

Short communication

Performance of an integrated composite membrane electrode assembly in DMFC

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Abstract

We report here the performance of a metal-based integrated composite membrane electrode assembly (IC-MEA) in direct methanol fuel cell (DMFC). The IC-MEA integrates the multi-functions of a conventional MEA, gas diffusion layer (GDL) and current collector. It was fabricated by impregnating Nafion electrolyte into a sandwiched structure containing expanding-Polytetrafluoroethylene (e-PTFE) and porous titanium sheets and subsequently coating with catalyst layer and microporous layer (MPL). While operating with air and 2 M methanol under ambient pressure, the IC-MEA in DMFC can yield a maximum power density of 19 mW cm^{-2} at 26°C , higher than a in-house made Nafion 115 MEA under the same working conditions. The IC-MEAs has been successfully applied to planar multi-cell stacks.

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Keywords: Integrated composite membrane electrode assembly; Porous titanium sheet; DMFC; Planar stack

1. Introduction

Direct methanol fuel cell (DMFC) is a promising power option for portable and micro devices. Theoretically, methanol has a superior specific energy density in comparison with the best rechargeable battery [1]. The liquid-feed DMFC system may be advantageous with respect to easy fuel storage, water management and elimination of complex reformer. These advantages are important for portable electronics devices such as cell phone, notebook computers, etc. However, some technological hurdles still need to be overcome before the commercialization of DMFC. The main problems associated with DMFC are methanol crossover and poor methanol electro-oxidation kinetics, which lead to low power density and reduced fuel utilization. Furthermore, especially for portable applications, it is desirable to make the DMFC system more compact, lightweight and cost competitive.

A single DMFC consists of the similar components as a H_2 fueled PEMFC, including proton exchange membrane, catalyst layer, gas diffusion layer, bipolar plate, and seals. All of these

components are layered structure and required to be compressed by sufficient and uniformly distributed pressure so as to reduce electrical contact resistance or ensure good conductive properties between each interfaces. Consequently, some ancillary equipment such as heavy tie rods and end-plates are indispensable in such a fuel cell stack. The bipolar plates, serving as current collector and containing the flow field to distribute reactant and remove product, takes the major volume and weight of the whole fuel cell stack. The lack of mechanical strength inherent with graphite-based bipolar plates imposes limitations on plate thickness. With respect to the development of micro fuel cells for portable applications, these drawbacks need be overcome.

In recent years, great attentions have been paid on new materials and fabrication technology in the development of portable DMFC. The silicon-based Micro-Electro-Mechanical Systems (MEMS) technology has been introduced to micro fuel cells and become a hot research field [2–7]. However, silicon wafer is a high-cost and non-conductive material. It needs to be coated with a precious metal layer to conduct electricity. The relative fragility makes it difficult to suffer great compressing pressure for good sealing and hence the contact resistance is high in fuel cell [8]. Novel MEA structures and fabrication processes for DMFC have also been proposed. Frey et al. fabricated MEA for

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DMFC onto a porous substrate by a layer-upon-layer method and achieved $5\text{--}7\text{ mW cm}^{-2}$ with single cell at ambient conditions [9]. Shao, Lim et al. prepared an electrode structure based on Ti mesh which showed a performance comparable to that of the conventional porous carbon-based structure in DMFC [10,11].

We have proposed a concept of an integrated composite membrane electrode assembly (IC-MEA), which has showed acceptable performance in small H_2/air fuel cell [12]. The basic idea of the concept is to integrate the layered components of fuel cells such as the membrane, catalyst layer, gas diffusion layer, bipolar plate, etc. into a monolithic structure. This integrated monolithic structure can act as multi-functional component. To achieve this goal, we propose the structure of an IC-MEA, which consists of impregnated electrolyte membrane, internal reinforcement media, incorporated porous metal sheets, catalyst layer and microporous layer. In this technique, the metal sheet is titanium with fine pores and channels fabricated by photochemical etching method. The titanium sheets can serve as supporting substrate, flow field and current collector. An e-PTFE substrate was used as an internal reinforcement media of the membrane. The e-PTFE substrate was sandwiched between the titanium sheets (Fig. 1a). The electrolyte ionomer dispersion was impregnated into the sandwiched structure to form the electrolyte membrane. The impregnated membrane was filled into the e-PTFE media completely and partly bonded with the titanium sheets. Consequently, these substrates and media can be bonded together as a monolithic structure (Fig. 1b). Catalyst layer can be coated onto the open area of the electrolyte membrane (Fig. 1c).

As a consequence, this IC-MEA can integrate the multi-functions of a conventional MEA, flow field and current collector. Supported by the metal sheet, the IC-MEA has high mechanical strength. It is possible to make an extremely thin and lightweight fuel cell with IC-MEA, for the metal sheet can be made as thin as only hundreds of microns. The membrane is impregnated between two metal sheets and bonded together with them. Reinforced by e-PTFE internal and strengthened by the metal sheets outside, the membrane is not prone to swell with water uptake or retract when drying, especially in the direction of in-plane. The suppression of its swell may make the fuel crossover problem become less serious. Furthermore, the different layers are integrated together and the contact resistance between each interface is eliminated or reduced. It is unneces-

sary to exert high mechanical compression on these layers and hence some sub-systems of the cell are dispensable.

In this study, the performance of the IC-MEA in application to DMFC was firstly reported. Some critical issues about the fabrication of IC-MEA were discussed and the performance under different working conditions was shown.

2. Experimental

2.1. Impregnation process

Expanded porous PTFE with high void volume of about 70% and with a thickness of $30\text{ }\mu\text{m}$ was used as internal reinforcement media. Prior to use, the e-PTFE was immersed with alcohol, then rinsed in diluted nitride acid solution and deionized water.

For the fabrication of IC-MEA, details of the procedure have been elaborated in [12]. The treated porous PTFE were put between two titanium sheets with a thickness of $100\text{ }\mu\text{m}$ in a sandwiched structure. The interspace between the nonporous edges the two metal sheets was sealed by a plastic film, also serving as an electrically insulating substrate. The ionomer dispersion was prepared by adding dimethylformamide (DMF) to DE 2021 Nafion dispersion (DuPont, Total Acid Capacity, $0.95\text{--}1.03\text{ meq g}^{-1}$, H^+ polymer basis). A calculated amount of the dispersion was impregnated into the pores of the PTFE membrane and the metal sheets, followed by putting in an extremely clean environment to dry for 2 h at ambient temperature. After that, it was annealed at $130\text{ }^\circ\text{C}$ for 1 h.

2.2. Fabrication of membrane electrode assembly

The cathode catalyst ink was prepared by mixing 47 wt.% Pt/C (Tanaka), 100 wt.% Pt black (Johnson Matthey), 5 wt.% Nafion dispersion (DuPont) and isopropanol together. The anode catalyst ink was prepared from a mixture of 20 wt.% Pt–10 wt.% Ru, 60 wt.% Pt–30 wt.% Ru, 5 wt.% Nafion dispersion and isopropanol. After the mixture was stirred and dispersed uniformly, a certain amount of NaOH was added into it to convert the H^+ form Nafion into Na^+ form. The electrolyte membrane was converted into Na^+ form by rinsing in hot NaOH solution for 1 h prior to use. Then the catalyst ink was directly coated onto the open area of the electrolyte membrane. The precious metal loading was 3 mg cm^{-2} and 4 mg cm^{-2} for cathode and anode, respectively. After that, a carbon layer composed of 5 mg cm^{-2} Vulcan XC-72 carbon and 2 mg cm^{-2} Nafion was brush-coated outside the catalyst layer as a microporous layer (MPL), followed by drying under vacuum at $185\text{ }^\circ\text{C}$ for 1 h. Lastly, the membrane and the catalyst layer were re-protonized by immersing in light boiling 3 wt.% sulfuric acid solution for 3 h, followed by rinsing in deionized water.

For comparison, a catalyst coated membrane (CCM) was fabricated by similar procedure with the same catalyst species and loading. The same catalyst ink as prepared above was directly coated onto Nafion 115 membrane (Na^+ form) by a spraying gun, followed by drying and converting into H^+ form. Toray carbon paper coated with 2 mg cm^{-2} vulcan 72 carbon and 30 wt.% PTFE was used as backing layer on both anode and cathode.

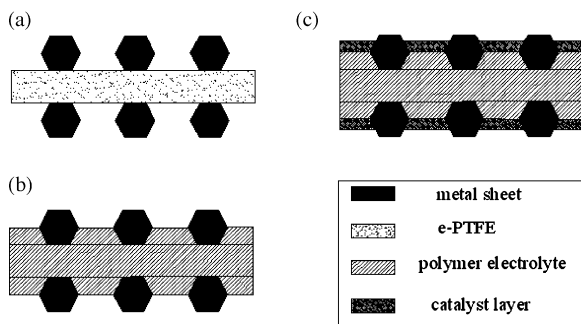


Fig. 1. Schematic diagram of the structure of IC-MEA (part of the cross-section): (a) before impregnation; (b) after impregnation; (c) catalyst coated IC membrane.

2.3. Test of DMFC performance

A single IC-MEA with an active electrode area of $2\text{ cm} \times 2\text{ cm}$ was inserted into a fuel cell hardware, which consisted of two graphite plates with serpentine flow field and two copper end plates coated with Au as corrosion protection layer. Rod-like heaters were inserted into the plates to control the cell temperature. Dry air was conducted into the cathode inlet at a fixed flow rate of 100 ml min^{-1} controlled by a mass flowmeter at ambient pressure. The dilute methanol solution was fed to the anode at a flow rate of 1 ml min^{-1} by a peristaltic pump (LB-05, Beijing Weixing) without backpressure. Before measuring the current–voltage curve, the IC-MEA was preliminarily conditioned in the single cell by circulating 1 M methanol solution into the anodic compartment for 12 h. The current–potential (I – V) characteristics were measured by an electronic load system. The I – V data were collected by measuring cell voltages which were stabilized for about at least 1 min after applying currents in the galvanostatic mode. The test of Nafion 115 CCM was carried out with the same fuel cell hardware and procedures.

3. Results and discussion

3.1. The metal sheet

The metal sheet is a multi-function component in IC-MEA. Acting as the supporting substrate for the MEA, it is required to have high mechanical strength. As the passage of reactant and product, it is necessary to be porous and with flow passage on it. Additionally, functioning as current collector, good electrical conductivity is a prerequisite. Comparing with graphite and silicon, metal material is advantageous in its higher mechanical strength and electrical conductivity. Thus, it can better fulfill these requirements. However, two issues must be considered concerning the development of metal substrates. One is how to fabricate micro flow field and pores on it, the other is its susceptibility to corrosion under the working environment of fuel cells.

In this study, the function of the metal substrate requires highly precise micro fabrication technique. Comparing with conventional large flow field, usually in order of millimeter in channel size, micro flow field with appropriate channel width and depth can increase the performance of fuel cell due to the improved mass transport [13]. A uniformly distributed pores and large opening area can ensure good access of reactant towards the electroactive sites and effective removal of product from the electrode. In this study, photochemical etching, which is a high-quality, low-cost technique and suitable for mass production, was adopted to fabricate micro flow field and pores. Here the width of channels was $150\text{ }\mu\text{m}$ and that of the ribs between the channels was $80\text{ }\mu\text{m}$ (Fig. 2).

As described above, the metal sheet is in direct contact with the electrolyte membrane in the IC-MEA structure. The electrolyte membrane has fluoropolymer backbone with side chains terminating in sulfonic acid. The metal sheets work in a strong acid and electrochemical environment. So, it must have enough corrosion resistance to prevent the membrane be contaminated

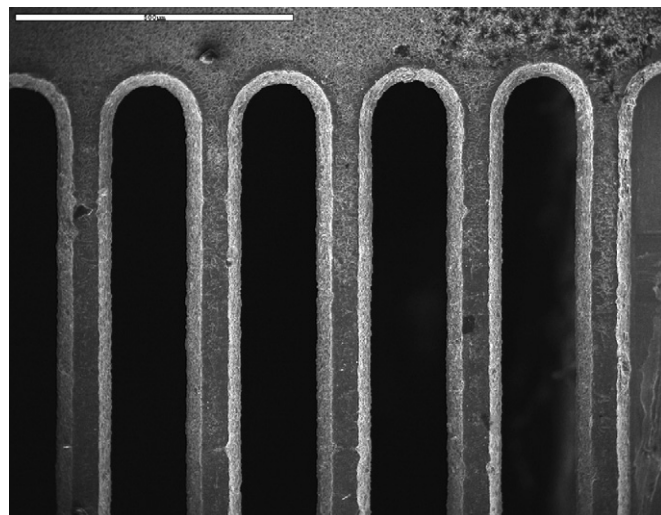


Fig. 2. The micro channels of titanium sheet fabricated by photochemical etching.

by metal ion to deteriorate the proton conductivity. The processes of surface-treatment are essential for long-term durability. The surface-treatment processes of metal bipolar plate in fuel cells have been widely studied before [14–18]. In this study, we use titanium material, which has good corrosion resistance. But the question of titanium is that it is prone to form an electrical-insulating layer on its surface. Prior to application, it was etched and coated with a Ru layer. During the long-term performance test for about 100 h, no obvious performance degradation has been observed induced by the corrosion problem. Other more economical and better surface-treatment methods can also be utilized and explored to this application.

3.2. Effects of MPL

The adding of a MPL incorporated with the IC-MEA is of significantly importance to the performance. Firstly, it can reduce the in-plane resistance of the electrode. The in-plane resistance of the electrode can be given by

$$R = \frac{\rho l}{mt} \quad (1)$$

Here ρ is the specific resistance coefficient of the catalyst layer. Considering the catalyst layer is mainly composed of carbon particles, the value ρ may be approximately equal to carbon, which is more than $1000\text{ }\mu\Omega\text{ cm}$, several orders of magnitude higher than titanium ($42\text{ }\mu\Omega\text{ cm}$). Presuming the length of catalyst layer l is equal to the width m , the electrical conductivity of the catalyst layer is poor because the thickness of catalyst layer t is only several tens microns and the value ρ is relatively low. As a consequence, the voltage drop along the in-plane direction of the electrode is relatively high. By adding a MPL upon the catalyst layer, which simultaneously filled into the pores of titanium sheets, the electrical conductivity can be improved due to the increased value t and better contact with the titanium sheets.

The adding of MPL can result in other effects. At the anode, the MPL provides a barrier to methanol diffusion and thereby

reduce methanol crossover [19]. At the same time, it decreases the methanol transport rate to the catalyst layer, resulting in higher mass transport overpotential. However, the IC-MEA is mainly for portable low power applications, where it is operated under ambient conditions and at relatively low current densities. In addition, it is noteworthy that the membrane impregnated is only as thin as 40 μm . As a result, the overpotential caused by crossover may be the primary loss in comparison with that caused by methanol transport in this case. It is still necessary to optimize the membrane thickness and MPL to best minimize the losses caused by crossover and concentration overpotential. At the cathode, the MPL can build up a hydraulic pressure difference across the membrane [20–22], which promotes the water back-diffusion from the cathode side to the anode side and offsets the electro-osmotic drag. Therefore, the net water transport coefficient can be significantly reduced.

3.3. Performance in DMFC

Fig. 3 shows the performance of IC-MEA in DMFC at 26 °C fed with forced air. The maximum power density obtained is 19 mW cm^{-2} . Although the thickness of the membrane impregnated is only about 40 μm , the IC-MEA showed a value of OCV of about 0.67 V. The relatively high value of OCV indicated that the crossover is not serious considering the thinness of the membrane. The performance of IC-MEA increased with the temperature, as shown in Fig. 3. At 60 °C, the maximum power density is about 55 mW cm^{-2} at 0.3 V with 2 M methanol input. By contrast, Fig. 4 presents the performance of CCM using Nafion 115 under the same working conditions. At 26 °C, the maximum power density achieved is about 12 mW cm^{-2} . At 60 °C, it is 50 mW cm^{-2} . The performance of the regular CCM is obviously lower than that of the IC-MEA.

For portable applications, the use of high concentration methanol is highly desirable in order to get greater power density. Fig. 5 depicted the influence of methanol concentration on performance. It can be observed that the value of OCV decreased with increasing methanol concentration. When 0.5 M methanol was used, the value of OCV was the highest. The

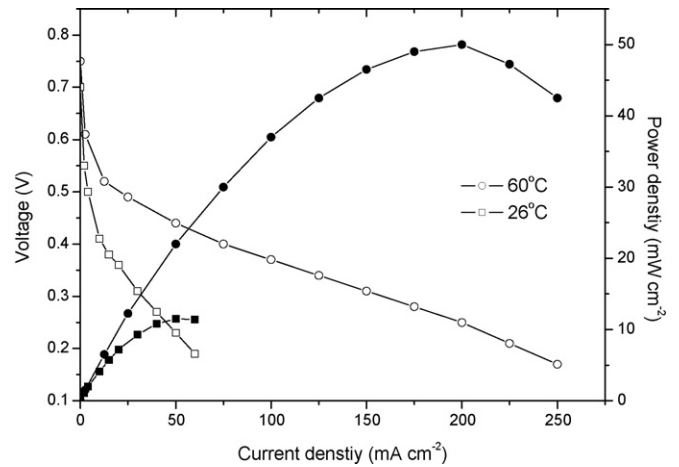


Fig. 4. The performance of CCM (ambient air and 2 M methanol).

OCV is affected by the crossover of methanol, which causes a mixed potential at the cathode and reduces the cell voltage. The crossover is more serious with high concentration of methanol and hence the value of OCV declines. This is consistent with the commonly used Nafion membrane as expected. At low current density region, lower concentration methanol yields higher power density due to the lower crossover of methanol. As the current density increases, the crossover becomes less serious. As shown in Fig. 5, at high current density region, the cell voltage using 1 M methanol is obviously higher than that using 0.5 M methanol at the same current density. The lower performance with lower concentration of methanol is probably attributed to the concentration polarization effects. When the cell voltage is below 0.3 V, the highest value of power density was obtained using 2 M methanol. The performance of using 1 M methanol is similar to that using 3 M at this region. While using 4 M methanol the performance is relatively poor because the crossover problem becomes dominated again. When 2 M methanol was used, the IC-MEA gave the maximum power density. In contrast, when a Nafion 112 membrane with a comparable thickness (50 μm)

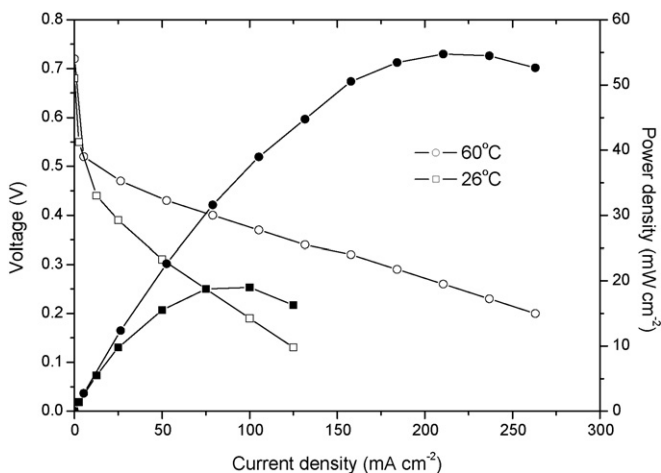


Fig. 3. The performance of IC-MEA in DMFC (ambient air and 2 M methanol).

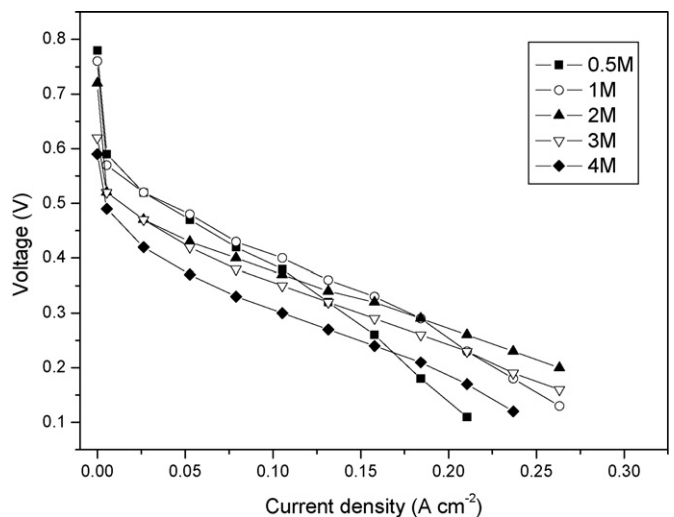


Fig. 5. The performance of IC-MEA with different methanol concentration (ambient air, at 55 °C).

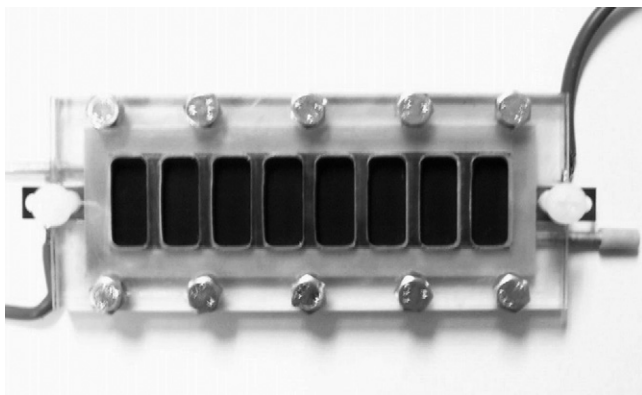


Fig. 6. Prototype of planar IC-MEA stack with eight cells in series.

is used, the maximum power density is usually achieved using about 1 M methanol [23].

Restricted by the e-PTFE and the porous titanium substrate, the IC-MEA has good dimensional stability. Especially in the in-plane direction, its dimension cannot be changed much by soaking with water or methanol. Due to the suppression of the swell of the impregnated membrane in IC-MEA, the crossover can be reduced to some extent. In our later work, we will discuss the crossover problem of IC-MEA in detail.

3.4. Planar stack of multicells

This concept of IC-MEA is especially suitable for small fuel cells. The total thickness of the IC-MEA fabricated is only about 240 μm . Supported by titanium substrate, the IC-MEA has high mechanical strength. For the space-efficient consideration, the configuration of small fuel cells is usually planar, including banded [24] or flip-flop [25]. In this concept, a planar multi-cell stack with the IC-MEA can be assembled by simply connecting the titanium sheet of the anode of one cell to that of the cathode of the adjacent cell. The electrolyte membrane of each cell is entirely segmented by insulating plastic, so the problem of lateral ionic conduction in planar multiple cells sharing the same electrolyte membrane [26] does not exist.

Fig. 6 is a prototype of planar IC-MEA stack with eight unit cells in series. Each cell has an active area of 2.5 cm^2 . The size and weight of the planar stack can be greatly reduced by further optimum design and fabrication processes. Here we only show the feasibility of the application of IC-MEA in planar stacks. The cathodes were directly open to the ambient air. The anodes were a reservoir containing 2 M methanol. The methanol is passively diffused to the anode of IC-MEA driven by concentration gradient, not flowing through a flow field with fixed rate as mentioned above while testing a unit MEA. At 23 $^{\circ}\text{C}$, this passive-feed planar stack gave a maximum power density of about 6 mW cm^{-2} (Fig. 7). The performance is nonetheless too low to meet the requirement for practical application. To improve the performance, it is necessary to further optimize the fabrication processes of a planar stack with IC-MEA including impregnating more conductive and uniform membrane, adopting more active catalyst and optimizing the electrode components, etc.

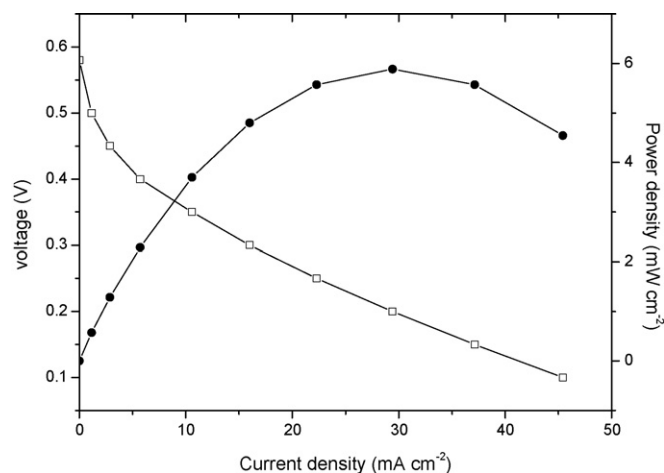


Fig. 7. The performance of planar stack using IC-MEA (passively fed with 2 M methanol and air-breathing, at 23 $^{\circ}\text{C}$).

4. Conclusions

In this study, an integrated MEA structure based on metal sheet was developed and fabricated. The performance of IC-MEA in DMFC was evaluated under different conditions. The IC-MEA gave the highest performance when feeding with 2 M methanol. At 26 $^{\circ}\text{C}$ fed with atmospheric air, the maximum power density obtained is 19 mW cm^{-2} , higher than a in-house made Nafion 115 CCM fabricated by similar procedure under the same working conditions. The IC-MEA has been successfully fabricated into a planar multi-cell stack. These results show that IC-MEA is a promising candidate in the development of portable DMFC systems.

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