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Performance and endurance of a PEMFC operated with synthetic reformate fuel feed

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Abstract

Widespread implementation of polymer electrolyte membrane fuel cell (PEMFC) powerplants for stationary and vehicular applications will be dependent in the near future on using readily available hydrocarbon fuels as the source of the hydrogen fuel. Methane and propane are ideal fuels for stationary applications, while methanol, gasoline, and diesel fuel are better suited for vehicular applications. Various means of fuel processing are possible to produce a gaseous fuel containing H_2, CO_2 and CO. CO is a known electrocatalyst poison and must be reduced to low (10's) ppm levels and CO_2 is said to cause additional polarization effects. Even with no CO in the feed gas a $H_2/CO_2/H_2O$ gas mixture will form some CO. Therefore, as a first step of developing a PEMFC that can operate for thousands of hours using a reformed fuel, we used an anode gas feed of 80% H_2 and 20% CO_2 to simulate the reforming of CH_4. To investigate the effect of reformate on cell performance and endurance, a single cell with an active area of 58 cm^2 was assembled with a membrane electrode assembly (MEA) furnished by Texas A&M University using IGT's internally manifolded heat exchange (IMHEX™) design configuration. The MEA consisted of a Nafion 112 membrane with anode and cathode Pt catalyst loadings of 0.26 and 1.46 mg/cm^2, respectively. The cell was set to operate on a synthetic reformate–air at 60°C and 1 atm and demonstrated over 5000 h of endurance with a decay rate of less than 1%/1000 h of operation. The cell also underwent four successful thermal cycles with no appreciable loss in performance. The stable performance is attributed to a combination of the IGT IMHEX plate design with its inherent uniform gas flow distribution across the entire active area and MEA quality. The effects of temperature, gas composition, fuel utilization (stoics) and thermal cycle on cell performance are described. © 1998 Elsevier Science S.A.

Keywords: Polymer electrolyte membrane fuel cell (PEMFC); Reformate; Membrane electrode assembly (MEA)

1. Introduction

Stable operation of a polymer electrolyte membrane fuel cell (PEMFC) on a feed stream of reformate is a goal that has to be obtained in order to demonstrate the utilization of PEMFCs for stationary power generation. Fuel feed streams based on reformate obtained by reforming methane or methanol could result in somewhat inferior cell performance as compared to the conventional operation with pure hydrogen. The reformate after suitable CO removal techniques such as water–gas shift and selective oxidation or methanation will contain 20–25% carbon dioxide (CO_2) and trace amounts of carbon monoxide (CO), <100 ppm at steady-state operation. CO strongly chemisorbs onto Pt at the operating potential of the anode, effectively poisoning the surface for H_2 oxidation resulting in degradation of cell performance. In addition, it has been reported in the literature that CO_2 also has a degrading effect on cell performance. Although not as severe an effect as CO, at the levels present in reformate, a significant performance loss was observed [1,2]. Also CO could be produced in situ at a ppm level at the PEMFC anode by either the reverse water–gas shift reaction,

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (1)$$

or by the electroreduction of the carbon dioxide,

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \quad (2)$$

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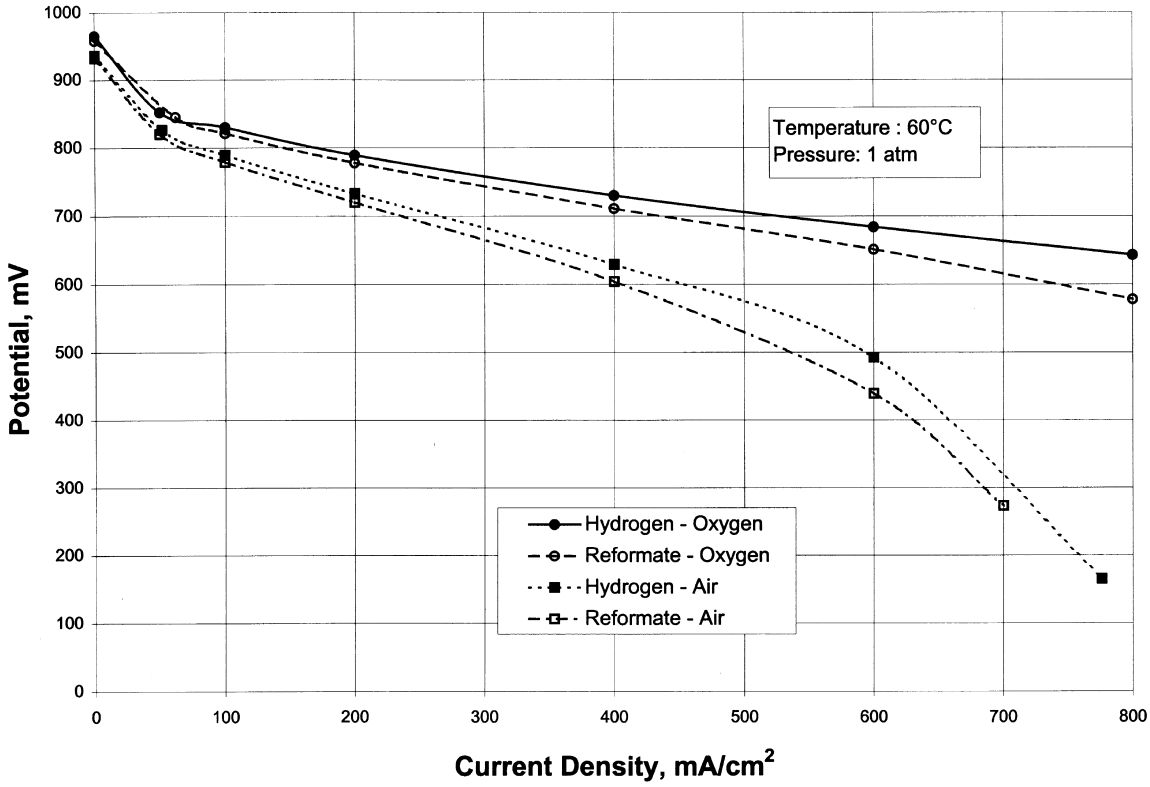

Fig. 1. Effect of oxidant gas composition on performance with hydrogen and reformate.

Also, at high fuel utilizations (above 70% or below 1.4 stoics) any increase in the anode polarization can decrease the cell performance. This increased anode polarization might be associated with restricted diffusion of hydrogen through the inert CO_2 in the reformate [3]. Therefore a cell test was conducted with Pt-loaded gas diffusion electrodes

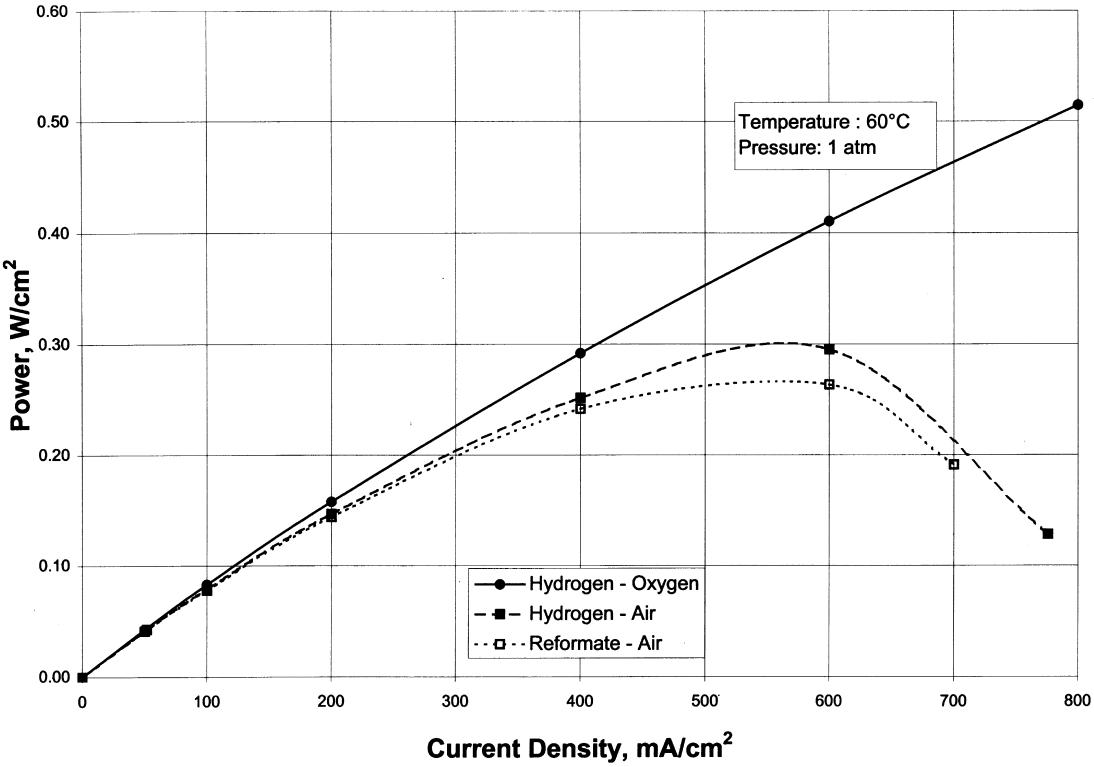

Fig. 2. Cell power output comparison for various fuel/oxidant types.

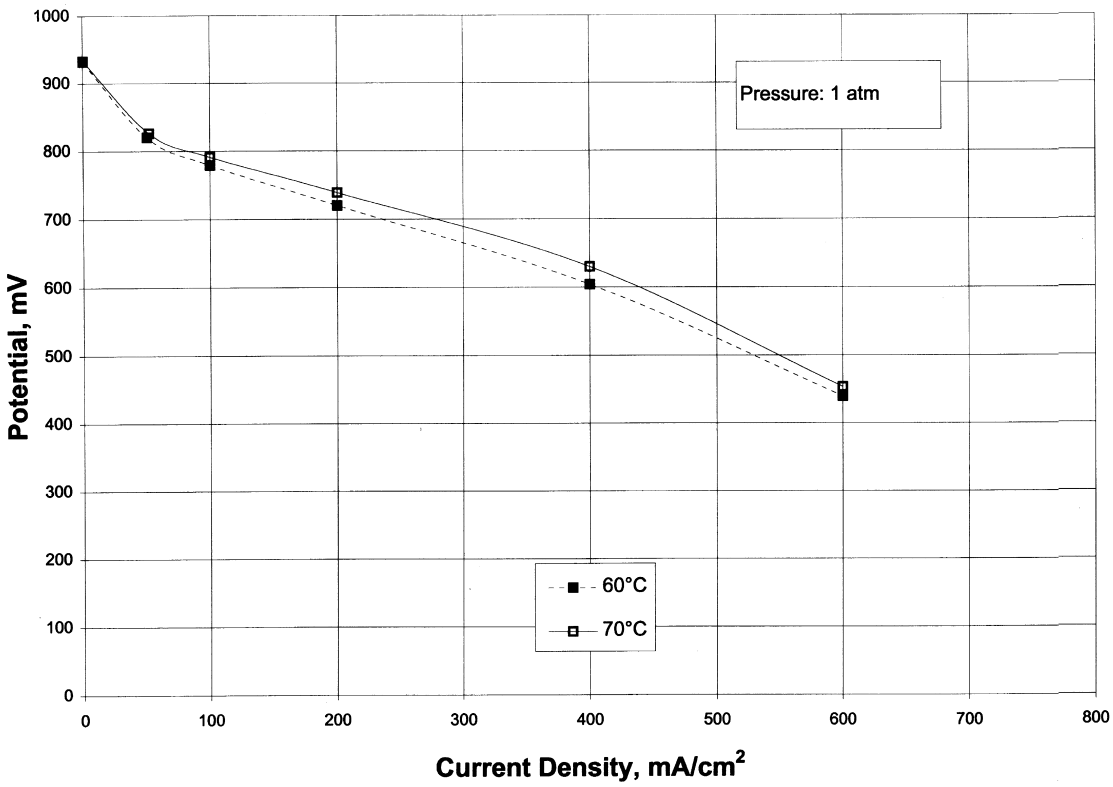

Fig. 3. Effect of temperature on performance with reformate/air.

to determine the effect of a carbon monoxide free synthetic reformate (80% H_2/20% CO_2) on cell performance and endurance.

2. Experimental

The gas diffusion electrodes were fabricated at Texas

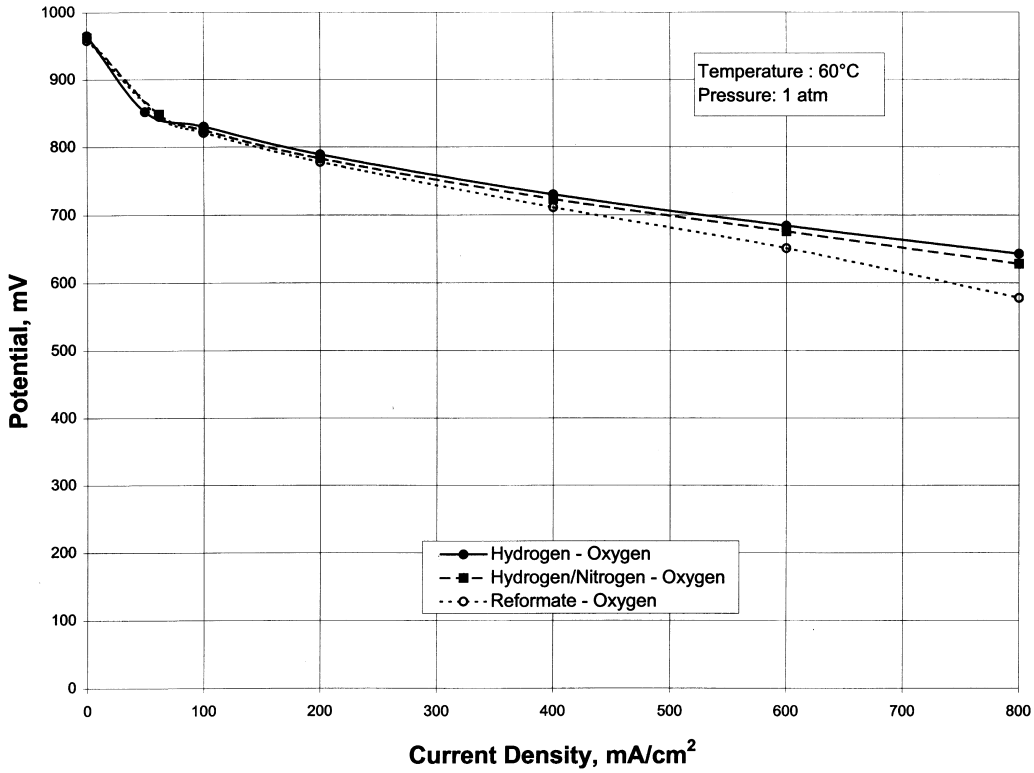

Fig. 4. Effect of anode gas composition on performance.

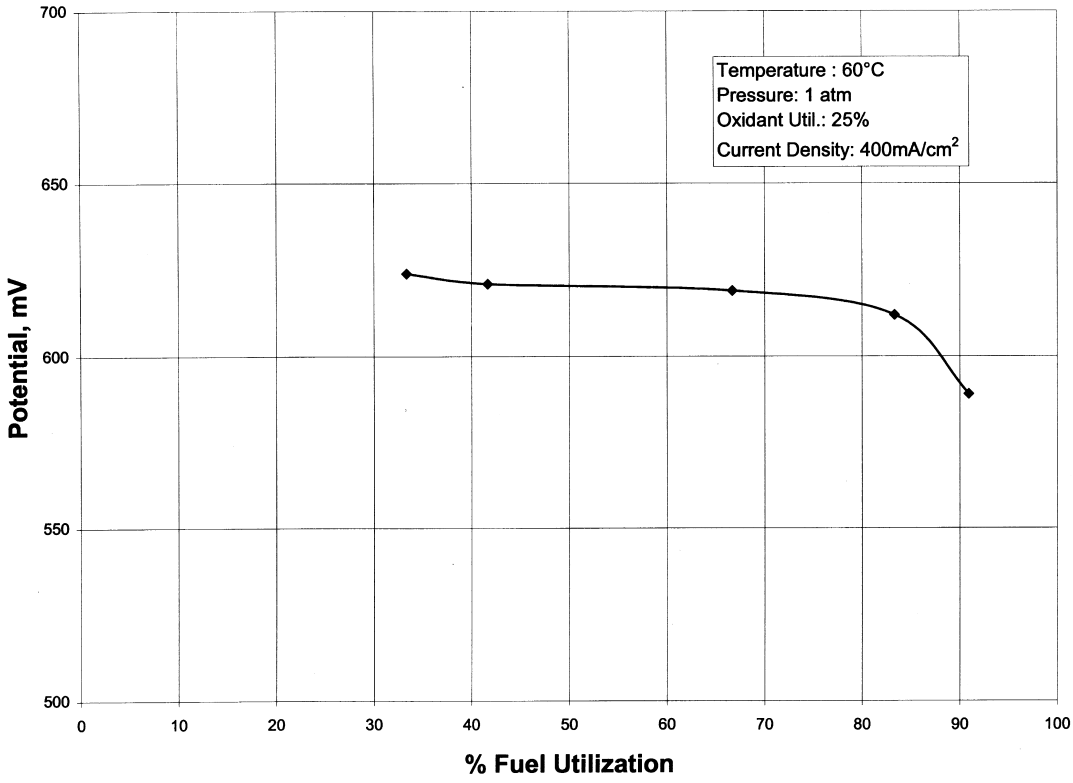

Fig. 5. Effect of fuel utilization on cell performance.

A&M University by spreading and rolling an intimate mixture [4] of platinum-supported catalyst and perfluorosulfonated ionomer onto an electrically conductive porous layer consisting of carbon black and PTFE incorporating a carbon cloth layer [5]. The platinum loadings for the anode (hydrogen) and cathode (air) electrodes (with an active area of

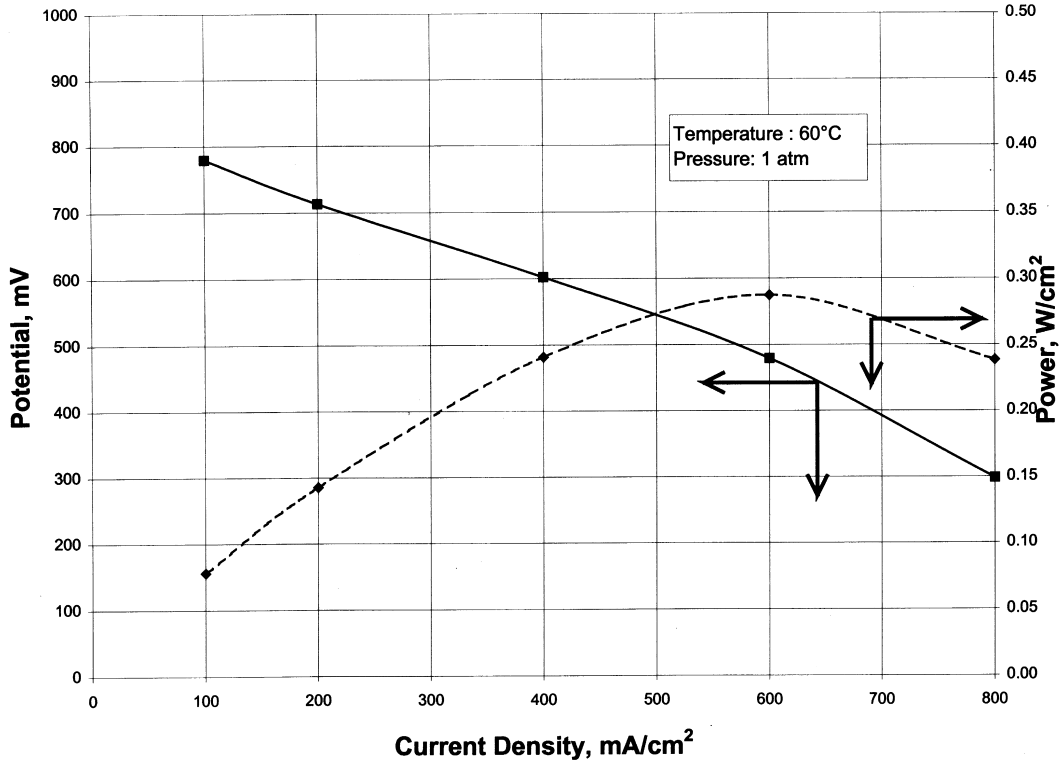

Fig. 6. Performance as a function of current density at constant fuel and oxidant utilization.

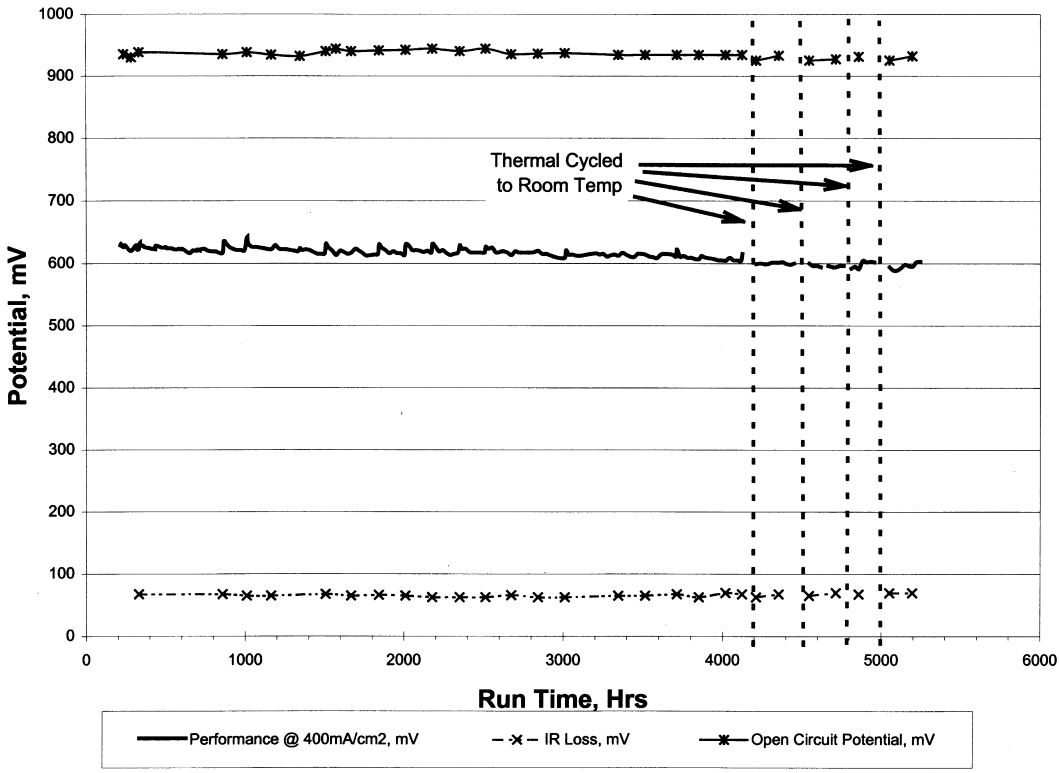

Fig. 7. Endurance on synthetic reformate and air at 60°C and 1 atm.

58 cm^2) were 0.26 and 1.46 mg/cm^2, respectively. The electrodes after drying were hot-pressed on both sides of a 50-μm thick polymer electrolyte Nafion 112 membrane to form the MEA.

A single cell with an active area of 58 cm^2 was assembled with the membrane electrode assembly (MEA) using IGT's internally manifolded heat exchange (IMHEX™) design configuration machined in 0.5-inch thick graphite plates. The cell was set to operate on synthetic reformate (80% H_2/20% CO_2 with no carbon monoxide) and air at 60°C and 1 atm to determine the effect on performance and endurance. The anode (reformate) and cathode (air) gas flows were set for 1.2 and 4.0 stoics (83% and 25% utilizations) at a current density of 400 mA/cm^2. The anode and cathode reactant gases were humidified by passing through saturators prior to entering the cell. The dew points for the anode and cathode gas streams were set at 10°C and 5°C, respectively, above the cell operating temperature. Product water was removed by gravity and entrainment. Polarization runs at constant flow (to determine I–V characteristics) were conducted periodically to monitor the cell performance. Measurements of I–V characteristics were also carried out with H_2 and H_2/N_2 (as the anode gas reactants) and oxygen and air (as the cathode gas reactants) to determine the effect of gas composition and temperature on cell performance. For all the polarization runs the anode and cathode gas flows were set for 1.2 and 2.0 stoics (83% and 50% utilizations) at a current density of 800 mA/cm^2. The effect of fuel utilization and thermal cycling on cell performance was also investigated.

3. Results and discussion

3.1. Effect of oxidant gas composition

The effect of oxidant gas composition, oxygen and air, on cell performance was determined for both pure hydrogen and reformate as the anode reactants shown in Fig. 1. The data indicate that the cell polarization trends for both fuel types tested with oxygen and air are similar. Above a current density of 400 mA/cm^2, the performance with air decreases substantially for both fuel types as compared to that obtained with oxygen. This decrease is due to the well documented mass transfer limitations that occur when operating on air. The results also indicate that a further performance decrease is observed for the reformate operated with both oxidant types. This is probably due to the additional mass transport problems caused by the presence of carbon dioxide (CO_2).

3.2. Cell power output for various fuel/oxidant types

A comparison of the cell power output for the three fuel/oxidant types employed in this test is shown in Fig. 2. The results indicate that for the hydrogen/oxygen (H_2/O_2) system

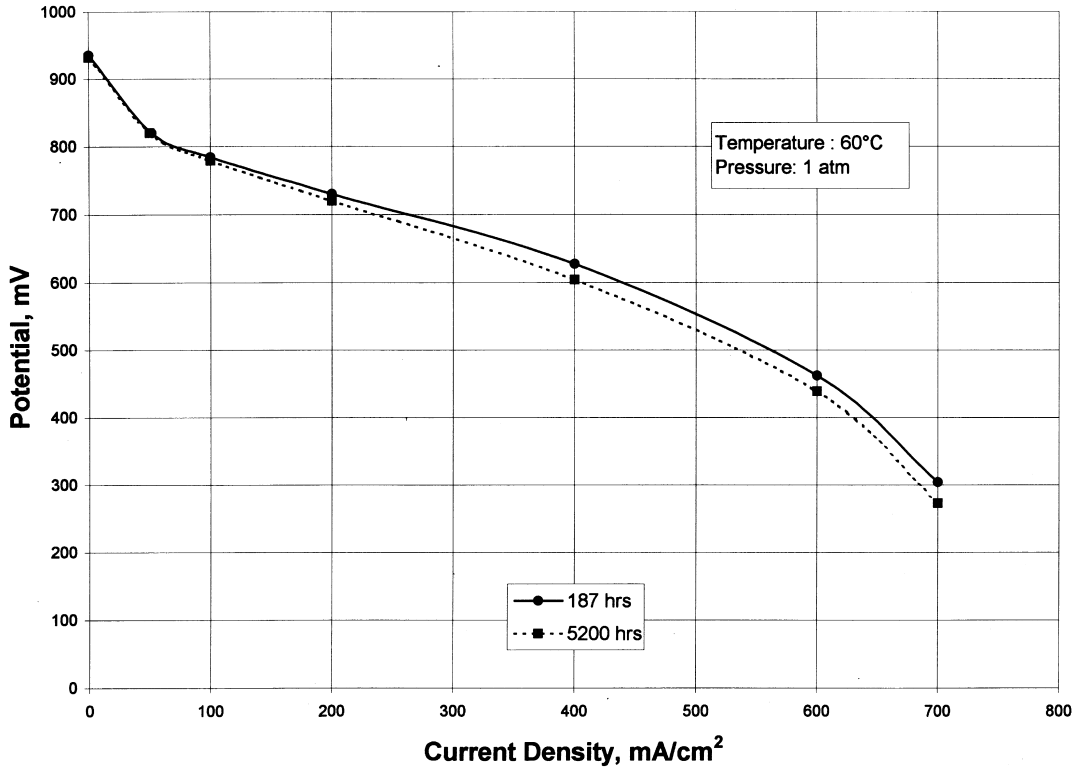

Fig. 8. Comparison of polarization curves at the beginning and end of life.

the cell attained a power output of 0.51 W/cm^2 at the maximum current density of 800 mA/cm^2 and appears to be still increasing. However, for the hydrogen/air and reformate (80% H_2/20% CO_2)/air systems maximum power outputs of 0.30 and 0.26 W/cm^2, respectively, occurred at a current density of 600 mA/cm^2.

3.3. Effect of temperature

The effect of temperature on cell performance is shown in Fig. 3. The effect of an increase in temperature is a lowering of the internal resistance of the cell, mainly by a decrease in the ohmic resistance of the electrolyte. In addition, mass transfer limitations are also reduced at high temperature. The overall result is an improvement in cell performance. Experimental data [6] suggest a voltage gain in the range of 1.1 mV to 2.5 mV for each degree (°C) of temperature increase. Results shown in Fig. 3 obtained with reformate/air indicate performance gain of ~17 mV when the cell temperature was increased from 60° to 70°C. This is in good agreement with the reported experimental gain stated above.

3.4. Effect of anode gas composition

The effect of anode gas composition on cell performance is shown in Fig. 4. The presence of 20% carbon dioxide (CO_2) in the reformate should result in a reduction in cell voltage of ~4 mV, due to the effect of decrease in hydrogen partial pressure on equilibrium (Nernst) potential. At low current density (up to 300 mA/cm^2), a voltage reduction close to this value was measured. At high current density, greater than 300 mA/cm^2, the increase in cell polarization exceeded this value. This increase could be due to a restricted diffusion of hydrogen through the inert carbon dioxide. Also, some of this loss could be caused by the partial reduction of carbon dioxide to carbon monoxide (CO) in a reverse shift reaction (eqn (1)). Thermodynamic equilibrium for this reaction predicts ~29 ppm of CO at cell conditions (60°C). Gas chromatographic analysis of the anode outlet, however, showed CO to be below the detectable limit of 1 ppm for the CO free gas, indicating that the kinetics of reverse shift reaction are slow at the 60°C cell operating temperature. The performance loss due to the hydrogen dilution effect was determined to be 15 mV from the polarization test conducted with hydrogen containing 20% nitrogen. Compared with pure hydrogen the loss in performance at a current density of 800 mA/cm^2 for the reformate is 65 mV (see Fig. 4). This polarization loss could therefore be due to the restricted diffusion of hydrogen through the stagnant CO_2 in the anode [7].

3.5. Fuel utilization sensitivity to cell performance

The fuel utilization sensitivity data on cell performance is shown in Fig. 5. The fuel utilization sensitivity value provides an indication of the magnitude of anode polarization.

Table 1
Effect of thermal cycling on cell performance

Thermal cycle no.	Duration (h)	Performance[a] (mV)		
		Before	After	ΔmV
1	72	605	600	−5
2	72	600	596	−4
3	16	596	598	+2
4	96	598	595	−3

[a]Flows set for 1.2 and 4.0 stoics at 400 mA/cm^2 for reformate–air.

In this test the fuel (80% H_2/20% CO_2 reformate) utilization was varied from 33% to 91% (3 to 1.1 stoics) at a current density of 400 mA/cm^2 while holding the oxidant (air) utilization constant at 25% (4 stoics). The data in Fig. 5 indicate that (a) increasing the fuel utilization from 33% to 68% decreases the performance by only 5 mV, and (b) a further increase from 68% to 91% results in a loss of 30 mV. The relatively small performance loss experienced above 70% fuel utilization suggests that no additional carbon dioxide (CO_2) inhibition occurred in the cell and the loss was primarily due to polarization caused by mass transport limitations.

3.6. Constant utilization polarization test

A constant utilization polarization test was conducted to determine the cell power output as a function of current density. The power curve is shown in Fig. 6. In this figure for each current density the anode and cathode gas flows were set for 1.2 (83% utilization) and 4.0 (25% utilization) stoics, respectively. The results in Fig. 6 indicate that the maximum power output of ~0.29 W/cm^2 occurs at a current density of 600 mA/cm^2.

3.7. Effect of reformate on performance and endurance

The effect of reformate on cell performance and endurance is shown in Fig. 7. The cell was set to operate on synthetic reformate (with no CO) and air at 60°C, 1 atm and a constant current density of 400 mA/cm^2. This current density was chosen to simulate typical stationary power plant test conditions [8]. The anode (80% H_2/20% CO_2 reformate) and cathode (air) gas flows were set for 1.2 (83% utilization) and 4 (25% utilization) stoics. The cell exhibited 5100 h of stable performance with a decay of less than 1%/1000 h. This demonstrates that a polymer electrolyte membrane fuel cell (PEMFC) can endure synthetic reformate/air operation without a Pt/Ru alloy anode catalyst and/or air bleeding on the anode side. Also, during the 5100 h of cell operation over 71 kWh was generated. Periodic collection and analysis of the condensate showed no membrane degradation. The stable cell performance is attributed to the IGT IMHEX plate design with its inherent uniform flow of reactant gases across the active area (and partly to the MEA quality used in the test). This lowers the probability of cell failure by reducing non-uniform current densities and membrane degradation. A comparison of the beginning of life (BOL) and end of life (EOL) polarization curves in Fig. 8 shows the stable performance after more than 5000 h of continuous operation.

3.8. Effect of thermal cycling on cell performance

Stationary power plant PEMFC cells/stacks will need to endure thermal cycling because of operational problems and maintenance schedules. In view of this the cell was thermal cycled four times during the last 1200 h of its operation and the effect on performance is shown in Table 1. The results indicate little effect on performance (1.7% loss) and demonstrate the resiliency of the PEMFCs to thermal cycling.

4. Conclusions

A single cell with an active area of 58 cm^2 was operated with synthetic reformate (CO free) and air and demonstrated 5100 h of endurance without the use of a Pt/Ru alloy anode catalyst and/or air bleeding. The stable cell performance with a decay rate of less than 1%/1000 h is attributed to a combination of the IGT IMHEX plate design with its inherent uniform gas flow distribution across the entire active area and the membrane electrode assembly (MEA) quality.

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References

[1] M.S. Wilson, C.R. Derouin, J.A. Valerio and S. Gottesfeld, *28th Intersoc. Energy Convers. Eng. Conf., 1* (1993) 1203.
[2] S. Swathirajan, *Fuel Cell Seminar Abstracts 1994*, San Diego, CA, 1994, p. 204.
[3] J. Fujta, J. Ohtsuki, A. Kabasawa, K. Urabe and K. Koseki, presented at the *Second IFCC Conference*, Japan, February 5–8, 1996, Paper P5–06.
[4] M.S. Wilson and S. Gottesfeld, *J. Electrochem Soc., 139* (1992) L28.
[5] S. Srivinvasan, S. Gamburzev, O.A. Velev, F. Simoneaux and A.J. Appleby, *Fuel Cell Seminar*, Orlando, FL, November 17–20, 1996, p. 513.
[6] K. Ledjeff et al., *Fuel Cell Seminar Abstracts*, 1992, p. 171.
[7] S. Kawatsu, S. Aoyama and M. Iwase, *Fuel Cell Seminar*, Orlando, FL, November 17–20, 1996, p. 262.
[8] T.R. Ralph, *Platinum Metals Rev., 41(3)* (1997) 102.