Effect of Reduction Temperature of Fe-Co-Ni/C Catalyst on the Solid Alkaline Fuel Cell Performance

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In this present work, the effect of reduction temperature of Fe-Co-Ni/C anode catalyst on the solid alkaline fuel cell performance was investigated. Fe-Co-Ni/C anode catalysts were prepared by the impregnation method, and reduced at 360°C, 500°C, and 900°C in hydrogen flow for 2 h. The order of the maximum power density was as follows: Fe-Co-Ni/C with reduction at 360°C > reduction at 500°C > reduction at 900°C. The maximum power density of 17 mW cm\textsuperscript{-2} was obtained for the cell with Fe-Co-Ni/C anode reduced at 360°C. The order of the particle size was as follows: Fe-Co-Ni/C with reduction at 360°C < reduction at 500°C < reduction at 900°C. Fe-Co-Ni/C reduced at 360°C with the smallest particle size showed the highest activity for hydrogen oxidation reaction.

Introduction

Fuel cells, as devices for direct conversion of the chemical energy of a fuel into electricity by electrochemical reactions, are one of the key technologies for effective use of energy. Recently, alkaline fuel cell (AFC) has regained attention because an alkaline media provides a less corrosive environment to the catalysts and electrodes than the acid environment of a polymer electrolyte fuel cell (PEFC) (1-4). Furthermore the rate of oxygen reduction reaction (ORR) in the cathode is much faster in an alkaline media than in an acid media (5, 6). The normal electrode potentials of AFC are as follows (eq. 1, 2).

\begin{align*}
\text{Anode} & : \quad H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad E_0(V) = -0.83 \quad (1) \\
\text{Cathode} & : \quad \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad E_0(V) = 0.40 \quad (2)
\end{align*}

So it is imperative to develop non-precious metal electrocatalysts for AFC (7).

In recent years, AFC using solid electrolyte (solid alkaline fuel cell; SAFC) has attracted great attention due to its easiness of handling. Until now it is well known that Fe-Co-Ni/C can function well as an anode catalyst in a SAFC.

In the present work, we investigated the effect of reduction temperature of Fe-Co-Ni/C anode catalyst on the SAFC performance.
Experiment

Preparation of NaCo$_2$O$_4$/C

NaCo$_2$O$_4$ was prepared by dry-up method (8). First, CH$_3$COONa and (CH$_3$COO)$_2$Co·4H$_2$O were dissolved in distilled water. The weight ratio of Na to Co is 1.6 to 2.0. This aqueous solution was heated to evaporate water and dried in oven at 80°C, followed by calcinations at 750°C. The calcined powder was ground to fine powder and pressed into disks with diameter of 20 mm and thickness of 3.0 mm. After uniaxial pressing, the disks were calcined at 790°C. The disks were ground to fine powder. The powder was characterized by XRD and pressed into disks with diameter of 20 mm and thickness of 1.0 mm. After uniaxial pressing, the disks were sintered at 900°C.

Preparation of Fe-Co-Ni/C

Fe-Co-Ni/C was prepared by the impregnating method. The molar ratio of Fe, Co and Ni were 1:1:1 with Fe-Co-Ni loading of 55 wt%. First, Fe(NO$_3$)$_3$·9H$_2$O, Co(NO$_3$)$_2$·6H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O were dissolved in distilled water. Then carbon black powder (Vulcan XC-72R, Cabot Corp.) was added to this aqueous solution. The mixture was heated to evaporate water in water bath at 80°C and dried in oven at 80°C. The residue was ground to fine powder. The powder was reduced in a hydrogen flow for 2 h at 360°C, 500°C and 900°C. The reduced powder was used for structural characterization by X-ray diffraction (XRD) and applied on NaCo$_2$O$_4$ electrolytes.

Electrochemical measurements

NaCo$_2$O$_4$ electrolyte painted with 360°C-reduced Fe-Co-Ni/C was calcined in a helium flow at 360°C for 2 h. NaCo$_2$O$_4$ electrolytes painted with 500°C- or 900°C-reduced Fe-Co-Ni/C were calcined in helium flow for 2 h at 400°C. Then calcined NaCo$_2$O$_4$ electrolytes were reduced in hydrogen flow for 0.5 h at 280°C. Fe-Co-Ni loading was 10 mg cm$^{-2}$.

The polarization curves were measured in humidified oxygen flow at a rate of 20 ml min$^{-1}$ and hydrogen flow at a rate of 20 ml min$^{-1}$ at the cathode and the anode, respectively. Cell temperature was room temperature, and the temperature of the cathode humidifier was 35°C.

Results

Figure 1 shows XRD patterns of Fe-Co-Ni/C before and after reduction. Before reduction (a), the nitrate peaks are observed at 10.9°, 13.6°, 16.6°, 20.5°, 21.9° and 25.2°. For all samples after reduction (b)-(d), the peaks assigned to Fe-Co-Ni alloy (44.2°, 51.5° and 76.0°) can be observed in the absence of the peaks assigned to pure Ni or Co. This suggests that Ni is easily alloyed with Co. For 360°C-reduced sample (b), peaks of oxides are observed at 30.2°, 35.4°, 37.0°, 43.9°, 56.9° and 62.5°, which are attributed to CoFe$_2$O$_4$, NiFe$_2$O$_4$, Fe$_2$O$_3$ or NiO. For 500°C-reduced sample (c), a big peak assigned to Fe is observed at 44.8° with relatively large peaks of alloy. For 900°C-reduced sample (d), large peaks of alloy were observed with a small peak of Fe. Even after reduction at 900°C, crystallite size of Fe-Co-Ni alloy was as small as 9.9 nm. The kinds and nature of active species strongly depend on the reduction temperature.
Figure 1. XRD patterns of Fe-Co-Ni/C (a) before reduction and after reduction at (b) 360°C, (c) 500°C, and (d) 900°C.

Figure 2 shows STEM images of Fe-Co-Ni/C reduced at 360°C, 500°C, and 900°C. Particle size of Fe-Co-Ni/C reduced at 360°C, 500°C, and 900°C, are 10~60 nm, 10~150 nm, 30~150 nm, respectively. The order of the particle size is as follows: Fe-Co-Ni/C with reduction at 360°C < reduction at 500°C < reduction at 900°C. Particle size increase with as increase in reduction temperature. Fe-Co-Ni/C reduced at 360°C has the smallest particle size.

Figure 2. STEM images of Fe-Co-Ni/C reduced at (a) 360°C, (b) 500°C, and (c) 900°C.
The polarization and power density curves for the AFC with anode Fe-Co-Ni/C catalyst are shown in Figure 3. For Fe-Co-Ni/C reduced at 360°C anode, the open circuit voltage (OCV) is 0.74 V, and maximum power density of 17 mW cm\(^{-2}\) is obtained at current density of 51 mA cm\(^{-2}\). For Fe-Co-Ni/C reduced at 500°C anode, OCV is 0.78 V. The maximum power density of 12 mW cm\(^{-2}\) is obtained at current density of 37 mA cm\(^{-2}\). For Fe-Co-Ni/C reduced at 900°C anode, OCV is 0.76 V. The maximum power density of 9.3 mW cm\(^{-2}\) is obtained at current density of 24 mA cm\(^{-2}\).

OCVs of AFC with Fe-Co-Ni/C reduced at 360°C, 500°C, and 900°C as an anode catalyst are essentially identical. The order of the maximum power density is as follows: Fe-Co-Ni/C with reduction at 360°C > reduction at 500°C > reduction at 900°C. The order of the maximum power density is reverse to the order of the particle size. This means that the maximum power density, that is activity for hydrogen oxidation reaction (HOR), is strongly related to the number of active site of the particle. The activity for HOR does not strongly depend on kind of active species in this experiment.

Figure 3. Cell polarization and power density curves of the AFC with Fe-Co-Ni/C reduced at 360 °C, 500°C, and 900°C as an anode catalyst. Pure hydrogen and oxygen were fed into the anode and cathode, respectively. Cell temperature was room temperature, and the temperature of the cathode humidifier was 35°C.
Conclusions

The effect of reduction temperature of Fe-Co-Ni/C anode catalyst on the SAFC performance was investigated. Cell polarization and power density curves were measured for AFC with Fe-Co-Ni/C reduced at 360°C, 500°C, and 900°C as the anode. The maximum power density of 17 mW cm\(^{-2}\) was obtained with a Fe-Co-Ni/C anode catalyst reduced at 360°C. Fe-Co-Ni/C reduced at 360°C with the smallest particle size showed the highest activity for HOR. The activity for HOR strongly depended on the particle sizes not on the kinds or nature of active species.

Acknowledgments

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References

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