



Short communication

A miniature passive direct formic acid fuel cell based twin-cell stack with highly stable and reproducible long-term discharge performance

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ABSTRACT

A miniature air-breathing twin-cell stack is designed and evaluated for direct formic acid fuel cell (DFAFC) applications. The stack consists of two face-to-face single cells with one shared fuel reservoir. This particular design has advantages in volume reduction relative to single cells in series connection. The performance, stability and reproducibility of the stack are investigated extensively for practical fuel cell applications. A maximum power density of 44.5 mW cm^{-2} is obtained with 5.0 M formic acid solution as the fuel and Pt catalysts in electrodes. It is also found that the stack yields high stability and reproducibility when discharged at a constant current of 20 mA. The output voltage can be maintained at 1.14 V for about 5 h by feeding 3.5 ml 5.0 M formic acid solution and the performance can almost be reproduced when the fresh fuel is injected.

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1. Introduction

Compared with direct methanol fuel cells, direct formic acid fuel cells (DFAFC) offer a broader range of advantages [1,2] including fast electro-oxidation kinetics [3], low fuel crossover through Nafion membrane [4,5], non-flammability and facile availability of fuel [2,6,7]. These benefits have made DFAFCs a viable candidate to replace batteries in portable power devices. Passive-mode DFAFCs are even more attractive [8–10] since they eliminate auxiliary devices such as pumps for feeding fuel and air blower for system cooling [11], which are mandatory for DFAFCs operated in active mode. The simplified stack configuration for passive DFAFC is highly desirable in the portable applications.

Printed circuit board (PCB) technology has many advantages when applied in fuel cells [12,13]. PCB integrates the end plate and current collector in one thin and light board, and the “two-in-one” assembly can simplify the fuel cell construction, thereby improving the volumetric and mass energy density. Our previous work confirmed that using PCB as the end plate and current collector was feasible in a passive DFAFC [14]. In consideration of the acidic nature of formic acid, electroplating a thin Au layer on Cu in PCB can effectively alleviate corrosion and contamination. However, voltage delivered by a single cell is too low (lower than 1 V) to meet the need for practical application since the minimum start-up voltage for DC/DC converter (MAX757) is 1.1 V [12]. Fuel cells in

series collection can certainly boost voltage but suffer from bulky volume.

Usage of effective electrocatalysts can help improve cell performance and increase the output voltage of the DFAFC consequently. Pd [15–18] and Pd-based non-platinum [19–22] catalysts have been proven to be most active to the formic acid oxidation relative to Pt-based catalysts. However, Pd catalysts alone are far from being satisfactory since they suffer from poor stability and serious degradation due to the poisoning effects in DFAFC [23–25]. As a compromise, Pt catalyst shows superior stability [23] and moderate electrocatalytic activity, which makes it more adoptable for DFAFC.

Against this background, we assembled a miniature air-breathing DFAFC twin-cell stack based on the PCB technology. The twin-cell stack consists of two face-to-face single cells with one shared fuel reservoir. This design is apparently advantageous over a fuel stack constructed by two single cells in series connection since it reduces volume. The voltage of twin-cell stack is high enough to trigger DC/DC converter for boosting voltage, satisfying practical applications. In addition, we have improved the stability and reproducibility significantly by using commercial Pt/C as the catalysts in both electrodes.

2. Experimental

2.1. Stack design and assembling

Two single cells (resemble with each other), gaskets and fuel reservoir are assembled together to fabricate the twin-cell stack, as

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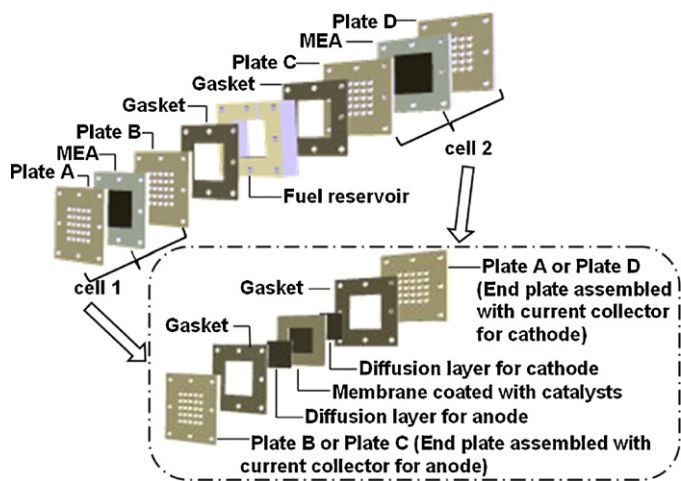


Fig. 1. Schematic of the DFAFC stack and single cells.

shown in Fig. 1. The function of the fuel reservoir was to store fuel and provide support to the cell. A polymethyl methacrylate (PMMA) board with a thickness of 8 mm was used to fabricate the reservoir. The square (2.1 mm × 2.1 mm) in the center served as the fuel tank with a total volume of about 3.5 ml. The surrounding area of the plate was evenly carved with eight small circular holes (Ø3 mm), so that the stainless steel bolts can travel through them and hold the cell parts together. In the top of the reservoir, two circular holes (Ø2 mm) were used as fuel entrance and gas exit. Gold coated PCBs are used as the current collectors *cum* end plates. The schematic configuration of a single cell is shown at the bottom right hand in Fig. 1 and more details can be found elsewhere [14].

Fig. 2 shows the zoomed-in view of the assembled twin-cell stack. The two single cells are assembled face-to-face and share one fuel reservoir. The anode wire of Cell 1 is connected to the cathode wire of Cell 2 and the rest two wires are connected to the external circuit.

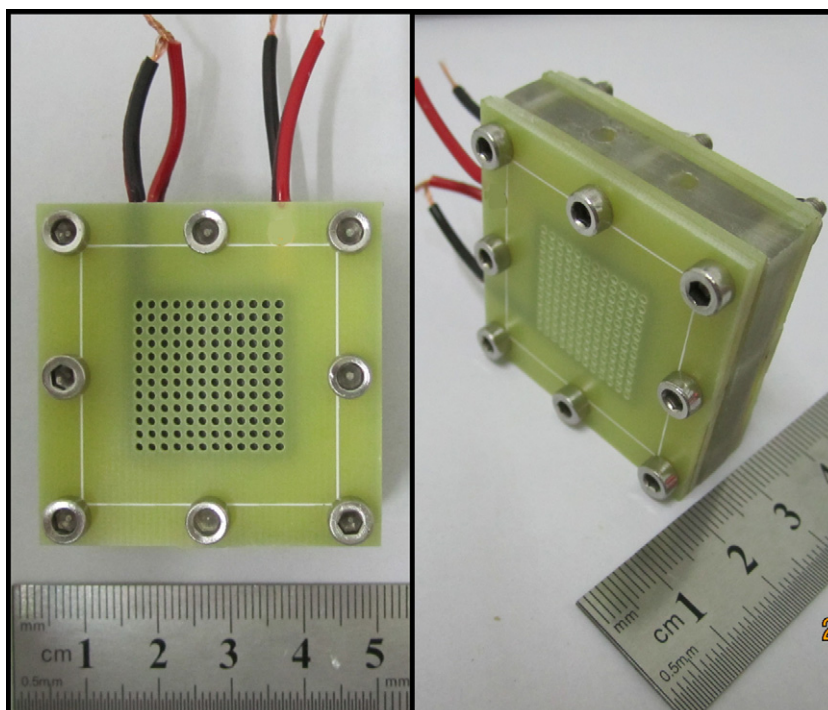


Fig. 2. Miniature air-breathing DFAFC twin-cell stack developed in this work.

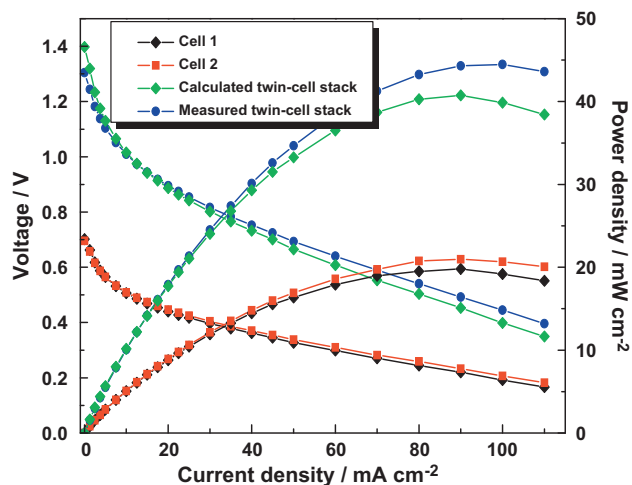


Fig. 3. The performance of the single cells and the stack (fuel solution: 5.0 M formic acid solution).

2.2. Membrane electrode assembly

Membrane electrode assembly (MEA) was fabricated using a 'direct catalyst spraying' technique developed in our group [26]. 20 mg Pt/C (Johnson Matthey, 40 wt.%) powders were dispersed into the mixture of 5 ml isopropyl alcohol (Analytical grade, Sinopharm Chemical Reagent Co.) and 200 mg 5 wt.% Nafion solution (DuPont). After sonicating for 15 min, the homogenized ink was then sprayed onto either side of Nafion[®] 212 membrane (DuPont) using an airbrush. Finally, the MEA was vacuum-dried at 70 °C overnight before usage. The catalyst loading was kept at 2 mg cm⁻² in both anode and cathode.

Different carbon papers were used as the diffusion layer in the anode and cathode for desired mass transfer of the reactants and products [27]. For better permeation of formic acid, pristine carbon paper was directly used in the anode without any pretreatment.

Alternatively, hydrophobic carbon paper with PTFE loading of ca. 12 wt.% was used in the cathode side for facile access of oxygen and removal of the produced water.

2.3. Fuel cell performance measurement

Formic acid (88% analytical grade, Enox[®]) was diluted with deionization water to form aqueous solution ranging from 2.0 to 8.0 M. The solution was then fed into the fuel reservoir and left conditioning for 1 h. The cell performance curve (I - V) was recorded on a home-made electrochemical workstation in galvanostatic discharging mode with current range of 5–440 mA at uneven intervals. In each step, the cell was discharged for 20 s followed by rest for 60 s before the next step. Voltage data were collected at an interval of 0.5 s and then averaged to plot the I - V curve. The measured voltage data in the rest time were averaged to give the open circuit voltage (OCV) change during the performance test.

2.4. Long-term performance test

The long-term (in terms of hours) discharging test was performed on a high-precision cell testing system (Neware[®], CT-3008W-5V1A-S4, China) in the constant-current mode by setting the current at 20 mA. Electrochemical impedance spectra (EIS) were recorded by using an IM-6e (Zahner, Germany) in the frequency range of 0.1 Hz to 100 kHz using a sinusoidal amplitude modulation of ± 5 mV at the OCV.

3. Results and discussion

Fig. 3 shows the performance of the single cells and the stack fed with 5.0 M formic acid solution. I - V curves of the two single cells were collected before stack performance evaluation. It can be seen that I - V curves for two single cells are almost overlaid, indicating similar performance and OCV of the two. It needs to be emphasized that similar single cell performance often infers better stack performance since charging and discharging between adjacent cells can be avoided. Fig. 3 also includes the calculated stack I - V curve by simply summing the performance of the two individual cells. It can be seen that the calculated curve deviates from the measured one. At lower current density section (lower than 10 mA cm^{-2}), the calculated performance was higher than the measured one; with the increase of current density, the measured performance increases and surpasses the calculated performance when current density is above 40 mA cm^{-2} . To explain this phenomenon, thermal behavior of the cell and mass transfer has to be taken into consideration. It is understandable that more heat will be generated and accumulated in the stack when two single cells simultaneously discharge than one single cell, especially at high current densities in a direct liquid fuel cells (DLFCs) [28]. As a result of thermal effect alone, the temperature of the stack increases significantly during the discharge process. Firstly, the increased temperature is beneficial for ion transfer in the electrolyte [27,29], thereby lowering the internal cell resistance. Fig. 4 shows the EIS of the single cells and stack. It can be seen that the internal resistance of the stack is indeed smaller than the sum of the two single cells (Cell 1: $97 \text{ m}\Omega$, Cell 2: $74 \text{ m}\Omega$, Stack: $149 \text{ m}\Omega$). Therefore, it is reasonable that the stack exhibits better performance at high current densities than the sum of the individual single cells (the maximum power density of the stack: 44.5 mW cm^{-2} at 100 mA cm^{-2} ; Cell 1 plus Cell 2: 40.7 mW cm^{-2} at 90 mA cm^{-2}). Secondly, the accelerated mass transfer at higher temperatures also contributes to the performance improvement at higher current densities [6]. Finally, it should be noted that the accelerated mass transfer of formic acid negatively affects the cell performance on the other hand. As is well acknowledged in direct methanol fuel cells (DMFCs), the increase in the cell temperature

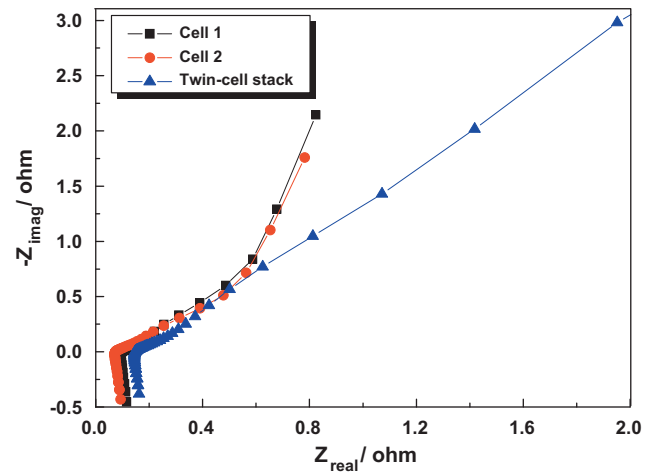


Fig. 4. Nyquist plots of the single cells and stack.

deteriorates the fuel crossover through the Nafion membrane in the stack and increases the mixed-overpotential at the cathode, leading to decreased performance at low current densities [27,30].

Fig. 5 displays the stack performance and OCV by feeding formic acid solution of various concentrations (2.0, 5.0, 8.0 M). From Fig. 5A, it can be seen that at low current densities (lower than 40 mA cm^{-2}), the cell performance is almost unaffected by fuel concentration. At high current densities, the stack performance is significantly improved when the concentration increased from 2.0 to 5.0 M. Further increase in the formic acid concentration to 8.0 M leads to a slight drop of the stack performance.

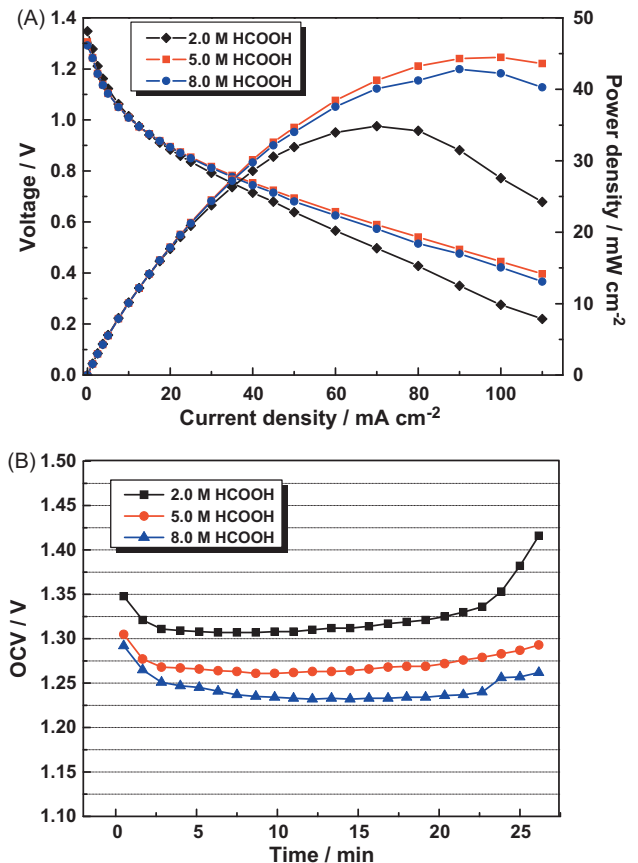


Fig. 5. The effect of formic acid concentration on the stack performance (A) and the OCV during the performance test (B) (formic acid concentration: 2.0, 5.0, 8.0 M).

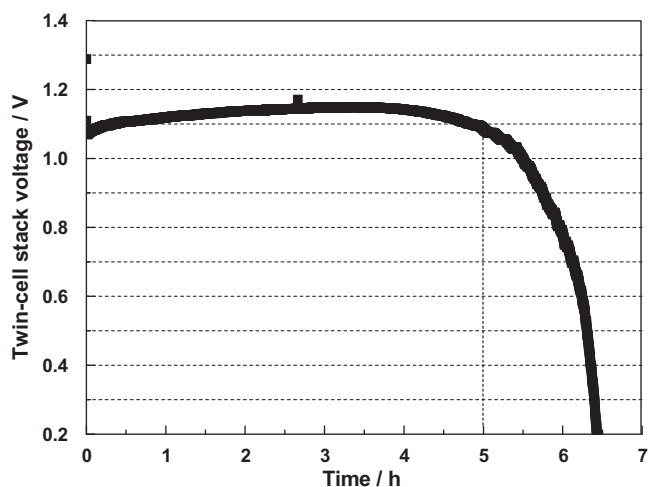


Fig. 6. Constant-current discharging curve of the stack at 20 mA (fuel solution: 3.5 ml of 5.0 M formic acid solution).

At low current densities, fuel crossover dominates cell performance, yielding the so-called ‘mixed-overpotential’ at the cathode, as mentioned above. Therefore, it is not surprising that the OCV and the performance at low current densities decreases in the order of 2.0, 5.0, 8.0 M. At high current densities, the cell performance is governed by the ionic and mass transfer [31]. Firstly, the increase in concentration from 2.0 to 5.0 M can greatly enhance the mass transfer of formic acid into the anode catalyst layer, thereby contributing to the improvement in the performance. Secondly, thermal effect of the stack has to be considered in the presence of high concentration of formic acid. High formic acid concentration can deteriorate the fuel crossover and thus increase the stack temperature, which further enhances the mass transfer both at the anode and cathode and improves the performance at high current densities.

The negligible difference in the cell performance between 5.0 and 8.0 M can be explained as follows. It has been well understood that high formic acid concentration facilitates the mass transfer but yields negative effect on the proton transfer in Nafion membrane. As a compromise, the cell performance remains similar when the concentration increases from 5.0 to 8.0 M. Experimentally, it is observed that 5.0 M is the optimal concentration for the present stack at 2 mg cm⁻² catalysts loading in anode and cathode in this study.

Fig. 5(B) shows the effect of formic acid concentration on the stack OCV during the performance evaluation. It can be seen that the OCV decreases with increasing formic acid concentration and each OCV curve shows a U-shape when time prolongs. The decrease in OCV with increasing concentration is due to the deteriorated ‘mixed-overpotential’ at the cathode, as discussed previously [10,31]. The initial steep decrease in OCV curve can be attributed to the poisoning effect of the catalyst in the electrode. As the discharging proceeds, more heat is generated and accumulated in the stack. As a result, the fuel crossover is gradually exacerbated, resulting in the slight decay of the OCV in the middle stage. In the last time section, continuous discharge leads to a further increase in the cell and stack temperature and decrease in the fuel crossover, which is beneficial for the electrode kinetics and leads to a slight increase in OCV.

Fig. 6 shows the constant-current curve of the stack discharging at 20 mA by feeding 3.5 ml of 5.0 M formic acid in the reservoir. The stack voltage can be maintained between 1.08 and 1.15 V for about 5 h, followed by a steep decrease from 1.10 to 0.20 V in the last 1.5 h. Compared with our previous work (maintained between 0.64 and 0.51 V for 3 h), the stability of the DFAFC performance is

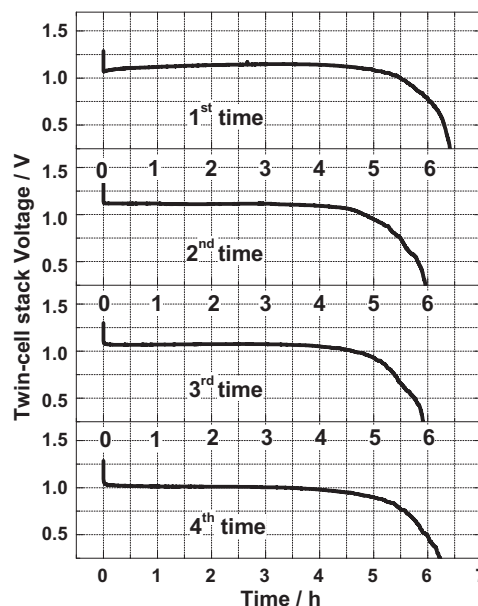


Fig. 7. Reproducibility of the stack discharging at constant current of 20 mA (3.5 ml of 5.0 M fresh formic acid solution was fed each time).

significantly improved [14], probably due to the replacement of Pd catalyst by commercial Pt catalyst. As mentioned in Section 1, Pd catalyst is inclined to poisoning in formic acid solution, whereas Pt shows superior stability in the formic acid oxidation reaction. The last sharp decrease in performance can be ascribed to the mass transfer polarization loss, which is induced by the consumption of formic acid in reservoir. The concentration of the formic acid, measured by titration, is found to be 0.20 M (5.0 M initially) after the long-term discharging experiment. Faradic efficiency (η) of the stack can be calculated by the following equation [32]:

$$\eta = \frac{It}{nF\Delta C_F V_F}$$

where I is the discharging current ($I = 20$ mA), t the discharging time, n the number of the electrons exchanged per formic acid ($n = 2$), F Faraday constant ($F = 9.64 \times 10^4$ C mol⁻¹), ΔC_F the formic acid concentration difference between the beginning and end of the test and V_F is the volume of formic acid solution in the reservoir ($V_F = 3.5$ ml).

The Faradic efficiency is thus calculated to be 14.4%, indicating that 85.6% formic acid is wasted other than generating electricity. One reason for low Faradic efficiency is due to formic acid crossover, in which the electron is directly consumed as the so-called parasitic current at the cathode. On the other hand, evaporation of formic acid through the open holes ($\varnothing 2$ mm, which are designed for balancing the pressure for the fuel entrance and gas exit in the anode chamber) on the top of the reservoir cannot be neglected. Further work on the design is still needed to address this issue.

Fig. 7 shows the results of the reproducibility test and the corresponding EIS patterns are shown in Fig. 8. The experiment is performed by refilling the fuel reservoir with fresh formic acid solution to replace the used formic acid. From Fig. 7, it can be seen that the stack can be discharged for about 6 h and a stable output voltage is generated at 1.14–1.01 V for ca. 4.5 h (the first time: 1.14 V for 5.0 h; the second time: 1.11 V for 4.5 h; the third time: 1.06 V for 4.5 h; the fourth time: 1.01 V for 4.3 h). It is thus concluded that the stack shows rather high reproducibility, confirming that Pt-based DFAFC yields superior reliability over the Pd-based one (a goal set by our experiment design). The slight decrease in the discharging voltage can be attributed to the increased internal resistance of the stack, as shown in Fig. 8.

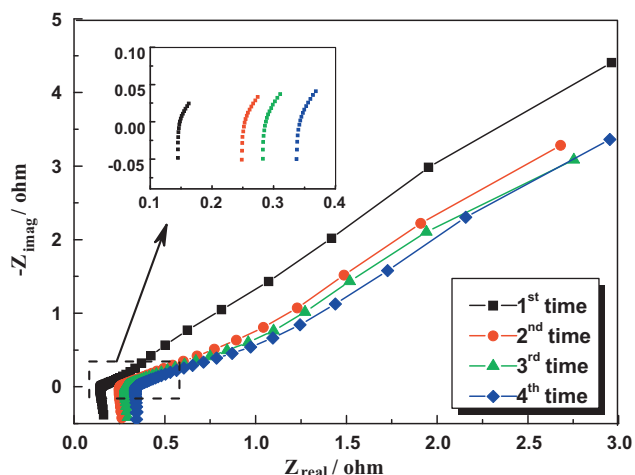


Fig. 8. Nyquist plots of the stack before each long-term discharging test.

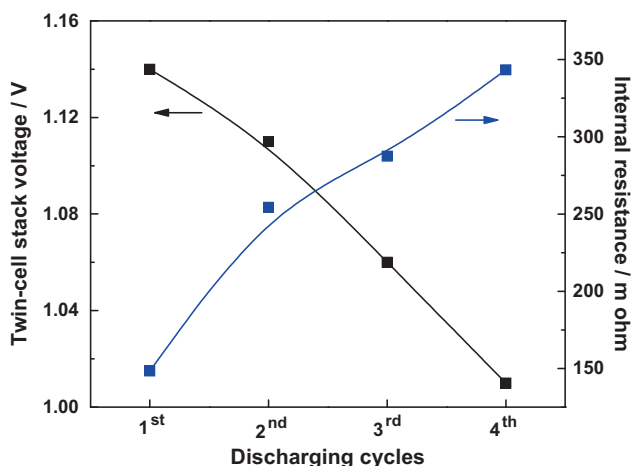


Fig. 9. Changes of the stack voltage and internal resistance with times of long-term discharging test.

To make it clearer, we have plotted the changes of plateau voltage and the internal resistance with discharging times in Fig. 9. It can be seen that the increased cell resistance can be roughly correlated with the decreased discharging voltage. The increased cell resistance may be caused by the MEA de-lamination or contamination, as were well clarified in typical DMFCs and PEMFCs [33–36]. Finally, the catalyst degradation and the cathode flooding cannot be excluded, which may also contribute to decrease in the stack performance.

4. Conclusions

A miniature air-breathing DFAFC twin-cell is designed and evaluated. Effects of formic acid concentration are studied and it is found that 5.0M formic acid solution yields the best performance. The maximum power density of the stack (44.5 mW cm^{-2}) is higher than that the summed power density of two individual cells (40.7 mW cm^{-2}), probably due to more heat generated in the

fuel cell stack. Stable output voltage of 1.14V is achieved for 5 h with 3.5 ml 5.0M fuel solution. Only slight voltage drop is observed when refilling the fuel for four times, an indication of high reproducibility. The high stability and reproducibility could be attributed to the usage of Pt catalysts instead of less stable Pd catalysts. It is believed that the high performance, stability and reproducibility of the stack make it very promising to be used in the real application of portable power sources.

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