Manufacture of Electrode for Polymer Electrolyte Fuel Cell with Woodceramics Sheet

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A polymer electrolyte fuel cell (PEFC) with electrodes manufactured with woodceramics sheet was investigated experimentally. We made a woodceramics sheet from a postcard paper. Two kinds of annealing temperature, i.e., 800 °C and 900 °C were considered. The factors of shrinkage due to the annealing at both temperatures were about 70 %. The electrode made of carbon paper which is widely-used as the electrode material was also considered for comparison. The values of the resistivity of the woodceramics made at 800 °C and 900 °C were 13.3 and 3.3 times as large as that of the carbon paper. The bulk density of woodceramics sheet was about twice as large as that of carbon paper regardless of the annealing temperature. We confirmed that the PEFC practically generated electric power. The PEFC with the electrodes made at the annealing temperature of 900 °C generated higher output voltage and power than that with the electrodes annealed at 800 °C. Hence, the annealing temperature of 900 °C might be more desirable than that of 800 °C. Furthermore, we suggested that the output power might be increased by improving the porosity of the woodceramics sheet.

Key words: woodceramics, polymer electrolyte fuel cell (PEFC), electrode, postcard paper, annealing

1. INTRODUCTION

In recent years, fuel cell has got into the spotlight as an ecological power generation method[1]. Especially, the research and development task on the application of polymer electrolyte fuel cell (PEFC) is now energetically pushed forward. That is because the PEFC may be made lighter and smaller and work at lower temperature than the other types of fuel cells such as phosphoric acid fuel cell, molten carbonate fuel cell and solid oxide fuel cell. However, there are some problems to be solved for further spread at present. One of the biggest problems is how to reduce the price.

On the other hand, woodceramics is attracting an attention as an ecological and low-cost material[2]. That is because woodceramics is made from ligneous waste such as waste paper. We have investigated the application of woodceramics to the PEFC to solve the problem of fuel cell system mentioned above[3]. In this paper, the PEFC was practically manufactured with electrodes made of the woodceramics and the power generation characteristics were estimated experimentally.

2. POLYMER ELECTROLYTE FUEL CELL WITH WOODCERAMICS

Figure 1 illustrates a schematic construction of a PEFC. A proton exchange membrane was sandwiched by electrodes with catalyst layer. The structure of the electrode was thin and porous so that both the electrolyte from one side and the gas from the other side could penetrate. In general, the membrane and electrodes were united by hot-press and membrane electrode assembly (MEA) was formed. It was also sandwiched and fixed by conductive plate which was called separator. As shown in Fig. 1, the separator had grooves and the gas was provided though those.

Woodceramics can be applied to the electrode and/or separator of the PEFC as the electrically-conductive material. We investigated the manufacture of electrode made of a woodceramics sheet.



Fig. 1. Schematic construction of PEFC.

3. WOODCERAMICS SHEET

3.1 Manufacturing procedure

Figure 2 shows an outline of the manufacturing procedure for the woodceramics sheet. We adopted a postcard paper as the material for the woodceramics sheet[4]. The thickness of the postcard paper was 0.023 cm. The postcard paper was cut into a size of 12.3 cm² (3.5 cm \times 3.5 cm) as a sample. We immersed the sample paper into a methanol solution of phenolic resin (Bellpearl, Air Water Bellpearl Inc.) of 15 wt% for about 48 hours. Then, we vacuum-dried the sample at a temperature of 150 °C for 15 min. In the carbonization, we changed the temperature as shown in Fig. 3 (a). The temperature was increased at a rate of 1 °C /min and was maintained at 300 °C for 3 hours. After that, we raised the temperature at the same rate again and maintained 600 °C for 3 hours. In this paper, the influence of the temperature in the annealing on the electric power generating characteristics was investigated. We considered two kinds of temperatures of 800°C and 900 °C in the annealing. In this paper, we defined the temperature as annealing temperature although the carbonization might also proceed during this treatment. Figure 3 (b) and (c) describe the temperature change with time. The increasing rate of the temperature was 10 °C /min and the time when the constant temperature was maintained was 3 hours.



Fig. 2. Outline of manufacturing procedure for woodceramics sheet.



Fig. 3. Temperature changes in carbonization and annealing.

3.2 Fundamental properties

Figure 4 shows the photo of the woodceramics sheet manufactured by the method mentioned above (annealing temperature: 900 °C). The photo of the postcard paper is also described in this figure. As shown in Fig. 4, it was found that the woodceramics sheet contracted. The dimensions and shrinkage factors of the woodceramics sheets are summarized in Table 1. In this paper, we defined shrinking factor as the rate of the volume of the woodceramics sheet to that of the postcard paper. The shrinkage factors of both woodceramics sheets were about 70 % and there was almost no recognizable difference due to the annealing temperature.

Figure 5 shows the measured resistivity (in plane) of the carbon paper and woodceramics sheets. The resistivity of woodceramics made at the annealing temperature of 800 and 900 °C were 0.173 Ω cm and 0.043 Ω cm. Those were equal to 13.3 and 3.3 times as large as the resistivity of the carbon paper (0.013 Ω cm), respectively.

The bulk densities of the carbon paper and woodceramics sheets are shown in Fig. 6. The densities of woodceramics sheets were about 0.8 g/cm^2 regardless of the annealing temperature. This value corresponded to about twice as large as that of the carbon paper. From this result, it might be said that the porosity of woodceramics is lower than that of the carbon paper. This means that the gas permeability of the woodceramics might also be lower than that of the carbon paper.



Fig. 4. Photographs of postcard paper and woodceramics sheet (annealing temperature: $900 \degree C$).

Table 1. Dimensions and shrinkage factors of woodceramics sheets

| Annealing temperature | Dimension | Shrinkage factor |
|--------------------------|------------------------------|---------------------|
| 800 °C | 7.13cm ² ×0.013cm | 67.2% |
| 900 ℃ | 7.18cm ² ×0.012cm | 69.5% |



Fig. 5. Resistivity of woodceramics sheet.



Fig. 6. Density of woodceramics sheet.

4. POWER GENERATION CHARACTERISTICS 4.1 Membrane electrode assembly (MEA)

Figure 6 illustrates the manufacturing procedure of the MEA. First, we gave the woodceramics sheet a water-repellent treatment. The woodceramics sheet was immersed into a diluted suspension of FEP and was heat-treated at 300 °C for 30 minutes. Secondly, they were cut into an electrode size of 4.8 cm^2 (2.2 cm× 2.2 cm). We made a catalyst paste by mixing carbon

support (VulcanXC72R) with catalyst and the electrolyte solution. Pt and Nafion were adopted as a catalyst and electrolyte. The catalyst paste was applied to the woodceramics sheet so that the amount of Pt was 1 mg/cm². Sandwiching a proton exchange membrane (Nafion115) between the electrodes and hot-pressing that, we manufactured the MEA. The hot-pressing temperature and pressure were 130 °C and 50 kgf/cm². Figure 7 shows the manufactured MEA using the woodceramics sheet (annealing temperature: 900 °C). We made the MEA with the carbon papers as well as the woodceramics sheets for comparison.

4.2 Experimental procedure

Incorporating the MEA made by the method mentioned in previous section into a PEFC single cell, we measured the voltage-current density characteristics. The experimental conditions are listed in Table 2. The cell temperature and dew-point temperature were 70 °C. H₂ and O₂ volumetric flow rates were 300 ml/min and 150 ml/min, respectively. The gas pressure was atmospheric pressure. Changing the output current of the cell, we measured the output voltage.







Fig. 7. Photograph of MEA manufactured.

| Table | 2. Ex | perimental | conditions. |
|--------|----------|------------|-------------|
| 1 4010 | T. T. Y. | permenten | conditions. |

| Cell temperature | 70 ℃ |
|-------------------------------------|----------------------|
| Dew-point temperature | 70 °C |
| H ₂ volumetric flow rate | 300 ml/min |
| O2 volumetric flow rate | 150 ml/min |
| Gas pressure | Atmospheric pressure |

4.3 Results and discussion

voltage-current Figure 8 shows the density characteristics of the PEFC with woodceramics sheets. It was confirmed that the PEFC with woodceramics sheet electrodes practically generated electric power. The open circuit voltages for the PEFC with woodceramics sheet annealed at 800°C and 900°C were 0.80 V and 0.72 V. The difference was small. The voltage for the annealing temperature of 800 °C decreased with an increase in the current density more sharply than that of $900\ensuremath{\,^\circ C}\xspace$. Figure 9 shows the power density as a function of the current density. The maximum power density for 800 °C and 900 °C were 12.1 mW/cm^2 and 37.5 mW/cm². From these results, it can be said that the annealing temperature of 900 °C is more desirable than that of 800 °C.

In Fig. 8 and 9, the results for the PEFC with carbon paper were also described. The voltages and power densities of the PEFC with woodceramics were lower than that with carbon paper. In general, the larger resistivity and lower porosity of the electrode are considered to cause the lower output voltage and power. As mentioned above, the resistivity of the woodceramics sheets was larger and the porosity may be lower than that of the carbon sheet. However, the large resistivity of woodceramics electrode can not be large cause in this case because the range of the current density was relatively low. Hence, it is important to increase the porosity to improve the power generating characteristics of woodceramics electrode.

The woodceramics sheet made from the postcard paper may include some impurities. It is necessary to investigate the chemical composition of the woodceramics sheet and the influence of the impurities on the electric power generating characteristics.



Fig. 8. Voltage-current density characteristics.



Fig. 9. Power density-current density characteristics.

5. CONCLUSIONS

We manufactured the electrode for the PEFC using the woodceramics sheet. A postcard paper was adopted as the material for woodceramics sheet. It was confirmed that the PEFC with woodceramics electrodes generated electric power. The output voltage and power density for the woodceramics made at 900 °C was higher than that at 800 °C. It was pointed out that increasing the porosity of the woodceramics sheet might be effective to improve the characteristics as the electrode.

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