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Development of Direct-Ethanol Anion-Conducting Solid Alkaline Inorganic Fuel Cell

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Anion-conducting solid alkaline inorganic fuels cell was developed. This fuel cell could be operated at high temperature of 110ºC. $NaCo_2O_4$ showed OH^- conduction and activity for oxygen reduction reaction. The Fe-Co-Ni alloy catalyst prepared in this experiment showed activity not only for hydrogen oxidation reaction but also for ethanol oxidation reaction. Completely precious metal-free fuel cell composed of $NaCo_2O_4$ and Fe-Co-Ni cell was made. The cell generated a high output power density of 64 mW/cm^2 directly from ethanol at current density of 160 mA/cm^2.

Introduction

In general, H_2 is used as a fuel for fuel cells. However, storage of H_2 is one of the serious problems for fuel cell system. Fuel cells with direct liquid feeds, such as alcohols, are desirable. Pt anode catalyst for Polymer electrolyte fuel cells (PEFCs) can activate both of H-H and C-H bond, but it cannot activate C-C bond. PEFCs can directly use methanol, but they cannot use ethanol as fuels.

On the other hand, since C-C bond can be activated by transition metal catalyst at basic condition, ethanol can be used for direct alkaline fuel cells. It is well known that the rate of oxygen reduction reaction (ORR) ($2H_2O + O_2 + 4e^- \rightarrow 4OH^-$) in an AFC is much higher than ORR ($4H^+ + O_2 + 4e^- \rightarrow 4H_2O$) of a PEFC. Therefore, non-precious metals can be used as the cathode catalyst in an AFC instead of Pt. Since a KOH electrolyte solution is usually used for AFC, it reacts easily with dissolved CO_2 to form carbonate. When anion-exchange membrane is used, the maximum temperature is around 60ºC (1-3). Fuel cells available over 100ºC is strongly desired especially for vehicles without a huge size of radiator (4). If fuel cells could be operated in the high temperature over 110ºC, the wide spread use of fuel cell is expected.

In this study, to prevent formation of carbonate species, inorganic anion-exchange membrane composed of $NaCo_2O_4$ having layered structures (5) was used. Thermal resistance over 110ºC was confirmed. Fe-Co-Ni alloy catalysts were prepared, and direct-ethanol fuel cell was developed.

Experimental section

Preparation of Electrolyte and Catalyst

CH_3COONa and $(CH_3COO)_2Co•4H_2O$ were dissolved in water. This solution was dried at 80ºC with stirring, and kept in an oven overnight at 80ºC. The dried powder wase milled, and calcined at 750ºC for 5 h. The calcined sample was crushed and pelleted. The

pellets were calcined at 790ºC and crushed. The $NaCo_2O_4$ powder was obtained (1) and used to prepare a $NaCo_2O_4$ disk for a fuel cell device. The $NaCo_2O_4$ powder was pressed at 30 MPa for 5 min, and pelleted into a 20 mm diameter, 1 mm thick disk. The disks were calcined at 900 ºC for 32 h to form the final $NaCo_2O_4$ disks, and one of the disks was crushed to form powders.

The $NaCo_2O_4$ powders were impregnated with an aqueous solution of $Pd(NH_3)_2(NO_2)_2$. These were dried at 80ºC and calcined at 600ºC for 2 h to form 15 wt% $Pd/NaCo_2O_4$. 10 mg of 15 wt% $Pd/NaCo_2O_4$ was mixed with 4 μL of ethylene glycol to form $Pd/NaCo_2O_4$ paste. The anode of the remaining $NaCo_2O_4$ disk was painted with the $Pd/NaCo_2O_4$ paste. The painted $NaCo_2O_4$ disk was calcined at 400ºC to form $Pd/NaCo_2O_4/NaCo_2O_4$ disk. The disk was reduced at 280ºC in H_2 humidified at room temperature. The area of the anode was 0.28 cm^2 and the Pd loading was 2 mg/cm^2.

Fe-Co-Ni catalyst (6): Vulcan powders were impregnated with a mixed aqueous solution of nitrate of Fe, Co, and Ni, followed by drying and reduction. Fe-Co-Ni loading was 55 wt% with molar ratio of Fe/Co/10=1/1/1. The anode of the $NaCoO_4$ disk was painted with Fe-Co-Ni/C past mixed with ethylene glycol. Fe-Co-Ni loading was 10 mg/cm^2.

Cell Performance Test

The $Pd/NaCo_2O_4/NaCo_2O_4$ disk was placed between two sheets of platinum mesh current collectors at anode and carbon paper current collectors. Fuel-cell polarization curves were collected at the room temperature and 110ºC. The current densities were measured in 20 mL flow of dry H_2 at the anode and in 20 mL flow of H_2O-saturated O_2 at 75ºC at the cathode.

Apparatus for direct-ethanol fuel cell is shown in Figure 1. Fe-Co-Ni/$NaCo_2O_4$ disk was placed between two sheets of platinum mesh current collectors at anode and carbon paper current collectors. Fuel-cell polarization curves were collected at 80ºC. The current densities were measured in 20-mL flow of ethanol gas diluted with He and N_2 at the anode and in 20-mL flow of H_2O-saturated O_2 at 75ºC at the cathode.

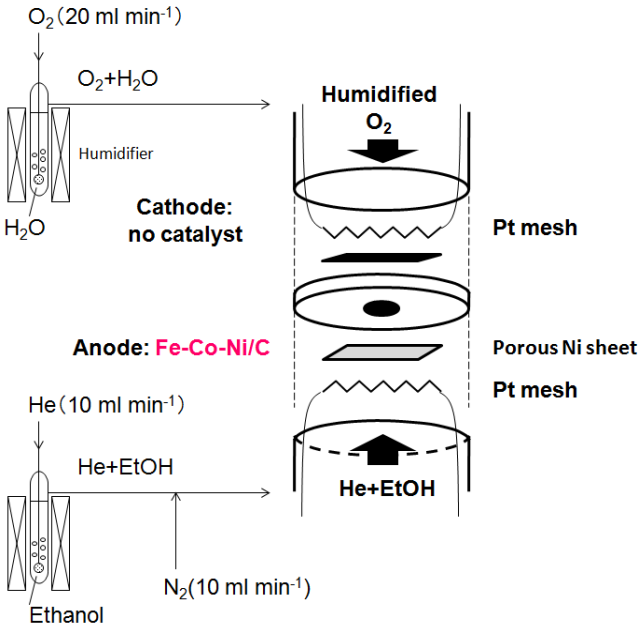

Figure 1 Apparatus for direct-ethanol fuel cell testing

Results and discussion

From XRD measurement, formations of the $NaCo_2O_4$ structure and Fe-Co-Ni alloy were confirmed. OH^- conductivity of $NaCo_2O_4$ was confirmed by concentration cell and water transfer experiments,

Results of the hydrogen oxidation are shown in Figure 2. Although the cathode is catalyst-free, the open-circuit voltage is as high as 0.8 V even at room temperature (a). If proton was charge carrier, oxide could not promote oxygen reduction reaction. If anion is charge carrier, oxide can promote oxygen reduction reaction. It is confirmed that the $NaCo_2O_4$ electrolyte, functions not only as an OH^- conductor but also as a cathode catalyst.

Anode	$H_2 + 2OH^-$	$\rightarrow$	$2H_2O + 2e^-$	$E^0 = -0.83$ V
Cathode	$1/2O_2 + H_2O + 2e^-$	$\rightarrow$	$2OH^-$	$E^0 = +0.40$ V

When operation temperature increases to110°C (b), current density increases. Both of a catalytic activity and OH- conductivity increased with temperature. The performance is high enough even at 110°C, although ordinary AEM cannot be operated over 70°C. This property is indispensable for vehicles.

At anode, Pd activates H-H bond, but it is difficult for Pd to activate C-C bond. Since Pd is precious metal, non-precious metal catalyst is desired.

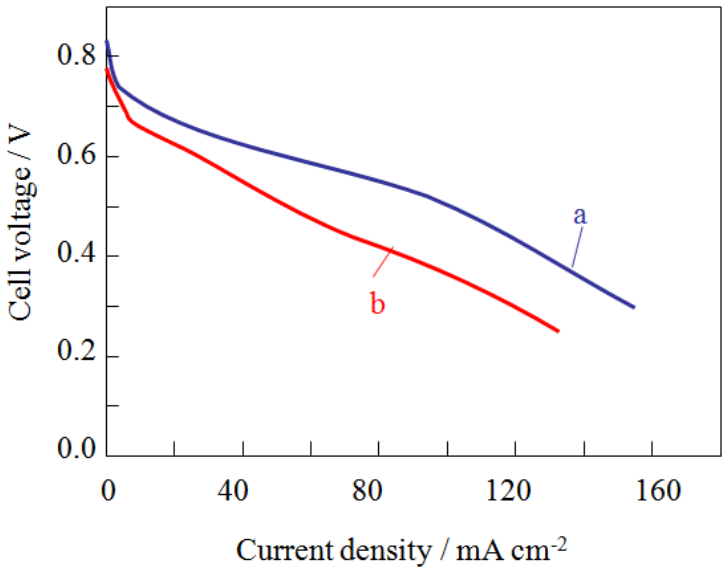

Figure 2 Performance of $Pd/NaCo_2O_4/NaCo_2O_4$ fuel cell at a) the room temperature and b) 110ºC.

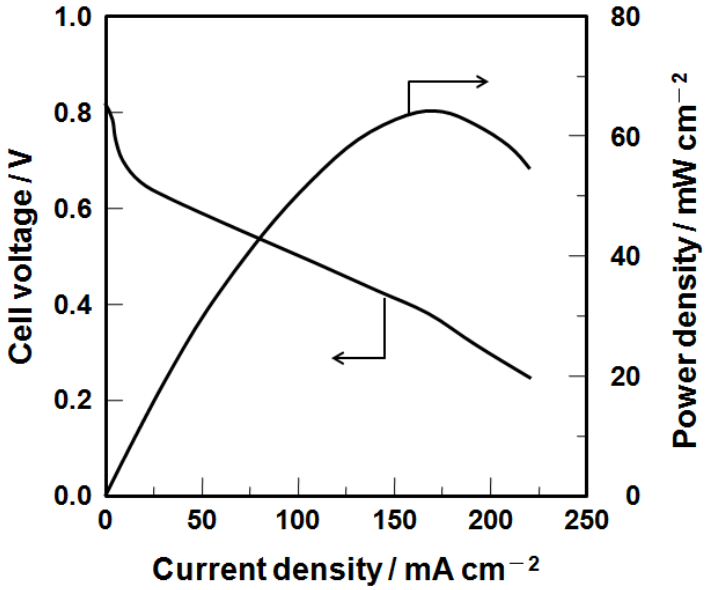

Figure 3 Performance of direct-ethanol solid alkaline inorganic fuel cell testing Anode, Fe-Co-Ni; electrolyte: $NaCo_2O_4$; cathode: catalyst free; Cell Temp., 80ºC; Anode gas, 20-mL flow of ethanol/He+N_2; Cathode gas, 20-mL flow of H_2O-

Figure 3 shows the performance of direct-ethanol solid alkaline inorganic fuel cell. Although the cathode was catalyst-free and anode is precious metal free, the open-circuit voltage is over 0.8 V. The fuel cell composed of Fe-Co-Ni/$NaCo_2O_4$ generated directly from ethanol a high output power density of 64 mW/cm^2 at current density of 160 mA/cm^2. If the reaction proceeds ideally, the following reaction is expected.

Anode	$C_2H_5OH + 12\ OH^-$	→	$2\ CO_2 + 9\ H_2O + 12\ e^-$	E° = -0.743 V
Cathode	$3\ O_2 + 6\ H_2O + 12\ e^-$	→	12OH-	E° = + 0.40 V

Fe-Co-Ni alloy catalysts have activity for ethanol oxidation reaction. At least, C-H bond was activated by the Fe-Co-Ni alloy catalysts. Indeed, formation of CO_2 must be confirmed for next study. As relatively high voltage was obtained directly from liquid fuel with high energy density, this technology will be desirable for mobile fuel cell systems.

Conclusions

Anion-conducting solid alkaline inorganic fuels cell could be operated at high temperature of 110ºC. $NaCo_2O_4$ showed an activity for oxygen reduction reaction. The Fe-Co-Ni alloy catalyst prepared in this experiment showed activity not only for hydrogen oxidation reaction but also for ethanol oxidation reaction. Completely precious metal-free fuel cell composed of $NaCo_2O_4$ and Fe-Co-Ni cell generated a high output power density directly from ethanol.

Acknowledgments

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