Development of the Ni-based Metallic Glassy Bipolar Plates for Proton Exchange Membrane Fuel Cell (PEMFC)

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Abstract. Alloy optimization in the Ni₈₀₋ₓCrₓP₁₆B₄ (x=9-30 at%) alloy system was conducted in order to achieve low Tₕ and a large ΔTₓ. From this study, the Ni₆₅Cr₁₅P₁₆B₄ glassy alloy was found to be the optimal alloy. The static and potentiodynamic corrosion behaviours of this alloy were measured. As a result of polarization measurements, it was found that the current density of the non-polished glassy alloy sample was smaller than that of a SUS316L sample. By contrast, the current density of the surface-polished glassy sample was slightly larger than that of the SUS316L sample in the voltage range of 0.3-0.8 V. A bipolar plate was successfully produced by hot-pressing the glassy alloy sheet in a supercooled liquid state. The I-V characteristics of a single cell with the glassy bipolar plates were measured.

1. Introduction
Proton exchange membrane (PEM) fuel cells have been receiving considerable attention as clean energy sources that may be used in the near future. Bipolar plates are one of the most important components of PEM fuel cells and are multifunctional as they conduct electricity from cell to cell, they separate the fuel gas from the oxidant gas, and their flow field supplies the gases to the electrodes. Bipolar plates are conventionally made of carbon graphite [1]. However, it cannot be used to produce thin bipolar plates because of its brittleness. Thinner bipolar plates will result in lighter and more compact fuel cell stacks, saving costs and enhancing the usefulness of fuel cells.

Recently, many research groups have tried to develop metallic materials for bipolar plates. The corrosion-resistant stainless steel SUS316L is recognized as a standard material for comparison [2]. Many different types of metallic bipolar plates have subsequently been developed, including those based on stainless steels or other alloys with coatings [3-5].

Metallic glassy alloys are also potential materials for bipolar plates because they have many advantageous characteristics over crystalline alloys. For example, glassy alloys exhibit higher mechanical strengths and higher corrosion resistance [6, 7]. Furthermore, metallic glasses can show viscous flow (plastic) deformation in a supercooled liquid state at temperatures between the glass transition temperature, Tₚ, and the crystallization temperature, Tₓ.

A large number of Ni-based amorphous alloys with non-metal such as Ni-P [8], Ni-B [9], Ni-Si-B [10] have been developed up to date. For example, Hashimoto’s group reported that the Ni-Cr-P-B quaternary glassy alloys possessed excellent corrosion resistance [11]. Recently, we found that a Ni-

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Cr-P-B glassy alloy could be melt-spun even in air without any degradation in its thermal or other properties and that it had a wide supercooled liquid region $\Delta T_x$ [12].

In this work, we adopted the above mentioned Ni-Cr-P-B quaternary system and optimized the alloy compositions suitable for bipolar plate production. Corrosion behaviours of the optimal alloy were examined. A bipolar plate was then produced by hot-pressing in a supercooled liquid state. Finally the I-V characteristics were tentatively obtained for the glassy alloy.

2. Experimental
Melt-spun samples of Ni$_{80-x}$Cr$_x$P$_{16}$B$_4$ alloys ($x=9$-30 at%) were produced by a Cu-roller melt-spinning technique in an Ar atmosphere. The glass transition behaviour of the samples was examined by differential scanning calorimetry (DSC) at a heating rate of 0.67 K·s$^{-1}$ in Ar flow.

The static corrosion rate was evaluated from the weight reduction of samples immersed in 1 mass% H$_2$SO$_4$ solution at 353 K for 1 week. The sample coupons were manually polished with 1500 grit SiC paper prior to the measurements.

Potentiodynamic polarization curves were obtained using a potentiostat/galvanostat at a potential sweep rate of 50 mV·min$^{-1}$ in 1 mass% H$_2$SO$_4$ solution open to air at 348 K. The counter electrode was Pt net and the reference electrode was SCE.

Auger electron spectroscopy (AES) analysis was conducted to study the surface condition of the glassy samples. The sputter rate was 60 nm·min$^{-1}$.

The I-V characteristics of single cells with the metallic glassy bipolar plates and with SUS316 bipolar plates were measured by an automatic fuel-cell test system. A standard PEM fuel cell was purchased from Electrochem Inc. The MEA area is 5 cm$^2$. Humidification was 100 % RH for H$_2$ and air at 343 K. The cell temperature was 353 K and the gas flow rate was 0.5 L·min$^{-1}$.

3. Results and Discussion
Figure 1 summarizes the thermal parameters of the Ni$_{80-x}$Cr$_x$P$_{16}$B$_4$ ($x=9$-30 at%) alloys. All the melt-spun ribbons were found to consist only of a single glassy phase by X-ray diffraction observations. The figure shows that the $T_g$ and $T_x$ increase with increasing Cr content and that $\Delta T_x$ is saturated and kept constant with Cr content more than 15 at%. Therefore, Ni$_{65}$Cr$_{15}$P$_{16}$B$_4$ metallic glass was selected in this study as an optimal alloy having an as wide $\Delta T_x$, and as low $T_g$ and $T_x$ as possible. The $T_g$, $T_x$ and $\Delta T_x$ of the Ni$_{65}$Cr$_{15}$P$_{16}$B$_4$ glassy alloy are 659 K, 702 K and 43 K, respectively.

As a result of static corrosion tests, it was found that the corrosion rate of the Ni$_{65}$Cr$_{15}$P$_{16}$B$_4$ glassy alloy was 6.94×10$^{-3}$ mm·y$^{-1}$ and was smaller than that of SUS316L (1.48×10$^{-2}$ mm·y$^{-1}$).

![Figure 1. Compositional dependence of $T_g$, $T_x$, and $\Delta T_x$ for melt-spun Ni$_{80-x}$Cr$_x$P$_{16}$B$_4$ ($x=9$-30 at%) alloys.](image)
Figure 2. Polarization curves at 50 mV s⁻¹ of the Ni₆₅Cr₁₅P₁₆B₄ glassy and SUS316L samples in a 1 mass%H₂SO₄ solution open to air at 348 K. (a) non-polished samples and (b) polished samples.

Figure 3. AES depth profile for the as-spun Ni₆₅Cr₁₅P₁₆B₄ glassy alloy.

Figure 2 shows polarization curves of the Ni₆₅Cr₁₅P₁₆B₄ glassy alloy. Figure 2(a) indicates the results for as-spun (non-polished) samples and Fig. 2(b) shows those for the surface-polished samples. As Fig. 2(a) clearly shows, the current density of the as-spun glassy alloy is smaller than that of the SUS316L sample, indicating excellent corrosion resistance of the as-spun glassy alloy. However, the current density of the surface-polished glassy alloy is slightly larger than that of the SUS316L samples in the voltage range 0.3-0.8 V. Since a glassy sample is generally produced by rapidly quenching the molten alloy, the surface of the sample is most likely covered with a thin oxide or an enriched layer of the main elements. Hence, the non-polished glassy sample is more corrosion-resistant than the polished one due to its thin protective surface layer.

To understand the surface condition of the as-spun Ni₆₅Cr₁₅P₁₆B₄ glass, the alloy surface was investigated by AES. The depth profile of the alloy is shown in Fig. 3. No Cr-oxide layer is evident in this measurement, but Ni and P are concentrated on its surface. Since the other constituent elements were not concentrated on the surface, it can be concluded that a Ni-P composite surface layer was formed, that functions as a protective film in a corrosive environment.

Figure 4 shows a bipolar plate produced by hot-pressing the Ni₆₅Cr₁₅P₁₆B₄ glassy alloy sheet at 679 K (=Tₘ+20 K) for 300 s in a dilute Ar atmosphere in the supercooled liquid state. The groove depth is 0.7 mm. Excellent viscous flow deformation was obtained as clearly demonstrated in this figure.

Figure 5 indicates the I-V curves of single cells with Ni₆₅Cr₁₅P₁₆B₄ glassy and SUS316 bipolar plates. The as-processed glassy plates were used for these measurements without any further surface-treatment. The SUS316 bipolar plates were produced by machining. The same flow field design was adopted for both bipolar plates. The metallic glassy bipolar plates were mounted on a carbon frame and used for measurement. From Fig. 2a, the current density of the non-polished sample is smaller than that of the SUS316L alloy. This is also reflected in the better performance of the single cell with Ni₆₅Cr₁₅P₁₆B₄ glassy plates. However, the carbon bipolar plates seem to have a better I-V performance. We are currently conducting further study to improve the performance of metallic glassy bipolar plates.
Figure 4. Optical micrograph of the Ni$_{65}$Cr$_{15}$P$_{16}$B$_{4}$ glassy alloy bipolar plate produced by hot-pressing in the supercooled liquid state.

Figure 5. Comparison of I-V characteristics between cells with Ni$_{65}$Cr$_{15}$P$_{16}$B$_{4}$ glassy alloy bipolar plates and SUS316 plates.

4. Summary

(1) After the screening test, the Ni$_{65}$Cr$_{15}$P$_{16}$B$_{4}$ glassy alloy was selected for further investigation. The thermal stability parameters, T$_g$, T$_x$, and $\Delta$T$_x$, of the Ni$_{65}$Cr$_{15}$P$_{16}$B$_{4}$ glassy alloy are 659 K, 702 K and 43 K, respectively.

(2) The static corrosion rate of the glassy alloy was smaller than that of the highly corrosion-resistant stainless steel SUS316L. As a result of polarization measurements, the current density of the non-polished glassy alloy sample was found to be smaller than that of the SUS316L sample. On the contrary, the current density of the surface-polished glassy sample was slightly larger than that of the SUS316L sample in the voltage range 0.3-0.8 V in a polarization measurement.

(3) A bipolar plate was successfully produced by hot-pressing the glassy alloy sheet at 679 K (=T$_g$+20 K) for 300 s in a dilute Ar atmosphere in the supercooled liquid state. The I-V performance of a single cell with glassy bipolar plates was superior to that of one with SUS316 plates.

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