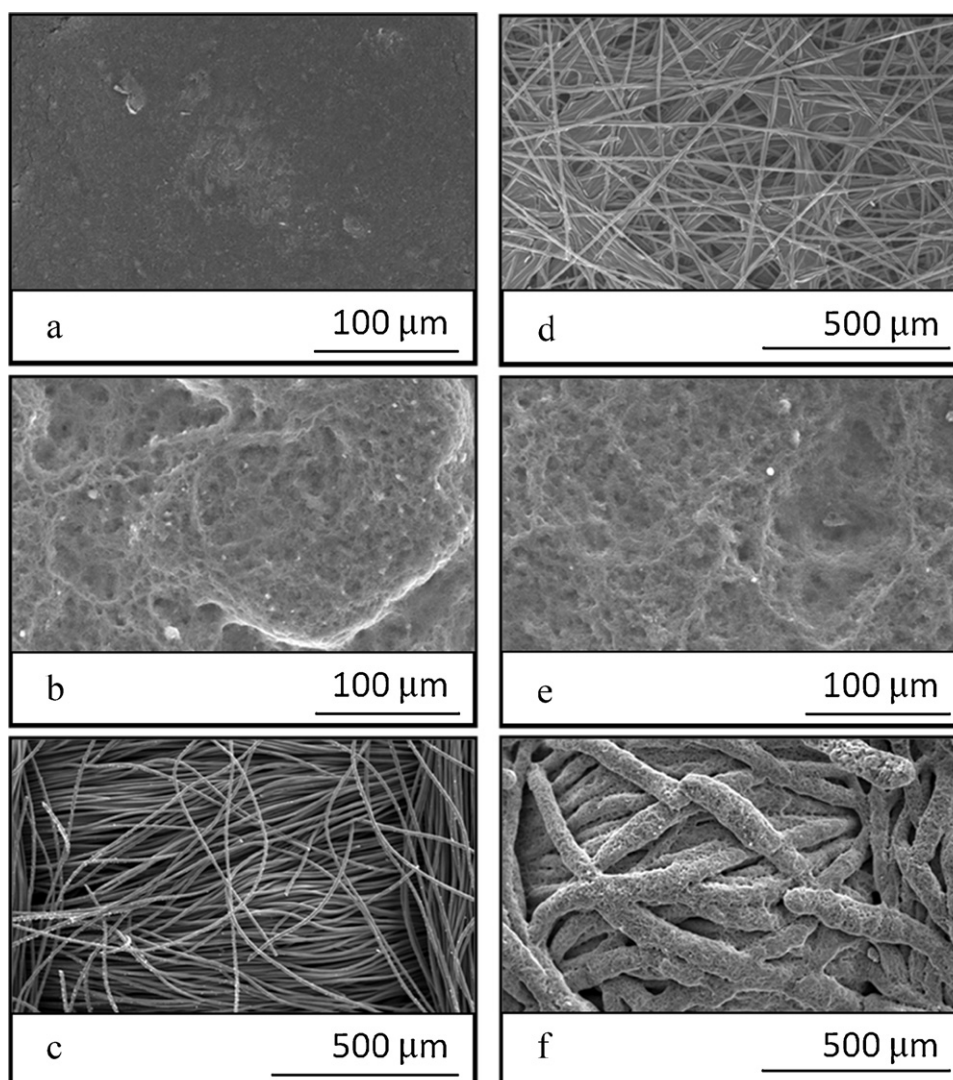


Fig. 2. SEM images of diffusion media before and after spraying catalyst layer: (a and d) CFP with MPL, (b and e) CFP and (c and f) CFC.

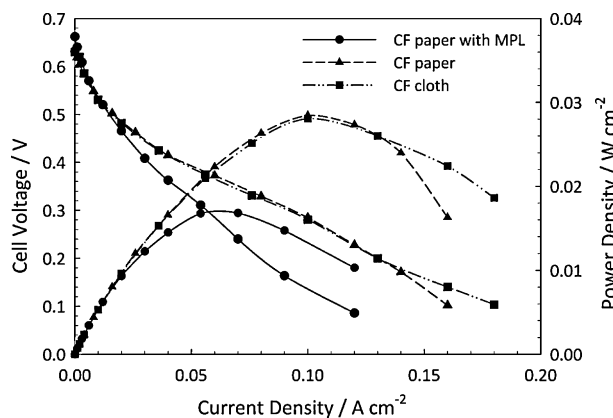


Fig. 3. Polarization and power curves with different anode diffusion media for 1 M EtOH feed (2 mL min^{-1} and 0 psig) and non-humidified oxygen (300 mL min^{-1} and 30 psig) at 90°C .

by increasing both the porosity and the PTFE content (20%) in the catalyst layer. However, in their case the catalyst layer was fabricated using pore formers, therefore the PTFE content could have a very different effect compared to the present work.

For this experimental system the majority of the products are in liquid phase, for the ideal DEFC system the reaction product is CO_2 , therefore the flow dynamics would be very similar to the direct methanol fuel cell. Gas management has been a critical factor for direct methanol fuel cells design given that CO_2 bubbles can remain in the diffusion layer. These bubbles generally block the pores used for the methanol diffusion to the catalyst layer, leading to fuel starvation and therefore decreasing the cell performance. A comprehensive review was published on the mass transport phenomena in a DMFC system [20]. For example, in an experiment performed by Lu and Wang [21], the effect of the anode diffusion media of a DMFC was evaluated. Untreated (hydrophilic) CFC was compared with a 20% PTFE treated CFP, which had a homemade MPL. The authors concluded that the addition of this layer decreased the rate of methanol crossover due to the low-permeability that the MPL provides. On the other hand the removal of CO_2 bubbles from the backing layer was easier in the CFC from visual experiments, although it was not clear whether this difference was due to the pore distribution differences or the PTFE content in the materials. Therefore the optimum diffusion media for DEFC anodes would depend on the reactant flow regime, including the amount of gas produced in the anode.

3.2. Effect of cathode backpressure and cell temperature

Fig. 4 shows the effect of cathode backpressure on the cell performance. In general the performance improves with increasing the backpressure, mainly because of the reduction of the activation overpotential. In the ohmic region, the four curves have similar behaviour. However, in the mass transport region, the effect of increasing the backpressure seems to diminish as the current density increases. Ethanol transport in the Nafion membrane takes place through three different phenomena: electro-osmosis; diffusion and hydraulic permeation. When the pressure at the cathode is higher than at the anode, there is back convection of ethanol from the cathode to the anode due to the hydraulic permeation. This results in an overall reduction of ethanol crossover. The reduction of ethanol concentration in the cathode will reduce the parasitic currents and poisoning created by the reaction of ethanol on the cathode active sites. This enhances the oxygen reduction reaction kinetics and reduces the activation overpotential as seen in Fig. 4. The cathode backpressure also increases the oxygen solubility in

the Nafion ionomer present in the catalyst layer. This will produce a higher oxygen concentration in the triple phase boundary, enhancing the oxygen reduction reaction rate.

As mentioned previously, the maximum current density values are very similar at the four tested backpressures. At higher current densities the concentration of ethanol in the anode catalyst layer is lower, which affects the fuel cell performance in two ways. First, the concentration overpotential at the anode increases and second, the crossover of the ethanol due to diffusion decreases as the difference in concentration between the anode and the cathode is reduced. Therefore, the fact that the maximum current density is nearly independent of the cathode backpressure suggests that in this region of the polarization ethanol mass transfer is governing the cell performance. The reduction of the crossover rate and therefore the parasitic current with increasing cell current has been also reported by Andreadis et al. through a modelling study [22]. In the same modelling work, it was reported that the ethanol crossover is maximal at OCV. In the present study, Fig. 4b shows that the OCV is almost unaffected by backpressure with a stable value at 0.64 V (variations are in the order of mV). It is important to note that a stabilization period of 30 min was used before measuring each polarization curve. The OCV was found to be very sensitive to the change of conditions but only at the moment when the perturbation was made. For example, an OCV of 0.8 V was recorded with increasing backpressure but only for a few seconds, and it would slowly decrease until reaching a stable lower point. It would have been expected that a higher backpressure would result in a higher OCV due to the reduction of the ethanol crossover. The fact that the steady state OCV is almost unchanged with increasing backpressure can be due to a steady poisoning of the cathode catalyst layer. This may be due to an accumulation of ethanol at the cathode side of the membrane, which lowers the initially recorded high OCV after a pressure increase. As for the maximum power density, it increases almost linearly with increasing backpressure up to 20 psig (Fig. 4b). By increasing the pressure from 20 to 30 psig the performance does not improve, therefore a saturation point might have been reached at 20 psig. It is important to note that there is also the crossover of species from the cathode to the anode such as oxygen, ethanol and/or reaction products of ethanol oxidation that may accumulate at the cathode side of the membrane, which would increase by increasing the cathode backpressure. James and Pickup have discussed the issue of ethanol oxidation products (acetic acid and acetaldehyde) crossing to the anode side [23]. While Jablonski et al. reported the effect of oxygen crossing from the cathode to the anode and reacting chemically [24] with ethanol to produce acetic acid and acetaldehyde. In either case the presence of electrochemical reaction products in the anode would lower the cell's OCV and performance and counteract the positive effect of backpressure on the cathode kinetics.

Fig. 5 shows the effect of temperature on the DEFC performance with cathode backpressure (30 psig) and without cathode backpressure (0 psig). The polarization curves in Figs. 5a and b show a similar behaviour with increasing the temperature. The kinetic region is enhanced and the slope of the ohmic region decreases. Electrode kinetics, membrane conductivity and mass transfer properties are thermally activated, therefore it is expected that an increment in fuel cell temperature will result in a performance enhancement. On the other hand, fuel crossover is also a thermally activated process. With increasing temperature the Nafion polymer backbone relaxes and expands allowing higher transport rates, in addition the ethanol diffusivity is also enhanced [13,25]. Therefore the cathode kinetics has two competing effects with increasing temperature. Li and Pickup reported that the effect of ethanol crossover is so significant that the cathode performance decreases with increasing temperature although the oxygen reduction reaction rate increases with temperature. They concluded that

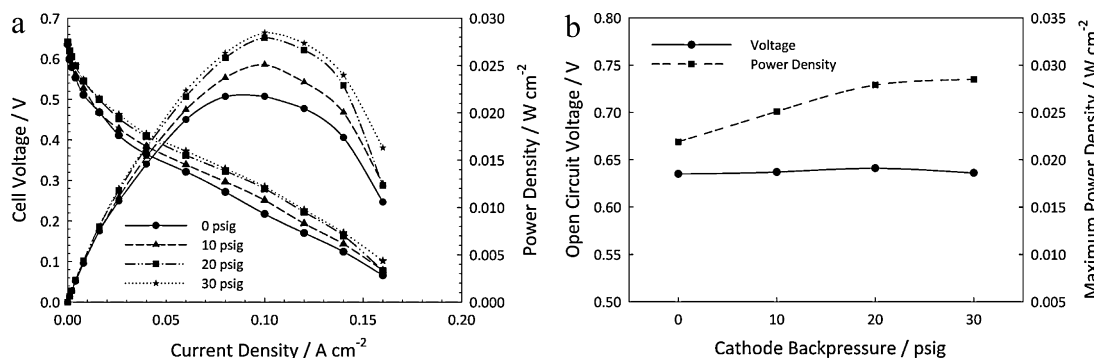


Fig. 4. Effect of cathode backpressure on fuel cell performance for 1 M EtOH feed (2 mL min⁻¹ and 0 psig) and non-humidified oxygen (300 mL min⁻¹) at 90 °C, (a) polarization and power curves and (b) open circuit voltage and maximum power density.

the overall cathode behaviour may be the result of an opposing dependence with temperature due to the parasitic current and poisoning of the catalyst [14]. But overall, the dependence of other cell processes with temperature seems to be greater than the crossover since the performance is enhanced despite the increase in ethanol crossover.

The maximum power density increases with temperature almost linearly for both conditions as seen in Fig. 5c, with the exemption of the 60 °C point for the unpressurized condition. The difference in power density for the systems at the same temperature but with and without backpressure is in the 6–7 mW cm⁻² range for all the points except for the 60 °C point where the difference is 3 mW cm⁻². The smaller difference at a lowest temperature suggests that at 60 °C the crossover effect is less important. Therefore the effect of the backpressure is reduced. The OCV showed a very small positive dependence with temperature in both circumstances (Fig. 5c) and was slightly higher with cathode backpressure. While Song et al. [13] showed that the OCV was greatly affected by temperature, although their work was done at a range lower than 75 °C. For example, when the temperature was reduced from 75 °C

to 55 °C the OCV decreased from 0.62 to 0.53 V. This could indicate that, at lower temperatures, the anode kinetics are more important than the effect of ethanol crossover. Therefore an increase in the temperature would improve the OCV. In this work, at higher temperatures as in Fig. 5a and c, competing effect between enhanced anode kinetics and higher crossover with increasing temperature, resulted in an almost invariable OCV with temperature.

3.3. Effect of ethanol flow rate and ethanol concentration

Fig. 6 shows the effect of flow rate of ethanol solution on the fuel cell performance in the range of 0.6–5 mL min⁻¹. The performance is almost invariable in the 1–5 mL min⁻¹ range but for 0.6 mL min⁻¹ the maximum power density is around a 10 mW cm⁻² lower than at the higher flow rates (Fig. 6b). The difference in the performance between 0.6 mL min⁻¹ and other flow rates starts to appear at higher current densities of the kinetic region of the polarization curve (Fig. 6a). With increasing current, the difference between the 0.6 mL min⁻¹ curve and the other curves remains constant, i.e., the curves are almost parallel. Therefore the ohmic and mass transfer

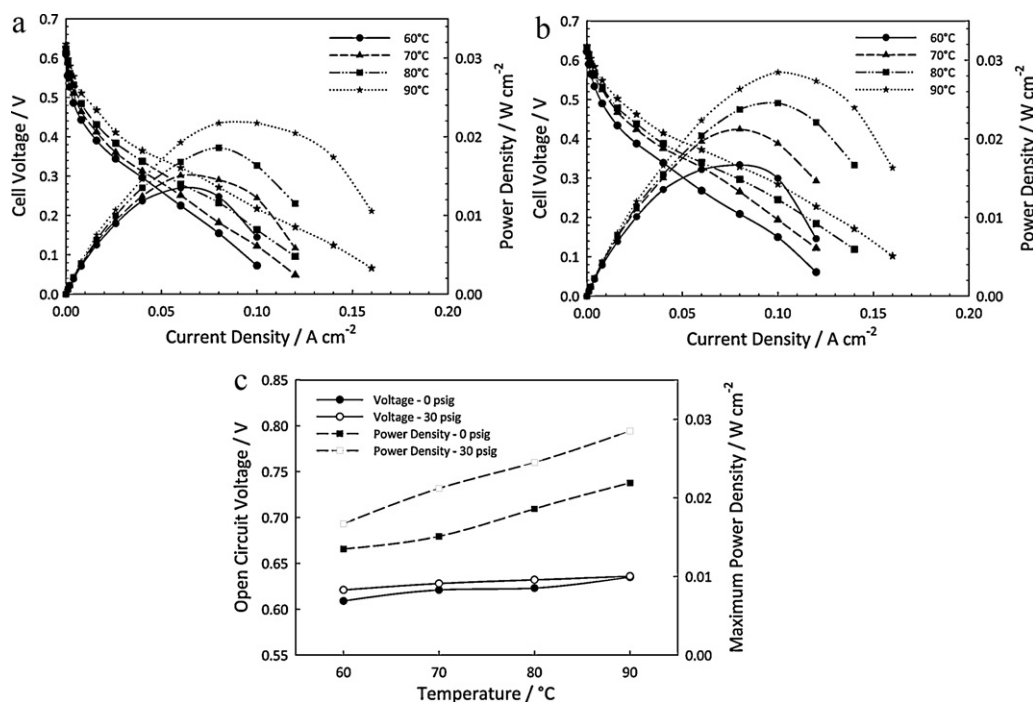


Fig. 5. Effect of cell temperature on fuel cell performance for 1 M EtOH feed (2 mL min⁻¹ and 0 psig) and non-humidified oxygen (300 mL min⁻¹) at 90 °C, (a) polarization and power curves with no cathode backpressure, (b) polarization and power curves with 30 psig cathode backpressure and (c) open circuit voltage and maximum power density.

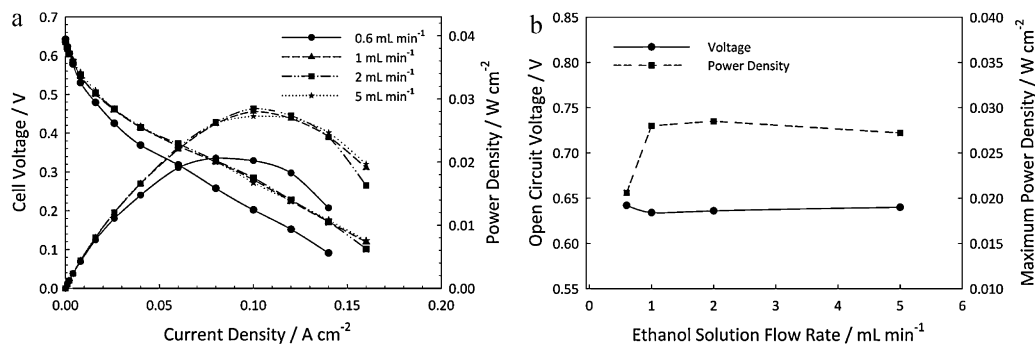


Fig. 6. Effect of ethanol solution flow rate on fuel cell performance for 1 M EtOH feed (0 psig) and non-humidified oxygen (300 mL min^{-1} , 30 psig) at 90°C , (a) polarization and power curves and (b) open circuit voltage and maximum power density.

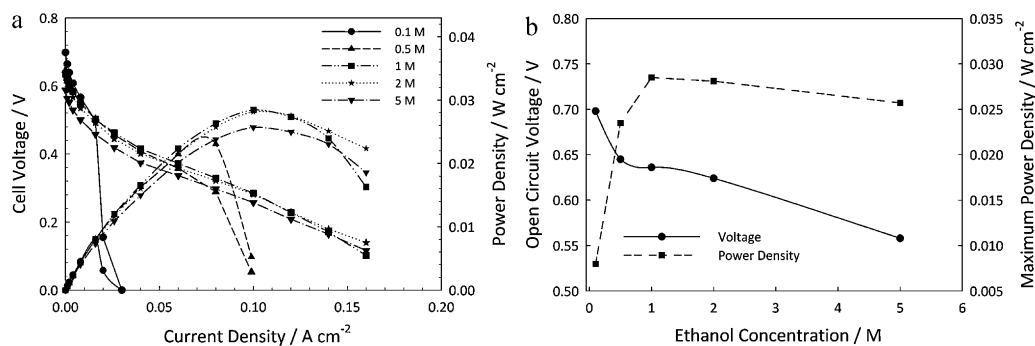


Fig. 7. Effect of ethanol concentration on fuel cell performance for aqueous EtOH feed (2 mL min^{-1} and 0 psig) and non-humidified oxygen (300 mL min^{-1} , 30 psig) at 90°C , (a) polarization and power curves and (b) open circuit voltage and maximum power density.

overpotentials are not affected by the ethanol flow rate. This suggests a surface phenomenon effect at low ethanol flow rates, such as lower removal of reaction products that block active sites or the decrease of in-plane transport of reactant and therefore a lower utilization of the available catalyst sites.

The effect of ethanol concentration on the cell performance is illustrated in Fig. 7. It is seen that the different regions in the polarization curve have different dependence on the ethanol concentration (Fig. 7a). Both, the OCV (Fig. 7b) and the fuel cell performance in the kinetic region increase with decreasing ethanol concentration. While in the mass transfer region the performance increases with increasing ethanol concentration up to 2 M. At very low ethanol concentration the performance suddenly drops due to mass transfer limitations. With 0.1 M the performance drops at a current density of approximately 0.015 A cm^{-2} , whereas this happens at 0.06 A cm^{-2} for a concentration of 0.5 M. In the case of 1 M ethanol solution, there is a slight inflection in the curve at 0.14 A cm^{-2} . At these three points the ethanol stoichiometries

are 8.04, 10.72 and 9.18, respectively (assuming the partial oxidation reaction of ethanol to acetic acid, i.e., 4 electrons per molecule of ethanol). Therefore, one can conclude that under these conditions a minimum stoichiometry of approximately 10 is necessary to avoid mass transfer limitations. By increasing the concentration from 1 M to 2 M the performance is almost invariable, differences are only seen at the maximum current density. While increasing ethanol concentration from 2 M to 5 M produces a drop in the performance in all regions of the polarization curve. In terms of the maximum power density there is a maximum between 1 M and 2 M (Fig. 7b). As seen from these results, by varying the ethanol concentration there is a clear contribution of two effects to the cell performance. Better mass transfer at high ethanol concentrations and lower ethanol crossover at low ethanol concentrations. At low currents there is a low consumption of ethanol; therefore a variation of ethanol concentration does not affect the anode kinetics in the studied concentration range. On the contrary, the cathode kinetic seems to be enhanced by the lower ethanol concentration

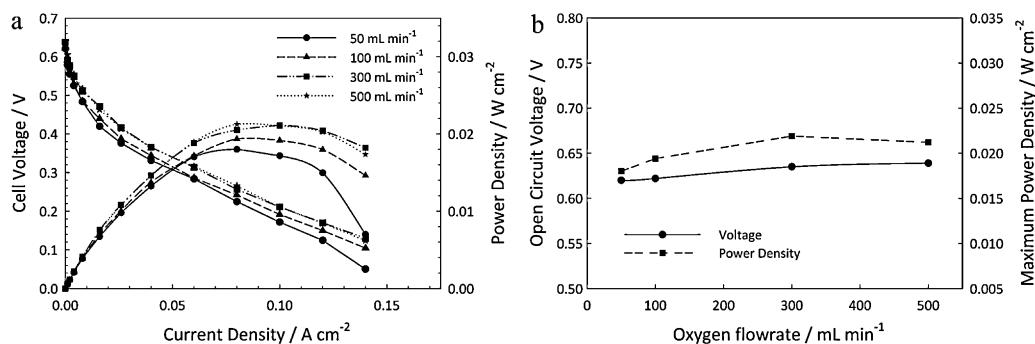


Fig. 8. Effect of oxygen flow rate on fuel cell performance for 1 M EtOH feed (1 mL min^{-1} , 0 psig) and non-humidified oxygen (300 mL min^{-1} , 0 psig) at 90°C , (a) polarization and power curves and (b) open circuit voltage and maximum power density.

due to the lower ethanol crossover. With increasing current density, the ethanol concentration starts to play a role in the anode response and the extreme case is seen when very low ethanol concentrations were tested with the presence of a limiting current.

3.4. Effect of oxygen flow rate

Fig. 8 shows the effect of oxygen flow rate on the fuel cell performance. These tests were performed at atmospheric pressure. No effect on the performance was observed in the 50–500 mL min⁻¹ range with 30 psig backpressure (results are not shown). In Fig. 8a it is seen that the performance increases with increasing oxygen flow rate up to 300 mL min⁻¹, increasing the flow rate further does not produce any change on the performance. Fig. 8b shows that the OCV and the maximum power density increase with increasing the flow rate, which is due to a higher concentration of oxygen at the cathode with respect to the crossover products and to an increase in the rate of removal of crossover substances that can poison the cathode catalyst.

4. Conclusions

The effect of operating parameters on the DEFC polarization curve, OCV and maximum power density was tested and analyzed. The OCV was highly dependant on the concentration of ethanol in the fuel stream and increases by decreasing the ethanol content. In contrast, the effect of the other studied parameters on the OCV was very small. Taking into account these small variations it can be summarized that the OCV increased with the oxygen flow rate, cathode backpressure and temperature, and was independent of fuel flow rate and anode backing layer.

In general, the kinetically controlled region of the polarization curves was enhanced by increasing the temperature, the backpressure and the oxygen flow rate, while it decreased by increasing the ethanol concentration. These parameters affected either or both the electrode intrinsic kinetics and the ethanol crossover. Furthermore, the kinetic response of the fuel cell was found to be independent of ethanol solution flow rate and anode diffusion layer. The cell's mass transfer properties were particularly affected by the ethanol concentration and in lesser extent by the anode backing layer and reactant flow rates.

Increasing the temperature improved the maximum power density almost linearly. With backpressure the performance increased up to 20 psig, further increments in the backpressure did not produce higher performance. Similar behaviour was seen for the oxygen flow rate at values higher than 300 mL min⁻¹. Higher power densities were found for ethanol concentration of 1 M and ethanol flow rate higher than 1 mL min⁻¹.

The gas diffusion layers that did not have an MPL showed superior performance. In terms of the diffusion layer, the DEFC system is unique since reactants and products are all liquids. This is not the case for the more extensively studied systems using methanol (liquid fuel–gas product) and hydrogen (gas fuel–liquid product) as fuels. Therefore more work is needed in the optimization of the DEFC electrode properties, including diffusion layers.

Acknowledgments

The National Research Council Canada-Institute for Fuel Cell Innovation (NRC-IFCI) and Agriculture Agri-Food Canada (AAFC) through the Agricultural Bioproducts Innovation Network Program (ABIP) supported this work. The authors thank Marius Dinu, Andrew Mattie, Kevin Berera and Tom Vanderhoek for their contribution in the fabrication of the ink auto-spray system and fuel cell hardware.

References

- [1] C. Lamy, S. Rousseau, E.M. Belgsir, C. Coutanceau, J.M. Léger, *Electrochim. Acta* 49 (2004) 3901.
- [2] S. Song, P. Tsiakaras, *Appl. Catal. B: Environ.* 63 (2006) 187.
- [3] K. Fatih, V. Neburchilov, V. Alzate, R. Neagu, H. Wang, *J. Power Sources* 195 (2010) 7168.
- [4] E. Antolini, E.R. Gonzalez, *Catal. Today* 160 (2011) 28.
- [5] E.V. Spinacé, M. Linardi, A.O. Neto, *Electrochem. Commun.* 7 (2005) 365.
- [6] E. Antolini, F. Colmati, E.R. Gonzalez, *Electrochem. Commun.* 9 (2007) 398.
- [7] A. Kowal, M. Li, M. Shao, K. Sasaki, M.B. Vukmirovic, J. Zhang, N.S. Marinkovic, P. Liu, A.I. Frenkel, R.R. Adzic, *Nat. Mater.* 8 (2009) 325.
- [8] E. Lee, A. Murthy, A. Manthiram, *Electrochim. Acta* 56 (2011) 1611.
- [9] J. Ribeiro, D.M. dos Anjos, K.B. Kokoh, C. Coutanceau, J.M. Léger, P. Olivi, A.R. de Andrade, G. Tremiliosi-Filho, *Electrochim. Acta* 52 (2007) 6997.
- [10] R.F.B. De Souza, M.M. Tusi, M. Brandalise, R.R. Dias, M. Linardi, E.V. Spinacé, M.C. dos Santos, A.O. Neto, *Int. J. Electrochem. Sci.* 5 (2010) 895.
- [11] J.E. Thomas, A.R. Bonesi, M.S. Moreno, A. Visintin, A.M. Castro Luna, W.E. Triaca, *Int. J. Hydrogen Energy* 35 (2010) 11681.
- [12] X. Zhao, W. Li, L. Jiang, W. Zhou, Q. Xin, B. Yi, G. Sun, *Carbon* 42 (2004) 3263.
- [13] S. Song, W. Zhou, J. Tian, R. Cai, G. Sun, Q. Xin, S. Kontou, P. Tsiakaras, *J. Power Sources* 145 (2005) 266.
- [14] G. Li, P.G. Pickup, *J. Power Sources* 161 (2006) 256.
- [15] H. Pramanik, A.A. Wragg, S. Basu, *J. Appl. Electrochem.* 38 (2008) 1321.
- [16] S. Song, G. Wang, W. Zhou, X. Zhao, G. Sun, Q. Xin, S. Kontou, P. Tsiakaras, *J. Power Sources* 140 (2005) 103.
- [17] S.K. Biswas, P. Sambu, S. Basu, *Asia-Pac. J. Chem. Eng.* 4 (2009) 3.
- [18] M. Blanco, D.P. Wilkinson, in: D.P. Wilkinson, J. Zhang, R. Hui, J. Fergus, X. Li (Eds.), *Proton Exchange Membrane Fuel Cell—Materials Properties and Performance*, CRC Press, Boca Raton, 2010, pp. 191–303.
- [19] G.M. Andreadis, A.K.M. Podias, P.E. Tsiakaras, *J. Power Sources* 194 (2009) 397.
- [20] T.S. Zhao, C. Xu, R. Chen, W.W. Yang, *Prog. Energy Combust. Sci.* 35 (2009) 275.
- [21] G.Q. Lu, C.Y. Wang, *J. Power Sources* 134 (2004) 33.
- [22] G.M. Andreadis, A.K.M. Podias, P.E. Tsiakaras, *J. Power Sources* 181 (2008) 214.
- [23] D.D. James, P.G. Pickup, *Electrochim. Acta* 55 (2010) 3824.
- [24] A. Jablonski, P.J. Kulesza, A. Lewera, *J. Power Sources* 196 (2011) 4714.
- [25] S. Kontou, V. Stergiopoulos, S. Song, P. Tsiakaras, *J. Power Sources* 171 (2007) 1.