

# High power density direct formic acid fuel cells

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## Abstract

A demonstration of direct formic acid fuel cells (DFAFCs) generating relatively high power density at ambient temperature is reported. The performance of Nafion 112-based DFAFCs with different concentrations of formic acid at different temperatures has been evaluated. DFAFCs operated with dry air and zero back-pressure can generate power densities of 110 and 84 mW cm<sup>-2</sup> at 30 and 18 °C, respectively, which are considerably higher than direct methanol fuel cells (DMFCs) operated under the same conditions. The DFAFCs are especially suited to power portable devices used at ambient temperature because the significant high power density can be achieved with highly concentrated formic acid.

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*Keywords:* Direct formic acid fuel cell; Portable power; High power density; Polymer electrolyte membrane

## 1. Introduction

The need of power and energy for portable devices such as cellular phones, personal digital assistants (PDAs), laptop computers, etc. is rapidly growing. But the progress of reduction in weight and size of power sources is not keeping up with the miniaturization of consumer electronic devices. The energy density of the advanced batteries, e.g. Li ion batteries, is limited and does not meet the demand. Therefore, polymer electrolyte membrane (PEM)-based fuel cells, in particular, the direct liquid-feed fuel cells (e.g. direct methanol fuel cells, DMFCs) become an attractive candidate [1–3] for powering these devices, because H<sub>2</sub>/air fuel cell is limited by the high cost of miniaturized hydrogen bottles and the potential danger in transport and in use. Unfortunately, there are significant drawbacks for DMFCs. A catalyst activity for methanol oxidation at room temperature is relatively low. Methanol crossover from anode through electrolyte membrane to cathode decreases the mixed potential of cathode, poisons cathode catalyst and reduces the fuel efficiency [4–6]. The methanol crossover limits utilization of high concentration of methanol, generally less than 2 M.

In recent publications of our group, feasibility of the PEM-based direct formic acid fuel cells (DFAFCs) have

been demonstrated [7–10]. Although neat formic acid (2086 Wh l<sup>-1</sup>) has a lower energy density than neat methanol (4690 Wh l<sup>-1</sup>), one can run the fuel cell fed with high concentration of formic acid solutions. Consequently, the DFAFCs are quite competitive on an actual fuel energy density basis (based on the maximum fuel concentration). On the other hand, the membrane electrode assemblies (MEAs) and fuel cell components definitely need to be developed for improving the performance of DFAFCs, which is the key issue for reduction in weight and size as well as cost.

In this paper, we demonstrate that DFAFCs can provide quite high power density under liquid formic acid—ambient air cell operation even at ambient temperature. It should not be surprised because formic acid/air fuel cells have a high theoretical open circuit voltage i.e. emf (1.45 V) and limited fuel crossover due to anodic repulsion between the Nafion sulfonic groups and the formate anions dissociated partially from formic acid [7,11]. In addition, formic acid is a strong electrolyte, hence, is expected to facilitate both electronic and proton transport within the anode compartment of the fuel cell [7]. The electro-oxidation of formic acid occurs via a dual reaction pathway, reducing the relative percentage of surface poisoning reaction intermediates [12–18]. The most desirable reaction pathway for DFAFCs is via the dehydrogenation reaction, which does not form CO as a reaction intermediate but forms CO<sub>2</sub> without CO intermediate. Based on the low crossover of formic acid, we utilize Nafion 112 as a polymer electrolyte membrane in this work. A technical improvement in MEA fabrication enhances the

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performance of DFAFCs. The evaluation results of the DFAFCs are reported in this paper.

## 2. Experimental

The single-cell test fixture was designed for use with formic acid and built by Fuel Cell Technologies, Inc. [7]. The anode/cathode flow fields were machined into graphite blocks. The formic acid/air is fed into the cells graphite blocks through Teflon swagelock fittings, directly mounted onto the anode/cathode graphite blocks, respectively.

The MEAs were fabricated using a ‘direct paint’ technique to apply the catalyst layer. The active cell area is  $5 \text{ cm}^2$ . The ‘catalyst inks’ were prepared by dispersing the catalyst nanoparticles into appropriate amounts of deionized water and a 5% recast Nafion solution (1100 EW, from Solution Technology, Inc.). Then both the anode and cathode ‘catalyst inks’ were directly painted onto either side of a Nafion 112 membrane. For all MEAs prepared in this study, the cathode consisted of unsupported platinum black particles (Johnson Matthey, HiSpec 1000) at a loading of  $5 \text{ mg cm}^{-2}$ . The anode consisted of unsupported platinum-ruthenium black catalyst particles at a loading of  $8 \text{ mg cm}^{-2}$  (Johnson Matthey, HiSpec 6000). A carbon cloth diffusion layer (E-Tek) was placed on top of both the cathode and anode catalyst layers. Both sides of the cathode side carbon cloth, were Teflon-coated for water management.

The MEAs were initially conditioned within the testing fixture at  $60^\circ\text{C}$  under  $\text{H}_2/\text{air}$  fuel cell operation mode for 1–2 h, while holding the cell potential at 0.7 V using a fuel cell testing station (Fuel Cell Technologies Inc.). The  $\text{H}_2$  flow rate was set to  $200 \text{ ml min}^{-1}$ , the gas stream was humidified to  $70^\circ\text{C}$  prior to entering the cell, and a back-pressure of 2 atm was applied. The air flow rate was  $390 \text{ ml min}^{-1}$ , the gas stream was humidified to  $65^\circ\text{C}$ , and a back-pressure of 2 atm was applied.

In this paper, both upward and downward voltage scans were used for each polarization measurement. Polarization plots were taken using a voltage interval of 50 mV and 25 s waiting time between points. The plots in the two scan directions were averaged and presented here as a single curve. For the cell polarization measurements, the anode fuel used was different concentration solution of formic acid (GFS Chemicals, 88% ACS grade) at a flow rate of  $0.5 \text{ ml min}^{-1}$ . On the cathode, air was supplied at a flow rate of  $390 \text{ ml min}^{-1}$  without any back-pressure and humidification. For DMFC operation, different concentration of methanol (Fisher Scientific, ACS grade) was fed through anode.

To evaluate formic acid crossover in the fuel cell test fixture, the cells were operated in a driven mode, and the crossover formic acid was oxidized at the fuel cell cathode. A linearly voltammetric scan was applied to the fuel cell cathode and current response recorded. This measurement allows to directly determine the magnitude of crossover using limiting current density. The working potential was controlled

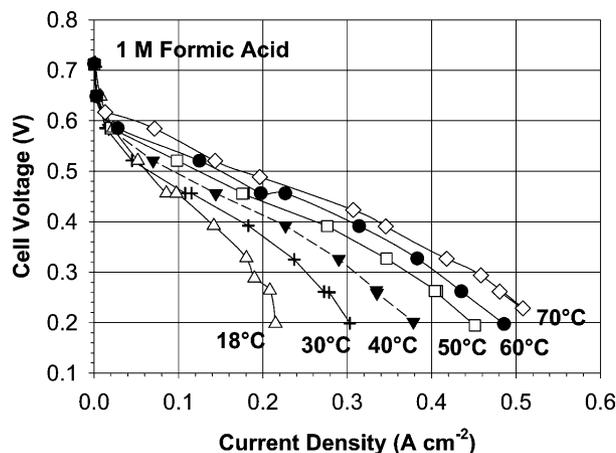


Fig. 1. Formic acid/air fuel cell polarization plots at 18, 30, 40, 50, 60, and  $70^\circ\text{C}$ . The flow rate of formic acid (1.0 M) to the anode was  $1 \text{ ml min}^{-1}$ . Air was supplied to the cathode at a flow rate of  $390 \text{ ml min}^{-1}$  without any back-pressure and humidification.

with a power supply (Hewlett-Packard, model 6033 A) and the potential was stepped in 10 mV increments at 5 s intervals.

## 3. Results and discussion

The range of applicable formic acid concentrations in the DFAFCs is currently dictated by the mass transport limitation of formic acid in catalysts layer, and the hygroscopicity of concentrated formic acid fed on the anode. A highly concentrated formic acid will dehydrate a MEA and hence result in a sharp increase of high frequency resistance of the MEA, which damages the MEA. To systematically evaluate effect of formic acid concentration on DFAFCs' performance without damaging MEA, an upper limit of formic acid concentration is selected as 10.0 M. At a lower formic acid concentration the performance is limited by mass transport of formic acid at anode, 1.0 M is a reasonably lower concentration of formic acid.

Fig. 1 is polarization plot of the DFAFCs with 1.0 M formic acid at different cell temperatures. At  $70^\circ\text{C}$ , current densities of 120, 170, and  $260 \text{ mA cm}^{-2}$  are achieved at 0.55, 0.50, and 0.40 V, respectively. Below 0.40 V, the mass transport of formic acid begins to limit the cell performance. The DFAFCs can be well operated at different cell temperatures from 18 to  $70^\circ\text{C}$ . The maximum power densities are relatively encouraging even around ambient temperatures, 60 and  $76 \text{ mW cm}^{-2}$  at 18 and  $30^\circ\text{C}$ , respectively. There is a very good performance in the kinetic region of polarization (e.g.  $120 \text{ mA cm}^{-2}$  at 0.55 V), which is an indication of low crossover of formic acid [4,19].

The formic acid permeating from anode to cathode through membrane should be measured in a fuel cell configuration to diagnose cell performance. We measured crossover by flowing argon through the fuel cell cathode

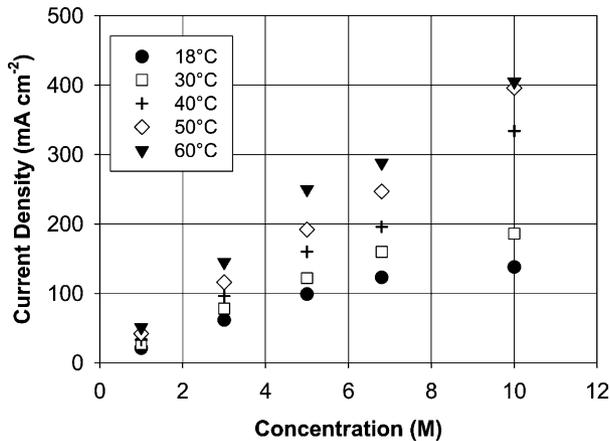


Fig. 2. Plots of the crossover current density of formic acid fed with different concentrations, 1.0, 3.0, 5.0, 6.8, 10.0 M, at different cell temperatures, 18, 30, 40, 50, and 60 °C. The data are based on the limiting currents produced by the electro-oxidation of crossover formic acid when a reverse bias of about 0.8 V was applied. The formic acid flow rate was 1 ml min<sup>-1</sup>. Argon gas was supplied to the cathode/working electrode at a flow rate of 300 ml min<sup>-1</sup>. These measurements are for qualitative comparisons only, since the 0.8 V bias substantially enhances the crossover current.

and applying a 0.8 V reverse bias on the cell. The formic acid is completely electro-oxidized on the opposite side in an inert atmosphere at sufficiently high electrode potential. Although the applied electric field will likely substantially increase the crossover flux than its true value because the positive potential drives formate ions to the cathode, it is still very helpful to a qualitative diagnosis of fuel cell measurement. Fig. 2 is the relationship between crossover current and formic acid concentration at several cell temperatures. For 1.0 M formic acid, the crossover current densities are indeed relatively low at all cell temperatures tested. The crossover currents increase with the formic acid concentration as generally expected. The currents are much higher than those reported previously [9] because the 0.8 V bias drives formic acid to the cathode.

Increasing concentration of formic acid moves mass transport limitation toward higher current densities, as shown in Fig. 3. The DFAFC with 3.0 M formic acid allows to be well operated even at 0.10 V, which generates very high current densities, up to ca. 0.8 A cm<sup>-2</sup> around 50–60 °C. At the same time, the performance in kinetic region is lower than that of 1.0 M formic acid (Fig. 2). The crossover increases as the formic acid concentration increases, which lowers cell performance in the kinetic region [4–6,19].

There is no further benefit if the concentration of formic acid is continually increased to 5.0 and 6.8 M. However, the DFAFC can be also well operated with 10 M formic acid, as shown in Fig. 4.

There is a significant enhancement of the DFAFC performance, e.g. from 0.2 to 0.3 A cm<sup>-2</sup> at 0.30 V, if the cell temperature is raised from 18 to 30 °C. Further raising cell temperature to 40 °C does not enhance the cell performance.

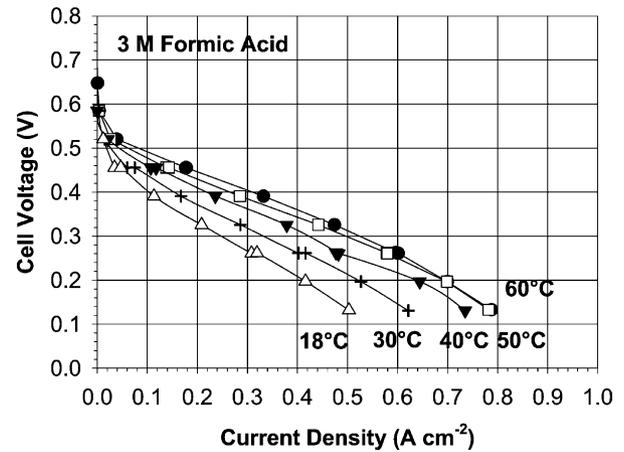


Fig. 3. Formic acid/air fuel cell polarization plots at 18, 30, 40, 50, and 60 °C. The flow rate of formic acid (3.0 M) to the anode was 1 ml min<sup>-1</sup>. Air was supplied to the cathode at a flow rate of 390 ml min<sup>-1</sup> without any back-pressure and humidification.

There is improvement of the DFAFC performance when the cell temperature is continually increased, but still not as much as expected according to kinetic theory. The formic acid crossover seems become a dominant factor in this case because the crossover currents are significant high beyond 40 °C (Fig. 2). However, the overall performance of DFAFCs with 10 M formic acid is still very good, which demonstrates a promising prospective to apply the DFAFCs as portable power sources because the high power density may be generated by using highly concentrated formic acid solution.

The power density–current density plots at different formic acid concentrations and at different cell temperatures are shown in Fig. 5. Five different formic acid concentrations were examined, 1.0, 3.0, 5.0, 6.8, and 10.0 M, respectively. Fig. 5 illustrates the typical variation of power density in the range of formic acid concentration 1.0–10.0 M. It is very obvious that 3.0 M formic acid generate the largest

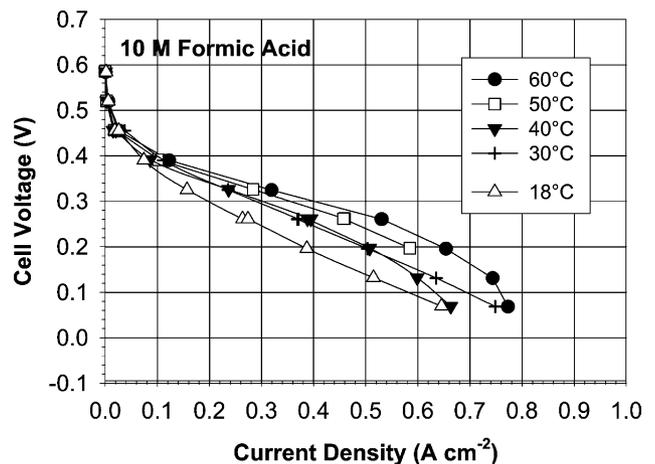


Fig. 4. Formic acid/air fuel cell polarization plots at 18, 30, 40, 50, and 60 °C. The flow rate of formic acid (10.0 M) to the anode was 0.5 ml min<sup>-1</sup>. Air was supplied to the cathode at a flow rate of 390 ml min<sup>-1</sup> without any back-pressure and humidification.

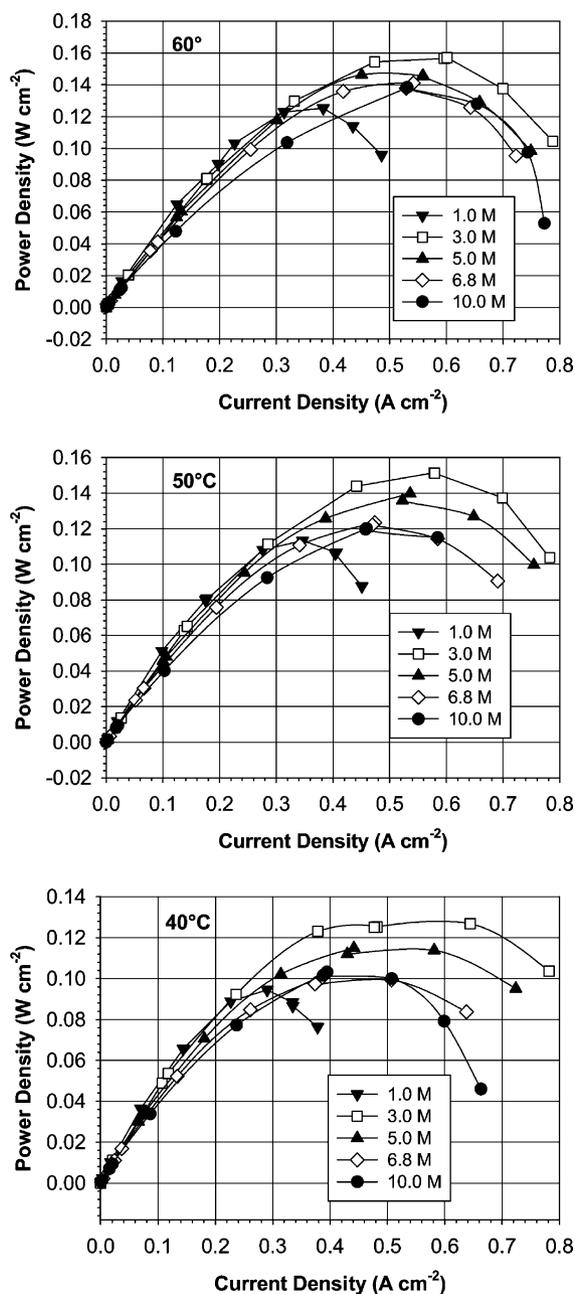


Fig. 5. The power density plots of formic acid/air fuel cells with different concentration of formic acid, 1.0, 3.0, 5.0, 6.8, and 10.0 M, at 40, 50, and 60 °C. The flow rate of formic acid to the anode was  $1 \text{ ml min}^{-1}$ . Air was supplied to the cathode at a flow rate of  $390 \text{ ml min}^{-1}$  without any back-pressure and humidification.

maximum power densities at every cell temperatures. Formic acid (1.0 M) cannot sustain fuel cell operation at higher current densities because of appearance of mass transport limitation. Interestingly, the maximum power densities of the cells with formic acid in concentrations from 3.0 to 10.0 M are not very sensitive to changes in concentration at higher temperature, 40–60 °C, in particular, at 60 °C. In addition, power density–current density relationship with 10.0 M formic acid is very close to that with 6.8 M formic

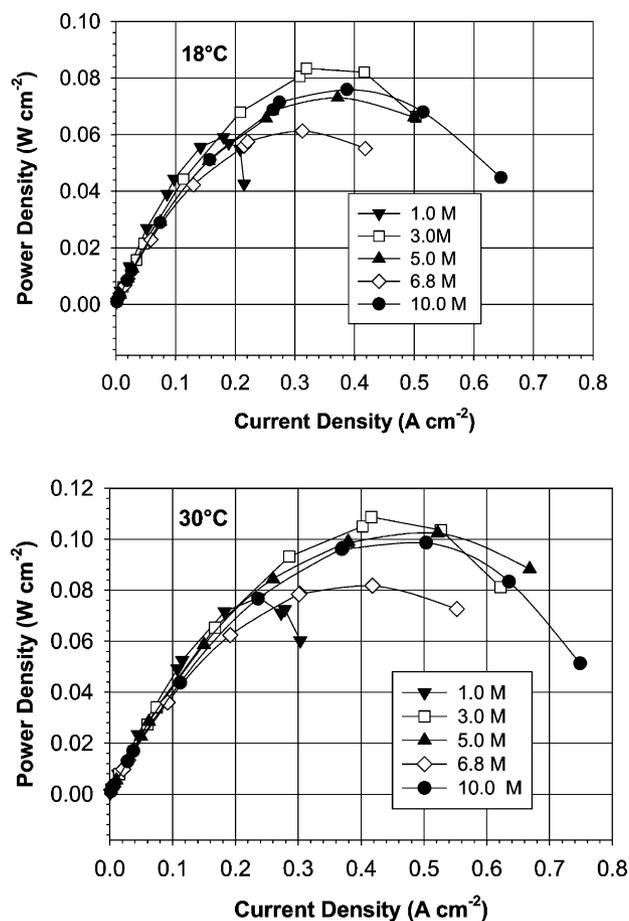


Fig. 6. The power density plots of formic acid/air fuel cells with different concentration of formic acid, 1.0, 3.0, 5.0, 6.8, and 10.0 M, at 18, and 30 °C. The flow rate of formic acid to the anode was  $1 \text{ ml min}^{-1}$ . Air was supplied to the cathode at a flow rate of  $390 \text{ ml min}^{-1}$  without any back-pressure and humidification.

acid, and seems to outperform that with 6.8 M formic acid when the cell temperature decreases.

It is surprised that 10.0 M formic acid performs very close to 5.0 M formic acid if the DFAFCs are operated around ambient temperatures, 18 and 30 °C (Fig. 6).

The crossover data in Fig. 2 may be helpful to explain the phenomenon. When temperatures are between 40 and 60 °C, linear relationship of formic acid crossover current with concentration can be observed for all concentrations of formic acid used (1.0–10.0 M). If the membrane properties were constant, one would expect a permeation rate proportional to concentration of formic acid. It is also reasonable that lower crossover corresponds to better performance if there is no mass transport limitation. However, a linear relationship between crossover current density and formic acid concentration is not valid if the concentration is increased to 10.0 M at 18 or 30 °C. The experimental data of formic acid permeation through Nafion membrane in a diffusion cell, published previously by this group, indicated that the Nafion membrane may be changed in the case of 10 M formic acid at room temperature. The membrane change results in a

lower formic acid crossover. Why did the change occur at lower temperatures, rather than at higher temperatures? It is well known that concentrated formic acid is strongly hydroscopic. Highly concentrated formic acid fed in the anode flow paths may somewhat dehydrate catalyst layer and membrane at low temperature and hence reduce the formic acid crossover. However, such a dehydration effect does not significantly increase high frequency resistance in the case of 10.0 M formic acid. The resistance rapidly increases if the concentration is 15.0 or 20.0 M. Raising temperature will reduce the hydroscopic ability of formic acid because the interaction between molecules decreases. If an oxygen plasma treated carbon cloth is used as an anode backing, which is more hydrophilic and hence absorbs more water in there, the dehydration effect will not be observed in the case of 10.0 M formic acid (unpublished results). Also if pressurized humidified cathode gas is used, the membrane can be hydrated from cathode side so that the dehydration effect may also be avoided (unpublished results). This is an indication of that the hydration status of MEA has a significant effect on cell performance. Consequently, DFAFCs' performance is dependent on crossover, mass transport, and hydration status of MEAs (in particular, catalyst layers). The hydration status is a quite complicated issue. More research needs to be done in future.

It should be emphasized that the DFAFCs with well-performed 3.0 M formic acid generate amazing maximum power densities using dry air without any back-pressure, 84 and 110  $\text{mW cm}^{-2}$ , respectively, around ambient temperatures, 18 and 30  $^{\circ}\text{C}$  (Fig. 6). The dependence of the maximum power densities on temperature is shown in Fig. 7. At the chosen air flow rate and formic acid concentration, the electric power rises with increasing temperature. A maximum power density of 158  $\text{mW cm}^{-2}$  can be achieved at 60  $^{\circ}\text{C}$ . The curve of the cell power in the temperature range studied shows that the linearization is not valid at elevated temperatures. The mass transport limitation is one of the reasons, which can be confirmed by the result of cell polarization with 3.0 M formic acid at 60  $^{\circ}\text{C}$  (Fig. 3).

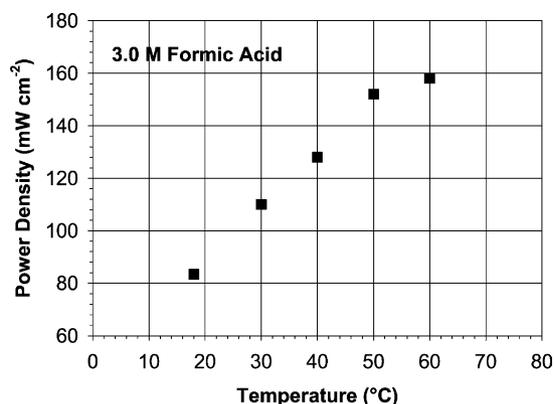


Fig. 7. The dependence of power density on cell temperature for formic acid/air fuel cells with 3.0 M formic acid, at 18, 30, 40, 50, and 60  $^{\circ}\text{C}$ . Data from Figs. 5 and 6.

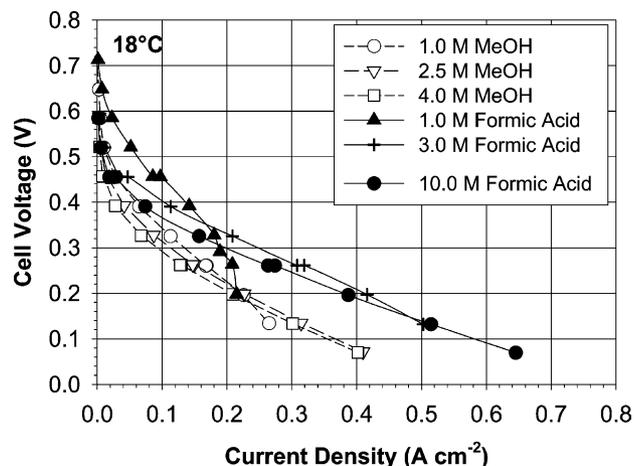


Fig. 8. The polarization plots of fuel cells with methanol (1, 2.5, 4 M) and formic acid (1, 3, and 10 M), at 18  $^{\circ}\text{C}$ . The flow rate of formic acid was 1  $\text{ml min}^{-1}$ . The air flow rate was 390  $\text{ml min}^{-1}$ .

In general, some effects mentioned below may also lead to a non-linear dependence of the power density as a function of the operating temperature. On one hand, the temperature influences the electrodes' kinetics [20,21], but at the same time high temperatures lead to an increased water vaporization at the cathode which reduces, e.g. the partial pressure of the oxygen. In addition, in DFAFCs the water permeation by electro-osmosis and formic acid crossover increase with higher temperatures due to swelling effects of the membrane [22]. In the temperature range from 18 to 50  $^{\circ}\text{C}$ , the electrodes' kinetics may be a dominant factor, which results in a rapid increase in the power density with temperature.

How significant is the DFAFC's performance demonstrated in this paper? By comparison, the DMFCs are carried out by using 1.0, 2.5, 4.0 M methanol under the same conditions as the DFAFCs'. The results in Fig. 8 demonstrate that the DMFC with 1.0 M methanol performs better than that with 2.5 and 4.0 M methanol at 18  $^{\circ}\text{C}$  even though the current density goes up to 0.22  $\text{A cm}^{-2}$  (maximum power density is around 0.2  $\text{A cm}^{-2}$ ). The methanol crossover limits the utilization of higher methanol concentration solution. Methanol concentration lower than 1.0 M may suffer a mass transport limitation at even lower current density. Obviously, the DMFC with 1.0 M methanol and dry air without any back-pressure has generated a very good performance at ambient temperature. However, the DFAFC with 1 M formic acid provides 110 mV advantage over 1.0 M methanol at 0.1  $\text{A cm}^{-2}$ , which is an indication of low formic acid crossover. But it clearly suffers a mass transport limitation at higher current density. The data in Fig. 9 confirm that the crossover of 1 M formic acid (21  $\text{mA cm}^{-2}$ ) is much lower than that of 1 M methanol (94  $\text{mA cm}^{-2}$ ).

Formic acid in a concentration higher than 3.0 M may run the fuel cell down to 0.1 V without mass transport limitation and provide ca. 120 mV advantages over methanol beyond 0.3  $\text{A cm}^{-2}$  (Fig. 8). DFAFCs with 3.0 and 10.0 M formic acid still offer 30–70 mV advantages over methanol at a

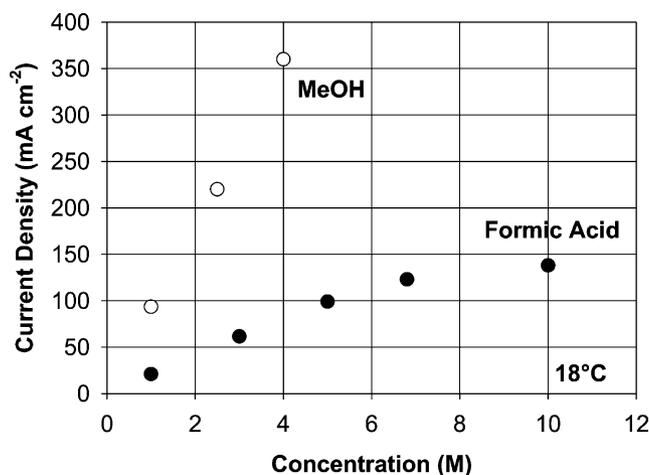


Fig. 9. Plots of the crossover current density of formic acid (1.0, 3.0, 5.0, 6.8, and 10.0 M), and methanol (1.0, 2.5, and 4.0 M), at 18 °C. The data are based on the limiting currents produced by the electro-oxidation of crossover formic acid when a reverse bias of about 0.8 V was applied. The flow rate for both formic acid and methanol was 1 ml min<sup>-1</sup>. Argon gas was supplied to the cathode/working electrode at a flow rate of 300 ml min<sup>-1</sup>. These measurements are for qualitative comparisons only, since the 0.8 V bias substantially enhances the crossover current.

lower current density of 0.1 A cm<sup>-2</sup>. The crossover of 10 M formic acid is higher than that of 1 M methanol, but much lower than that of 2.5 or 4 M methanol (Fig. 9). The observed voltages from the polarization plots at a very low current density in Fig. 8 reflect the crossover-controlled features. Formic acid (3.0 M) has a much lower crossover than that of 1.0 M methanol (Fig. 9). Therefore, a clear voltage advantage of the DFAFC with 3.0 M formic acid can be achieved in comparison with 1.0 M methanol (Fig. 8).

Comparing the power densities of the fuel cells with 1.0 M methanol and 3.0 M formic acid, as shown in Fig. 10, there are ca. 87% advantage of formic acid (84 mW cm<sup>-2</sup>) over methanol (45 mW cm<sup>-2</sup>) at 18 °C, and ca. 64% advantage of formic acid (110 mW cm<sup>-2</sup>) over methanol (67 mW cm<sup>-2</sup>) at 30 °C. Thus, the DFAFCs are especially suited to power portable devices used at ambient temperatures because the significantly high power density can be generated with relatively high concentration of formic acid.

As indicated by the data in Fig. 11, replacing air by pure oxygen gas has a strong effect on the fuel cell performance at ambient temperatures, 18 and 30 °C. The performance gain may result from the higher partial pressure of oxygen. An increase in the cathode operating pressure from 1.00

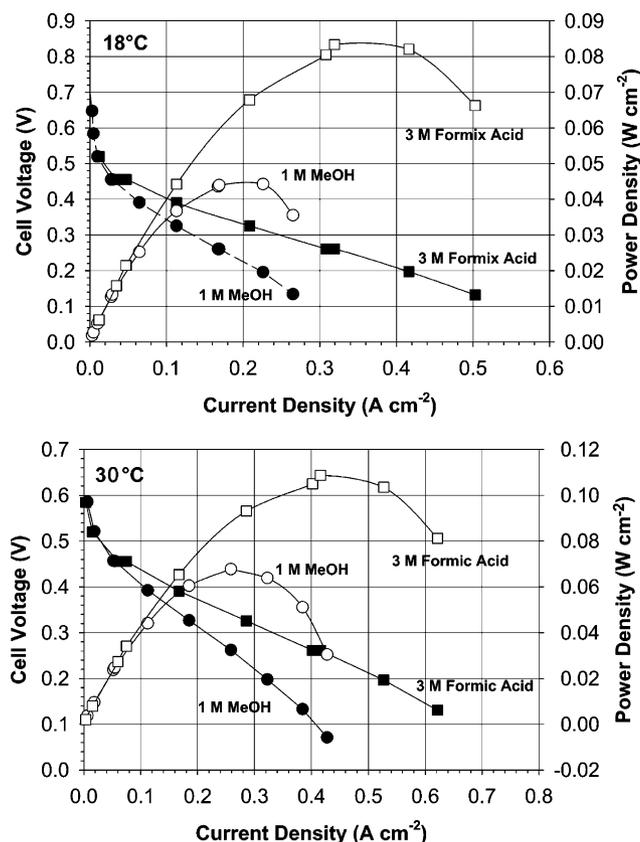


Fig. 10. The power density plots of fuel cells with methanol (1 M) and formic acid (3 M), at 18 and 30 °C. The flow rate of formic acid to the anode was 1 ml min<sup>-1</sup>. Air was supplied to the cathode at a flow rate of 390 ml min<sup>-1</sup> without any back-pressure and humidification.

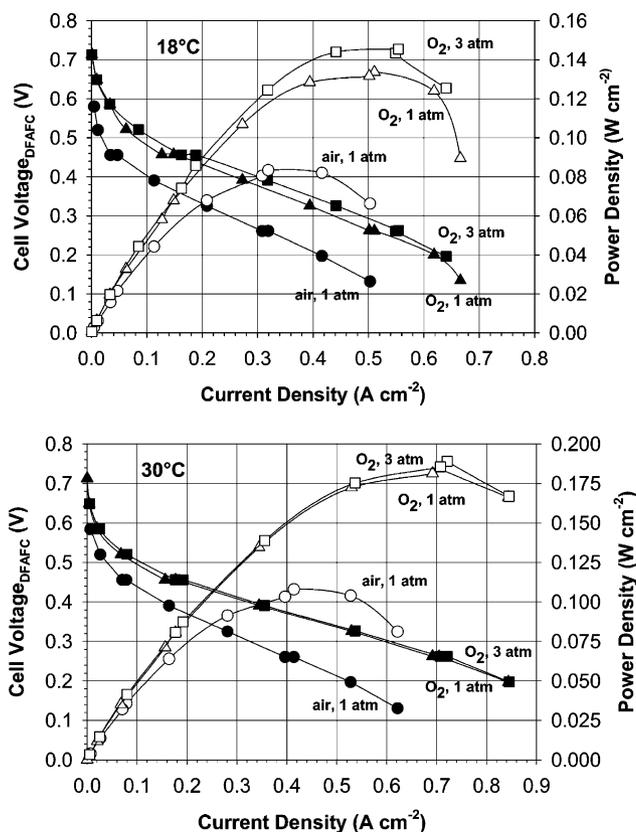


Fig. 11. The power density plots of fuel cells with 3 M formic acid, at 18 and 30 °C. The flow rate of formic acid to the anode was 1 ml min<sup>-1</sup>. The cathode was fed by dry air or dry oxygen without back-pressure (total pressure, 1 atm) or dry oxygen with 2 atm back-pressure (total pressure, 3 atm). The cathode flow rate was 390 ml min<sup>-1</sup>.

to 3.00 atm, brings no further improvement to the performance at 30 °C (maximum power density, 180 mW cm<sup>-2</sup>), but some improvement at 18 °C (maximum power density, 145 mW cm<sup>-2</sup>). The results indicate that the DFAFC performance will be limited by anode activity if sufficient oxygen is fed to cathode at 30 °C. Further development and optimization of DFAFC anode will provide more power density at ambient temperatures.

#### 4. Conclusions

The DFAFCs generating relatively high power density at ambient temperature have been demonstrated in this paper. The performance of DFAFCs with different concentrations of formic acid at different temperatures has been evaluated. It has been confirmed that formic acid is a viable fuel for direct liquid-feed fuel cell systems. Using the same concentration of 1.0 M, formic acid clearly outperforms methanol, with a 110 mV advantage at lower current density of 0.1 A cm<sup>-2</sup>, which is dominated by the crossover of formic acid or methanol. Comparing the power densities of the fuel cells with 1.0 M methanol and 3.0 M formic acid, there are ca. 87% advantage of formic acid (84 mW cm<sup>-2</sup>) over methanol (45 mW cm<sup>-2</sup>) at 18 °C, and ca. 64% advantage of formic acid (110 mW cm<sup>-2</sup>) over methanol (67 mW cm<sup>-2</sup>) at 30 °C. Formic acid (10.0 M) still generates the power densities of 76 and 99 mW cm<sup>-2</sup> at 18 and 30 °C, respectively. Thus, the DFAFCs are especially suited to power portable devices used at ambient temperatures because the significant high power density can be achieved with highly concentrated of formic acid. Further development and optimization of DFAFC anode will provide more power density at ambient temperatures.

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