



Study of operating conditions and cell design on the performance of alkaline anion exchange membrane based direct methanol fuel cells

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ABSTRACT

Direct methanol fuel cells using an alkaline anion exchange membrane (AAEM) were prepared, studied, and optimized. The effects of fuel composition and electrode materials were investigated. Membrane electrode assemblies fabricated with Tokuyama® AAEM and commercial noble metal catalysts achieved peak power densities between 25 and 168 mW cm⁻² depending on the operating temperature, fuel composition, and electrode materials used. Good electrode wettability at the anode was found to be very important for achieving high power densities. The performance of the best AAEM cells was comparable to Nafion®-based cells under similar conditions. Factors limiting the performance of AAEM MEAs were found to be different from those of Nafion® MEAs. Improved electrode kinetics for methanol oxidation in alkaline electrolyte at Pt–Ru are apparent at low current densities. At high current densities, rapid CO₂ production converts the hydroxide anions, necessary for methanol oxidation, to bicarbonate and carbonate: consequently, the membrane and interfacial conductivity are drastically reduced. These phenomena necessitate the use of aqueous potassium hydroxide and wettable electrode materials for efficient hydroxide supply to the anode. However, aqueous hydroxide is not needed at the cathode. Compared to AAEM-based fuel cells, methanol fuel cells based on proton-conducting Nafion® retain better performance at high current densities by providing the benefit of carbon dioxide rejection.

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1. Introduction

Direct methanol fuel cells (DMFCs) – based on a proton-conducting polymer electrolyte membrane and a circulating feed of an acid-free, aqueous methanol solution – underwent rapid development between 1990 and 2005 [1–13]. Nafion® and other proton exchange membrane (PEM) systems have been widely investigated as electrolytes for DMFCs [14–18]. Operating systems have been demonstrated and a few commercial systems are now available [19–21]. However, more recently, there has been renewed interest [22–28] in DMFCs based on alkaline membrane electrolytes because of the possibility of improved electrode kinetics and lower catalyst loading. A recent review by Yu *et al.* presents a comprehensive overview of the current state of the art on direct alcohol fuel cells based on alkaline electrolytes [29]. Recent reports of DMFCs using Tokuyama® [30] and other membranes [31] are promising, but the power and current densities are lower than those of PEMs. Our goal is to optimize the membrane electrode assembly (MEA) construction and operating conditions in order to maximize the performance of DMFCs based on alkaline anion exchange membranes (AAEM) to a practical level.

An alkaline membrane electrolyte can be advantageous to a direct alcohol fuel cell for several reasons. It is known that the kinetics of electro-oxidation of methanol and other alcohols are more rapid in alkaline media [32] compared to acid media due to the weaker binding of chemisorbed intermediates, such as CO; the oxygen reduction reaction is also more facile in alkaline media [33]. The less corrosive alkaline environment invites the possibility of using non-noble metal catalysts at both the anode and the cathode [34]. This presents an opportunity for discovering more selective catalysts, that could facilitate the development of mixed reactant fuel cells [35]. Furthermore, one of the most problematic issues facing Nafion®-based DMFCs is methanol crossover from the anode to the cathode compartment through the membrane, resulting in a mixed potential at the cathode, flooding of the cathode, and parasitic consumption of fuel. This problem has been partially solved by using polyvinylidene fluoride–polystyrene sulfonic acid (PVDF–PSSA) membranes developed in our laboratory [14,15]. In alkaline fuel cells, this crossover is likely to be hindered by the electro-osmotic flux of water from the cathode to the anode. Finally, the price of Nafion® and similar polymers adds significantly to the cost of materials; less expensive membrane materials are desirable. The possibility of using non-noble-metal catalysts with alkaline membranes presents an opportunity for further cost reduction.

However, alkaline fuel cells (AFC) are not without disadvantages. Most alcohol AFCs include an electrolyte such as potassium

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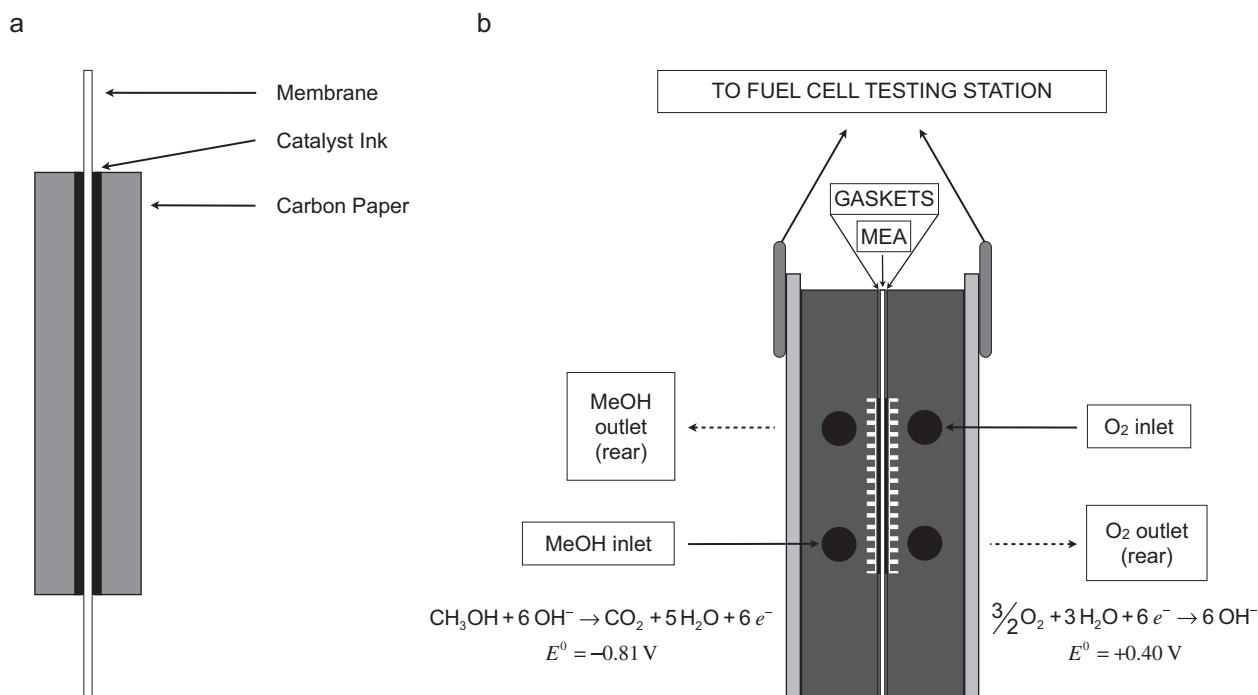


Fig. 1. (not to scale) (a) Cross-sectional diagram of the MEA, showing painted electrodes affixed onto either side of the membrane; (b) diagram of the MEA enclosed in the cell housing, showing the MEA, PTFE gaskets controlling compression, a cross-section of the pin-type graphite flow fields, and gold-plated current collectors.

hydroxide in the aqueous fuel to improve the cell performance; the conductivity of alkaline anion exchange membranes is generally found to be lower than that of proton exchange membranes [32]. Carbon dioxide formed at the anode in the presence of a basic aqueous electrolyte reacts with the hydroxide ions to form carbonate and bicarbonate species and decreases the overall cell performance [36]. The incorporation of these anions into the membrane creates an unfavorable pH gradient across the membrane, resulting in loss of voltage [37].

In the present study, alkaline direct methanol fuel cell based on a polymer electrolyte membrane has been shown to provide similar performance to that of Nafion[®]-based DMFCs. Specifically, we have investigated the effects of fuel composition, oxidant flow, and electrode materials on the performance in an operating cell.

2. Materials and methods

Fuel solutions were prepared from HPLC-grade methanol (Sigma–Aldrich) and reagent grade potassium hydroxide (Mallinckrodt) with deionized water (18.2 MΩ cm, Millipore Direct-Q 3).

Membrane electrode assemblies (MEAs) for alkaline DMFCs were prepared using the Tokuyama A-006 membrane (~50 μm thick, Tokuyama Corp.) and Toray carbon paper (TGPH-60) with and without 10 w/w% Teflon[®] wet-proofing. Catalyst inks were prepared from platinum black or platinum–ruthenium (1:1 atom ratio) black (Alfa-Aesar; Hi-Spec 1000 and Hi-Spec 6000, respectively), an ionomer solution (AS-4, quaternary ammonium type, Tokuyama Corp.), and deionized water in the mass ratio of 1:1:3 (catalyst:ionomer:water). The inks were painted onto 25 cm² carbon paper electrodes to achieve a catalyst loading of 8 mg cm⁻² and the MEAs were hot-pressed at 110 °C. For comparison, similar MEAs were prepared with Nafion[®] 117 (Du Pont, Inc.) using a 5% Nafion[®] ionomer solution (Sigma–Aldrich) and hot-pressed at 140 °C. A cross-sectional diagram of the MEA is shown in Fig. 1a.

Characterization of the MEAs was carried out in a standard cell housing with pin-type flow fields (Electrochem, Inc.) using a Fuel

Cell Test System 890B (Scribner Associates, Inc.). Fuel solutions were circulated using a Micropump[®] pump, and the temperature was controlled using a Digi-Sense[®] temperature controller (Cole-Parmer, Inc.). Pure O₂ was supplied to the cathode at various flow rates using an Accucal[®] controller (Gilmont, Inc.). A diagram of the cell housing is shown in Fig. 1b.

Both membranes require continuous water channels surrounding their hydrophilic side chains to provide sufficient ionic conductivity, and should be fully swelled with water prior to operation. Following hydration for a minimum of 6 h at 60 °C, and MEA conditioning at 90 °C, current–voltage curve measurements were taken in 0.5 A steps at 90 s intervals, at 30, 60 or 90 °C with O₂ supplied at 200, 700, or 1270 mL min⁻¹. Methanol solution was supplied at a constant flow rate of 200 mL min⁻¹, which ensured that the formed CO₂ was transported out of the cell and that methanol utilization was not more than 1% in a single pass for 1 M methanol while operating at 500 mA cm⁻².

3. Results and discussion

3.1. Operating conditions

3.1.1. Effects of temperature

MEAs were prepared at first using Toray paper (TGPH-60) that was wet-proofed with 10 w/w% Teflon[®]. These cells were supplied with 1 M methanol + 1 M KOH at the anode, and an ambient pressure oxygen flow at 1270 mL min⁻¹ to the cathode. Fig. 2 shows the performance of such a cell as a function of temperature. As expected, the current and power density maxima increased in value with an increase in temperature; at 90 °C, the peak power density was more than double (63 mW cm⁻²) the value observed at room temperature (27 mW cm⁻²). The cell behavior at 60 °C was very similar to that at 90 °C until the current density reached 140 mA cm⁻² (where both cells were at 0.44 V). However, at current densities greater than 140 mA cm⁻², the performance at 60 °C seemed to be limited by mass transport issues. This is attributed largely to the Teflon-coated anode and was confirmed by exper-

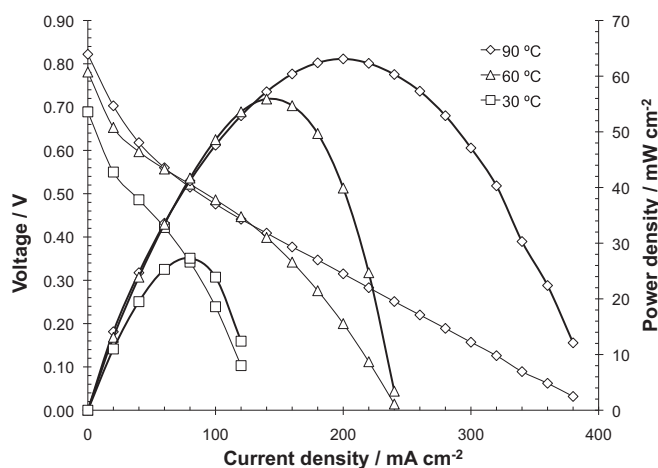


Fig. 2. Effect of temperature: polarization and power density curves, 1 M methanol + 1 M KOH, $1270 \text{ mL min}^{-1} \text{ O}_2$, wet-proofed electrodes.

iments with an electrode with no Teflon® (see Section 3.3.1). At 90°C , the mass transport limitations were not observed and ohmic control prevailed into high current densities.

3.1.2. Effects of oxidant flow rate

When the oxygen flow rate was decreased from 1270 mL min^{-1} to 200 mL min^{-1} , the reduction in performance was found to be 5–6% at all three temperatures based on both power densities as well as current densities. For example, at 90°C , the peak power density decreased only to a very small extent from 63 mW cm^{-2} to 59 mW cm^{-2} . These results indicate that the mass transport of oxygen is not a limiting factor in the range of current densities investigated for this type of MEA. Further MEA optimization, which allowed operation at higher current densities, showed that oxygen mass transport became important at high current densities (Section 3.3.2).

3.2. Fuel supply

3.2.1. Effects of methanol concentration

The baseline fuel solution used in the previously described experiments was 1 M methanol + 1 M KOH. The effect of increasing the fuel concentration at 90°C with an oxygen flow rate of 1270 mL min^{-1} was investigated. At first, the KOH concentration was held constant and the methanol concentration was increased. With 1 M KOH, the performance of the MEA decreased with increasing methanol concentration (Fig. 3). Although methanol crossover is expected to be less problematic with alkaline fuel cells, it is likely that the relatively thin Tokuyama membrane ($50 \mu\text{m}$) made these MEAs more susceptible to crossover compared to a thicker 117 Nafion® membrane ($175 \mu\text{m}$). Thus, increasing the concentration of methanol beyond 1 M was not beneficial. For example, at 50 mA cm^{-2} the observed cell voltages for 1 M, 2 M, and 3 M methanol were 0.59 V, 0.55 V, and 0.39 V, respectively, demonstrating the negative impact of crossover on overall cell performance. Based on these data and the results presented in Section 3.1.1, 1 M methanol was found to be the optimal fuel concentration.

3.2.2. Effects of potassium hydroxide concentration

Experiments with aqueous methanol fuel (1–2 M) with no added KOH electrolyte resulted in no measurable performance at all temperatures. This ultra-low performance is often attributed [38–40] to a poorly formed interface between the electrode and the alkaline anion exchange membrane, which is considered to be insufficiently conductive to allow facile hydroxide transfer. We suggest an alter-

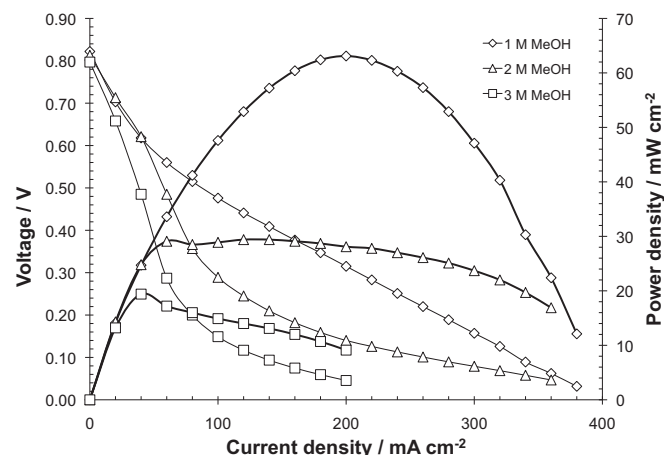


Fig. 3. Effect of methanol concentration: polarization and power density curves, 1 M KOH, 90°C , $1270 \text{ mL min}^{-1} \text{ O}_2$, wet-proofed electrodes.

native explanation based on our subsequent experiments (also see Section 3.3.1).

Previous experiments in Section 3.2.1 were conducted with 1 M KOH. Subsequently, the peak power density was found to increase upon raising the KOH concentration from 1 M to 2 M (Fig. 4). This effect was the same when using 2 M and 3 M methanol. This supports the hypothesis (Section 3.2.2) that KOH increases the conductivity of the electrode/electrolyte interface. However, no further improvement was observed by increasing the KOH concentration to 3 M; in fact performance was inferior to that at 2 M KOH and very similar to that at 1 M KOH. Based on these data, 1 M methanol + 2 M KOH was chosen as the ideal fuel/electrolyte composition for further studies.

There are many factors to consider when examining the effect of electrolyte concentration on electrode performance, especially the effect of pH on the membrane potential, carbonate formation, and their interdependence. The effects of these factors could not be easily separated in the present experiment. For example, as CO_2 is formed in the anode diffusion layer, the rate of the bicarbonate/carbonate formation reaction is determined by the concentration of OH^- at the interface. The concentration of OH^- is in turn dependent on the diffusion rate of OH^- through the electrode structure and on the bulk concentration of KOH. AAEM conductivity and the effectiveness of the ionomer are often cited [38–40] as the causes of inferior performance in the absence of added hydroxide. However, in our studies, the ohmic resistance

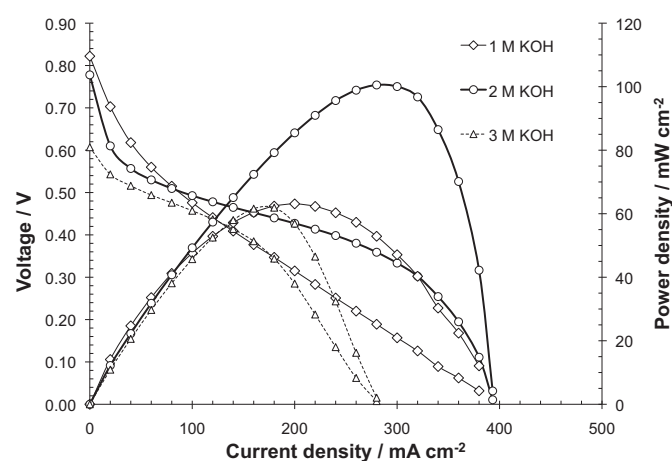


Fig. 4. Effect of increasing KOH concentration: polarization and power density curves, 1 M methanol, 90°C , $1270 \text{ mL min}^{-1} \text{ O}_2$, wet-proofed electrodes.

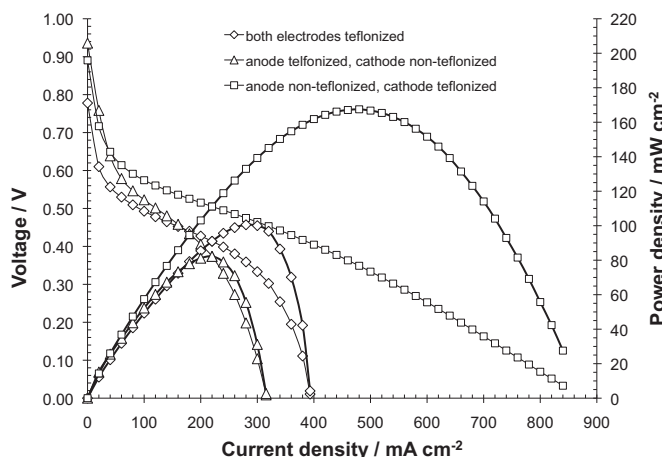


Fig. 5. Effect of electrode wet-proofing: polarization and power density curves, 2 M KOH + 1 M methanol, 90 °C, 1270 mL min⁻¹ O₂.

of the AAEM and Nafion® MEAs were quite similar. Furthermore, the addition of KOH would offer conductivity benefits only to the anode. If the membrane interface or ionomer were the underlying cause, we would expect the cathode interface to be similarly impacted, since the same ionomer was used at the anode and cathode. Therefore, we suggest that the underlying issue is the availability of the hydroxide anion as a necessary reactant in the methanol oxidation reaction. The competing, non-Faradaic reaction of OH⁻ with carbon dioxide, in the absence of a large excess of hydroxide, reduces the availability of OH⁻ needed for the methanol oxidation reaction; when hydroxide is available in excess, the effect of formation of bicarbonate or carbonate is less significant. Therefore, we suggest that the increase in performance from 1 M to 2 M KOH was due to the beneficial effect on hydroxide availability.

3.3. Membrane–electrode assembly materials

3.3.1. Effects of electrode wettability

All previous experiments were conducted with Toray TGPB-60 with 10% wet-proofing. These were designated as “standard” MEAs. Using all the previously optimized conditions, the impact of the Teflon® wet-proofing on the carbon paper electrodes was examined. Fig. 5 shows the current–voltage characteristics and power densities of various MEAs with both “standard” and “non-wet-proofed” Toray electrodes. Replacing the “standard cathode” with “non-wet-proofed” carbon paper decreased the maximum current density by nearly 25%, and the maximum power density by 20%. On the other hand, replacing only the anode with “non-wet-proofed” carbon paper more than doubled the maximum current density (from 400 mA cm⁻² to 840 mA cm⁻²) and increased the maximum power density from 101 mW cm⁻² to 168 mW cm⁻². This is consistent with expectation that the Teflon® coating at the anode would impede the diffusion of the aqueous electrolyte at the anode, and aid in water rejection and prevent flooding at the cathode.

The performance of cells with and without Teflon® coating at the anode at 30 °C are compared in Fig. 6. The polarization curves confirmed that the Teflon coating impeded mass transport at low temperature, while the anode without the Teflon® wet-proofing appeared to be only under ohmic control even at high current densities.

The hydroxide exchange membrane MEA requires rapid and efficient distribution of electrolyte into the pores at the anode/membrane interface in order to ensure hydroxide anion availability. For this reason, wet-proofing at the anode impedes the diffusion of the hydroxide ions and results in reduced cell performance. Acidic fuel cells using Nafion®, on the other hand,

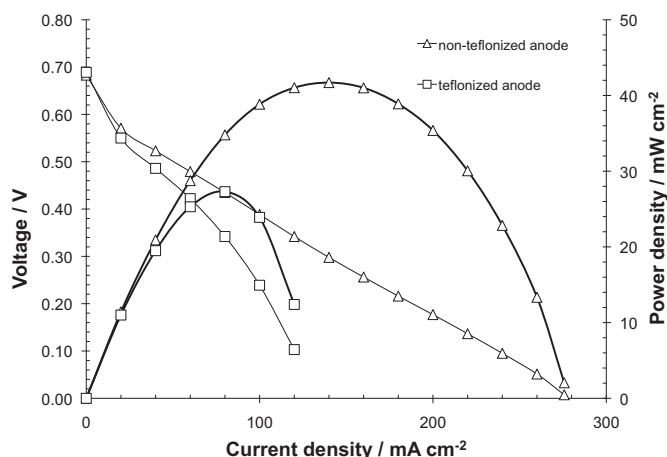


Fig. 6. Mass transport limitation at low temperature with wet-proofed anode: polarization and power density curves, 2 M KOH + 1 M methanol, 30 °C, 1270 mL min⁻¹ O₂.

require only methanol to be transported and the proton concentration is unaffected by the production of CO₂ [41]. Consequently, wet-proofing has only a marginal effect on overall performance.

3.3.2. Comparison of performance of AAEM and Nafion® cells

For comparison, a Nafion® 117 MEA was tested with 1 M methanol with no added KOH at 90 °C with wet-proofed electrodes. The maximum power density for the Nafion cell was 173 mW cm⁻², about 4% greater than the AAEM cell (see Fig. 7). Furthermore, the maximum power density of the Nafion® MEA was observed at a lower cell voltage, suggesting a higher voltage efficiency for the AAEM cell at the peak power density. At peak power point, the voltage of the Tokuyama cell was 0.35 V; the power density of the Nafion® cell at this voltage was about 4% lower. Fig. 7 also includes a plot of the cell voltage corrected for internal resistance losses. The ohmic resistance measurements made at the start of the tests were used in calculating the resistance-corrected voltage values. The resistance of the AAEM was quite similar to the Nafion® cell resistance, about 250 mΩ cm². Tafel slopes calculated using the resistance-corrected curves for the AAEM and Nafion® MEAs were very similar. These results are consistent with the absence of any difference in the catalyst compositions between the cells.

The Nafion® cell exhibited better performance at high current densities; this is plausibly due to the higher solubility of O₂ in

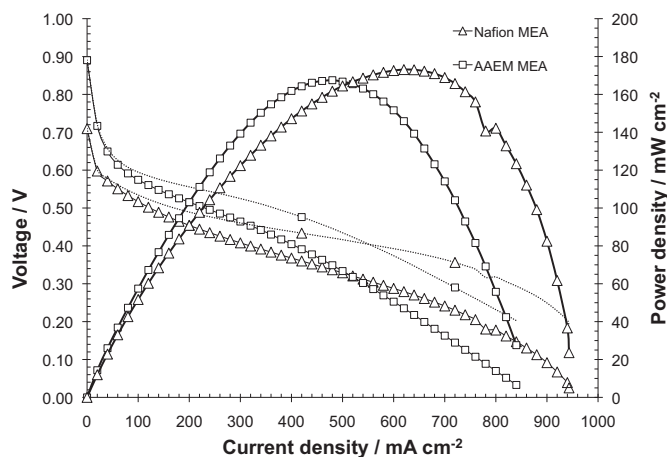


Fig. 7. Comparison of Tokuyama MEA with Nafion MEA: polarization and power density curves, 2 M KOH + 1 M methanol, 90 °C, 1270 mL min⁻¹ O₂ (dotted lines represent iR-corrected polarization curves).

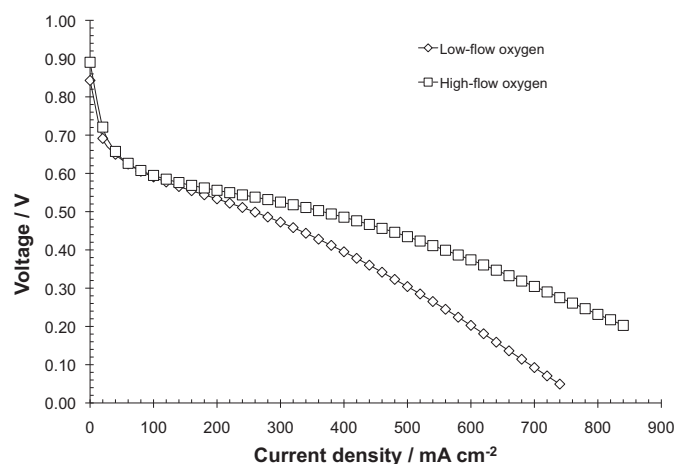


Fig. 8. Polarization curves showing the effect of reduced oxygen flow rate at high current densities; 2 M KOH + 1 M methanol, 90 °C; "high-flow" signifies 1270 mL min⁻¹ O₂, "low-flow" signifies 200 mL min⁻¹ O₂.

the catalyst layer containing Nafion[®] ionomer. The cathode in the AAEM cell was relatively unoptimized with respect to the formation of the electrode/electrolyte interface, and the solubility of O₂ is lower than in Nafion[®]. Consequently, O₂ mass transport issues were seen at current densities greater than 500–600 mA cm⁻². Fig. 8 shows the performance decrease observed when the oxygen flow rate was decreased, which confirms the mass transport limitations of oxygen in the AAEM cell. Such a limitation was not observed in the results reported in Section 3.1.2 due to the low current densities involved and the non-optimal fuel composition and electrode materials. In a previous report [14], we have observed a negative effect of increasing oxygen flow which was attributed to faster drying-out of the Nafion[®] membrane. The opposite effect, observed here, demonstrates that water transport to the cathode as a necessary reactant is not a limiting factor, possibly due to the thinner Tokuyama membrane. In acidic DMFCs, backdiffusion of water from the cathode to the anode is desirable to prevent cathode flooding, and therefore oxygen backpressure is often beneficial. The oxygen reduction reaction in alkaline DMFCs, on the other hand, depends on water transport from the anode to the cathode. As a consequence, oxygen backpressure may hinder the cathode reaction and was therefore not employed in this study.

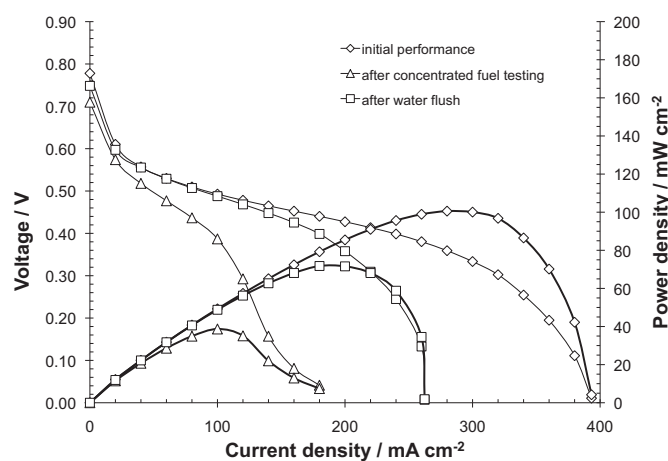


Fig. 9. Degradation behavior of a Tokuyama MEA with wet-proofed electrodes: initial performance, followed by observed degradation after high concentration fuel experiments, and finally partial recovery after 12 h/60 °C water flush (experiments were carried out at 48 h intervals); polarization and power density curves, 2 M KOH + 1 M methanol, 90 °C, 1270 mL min⁻¹ O₂.

3.3.3. Cell durability

The current voltage curves for the AAEM cell recorded over several days of testing under different conditions are shown in Fig. 9. Initially, the cell was tested repeatedly for two days at 60 °C with low concentration fuel (1 M methanol + 1 M KOH). After these tests, any decrease in performance was completely recovered by replacing the fuel solution. Subsequently, the temperature was increased to 90 °C and tests were conducted with 2 M and 3 M methanol. Fig. 9 shows the performance on the first day of more extended testing at the optimized fuel concentration (1 M methanol + 2 M KOH). The second curve represents the same cell tested under similar conditions after using solutions reaching 3 M in methanol or KOH: the power density was approximately 40% of the value from the previous tests. Finally, the last curve shows the performance after continued testing with 2 M and 3 M methanol, but with both electrodes flushed overnight with deionized water at 60 °C before the tests. About 70% of the original performance was recovered after the flushing of the electrodes with deionized water.

The durability of Nafion[®] DMFCs has been well-studied and the effective lifetime determined to be approximately 1000 h [42]. Degradation reactions of AAEMs in strongly basic environments (particularly by Hofmann elimination [43]) are well known; operating at 90 °C could result in permanent chemical degradation. However, the reversible loss in performance was more likely due to the formation of bicarbonate carbonate species through the reaction of carbon dioxide with hydroxide anions in the electrolyte. In addition to reducing the number of hydroxide ions available for the methanol oxidation reaction, the bicarbonate and carbonate ions decreased the conductivity of the membrane by exchanging with the hydroxide ions in the membrane. Thus, flushing with water over an extended period of time restored the membrane sites at least partially.

4. Conclusions

The peak performance of MEAs with the alkaline anion exchange membrane (Tokuyama A-006) and the Nafion[®] DMFC were comparable under similar test conditions. However, the factors that limited the performance of the two types of cells were different. It appears that the oxygen reduction reaction at the cathode becomes a limiting factor in the Tokuyama cells at high current densities. Furthermore, performance loss in AAEM-based MEAs is more rapid than in Nafion[®] DMFCs due to the less robust membrane. Nevertheless, using an optimized fuel and electrolyte mixture and by careful choice of electrode materials, we obtained high power densities and current densities compared to known reports of alkaline DMFCs with only 1 M methanol as fuel at both high and low temperatures [29].

Importantly, the addition of KOH was found to be necessary for performance; based on our results, we believe that for the facile electrooxidation of methanol to occur, hydroxide needs to be supplied. The use of an alkaline anion-exchange ionomer in the electrodes does not by itself ensure high performance. The carbon dioxide produced at the anode depletes the interface of the hydroxide transported through the membrane, which is necessary for the methanol oxidation reaction, resulting in continually decreasing current. This conclusion is consistent with observations reported by others [44] and has important implications for the design of future alkaline DMFCs.

While problems of interfacial conductivity and exchange may contribute to the reduction in performance, the fundamental insufficiency of hydroxide ions due to their reaction with carbon dioxide is a very important performance-limiting factor in AAEM-based alkaline DMFCs. The depletion of hydroxide ions through bicarbonate/carbonate formation and exchange leads to reversible loss of

performance while the chemical degradation of the membrane in the strongly alkaline environment leads to unrecoverable losses. Under these conditions, DMFCs based on AAEMs will unavoidably require addition of hydroxide electrolyte for sustained operation. Therefore, the discovery of more robust membranes in alkaline environments, coupled with better anode and cathode catalysts, offers the most promise for attaining higher performance alkaline DMFCs.

Acknowledgements

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