Ni-based amorphous alloy-coating for bipolar plate of PEM fuel cell by electrochemical plating

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Abstract. In this study, the Ni-Cr-P amorphous alloy-coated bipolar plates were produced by electro-plating on the Cu base plates with a flow field. The power generation tests of a single fuel cell with those Ni-Cr-P bipolar plates were conducted at 353 K. It was found that the single fuel cell with those Ni-Cr-P bipolar plates showed excellent I-V performance as well as that with the carbon graphite bipolar plates. It was also found that the single cell with those Ni-Cr-P bipolar plates showed better I-V performance than that with the Ni-P amorphous alloy-coated bipolar plates. Furthermore, the long-time operation test was conducted for 440 h with those Ni-Cr-P bipolar plates at the constant current density of 200 mA cm⁻². As a result, it was found that the cell voltage gradually decreased at the beginning of the measurement before 300 h and then the voltage was kept constant after 300 h.

Introduction

The bipolar plates are one of the most important components of the proton exchange membrane fuel cells (PEMFC), as they distribute reactant gases (H₂ and O₂/Air) to the electrodes and provide mechanical support and electrical connection between the adjacent cells in the fuel cell stack [1]. Conventionally, bipolar plates have been constructed from carbon graphite because of its high corrosion resistance in the fuel cell environment and high electrical conductivity [2]. However, the brittleness of carbon graphite necessitates the use of thick bipolar plates, resulting in low volumetric power density of the fuel cell stack. Machining of flow fields into carbon graphite plates is also expensive, making carbon graphite impractical for wide-scale commercial uses.

Alternative candidate for bipolar plates is metallic material [3-7]. The metallic materials are suitable to produce thinner bipolar plates since they have many advantages, such as high mechanical strength and excellent machinability to desired shapes. Thinner bipolar plates enable us to make a compact fuel cell stack, leading to enhancing the usefulness of fuel cells. For this purpose, some metallic materials such as the Nb/stainless steel clad material [3], SnO₂:F-coated stainless steel [4] and Cr-N-coated stainless steel [5, 6], were used tentatively to produce thin bipolar plates and the power generation properties of a single fuel cell with those bipolar plates were studied.

Amorphous alloys are known for their advantageous characteristics over crystalline alloys. In particular, they exhibit very high mechanical strength [8] and excellent corrosion resistance [9]. We have tried to develop an amorphous/glassy alloy bipolar plate. In our previous works, the glassy alloy

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bipolar plates were produced by hot-pressing the melt-spun glassy alloy sheets [10, 11]. Then the Ni-Cr-P-B glassy alloy-coated bipolar plates were produced by high velocity oxy-fuel (HVOF) spray-coating on Al bipolar plates and the power generation properties of a single fuel cell with those bipolar plates were also examined [12]. As the result, it was found that the single fuel cell with those glassy alloy-coated bipolar plates showed excellent I-V performance. The HVOF spray-coating is suitable for mass-production. However, it needs a special equipment and facility. Then we have adopted electrochemical plating to produce amorphous alloy surface film since it does not need special equipments in a laboratory.

A large number of metal-metalloid amorphous alloys such as Ni-P [13-15], Ni-B [16], Ni-Cr-P [17], Fe-Ni-P [18], Fe-Cr-Ni-P [19] have been developed up to date. For example, electro-less deposited Ni-P amorphous alloy has been widely used in commercial scale. Furthermore, the Ni-Cr-P amorphous alloy was synthesized by electrodeposition and its corrosion resistance was previously studied [17]. In this Ni-Cr-P alloy, P and Cr were added to Ni for amorphization and passivation, respectively. As a preliminary work, we produced the Ni-P amorphous alloy-coated bipolar plates by electro-less plating and examined the I-V performance of a single fuel cell with those bipolar plates [20]. As a result, it was found that the single fuel cell with those Ni-P bipolar plates did not show good I-V performance maybe because the alloy does not contain corrosion resistant elements such as Cr.

In this study, we produced the Ni-Cr-P amorphous alloy-coated bipolar plates by electro-plating and examined the I-V performance and long-time durability of a single fuel cell with those Ni-Cr-P amorphous alloy-coated bipolar plates.

**Experimental procedure**

The Cu plates (100 mm × 100 mm × 0.3 mm) with a flow field were prepared by hot-pressing. Figure 1 shows a schematic illustration of the flow field designed in this work [12]. The flow field area is 5 cm$^2$. Surface of the Cu plates with a flow field were cleaned with a nitric acid solution and then with distilled water supersonically before electro-plating.

The electro-plating bath is shown in Fig. 2. The working electrode was the Cu plate and the counter electrode was a Pt net. The electro-plating was carried out at the constant current density of 400 mA·cm$^{-2}$, at the bath temperature of 303-318 K for 24 h. The Cu plate was covered with a polymer film and only the flow field area was exposed to the chemicals. The chemicals for the Ni-Cr-P plating bath were mainly composed of chromium chloride, nickel chloride, citric acid, sodium hypophosphate, formic acid and so on. All the chemicals used in this study were shown in Table 1.

The amorphicity of the electro-plated Ni-Cr-P alloy samples were examined by X-ray diffractometry (XRD) with a monochromatic Cu-K$\alpha$ radiation at 40 kV and 40 mA. The surface morphology and the
Table 1. Chemical reagents used for Ni-Cr-P plating.

| Chemicals       | Contents   |
|-----------------|------------|
| NiCl$_2$·6H$_2$O | 25 g/L     |
| CrCl$_3$·6H$_2$O | 120 g/L    |
| HCOOH           | 50 cc/L    |
| KBr             | 17.3 g/L   |
| NH$_4$Cl        | 50 g/L     |
| Na$_3$cit·2H$_2$O | 80 g/L   |
| H$_3$BO$_3$     | 35 g/L     |
| NaH$_2$PO$_4$·H$_2$O | 10 g/L |
| HCl             | pH=1.0     |
| NH$_4$OH        |            |

The chemical compositions were obtained by scanning electron microscope with energy dispersive X-ray spectroscopy (SEM-EDX).

The I-V characteristics of the single cells with the bipolar plates prepared in this study were measured by an automatic fuel-cell test system (Toyo Corporation, PEMTest8900). A standard fuel cell and membrane-electrode assemblies (MEA) were purchased from Electrochem Inc. Humidification was 100%RH for H$_2$ and O$_2$ at 343 K. The cell temperature was 353 K and the gas flow rate was 0.1-0.3 L·min$^{-1}$. After the I-V measurement, the long-time operation test was carried out for 440 h.

Results and discussion

1.1. Bipolar plate preparation

Figure 3 shows an outer view of a Ni-Cr-P alloy-coated bipolar plate produce by electro-plating. The Cu plate was covered with polymer film, but the flow field area was only exposed to the chemicals. So, the Ni-Cr-P alloy was deposited only around a flow field on both sides of the plate.

Figure 4 shows a typical surface morphology of the electro-plated Ni-Cr-P alloy. It was found that

![Figure 3. Ni-Cr-P amorphous alloy-coated bipolar plate.](image)

![Figure 4. Surface morphology of the Ni-Cr-P alloy deposited on Cu plate by electro-plating.](image)
the surface was not smooth and that some small cracks can be seen. Furthermore, the thickness of the layer was not constant because of a large distribution of electric field depending on the position along the flow field. The thickness of the plated layer was 5-100 µm.

Figure 5 shows the XRD pattern of the electro-plated Ni-Cr-P amorphous alloy. As clearly seen in the figure, the sample showed a broad halo peak and a distinct crystalline peak. The broad halo peak comes from a single amorphous phase and the distinct peak may come from the Cu base plate detected from the outside Cu area around the flow field.

![Figure 5. XRD pattern of the Ni-Cr-P alloy electro-plated on Cu plate.](image)

Table 2 shows the detailed alloy compositions of the electro-plated Ni-Cr-P alloy. According to the analysis, the alloy produced in this study was Ni$_{52}$Cr$_{25}$P$_{23}$ in at% description. This alloy has P content of more than 20 at%, resulting that the single amorphous phase can be formed. According to the previous papers, it was reported that Ni-P amorphous single phase was formed when P content is as large as 20 at% [13]. So, it was concluded from Fig. 5 and Table 2 that the Ni-Cr-P alloy prepared by electro-plating in this study possessed a single amorphous phase.

| Element | Wi% | At% |
|---------|-----|-----|
| P       | 14.37 | 23.45 |
| Cr      | 25.51 | 24.80 |
| Ni      | 60.12 | 51.75 |

1.2. Power generation tests

Figure 6 shows the I-V curve of a single fuel cell with two Ni-Cr-P amorphous alloy-coated bipolar plates (hereafter denoted as Ni-Cr-P bipolar plates) measured at 353 K after 50 cycles repetition. The gas flow rate of both H$_2$ and O$_2$ was 0.1 L·min$^{-1}$. The I-V curves measured with the carbon graphite and electro-less plated Ni-P bipolar plates were reported in our previous paper [20] and were also superimposed on the figure for comparative purpose. We used a new MEA for each single fuel cell assembly. When a new MEA is set in a single fuel cell, it needs activation period for a few tens of I-V cycles to show the maximum performance. So, we showed the I-V curve after 50 cycles repetition. As seen in the figure, the single fuel cell with the Ni-Cr-P bipolar plates shows excellent I-V performance as well as that with the carbon bipolar plates. Furthermore, it was found that the single cell with the
Ni-Cr-P bipolar plates showed better I-V performance than that with the Ni-P bipolar plates. This is because the former one includes high content of corrosion resistant element, Cr. According to the previous paper, the protective chromium oxide passive film can be formed on the surface of the alloy containing both Cr and P [21].

The MEA was fully activated after 50 repetitions of I-V measurement and was ready for long time operation. So, then we started the long time power generation test soon after the I-V measurement shown in Fig. 6.

Figure 7 indicates the result of the long time power generation test conducted at the current density of 200 mA∙cm\(^{-2}\) at 353 K for 440 h. Final product inside a fuel cell is water. Water should be removed from fuel cell quickly so as not to degrade the cell performance especially in the long time operation. So, the gas flow rate of H\(_2\) and O\(_2\) was increased to 0.3 L∙min\(^{-1}\) for this test in order to drain off the water produced inside the fuel cell completely from the flow field of the fuel cell. As seen in the figure, the voltage decreased gradually with time at the beginning of the measurement before 300 h and then the voltage was almost kept constant after 300 h. This may be because the protective passive film was formed on the surface of the Ni-Cr-P bipolar plates during the test, leading to fully passivated surface of the bipolar plates. Although some small microcracks were observed in the microstructure as shown in Fig. 4, they did not affect significantly the I-V performance shown in Fig. 6. The result of the long-time operation test in this work was not affected significantly by those microcracks. However, it is not clear whether the microcracks degrade the cell performance after longer operation. We need further investigations. It is also important to optimize the conditions to prepare electro-plated amorphous alloy film having smooth surface without microcracks.

At any rate, the Ni-Cr-P amorphous alloy-coated bipolar plates were produced by electro-plating. The potential of the amorphous alloy-coated bipolar plates produced by electro-plating was successfully shown in this work.

**Figure 6.** I-V performance of a single fuel cell with the Ni-Cr-P amorphous alloy-plated bipolar plates. Those with the carbon and Ni-P bipolar plates are also shown in the figure for comparative purpose [20].

**Figure 7.** A result of long time power generation at constant current density of 200 mA∙cm\(^{2}\) for 440 h.

**Summary**

In this study, the Ni-Cr-P amorphous alloy-coated bipolar plates were produced by electro-plating on the Cu base plates with a flow field. The detailed analysis revealed that the alloy composition was Ni\(_{52}\)Cr\(_{25}\)P\(_{23}\).

The I-V characteristics of the single fuel cell with the Ni-Cr-P amorphous alloy-coated bipolar plates produced in this study were examined at 353 K with pure H\(_2\) and O\(_2\) gases. As a result, it was found that the cell with the Ni-Cr-P amorphous alloy-coated bipolar plates showed excellent I-V
performance as well as that with the carbon graphite bipolar plates. It was also found that the cell with the Ni-Cr-P amorphous alloy-coated bipolar plates showed better I-V performance than that with the Ni-P amorphous alloy-coated bipolar plates. This may be because the protective passive film was formed on the surface of the Ni-Cr-P amorphous alloy, leading to its high corrosion resistance. Furthermore, the long-time operation test was conducted for 440 h with the Ni-Cr-P amorphous alloy-coated bipolar plates at the constant current density of 200 mA cm\(^{-2}\). The cell voltage gradually decreased at the beginning of the measurement before 300 h. However, the voltage was kept constant after 300 h. This may be because the alloy surface was fully passivated after 300 h.

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