NAFION SPIN COATING INSIDE NANO/MICRO STRUCTURED CATHODE FOR THREE-PHASE INTERFACE CONTROL IN MICRO-DMFC

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Abstract: A high surface area and micro process integrated cathode for μ-DMFC is introduced in this study. CNTs growth inside micro structured cathode for catalyst support was employed for reaction surface increment, while liquid Nafion spun into radial arranged micro reaction holes controlled by centrifugal force was carried out to provide proper immersion ratio of CNTs in Nafion. The process is all integrated by MEMS process and the device is expected to improve proton transport and oxygen reaction efficiency over traditional carbon cloth based DMFC systems.

Key words: Micro-DMFC, Micro-structure, CNTs

1. INTRODUCTION

Owing to the high theoretical energy density, there is a high potential for the micro-DMFC (μ-DMFC) embedded into the portable electronic devices. In order to integrate successfully, the size of DMFC must be reduced to a proper scale to be carried more flexible. By the progress of MEMS technology, high performance μ-DMFC can be easily achieved1-4. However; to operate μ-DMFC, both the anode and cathode reaction should be processed smoothly. At the anode, methanol should be delivered successfully and the CO2 must be removed quickly. At the cathode, oxygen should be supplied continuously and the H2O product must be eliminated soon. In other words, both the two electrodes include liquid and vapor phase dynamics. In fact, MEMS technology is an excellent tool to manipulate the micro scale issues. Therefore; MEMS technology not only can fabricate μ-DMFC but also overcome the problems in μ-DMFC.

In this study, a high surface area anode structure with radial pattern was designed to improve the diffusivity of oxygen at the anode. A silicon based structure was fabricated by lithography and deep reactive ion etching (DRIE) technique5. Carbon nanotubes (CNTs) were employed as the electrode. Catalyst (Pt) was loaded on the CNTs by chemical reduction method. Proton exchange membrane was first dropped in the CNTs matrix and dispersed by centrifugal force. Finally; a cathode structure with high 3-phase interface was constructed.

2. EXPERIMENTAL

The experiment was started with a P-type (Boron doped) Si (100) wafer. Si wafer was first cleaned by acetone and isopropyl alcohol. Afterward, the first pattern was transferred on the wafer by lithography technique. The wafer was then etched 400μm by DRIE to form a shallow container shape. Consecutively, a radial pattern was then transferred on the other side of the wafer. Finally, the DRIE process was then employed again to complete the structure. After the structure was fabricated, the metal layers for CNTs growth were deposited sequentially by sputtering technique. The metal layers were Aluminum(Al), Tatinium(Ti) and Nickle(Ni) separately. Al was used for electron conduction, Ti was used to improve the adhesion of CNTs and Ni enacts the catalyst for CNTs growth. The CNTs was grown by thermal CVD system. The detail of the process is shown as Fig 1.

Fig 1 The fabrication process of the radial patterned cathode structure.
After CNTs were successfully grown on the wall of the structure, Pt catalyst will be deposited on immediately. To deposit Pt successfully, the CNTs need to be hydrophilized in 6M H$_2$SO$_4$ at 80°C for 1 hour first. Then the sample with hydrophilic CNTs was immersed into the solution of 0.04392mg H$_2$PtCl$_6$ and 100 ml 3M ethylene glycol(EG) and heated from room temperature(25°C) to 160°C for 3 hours to deposit Pt on the CNTs via a reduction process. Cyclic Voltammetry (CV) was then employed to identify the catalyst character. The test condition is 0.5 M H$_2$SO$_4$ electrolyte, SCE reference electrode, scan from -0.25V~1V by 50mV scan rate.

The next step is to construct the half cell structure. 20% liquid Nafion was dropped into the structure to interconnect pt and CNT to form 3-phase boundary. Since the dimension of the structure is in the order of micro scale, liquid Nafion will be trapped in the hollow structure due to surface tension, as shown in Fig 2(a). If the trapped Nafion cannot be removed, the cathode fuel, oxygen, will spend more time to diffuse to the 3-phase boundary. In general; the liquid phase solution can moving as a radial path when it was spun on a flat substrate as a result of centrifugal force. Therefore, the purpose of the radial structure is to release the space of the structure via a spinning process. The dispensable Nafion could be spun out of the structure along the radial path and then the Nafion which covers the CNTs electrode will be reduced, hence the diffusion time of oxygen from ambient to the 3-phase boundary at cathode could be reduced. Fig 2(b) is the scheme of the structure after spinning process. Theoretically, the amounts of Nafion can be adjusted by rotation speed. Thus, three conditions, 1000, 2000 and 3000RPM, were compared in this experiment.

The full cell can be completed by hot pressing 2 electrode structure with solid Nafion. Fig 3 shows the idea of the cell structure.

3. RESULTS AND DISCUSSION

The CNTs profile on the side wall of the structure is shown as Fig 4. The CNTs are well distributed along the side wall and length of the CNTs is about 8-10µm. The SEM image after Pt deposited is shown as Fig 5. Pt particles can be clearly identified from the insert, and it seems that the particles prefer to aggregate at the top of CNTs. EDX analysis has also been employed to examine the elements on CNTs. The signal shows that there are 100wt% Pt on the top of CNTs and 65.64wt% Pt, 28.51wt% Carbon and 5.84wt% Si at the root of CNTs. Table 1 shows the detail of the EDX results.
Table 1 Element analyzing at the top and the root of CNTs.

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<tr>
<th>Elements</th>
<th>Top</th>
<th>Root</th>
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<tbody>
<tr>
<td>C</td>
<td>49.51</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td></td>
<td>5.84</td>
</tr>
<tr>
<td>Pt</td>
<td>0.108</td>
<td>65.44</td>
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<tr>
<td>Total</td>
<td>100</td>
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The CV testing results as shown in Fig 6. It is clear that the Pt exactly react with the solution. The loading of the Pt is about 0.108mg. The current density shown in Fig 6 is the current divide by the projection area instead of the real area.

Fig 6  Cyclic voltammograms for 0.5M H2SO4 solution.

After liquid Nafion had been dropped into the structure, the distribution of Nafion with different treatment was observed by SEM. Fig 7 shows the Nafion distribution without any treatment. Definitely, the Nafion blocks the channel. After spinning treatment, the channel had been released obviously as shown in Fig 8. Fig 8 also shows the detail of Nafion in CNTs on the structure wall. Three different locations A, B and C represent the center, intermediate and peripheral along the channel separately. It could also be found that the immersion ratio of CNTs in Nafion was reduced under higher spinning speed as indicated by the dash line. With more Nafion spun out from the channel, not only the channel can be released but the Nafion which covers the catalysts will be diminished. Namely; the diffusion length of oxygen from environment to the catalyst can be reduced and the cathode reaction efficiency could be promoted.

Fig 7 Nafion distribution in the structure without any treatment.

Fig 8 The Nafion distribution under different rotation speeds, 1000/2000/3000rpm, respectively. Three different positions at (A)center(B)intermediate and (C)periphery.

Fig 9 The comparison of Nafion thickness in different rotation speed and position.

The activity of catalysts which covered by different Nafion thickness was examined by CV analyzing. Two conditions, 2000rpm and 3000rpm, were compared in Fig 10. The Pt characteristic in H2SO4 can be observed in both the samples. It is clear that the condition with thinner Nafion which displays the better performance. It could be attributed to that the higher ratio of Pt emerge from the CNT accompany with the thinner Nafion coating. Therefore; the sample with thinner Nafion reveals the higher current density in CV testing. The result can imply to
that if the sample with higher speed while Nafion is spinning in, it could perform the better efficiency while oxygen reduction reaction is occurring.

Fig 10 Cyclic voltammograms for 0.5M H2SO4 solution with different Nafion spinning condition.

4. CONCLUSIONS

Through the combination of spinning conditions and radial structure designs, the desired Nafion thickness can be adjusted inside the micro holes, thus provides the path for oxygen to flow in and reduces the path for proton transport. The device is expected to improve proton transport and oxygen reaction efficiency over traditional carbon cloth based DMFC systems by more reaction surface and efficient proton/gas transport path.

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REFERENCES