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Development of a passive direct methanol fuel cell (DMFC) twin-stack for long-term operation

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ABSTRACT

Direct methanol fuel cell (DMFC), with benefits such as high energy efficiency, quick start capability and instantaneous refueling, is a promising power source to meet the ever-increasing power demand for portable electronic products. In this paper, a novel CO_2-driven fuel-feed device was produced and equipped in a passive 8-cell DMFC twin-stack for long-term operation. It was shown that this fuel-feed device was capable of supplying methanol solution continuously in response to the change in discharging current of the stack. Stainless steel sheet was photochemically etched as current collectors based on MEMS techniques. Series interconnections between two neighbor cells were realized in banded configuration which avoided the external connection. TiN-plated mesh was placed between current collector and membrane electrode assembly (MEA), which was used to lessen the internal resistance of the stack. A peak power density of 16.9 mW cm^{-2} was achieved with 4 M methanol at ambient temperature and passive operation. The stack equipped with the fuel feed device successfully powered a sensor node for 39 h with the consumption of 80 ml of 4 M methanol.

1. Introduction

Recent years have witnessed increasing energy demand for commercial electronics and micro devices. The use of conventional battery technology is problematic due to battery self-discharge, number of recharge cycles and environmental impact [1]. However, direct methanol fuel cell (DMFC) is a promising power source candidate to meet that demand because of their benefits such as high energy efficiency, quick start capability, low emission, reduced size and weight, facile construction, instantaneous refueling, ease of storage and transportation of the fuel, and ability to adjust the power output according to the demanded load. Passive air-breathing DMFCs are more attractive than active ones because they eliminate parasitic power loss from fuel pump and other ancillary devices and consequently have much simpler structures, higher reliability, lower cost and higher fuel utilization [2,3].

Methanol crossover from the anode to the cathode of DMFC causes a mixed potential on the cathode and thus reduces the overall cell voltage. Therefore, low methanol concentrations are usually used to achieve a desirable cell performance. However, too low methanol concentration leads to a low energy density of the fuel cell, which cannot meet the requirement of electrical applications. In order to supply enough fuel during operation, passive fuel delivery methods for DMFCs have been reported in recent years [4–7]. Guo and Cao [4] proposed a capillary pump which provided a much simpler, cost effective and reliable fuel delivery system for DMFCs. In this system, methanol and water were carried separately and mixed in situ during fuel cell operation. A controlled three-way valve to direct the exhaust gas was used to drive liquid fuel into the anode by Zhang et al. [5]. A higher power density was achieved while minimal electrical power was consumed by the valve. Zhao and co-workers [6] proposed a self-regulated passive fuel-feed system that not only enabled the passive DMFC to operate with high-concentration methanol solution without serious methanol crossover, but also allowed a self-regulation of the feeding rate of methanol solution in response to discharging current. Based on the theoretical analysis of the natural-circulation system, Zhao and Ye [7] also presented a passive fuel delivery system for a DMFC with a single serpentine flow field and they compared this DMFC with that fed by conventionally pump. This system was simple and could naturally circulate the fuel but may lead to various methanol concentration in the total active area of the fuel cell.

On the other hand, series interconnection of the fuel cells is necessary to achieve a useful output voltage for electric appliance. The connection methods that have been reported include bipolar plate [8], banded [9] and flip-flop [10] configuration. However, bipolar plate structure can hardly be utilized in passive mode because liquid

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fuel and ambient air are difficult to deliver, and flip-flop interconnection is complicated because reactant chambers must alternate between liquid fuel and ambient air. Traditional banded scheme which is realized by using spot welding [11], conductive adhesive [12] or bolt [13] exhibits better volumetric packaging compared with bipolar plate stacks in low-power applications but may have high resistive loss.

This paper presents the design and fabrication of a planar banded DMFC twin-stack with a total active area of 32 cm^2 which can be used in portable applications such as radios, sensor node and palmtop computers. The fuel was driven by CO_2 from an accessible fuel reservoir, while the oxygen was supplied from the ambient air. Banded method was adopted to the interconnection of the stack, which eliminated auxiliary wire and contact resistive loss. Experimental results showed that the stack had low inherent resistance and continuously powered a sensor node for 39 h with the consumption of 80 ml of 4 M methanol solution.

2. Experimental

2.1. Membrane electrode assembly

A piece of catalyst coated membrane (CCM) with an active surface area of 3.1×1.3 cm^2 consists of a Nafion 115 membrane, anode catalyst layer of PtRu black (4.5 mg cm^{-2}) and cathode catalyst layer of Pt black (2.4 mg cm^{-2}). The CCM was sandwiched between two telfonised carbon papers (TGP-H-090, Toray), which served as gas diffusion layers (GDLs), and then hot-pressed at 140 °C and 30 atm for 2 min to form the membrane electrode assembly (MEA). Gaskets (FJ011, GORE-TEX®) with a thickness of 0.2 mm were used at both anode and cathode of the MEA. The gaskets served as sealant for fuel and thickness matching to the GDLs. In order to decrease the contact resistance, titanium nitride (TiN)-plated stainless steel mesh was employed between the MEA and current collectors. Fig. 1 is one side of the MEAs stuck with meshes and gasket.

2.2. Banded current collectors

Silicon wafer is usually used as the substrate of current collector for micro DMFC [3]. However, the Si substrate is quite fragile, making difficult to compress the fuel cell tightly for good seals and for lowering the contact resistance between MEA and Si-based current collectors [14]. Furthermore, silicon wafer is nearly electrically insulated and the conductivity for current collection fully depends on the thickness of the conductive layer coated on Si. So, the cost will significantly increase in order to minimize the resistance by thickening the conductive layer. The interconnection between Si-based current collectors is also intractable because of its fragility and electrical insulation. An alternative method to fabricate the current collector is using stainless steel plates instead of silicon wafer because stainless steel has much higher conductivity and mechanical strength. The current collectors used in this experiment were made of stainless steel (SS 316L) sheet with a thickness of 100 μm.

The preparation of current collectors was based on MEMS techniques, as shown in Fig. 2. An array of circular holes (2 mm and 1.5 mm diameter) was photochemically etched as fuel and oxidant feed path. Anode current collector of one cell, cathode current collector of the adjacent cell and interconnection conductor between them were etched from one piece of SS 316L sheet. Therefore, the interconnection of the DMFC stack was realized in banded configuration, which avoided additional spot welding and contact resistive loss. The folding operation was rather timesaving as all current collectors were thin and flexible. The current collectors were also plated with TiN to prevent corrosion [15], as shown in Fig. 3.

2.3. Fuel-feed device

The passive CO_2-driven fuel-feed device is shown in Fig. 4, which consists of four separate reaction chamber, a fuel reservoir, four feed pipes, four gas outlets and a gas–liquid separator.

Methanol solution was stored in all the reaction chambers and methanol reservoir. The consumed methanol in the reaction chambers was supplied by the methanol solution in the fuel reservoir. The feeding rate from the fuel reservoir to reaction chambers was controlled by the gas CO_2 generation rate, which is proportional to current density.

The working principle of the fuel-feed system is described as follows. At the beginning, when the DMFC stack discharges, gas CO_2 is produced at the anodes of cells and flow to the separate reaction chambers. If the dimensions of gas outlet and feed pipe are suitable, the gas CO_2 will accumulate at the top in each reaction chamber to form a large bubble. The pressure and volume of the bubble increase with time. Once the pressure and volume reach a critical value, the large bubble will be ejected through the gas outlet. Subsequently, fuel in reservoir is fed into the bottom of reaction chamber through feed pipe. Meanwhile, small CO_2 bubbles which are generated continuously agitate the aqueous methanol solution in reaction chamber and consequently the methanol concentration in reaction chamber reaches uniform rapidly. As such, the methanol solution in reservoir is periodically fed into the reaction chamber and the feeding rate depends on the generation rate of the gas CO_2, which is proportional to current density. When the current density is increased, more methanol will be consumed due to the electrochemical reaction and more CO_2 is generated, leading to a faster

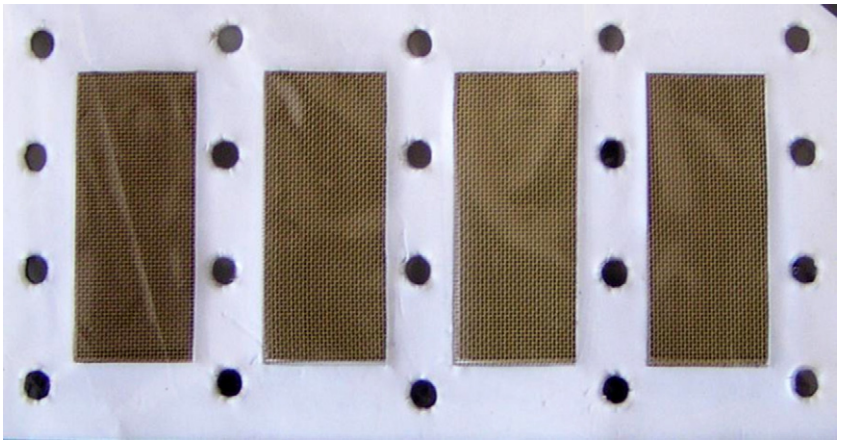

Fig. 1. MEA with mesh and gasket.

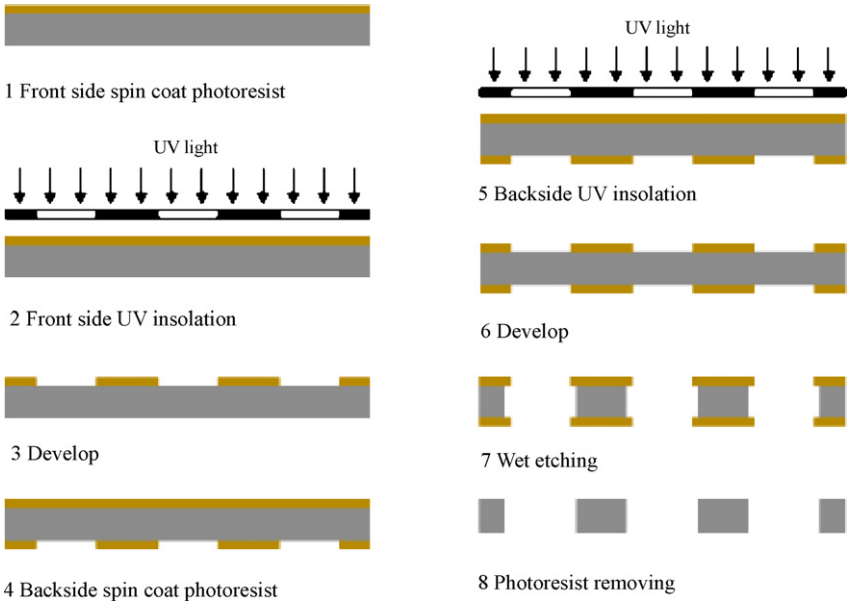

Fig. 2. Schematic fabrication process of the current collector.

increase in the volume of the large bubble at the top in each reaction chamber. As a consequence, the feeding rate will be higher. Hence, this CO_2-driven fuel-feed device can self-regulate the feeding rate in response to a change in the discharging current of the fuel cell. The successful operation of this passive fuel-feed system depends on the suitable dimensions of the gas outlet and feed pipe. Based on our previous experiments, the inner diameters of the pipes were 3 mm and the diameters of the gas outlets were 4 mm in this study.

Holes in bakelite end plates were machined corresponding to those in current collectors, which had the benefits of improving the rigidity of end plates and the transportation of fuel. Finally, the completed MEAs, current collectors, fuel feed device and end plates mentioned above were assembled, as shown in Fig. 5. Four cells were connected in series on either side of the reaction chamber and then the two 4-cell sub-stacks were series connected by the method mentioned in Section 2.2. The final DMFC twin-stack is shown in Fig. 6. The dimensions of the stack were: 13 cm (l) × 2 cm (w) × 10 cm (h).

3. Results and discussion

The assembled 8-cell DMFC stack was tested at room temperature under ambient pressure. The polarization curve and Nyquist plot of the stack were obtained on a DC electronic load and electrochemical station, respectively. Aqueous methanol was supplied into the fuel reservoir and all reaction chambers, while oxygen was obtained from ambient air. The polarization curves were obtained by the constant voltage method, which meant that the DMFC stack was forced to operate under a constant voltage until the output current became stable. The Nyquist plot was measured by AC impedance method at frequencies from 100 kHz to 1 Hz. The following sections are the performance of the stack from different design configurations and test conditions.

3.1. Performance of the stack

Fig. 7 is the performance of the stack with TiN-plated mesh at a methanol concentration of 4 M. According to the *I–V* and *I–P* curves, the passive 8-cell stack had a maximum output of 540 mW at 1.8 V. Performance testing of individual cell was also carried out, and results showed that the voltage difference of all cells was less than 0.03 V when the cells were at the same discharge current of 300 mA. This indicated that the performances of the cells in the stack were rather uniform.

The impedance data of the stack at an applied potential of 2.4 V were shown in Fig. 8. The total internal resistance of the 8-cell stack was 1.2 Ω. If the bulk resistance of current collectors is ignored, a mean area resistance of 0.6 Ω cm^2 can be obtained with the known active area of 4 cm^2 of each cell.

3.2. Influence of methanol concentration

Fig. 9 shows the performance comparison of the stack with different methanol concentrations. By using 4 M methanol, the peak power density increased from 10.2 mW cm^{-2} at 3 M to 16.9 mW cm^{-2}. This was because the rate of methanol crossover from the anode to the cathode at 4 M methanol concentration was higher than that at 3 M. The exothermic reaction between the permeated methanol and oxygen on the cathode generated more heat with higher methanol concentration, leading to a higher operating temperature. The increased cell temperature speeded up both the methanol oxidation and oxygen reduction reactions, thereby leading to the improved cell performance [16]. This is different from that of active fuel supply DMFCs [17], in which lower concentration (e.g. 1 M) may generate better performance because enough methanol is near the surface of the MEA, although the cell is supplied with lower concentration.

However, the peak power density of this stack decreased to 11.6 mW cm^{-2} when it was supplied with 5 M methanol solution. This was because the effect of mixed potential generated by methanol crossover on the performance of the stack exceeded that of the temperature. This indicated that 4 M might be the optimum concentration for this stack. These experimental results indicated that the passive fuel-delivery DMFCs had better performance at higher methanol concentration and that there was an optimal methanol concentration for DMFCs.

3.3. Influence of stainless steel mesh

Fig. 10 presents the influence of TiN-plated mesh on the performance of the stack. The peak power density of the stack was

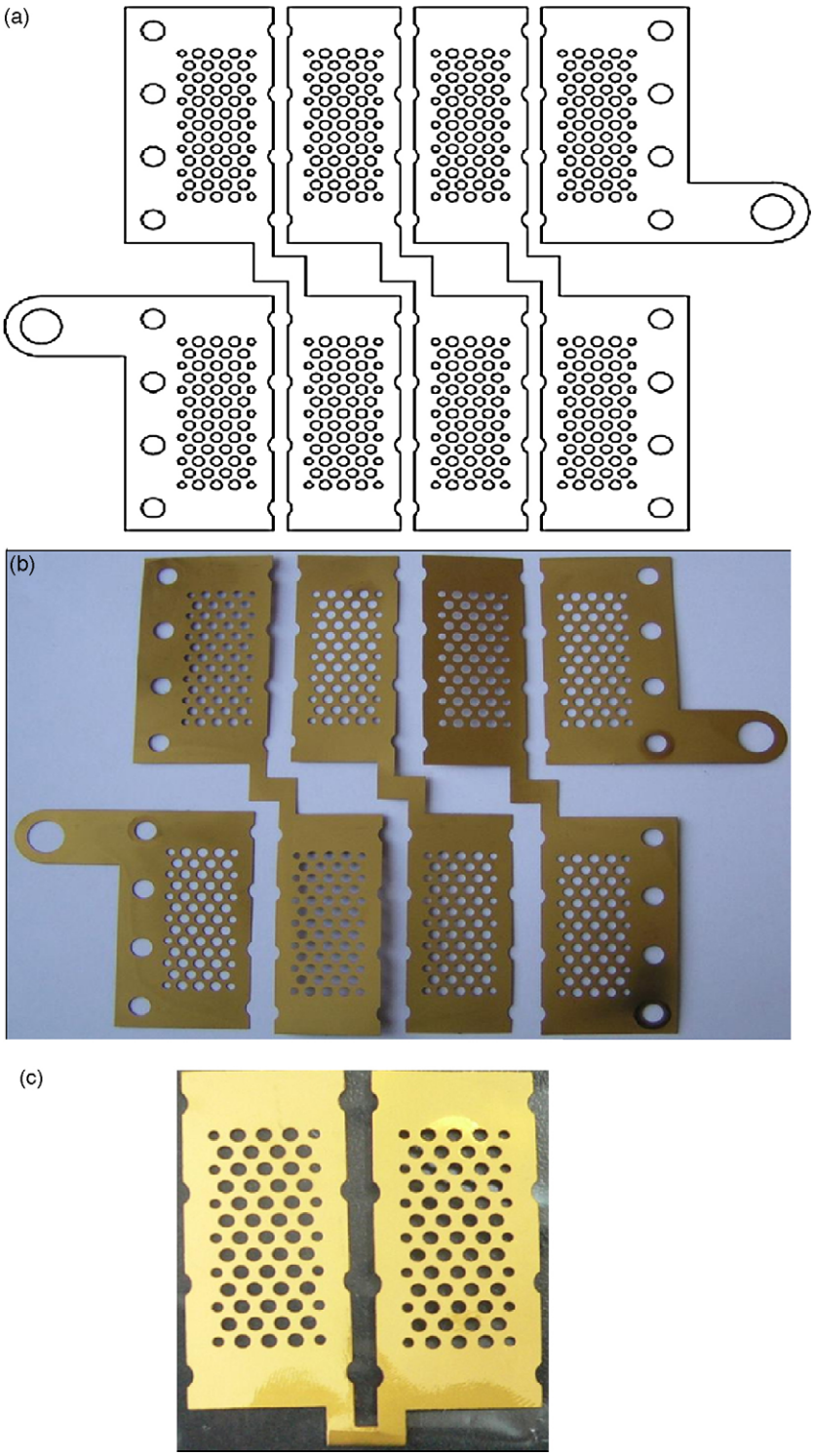

Fig. 3. (a) Layout of current collectors, (b) TiN-plated current collectors and (c) folded current collectors.

7 mW cm^{-2} and 10.2 mW cm^{-2} at 3 M methanol without and with mesh, respectively. Fig. 11 shows that the total internal resistance of the stack decreased from 2 Ω to 1.2 Ω by using mesh. One reason may be that the whole GDL supported by the mesh had a more homogeneous compression and then had a smaller bulk resistance. The other reason may be that the mesh collected the current of the GDL in the holes of current collector and lowered the contact resistance between the MEAs and the current collectors. Therefore, by using the mesh, an internal resistance decrease of 40% and a power density increase of 46% were obtained.

3.4. Influence of the fuel-feed device

Fig. 12 is the comparison of output voltages of the stack operating at current density of 50 mA cm^{-2} with and without fuel

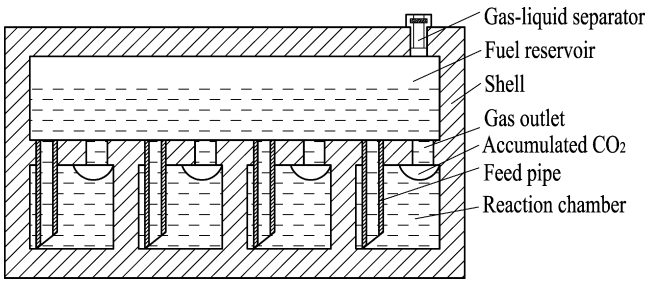

Fig. 4. Schematic of the passive fuel-feed device.

reservoir. In the case without fuel reservoir, each reaction chamber was fueled with 2 ml of 3 M methanol concentration and the fuel reservoir was empty. In the case with fuel reservoir, each reaction chamber and the fuel reservoir were fueled with 2 ml and 8 ml of 3 M methanol, respectively. It was found in Fig. 12 that the voltage was steady for more than 8 h in the case with fuel reservoir, while the voltage dropped rapidly after 2 h in the case without fuel reservoir. This indicated that the working duration of the stack equipped with the fuel-feed device was about twice of that without this supplement. This was because that the methanol crossover was mitigated when the supply process was controlled by the CO_2 generation rate.

To further verify the fuel-feed device, the stack was used to continuously power a sensor node of wireless network which was ACTIVE (75 mA) for 15 min and SLEEP (15 mA) for 15 min and then went round and round in circles, as shown in Fig. 13 shows the sensor node driven by the DMFC stack. In this experiment, the stack was fueled with 80 ml of 4 M methanol solution and the output voltage of the stack was measured when the sensor node was ACTIVE.

Fig. 15 shows the long-term performance of the stack. It was shown that the voltage gradually decreased with operation time, which was due to methanol crossover and the gradual accumulation of water at the cathode sides. The voltage fluctuation was caused by the local environmental variation such as temperature, humidity and ventilation around the passive air-breathing stack. This phenomenon was also observed in other researcher's work [18]. The figure showed that the stack powered the sensor node for 39 h at the voltage higher than 2.1 V. The concentration of the methanol solution in the reservoir decreased to 2.8 M after the experiment. To obtain the fuel utilization efficiency, the Faradic efficiency can be calculated by. Fig. 14

$$\eta = \frac{It}{6C_M V_M F} \quad (1)$$

where t is the time of the discharging process, I is the transient discharging current, C_M is the differential concentration between the initial methanol solution and the final solution, V_M is the volume of methanol solution and F is the Faraday constant. By using Eq. (1), a Faradic efficiency of 12% was obtained in this experiment. This low Faradic efficiency was primarily caused by the higher rate of methanol crossover with higher methanol concentration [16] and the nonoptimal dimensions of gas outlet and feed pipe. Future experimental analysis will be carried out involving the dimensions of gas outlet and feed pipe. However, the above test results indicated that the fuel in the reservoir was successfully supplied into the reaction chamber and that the fuel-feed device was effective. This device significantly simplified the structure and decreased the cost of the DMFC stack.

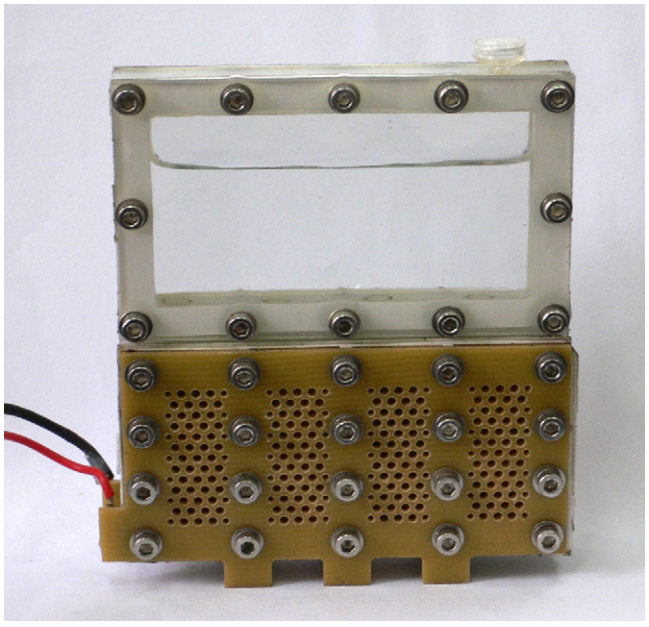

Fig. 6. Assembled DMFC stack.

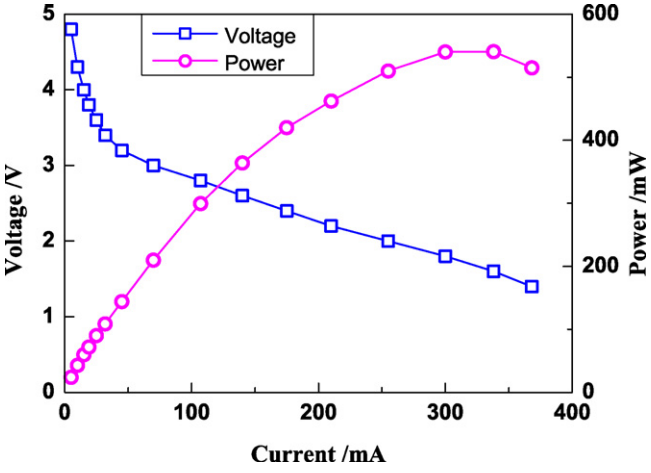

Fig. 7. Performance of the stack with 4 M methanol.

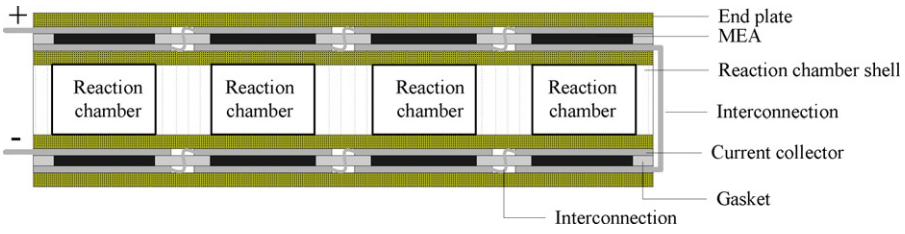

Fig. 5. Structural schematic of the 8-cell stack.

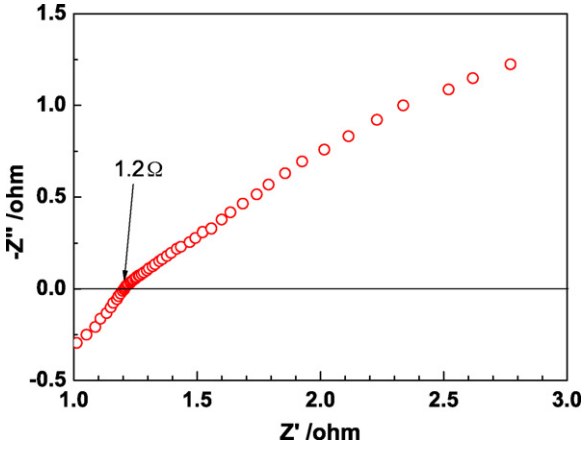

Fig. 8. Nyquist impedance plot of the stack at 2.4 V.

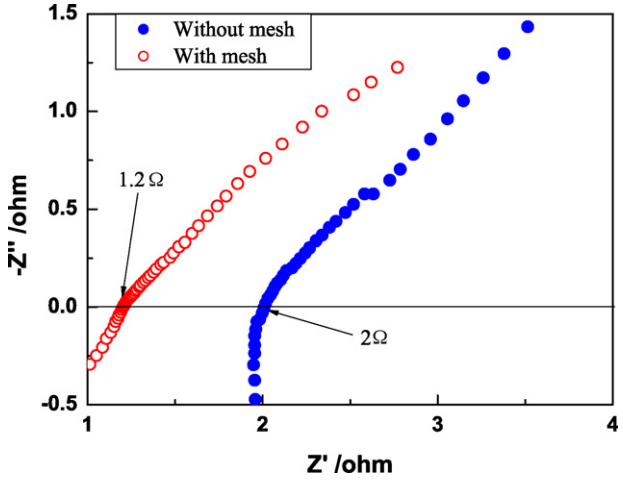

Fig. 11. Nyquist plots of the stack with and without mesh.

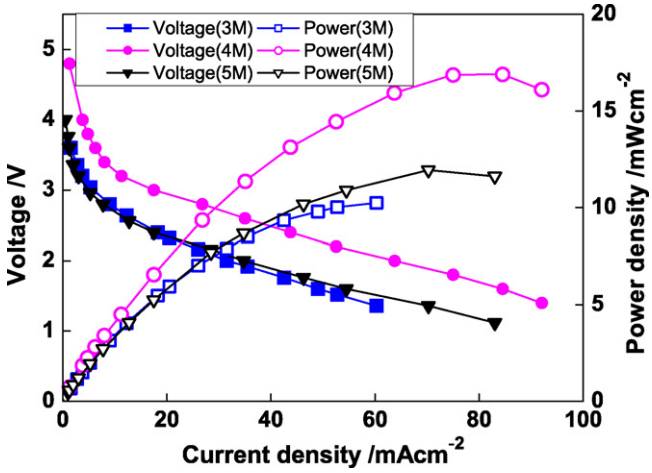

Fig. 9. Effect of methanol concentration on the performance of the stack.

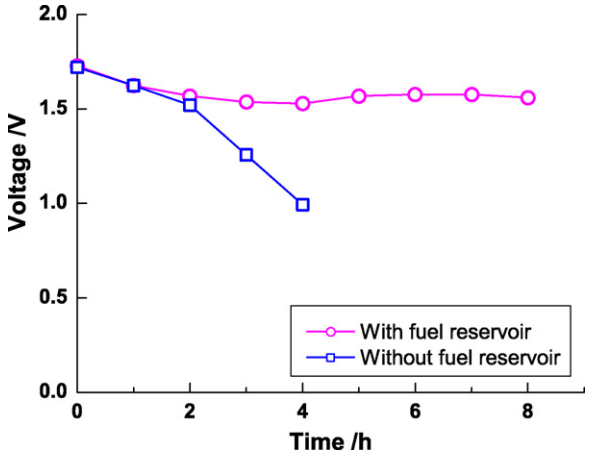

Fig. 12. Performance of the stack operating at current density of 50 mA cm^{-2} with and without the fuel reservoir.

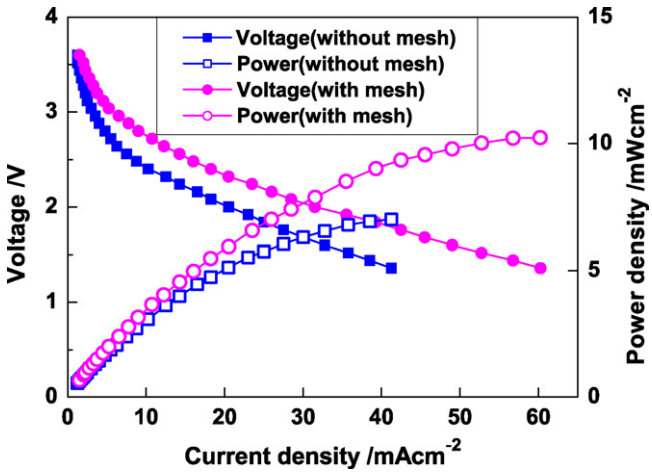

Fig. 10. Effect of TiN-plated mesh on the performance of the stack at 3 M methanol.

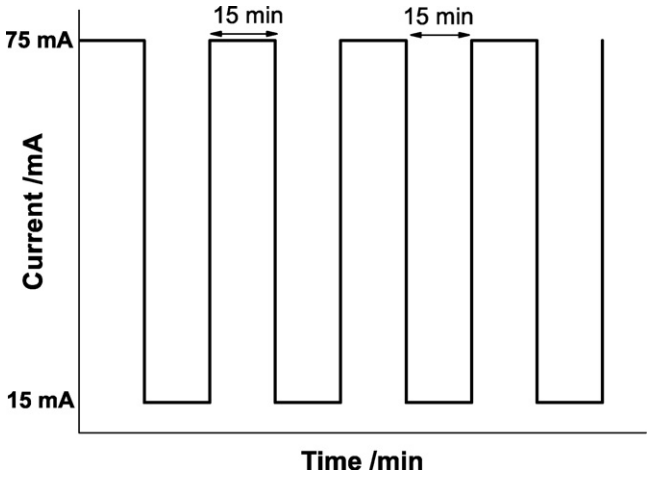

Fig. 13. The operation mode of the stack used for a sensor node.

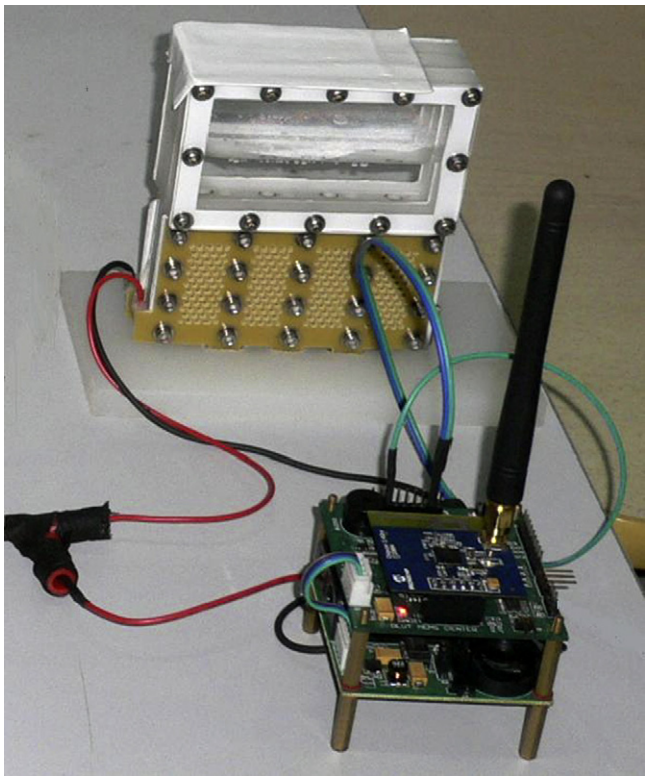

Fig. 14. A sensor node driven by the DMFC stack.

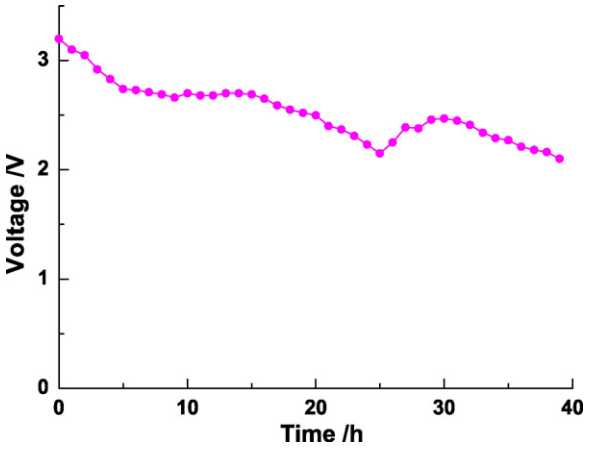

Fig. 15. Output voltage of the stack when the sensor node was ACTIVE.

4. Conclusions

A planar 8-cell DMFC twin-stack with a total active area of 32 cm^2 was designed, fabricated and tested. A peak power density of 16.9 mW cm^{-2} was achieved with 4 M methanol at ambient temperature and passive operation. An internal resistance decrease of 40% and a power density increase of 46% were obtained by using the TiN-plated mesh. A new CO_2-driven fuel feed device was produced which can self-regulate the feeding rate in response to a change in the discharging current of the fuel cell. The stack equipped with this fuel-feed device successfully powered a sensor node for 39 h with the consumption of 80 ml of 4 M methanol. The feeding rates can be optimized for different methanol concentrations by adopting more suitable dimensions of gas outlet and feed pipe. So, it is expected that, with an improved design, a prolonged operation time could be achieved with the same fuel loading.

Acknowledgments

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