JOURNAL OF APPLIED ELECTROCHEMISTRY **26** (1996) 751–756

A direct methanol fuel cell using acid-doped polybenzimidazole as polymer electrolyte

J.-T. WANG,[‡] J. S. WAINRIGHT,[‡] R. F. SAVINELL,*[,‡] M. LITT[§]

Ernest B. Yeager Center for Electrochemical Sciences, Department of Chemical Engineering[‡] *and Department of Macromolecular Science,*[§] *Case Western Reserve University, Cleveland, OH 44106, USA*

Received 19 July 1995; revised 21 December 1995

A direct methanol/oxygen solid polymer electrolyte fuel cell was demonstrated. This fuel cell employed a 4 mg cm^{-2} Pt-Ru alloy electrode as an anode, a 4 mg cm^{-2} Pt black electrode as a cathode and an acid-doped polybenzimidazole membrane as the solid polymer electrolyte. The fuel cell is designed to operate at elevated temperature (200 °C) to enhance the reaction kinetics and depress the electrode poisoning, and reduce the methanol crossover. This fuel cell demonstrated a maximum power density about 0.1 W cm^{-2} in the current density range of 275–500 mA cm^{-2} at 200 °C with atmospheric pressure feed of methanol/water mixture and oxygen. Generally, increasing operating temperature and water/methanol mole ratio improves cell performance mainly due to the decrease of the methanol crossover. Using air instead of the pure oxygen results in approximately 120 mV voltage loss within the current density range of 200–400 mA cm^{-2}.

1. Introduction

Fuel cells employing solid polymer electrolytes such as perfluorosulfonic acid polymer membranes (Nafion®) are receiving increasing attention due to their promise as a high energy density power plant for both stationary and mobile applications. The main features of the polymer electrolyte fuel cell (PEFC) are pollution free operation, less corrosion and high power density. During the last five years, significant efforts have been made to advance the H_2/O_2 PEFC, such as decreasing the noble metal catalyst loading and improving the conductivity of the polymer electrolyte [1–4]. Now for the H_2/O_2 PEFC, the catalyst loading can be as low as 0.05–0.15 mg cm^{-2} with similar fuel cell performance to a high loading PEFC (4 mg cm^{-2} Pt).

Recently, there is an increasing motivation to develop a direct methanol/oxygen fuel cell (DMFC) [5–8]. Using methanol as fuel has several advantages compared to hydrogen. Methanol is a relatively plentiful liquid fuel which can be easily handled, stored and transported. Moreover the infrastructure built for gasoline can be used, if the methanol/oxygen fuel cell is used in transportation. However, there are at least two technical challenges impeding direct methanol/oxygen fuel cell commercialization. One is lack of a sufficiently active anode catalyst, although Pt–Ru alloy is still recognized as the best catalyst for direct methanol oxidation. The other is that the solid polymer electrolytes currently available, such as Nafion®, have a large methanol crossover rate. The methanol crosses the membrane to the cathode and not only wastes fuel but also polarizes the oxygen electrode, consequently lowering the energy efficiency and cell performance. To overcome these problems, Savinell *et al.* [9] proposed to increase the cell operating temperature to 200 °C. Operating a fuel cell at elevated temperature can enhance the reaction kinetics and depress the electrode poisoning, and cut down the methanol crossover rate due to lower gas permeability of the polymer electrolyte at elevated temperature. For such a DMFC, a new polymer electrolyte which can be operated at elevated temperature is required.

Polybenzimidazole (PBI) was suggested by Wainright *et al.* [10] for use as a polymer electrolyte when doped with an amphoteric acid such as phosphoric acid or sulfuric acid. PBI is a basic polymer ($pK_a = 5.5$) and it can be easily doped with an acid to form a single phase polymer electrolyte. The acid-doped PBI membrane exhibits excellent oxidative and thermal stability, and good mechanical flexibility at elevated temperature (200 °C). Compared to a Nafion® membrane, there are several advantages of acid doped PBI membrane. First, acid doped PBI membrane has good protonic conductivity at elevated temperature. Second, it has an almost zero electro-osmotic drag number [11], compared to the drag number of 0.6–2.0 for Nafion® membrane [12, 13]. This means that when protons transport through the PBI membrane, they do not carry water with them. This unique feature of the acid doped PBI membrane allows the PBI fuel cell to be operated at high temperature and low gas humidification without membrane dehydration. Third, acid doped PBI membrane has low methanol gas permeability. The methanol crossover rate of the acid-doped PBI membrane with a thickness of 0.008 cm is one-tenth of that of the Nafion® membrane with a thickness

---

*Author to whom correspondence should be addressed.

of 0.021 cm [10]. These properties suggest that acid-doped PBI membrane is a promising polymer electrolyte for DMFC.

This paper presents the results of testing a DMFC with acid-doped PBI membrane as the polymer electrolyte. The PBI fuel cell was operated at temperatures above 150 °C with a mixture of methanol and water and oxygen or air at atmospheric pressure. The effects of the operating temperature, anode gas composition, and air instead of oxygen were examined. The catalyst loading, and catalyst layer thickness effects on the electrode performance were also investigated.

2. Experimental details

Polybenzimidazole (Celanese) films were cast from a solution of high molecular weight (HMW) PBI in dimethylacetamide (DMAc). The films were then doped by immersion in a 11 M phosphoric acid solution for at least 24 h. The resulting doping level was approximately five phosphoric acid molecules per polymer repeat unit. The film thickness after doping was around 0.008 cm.

Platinum black (Johnson Matthey) and platinum–ruthenium alloy (Giner Inc.) were used as cathode and anode catalysts, respectively. The electrodes were prepared as follows. The desired amount of catalyst and PTFE suspension were mixed with distilled water. For low catalyst loadings, a small amount of carbon powder was added to facilitate handling. The resulting mixture was filtered through a polycarbonate filter membrane (1 μm pore size) to remove water. After most of the water was removed, a thin, uniform catalyst layer remained on the filter membrane. To reduce cracking of the catalyst layer in the drying process, a small amount of glycerol was added on the top of the catalyst layer. The glycerol was then filtered through the catalyst layer and replaced the residual water in the catalyst layer. The catalyst layer was then transferred onto a gas backing material (Spectracarb 2050 carbon paper) by lightly pressing the catalyst layer onto the gas backing, and carefully peeling off the filter membrane. The electrode was dried at room temperature in a vacuum oven for 4–5 h, then further dried at 60 °C in a vacuum oven overnight. Finally, the electrode was treated in a nitrogen atmosphere at 200 °C for 2 h to decompose the surfactant in the PTFE suspension.

The membrane/electrode (M&E) assemblies were formed by hot pressing the electrodes on an acid doped PBI membrane at 150 °C, 2.2×10^4 kPa for 10 min. The M&E assemblies were then impregnated with phosphoric acid by adding a few microlitres of 5 M H_3PO_4 solution on the gas backing side, and letting the acid solution penetrate into the electrode structure. The function of the added acid was to soften the PBI/electrode interface to improve ionic contact when the electrode is heated to 150 °C.

The electrochemical experiments were carried out in a single cell test station. Figure 1 shows the fuel cell hardware which consisted of two PTFE blocks supported by two stainless steel plates at the outside. The gas distribution channels and feed-throughs were machined into the PTFE blocks. The active electrode area was 1 cm^2. The whole unit was held together by four threaded studs and nuts. At the anode side, a reference electrode was held against the membrane. The reference electrode consisted of a E-TEK electrode (0.5 mg cm^{-2} Pt on carbon), which was fed continuously with humidified hydrogen gas during the experiment. Its potential was assumed to be equal to that of the reversible hydrogen electrode (RHE), and all potentials reported are with respect to this reference electrode. The fuel cell hardware was placed in an oven and heated to the desired temperature. Humidified oxygen or air was fed to the cathode chamber. Gas humidification was achieved by bubbling the gases through the distilled water at room temperature. A liquid mixture of methanol and water was vaporized in the oven and then fed to the anode chamber. The fuel cell was operated at atmospheric pressure. The cell resistance between anode and cathode was measured using the current interrupt method.

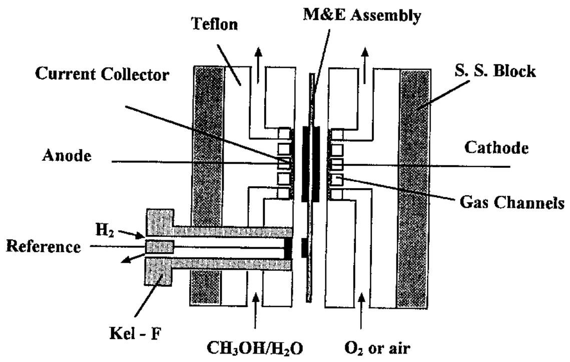

Fig. 1. Schematic of single cell with an electrode area of 1 cm^2.

3. Results and discussion

3.1. *Temperature effect*

Figure 2 shows the operating temperature effect on the cell performance. Increasing the operating

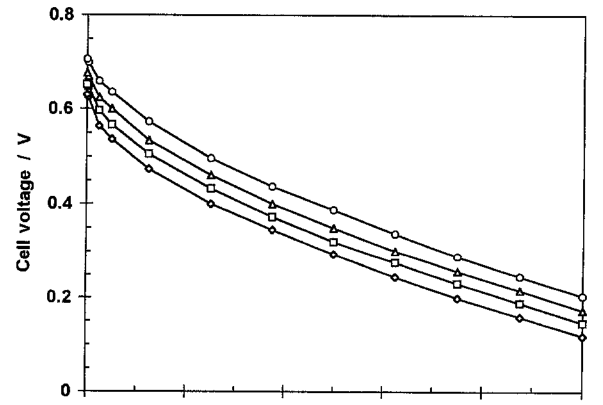

Fig. 2. Operating temperature effect on the fuel cell performance. PBI membrane doped with 500 mol% H_3PO_4. Cathode: 4 mg cm^{-2} Pt black, oxygen 1 atm, humidified at room temperature. Anode: 4 mg cm^{-2} Pt/Ru, water/methanol mole ratio of 2. Temperatures: (◇) 150, (□) 170, (△) 190 and (○) 200 °C.

temperature improves cell performance. The open circuit voltage of the cell varied from 0.630 to 0.706 V as the operating temperature was increased from 150 to 200 °C. The open circuit voltage change reflects the polarization of the anode and cathode due to the gas crossover (methanol crossover to cathode, and oxygen crossover to anode). Both factors will result in an open circuit voltage increase as the operating temperature increases. The cell voltage also increased over a broad current density range with increasing operating temperature. The cell voltage increase at 250 mA cm^{-2} was 70–90 mV when the operating temperature was increased from 150 to 200 °C. In the same temperature range, the cell resistance was almost constant (0.45–0.5 Ω cm^2 for a 0.008 cm thick PBI membrane). This measured cell resistance is consistent with the PBI membrane conductivity measured by a four-probe a.c. technique [10].

From the polarization curves of the anode and the cathode, it was found that the performance of the methanol electrode depends only slightly on temperature. This observation was made for both Pt and Pt/Ru catalysts. In the literature, it has been reported that the methanol oxidation on the Pt and Pt–Ru alloy in an aqueous solution is temperature dependent. For instance, Aramata [14] and Gasteiger *et al.* [15] report that the electrooxidation of methanol in 0.5–5 M H_2SO_4 solution on Pt–Ru alloys is strongly temperature dependent in the temperature range of 25–80 °C. Gasteiger also pointed out that the temperature effect is due to a shift in the rate determining step from methanol adsorption/dehydrogenation at low temperature to the surface reaction between the dehydrogenation intermediate and surface oxygen at high temperature. The cyclic voltammetry of electro-oxidation of methanol in a 85% H_3PO_4 solution on Pt also showed a temperature dependency in the range of 150–200 °C [16]. The difference between the literature measurements and the present results is that the latter DMFC is operated at elevated temperature, and the anode oxidizes gas phase methanol and water. Possible reasons for the temperature independence include low gas solubility at high temperature and electrode structure which limit gas transport or inhibit CO_2-product removal.

In contrast to the methanol electrode, the performance of the oxygen electrode was found to be dependent on the operating temperature. The higher the operating temperature, the better the cathode performance. Increasing the operating temperature not only enhances the kinetics of the oxygen reduction, but also reduces the methanol crossover. Both factors will improve the oxygen electrode performance.

3.2. *Anode gas composition effect*

The effect of the anode gas composition on fuel cell performance is shown in Fig. 3. It can be seen that increasing the water content significantly improves the performance of the cell. Increasing the water content decreases the methanol concentration and increases water concentration in the feed gas. The former reduces the methanol crossover, and the latter enhances the conductivity. The cell resistance observed changed from 0.522 to 0.475 Ω cm^2, when the mole ratio of water/methanol in the feed was changed from 1 to 4.

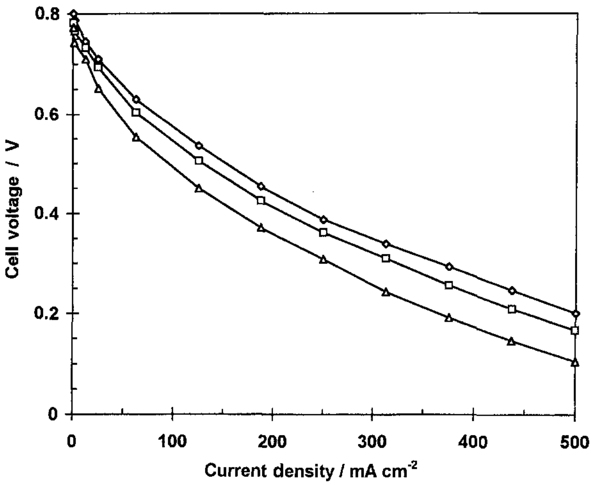

Fig. 3. The water/methanol mole ratio effect on the fuel cell performance. PBI membrane doped with 500 mol% H_3PO_4. Cathode: 4 mg cm^{-2} Pt black, oxygen 1 atm, humidified at room temperature. Anode: 4 mg cm^{-2} Pt/Ru. Cell operating temperature: 200 °C. Water/methanol mole ratio: (◇) 4, (□) 2 and (△) 1.

The effects of anode gas composition on the methanol and oxygen electrodes are shown in Fig. 4. The methanol electrode is only slightly sensitive to the gas composition in the activity range investigated. The polarization curves show that increasing methanol activity actually degrades the performance of the methanol electrode slightly, indicating that the methanol concentration is not a dominant factor controlling the electrode performance in this concentration range. The slightly increased performance at high water/methanol ratio may be due to higher ionic conductivity within the electrode structure. However, further increasing the mole ratio of the water/methanol may lower the electrode performance because of low methanol concentration and water flooding in the

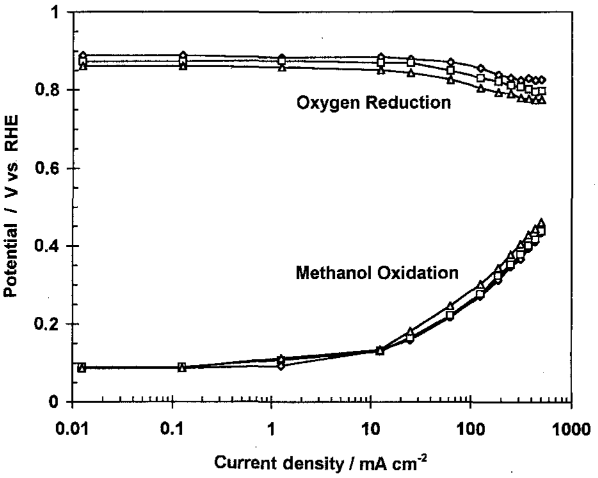

Fig. 4. The water/methanol mole ratio effect on the electrode performance. PBI membrane doped with 500 mol% H_3PO_4. Cathode: 4 mg cm^{-2} Pt black, oxygen 1 atm, humidified at room temperature. Anode: 4 mg cm^{-2} Pt/Ru. Cell operating temperature: 200 °C. Water/methanol mole ratio: (◇) 4, (□) 2 and (△) 1.

electrode structure. Obviously, there is an optimal mole ratio of water/methanol depending on the operating conditions of the fuel cell, such as operating temperature, current density, and gas flow rate.

Recently, the exhaust gases of the anode were investigated by the DEMS (differential electrochemical mass spectroscopy) method [17]. The methanol oxidation product distributions on Pt–Ru catalyst showed that the main products of the methanol oxidation on the Pt–Ru under these fuel cell operating conditions were carbon dioxide, methanaldimethylacetal and methylformate. The relative product distribution was strongly dependent on the mole ratio of water/methanol. When the mole ratio of water/methanol was greater than 2, carbon dioxide was the dominant product (> 99%), indicating complete methanol oxidation. When the mole ratio of water/methanol is less than 1, the methanaldimethylacetal becomes the more predominate product. However, although the product distributions change in the range of the mole ratio of water/methanol 1 to 4, no significant change of the anode polarization was observed.

Figure 4 also shows that as the water content in the anode feed increases, the performance of the oxygen electrode becomes better. This result is not surprising, because increasing the water content will reduce the methanol crossover and improve the polymer conductivity. The same reason may explain why the polarization curves become flat at high current density. The open circuit potential of the oxygen electrode is about 35 mV higher for a water/methanol mole ratio of four as compared to a mole ratio of one, probably because of the lower amount of methanol crossover.

3.3. *Air versus oxygen*

Since air is a more realistic oxygen source for a DMFC than pure oxygen, the effect of air on the cell performance was examined. A typical cell performance and corresponding polarization curves of the anode and the cathode are shown in Fig. 5 and Fig. 6, respectively. The open circuit voltage of the fuel cell decreases from 0.784 V for oxygen to 0.678 V with air. The cell voltages at a current density of 250 mA cm^{-2} with oxygen and air are about 0.390 V and 0.270 V, respectively. The cell performance curve of a methanol/air fuel cell is not parallel to that of methanol/oxygen fuel cell, indicating that factors other than oxygen concentration affect the cell performance.

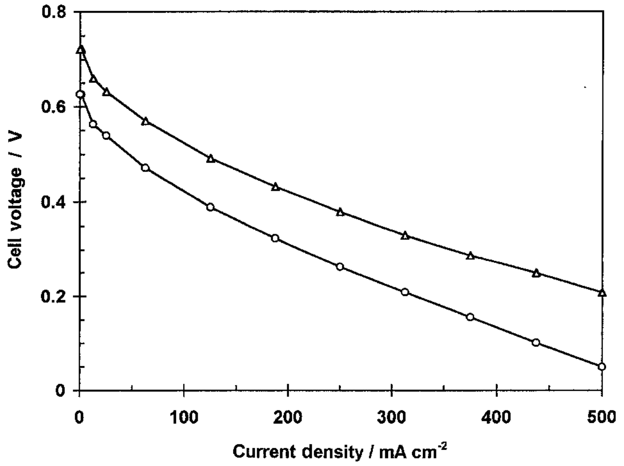

Fig. 5. Cell performance of PBI methanol/oxygen fuel cell with oxygen (△) or air (○). PBI membrane doped with 500 mol% H_3PO_4. Cathode: 4 mg cm^{-2} Pt black, oxygen 1 atm, humidified at room temperature. Anode: 4 mg cm^{-2} Pt/Ru, water/methanol mole ratio of 2. Cell operating temperature: 190 °C.

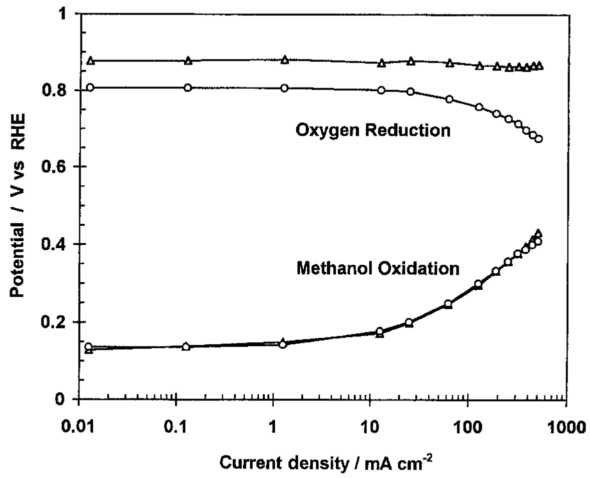

Fig. 6. Comparison of the electrode polarization curves with oxygen (△) or air (○) feeding at cathode. PBI membrane doped with 500 mol% H_3PO_4. Cathode: 4 mg cm^{-2} Pt black, oxygen or air 1 atm, humidified at room temperature. Anode: 4 mg cm^{-2} Pt/Ru, water/methanol mole ratio of 2. Cell operating temperature: 190 °C.

For a PBI H_2/O_2 fuel cell [18], the cathode polarization curve for air is parallel to the curve of oxygen with a 80 mV potential difference because of the lower oxygen partial pressure of air. From Fig. 6, it can be seen that the DMFC cathode polarization curve for air is not parallel to the curve of oxygen, and looses potential severely in the high current density region. This suggests that oxygen mass transport is controlling. A contributing factor to oxygen limitation could be due to methanol crossover. Additional oxygen is needed since methanol reaching the cathode consumes oxygen by direct reaction. Since a larger oxygen flux is then needed, transport within the electrode structure could become limiting. If this is true, one can expect that by reducing the methanol crossover rate or by pressurizing the air, the cell performance can be further improved. The anode polarization curve of the methanol/air cell is parallel to the curve of the methanol/oxygen cell. A 20–50 mV improvement in the anode potential was observed when air was used instead of oxygen, probably because of lower oxygen crossover to the anode. These results indicate that for the direct methanol fuel cell, oxygen crossover to the anode may also need to be considered because of the low anode catalyst activity.

3.4. *Catalyst loading effect on cathode performance*

Reducing the methanol crossover presents a great challenge for developing a direct methanol fuel cell. One unique feature of the acid doped PBI membrane is its low gas permeability. A typical value of methanol crossover [10] for a 0.008 cm thick PBI membrane

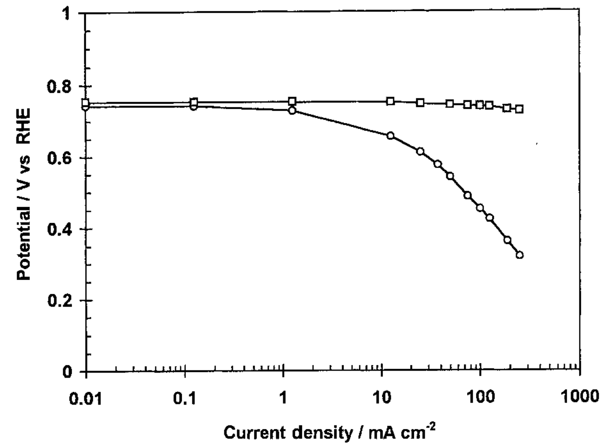

Fig. 7. Catalyst loading effect on the oxygen electrode performance under methanol/oxygen fuel cell operating condition. PBI membrane doped with 483 mol% H_3PO_4. Cathode side: oxygen 1 atm, humidified at room temperature. Anode side: 1 : 2 CH_3OH/H_2O feed. Cell operating temperature: 150 °C. Key: (□) 4 mg Pt cm^{-2}; (○) 0.5 mg Pt cm^{-2}.

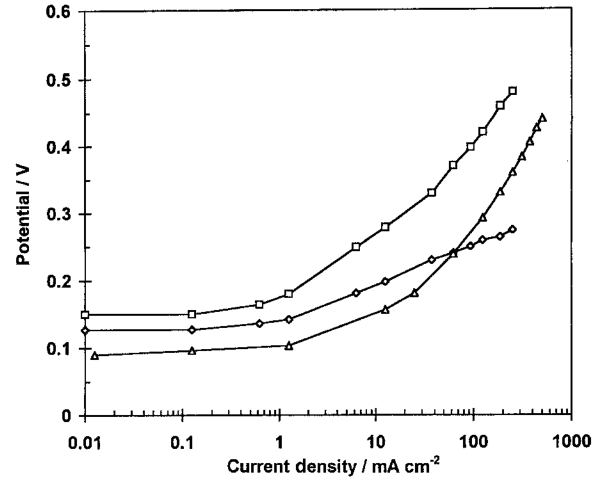

Fig. 8. Catalyst loading and electrode thickness effects on the anode performance under methanol/oxygen fuel cell operating condition. PBI membrane doped with 483 mol% H_3PO_4. Cathode side: oxygen 1 atm, humidified at room temperature. Anode side: 1 : 2 CH_3OH/H_2O feed. Cell operating temperature: 150 °C. Thickness: (◇) electrode A: 15 mg cm^{-2} Pt–Ru, 150 μm; (□) electrode B: 4 mg cm^{-2} Pt–Ru, 150 μm; (△) electrode C: 4 mg cm^{-2} Pt–Ru, 12 μm.

doped with 500 mol% phosphoric acid under fuel cell operating condition is 10–15 mA cm^{-2}. However, even this small amount of methanol across the membrane can adversely affect oxygen electrode performance. To address this problem, the effect of the catalyst loading and electrode structure on oxygen electrode performance was investigated. Figure 7 shows the comparison of the polarization curves of oxygen electrode with low loading (E-TEK electrode 0.5 mg cm^{-2} Pt on carbon) and high loading (4 mg cm^{-2} Pt). It shows that for a low loading electrode the polarization curve bends down severely at high current density. However, the electrode which has high Pt loading and a relatively thin catalyst layer shows a small performance decay at high current density, indicating that by increasing the catalyst loading the oxygen electrode becomes more methanol tolerant. Although an increased cathode platinum loading improves the cathode performance, a high loading electrode will increase catalyst cost. Therefore, there is an incentive to search for active oxygen reduction catalysts which are methanol tolerant and, preferably, non-precious metal based.

3.5. *Catalyst loading and catalyst layer thickness effects on anode performance*

The effects of catalyst loading and the electrode thickness on anode performance were investigated. Different catalyst loadings and catalyst layer thicknesses were achieved by adjusting the amounts of catalyst and carbon powder used in preparation of the electrodes. Figure 8 shows the comparison of three electrodes with different catalyst loading and electrode thickness. Electrode A and the electrode B have the same catalyst layer thickness (about 150 μm), but different catalyst loadings. As expected, the polarization curves show that the electrode with low catalyst loading is not as good as that with high catalyst loading due to fewer active catalyst sites. Electrode C has the same catalyst loading as the electrode B, but with less than one tenth of the electrode thickness. The polarization curves show that the performance of the thin electrode is significantly improved at high current density. The potential for methanol oxidation at 250 mA cm^{-2} is 0.36 V for the electrode C, which is about 100 mV lower than the thick electrode. These observations are consistent with our simulation results [19]. A thinner catalyst layer has lower mass transport and ion transport limitations and, therefore a higher catalyst utilization and better electrode performance.

4. Summary

A prototype direct methanol/oxygen solid polymer electrolyte fuel cell was tested. This fuel cell employed a 4 mg cm^{-2} Pt–Ru alloy anode, a 4 mg cm^{-2} Pt black cathode, and acid doped polybenzimidazole as the solid polymer electrolyte. The fuel cell is designed to operate at elevated temperature (200 °C) to enhance the reaction kinetics and depress electrode poisoning, and to lower methanol crossover. The fuel cell delivered a maximum power density of about 0.1 W cm^{-2} in the current density range of 275–500 mA cm^{-2} at 200 °C and atmospheric pressure water/methanol and oxygen feeds. Generally, increasing the operating temperature and the water/methanol mole ratio improved cell performance, mainly by decreasing methanol crossover. Using air instead of pure oxygen results in approximately 120 mV voltage loss in the current density range of 200–400 mA cm^{-2}. The experimental results show that a high Pt loading cathode is necessary to reduce sensitivity to methanol crossover.

Acknowledgement

This work was supported under a University Research Initiative Grant from the Advanced Research Projects Agency, ONR contractor NOOO14-92-J-1848. We thank H. Moadell for preparation of the PBI membranes.

References

[1] M. S. Wilson and S. Gottesfeld, *J. Electrochem. Soc.* **139** (1992) L28.

[2] M. S. Wilson and S. Gottesfeld, *J. Appl. Electrochem.*. **22** (1992) 1.

[3] E. J. Taylor, E. B. Anderson and N. R. K. Vilambi, *J. Electrochem. Soc.* **139** (1992) L45.

[4] S. Mukerjee, S. Srinivasan and A. J. Appleby, *Electrochim. Acta* **38** (1993) 1161.

[5] M. Wilson, J. Bett, X. Ren, F. Uribe and S. Gottesfeld, Ext. abstract 477, 187th Electrochemical Society Meeting, Reno, NV, 21–26 May (1995).

[6] D. Maricle and B. L. Murach, Ext. abstract 478, 187th Electrochemical Society Meeting, Reno, NV, 21–26 May (1995).

[7] J. A. Kosek, C. C. Cropley, G. Wilson and B. LaConti, Ext. abstract 479, 187th Electrochemical Society Meeting, Reno, NV, 21–26 May (1995).

[8] M. S. Wilson, J. A. Bett, T. A. Zawodzinski, and S. Gottesfeld, Ext. abstract 626, 185th Electrochemical Society Meeting, 22–27th May 1994, San Francisco, CA (1994).

[9] R. F. Savinell, E. Yeager, D. Tryk, U. Landau, J. Wainright, D. Weng, K. Lux, M. Litt, and C. Rogers, *J. Electrochem. Soc.* **141** (1994) L46.

[10] J. S. Wainright, J.-T. Wang, D. Weng, R. F. Savinell and M. Litt, *ibid.* **142** (1995) L121.

[11] D. Weng, J. S. Wainright and R. F. Savinell, Ext. abstract 667, 188th Electrochemical Society Meeting, Chicago, IL, 8–13 Oct. (1995).

[12] T. A. Zawodzinski, Jr, T. E. Springer, J. Davey, R. Jestel, C. Lopez, J. Valerio and S. Gottesfeld, *J. Electrochem. Soc.* **140** (1993) 1981.

[13] T. F. Fuller and J. Newman, *ibid.* **139** (1992) 1332.

[14] A. Aramata and M. Masuda, *ibid.* **138** (1991) 1949.

[15] H. A. Gasteiger, N. Markovic, P. N. Ross, Jr., and E. J. Cairns, *ibid.* **141** (1994) 1795.

[16] Q. Zhao and R. F. Savinell, Ext. abstract 615, 186th Electrochemical Society Meeting, Miami Beach, FL, 9–14 Oct. (1994).

[17] S. Wasmus, J-T., Wang and R. F. Savinell, *Electrochem. Soc.* **142** (1995) 3825.

[18] J.-T. Wang, R. F. Savinell, M. Litt and H. Yu, *Electrochim. Acta* **41** (1996) 193.

[19] J.-T. Wang and R. F. Savinell, 'Simulation Studies on the Fuel Electrode of a Methanol Air Polymer electrolyte Fuel Cell', Proceedings of the Symposium on Electrode Materials and Processes for Energy Conversion and Storage III (edited by S. Srinivasan), San Francisco, CA, The Electrochemical Society, Pennington, NJ (1994).