

An integrated composite membrane electrode assembly (ICMEA) and its application in small H₂/air fuel cells

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Abstract

The commercialization of small fuel cells requires both the reduction of components cost and improvement of power density. To meet these requirements, we proposed the concept of an integrated composite membrane electrode assembly (ICMEA) which integrates the functions of conventional MEA, flow field, and current collector. Compared to conventional ones, it is advanced in simplification of fuel cell components, higher mechanical strength and dimensional stability, reduction in volume and weight, lower clamping pressure, and lower cost. A 200 μm thick ICMEA was successfully fabricated. A sandwiched structure was fabricated by attaching an e-PTFE substrate with two finely porous thin metal sheets on each side. After the impregnation of polymer electrolyte, the porous PTFE was filled with the polymer electrolyte and was bounded with the two metal sheets. Catalyst layer was directly coated on the surface of the composite membrane. At ambient conditions, the achieved maximum power density of ICMEA in H₂/air fuel cell was nearly 80 mW cm⁻².

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1. Introduction

Polymer electrolyte membrane fuel cell (PEMFC) is one of the attractive power sources for a wide range of applications. In recent years, portable electronics, such as cell phone, laptop, PDAs, etc., have shown an ever-increasing requirement for the new concepts of power sources. For the portable applications, PEMFCs have many advantages compared with conventional batteries: higher power density, higher power-to-weight ratio, and convenient in refilling fuel instead of electrical charging. These advantages make PEMFCs promising power option in portable applications. Rapid progress has been made in small PEMFCs in the past years. However, small fuel cells are different from large fuel cells in many respects, such as cell configuration, material selection, and components manufacture. To accelerate the commercialization of small fuel cells, both the components cost and the power density are of paramount importance.

2. Design concept of ICMEA

Conventionally, a single PEM cell comprises several components and layers, including proton exchange membrane, catalyst layer, gas diffusion layer, bipolar plate, and seals. The catalyst layer is usually cast as thin films, transferred to the membrane, or applied directly on the membrane. Alternatively, the catalyst–electrode layer may be deposited onto the gas diffusion layer. All of these layers in fuel cell must be compressed by high and evenly-distributed pressure to maintain electrical contact and improve conductive properties between each interface. Consequently, the complexity of many layers requires ancillary equipment, such as heavy tie rods and end-plates. One of the main obstacles towards the commercialization of fuel cell is its high-cost materials (membrane, noble metal catalyst, carbon based gas diffusion layer, bipolar plate, etc.), which are indispensable in the current technology. The bipolar plates, serving as current collector and containing the flow field for fuel supply to the electrode area, are usually manufactured by machining, milling, or pressure-moulding processes from materials of graphite, amorphous carbon, and composite carbon materials in combination with polymers. These traditional manufacturing

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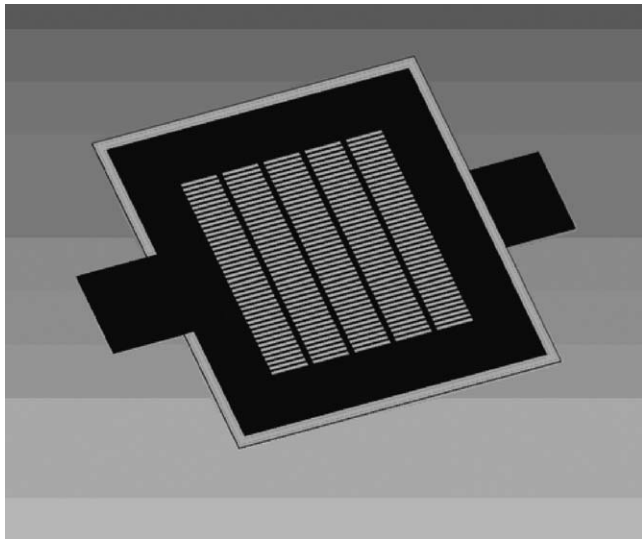


Fig. 1. The concept of ICMEA.

processes are neither suitable to mass production nor appropriate for more precise manufacture of micro-fuel cells. Furthermore, the lack of mechanical strength inherent with graphite imposes limitations on plate thickness and consequently, on specific energy. In recent years, many studies have been conducted on the basis of Micro-Electro-Mechanical System (MEMS) technology using silicon wafer as supporting substrate, flow field, and current collector [1–6] as well as on the printed circuit board (PCB) technology [7,8]. For the portable application, fuel cells need to be operated at ambient conditions concurrently with high and stable power density. In this case, a thin and highly conductive membrane with high mechanical strength becomes a key research issue. W.L. Gore and Associates have successfully developed thin membrane (25 μm) for small fuel cells using e-PTFE as supporting media and showed improvement of MEA durability [9]. Yamaguchi et al. [10] and Pichonat et al. [11] proposed pore-filling electrolyte membrane for PEM fuel cells.

For portable application, in order to make fuel cells more lightweight, cost competitive, and suitable for batch production, it is desirable to simplify the cell configuration, reduce layers, and integrate functions of components.

In this study, we proposed a concept of integrated composite membrane electrode assembly (ICMEA). This ICMEA integrates the functions of conventional MEA, flow field, and current collector. Two finely thin porous metal sheets are incorporated with a MEA on both sides, serving as flow field and current collector (Figs. 1 and 2). The fabrication procedure is shown

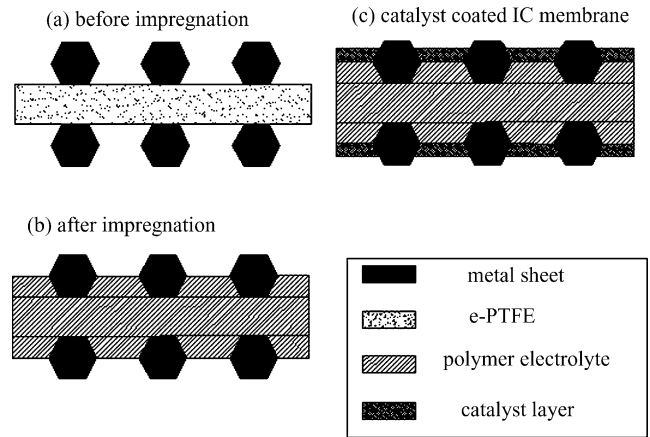


Fig. 3. Schematic diagram of the fabrication procedure (part of the cross-section): (a) before impregnation, (b) after impregnation, and (c) catalyst coated IC membrane.

in Fig. 3. An expanded PTFE substrate was attached with two finely porous thin metal sheets on each side, forming a sandwiched structure as shown in Fig. 3(a). The polymer dispersion is impregnated into the porous structure. When being dried, the polymer ionomer is filled into the porous PTFE substrate completely and embedded into part of the depth of the pores on metal sheets, as shown in Fig. 3(b). Thus, the polymer bounds the three substrates together. Catalyst layer can be coated onto the surface of the electrolyte polymer, concurrently in contact with the walls of the pores of the metal sheets Fig. 3(c) which conduct electrical current to external circuit.

As a result, the ICMEA integrates the functions of MEA, flow field and current collector. For this technique, it is unnecessary to use the same bipolar plate as in those conventional cell configurations. The metal sheets can serve as current collector, flow field and supporting substrate. Thus, it is possible to make an extremely thin fuel cell with ICMEA, for the metal sheet can be as thin as only hundreds of microns. Moreover, the ICMEA has high mechanical strength and dimensional stability. The membrane is impregnated between two metal sheets and bounded together with them. It is reinforced not only by e-PTFE internal but also by the metal sheet outside so that it is not prone to swell with water uptake or contract when drying. Furthermore, the different layers are integrated together and the contact resistance in each interface is reduced or eliminated. It is unnecessary to exert high pressure to compress the layers. As a result, some sub-systems of the cell can be eliminated. In addition, reinforced by porous PTFE and metal sheet, the membrane can be made very thin (<50 μm). Correspondingly, the resistance of the elec-

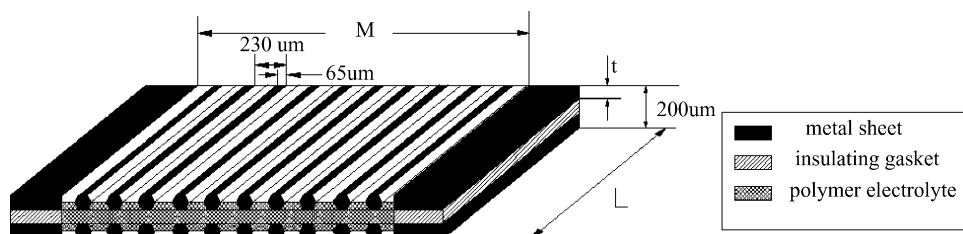


Fig. 2. Schematic diagram of the dimensions of ICMEA.

trolyte becomes less and back diffusion of water from cathode to anode enhances. This concept of ICMEA is suitable for small fuel cells. For the space-efficient consideration, the configuration of small fuel cells is usually planar, including banded [12] or flip-flop [13]. In this concept, a planar multi-cell stack with the ICMEA can be easily assembled, which is more compact and lightweight than vertical-series fuel cell stacks.

3. Experimental

3.1. Porous metal sheet and its surface treatment

The porous metal sheets were made with titanium ranging from 50 to 300 μm thick. Different types of through-pores were fabricated by photolithography and wet etching techniques. In order to enhance the capability of corrosion resistance, the metal must be surface treated (coated with Ru layer) prior to application.

3.2. Porous PTFE membrane

Expanded porous PTFE with high void volume at least of 70%, with a thickness ranging from 10 to 100 μm (40 μm was selected in this experiment), was used. Prior to use, the membrane was immersed with alcohol, then rinsed in nitride acid solution and deionized water.

3.3. Impregnation of electrolyte dispersion

The treated porous PTFE and two metal sheets were put together in a sandwiched structure. The marginal interspace between the nonporous areas of the two metal sheets (Fig. 2) was sealed by a plastic film, also serving as an electrically insulating substrate. The electrolyte dispersion, from DuPont, DE 2021 (total acid capacity, 0.95–1.03 meq g^{-1} , H^+ polymer basis), was impregnated into the pores of the PTFE membrane and the metal sheet. Then it was put in an extremely clean environment and dried at ambient conditions for 3–4 h. Lastly, it was annealed at 130 $^{\circ}\text{C}$ for 30 min. When the solvent was completely evaporated, the layers were bounded together, forming an integrated composite membrane. Then it was protonized by immersing in light boiling 5% sulfuric acid solution for 30 min, followed by rinsing in deionized water.

3.4. Fabrication of membrane electrode assembly

The catalyst ink was prepared by dispersing Pt/C (20%, E-Tek) in alcohol, with additive of Nafion dispersion (5%, DuPont). After well mixed by stirring, it was directly brush-coated onto the surface of electrolyte membrane with a Pt loading of 0.5 mg cm^{-2} in the cathode and 0.2 mg cm^{-2} in the anode. Then the catalyst ink was dried at 130 $^{\circ}\text{C}$ for 1 h.

3.5. Test in small fuel cells

The H_2 /air self-breathing fuel cell was assembled as shown in Fig. 4. An ICMEA with active electrode area of 2 $\text{cm} \times 2 \text{ cm}$

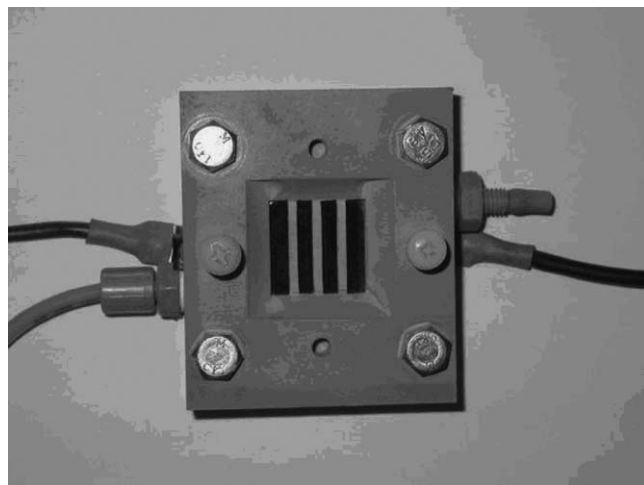


Fig. 4. Air-breathing small fuel cell with ICMEA (cathode side, active area = 2 $\text{cm} \times 2 \text{ cm}$).

was inserted into the fuel cell hardware, which consisted of two plastic end plates. Because we used silicon gasket as seal, the bolt and screw were needed to compress the gasket. This can be eliminated by some further design of seal technology. The cathode side was directly open to the environment. The flow field of the anode was void without any supporting ribs. Pure and dry hydrogen was conducted into it at normal pressure with dead-ended stream. All of the tests were operated at ambient conditions. Current–voltage characteristics were measured using two digital multimeters and a rheostat. Open circuit voltage (OCV) was measured by directly connecting the anode and cathode of the fuel cell to a digital multimeter.

4. Results and discussion

4.1. The porous metal sheet

To reduce the volume and weight of the cell, the metal sheet should be made as thin as possible. But when it becomes thin, it has increased electrical resistance and too flexible to be used as a supporting substrate. The open ratio of the metal sheet is another important factor. In this experiment, the metal sheet was 80 μm thick, with 65 μm width of rib and 165 μm width of channel (as shown in Fig. 2). The open ratio of the sheet is about 72%. The open areas of the metal sheet are equal to the areas of the interfaces between the catalyst layer and the electrolyte membrane. A greater ratio of open areas indicates a larger electrochemically active zone. It is necessary to enlarge the ratio of open area so as to gain maximum power output. But when the ratio of open area becomes large, the filaments of the metal sheet turn thin and mechanically weak. Most importantly, this results in a higher electrical resistance of the metal sheet and higher ohmic losses. If we use metal sheet with pore shape as shown in Fig. 1, the relationship between these factors can be explained and calculated by the equations as follows:

- The voltage drop along the metal sheet can be given by

$$\Delta V = \frac{jL^2(1-r)}{2rt\sigma} \quad (1)$$

- The power wasted on the electrical resistance of metal sheet can be expressed as

$$\Delta P = \frac{j^2L^3M(1-r)^2}{2rt\sigma} \quad (2)$$

- If only the power wasted on the electrical resistance of the metal sheet is considered, the power output can be given by

$$P = VjLM(1-r) - \frac{j^2L^3M(1-r)^2}{2rt\sigma} \quad (3)$$

where L (Fig. 2) is the length of the electrode perpendicular from the current-collector edge, M the length of the electrode normal to L , j the average current density of the active electrode surface normal to the surface and assumed to be uniform, r the ratio of the sum width of metal filaments to the value of M , t the thickness of the metal sheet and σ the electrical conductivity of the metal sheet, and V is the voltage output of fuel cell.

Obviously, the power wasted on electrical resistance is inversely proportional to the value of the conductivity and the thickness of metal sheet. A less value of r indicates a larger electrochemically active area and accordingly higher total power generated. But when the value of r becomes less, the voltage drop along the metal sheet increases. If other parameters are fixed and only the power wasted on the metal sheet is considered, then the value r is equal to:

$$r = L \sqrt{\frac{j}{(2Vt\sigma + jL^2)}} \quad (4)$$

the power output P has maximum value.

We must point out that if we consider the electrical resistance along the catalyst layer, the problem becomes complicated and

some revision is necessary to optimize the parameters. Here we only show the feasibility of the concept of ICMEA.

The metal sheet must be corrosion resistive in the acid and electrochemical environment. So processes of surface-treatment are necessary for a long-term application. We coated Ti metal sheet with Ru layer. Also, other surface-treatment processes can be utilized and explored.

4.2. The process of electrolyte impregnation

It should be precise to control the amount of dispersion impregnated. The void volume of e-PTFE substrate should be filled completely with electrolyte to prevent the mixture of reactive fuel and oxidant. The amount of electrolyte should exceed the value that needed to completely fill the e-PTFE, so as to ensure that the electrolyte membrane can be partly embedded into the through-pores of metal sheet. Thus, the metal sheet and the electrolyte membrane are bounded together. But the amount of electrolyte and the process of impregnation should be controlled so as to prevent the surface of the metal sheet from being coated with a layer of polymer electrolyte which hinders the transport of electron.

4.3. Physical properties of the composite membrane

The composite membrane with metal sheet support is shown in Fig. 5. The membrane has shown good dimensional stability and mechanical strength. Its dimension cannot be easily changed by water soaking or drying. It does not crinkle when wet catalyst ink applied on it, but this often happens with unsupported membranes. Thus, the catalyst layer can be directly applied onto the composite membrane and the catalyst coated membrane (CCM) fabrication can be easily achieved. As a result, the procedures of MEA fabrication become more convenient and suitable to streamlining production.

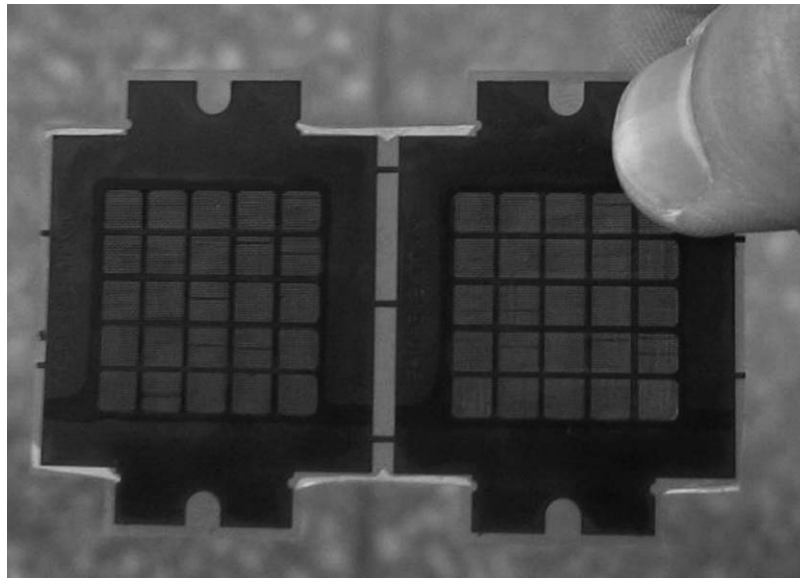


Fig. 5. The ICMEA fabricated (active area = 2 cm × 2 cm).

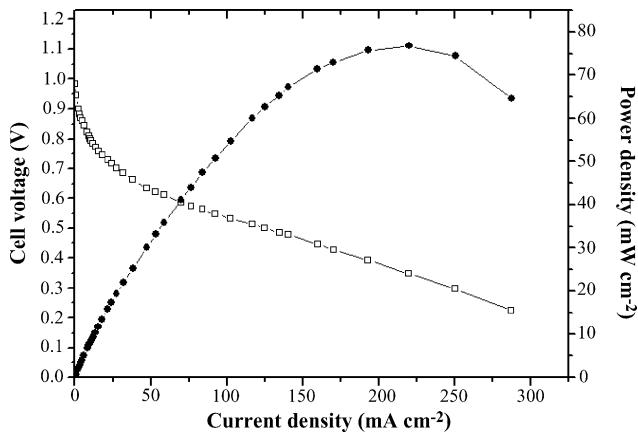


Fig. 6. The performance of ICMEA in air-breathing small H₂/air fuel cell (at ambient conditions, dry hydrogen at normal pressure).

4.4. Performance in small fuel cells

Open circuit voltage and current–voltage characteristics were measured at ambient conditions. The performance of ICMEA in a small fuel cell is shown in Fig. 6. The open circuit voltage of the cell is 0.985 V. The maximum power output of about 80 mW cm⁻² was achieved at voltage of 0.4 V. At 0.6 V, the power obtained is 40 mW cm⁻². There are mainly two reasons to account for the low voltage at the maximum power output: One is the lower pressure of hydrogen and air, the other is due to the high electrical resistance along the metal sheet and the lateral surface of catalyst layer.

The fuel cell with ICMEA was operated continually at a current density of 150 mA cm⁻² for several days. Only a slight degradation of cell performance was recorded. There is no liquid water accumulated on the surface of the membrane and metal sheet on both sides of the cathode and anode. The cathode was directly exposed to the external environment, so water can be evaporated without the restriction of gas diffusion layer. This may lead to water losses during long time operation. The long-term performance of ICMEA needs to be further studied.

5. Conclusions

In this paper, the concept of an integrated composite membrane electrode assembly was proposed. The ICMEA suc-

cessfully fabricated using finely porous metal sheet and e-PTFE substrate was experimentally proved to have some unique characteristics compared with conventional MEA structure:

1. simplification of components, integrating functions of MEA, flow field, and current collector;
2. very thin (about 200 μm), reduction in volume and weight, compact, and lightweight;
3. high mechanical strength, high dimensional stability, suitable for CCM fabrication;
4. low clamping pressure of fuel cell stack;
5. low cost, reduced amount of electrolyte ionomer.

ICMEA has showed acceptable performance in air-breathing fuel cell. The maximum and stable power obtained was nearly 80 mW cm⁻². Better performance of ICMEA can be achieved with optimized parameters for each process. ICMEA is a promising candidate in the application and commercialization of small fuel cells due to its unique characteristics.

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