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Study of Anode Catalysts and Fuel Concentration on Direct Hydrazine Alkaline Anion-Exchange Membrane Fuel Cells

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A platinum-free fuel cell using liquid hydrazine hydrate $(N_2H_4 \cdot H_2O)$ as the fuel and comprised of a cobalt or nickel anode and a cobalt cathode exhibits high performance. In this study, the fuel cell performances using nickel, cobalt, and platinum as anode catalysts are evaluated and compared. It is found that fuel cell performance in the case of nickel and cobalt is higher than that in the case of platinum. Further, anodic reactions are discussed by comparing the hydrazine consumption and ammonia generation when cobalt and nickel are used as anode catalyst. Cobalt exhibits a higher rate of decomposition than nickel. Nickel is found to be the most suitable anode catalyst among the above mentioned anode catalysts for this fuel cell. The influence of hydrazine hydrate and KOH concentrations in the fuel on cell performance is also discussed. Cell performance is the highest at a hydrazine hydrate concentration of 4 M and a KOH concentration of 1 M. The maximum power density of the alkaline anion-exchange membrane fuel cell, comprised of a nickel anode and a Co–PPY–C (cobalt polypyrrole carbon) cathode, is 617 mW cm^{-2}.
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Proton-exchange membrane (PEM) fuel cells have been recognized as the future power source for vehicles. These fuel cells do not adversely affect air quality, health, and the environment, because they do not emit toxic substances and carbon dioxide. However, economic problems associated with the large-scale use of platinum and many restrictions associated with the infrastructure and storage of hydrogen have limited the widespread use of fuel cell vehicles.

In order to solve these problems, a platinum-free direct hydrazine fuel cell has been developed.[1] In conventional fuel cells, materials with high corrosion resistance are required for the fabrication of electrodes because the PEMs used in these cells are highly acidic in nature. Thus far, metals other than platinum have not been used for the fabrication of electrodes for fuel cells. In alkaline anion-exchange membrane fuel cells, basic hydroxide anion (OH^-) exchange polymer membranes are used. These fuel cells have a mildly corrosive environment. Therefore, various types of metals can be used in these fuel cells.[2-6] A platinum-free fuel cell using liquid hydrazine hydrate $(N_2H_4 \cdot H_2O)$ as the fuel and comprised of a cobalt or nickel anode and a cobalt or silver cathode has been developed. The power generation performance of this fuel cell is comparable to that of hydrogen fuel cells, and this fuel cell is characterized by zero CO_2 emissions (Fig. 1).

Hydrazine-air fuel cells were developed in the 1960s.[7] A high-concentration alkaline liquid (9 M KOH) is used as the electrolyte in these cells. However, in these fuel cells, CO_2 neutralization of the electrolyte takes place. The CO_2 tolerance of the anion-exchange membrane fuel cells is discussed in Ref. 1. The power density of these cells reduces slightly when the concentration of CO_2 inside them is approximately 50 times that in the atmosphere. However, the cell performance reverts back to the original level shortly after the removal of CO_2. This result shows that CO_2 neutralization is not a serious problem for anion-exchange membrane fuel cells. Vorcoe et al. have reported similar results in the case of hydrogen–oxygen fuel cells comprising an anion-exchange membrane.[2]

High-concentration hydrazine hydrate is not only poisonous but also mutagenic. Although the flash point of hydrazine hydrate (74°C) is higher than that of gasoline (< -40°C), hydrazine hydrate has to be handled carefully. A detoxification method has been developed previously[1] which repeatedly fixes hydrazine to the carbonyl groups in the polymer. The onboard readsorption of hydrazine hydrate is possible; the polymer releases the required amount of liquid hydrazine hydrate in a timely manner for generation and the hydrazine hydrate supply in a filling stand can also be attained without returning to a factory. Therefore, hydrazine hydrate can be regarded as a promising carrier for realizing a hydrogen society.

The new platinum-free anion-exchange membrane fuel cell can be potentially used for a wide range of applications. Moreover, this technology attracted considerable attention at the Environmental Showcase of the G8 Hokkaido Toyako Summit held in July 2008.[8] In this study, the power densities of the anion-exchange membrane fuel cell using nickel, cobalt, and platinum as an anode catalyst are compared. The influence of hydrazine and KOH concentrations in the fuel on fuel cell performance is also investigated.

Experimental

Materials.— Three types of unsupported nanoparticles, Ni (Inco, type 210H), Co (Junye Nano Material Co., Ltd.), and Pt (Tanaka K.K.), were used as an anode catalyst in the anion-exchange membrane fuel cell. The specific surface areas of Ni, Co, and Pt were 6.2, 33, and 6.9 $m^2 g^{-1}$, respectively. In all three cases, Co–polypyrrole(PPY)–C was used as the cathode catalyst. A Co–PPY–C cathode was used in previous research by Bashyam and Zelenay.[9] The concentration of Co in Co–PPY–C was 10 wt %. An anion-exchange membrane (ion exchange capacity 1.7 meq g^{-1}; thickness 30 μm; quaternary ammonium form) and an anion-exchange resin solution (ion exchange capacity 2.0 meq g^{-1}), both provided by

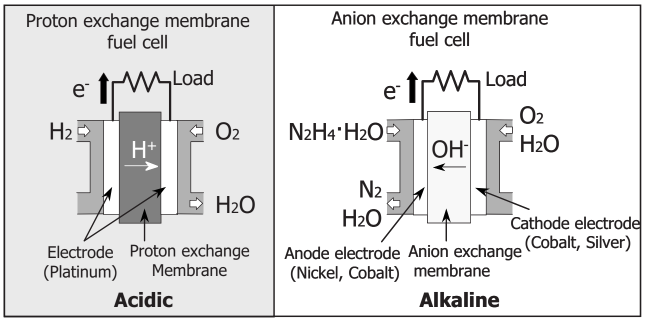

Figure 1. Working principle of alkaline anion-exchange membrane fuel cell.

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Tokuyama Corp., were used to fabricate the membrane electrode assembly (MEA). Hydrazine hydrate (60 wt %) was obtained from Otsuka Chemicals, and potassium hydroxide (85 wt %) was purchased from Hayashi Junyaku K.K.

Methods.— Comparison of anode catalysts.— For preparation of anode ink, 0.2 g of Ni and 2 g of a solvent (1-propanol 80:THF 20 by weight) were sonicated for 3 min. Then, 1.1 g of an ionomer (2 wt %) and 1.4 g of the solvent were added to the mixture. The ink was dispersed by using a rotary shaker for 15 min. For the preparation of cathode ink, 0.2 mg of Co–PPY–C and 1.3 g of the solvent were sonicated for 3 min. Then, 1.9 g of an ionomer solution (2 wt %) was added to the mixture. Finally, the ink was dispersed by using a rotary shaker for 15 min.

The inks were splayed onto the MEA (geometric surface area of the electrodes: 1.33 cm^2). The spray-painted MEA was then pressed at 110 MPa at room temperature for 30 s. The loading amounts of Ni, Co, and Pt on the MEA were 2.7, 2.7, and 2.8 mg cm^{-2}, respectively. In all three cases, Co–PPY–C was used as the cathode catalyst, and the loading amount of Co on the cathode was 0.24 mg cm^{-2}.

For the preparation of fuel, 5 M KOH aqueous solution was prepared by diluting KOH (85 wt %) in ultrapure water. Hydrazine solutions of the required concentration were prepared from a concentrated aqueous solution (60 wt %) and the 5 M KOH aqueous solution by diluting these solutions in ultrapure water (Millipore Milli-Q system, 18.2 M Ω cm).

The fabricated MEA (spherical shape; working electrode area 1.33 cm^2) was inserted in a single cell to measure the cell performance. An aqueous solution of 1 M hydrazine hydrate and 1 M KOH preheated at 55°C was supplied to the anode at 2 mL min^{-1}, and oxygen humidified at 50°C was supplied to the cathode at 500 mL min^{-1}. The cell temperature was controlled and maintained at 80°C. The cell performance was evaluated after continuously operating the cell for 10 h as a conditioning. Current–voltage (*I-V*) measurements were performed in the potentiostatic mode. The *I-V* measurements were started only after voltage remained constant at 0.4 V for at least 15 min. Then, it was increased in steps of 20 mV at time intervals of 6 s. The high-frequency resistance of the cell was determined by ac impedance spectroscopy at 0.4 V.

In order to analyze the reaction during power generation by determining the difference in the anode catalysts, the concentrations of hydrazine and ammonia were measured by absorption spectrophotometry and ion chromatography, respectively. The schematic diagram of the equipment used for exhaust composition analysis is shown in Fig. 1 of Ref. 10.

Influence of hydrazine hydrate and KOH concentration on cell performance.— The influence of hydrazine hydrate and KOH concentration on fuel cell performance was investigated. During the measurements, the hydrazine hydrate concentration in the aqueous solution was varied at 1, 2, 4, and 8 M, while the KOH concentration was 1 M. Further, the influence of KOH concentration on fuel cell performance was measured by using an aqueous solution of 4 M hydrazine hydrate in the absence of KOH, and for 0.1 and 1 M KOH. The cell performance was measured on the Ni anode (2.5 mg cm^{-2}) and Co–PPY–C cathode (0.21 mg cm^{-2}). Other experimental conditions were fundamentally the same as the abovementioned.

Results and Discussion

Comparison of anode catalysts.— The fuel cell performances using Ni, Co, and Pt as an anode catalyst were measured. The *I-V* performance and the power density performance of the cell using Ni and Pt as an anode catalyst are shown in Fig. 2. It is observed that in the anion-exchange membrane fuel cell using hydrazine as the fuel, use of Ni and Co as anode catalysts results in a high power density as compared to Pt. The anodic reaction of hydrazine in an alkaline environment takes place through the following reactions

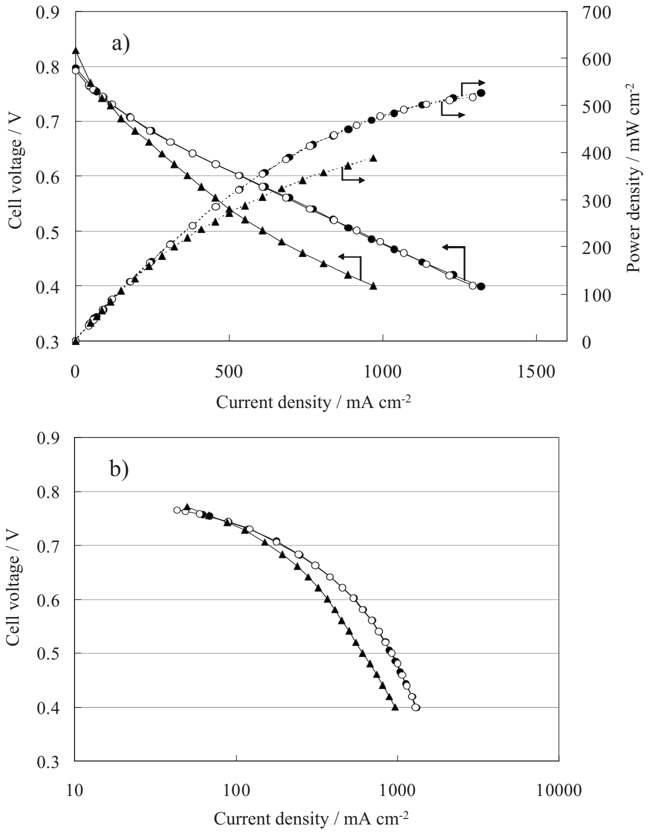

Figure 2. Influence of concentration of hydrazine hydrate on the cell voltages and power density vs current density at (●) 1, (○) 2, (▲) 4, and (■) 8 M. The cell temperature was 80°C. An aqueous solution of hydrazine and KOH (2 mL min^{-1}, λ_{stoic} = 10, 20, 40, and 80 at i = 1 A cm^{-2}) was supplied to the anode, and humidified oxygen (55°C, relative humidity (RH) 27%, 500 mL min^{-1}, λ_{stoic} = 23 at i = 1 A cm^{-2}) was supplied to the cathode.

(a) Electrochemical reaction

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^- \quad \text{(four-electron reaction)} \qquad [1]$$

$$N_2H_4 + 3OH^- \rightarrow N_2 + (1/2)H_2 + 3H_2O + 3e^- \quad \text{(three-electron reaction)} \qquad [2]$$

$$N_2H_4 + 2OH^- \rightarrow N_2 + H_2 + 2H_2O + 2e^- \quad \text{(two-electron reaction)} \qquad [3]$$

$$N_2H_4 + OH^- \rightarrow N_2 + (3/2)H_2 + H_2O + e^- \quad \text{(one-electron reaction)} \qquad [4]$$

$$N_2H_4 + OH^- \rightarrow (1/2)N_2 + NH_3 + H_2O + e^- \quad \text{(one-electron reaction)} \qquad [5]$$

(b) Chemical reaction

$$N_2H_4 \rightarrow N_2 + 2H_2 \quad \text{(decomposition)} \qquad [6]$$

$$3N_2H_4 \rightarrow 4N_2 + NH_3 \quad \text{(decomposition)} \qquad [7]$$

In the electro-oxidation reaction of hydrazine, the most desirable reaction is the four-electron reaction given by Eq. 1.

In the graph shown in Fig. 3, Pt (829 mV) has a higher open-circuit potential (OCP) than Ni (797 mV) and Co (792 mV). Ni (527 mW cm^{-2}) and Co (517 mW cm^{-2}) exhibit a higher power density than Pt (389 mW cm^{-2}). The difference between the *I-V*

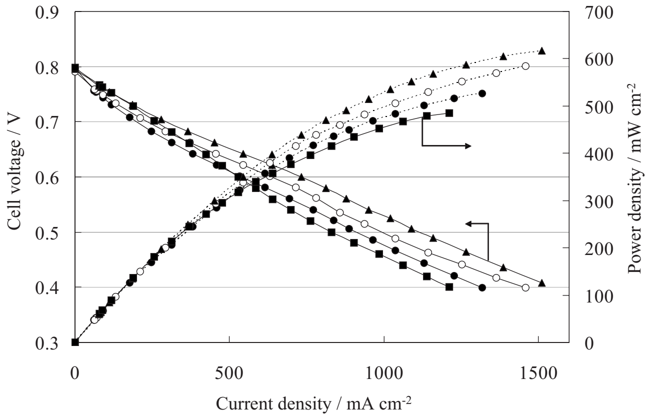

Figure 3. Effect of anode catalysts on (a) cell voltage and power density vs current density: (●) nickel, (○) cobalt, and (▲) platinum. The loadings of nickel, cobalt, and platinum were 2.7, 2.7, and 2.8 mg cm^{-2}, respectively. The cell temperature was 80°C. An aqueous solution of hydrazine and KOH (2 mL min^{-1}; $\lambda_{stoic} = 10$ at $i = 1$ A cm^{-2}) was supplied to the anode, and humidified oxygen (55°C, RH 27%, 500 mL min^{-1}, $\lambda_{stoic} = 23$ at $i = 1$ A cm^{-2}) was supplied to the cathode. (b) Tafel plots derived from *I-V*. (Same conditions as Fig. 2a.)

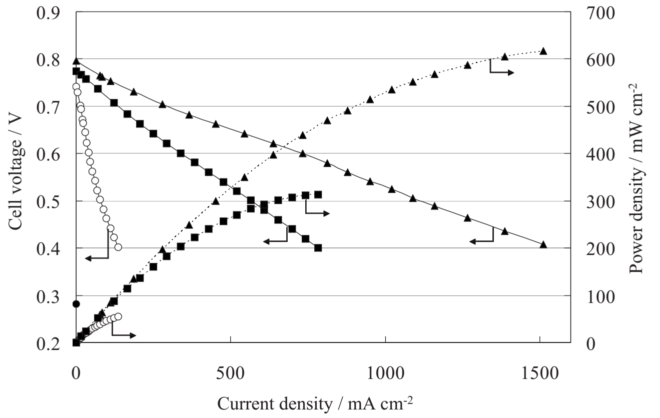

Figure 4. Influence of KOH concentration in fuel on the cell voltage and power density vs current density: (●) without KOH, (○) 0.1 M KOH, and (▲) 1 M and (■) 3 M KOH. The cell temperature was 80°C. An aqueous solution of hydrazine and KOH (2 mL min^{-1}, $\lambda_{stoic} = 40$ at $i = 1$ A cm^{-2}) was supplied to the anode, and humidified oxygen (55°C, RH 27%, 500 mL min^{-1}, $\lambda_{stoic} = 23$ at $i = 1$ A cm^{-2}) was supplied to the cathode.

slopes of these anode catalysts does not influence the high-frequency resistance of the cell because the resistance of these anode catalysts is the same (0.15 Ω cm^2). In the Tafel plot shown in Fig. 3, although a clear difference is observed in the characteristics of these anode catalysts in high-current regions, no clear difference in the low-current regions below 100 mA cm^{-2} is observed. This plot shows that the low ion-conductive anion-exchange ionomer does not show a difference in catalytic activities of the above-mentioned anode catalysts.

Because Ni and Co exhibited equivalent *I-V* characteristics, the reaction at each anode was investigated. The concentrations of hydrazine and ammonia in the exhaust measured by absorption spectrophotometry and ion chromatography, respectively, are shown in Table I. Ammonia is formed as a by-product of hydrazine decomposition. However, ammonia does not deactivate the catalysts, unlike carbon monoxide of direct methanol fuel cells.[11] However, the concentration of ammonia should be low to achieve high efficiency and zero emissions. Hydrazine consumption and ammonia generation in the case of the Ni catalyst were less than that in the case of Co catalyst. In the case of Co catalyst, the consumption of hydrazine was considerably high, and the decomposition reaction given by Eq.7 occurred at the OCP. There was no relationship between current densities and ammonia concentrations, implying that ammonia was generated by the chemical reaction.[7] Moreover, this indicated that Co was in the metal form at the OCP, because Co exhibited a high rate of decomposition. An increase in the current density resulted in the oxidation of Co and a decrease in the rate of decomposition. From these results, it can be assumed that Ni is the most suitable anode catalyst among Ni, Co, and Pt for use in the direct hydrazine alkaline anion-exchange membrane fuel cell.

Table I. The exhaust composition from the anode side of the fuel cell during operation.

Anode	Cathode	Current density (mA cm^{-2})	Hydrazine hydrate (%)	Ammonia (ppm)
Ni	Co–PPY–C	0	4.98	33
		376	4.53	38
		752	4.34	75
Co	Co–PPY–C	0	4.77	1193
		376	4.12	617
		752	3.99	618

Influence of hydrazine hydrate and KOH concentrations on fuel cell performance.— The influence of the concentration of hydrazine hydrate on fuel cell performance is discussed in this section. The change in the *I-V* performance and power density performance with a change in the hydrazine hydrate concentration from 1 to 8 M is shown in Fig. 4. The cell performance improves until the hydrazine hydrate concentration is 4 M. However, the cell performance deteriorates at a KOH concentration of 8 M. Crossover of hydrazine was almost the same because the difference between the OCPs is small. Although the high-frequency resistance of the cell remains almost the same (0.15–0.16 Ω cm^2) from 1 to 4 M, it increases rapidly (0.23 Ω cm^2) at 8 M. The increase in the hydrazine concentration from 1 to 4 M results in an increase in the reactivity. However, an excess concentration of hydrazine (8 M) adversely affects the cell performance because of a decrease in ion conductivity.

The anion-exchange membrane fuel cell, comprised of a Ni anode and a Co–PPY–C cathode, exhibits the maximum power density of 617 mW cm^{-2} at a hydrazine hydrate concentration of 4 M.

The influence of KOH concentration in the fuel on cell performance was also investigated. The hydrazine hydrate concentration was set to 4 M. The change in the *I-V* performance and power density performance of the cell with a change in the KOH concentration from 0 to 3 M is shown in Fig. 4. It was found that the addition of KOH improved the cell performance remarkably. The cell performance was very poor in the absence of KOH and for 0.1 M KOH. In particular, the cell exhibited a very low OCP of 0.282 V in the absence of KOH. Hydrazine is a weak base ($pK_a = 7.96$); at pH values well below pK_a, hydrazine exists primarily as hydrazinium ions ($N_2H_5^+$). This result indicates that the low OCP can be attributed to the restriction of the diffusion of hydrazinium ions into the catalyst layer due to the inverse effect of an anion-exchange resin of electrode. Further, it is considered that the addition of KOH improves the ion conductivity of anion-exchange membranes. However, the cell performance decreases when the KOH concentration is 3 M. This decrease in the cell performance is not due to its high-frequency resistance (0.13 Ω cm^2 at 3 M and 0.15 Ω cm^2 at 1 M). Therefore, an increase in the KOH concentration results in a decrease in cell performance; this decrease can be attributed to mass transportation that influences cathode polarization.[12,13] In alkaline fuel cells, alkaline liquid electrolytes with high concentration (9 M KOH) can be used. Electrolytes with low concentration (1 M KOH) can be used in this anion-exchange membrane fuel cell.

Conclusion

1. In an alkaline anion-exchange membrane fuel cell using hydrazine as the fuel, the power density was higher in the case of Ni and Co used as an anode catalyst than in the case of Pt used as an anode catalyst.

2. Ni was found to be the most suitable anode catalyst among Co, Ni, and Pt for use in the direct hydrazine anion-exchange membrane fuel cell, because the rate of decomposition of Ni was lower than that of Co, and Ni exhibits higher power density than Pt.

3. An increase in the hydrazine concentration from 1 to 4 M results in an increase in the reactivity. However, an excess concentration of hydrazine adversely affected the cell performance because of a decrease in ion conductivity.

4. Addition of KOH can improve cell performance remarkably. In the absence of KOH, hydrazine exists primarily as hydrazinium ions ($N_2H_5^+$). Low OCP can be attributed to prohibition of hydrazinium ion into the catalyst layer by an inverse affect of alkaline anion-exchange resin of the electrode.

5. The anion-exchange membrane fuel cell, comprised of a Ni anode and a Co–PPY–C cathode, exhibits a maximum power density of 617 mW cm^{-2} at a hydrazine hydrate concentration of 4 M.

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References

1. K. Asazawa, K. Yamada, H. Tanaka, A. Oka, M. Taniguchi, and T. Kobayashi, *Angew. Chem., Int. Ed.*, **46**, 8024 (2007).
2. L. A. Adams, S. D. Poynton, C. Tamain, R. C. T. Slade, and J. R. Varcoe, *Chem. Sus. Chem.*, **1.2**, 79 (2008).
3. J. R. Varcoe and R. C. T. Slade, *Fuel Cells*, **2**, 187 (2005).
4. J. R. Varcoe, R. C. T. Slade, and E. L. H. Yee, *Chem. Commun. (Cambridge)*, **2006**, 1428.
5. E. H. Yu and K. Scott, *J. Appl. Electrochem.*, **35**, 91 (2005).
6. K. Yamada, K. Yasuda, N. Fujiwara, Z. Siroma, H. Tanaka, Y. Miyazaki, and T. Kobayashi, *Electrochem. Commun.*, **5**, 892 (2003).
7. G. E. Evans and K. V. Kordesch, *Science*, **158**, 1148 (1967).
8. http://www.mofa.go.jp/Mofaj/Gaiko/summit/toyako08/showcase/pdf/E08.pdf, last accessed Feb 18, 2009.
9. R. Bashyam and P. Zelenay, *Nature*, **443**, 63 (2006).
10. K. Yamada, K. Asazawa, K. Yasuda, T. Ioroi, H. Tanaka, Y. Miyazaki, and T. Kobayashi, *J. Power Sources*, **115**, 236 (2003).
11. S. Gottesfeld and J. Pafford, *J. Electrochem. Soc.*, **135**, 2651 (1988).
12. Z. P. Li, B. H. Liy, K. Arai, A. Asaba, and S. Suda, *J. Power Sources*, **126**, 28 (2004).
13. W. X. Yin, Z. P. Li, J. K. Zhu, and H. Y. Qin, *J. Power Sources*, **182**, 520 (2008).