MINIATURE FUEL CELL WITH MONOLITHICALLY FABRICATED SI ELECTRODES
- ADHESION BETWEEN ELECTRODES AND PEM -

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Abstract: In this study, peak output of our miniature fuel cell was raised to 420mW/cm^2 which is comparable to the conventional large scale fuel cells. We have proposed monolithically fabricated Si electrodes for miniature fuel cells, on which porous Pt catalyst layer and fuel channels are formed on a Si wafer. Although our past prototype cells demonstrated relatively high outputs among MEMS based miniature fuel cells, compared with conventional large scale cells, performance was poor. In this study, in order to make spatial non-uniformity of the cell structure conspicuous, reaction area of the fuel cell was reduced to 1mm^2. Some cells showed high outputs though the majority showed little output. It was suggested that the adhesion between electrode chip and PEM (Polymer Electrolyte Membrane) was not tight. The electrode chip has a depression on the catalyst area. Two sheets of PEM were placed on the catalyst area to realize tight contact and increased output was obtained.

Keywords: miniature fuel cell, porous Si, plating, plasma etching, MEMS

INTRODUCTION

Portable electronic devices have driven research toward small electric power sources. At this point, Li ion batteries are widely used in the portable devices. Although the performance of the batteries are still increasing, recent accidents, such as explosion of the batteries, may suggest that we are facing difficulties in further improvement of the Li ion batteries. Then, fuel cells have attracted large attention as ultimate portable power sources. Prototypes have been demonstrated by many research groups and some of them seem to be fit for practical use. But, no miniature fuel cells are available in a usual consumer market yet. There may be problems in production cost and mass productivities. While in the recent trend, technology toward clean energy system needs to be developed. Fuel cells are considered as key technology in the hydrogen energy cycle system. The portable miniature fuel cell will be attractive devices in various fields when the hydrogen energy cycle is realized.

For the practical application, further miniaturization will be still needed in the miniature fuel cell field. MEMS (Micro Electromechanical Systems) fabrication technology is an important tool to reduce the fuel cell structure to micrometer scales and is advantageous for mass production. Therefore, a lot of studies for fuel cell miniaturization using MEMS techniques were made in these several years [1-12]. In most of those studies, conventional catalyst layers, in which carbon black with catalyst metal particles is splayed, were used. However, MEMS fabrication techniques treat basically monolithic structures and treating powders such as carbon black is not preferable. In order to adapt the construction process

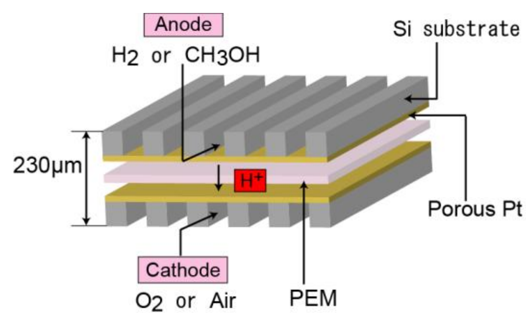

Fig. 1 Schematic view of the Si based fuel cell

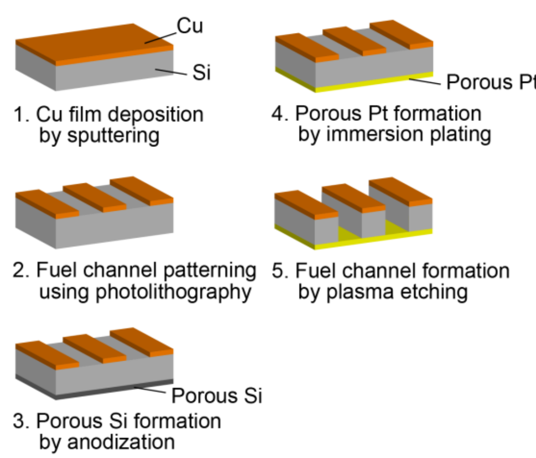

Fig. 2 Fabrication process of the monolithic electrode

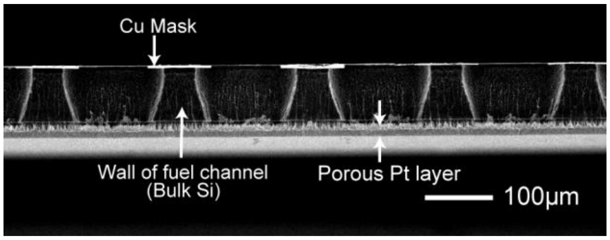

Fig. 3 Cross sectional SEM image of the Si electrode after plasma etching.

to more MEMS fabrication procedures, various approaches were attempted. Recently, some attempts with SOFC (Solid Oxide Fuel Cell) showed fairly good outputs [12], but the performance of the MEMS based fuel cells was generally poor.

Recently, we discovered that a porous Pt layer can be obtained by just immersing high porosity porous Si into a Pt plating bath containing HF [13]. Using the porous Pt as a catalyst layer, we built novel fuel cell electrodes [14]. On the electrodes, fuel channels were etched after forming the porous Pt catalyst layer and the catalyst layer was expected to work as a stopping layer of plasma etching. Then, through-chip porous Pt layer were successfully fabricated and monolithic fuel cell electrodes were demonstrated. Prototype cell showed a relatively high output of 108mW/cm^2 in the last PowerMEMS2008. But the performance was far from practical application and continuous efforts have been paid for improvements. In these studies, reproducibility of the cell output was poor and it was difficult to find out the cause of the poor performance.

In this study, in order to eliminate the effect of spatial non-uniformity of the cell structure, reaction area was reduced to 1mm × 1mm from 3mm × 3mm and attempted to find out the dominant cause of the poor performance.

CELL FABRICATION

The fuel cell design we proposed is shown in figure 1. The electrode plate has quite simple structure, in which catalyst layer and fuel channels are monolithically fabricated on a Si wafer. A highly doped Si wafer, that has low resistivity, works as a current path. PEM (Polymer Electrolyte Membrane) is hotpressed with two Si electrodes using Nafion solution as an adhesive. Thickness of the Si wafer is about 100µm and the total thickness of a cell can be less than 230µm. Figure 2 shows the fabrication procedure. After removing oxide by HF, copper thin film is deposited on the Si wafer by sputtering. Using usual photolithographic patterning with photoresist and wet etching, fuel channel mask is made on the copper film for plasma etching. Cu mask pattern prepared in this study has 5 × 5 openings in a 1mm × 1mm region. The shape of the openings is a square 100 µm on a side. Porous Si layer is formed on the opposite side of the Si wafer by anodization in an electrolyte containing HF. The porous Si layer is subsequently submerged in a Pt plating bath and porous Pt layer is obtained. Detailed description about porous Pt layer formation can be seen in ref. [13]. Fuel channels are opened by applying plasma etching on the backside of the porous Pt layer with the copper film mask. Conventional parallel plate reactive etching system is used, and SF_6 and O_2 gases are used for the etching. In this plasma etching process, porous Pt layer is supposed to work as a stopping layer of the etching, because the etching rate is low at the porous metal layer, and through-chip porous Pt layer can be relatively easily fabricated.

Table 1 Outputs of 4 prototype cells with 1mm × 1mm reaction areas.

Fuel cells	Output power
cell #1	141 mW/cm^2
cell #2	less than 1 mW/cm^2
cell #3	less than 1 mW/cm^2
cell #4	less than 1 mW/cm^2

RESULTS AND DISCUSSION

Figure 3 shows a cross sectional SEM image of the monolithically fabricated Si electrode. Through chip porous Pt catalyst layer was successfully built as we intended. Using those electrode chips, four prototype cells were constructed with identical fabrication procedures and power generation tests were performed with H_2 and O_2 feeds at 313K. Table 1 shows peak outputs of the 4 prototype cells. Three of four cells had almost no power output, while the rest one cell showed large output which was the highest performance at that point among our prototypes. Therefore, the poor reproducibility was supposed to be caused by some spatial non-uniformity.

Though microscopic observations were carefully performed, we could not find obvious characteristic differences from outside view. We also have attempted cross sectional observation of the prototype cells. But due to the material nature of brittle Si and flexible PEM sheet, fine cross sectional edge is not available and no meaningful information is obtained yet. Then we discussed about the major factor of the non-uniformity and the thickness of the porous Pt catalyst layer was focused. It had been noticed that the thickness of the porous Pt layer tends to decrease from the original porous Si layer by some SEM

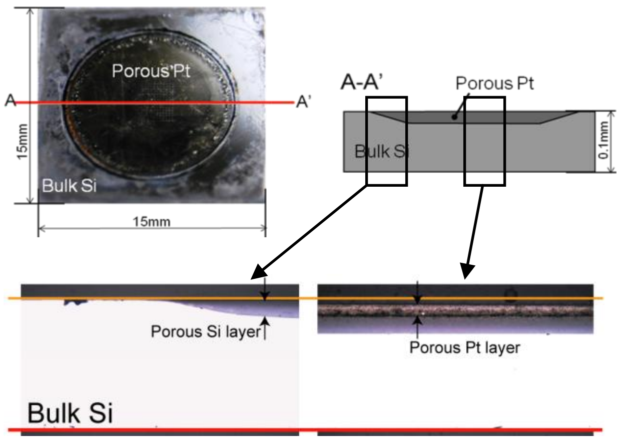

Fig. 4 Cross sectional images of the Si chip with catalyst layer.

observations, but we did not have quantitative data because the precision of the SEM length scale is not reliable.

In order to estimate the shrinkage of the porous layer by Pt deposition, a specimen chip which has the porous Pt catalyst layer was mounted in a resin and cross section was observed by an optical microscope. Figure 3 shows the result. It is obvious that the thickness of the chip became thinner on the porous layer area and it was found that the originally flat Si electrode chip had a depression on the porous catalyst layer. The depth of the depression was about 6 μm. Two electrode chips are used for constructing cells and total 12 μm gap might be formed in the cells.

DOUBLE PEM TREATMENT

As shown in figure 5, the electrode surface was supposed not to be level. Though Nafion solution is used as an adhesive between the Si electrode and PEM, it is supposed that the 12μm gap is large and the adhesion between the catalyst layer and PEM sheet might be insufficient. Thickness of the PEM used in this study is about 15μm which is close to the estimated gap of 12μm. In order to improve the contact between the catalyst layer and PEM, we placed 2 sheets of PEM on the catalyst layer as shown in figure 6. Then, a new prototype cell was fabricated.

Figure 7 shows the polarization curve obtained by the prototype. Peak output of 420mW/cm^2 was obtained at 313K with H_2 and O_2 feeds that is comparable to the conventional large scale fuel cells. Figure 8 shows a demonstration of two cell series connection with plastic casings. In an open circuit condition, each cell showed more than 900mV. Both cell showed about 600mV with LED.

Thickness of our prototype cell is only 230μm and large power density of 16W/cm^3 can be expected if

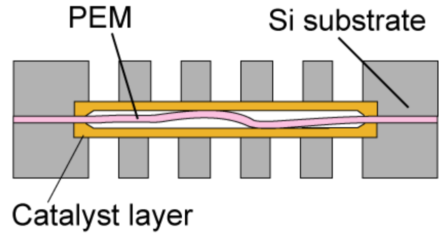

Fig. 5 Insufficient contact between the electrode and PEM.

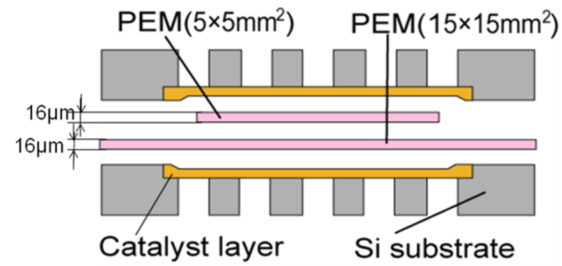

Fig. 6 Putting two sheets of PEM on the catalyst layer to fill the gap.

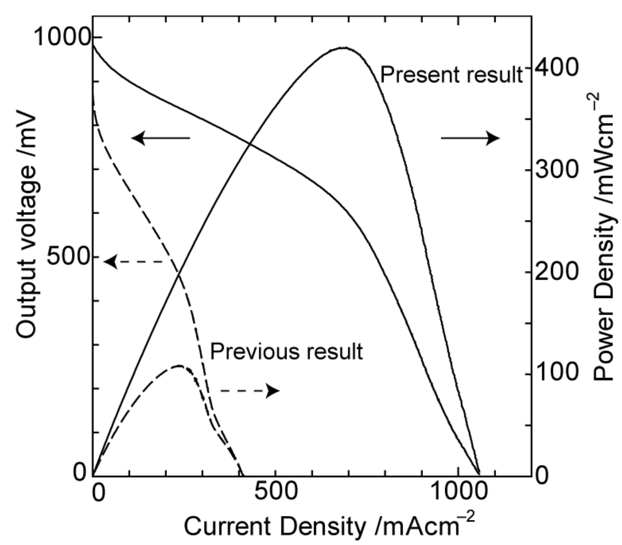

Fig. 7 Polarization curve of the double PEM prototype with H_2 and O_2 feed at 313K.

the stacking is made without loss. This result seems quite promising. However, the usage of Pt is large and the life time is unknown. Further study will be needed to make our miniature fuel cells more practical.

CONCLUSION

In order to find out major factor of the poor performance of our miniature fuel cells, reaction area was reduced to 1mm^2. Three of the four prototype cells showed little output, but rest one cell showed the highest output at that time. As a cause of the poor performance, poor contact between catalyst layer and PEM was focused, because gap between catalyst layer and PEM might be formed by the porous layer shrinkage. In order to avoid the gap, double PEM treatment was applied. The new prototype showed the highest peak output of 420mW/cm^2, which is comparable to the large scale conventional fuel cells. Large power density of 16W/cm^3 can be expected and the high potential of the miniature fuel cell was demonstrated.

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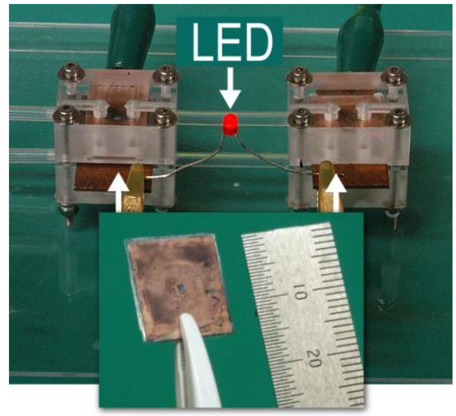

Fig. 8 Series connection was demonstrated with two prototype cell with 1mm^2 reaction area.

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