Miniature Fuel Cell with Monolithically Fabricated Si Electrodes
-Reduction of Pt Usage by Pd-Pt Catalyst-

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Abstract: A new Pd-Pt catalyst was discussed for reduction of Pt usage in our miniature fuel cells. Although our prototype cell showed high output among MEMS fuel cells, porous Pt was used as a catalyst layer and Pt usage was quite large. In order to reduce Pt usage, we attempted to deposit Pt on porous Pd. Using the Pd-Pt as anode catalyst, prototype cells were made and maximum output of 520mW/cm² at 313K, which was the highest in our study, was obtained. Pt usage was estimated to be less than 0.4mg/cm² and significant reduction of Pt usage was demonstrated.

Keywords: fuel cell, PEFC, porous silicon, MEMS, porous Pd, porous Pt

INTRODUCTION

High performance power sources are desired along with widespread use of electronic and electric devices. At this point, Li ion batteries are widely used as the power source. However, those batteries need charging, which interrupts continuous use of the devices. Besides, it is becoming difficult for the batteries to satisfy required storage capacity, because of the increasing power consumption with advances of the device function and performance. Then, miniature fuel cells have been studied actively by various groups.

For practical use, production cost and mass productivity are important and MEMS techniques are promising for the fuel cell miniaturization because of the good mass productivity. Therefore, various studies using Si substrate and MEMS techniques have been performed [1-10]. Recently, we employed a novel catalyst layer fabrication process, in which porous Pt layer was formed on a Si substrate by using anodized porous Si as a base material [11], and fuel cell electrodes were produced monolithically with Si substrates [12].

Schematic view of our fuel cell is shown in figure 1. Porous Pt layer, which works as a catalyst layer, was synthesized on a Si substrate by immersing porous Si into a Pt plating solution containing HF. Then, fuel channels were opened by applying plasma etching on a back side of the porous Pt layer. Porous Pt layer worked as an etching stopping layer and a through-chip porous Pt layer was made. Two Si electrodes were hot-pressed onto either side of a PEM (Polymer Electrolyte Membrane) and prototype fuel cells were made. Our prototype had only 230µm in thickness and showed relatively large output. at the last PowerMEMS 2009, we reported maximum output of 420mW/cm² at 313K with H₂-O₂ supply [13]. However, porous Pt was used as a catalyst and Pt usage was quite high. Estimated usage was 3.6mg/cm², which is only 0.1mg/cm² in conventional fuel cells.

In our fuel cells, porous Pt works not only as a catalyst, but also as a current path. It is assumed that most of Pt does not contribute to the catalyst activity. Therefore, in order to reduce the Pt usage, we discussed about making a porous conductive layer with other metal and depositing small amount of Pt on the porous metal layer as shown in figure 2. At this point, porous Au, Ru and Pd can be formed monolithically on a Si substrate. Those noble metals are still expensive, but cheaper than Pt. As a first trial, we employed Pd. After porous Pd formation, it is supposed that Pt can be deposited on Pd by galvanic displacement. In this study, fabrication of porous Pd-Pt layer and its application to our monolithic fuel cell structure were attempted.

Fig. 1: Schematic view of the miniature fuel cell and the cross section of monolithic fuel cell Si electrodes.

Fig. 2: Strategy for Pt usage reduction. Using ionization tendency difference, Pt can be deposited on a porous Pd.
FABRICATION PROCESS

Figure 3 shows a schematic view of the Si electrode fabrication process. Fabrication procedure follows the previously developed one for the porous Pt catalyst structure described in reference 13. Application of the porous Pd-Pt is a challenge in this study.

Cu Mask
At first, patterned Cu film is prepared on a Si chip. The Cu film works as a current path for anodization and a mask for plasma etching. Si substrate is a 15mm × 15mm chip diced from 4 inch wafer. Cu thin film is deposited by physical vapor deposition. Then, usual photolithographic patterning is applied on the Cu thin film. The mask pattern has 1mm × 1mm square region, in which 100μm × 100μm square openings are made as shown in figure 4.

Porous Pd Formation
Porous Pd is formed basically same way as our porous Pt layer formation described in reference 11. Si substrate is anodized in a solution containing HF and porous Si is formed. Then the porous Si is immersed in a Pd plating solution. In the plating bath, Si works as a reducing agent. Pd ion is reduced on Si surface and Pd particles deposit, while Si is oxidized. Oxidized Si is removed by HF added in the plating solution. The reaction continues until almost all Si is dissolved and the porous Pd layer is formed.

Many efforts were made to find conditions for obtaining utilizable porous Pd layer. Table 1 shows the conditions used in this study.

The Si chip is put in a fluorocarbon polymer vessel and anodization is performed. Anodization current is supplied by contact pins to the patterned Cu film on the backside of the Si chip. A Pt wire is used as a counter electrode. After porous Si formation, anodization electrolyte is removed from the vessel and a dilute NaOH solution is poured into the vessel.

It is known that anodized porous Si layer has a small pore top layer, which is different from main porous layer underneath. The top layer tends to form dense metal film during the immersion plating. Therefore, the top layer is removed by the NaOH etching. After NaOH etching, specimen chip is rinsed by acetone to avoid oxidation by water.

Immediately after the top layer etching, Pd plating solution is poured into the vessel and agitation is applied by a homemade syringe pumping equipment. Pd deposition is performed for 20min and the porous Pd is obtained.

Pt Deposition on Porous Pd
After the porous Pd formation, plating electrolyte is switched for Pt deposition. For Pt deposition, H₂PtCl₆ solution consisting Pt(IV) ion and H₂PtCl₄ solution consisting Pt(II) ion were prepared. After 5min of immersion, specimen chip is carefully rinsed by acetone.

Fuel Channel
Fuel channels are opened by plasma etching on the opposite side of the porous Pd-Pt layer with the Cu thin film mask. Conventional parallel plate reactive ion etching system (Samco RIE-10N, Japan) is used and 18sccm of SF₆ and 4sccm of O₂ gases are supplied for the etching. In this plasma etching process, porous Pd-Pt layer is supposed to work as an etching stopping layer, because the etching rate is assumed to be quite low at the porous metal layer. Therefore, the through-chip porous Pd-Pt layer can be fabricated relatively easily.

Table 1: Condition for porous Pd-Pt layer formation

<table>
<thead>
<tr>
<th>Property of Si substrate</th>
<th>Crystal Orientation</th>
<th>Type</th>
<th>Thickness of Si substrate</th>
<th>Resistivity [ȍcm]</th>
<th>Composition of solution</th>
<th>Current density [mA/cm²]</th>
<th>Time [s]</th>
<th>Composition of solution</th>
<th>Temperature [K]</th>
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<tr>
<td></td>
<td>(100)</td>
<td>N</td>
<td>100μm</td>
<td>0.004-0.006</td>
<td>Water:HF(46%):Ethanol=5:3:2</td>
<td>90, 0</td>
<td>620</td>
<td>20mM NaOH</td>
<td>283</td>
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<td>Anodization condition</td>
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<td>Alkali etching condition</td>
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<td>Pt immersion plating condition</td>
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Prototype Assembly

For electrical contact, a thin gold layer at the border of the catalyst layer was formed as described in our previous work (ref. 11), because direct electrical contact between the porous catalyst layer and silicon is poor. Then, two Si electrodes are hot-pressed onto either side of a PE. The PEM used was a TSF-1301 obtained from Toagosei Co. Ltd. (Japan). In order to obtain good contact between the catalyst layer and PEM, the double PEM treatment [13] is employed.

RESULT AND DISCUSSION

Porous Pd-Pt Layer

Cross sectional images of the porous Pd-Pt layers are shown in figures 5 and 6. EDS (Energy Dispersive X-ray Spectroscopy) analysis was also performed and atomic ratio was measured at several points as shown as A, B in figures 5 and 6. Table 2 shows the result. It was found that the porous Pd layers do not have obvious damages after the Pt deposition and it was supposed that the obtained porous Pd-Pt layer could be used for the miniature fuel cells. Difference with Pt sources could not be seen obviously from both SEM images and EDS data.

Table 2: Atomic ratio of the porous layer by EDS quantitative analysis. Two points at A, B in figure 5 and figure 6 were measured.

<table>
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<th>Pd[At%]</th>
<th>Pt[At%]</th>
<th>Si[At%]</th>
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<tr>
<td>Pd+Pt(IV) A</td>
<td>80</td>
<td>15</td>
<td>5</td>
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<tr>
<td>Pd+Pt(IV) B</td>
<td>85</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>Pd+Pt(II) A</td>
<td>76</td>
<td>16</td>
<td>8</td>
</tr>
<tr>
<td>Pd+Pt(II) B</td>
<td>91</td>
<td>0</td>
<td>9</td>
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</table>

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EDS data largely depends on the surface condition and sometimes the atomic ratio is not correct. Then, we attempted to estimate the Pt usage by measuring Pt ion concentration in plating solutions before and after the Pt deposition. Absorption spectrophotometry was performed and the estimated Pt usage was 0.16 mg/cm² with Pt(IV) and 0.36 mg/cm² with Pt(II) respectively. Pd usage could not be estimated by the spectrophotometry at this point, because the Pd plating solution does not have clear adsorption band. Further study will be needed to determine the Pd usage quantitatively.

Power Generation Test

Cathode reaction (O₂ side) needs higher catalytic...
activity and anode reaction is easier. As a first step, the new Pd-Pt catalyst was used only in the anode (H2 side) and the conventional porous Pt catalyst was used in the cathode. Pd also has a catalytic activity for H2 oxidation. Three prototypes were prepared. First one had a simple porous Pd catalyst. Second one had the porous Pd-Pt catalyst with Pt(IV) source. Third one had the porous Pd-Pt catalyst with Pt(II) source. Prototype cells were set into the aluminum casing and power generation tests were performed in a temperature controllable chamber. 10sccm of H2 and 5sccm of O2 were fed to the anode and cathode respectively.

Figure 7 shows the polarization curve of the prototype cells at 313K. Relatively high output of 350mW/cm2 was obtained with the porous Pd catalyst (red). With Pt deposition, much higher output of 400mW/cm2 and 520mW/cm2 were obtained with Pt(IV) and Pt(II) sources respectively. 520mW/cm2 at 313K is superior to the previous prototype output of 420mW/cm2 reported at the last PowerMEMS 2009 and is the highest output among our miniature fuel cells. Figure 8 shows the polarization curve obtained at 343K. All three prototypes show higher output than the one at 313K as usual fuel cells.

Then, the Pd-Pt catalyst was also examined in both anode and cathode. Figure 9 shows the result with black lines. The porous Pd-Pt catalysts with Pt(IV) source were used in both electrodes. Green line is the identical result to the green one in figure 7 and is drawn just for comparison. In the small current density range, green line showed better performance. But black line showed higher peak output. These differences can be caused by poor reproducibility, porous morphology that has impact on flooding, or other factors. Further study will be needed for discussion about the catalyst activity. Anyway, even in the cathode use, the new Pd-Pt catalyst showed satisfying peak output that is comparable to the one obtained by our previous prototype (420mW/cm2).

The reproducibility of the cell production is not satisfying at this point and the comparison is not easy. But it can be said that the new Pd-Pt catalyst have at least comparable catalyst activity to our conventional porous Pt catalyst.

CONCLUSION

In this study, a new Pd-Pt catalyst was discussed for reduction of Pt usage in our miniature fuel cells. After porous Pd layer formation, Pt was deposited by galvanic replacement reaction and the Pd-Pt catalyst was made. Two Pt sources of Pt(IV) ion and Pt(II) ion were tested for Pt deposition. The Pt usage was estimated to be 0.16mg/cm2 and 0.36mg/cm2 with Pt(IV) and Pt(II) respectively. The prototype cells with the new Pd-Pt catalyst showed higher output compared to the conventional porous Pt catalyst whose Pt usage was 3.6mg/cm2. Significant reduction of Pt usage was demonstrated by the new porous Pd-Pt catalyst structure. Further study about durability and more inexpensive material use will be needed for practical application.

REFERENCES