Fabrication and Testing of a Bi-Conductive Polymer Membrane Fuel Cell

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Abstract. This paper reports the fabrication process and testing of a bi-conductive polymer membrane (BCPM) fuel cell that integrates lateral current collectors on both sides with an ionic conductive path through the membrane. The new membrane shows major advantages over standard Nafion® membranes used in Polymer Electrolyte Fuel Cells (PEMFCs). In addition to being mechanically stable when wet, the flexible BCPM integrates efficient thin film current collectors (ICCs) on an ionic conductive membrane with a high active area ratio. Also, ICCs leave all the surface of the electrode free to eventually integrate a more efficient water and gas management system than traditional gas diffusion layers. Moreover, the fabricated membrane has shown superior volumetric power density than standard PEMFC (0.76 vs 0.47 mW/cm² µm).

1. Introduction

Polymer electrolyte fuel cells (PEMFCs) can deliver simultaneously high energy and power densities while providing power as long as they are supplied by reactants. These characteristics give PEMFCs potential advantages compared to lithium batteries to power small portable devices. At small scales however, packaging and peripheral components tend to dominate the size of the cell while poor water management causes non optimal [1] and unstable performance of the stack [2]. These issues stem from the use of gas diffusion layers (GDLs) simultaneously as current, water and air pathway.

GDLs are an inefficient water management solution for small PEMFCs that usually work in air-breathing mode, since they can only delay flooding or drying [2] without preventing it. Moreover, current is generally drawn from the GDLs with metallic grids, called bipolar plates, which are clamped with screws, bolts or by a hot pressing process to reduce electrical contact resistance [3–6]. This approach leads to bulky packaging and leaves no room on top of the electrodes to place a more efficient water or gas management system.

A better approach is to integrate current collectors directly on the ionic conductive membrane thus eliminating bipolar plates. Photosensitive glass and polymer [7,8] have been successfully used as a substrate but the active area in these designs covered only a very small portion of the total surface. A large pattern (1mm²) etched in an SOI wafer filled with ionic conductor and gold current collectors was used by Zhu et al. [9] to obtain substantial power density. In this case however, reducing the pattern size and repeating it multiple times could reduce electrical and ionic losses significantly.

To minimize low power PEMFCs and uncoupling gas, water and electrical path, a first attempt to fabricate a bi-conductive polymer membrane (BCPM) was described in previous work [10] but didn’t give the expected results. That membrane used polyimide as support material and had a large ratio of active-to-total area. It was the first to integrate lateral electrical conductive layers on both sides with
an ionic conductive path through the membrane. Unfortunately, the process was time consuming and lead to unrepeatable results mainly caused by poor gold adhesion and damaged current collectors during polyimide etching. Moreover, the membrane had gas hermeticity issues due to poor ionic conductor filling of the holes.

Therefore, an improved fabrication process of the BCPM is presented. The final device integrates on the same polymer sheet; mechanical support, ionic conduction and current collection while providing low ionic and electrical resistance and high active area ratio. The membrane is a 50µm thick patterned polyimide sheet (Kapton 200HN, Dupont®) between two Integrated Current Collectors (ICCs) consisting of metallic thin films (chromium, gold and titanium). The active area of the membrane is a square of 0.25cm$^2$ covered at 20% by through holes. Dimensions were selected to reduce ionic and electrical resistance while easing fabrication.

![Figure 1 - Isometric cut view of the Bi-Conductive Polymer Membrane (BCPM)](image)

In this work, we report the fabrication techniques that have been used to achieve the desired configuration and the characterization of the final device. The hermeticity, mechanical stability and efficiency of the ICCs are first tested. Then, the performances of the BCPM fuel cell are measured and compared to a standard PEMFC.

2. Fabrication process

The fabrication process of the BCPM (Figure 2) is subdivided in five major steps: ICCs deposition (Figure 2a-f), holes etching (Figure 2g), Nafion filling (Figure 2h-i), Nafion excess removal (Figure 2j-k) and electrode spray coating (Figure 2l). To solve the problems of gold adhesion, damaged ICCs and Nafion filling encountered in the first fabrication approach [10], two major changes have been made. First, metal wet etching and oxygen plasma etching of Kapton have been replaced by one quick and simple step of laser etching. This allows the use of an adhesion layer for gold in addition of being fast, low cost and repeatable. Secondly, a shear stress removal technique has been developed to remove excess Nafion and exposing the conductive layers while keeping the holes filled.

To start, a layer of α-gel (Taica®) 0.5mm thick thermo-conductive rubber is laid on a silicon substrate (Figure 2a) and a Kapton 200HN sheet (50µm thick, Dupont®) is rolled on top of it (Figure 2b). Three metallic layers are then evaporated in the same step; chromium (30nm) serves as an adhesion layer for the gold conductive layer (300nm) and titanium (30nm) protects the gold in the subsequent steps. The metallized Kapton is peeled-off (Figure 2d) and cleaned with acetone and ethanol. The membrane is flipped over (Figure 2e) and the evaporation process is repeated (Figure 2f). The metallized membrane is removed from the α-gel and prepared for laser etching.

Holes of 25µm in diameter separated by 25µm are etched with an excimer laser (Protolaser U3, LPKF) through the metallic and polymer layers on a 5mm x 5mm area of the metallized Kapton (Figure 2g).
The 10,000 holes must be completely filled with Nafion to ensure ionic conductivity through the membrane and to prevent gas leakage from the anode to the cathode. To do so, the membrane is reattached to a silicon substrate using Kapton tape and Nafion in solution (Liquion™ 15% wt, IonPower) is deposited on the metallized Kapton surface (Figure 2h). After a 30s vacuum, the assembly is put on a hot plate at 60°C for 30min and IPA drops are periodically added to the Liquion to dilute it and prevent cracking. The temperature is then raised to 100°C for 15min to eliminate all solvent (Figure 2i).

A 10min soaking in DI water (Figure 2j) softens the Nafion and makes it easier to remove by a shear stress technique. A 23µm thick sharp blade is inserted underneath the excess Nafion layer and is slid over the etched area (Figure 2k).

To complete the fuel cell, porous electrodes are deposited both sides of the membrane. A mix of Pt/C, carbon black, Liquion and IPA is sprayed on both sides of the membrane, following standard procedures [11] (Figure 2l).

3. Experimental Characterisation

After the Nafion shear stress removal step (Figure 2k), the etched region of the membrane is observed with SEM to evaluate the efficiency of the removal technique. Figure 3a shows that the metal layer that forms the ICC is free of Nafion while the holes seem to be entirely filled. This is also confirmed with a cross-section view of a filled hole (Figure 3b). Afterwards, a differential pressure test validates that the membrane will not allow gas leakage from the anode to the cathode. A four point probing station was also used to validate the electrical conductivity of the ICCs to ensure that its surface is indeed free of Nafion.

Mechanical stability in water of the BCPM is confirmed by immersing it in DI water for 10min and visually comparing the dry and wet states. The results show (Figure 3c) that the BCPM is not mechanically affected by water which is not the case for standard PEMFC that is substantially deformed when in contact with water.
Finally, polarization curves of the BCPM with two modes of current collection are performed to validate the efficiency of ICCs. First, traditional current collection normal to the electrodes using bipolar plates is used to draw the current from the top of the electrodes instead of using the ICCs as a reference condition (Figure 4a). Then, measurements are also taken for the same fuel cell but using the ICCs to extract the charges laterally and collect them at the periphery of the BCPM. In this case, the bipolar plates are electrically isolated from the fuel cells electrodes and are only used to ensure comparable gas flows and operating conditions (Figure 4b).

By comparing the polarization curves of these two collection modes (Figure 5), it is possible to see that there are no major discrepancies in output voltage or power of the BCPM. Therefore, no additional ohmic losses are generated by ICCs.

4. Comparison with standard PEMFC
The performance of the BCPM can be compared to a standard PEMFC in the same working conditions (Table 1). The PEMFC is made from a 25.4µm thick Nafion membrane (Membrane XL, Ion Power...
(inc.) with the same electrode recipe as for the BCPM. Both membranes were tested in the test bench setup showed at figure 4a and their maximum power density was determined.

|                        | New BCPM | Standard PEMFC |
|------------------------|----------|----------------|
| Surface Power Density  | 76       | 223            |
| (mW/cm²)               |          |                |
| Typical Thickness      | ~100     | ~600           |
| (µm)                   |          |                |
| Volumetric Power Density| 0.76     | 0.37           |
| (mW/cm² µm)            |          |                |

Table 1 shows that surface power density of BCPM is about 3 times lower than for PEMFC. This is mostly explained by the 10 times higher ionic resistance of the BCPM caused by the membrane thickness difference and that only 20% of BCPM cell area is covered with Nafion. Since some applications have surface limitations, surface power density of the BPCM could eventually be improved by bringing holes closer to each other thus increasing Nafion coverage. Low surface power density of BCPM is compensated by the presence of ICCs, which reduce its total thickness. For PEMFC, current collectors must be added to the thickness of the membrane to properly compare volumetric power densities. Here, current collectors were considered as two silicon wafers of 250µm bonded from each side of the membrane [5], a solution commonly used in microfabrication. In this scenario, BCPM volumetric power density is found to be twice as high as PEMFC. This validates the assumption that BCPM could help to improve the power density of a fuel cell stack.

5. Conclusion
The Bi-Conductive Polymer Membrane Fuel Cell presented in this work showed better volumetric power density than standard PEMFC (0.76 vs 0.37 mW/cm²µm) while being flexible and stable in water, making it easier to integrate in a microfabrication process. Also, the fabrication process of the membrane is simple and can potentially be used in large scale production. For the first time, current collectors have been integrated directly on an ionic conductive membrane with a high active area ratio and tested successfully. Moreover, the ICCs did not add ohmic losses, leading the way to a complete re-thinking of PEMFC packaging. Since gas diffusion layers are no longer required in the current path, ICCs leave all the top surface of the electrodes available to integrate a water management system that will better suit the needs of small air-breathing fuel cells.

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