Journal of Power Sources 83 (1999) 128–133

JOURNAL OF POWER SOURCES

www.elsevier.com/locate/jpowsour

# Performance of polymer electrolyte membrane fuel cell (PEMFC) stacks Part I. Evaluation and simulation of an air-breathing PEMFC stack

Deryn Chu *, Rongzhong Jiang

*U.S. Army Research Laboratory, Sensor and Electronic Devices Directorate, Mail Stop AMSRL-SE-DC, Adelphi, MD 20783-1197, USA*

Received 25 January 1999; received in revised form 6 April 1999; accepted 6 April 1999

**Abstract**

The performance of an air-breathing polymer electrolyte membrane fuel cell (PEMFC) stack was evaluated under different environmental conditions. The humidity of the surrounding air significantly affected the performance of the stack. When the humidity was less than 10% RH at 35°C, the stack lost almost 95% power. Acceptable operating temperature for the stack would be from 20 to 40°C for > 36% RH. An empirical equation was proposed to analyze the performance of the PEMFC stack instead of only for a single cell. The results calculated with the empirical equation are excellently fitted to the experimental polarization curves at various humidity and temperatures. The impedance and Tafel slope of the stack both increase with decreasing either the environmental humidity or temperature. Published by Elsevier Science S.A.

*Keywords:* Fuel cell; PEMFC; Fuel cell stack; PEMFC stack; Portable power source; Electrode kinetics

## 1. Introduction

Steadily increasing requirements for portable electric power have stimulated the interest to develop more efficient and more energetic fuel cell device. A polymer electrolyte membrane fuel cell (PEMFC) is one of the best candidates as a portable power source for commercial applications primarily because of its lightweight and high power density. The research and development of PEMFCs with Nafion membrane as electrolyte have received much attention since 1980's [1]. Nafion is a perfluorinated cation exchange polymer membrane, it has shown good conductivity and stability up to 100°C in the fuel cell operating environmental conditions. Most of these researches are mainly concentrated on a PEMFC single cell or one of its components, such as novel membrane electrolytes [2,3], catalysts and structure [4–7], electrochemical reaction mechanisms and kinetics [8], as well as electrode materials and preparation [9,10]. Most recently, many PEMFC stacks have been emerging, with variety of types and functions from many developers. However, only a few reports have been published about the research on an entire fuel cell stack including stack design and evaluation [11].

Understanding the performance and characteristic of PEMFC stacks is clearly important for realizing the optimum cost/weight/performance ratios. The objective of this study is to construct a bridge between the development and applications of PEMFC stacks for promoting their practical applications in military and civilian markets. Here, we report an air-breathing PEMFC stack, which is assembled with a series of bi-cell units, having a feature of lightweight and high power. The fuel is fed into the stack by compressed hydrogen and the oxidant is fed by spontaneous convection of air from the environmental. The heat dissipation of the stack is realized efficiently and automatically because of large contact area designed between the stack surface and environmental air.

## 2. Experimental

The air-breathing PEMFC stack was composed of 6 bi-cells in a series connected. The geometric area of each electrode is approximately 32 $cm^2$. The open circuit voltage was approximately 6 V. The air-supply to the cathode was spontaneously obtained by convection from environ-

* Corresponding author. Tel.: +1-301-721-3451; Fax: +1-301-721-3402; E-mail: dchu@arl.mil

0378-7753/99/$ - see front matter Published by Elsevier Science S.A.
PII: S0378-7753(99)00285-2

mental air. The high purity of hydrogen (99.99%) was used. A Matheson TF601 Rotameter was used for measuring the hydrogen flow rate. The temperature and humidity were controlled with a Tenney Environment Chamber (model No. BTRC) and a Heatless Dryers (model No. HF 200A). A Hewlett-Packard Electronic Load (Model No. 6050A) and a Hewlett-Packard Multimeter were used for measuring stack's current and voltage, respectively. The Tenney Environment Chamber was controlled through a computer with Linktenn II Software. In order to get reproducible results, all electrochemical measurements were carried out after the temperature and humidity were held constant for at least 2 h.

## 3. Results and discussion

It is well known that the performance of a PEMFC is a function of temperature and pressure. However, operating temperature increases will cause thermal management and membrane dry-out problems. Operating pressure increases will result in the system complications. Therefore, our present emphasis is on the evaluation of ambient pressure, normal environmental temperatures and humidity for a PEMFC stack that could be carried by one person.

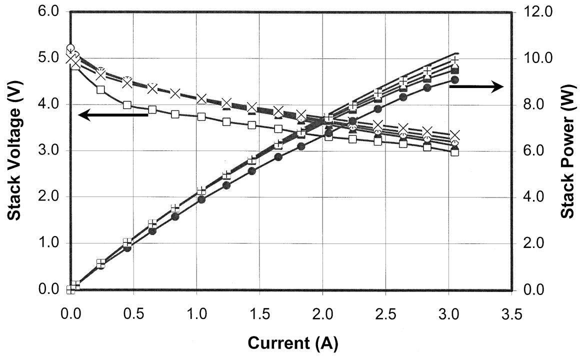


Fig. 2. Effect of %RH on stack power and voltage at 10°C. $H_2$ flow = 68 ml/min (dry $H_2$). From bottom to top the humidity are 22%, 30%, 40%, 60% and 90% RH, respectively.

### 3.1. Humidity effect

The air-breathing PEMFC stack was designed to use oxygen from the surrounding air, which let it be much lighter, simpler and lower cost than other types of stacks because of no needs for additional auxiliaries for providing oxygen or air. The reaction product of water at the cathode electrodes was automatically exhausted to environment. The disadvantage is that any factors, which are present in surrounding environment, may affect the stack performance. The first factor considered is humidity.

Fig. 1A shows the effect of relative humidity (%RH) on stack performance at 35°C. The polarization curve with 85% RH has the highest values of voltage at the same current. It means that the highest power output is at the 85% RH for the same other conditions. The performance of the stack decreases with decreasing the %RH. From the RH 85% to 30%, the voltage on each curve decreases smoothly with increasing of current. However, the curve for the 20% RH (see Fig. 1A and B) is not smooth.

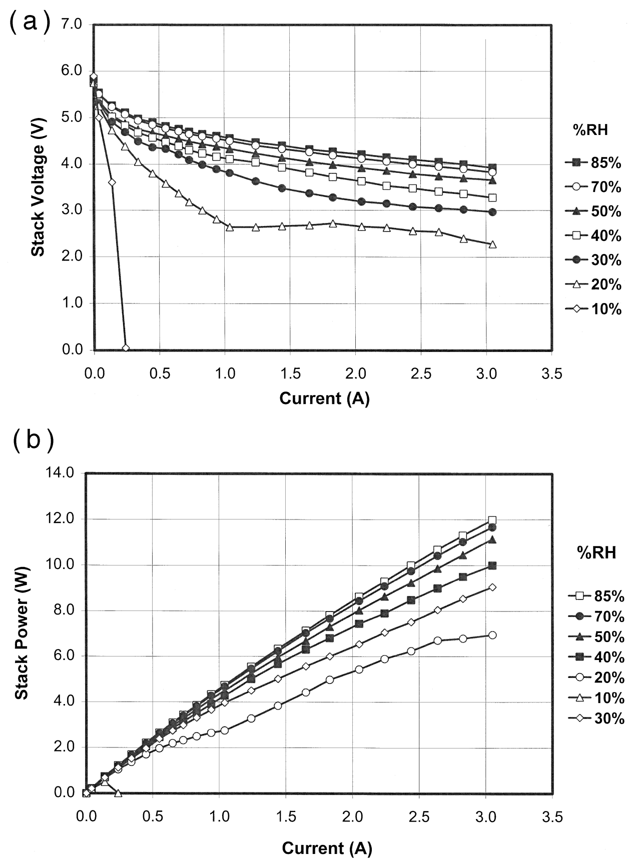


Fig. 1. (a) Effect of %RH on stack voltage. $T = 35°C$, $H_2$ flow = 68 ml/min (dry $H_2$). Each electrode geometrical area: 32 $cm^2$. (b) Effect of %RH on stack power. $T = 35°C$, $H_2$ flow = 68 ml/min (dry $H_2$).

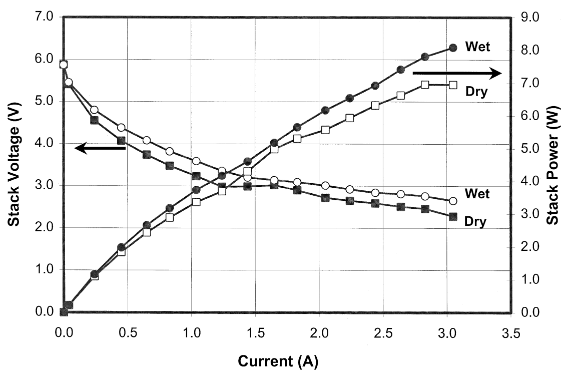


Fig. 3. Effect of wet $H_2$ fill on stack power and voltage. $T = 40°C$, RH as 20%, $H_2$ flow: 68 ml/min. Lines from top to bottom are wet and dry $H_2$ fill, respectively.

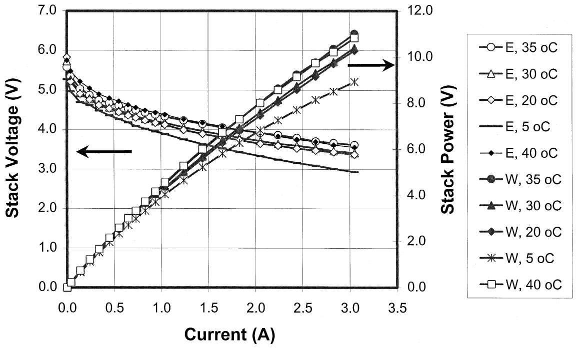


Fig. 4. Effect of temperature on stack voltage and power. RH = 50%, $H_2$ flow = 68 ml/min (dry $H_2$). Lines from bottom to top the temperature as 5, 20, 30, 35 and 40°C, respectively.

Surprisingly, the voltage drops sharply as the current goes from 0 to 1 A; when the current is greater than 1 A the voltage increases instead of decreases. This is because of stack's self-humidification due to water production at the cathode during its operating. When RH value is less than 10% the stack's voltage decreases considerably with increase of current. Fig. 1B shows the calculated stack power from the data in Fig. 1A. The stack's power increases with increasing of current until reaching to the highest current value. If it goes above the highest current value the voltage drops to zero rapidly because the rate of hydrogen permeation is limiting. When the RH ~ 10% the max stack power is 5% of the maximum stack power at the RH of 80%. The voltage and power vs. current relationship plots for different %RHs at 10°C are shown in the Fig. 2. The results show that the effect of humidity on stack performance at 10°C is less than that at 35°C.

Fig. 3 shows the polarization curves for the same flow rate of the dry and the wet hydrogen fed into the anode electrode compartment at 40°C and 20% RH. As expected, the stack performance for the hydrogen saturated with water fed into the anode compartment is slightly better than that for the dry hydrogen fed into the anode compartment.

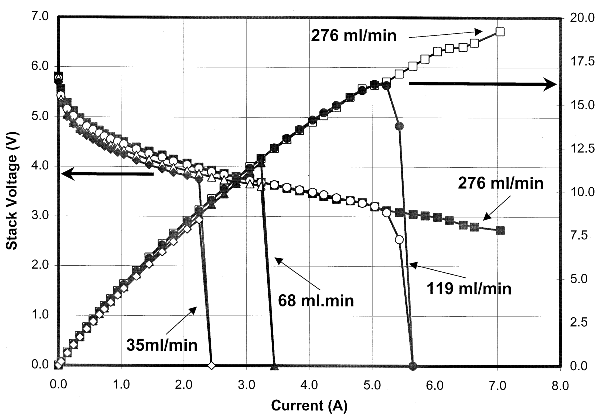


Fig. 5. Effect of $H_2$ flow rate (dry $H_2$) on stack power and voltage. $T = 35°C$, RH as 50%.

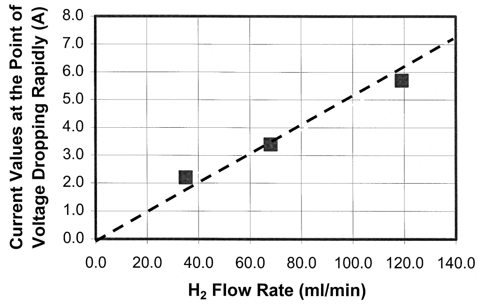


Fig. 6. Plot of $H_2$ flow rate (dry $H_2$) vs. the current values at the point of stack voltage dropping rapidly. $T = 35°C$ and RH = 50%.

The effect of humidity on Nafion's ionic conductivity at different temperatures was reported by Sone et al. [3]. The temperature ranges were from 20 to 50°C. They reported that Nafion's ionic conductivity is significantly affected by the humidity. Their results are consistent with our experimental data as shown in Fig. 1. Unfortunately, they did not report the impedance results for temperature below 20°C.

### 3.2. Temperature effect

Fig. 4 shows a series of polarization curves for the PEMFC stack at the constant humidity (50% RH) for different temperatures. With increasing of current, the voltage decreases but the power increases. The stack performance decreases with decreasing temperatures, especially at the temperature less than 5°C. Increasing of performance with increasing temperature is not only due to increase of the reaction rate of the electrode process but also to an increase of the ionic conductivity of the membrane electrolyte. At the low current density the electrochemical process is mainly controlled by a charge transfer reaction or activation of the electrodes. At the high current density the electrochemical process is mainly controlled by ohmic and/or mass transfer polarization. Because the Nafion's impedance becomes more appreciable at low temperature, larger IR drop is observed at 5°C in the potential–current curve especially for the high current density range.

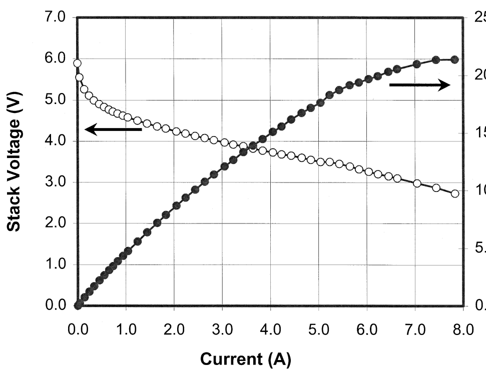


Fig. 7. Optimized performance of the air-breath PEMFC stack. RH = 85%, $H_2$ flow (wet $H_2$) = 276 ml/min and $T = 35°C$.

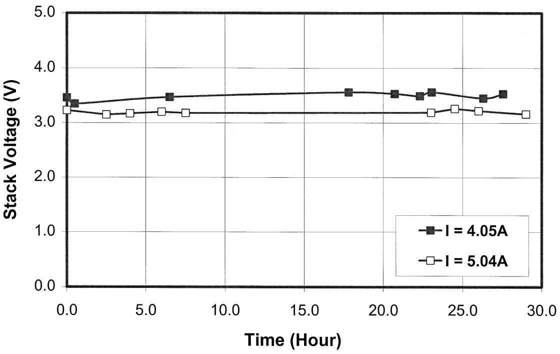


Fig. 8. Stack performance at constant current operation. The $T = 35°C$, RH = 50%. $H_2$ flows (dry $H_2$) were 110 ml/min and 134 ml/min for $I = 4.05$ A and $I = 5.04$ A, respectively.

### 3.3. $H_2$ flow rate effect

The air-breathing PEMFC stack was designed for working at low $H_2$ pressure. Therefore, the $H_2$ flow rate would be one of critical parameters for the performance of the stack. The $H_2$ flow rates were varied at the constant temperature and humidity. Fig. 5 shows a series of polarization curves for the stack at different $H_2$ flow rates. Surprisingly, the $H_2$ flow rate has no appreciable affection on the shape and magnitude of the potential–current curves until the current density goes to a definite high point at which the stack voltage drops rapidly. This is easy to understand because the air-breathing PEMFC stack is still maintaining approximately the same $H_2$ pressure even at different $H_2$ flow rates. However, the voltage will rapidly drop to zero when the current is larger than the definite value because the hydrogen at the anode compartment is completely consumed. We call the definite point where voltage is dropping rapidly as dead point. The stack cannot continue to be operated at currents equal to or higher than the dead point. If used, probably a significant damage of the stack would be caused because of incorrect ratio of hydrogen to oxygen. Fig. 6 shows the plot of dead point current vs. $H_2$ flow rate. As expected it is a straight line and passing through the origin point. If too high $H_2$ flow rate is applied, it may cause fuel waste, and vice versa, it may damage the stack. According to Fig. 6, for properly operating the stack, one needs to use an appropriate $H_2$ flow rate. On the other hand, the oxygen is provided from the environmental air, and the maximum performance of a PEMFC stack should be limited by the natural convection of the surrounding air. However, in the present stack the cathode electrode limitation was not observed within the test current range on the potential–current curves. This result implies that for our air breathing PEMFC stack the cathode electrode is not rate limiting.

### 3.4. System optimization and stability

After optimization of many parameters such as temperature, humidity and hydrogen flow rate, the best performance of the air-breathing stack was obtained. Fig. 7 shows the possible highest power output. It is approximately 22.5 W at operating conditions of 7.5 A, 3 V, 35°C and 85% RH humidity. The long-term performance of the air-breathing PEMFC stack was also evaluated at 35°C and 50% RH for 4.05 A and 5.04 A. Fig. 8 shows a plot of stack voltage vs. time at constant current. After 30 h test the stack voltage was still maintained as almost stable for constant current at 4 A and 5 A, respectively.

### 3.5. Analysis of electrode process

It is well known that the electrode process for a single cell of PEMFC can be analyzed with an empirical equation used by Kim et al. [12] and Rho et al. [13], which is described as follows,

$$E_i = E_o - b\log(i) - iR \tag{1}$$

$$E_o = E_r + b\log(i_o) \tag{2}$$

Here, $E_i$ is the potential from experimental observation. $E_r$ is the reversible potential for the stack, $b$ and $i_o$ are Tafel slope and exchange current density, respectively. $R$ represents the electrolyte resistance, which causes a linear variation of the stack potential with current.

However, there have no equations to describe the potential–current behaviors for a PEMFC stack. Here, we con-

Table 1
Electrode kinetic parameters calculated from the polarization curves in Fig. 1A for the PEMFC stack at different humidity (temperature as 35°C)

| Humidity (%RH) | Performance for PEMFC stack (6 cells) | | | Average performance for single cells | | |
|---|---|---|---|---|---|---|
| | $\Sigma(E_o)_j$ (V) | $\Sigma(R)_j$ (Ω) | $\Sigma(b)_j$ (mv/dec) | $E_o$ (V) | $R$ (Ω) | $b$ (mv/dec) |
| 85 | 6.3 | 0.22 | 488 | 1.05 | 0.0367 | 81.3 |
| 70 | 6.3 | 0.26 | 495 | 1.05 | 0.0433 | 82.5 |
| 50 | 6.2 | 0.25 | 532 | 1.03 | 0.0417 | 88.7 |
| 40 | 6.2 | 0.34 | 547 | 1.03 | 0.0567 | 91.2 |
| 30 | 6.2 | 0.43 | 630 | 1.03 | 0.0717 | 105.0 |
| 20 | 6.2 | 1.60 | 650 | 1.03 | 0.2667 | 108.3 |

Table 2
Electrode kinetic parameters calculated from the polarization curves in Fig. 4 for the PEMFC stack at different temperatures (humidity as 50% RH)

| Temperature (°C) | Performance for PEMFC stack (6 cells) | | | Average performance for single cell | | |
|---|---|---|---|---|---|---|
| | $\Sigma(E_o)_j$ (V) | $\Sigma(R)_j$ (Ω) | $\Sigma(b)_j$ (mv/dec) | $E_o$ (V) | $R$ (Ω) | $b$ (mv/dec) |
| 35 | 6.2 | 0.25 | 532 | 1.03 | 0.0417 | 88.7 |
| 20 | 6.1 | 0.26 | 568 | 1.02 | 0.0433 | 94.7 |
| 5 | 5.9 | 0.35 | 570 | 0.98 | 0.0583 | 95.0 |

sider a PEMFC stack, which is assembled by many single cells with series connection. Therefore, the current flowing to each cell must be the same and the total potential of the stack can be described as follows,

$$\Sigma(E_i)_j = \Sigma(E_o)_j - (\log(i))\Sigma(b)_j - i\Sigma(R)_j \quad (3)$$

Here, the subscript $j$ expresses the order of a single cell in the stack. For example, if there have $N$ number of single cells in the stack, the $\Sigma(E_i)_j$ means the sum of the all single cells' voltage from cell number $j = 1$ to cell number $j = N$. If all the single cells are exactly identical and the total single cell number is $N$, Eq. (3) can be rewritten as,

$$NE_i = NE_o - Nb\log(i) - iNR \quad (4)$$

Eq. (3) or Eq. (4) can be used to describe the potential–current behavior for a PEMFC stack and to calculate the electrode kinetic parameters for the single cells in the stack.

The electrode kinetic parameters obtained by fitting with Eq. (3) at different humidity and temperature are summarized in Tables 1 and 2, respectively. In order to confirm these fit parameters are accurate, the data from Tables 1 and 2 were used to construct the solid lines in Figs. 9 and 10. The points plotted from the experimentally observed results are excellent agreement with the solid lines calculated by the equations for the whole operating current regions at the humidity higher than 30%. However, the calculated curve (solid line) for the 20% RH only fitted well with experimental points for the operating currents equal to or lower than 1 A. For the operating current higher than 1 A, the calculated curve (solid line) deviated from the experimental points, because the electrochemical reaction product, water formed at the cathode electrode, is enough to result in self-humidifying. Therefore, the calculated curve for the 20% RH is not fitted well for the case when the operating current is larger than 1 A.

The $\Sigma(R)_j$ value increases with decreasing humidity because the Nafion membrane losses ionic conductivity. The $\Sigma(b)_j$ value increases because of the electrode process becomes less reversible. All calculated $\Sigma(E_o)_j$ values are slightly larger than those of experimental $\Sigma(E_o)_j$. This is because the full open circuit potential was unobtainable because hydrogen crossover to the cathode electrode was unavoidable. Even if only a very small amount of hydrogen crosses, the equilibrium potential decreases. As shown by experiment, as hydrogen was admitted to the stack the open circuit potential was increasing until a maximum value approximately 6.2–6.3 V was reached, then decreased gradually and maintained at 5.7–5.9 V for the conditions of 50% RH and temperature at 35°C.

With decreasing temperature the $\Sigma(E_o)_j$ value decreases as shown in the Table 2. This can be explained thermodynamically as a Nernst effect. Accordingly, the $\Sigma(R)_j$ values are increasing because the ionic conductivity of Nafion membrane is becoming smaller, and the $\Sigma(b)_j$ value are increasing due to the increasing irreversibility of hydrogen oxidation, the rate limiting electrode process.

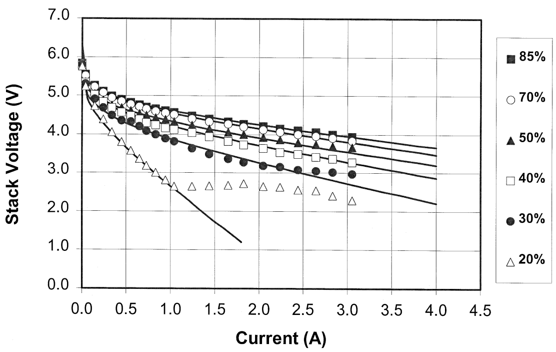


Fig. 9. Calculated polarization curves (points from Fig. 1A) for the PEMFC stack with different humidity. $T = 35$°C, $H_2$ flow = 68 ml/min. The lines from bottom to top with humidity as 20%, 30%, 40%, 50%, 70% and 85% RH, respectively.

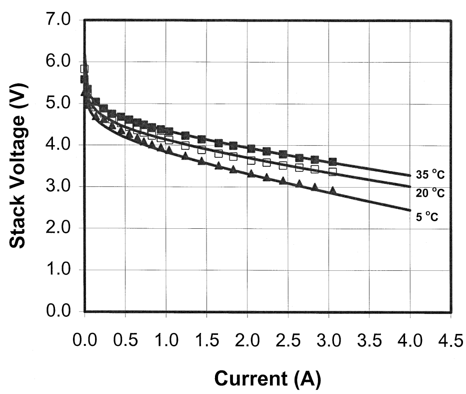


Fig. 10. Calculated polarization curves (points from Fig. 4) for the PEMFC stack with different temperatures. RH = 50%, $H_2$ flow = 68 ml/min. The lines from bottom to top with temperature as 5, 20 and 35°C, respectively.

## 4. Conclusion

The humidity in the surrounding air significantly affected the performance of the air-breathing PEMFC stack. When humidity was less then 10% RH, the stack power was less than 5% for a fully humidified stack. A phenomenon of self-humidifying by the product of water in the stack was observed at the operating current higher than 1 A for the humidity below 30% RH and temperature at 35°C. It is suggested that the appropriate humidity for operating the stack would be 30% RH or higher. The proper operation temperatures for the air breathing PEMFC stack would be from 20 to 40°C. Operating temperature lower than 5°C, the performance of the stack was poor. The rate of $H_2$ flow did not have apparent affect on the shape of the current–potential curve. It only determined the dead point of current, at which the voltage dropped to zero rapidly. The electrode processes were analyzed by an empirical equation, which is suitable for analysis of PEMFC stack in stead of only for a single cell. The computer calculated curves were fitted to the experimental polarization data points at varying humidity and temperature. With humidity or temperature decreasing the sum of stack impedance $\sum(R)_j$ and sum of Tafel slope $\sum(b)_j$ both increase, but the $\sum(E_o)_j$ value decreases. The calculated potential–current curves for the low humidity conditions (less than 30% RH) were not fitted well because hydration of membrane was inadequate and/or incomplete for the preconditioning time (about 2 h) used for this work.

## Acknowledgements

The authors wish to thank Army Materiel Command for financial support this project.

## References

[1] T.F. Fuller, Electrochemical Society Interface, Fall (1997) 26.
[2] N. Yoshida, T. Ishisaki, A. Watakabe, M. Yoshitake, Electrochimica Acta 43 (1998) 3749.
[3] Y. Sone, P. Ekdunge, D. Simonsson, J. Electrochem. Soc. 143 (1996) 1254.
[4] M.S. Wilson, S. Gottesfeld, J. Appl. Electrochem. 22 (1992) 1.
[5] J. Fournier, G. Faubert, J.Y. Tilquin, R. Cote, D. Guay, J.P. Dodelet, J. Electrochem. Soc. 144 (1997) 145.
[6] E. Passalacqua, F. Lufrano, G. Squadrito, A. Patti, L. Giorgi, Electrochimica Acta 43 (1998) 3665.
[7] O. Antoine, Y. Bultel, R. Durand, P. Ozil, Electrochimica Acta 43 (1998) 3681.
[8] D. Chu, Electrochimica Acta 43 (1998) 3711.
[9] K.Y. Chen, A.C.C. Tseung, J. Electrochem. Soc. 143 (1996) 2703.
[10] P.K. Shen, K.Y. Chen, A.C.C. Tseung, J. Electrochem. Soc. 142 (1996) L85.
[11] O.J. Murphy, A. Cisar, E. Clarke, Electrochimica Acta 43 (1998) 3829.
[12] J. Kim, S.M. Lee, Srinivason, C.E. Chamberlin, J. Electrochem. Soc. 142 (1995) 2670.
[13] Y.W. Rho, O.A. Velev, S. Srinivason, Y.T. Kho, J. Electrochem. Soc. 141 (1994) 2084.