

Short communication

Determination of energy efficiency for a direct methanol fuel cell stack by a fuel circulation method

Rongzhong Jiang*, Charles Rong, Deryn Chu

US Army Research Laboratory, Adelphi, MD 20783-1197, USA

Received 17 July 2003; accepted 14 August 2003

Abstract

A method of fuel circulation with a fixed amount of fuel was employed to investigate a direct methanol fuel cell (DMFC) stack that was built with metal foam flow fields for the air and fuel flows. The stack power output increases significantly with environmental temperature from 20 to 40 °C. The average peak power per cell at 40 °C is 26 mW cm⁻² per cell. The average discharge voltage per cell at peak power does not change with temperature but remains at 0.3 V. The energy output of the stack was determined at constant current or constant voltage with a fixed amount of methanol to feed the anode of the stack until the fuel was consumed. The results by constant current discharge show that at higher temperature the stack has remarkably higher energy output; while at the same temperature only a suitable magnitude of discharge current can achieve the highest energy output. The results by constant voltage discharge show that the Faradic efficiency is 86%, and the energy efficiency is 17% at 30 °C.

© 2003 Elsevier B.V. All rights reserved.

Keywords: DMFC; Fuel cell stack; Stack design; Energy efficiency; Faradic efficiency

1. Introduction

Direct methanol fuel cells (DMFCs), as one type of polymer electrolyte membrane fuel cells (PEMFCs), have received much attention [1–9] due to the high theoretical energy density and using a liquid fuel that can be stored and transported safely. Recently, research focused on practical applications of DMFCs, such as portable power sources for consumer electronics. Several DMFC stacks, or systems, have been demonstrated with the power ranging up to several hundreds of watts. A practical power source comprising fuel cells is usually composed of a number of single cells. Such a combination of single fuel cells is called as fuel cell stack, which provides higher voltage, or power. Although there are a variety of fuel cell stacks with different sizes, shapes, materials, and power ranges, the methods to assemble single cells into a fuel cell stack can mainly be classified as bipolar and mono-polar designs [10]. The most conventional method of configuring fuel cell stack is a bipolar design, where two adjacent single cells share one bipolar plate that provides fuel for one cell's anode and air for the other's cathode. The fuel cell stack with bipolar design has the advantages of lower internal resistance and smaller volume

than that with mono-polar design. Graphite materials are commonly used in bipolar plates. Complex flow-channels on both sides of a bipolar plate are required for fuel and air transfer, respectively. The work of fabricating bipolar plates can be a major cost in a fuel cell stack. Alternative materials are sought for making bipolar plates, such as a carbon-carbon composite [11,12], stainless steel, and metal alloys [13–17]. Most recently, metal foams [18] and metal meshes [19] are reported as possible materials for the flow fields on the bipolar plates to lower the cost. Two pieces of metal foam can be conveniently attached onto the sides of a metal sheet for the flow fields of a bipolar plate. Since little is known about the practical performance of such fuel cell stacks, we carried out investigative work on a DMFC stack with metal foam flow fields, by designing experiments in such a way that a fixed amount of fuel is circulated in the stack until the fuel is consumed. The method reported here allowed us to systematically examine the performance of the DMFC stack with a metal foam flow field, and this method in general would be suitable for other stack evaluations.

2. Experimental

A DMFC stack was used, in which the anode flow field was nickel foam, and the cathode flow field was stainless

* Corresponding author. Tel.: +1-301-394-0295; fax: +1-301-394-0273.
E-mail address: rjiang@arl.army.mil (R. Jiang).

steel foam coated with a thin layer of gold. Each of the bipolar plates in the fuel cell stack was built by the combination of two different pieces of metal foam and one piece of mass-separator, which separates the fuel from the anode and the oxidant from the cathode for two adjacent single cells. The bipolar plates have three functions, i.e. they provide (1) flow fields, (2) electric conduction, and (3) serve as mass separators between the cathode and the anode for two adjacent single cells. The membrane electrode assemblies (MEAs) consisted of a Nafion 117 electrolyte membrane, a cathode and an anode, which were combined by hot-pressing. The cathode was unsupported platinum black, with a catalyst loading of 4 mg/cm^2 pure Pt. The anode was an unsupported PtRu black (4 mg/cm^2 by total PtRu). Carbon cloth was used as the gas and fuel diffusion electrodes in the stack.

The fuel cell stack was tested in a Tenney Environmental Chamber (model no. BTRC), which was programmed to control the temperature. An Arbin battery-tester BT-2043 was used for electrochemical measurements.

A 1.0 M aqueous methanol solution was used as fuel, and fed into the anode with a flow rate of 200 ml/min. The methanol solution was warmed to the same temperature as that inside the environmental chamber at the beginning of each of the experiments. Compressed air was used to feed the cathode with an inlet pressure of 3 psi. The energy output of the stack was measured at constant current or constant voltage with a measured amount of fuel, 2000 ml 1.0 M methanol, and the discharge process was monitored continuously until the fuel was consumed.

3. Results and discussion

3.1. Polarization behaviors and power output

Fig. 1 shows the discharge voltage–current and power–current curves of a DMFC stack assembled with metal foam bipolar plates. The open circuit voltage was about 21 V at 20°C , which increased with temperature. The highest open circuit voltage was 27 V at 40°C . The stack voltage dropped sharply at the beginning of the discharge once a small current was passed, which is a typical behavior of a DMFC because of slow kinetic rate for methanol electrochemical oxidation. The polarization behavior of the DMFC stack can be explained by dividing each of these curves into three regions, i.e., low, medium, and high current regions. The polarization behaviors of the DMFC in the low current region (less than 0.3 A) are controlled by the kinetic rate of methanol oxidation. In the medium current region, the voltage–current curves are relatively straight due to the Ohmic controlled process. In the high current region, the voltage–current curves are depressed slowly because of slow mass transfer of fuel or air molecules to the electrode. Higher temperature expands the part of the Ohmic controlled region, which implies that the ionic resistance of the electrolyte membrane decreases with increasing temperature. The power–current curve forms a peak at the region of medium discharge current. With increasing temperature the power output increases. The highest discharge power is about 30 W at 40°C . Table 1 summarizes the results of the DMFC stack at different environmental temperatures, and the average

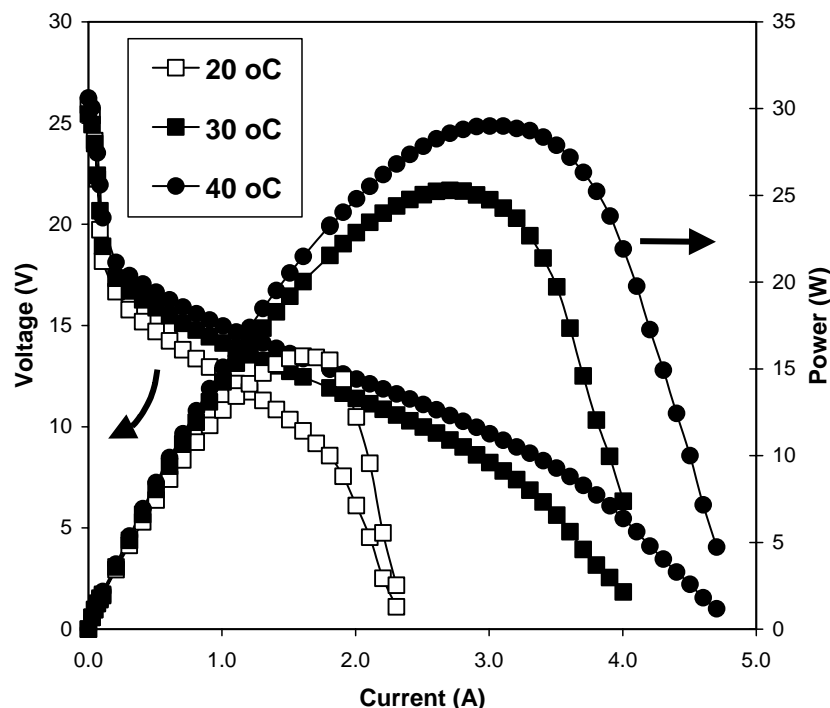


Fig. 1. Voltage–current and power–current curves of a DMFC stack. Anode flow: 200 ml/min 1.0 M MeOH; cathode flow: 3 psi air at inlet.

Table 1
Summary of the discharge performance of the DMFC stack^a

Temperature (°C)	Peak power		Voltage at peak power (V per cell)
	W	mW cm ⁻² per cell	
20	15.7	14.0	0.29
30	25.3	22.5	0.27
40	29.0	25.8	0.29

^a Anode flow: 200 ml/min 1.0 M MeOH and cathode flow: 3 psi air.

performance (mW cm⁻² per cell) per cell is also listed in the table. The average performance per cell in the stack is 14 and 25.8 mW cm⁻² per cell for 20 and 40 °C, respectively. Although the peak power of the DMFC stack varies significantly with temperature or discharge current, the voltage at the peak power is almost constant at about 0.3 V.

3.2. Energy output at constant current

3.2.1. Effect of discharge current

The energy output of the DMFC stack was investigated by constant current discharge with 2000 ml 1.0 M methanol until the fuel was exhausted. Fig. 2 shows the plots of discharge voltage versus time at 20 °C. During the first hour of the discharge, the curve of voltage versus time is relatively flat even as the methanol concentration decreases with the discharge. Then, the stack voltage decreases slowly, because of low methanol concentration. Finally, the stack voltage decreases rapidly due to the depletion of the fuel. The stack voltage is sensitive to the discharge current. With the current increased from 1.0 to 2.0 A, the stack voltage decreased correspondingly.

Having studied the power output of the DMFC stack shown in Fig. 1, we further investigated the energy output, which is the next important characteristic of a fuel cell stack. The energy output can be calculated from the data of the voltage–time curves shown in Fig. 2. Here, we describe a method of analyzing energy conversion in the DMFC stack for the operating condition of constant current discharge. The discharge capacity can be expressed by Eq. (1):

$$P = \frac{it}{3600} \tag{1}$$

where P (Ah) is the discharge capacity, i (A) the discharge current, t (s) the time of the discharge process. Because the voltage is a function of time, and at any given time the capacity is also known from Eq. (1), we can make a plot of voltage versus capacity, which means that the voltage can also be written as a function of capacity. Fig. 3 shows the plots of the stack voltage versus capacity and the discharge time versus capacity. The discharge capacity increases with time linearly due to the constant current discharge. The stack voltage decreases with increasing capacity non-linearly. The accumulated discharge energy can be obtained by integration

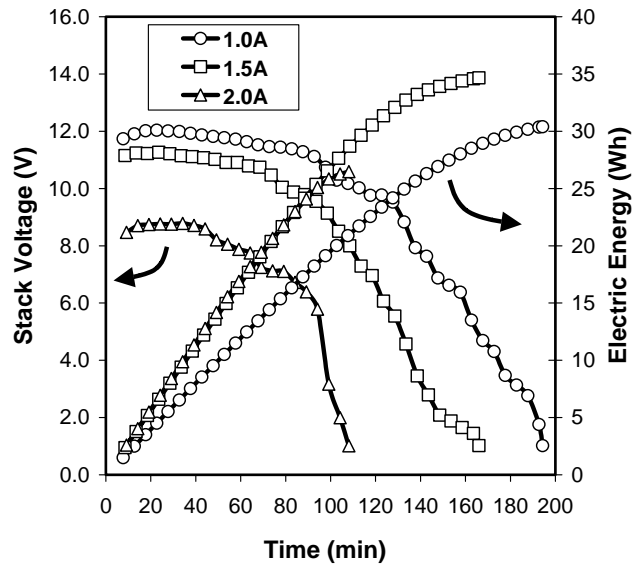


Fig. 2. Voltage–time and energy–time curves of a DMFC stack at constant current and 20 °C environmental temperature. Total fuel amount: 2000 ml 1.0 M MeOH; anode flow: 200 ml/min 1.0 M MeOH; cathode flow: 3 psi air at inlet.

of the area under the voltage–capacity curve in Fig. 3 with Eq. (2):

$$E = \int_0^P v(p) dp \tag{2}$$

where E (Wh) is the energy output of the fuel cell stack, v (V) the stack voltage, and $v(p)$ a function of stack voltage versus capacity.

The energy–time curves of the DMFC stack at constant current discharge can be calculated using Eq. (2), and are also shown in Fig. 2. Interestingly, the energy output varies with the discharge current. In this particular case, neither the high nor the low, but the middle level of discharge current

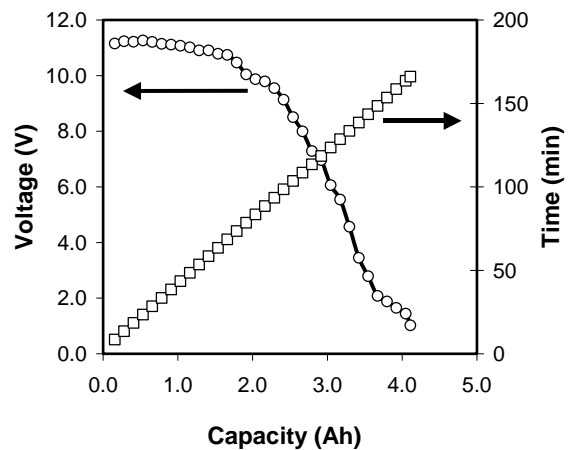


Fig. 3. Voltage–capacity and time–capacity curves for a DMFC stack at constant current (1.5 A) discharge at 20 °C. Total fuel amount: 2000 ml 1.0 M MeOH; anode flow: 200 ml/min 1.0 M MeOH; cathode flow: 3 psi air at inlet.

gives the highest energy output. At 20 °C, the use of 1.5 A discharge current gave the highest energy output. At the endpoint, where the methanol is used up, the accumulated energy output at 1.5 A is about 35 Wh with 2000 ml 1.0 M methanol as fuel. Although the use of 1.0 A discharge gives longer discharge time, the accumulated energy output is lower due to smaller integrated value of stack voltage versus capacity. The use of 2.0 A discharge gives about the same amount of energy as that of the 1.5 A discharge, but the discharge process is shorter due to fast consumption of the fuel, leading to lower accumulated energy output at the end of the discharge. If the methanol concentration were kept the same as that of the beginning of, discharge for all the time, the energy output would not be different for 1.5 and 2.0 A discharge. Therefore, only use of an appropriate magnitude of discharge current can achieve the highest energy output with the method we employed here.

3.2.2. Effect of the environmental temperature

Fig. 4 shows the plots of stack voltage versus time for constant current (2.0 A) discharge at different environmental temperatures. With increasing temperature from 20, 30 to 40 °C, the stack voltage increases almost proportionally. Apparently, higher temperature results in higher kinetic rates for both catalytic methanol oxidation and catalytic oxygen reduction, leading to higher stack voltage. In addition, higher temperature will also increase the ionic conductivity of the polymer electrolyte membrane. The amount of energy output is calculated with Eq. (2), and shown in the same figure, which increases with time until the fuel is consumed. At 40 °C the highest energy is obtained about 45 Wh at the endpoint of discharge.

Fig. 5 shows the plots of stack voltage versus time at a higher discharge current (3.0 A) than that in Fig. 4. With

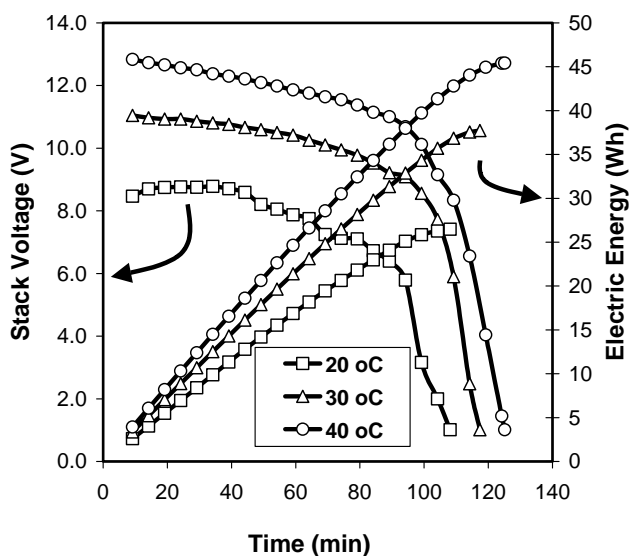


Fig. 4. Voltage–time and energy–time curves of a DMFC stack at constant current (2.0 A) discharge. Total fuel amount: 2000 ml 1.0 M MeOH; anode flow: 200 ml/min 1.0 M MeOH; cathode flow: 3 psi air at inlet.

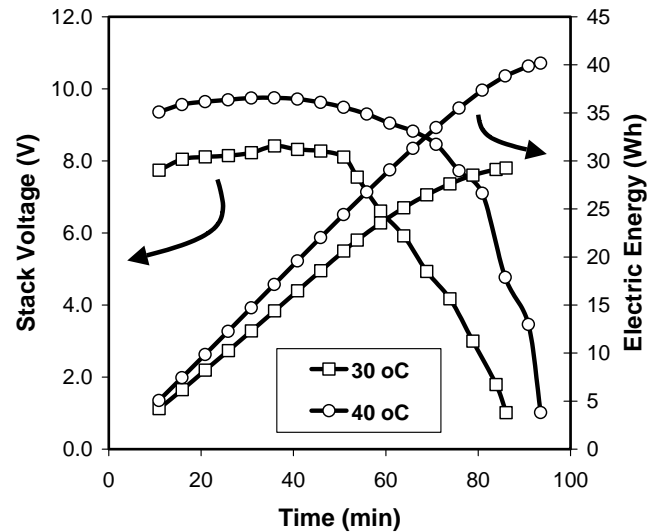


Fig. 5. Voltage–time and energy–time curves of a DMFC stack at constant current (3.0 A) discharge. Total fuel amount: 2000 ml 1.0 M MeOH; anode flow: 200 ml/min 1.0 M MeOH; cathode flow: 3 psi air at inlet.

increasing temperature, the stack voltage and energy output both increase apparently no matter what level of the discharge current is applied. However, as compared with Fig. 4, the stack voltage and the output energy both are lower due to too high discharge current. Therefore, for a specific environmental temperature only an appropriate discharge current can achieve the best stack performance with the method we employed here.

3.3. Faradic efficiency and energy output at constant voltage discharge

A method of constant voltage discharge until the fuel is exhausted was carried out in order to measure the possible highest Faradic efficiency of the DMFC stack. Fig. 6 shows the current–time curves of the DMFC stack at constant

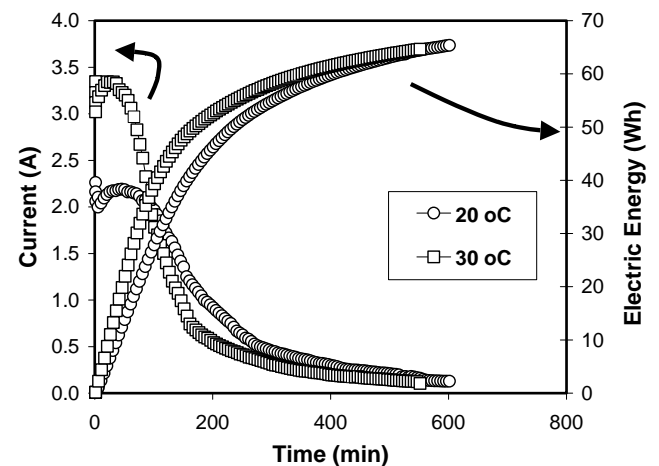


Fig. 6. Current–time and energy–time curves of a DMFC stack at constant voltage (8.0 V) discharge. Total fuel amount: 2000 ml 1.0 M MeOH; anode flow: 200 ml/min 1.0 M MeOH; cathode flow: 3 psi air at inlet.

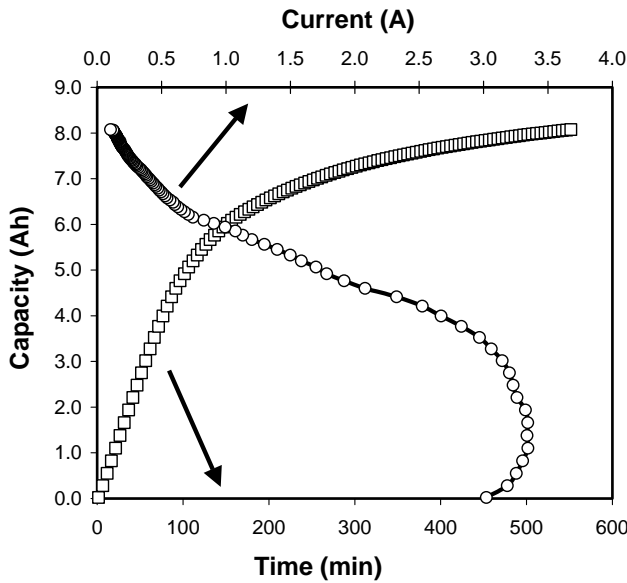


Fig. 7. Discharge capacity–time and capacity–current curves for a DMFC stack at constant voltage (8.0 V) discharge at 30 °C. Total fuel amount: 1.0 M MeOH, 2000 ml; fuel circulation: 200 ml/min; cathode flow: 3 psi air at inlet.

voltage (8.0 V) discharge with 2000 ml 1.0 M methanol. The discharge current decreases slowly with time due to fuel consumption. After 3 or 4 h the discharge current has decreased about 80%, then a small discharge current is maintained for additional 6 or 7 h until the fuel is fully used up. Higher temperature gives much higher discharge current at the beginning of the discharge process.

Here, we describe a method of analysis of energy conversion in the stack for the operating condition at constant voltage discharge (instead of the constant current discharge described above). The discharge capacity can be calculated using Eq. (3):

$$P = \frac{1}{3600} \int_0^t i(t) dt \quad (3)$$

where the current $i(t)$ is a function of time. Fig. 7 shows the plots of discharge capacity versus time and discharge capacity versus current for the DMFC stack at constant voltage discharge (8.0 V) at 30 °C. The discharge capacity increases with time, but decreases with increasing discharge current. The capacity–time curve is not a straight line. This behavior is very different from that of constant current discharge.

The Faradic efficiency, discharge energy and energy efficiency of the DMFC stack can be calculated with the following (Eqs. (4) and (5)):

$$\eta\% = \frac{3600 nP}{6 VCF} \times 100 \quad (4)$$

$$E = \frac{v}{3600} \int_0^t i(t) dt \quad (5)$$

$$\zeta = \frac{3600 vP}{1.21 \times 6 VCF} \times 100 = \frac{v\eta\%}{1.21 n} \quad (6)$$

where $\eta\%$ is the Faradic efficiency, n the number of single cells in the DMFC stack, V (l) the volume of the methanol solution used in the experiment, C (M) the concentration of methanol solution, F (C) the Faradic constant, and ζ the energy efficiency, i.e., the ratio of the practically obtained energy from the certain amount of fuel to the calculated theoretical energy from the same amount of fuel. The other parameters have the same meanings as described in Eqs. (1) and (2).

The discharge energy of the DMFC is also shown in Fig. 6. Even if the distributions of energy versus time between 20 and 30 °C are different, their accumulated energy at the end-point is approximately the same (65 W h). Higher temperature gives higher power and energy output at the beginning, leading to quicker consumption of the fuel than that at lower temperature. The accumulated energy output at the end of the discharge time seems to have no apparent relationship with the temperature in the case of constant voltage discharge. Fig. 8 shows the Faradic efficiency and energy efficiency of the DMFC stack at constant voltage (8.0 V) discharge at 30 °C. The final Faradic efficiency at the end-point of discharge is about 86%, which implies that the problem of fuel crossover through the electrolyte membrane can be limited as long as the discharge current is high enough, or the discharge voltage is low enough. However, the energy efficiency is affected by more factors, i.e., the Faradic efficiency, the discharge voltage and the number of cells in the stack, which is determined by Eq. (6). In addition, the factors of Faradic efficiency and energy efficiency are both affected by experimental conditions, such as temperature and pressure. Generally, the energy efficiency is much smaller than the Faradic efficiency for DMFC stacks or systems due to large voltage loss. Although the Faradic efficiency is high

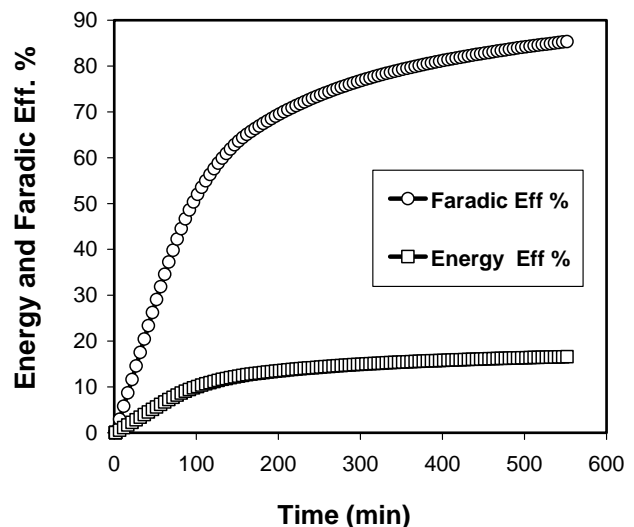


Fig. 8. Energy efficiency and Faradic efficiency of a DMFC stack at constant voltage (8.0 V) discharge. Total fuel amount: 2000 ml 1.0 M MeOH; anode flow: 200 ml/min 1.0 M MeOH; cathode flow: 3 psi air at inlet.

in Fig. 8, the final energy efficiency is only about 17% for constant voltage discharge at 8.0 V and 30 °C.

4. Conclusion

The DMFC stack with a metal foam flow field design performed well at temperatures from 20 to 40 °C. The method of fuel circulation with fixed fuel amount was used successfully to determine the Faradic efficiency, energy density and energy efficiency for the DMFC stack. The average power-output per cell at 40 °C is about 26 mW cm⁻² per cell. About 86% Faradic efficiency was achieved at constant voltage discharge until the fuel was consumed.

Acknowledgements

The authors wish to thank the US Department of Army and the Army Materiel Command for their financial support.

References

- [1] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. Laconti, J. Kosek, G.K.S. Prakash, G.A. Olah, *J. Power Sour.* 47 (1994) 377.
- [2] X.M. Ren, M.S. Wilson, S. Gottesfeld, *J. Electrochem. Soc.* 143 (1996) L12.
- [3] Q.B. Fan, C. Pu, E.S. Smotkin, *J. Electrochem. Soc.* 143 (1996) 3053.
- [4] D. Chu, S. Gilman, *J. Electrochem. Soc.* 143 (1996) 1685.
- [5] J.T. Wang, J.S. Wainright, R.F. Savinell, M. Litt, *J. Appl. Electrochem.* 26 (1996) 751.
- [6] C.K. Witham, W. Chun, T.I. Valdez, S.R. Narayanan, *Electrochem. Solid State Lett.* 3 (2000) 497.
- [7] X.M. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, *J. Power Sour.* 86 (2000) 111.
- [8] A.S. Arico, S. Srinivasan, A. Antonucci, *Fuel cells 1* (2001) 133.
- [9] S.C. Thomas, X.M. Ren, S. Gottesfeld, P. Zelenay, *Electrochim. Acta* 47 (2002) 3741.
- [10] R. Jiang, D. Chu, *J. Power Sour.* 93 (2001) 25.
- [11] T.M. Bestman, J.W. Klett, J.J. Henry, E. Lara-Curzio, Carbon/carbon composite bipolar plate for proton exchange membrane fuel cells, *J. Electrochem. Soc.* 147 (2000) 4083.
- [12] J. Scholta, B. Rohland, V. Trapp, U. Fochen, Investigations on novel low-cost graphite composite bipolar plates, *J. Power Sour.* 84 (1999) 231.
- [13] M.P. Brady, K. Weisbrod, C. Zawodzinski, I. Paulauskas, R.A. Buchanan, L.R. Walker, Assessment of thermal nitridation to protect metal bipolar plates in polymer electrolyte membrane fuel cells, *Electrochem. Solid State Lett.* 5 (2002) A245.
- [14] J. Wind, R. Spah, W. Kaiser, G. Bohm, Metallic bipolar plate for PEM fuel cells, *J. Power Sour.* 105 (2002) 256.
- [15] D.P. Davies, P.L. Adcock, M. Turpin, S.J. Rowen, Bipolar plate materials for solid polymer fuel cells, *J. Appl. Electrochem.* 30 (2000) 101.
- [16] R. Hornung, G. Kappelt, Bipolar plate materials development using Fe-based alloys for solid polymer fuel cells, *J. Power Sour.* 72 (1998) 20.
- [17] D.P. Davies, P.L. Adcock, M. Turpin, S.J. Rowen, Stainless steel as a bipolar plate material for solid polymer fuel cells, *J. Power Sour.* 86 (2000) 237.
- [18] A. Kumar, R.G. Reddy, Modeling of polymer electrolyte membrane fuel cell with metal foam in the flow-field of the bipolar/end plates, *J. Power Sour.* 114 (2003) 54.
- [19] K. Scott, P. Argyropoulos, P. Yiannopoulos, W.M. Taama, Electrochemical and gas evolution characteristics of direct methanol fuel cells with stainless steel mesh flow beds, *J. Appl. Electrochem.* 31 (2001) 823.