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Development of a polymeric micro fuel cell containing laser-micromachined flow channels

Siew Hwa Chan, Nam-Trung Nguyen, Zetao Xia and Zhigang Wu

Fuel Cell Strategic Research Programme, School of Mechanical and Production Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

E-mail: mntnguyen@ntu.edu.sg

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Abstract

This paper presents the development of a micro fuel cell (μFC) by polymeric micromachining technique. The membrane electrode assembly (MEA) is embedded in a gold-coated polymethyl methacrylate (PMMA) substrate, on which the gas flow channels are fabricated by laser micromachining. The special Gaussian shape of the microchannel allows the continuous sputtering of a gold layer, which works as the current collector for the fuel cell. The packed fuel cell has been characterized by an electronic load system. At room temperature, the power output of the 3 cm^2 micro fuel cell can reach 315 mW cm^{-2} when hydrogen and oxygen are supplied to the anode and cathode, respectively. When air is used for the cathode side, the power output can reach 82 mW cm^{-2}. During testing, the hydrogen flow is set to be dead-ended. That means the utilization of hydrogen in the μFC is close to 100%.

1. Introduction

Recently, the use of micro technology for realizing power generation has been the focus of many research groups. Despite the compact size, the miniaturization promises a higher efficiency and higher performance of such devices [1]. Epstein *et al* [2] proposed the miniaturization of heat engines to convert heat energy of fuel combustion into mechanical energy and then into electricity. This concept requires complex technologies, high-temperature materials, and poses a number of other challenges [3]. Another approach for micro-scale power generation is scaling down electrochemical concepts such as battery [4] and fuel cell.

Fuel cells are electrochemical devices that convert the chemical energy of a reaction directly into electricity. The basic physical structure of a fuel cell consists of an electrolyte layer in contact with a porous anode and cathode on either side. In a typical fuel cell, fuel (i.e., hydrogen) is fed continuously to the anode and an oxidant (i.e., oxygen from air) is supplied continuously to the cathode. The electrochemical reactions take place at the electrodes by the activation of catalysts:

$$\text{on the anode: } 2H_2 = 4H^+ + 4e^-$$
$$\text{on the cathode: } O_2 + 4H^+ + 4e^- = 2H_2O.$$

The protons pass through the electrolyte, and the electrons create a separate current that can be utilized before they return to the cathode. Since the energy is stored as a 'reservoir' of fuel rather than as an integral part of the power source, fuel cells have advantages over batteries. The battery is an energy storage device. The maximum energy available is determined by the amount of chemical reactant stored within the battery itself. The battery will cease to produce electricity when the chemical reactants are consumed. In a secondary battery, the reactants are regenerated by recharging, which involves putting electricity into the battery from an external source. The fuel cell, on the other hand, is an energy conversion device that theoretically has the capability of producing electricity for as long as fuel and oxidant are supplied to the electrodes.

Fuel cells have gained renewed interest for applications in high power consumption electronic devices such as data acquisition and communication devices. Since the energy is stored as a 'reservoir' of fuel rather than as an integral part of the power source, fuel cells have advantages over batteries. A miniaturized fuel cell power source can be realized through an approach that combines thin film materials with MEMS (micro-electro-mechanical system) technology. Micro

fuel cells (μFCs), which generally generate less than 5 W electricity, are developed either by silicon micromachining or polymeric micromachining with current collectors normally embedded in the flow channels.

A literature review showed that very few papers have reported work on μFCs. Lee *et al* [5] developed a 2-cell and a 4-cell μFC array with flip–flop interconnection. The former was supported on a borofloat glass with peak power density of 20 mW cm^{-2}, while the latter was on silicon substrate with peak power density of 42 mW cm^{-2}. Both stacks were supplied with hydrogen and tested at room temperature. Yen *et al* [6] fabricated a direct methanol μFC by silicon micromachining on a pair of 500±20 μm silicon wafers employed as the bipolar plates. The peak power density achieved was 47.2 mW cm^{-2} with 1 M CH_3OH at 60 °C. Yu *et al* [7] claimed that they have developed a miniature silicon wafer fuel cell with improved performance. Results showed that with the thickness of Cu/Au composite layers of 1.5/0.9 μm sputtered on the top of the silicon wafers as the current collectors, the peak power density has achieved 194.3 mW cm^{-2} (at 450 mA cm^{-2}) at room temperature. The superior performance of this μFC was due to the use of oxygen instead of air and the high flow rates of hydrogen/oxygen flow (50 ml min^{-1}). Based on our estimation, the fuel utilization of this μFC is around 6.8%. Lu *et al* [8] developed a silicon-based μFC fed with 2 M CH_3OH. The peak power density achieved was 16 mW cm^{-2} at 23 °C and 50 mW cm^{-2} at 60 °C. Blum *et al* [9] developed a water-neutral μFC fed with CH_3OH. The μFC, with a plastic housing, showed a stable operation for 900 h and has achieved a peak power density of 12.5 mW cm^{-2}. Shah *et al* [10] developed a hydrogen-fed μFC based on polymeric micromachining technology. Polydimethylsiloxane (PDMS) was used as the cell support and housing. Its peak power density has achieved 35 mW cm^{-2} when the cell was heated to 60 °C. Hsieh *et al* [11] claimed to have a novel design and microfabrication on a μFC, which consists of a polymethylmethacrylate (PMMA) flow field plate with narrow and deep channels cut by excimer laser. The peak power density achieved was 31 mW cm^{-2} at room temperature with an unusually high hydrogen pressure of about 4 atm. Li *et al* [12] developed a μFC using borohydride (10 wt% $NaBH_4$ and 20 wt% NaOH) as the fuel and has achieved a peak power of 100 mW cm^{-2} at 50 °C when fed with humidified O_2 at 200 ml min^{-1}. Min *et al* [13] developed a MEMS based polymer electrolyte fuel cell stack consisting of nine cells each with a size of 12 mm × 15 mm connected in series. The peak power density achieved (for a single cell) was about 0.45 μW cm^{-2} with H_2 fed at 0.01 MPa. Chan and Goh [14] developed a mathematical model to study the effect of operating conditions on water self-sufficiency in the membrane–electrode assembly of a μFC, which is useful to establish the water balance in the cell for reliable cell operation. In addition to the polymer-based fuel cells, there exist a few reports [15, 16] on micro scale solid oxide fuel cells. The peak power density could reach 110 mW cm^{-2} at 570 °C [15] and 170 mW cm^{-2} at 600 °C [16], which are comparable to the polymer fuel cells that operate at room temperature. But the micro scale solid oxide fuel cells that operate at high temperature need extra heating to start up and run, which is not practical for a stand-alone fuel cell system with output power less than 5 W.

This paper presents a polymeric μFC with a higher power density then all the above devices. The performance is due to the novel design of the fuel delivering microchannels as well as the channel shape. The micro channel was micromachined with a CO_2-laser and has a typical Gaussian shape. This channel shape cannot be achieved with other polymeric micromachining techniques such as molding [10] or excimer laser machining [11]. The curved channel wall allows sputtering of a smooth current collector layer, which definitely decreases the internal electrical resistance of the fuel cell.

2. Materials and methods

In this study, the polymeric micro fuel cell was developed on the basis of micromachining of PMMA, which is known under trade names such as Acrylic, Oroglass, Perspex, Plexiglas or Lucite. This material is commercially available in the form of extrusion sheets. PMMA is one of the thermoplastic polymers, which are usually linear-linked and can be softened by applying heat at above the glass transition temperature. The polymer can be reheated and reshaped before hardening in its form many times. PMMA has a non-crystalline structure with an optical property of 92% light transmittance in the visible spectrum. In addition, this material also offers other excellent properties such as low frictional coefficient, high chemical resistance and good electrical insulation. All the above features and properties make PMMA a good substrate for microfluidic devices, especially for those involved in chemical applications. A PMMA substrate can be micro machined in many ways, such as x-ray exposure and subsequent developing, hot embossing and laser machining. For the micro fuel cell described in this paper, laser machining was adopted with the fabrication steps shown in figure 1.

The microchannels for fuel flow and oxidant flow were first ablated with a CO_2-laser. Since a CO_2-laser has a relatively long characteristic wavelength of 10.6 μm, the ablation process depends more on thermal energy. The microchannel shown in figure 1(*a*) was fabricated by the Universal M-300 Laser Platform (Universal Laser Systems Inc.). The system uses a 25 W CO_2-laser. The maximum beam speed is about 640 mm s^{-1}. The ablation process of the CO_2-laser is determined by thermal energy. Therefore the cross section of the microchannel depends on the energy distribution of the laser beam, its moving speed, the laser power and the thermal diffusivity of the substrate material. The energy of the laser beam has a Gaussian distribution, thus the cross section of the channel also has a Gaussian shape. The typical cross sections of a Gaussian-shaped microchannel can be seen in figure 2. The next advantage of Gaussian-shaped microchannels is apparent in the subsequent fabrication step. About 40 nm gold layer was sputtered over the substrate surface (SC7640 sputter coater, Quorum Technologies Ltd), figure 1(*b*). This gold layer acts as the current collector and corrosion protection layer for the fuel cell. Since sputtering only allows straight deposition, the Gaussian shape allows gold to cover all sides of the channel. This feature is crucial for the application of a current collector.

The design of the base substrate needs to consider two basic aspects. The first aspect is the design of microchannels

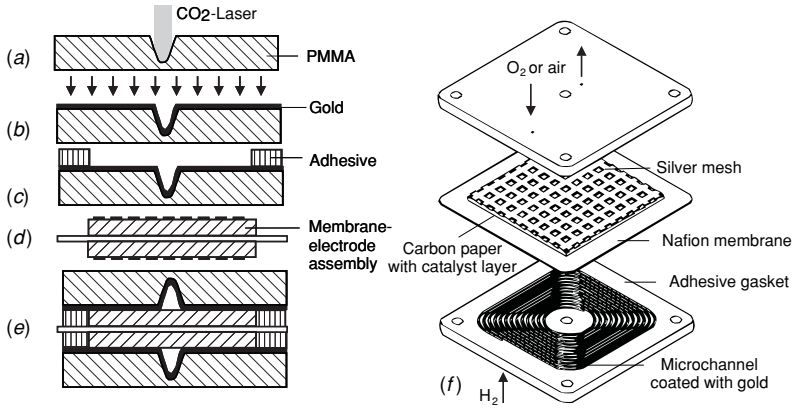


Figure 1. Fabrication process for the polymeric micro fuel cell: (*a*) the flow channels are ablated with a CO_2 laser, (*b*) a gold layer is sputtered over the substrate surface, (*c*) applying adhesive gasket for bonding, (*d*) the membrane electrode assembly, (*e*) the assembled micro fuel cell and (*f*) explosive view of the micro fuel cell.

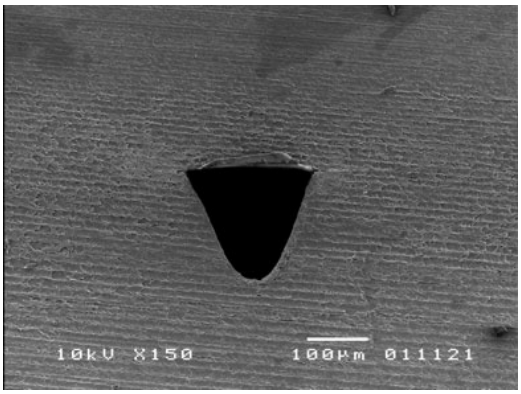


Figure 2. The Gaussian-shaped microchannel (4% beam speed and 6% laser power).

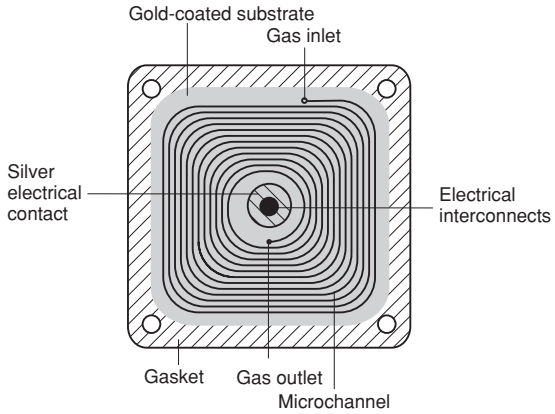


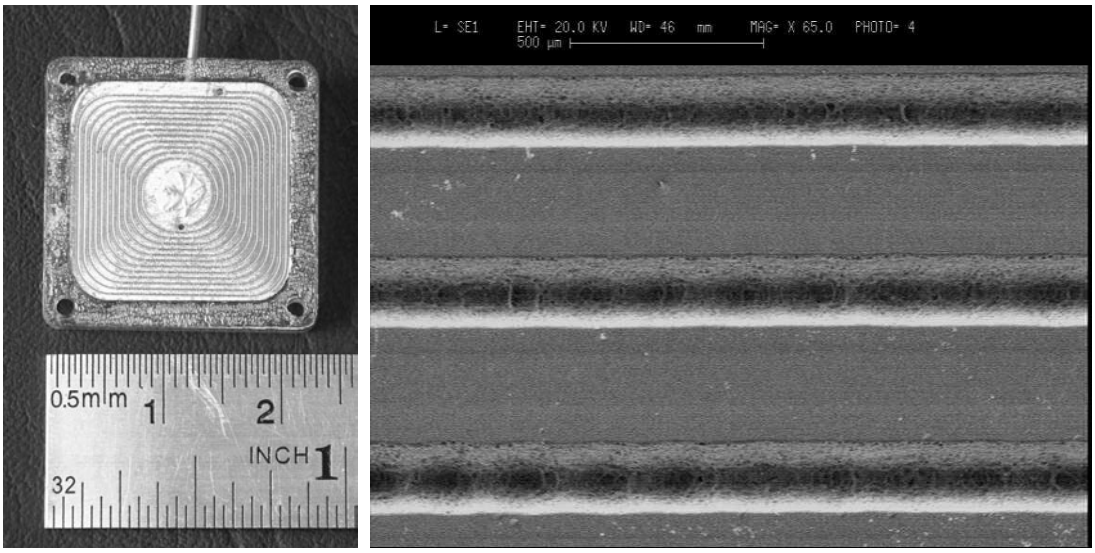
Figure 3. The base substrate of the polymeric micro fuel cell.

for fuel delivery with water management. The second aspect is the current-collecting method. The electrical resistance should be minimized by a large electrically conducting surface, while a large channel area improves the diffusion of reactants. An optimization regarding both aspects must be considered for the design.

Water management is the most important issue in the design of the microchannel of the fuel cell. On the one hand, water is the reaction product and should be transported away. On the other hand, supplied dry hydrogen should be humidified in the fuel cell for a better performance. Our micro fuel cell was designed in a way that can get rid of an external humidifying system for fuel and oxidant. The stand-alone micro fuel cell can use dry hydrogen on the anode side and ambient air or dry oxygen on the cathode side. In our micro fuel cell, water generated by the reaction was utilized for humidification. The design of our micro fuel cell is shown in figure 3.

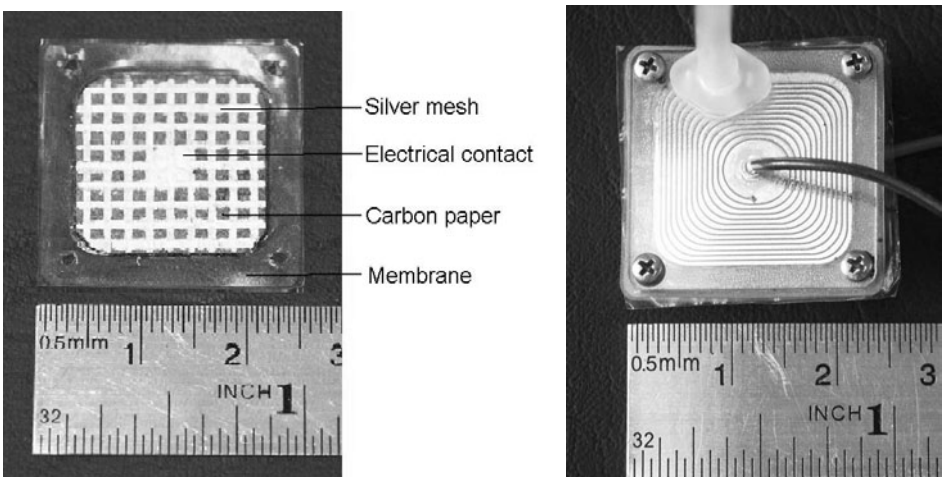
The flow channel is designed to have a spiral shape. Such a design enables the relatively dry gas in the outer spiral line to become hydrated by acquiring some of the moisture from the adjacent inner spiral line. The ablation process of the microchannels used a beam speed and a laser power of 4% and 6% of the maximum values, respectively. A channel width and channel depth of 220 μm can be expected from these parameters. The spiral design also enables the electrical contact to be placed in the middle of the cell, which minimizes the resistance of the current collector. In the middle of the base substrate, a small hole was drilled by the same laser and an electrical wire was inserted through the hole and bonded by a silver-loaded adhesive. Figure 4(*a*) depicts the fabricated base substrate with the spiral microchannel. The close-up image of the channel is shown in figure 4(*b*). In order to press the base substrate tightly with the membrane electrode assembly, four holes were also drilled in the corner of the base substrate to mount bolts and nuts for adjusting pressing force.

The heart of the fuel cell is the membrane electrode assembly (MEA). Nafion 1135 membrane (DuPont) was used in the experiments. The membrane was first treated with 5% hydrogen peroxide solution heated to boiling point to oxidize organic impurities, after rinsed in deionized water, and then immersed in 0.5 M hot sulfuric acid to get rid of the metallic residues. After being washed in boiling deionized water several times, the membrane was ready for use. In the fabrication process of the electrodes, Toray carbon paper (TGPH-090, typical thickness 260 μm, typical density 0.49 g cm^{-3}) was treated by hydrophobic PTFE, after applying a diffusion layer (carbon powder mixed with PTFE) on one side, a catalyst layer was coated. The catalyst layer was made of Nafion (Nafion solution 5112, from DuPont)



(*a*) (*b*)

Figure 4. The fabricated base substrate of the polymeric micro fuel cell: (*a*) the base substrate with the spiral microchannel and (*b*) close-up image of the microchannel.



(*a*) (*b*)

Figure 5. The fabricated micro fuel cell: (*a*) the membrane electrode assembly, (*b*) the assembled micro fuel cell.

bonded platinum on carbon (40% Pt/C, from E-TEK Div. of De Nora N.A., Inc.), which extends the three-phase boundary for electrochemical reaction. The catalyst layer contains 1 mg cm^{-2} platinum and 1 mg cm^{-2} Nafion. To increase the conductivity of the carbon paper, silver conductive paint (from RS Components) was printed on the other side of the carbon paper, which is used as a part of the current collector. The silver electrical conductor is designed to have the mesh shape. The printed part is mainly used as the current collector, and the non-printed part is mainly used as the gas diffusion area. In the middle of the electrode is the electrical pad, which should later be in direct contact with the base substrate. Finally, the membrane was sandwiched by two electrodes and pressed at 60 kg cm^{-2} and 130 °C for 3 min. Figure 5 shows the fabricated MEA. With a dimension of approximately 1.8 cm × 1.8 cm, the electrode area is about 3 cm^2.

In the final step, the two PMMA substrates and the MEA were bonded together using an adhesive gasket. The gasket (Adhesives Research, Inc., Arclad 8102 transfer adhesive) was also machined with the same laser system described above. The micro fuel cell was assembled by four screw bolts and nuts.

3. Characterization

The packed fuel cell has been characterized by the electronic load system (Arbin Corp.). The schematic testing facility is shown in figure 6. Hydrogen is supplied by a hydride storage. Air or oxygen flow rate is controlled by a flow meter. Arbin electronic load is controlled by a computer. The operation conditions are as follows.

- All tests are at room temperature of 24 °C.
- Hydrogen is set to be dead-ended during testing (the hydrogen outlet hole was open before testing, after the

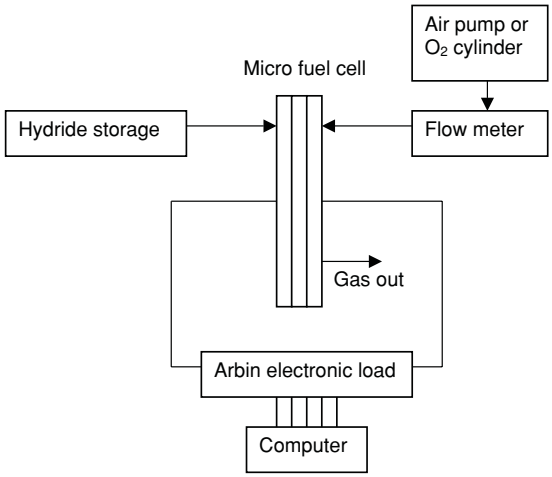


Figure 6. The schematic testing facility.

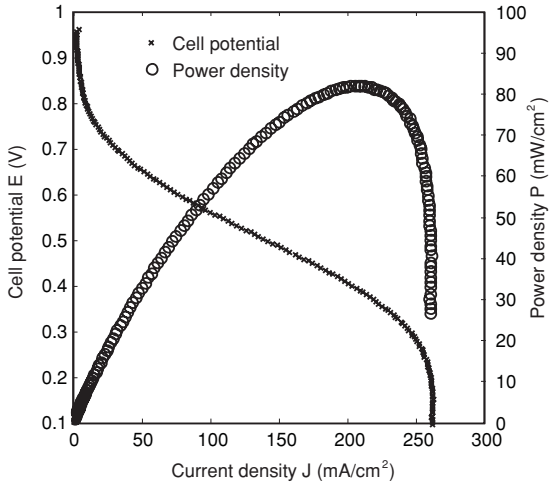


Figure 7. The performance of the polymeric micro fuel cell with air on the cathode side (hydrogen is set to be dead-ended).

hydrogen replaces the air, the outlet hole was closed) and the pressure of hydrogen is 10 psi.

- The air is supplied by an air pump, the flow rate is kept constant at 50 ml min^{-1}.
- The oxygen flow is controlled and kept constant at 20 ml min^{-1}.

Figure 7 shows the performance of our micro fuel cell for hydrogen/air reaction. The power density reaches a peak at a current density of 205 mA cm^{-2}. The voltage and power density corresponding to this point are 0.40 V and 82 mW cm^{-2}, respectively. Normally, fuel cells are designed to operate at a point slightly to the left of this point for a good compromise between cell efficiency, low capital cost and stable operation. For instance, if the operation voltage is set to be 0.50 V the power density is about 70 mW cm^{-2}. Figure 8 shows the long term performance of the micro fuel cell operating at 0.50 V. The performance is stable during operation for many hours.

Figure 9 shows the results of hydrogen/oxygen cell reaction. The power density reaches a peak at a current density of 901 mA cm^{-2}. The voltage and power density corresponding to this point are 0.35 V and 315 mW cm^{-2},

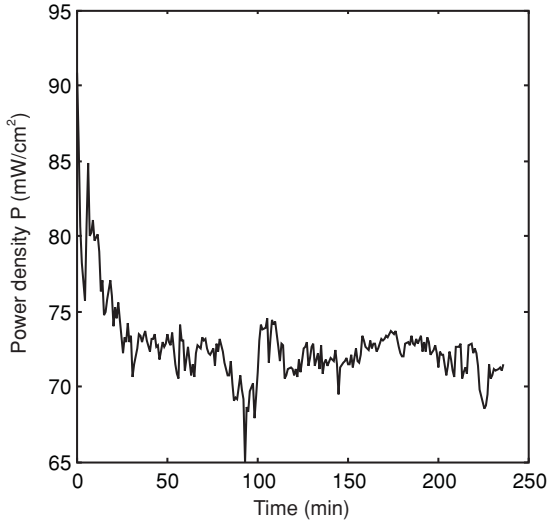


Figure 8. The long term performance of the polymeric micro fuel cell with air on the cathode side (operating voltage is 0.50 V).

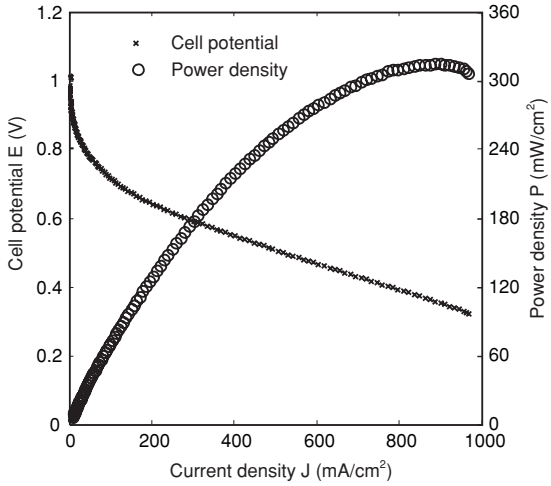


Figure 9. The performance of the polymeric micro fuel cell with oxygen on the cathode side (hydrogen is set to be dead-ended).

respectively. If the operation voltage is 0.50 V, the power density is 254 mW cm^{-2}.

4. Conclusions

The micro fuel cell investigated in this study has achieved the best performance compared with other devices reported in the recent literature. The main reason for the breakthrough is the good design of the base substrate and the electrodes. In the design of the base substrate, both water management and electrical interconnection are considered. In the electrode design, the area is well divided to reach a good compromise between current collecting and gas diffusion.

In conclusion, we designed and fabricated the micro fuel cell by polymeric micromachining. The membrane electrode assembly is sandwiched between two gold-coated PMMA base substrates. The gas flow channels are fabricated on the

substrate by CO_2 laser micromachining. The assembled fuel cell has been characterized by an electronic load system. At room temperature, the power output of the 3 cm^2 fuel cell can reach 0.947 W (315 mW cm^{-2}) when pure hydrogen is fed to the anode and pure oxygen is supplied to the cathode. When air is used on the cathode side, the power output can reach 0.246 W (82 mW cm^{-2}). During the characterization, the hydrogen is set to be dead-ended, which means the utilization of hydrogen is close to 100%.

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