Short communication

A miniature direct formic acid fuel cell battery

Hee Soo Kim, Robert D. Morgan, Bogdan Gurau, Richard I. Masel*

Chemical & Biomolecular Engineering, 600 South Mathews Avenue, University of Illinois, Urbana, IL 61801 USA

ARTICLE INFO

ABSTRACT

This work describes miniature formic acid fuel cell batteries, which are built based on a Nafion® membrane and thin metal foils. The intrinsic advantages of formic acid fuel allow for a very simple design of the fuel cell, and the volume of the complete system, including fuel reservoir, can be as small as 11 mm^3. This work examines the effect of membrane thicknesses and fuel concentrations on the cell performance. The optimized cell performance is obtained with N117 membrane and 12 M fuel. Peak power density of the optimized cell is 112 mW cm^{-2}. Life tests are conducted at various conditions using 6 μL of fuel. An energy density of 70 Wh L^{-1} with 40% fuel utilization rate is observed when 12 M formic acid is used at 0.5 V.

1. Introduction

The decreasing size of portable electronic devices with ever increasing power demand necessitates the development of micro power sources. Consequently, there have been substantial efforts in miniaturizing power sources including fuel cells and rechargeable batteries.

Miniature lithium batteries have been developed for implantable medical applications. The smallest Li primary battery reported so far is a pin-type battery with 155 mm^3 of total system volume [1]. Its energy density can be over 500 Wh L^{-1}, which is comparable to that of commercial coin-sized Li battery. Unfortunately, however, the energy density declines sharply when the size of the battery further decreases. For example, an 80 mm^3 Li ion battery is described in the same report with energy density lower than 150 Wh L^{-1}.

On the other hand, various methods to fabricate micro fuel cell systems have been suggested, including Si micro fabrication [2–5], porous Si [6], photochemically etched [7] or micro patterned [8] stainless steel foils, and gold-sputtered polymer [9]. While these millimeter to centimeter sized fuel cells are promising candidates for micro power sources, most of the measurements required additional devices such as Teflon holder or fuel reservoir. The additional devices are often larger than the fuel cell itself, but the total volume of the system is rarely reported.

The direct formic acid fuel cell is ideal for miniaturization because it requires very little balance of plant components, and

it has high power output compared to other liquid fuels such as methanol [10–12]. Although the intrinsic energy content of formic acid is lower than that of methanol (two electrons per molecule of formic acid versus six electrons per molecule of methanol), formic acid can be used in high concentration because of its low crossover rate [13,14].

Previous work on miniature direct formic acid fuel cells was mostly based on Si micro fabrication [2,4,5]. Although remarkable advances were made in terms of power density, only short performance test results have been reported.

In this paper, we report a strikingly simple yet fully functional direct formic acid fuel cell battery based on stainless steel plates and a Nafion® membrane. The total volume of this completely self-contained fuel cell battery is only 11 mm^3 including fuel reservoir. This is smaller than any type of fuel cell battery reported so far.

2. Experimental

2.1. Fuel cell fabrication

Fig. 1(a) shows the schematic of the cell design used in this work. In this design, 25 μm-thick stainless steel plates with 2.5 mm diameter holes are used as current collectors. A small piece of Nafion® membrane (Ion Power) is sandwiched between these two stainless steel plates, and the metal-membrane assembly was hot-pressed at 135 °C for 2 min at an appropriate pressure. The anode catalyst ink is prepared by mixing Pd black (Aldrich, high surface area) with 5% Nafion solution (Ion Power), Millipore water, and isopropanol (Sigma–Aldrich, >99.5%) in an appropriate ratio, and then ultrasonicating the mixture in an ice bath. The cathode ink is prepared in the same manner using Pt black (Alfa Aesar) instead of Pd black.

* Corresponding author. Tel.: +1 217 333 6841; fax: +1 217 333 5052.
  E-mail address: r-masel@uiuc.edu (R.I. Masel).
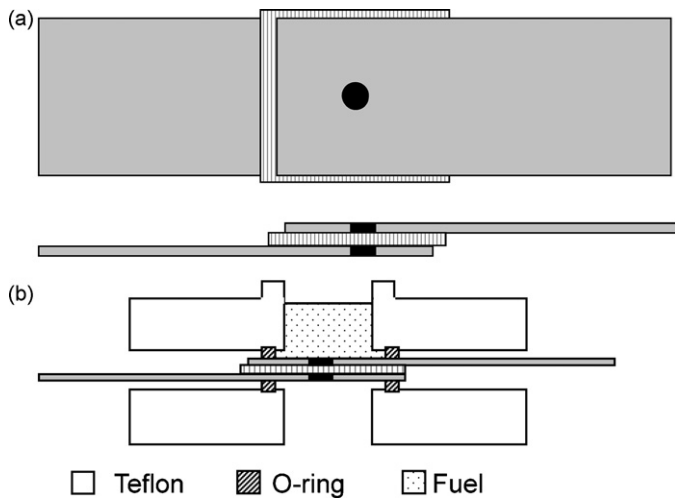
Fig. 1. (a) Top view and side view of a cell used for VI performance check. (b) A fuel cell built as in (a) placed in a Teflon holder for electrochemical testing.

The ink was then applied to the 2.5 mm exposed Nafion® using the direct paint method.

The larger cell shown in Fig. 1(a) is mostly used to check the VI performance of the membrane electrode assembly (MEA). The stainless steel plates can be made smaller to reduce the volume of the cell, down to 11 mm³. A complete, 11 mm³ fuel cell battery (without electrical leads) is shown placed on a penny in Fig. 2. Another battery with extended stainless steel plates for electrical leads is also shown in Fig. 2. The battery shown in Fig. 2 has a fuel reservoir for life tests. The reservoir is a cup, fabricated in house from titanium, with 6 μL capacity. This titanium fuel reservoir can be attached on the anode side of the stainless steel plate using a very small amount of epoxy adhesive (3 M Scotch-Weld™, 2216 B/A). A titanium cap, fabricated in house, with two holes is placed on top of the cup to prevent formic acid evaporation while ensuring CO_2 ventilation. In order to accomplish proper ventilation of CO_2, the inside of the cap is made hydrophobic by depositing heptadecafluoro-1,1,2,2-tetrahydrodecyltrichlorosilane (FDTS) by Molecular Vapor Deposition (Applied MicroStructures, Model 100). The hydrophobic surface promotes efficient delivery of fuel and CO_2 ventilation by preventing the fuel from sticking to the cap.

2.2. Testing

All electrochemical measurements are performed at room temperature using a Solartron 1287 potentiostat. To obtain VI curves,


Fig. 2. 11 mm³ cell placed on top of a penny (left) and another cell of same design with extended stainless steel plates for electrical connection (right).

the cell is placed in a Teflon holder, built in house, as depicted in Fig. 1(b). The fuel cell is held in the Teflon holder by tightening screws on each corner of the holder. Approximately 3 mL of fuel is placed in the anode reservoir, while the cathode is exposed to quiescent ambient air. Formic acid solutions of various concentrations are prepared from either a 50% formic acid solution (Fluka) or from an 88% formic acid solution (GFS Chemicals). For the life tests, 6 μL of fuel is placed inside the titanium cup using a micropipette, and the titanium cap is placed on the top to prevent evaporation of the fuel. A self-breathing cathode is used for all the experiments.

3. Results and discussions

3.1. VI performance

The cell is fabricated with Nafion® films of various thicknesses. Fig. 3 shows the VI curves obtained with a cell made with N112 membrane. Both the open circuit voltage (OCV) and the overall performance of the cell clearly reflect the effect of fuel concentration with this thin membrane. As more concentrated fuel is used, a significant drop in OCV as well as a decrease in performance is observed due to fuel crossover and catalyst poisoning. Consequently, 5 M fuel shows the highest performance in N112 cells, with peak a power density of 55 mW cm^{-2} at 0.50 V. In contrast, the N115 membrane cells display similar performance with 5 M, 8 M, and 12 M fuel in the low current density region (Fig. 4). As the current density increases, the performance with 5 and 8 M fuel begins to drop significantly due to mass transport limitation. On the other hand, more concentrated 15 M fuel performance is hampered by fuel crossover effects. Therefore, the highest power density is achieved with 12 M fuel, which is 84 mW cm^{-2} at 0.43 V.
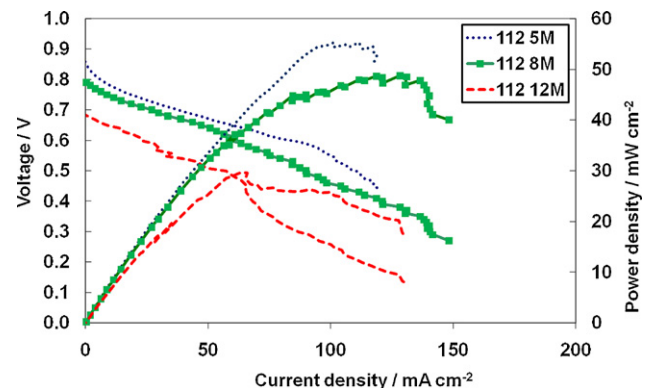
Fig. 3. VI performance of N112 cells with various fuel concentrations.
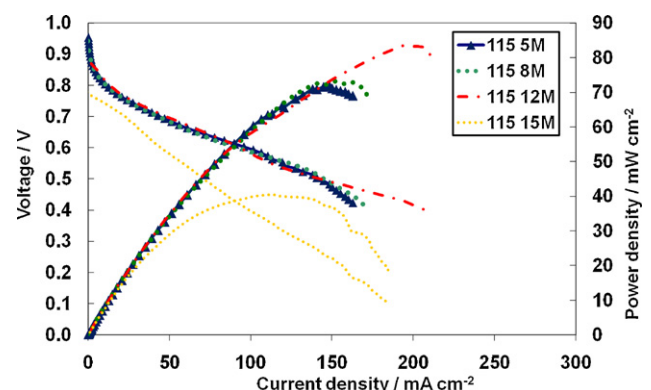
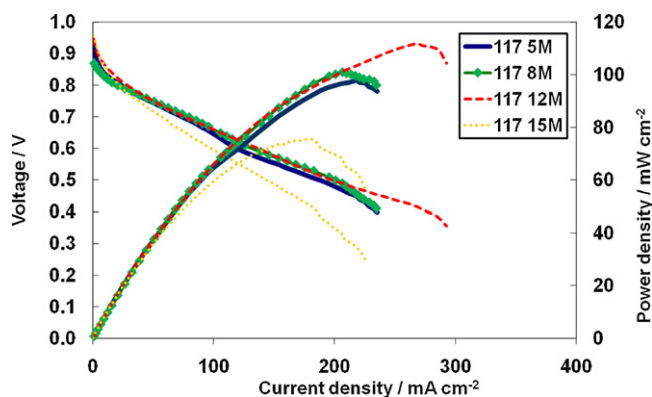**Fig. 4.** VI performance of N115 cells with various fuel concentrations.

Fig. 5. VI performance of N117 cells with various fuel concentrations.

Fig. 7. VI performance of various thickness membranes with 12 M formic acid.

Fig. 5 illustrates that N117 cells have a similar trend as that of N115 cells; i.e., 5, 8 and 12 M have similar performance in the low current region with 12 M showing highest performance at high current density and 5 and 8 M performance decreasing due to mass transport. The 15 M performance is lower than that of 12 M, but the difference is smaller compared to N115 cells since fuel crossover effect is smaller with the thicker membrane. The peak power density is 112 mW cm^{-2} at 0.42 V. For comparison, the peak power density of a 4 cm^2 passive direct formic acid fuel cell previously reported is 177 mW cm^{-2} at 0.53 V, which was obtained at 30 °C using 10 M fuel [11]. The effect of the formic acid concentration on the performance of N1110 cells is shown in Fig. 6. The performance increases with increasing fuel concentration up to 12 M, then decreases with 15 M fuel. This result indicates that the fuel crossover effect is less important than the mass transport effect when the concentration is less than 15 M. The best performance is again obtained with 12 M fuel, and the peak power density is 70 mW cm^{-2} at 0.40 V.

Fig. 7 compiles the 12 M performance of cells with various membrane thicknesses. Increasing OCV with increasing thickness of membrane is clearly the result of a reduction in fuel crossover with thicker membranes. However, in the case of N1110, this advantage of thicker membrane is quickly compromised by IR drop in the practical current density range. Consequently, the optimum performance is obtained with a N117 membrane.

3.2. Life tests

According to the design in Fig. 2, 11 mm^3 devices were built using N117 membrane. Four life tests were performed to evaluate the device, and the results are summarized in Fig. 8 and Table 1.
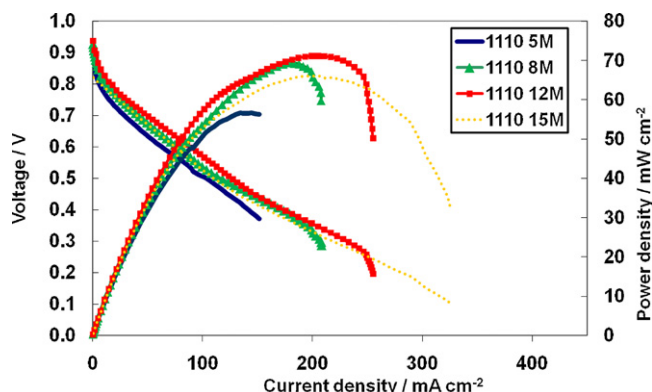

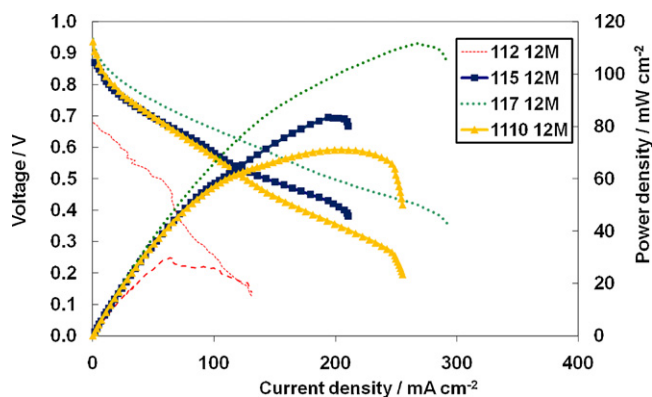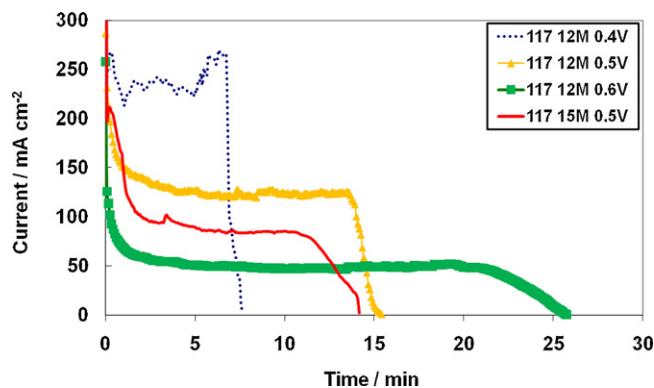**Fig. 6.** VI performance of N1110 cells with various fuel concentrations.

Fig. 8. Constant voltage life test result of N117 cells using 6 μL of fuel. The volume of the cell is 11 mm^3.

Life tests at various voltages prove that the device can handle various power outputs ranging from 123 to 388 W L^{-1}. The power density is highest at 0.4 V, but the energy density is low due to the low voltage efficiency and low fuel utilization rate. Higher current density at this low operating voltage may lead to higher fuel crossover rate resulting in a low fuel utilization rate. At 0.5 V, both the voltage efficiency and fuel utilization rate improve, and the energy density and the fuel utilization rate show their maximum values of 70 W L^{-1} and 40%, respectively. At 0.6 V, however, the energy density decreases despite the higher voltage efficiency, due to the low fuel utilization rate. Since the fuel reservoir is not completely sealed, some of the fuel can be lost by evaporation and the effect is more significant as the life test runs for a longer period of time.

The same N117 cell was tested with 15 M fuel in the hope of obtaining higher energy density. Unfortunately, the fuel utilization rate was too low to take advantage of the higher concentration. More concentrated fuel unavoidably has a higher fuel crossover

Table 1
Life test results obtained with N117 cells and 6 μL of fuel.

	Fuel concentration			
	12 M			15 M
	Operating voltage (V)			
	0.4	0.5	0.6	0.5
Average power density (W L^{-1})	388	272	123	208
Energy density (Wh L^{-1})	50	70	56	49
Fuel utilization rate (%)	36	40	26	23

rate. In addition, when formic acid comes into contact with the anode catalyst, hydrogen is spontaneously evolved from the catalyst surface, most of which will be lost as the evolved hydrogen bubbles escape the fuel reservoir. The more concentrated the fuel, the higher the hydrogen evolution rate is, which further lowers the fuel utilization. Therefore, the optimized performance can be achieved only when the fuel concentration at the catalyst surface is close to 12 M or lower.

4. Conclusions and future directions

A complete direct formic acid fuel cell battery of 11 mm^3 volume was built using metal foils and Nafion® membrane. The Peak power density was 112 mW cm^{-2} when N117 membrane and 12 M fuel were used. A life test was performed at 0.5 V with 6 μL of fuel to produce 70 W L^{-1} of energy density with 40% fuel utilization rate. These results suggest that higher energy density may be achieved by improving the following in the cell design:

(1) The fuel reservoir should have better sealing to prevent fuel evaporation.
(2) Adding a fuel control layer on top of the anode may enable the use of a fuel with a concentration greater than 12 M. If the fuel in contact with the anode catalyst is dilute, there will be less fuel loss due to crossover and hydrogen evolution.

References

[1] M. Nagata, et al., Journal of Power Sources 146 (1–2) (2005) 762–765.
[2] J. Yeom, et al., Journal of Power Sources 160 (2) (2006) 1058–1064.
[3] J.P. Meyers, H.L. Maynard, Journal of Power Sources 109 (1) (2002) 76–88.
[4] K.-L. Chu, M.A. Shannon, R.I. Masel, Journal of Micromechanics and Microengineering 17 (9) (2007) S243–S249.
[5] K.-L. Chu, M.A. Shannon, R.I. Masel, Journal of the Electrochemical Society 153 (8) (2006) A1562–A1567.
[6] T. Pichonat, B. Gauthier-Manuel, Fuel Cells (Weinheim, Germany) 6 (5) (2006) 323–325.
[7] G.Q. Lu, C.Y. Wang, Journal of Power Sources 144 (1) (2005) 141–145.
[8] R. Hahn, et al., Journal of Power Sources 131 (1–2) (2004) 73–78.
[9] S.H. Chan, et al., Journal of Micromechanics and Microengineering 15 (1) (2005) 231–236.
[10] S. Ha, B. Adams, R.I. Masel, Journal of Power Sources 128 (2) (2004) 119–124.
[11] S. Ha, Z. Dunbar, R.I. Masel, Journal of Power Sources 158 (1) (2006) 129–136.
[12] X. Yu, P.G. Pickup, Journal of Power Sources 182 (1) (2008) 124–132.
[13] X. Wang, J.-M. Hu, I.M. Hsing, Journal of Electroanalytical Chemistry 562 (1) (2004) 73–80.
[14] Y.-W. Rhee, S.Y. Ha, R.I. Masel, Journal of Power Sources 117 (1–2) (2003) 35–38.