

Investigation of PEM type direct hydrazine fuel cell

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Received 21 October 2002; received in revised form 16 December 2002; accepted 19 December 2002

Abstract

Hydrazine was examined as a fuel in a direct-liquid-fueled fuel cell employing proton exchange membrane (PEM) for the electrolyte. Hydrazine showed better performance than methanol in the direct fuel cell; the cell using hydrazine gave voltage twice as high as that using methanol in the low-current density region. The *I*–*V* characteristics were drastically changed depending on the surface area of the anode catalyst. Compositions of the exhaust materials from each electrode were analyzed in order to investigate the reaction that occurred at the electrodes. The analysis revealed that the catalytic decomposition reaction of hydrazine proceeded further than the electro-oxidation reaction on the anode side using a high specific surface area catalyst. The crossover of hydrazine and ammonia through the PEM was confirmed and the reduction of the hydrazine crossover is important in developing further high performance.

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Keywords: PEM; Direct-fueled fuel cell; Hydrazine

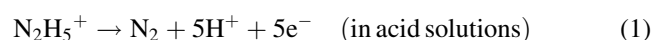
1. Introduction

Because of their high fuel efficiency, fuel cells are considered as the most promising power source of next generation, which will replace the internal combustion engine. There are several types of fuel cell, differentiated by the electrolyte and conducting ion. Proton exchange membrane fuel cells (PEMFCs) are suitable as a power source for vehicles and mobile electric appliances, because the electrolyte is a solid with high protonic conductivity and the power density is high at low operation temperature.

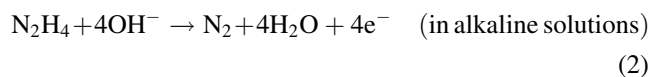
Because high-density storage of hydrogen, especially for vehicles, is difficult, the current mainstream method of storage is a high-pressure gas. However, from the viewpoint of possible running distance, it is desirable to use a liquid fuel that has high energy density and ease of handling. Direct fuel cell systems, where fuel is directly supplied to the fuel cell without reforming to hydrogen also have great benefits for vehicles and mobile electric appliances [1]. Direct methanol fuel cell (DMFC) is expected as a hopeful candidate of the direct fuel cell system [2]. However, major

problems remain unsolved. The anode overvoltage is high because reaction intermediates such as CO adsorb on the surface of the electrocatalyst and act as a severe poison to platinum [3]. This causes a low cell voltage and requires a high loading amount of platinum and ruthenium in the anode. Increasing operation temperature for reduction of this problem brings about other problems such as startup and cell durability. In addition, the methanol crossover through the electrolyte membrane further reduces the efficiency and power output [4,5]. Therefore, technological breakthroughs are necessary to enable practical applications.

Hydrazine (N₂H₄) fuel cells are ideal in that they do not exhaust environmentally loading materials such as CO₂ and can generate high voltage as a direct fuel cell system. As shown in Eqs. (1) and (2), since hydrazine is composed of only hydrogen and nitrogen, the anode reaction produces, theoretically, only nitrogen. Therefore, perfect zero emission equal to a pure hydrogen fuel can be realized. Since direct hydrazine fuel cell (DHFC) does not produce CO-like poisoning species in the direct electro-oxidation process, the overvoltage by the catalyst poisoning is low in DHFC. The theoretical electromotive force is also high at 1.56 V [6], and highly efficient high power density is expected:



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Hydrazine FC was investigated intensively in the 1970s, as an alkali fuel cell using liquid alkaline electrolyte [7,8]. The Governmental Industrial Research Institute, Osaka (GIRIO) and Daihatsu Motor Co. Ltd. produced a hydrazine-air fuel cell vehicle experimentally in 1972, and driving experiments were carried out [9]. The recent progress of PEMFC technology has been remarkable, reaching the test and demonstration phase. The application domain of PEMFC is also becoming wider to include a few watts level for portable devices. This study reconsiders hydrazine fuel cells using recent PEMFC technology. Although Saito and coworkers suggested hydrazine permeation through the membrane of DHFC [10], there is no report on the high performance and characteristics of DHFC, which uses the recent proton exchange membrane (PEM) technology. This study investigates the performance and influential factor of direct hydrazine fuel cells using PEM, and examines the possibility of practical application.

2. Experimental

2.1. Membrane electrode assembly (MEA) preparation

Two kinds of unsupported Pt black catalyst (Tanaka K.K.) that differ in specific surface area ($7 \text{ m}^2/\text{g}$ for Pt(LSSA), $35 \text{ m}^2/\text{g}$ for Pt(HSSA)) were used for the anode. The higher surface area catalyst, Pt(HSSA), was heat treated in an oven at 400°C for 2 h. The resulting catalyst was called Pt(HSSA treated). Unsupported Pt-Ru black catalyst ($67 \text{ m}^2/\text{g}$, Johnson Matthey) for DMFC was also used for comparison. The catalyst was mixed with 5 wt.% Nafion[®] solution (Aldrich) at the fixed ratio. The mixture was stirred for over 2 h, and then it was thoroughly dispersed in an ultrasonic bath to make the catalyst ink. For the preparation of membrane electrode assembly (MEA), the prepared ink was directly sprayed onto a Nafion[®] 117 (Du Pont) electrolyte membrane, after the viscosity had been moderately adjusted in ethanol. Carbon black supported 60 wt.% Pt catalyst

(Tanaka K.K.) was applied to the cathode, and formed into an electrode using a similar method to that for the anode. Both electrodes were fixed to the membrane by applying the electrode to both sides of the membrane and leaving at room temperature for 30 min, and then, hot-pressing for 5 min at 120°C . A sintered titanium fiber was used for the current collector on the anode side. A carbon cloth having a thin gas diffusion layer was used on the cathode side.

2.2. Characterization of electrocatalyst

Platinum dispersion and particle size were observed with a high-resolution transmission electron microscope (TEM) (Hitachi H-9000) operating at 300 kV, and half-width method from the Pt(1 1 1) peak of X-ray diffraction (XRD). The specific surface area and pore-volume distributions of electrocatalysts were measured by N_2 adsorption (Micromeritics ASAP2010) and calculated by the BET and BJH method.

2.3. The measurement of cell performance

The prepared MEA, with a round shaped working electrode area of 10 cm^2 , was inserted in a single cell to measure the cell performance. An aqueous solution of hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) of 10 wt.% was supplied to the anode at the flow rate of 2 ml/min, and oxygen gas humidified at 80°C was supplied to the cathode at the flow rate of 400 ml/min. The applied shape of the flow-fields was serpentine for the anode and comb-shaped for the cathode. Before measuring DHFC performance, the cell was operated for 1 h with pure hydrogen fuel, following 1 h operation by 10 wt.% $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ as fuel. The cell temperature was controlled at 80°C . For comparison, the performance of DMFC was measured under the condition of 3 wt.% methanol aqueous solution at the flow rate of 4 ml/min and cell temperature of 100°C .

2.4. The composition analysis of the exhaust materials

To analyze the reaction during cell operation, compositions of the exhaust from both electrodes were analyzed in various conditions. Fig. 1 is a schematic diagram of the measurement equipment. The gas composition (hydrogen,

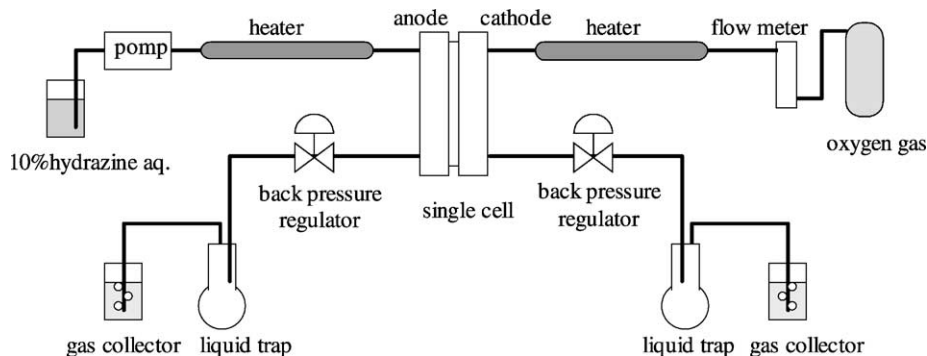


Fig. 1. Scheme of the equipment for exhaust composition analysis.

oxygen, nitrogen) was measured by gas chromatography. The water-soluble components (ammonia and hydrazine) were measured by ion chromatography and absorption spectrophotometry, respectively. Results are given in 10^{-6} mol/min units.

3. Results and discussion

Fig. 2 compares the performance of the DHFC, which used Pt black (LSSA) for the anode catalyst, with the DMFC, which used Pt-Ru black. Pt-Ru black is currently the most active electrocatalyst for methanol oxidation in DMFC. The

generally preferable condition for each fuel cell system was applied because of the optimum condition at which the high performance is obtained differs according to the system. Hydrazine generated much higher cell voltage than methanol in direct fuel cells using the proton exchange membrane. At a current density of 40 mA/cm^2 or less, DHFC generated over 1 V, about double that of DMFC even though the specific surface area of Pt black in the DHFC anode was much lower than that of Pt-Ru black in the DMFC anode. Moreover, the cell voltage of DHFC was higher, even though the cell temperature of DHFC was 20°C lower than that of DMFC. This means that, when it is used for the vehicles and mobile electric appliances, DHFC enables system simplification, cost

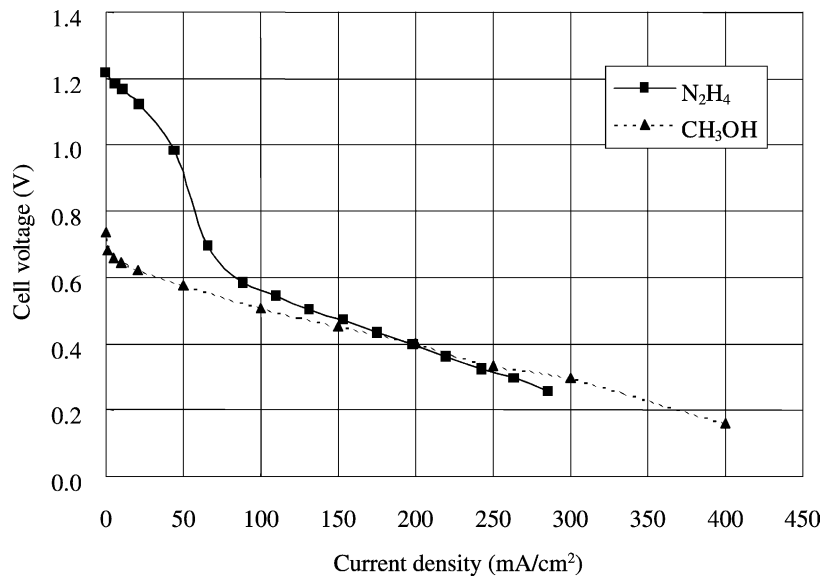


Fig. 2. Comparison of fuels for direct-fueled fuel cell. N_2H_4 (DHFC): loading of anode/cathode catalysts = Pt 2/Pt 3 mg/cm^2 , specific surface area of anode catalyst = $7 \text{ m}^2/\text{g}$, operating temperature = 80°C ; CH_3OH (DMFC): loading of anode/cathode catalysts = Pt 3Ru 1.5/Pt 3 mg/cm^2 , specific surface area of anode catalyst = $67 \text{ m}^2/\text{g}$, operating temperature = 100°C ; common conditions: anode/cathode pressures = $0.2/0.2 \text{ MPa}$.

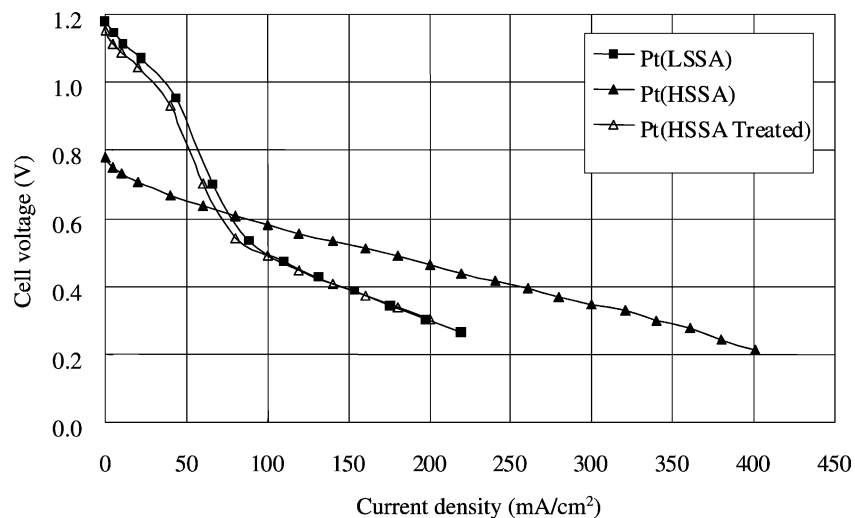


Fig. 3. Effect of anode Pt catalyst for direct hydrazine fuel cell. Specific surface area of anode catalyst: Pt(LSSA) = $7 \text{ m}^2/\text{g}$, Pt(HSSA) = $35 \text{ m}^2/\text{g}$, Pt(HSSA treated) = $6.3 \text{ m}^2/\text{g}$, loading of anode/cathode catalysts = Pt 2/Pt 3 mg/cm^2 , anode/cathode pressures = $0.1/0.15 \text{ MPa}$.

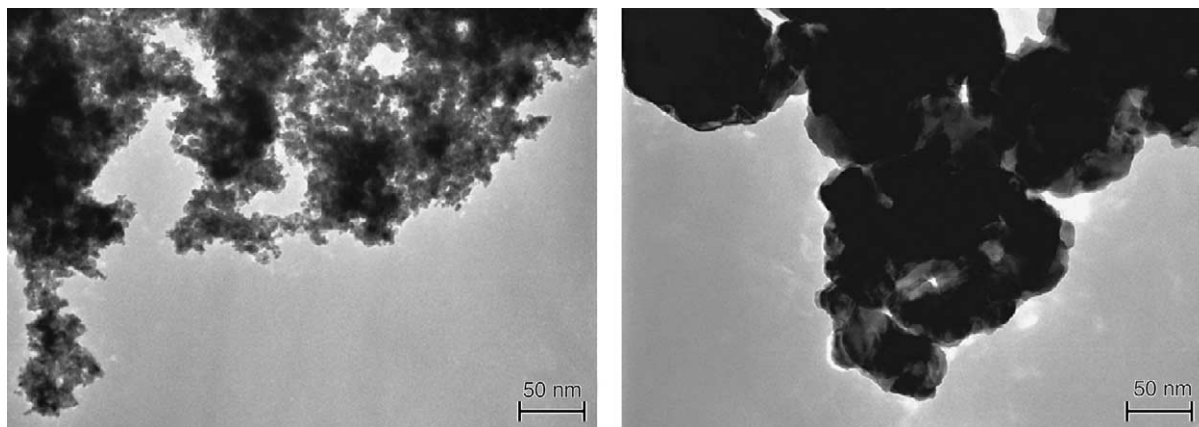


Fig. 4. TEM images of anode Pt(HSSA) catalyst before (left side) and after (right side) heat treatment at 400 °C for 2 h.

reduction, fewer cells required in the stack and the important merit of compactness. In spite of the better performance of DHFC, the internal resistance of DHFC was about 2.5 times larger than that of DMFC. This is one of the problems in the operation of DHFC in the high current density region. Such characteristics of DHFC are expected to be more useful in the power application of mobile electric appliances.

Fig. 3 shows the performances of DHFC, which use some kinds of anode electrocatalyst. These electrodes include the same loading amount of platinum. This figure shows the different I - V (current–voltage) characteristics when using the high specific surface area catalyst, Pt(HSSA). The open circuit voltage dropped below 1 V and the potential was lowered almost rectilinear with increasing the current density. Although surface property, morphology and the catalytic activity of the catalysts is dependent on the preparation method, the preparation processes of the two Pt black, Pt(LSSA) and Pt(HSSA), are not exhibited. This study prepared Pt(HSSA treated) by simple heat treatment of Pt(HSSA). In Fig. 3, DHFC performance was evaluated

using prepared Pt(HSSA treated) catalyst with a specific surface area of 6.3 m²/g, almost the same as Pt(LSSA). The I - V characteristic of the Pt(HSSA treated) was almost equal to Pt(LSSA) as shown in this figure. The changes of particle size and pore-volume distribution of Pt(HSSA) before and after the heat treatment were examined with TEM, XRD and N₂ adsorption. Fig. 4 shows the TEM images of Pt(HSSA) before and after the heat treatment, which confirmed that sintering of Pt particles occurred and the size of particles was increased by the heat treatment. Fig. 5 shows the XRD patterns of Pt(HSSA) before and after the heat treatment. From this figure, the average Pt particle sizes were calculated to be 7.0 and 27.6 nm, respectively. Furthermore, there was no large difference in the intensity ratio of each peak between before and after heat treatment, which means that there was no inclined growth of crystal plate. Fig. 6 shows the specific pore-volume distributions, $d(\text{pore volume})/d(\log(\text{pore radius}))$, of two Pt blacks measured by N₂ adsorption. The pore volume below 100 nm was drastically decreased by the heat treatment. Pores below 100 nm are

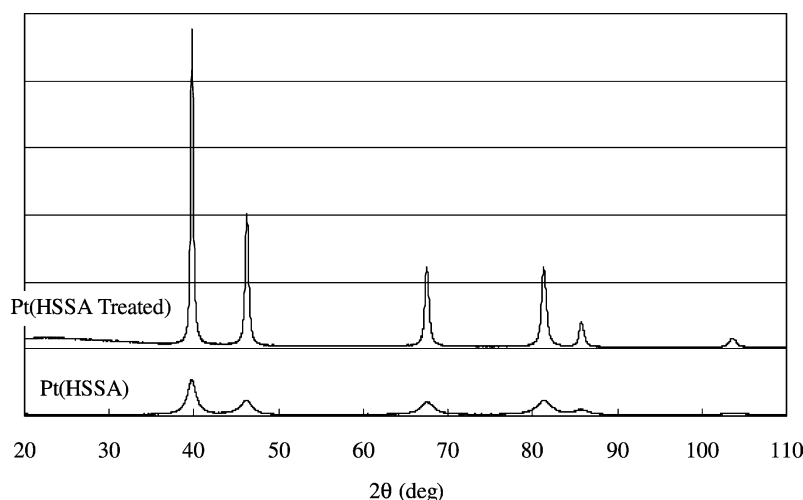


Fig. 5. XRD of anode Pt(HSSA) catalyst before and after heat treatment.

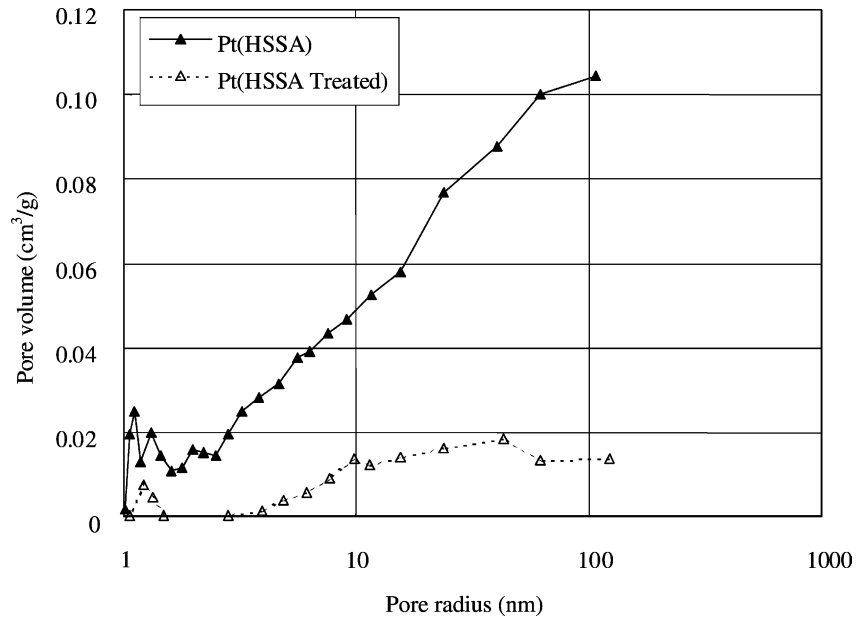


Fig. 6. Pore-volume distribution, $d(\text{pore volume})/d(\log(\text{pore radius}))$, of anode Pt(HSSA) catalyst before and after heat treatment.

those between primary particles and on the surface of primary particles. From these results, it is obvious that the sintering of primary particles and reduction of specific surface area occurred in Pt(HSSA treated). Taken together, the above-mentioned data reveal that $I-V$ characteristics are greatly changed by controlling the specific surface area or the particle size of the anode catalyst.

The composition of the exhaust from both electrodes under DHFC operation was measured to examine the scheme of reactions in DHFC with different specific surface area of the anode catalyst. Fig. 7 shows anode and cathode exhaust composition under operation at the current density of 50 mA/cm^2 with the anode catalyst Pt(LSSA) and Pt(HSSA), respectively. From the anode side composition

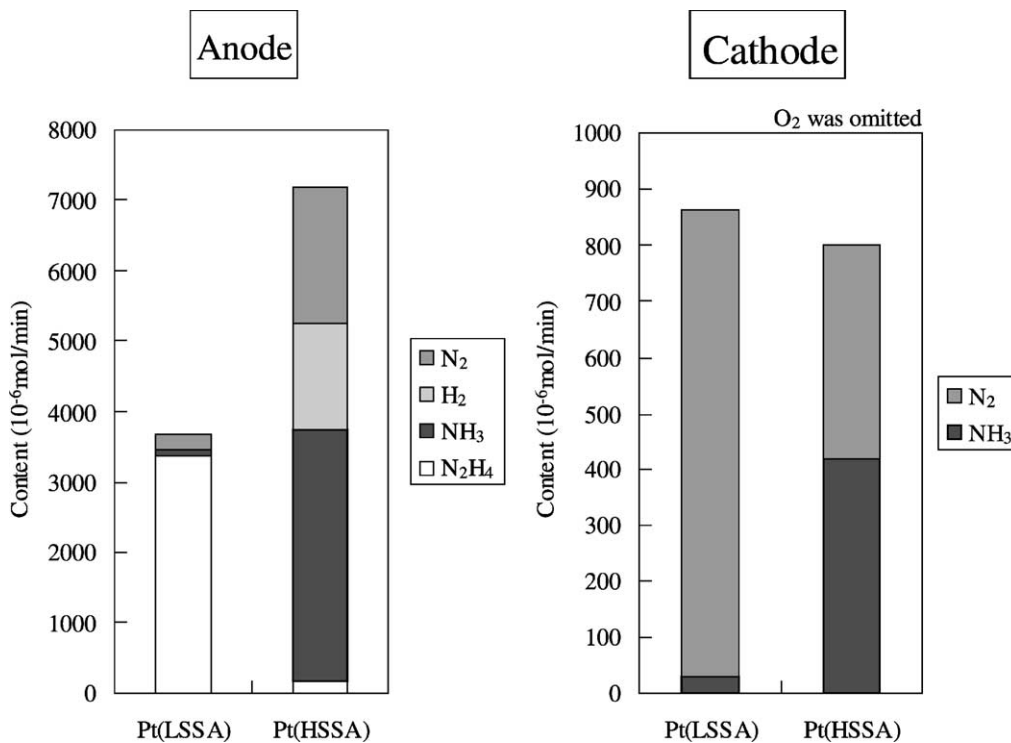


Fig. 7. The content of exhaust materials from each electrode with high and low specific surface area anode catalysts. Loading of anode/cathode catalysts = Pt 2/Pt 3 mg/cm^2 , current density = 50 mA/cm^2 , anode/cathode pressures = 0.1/0.1 MPa.

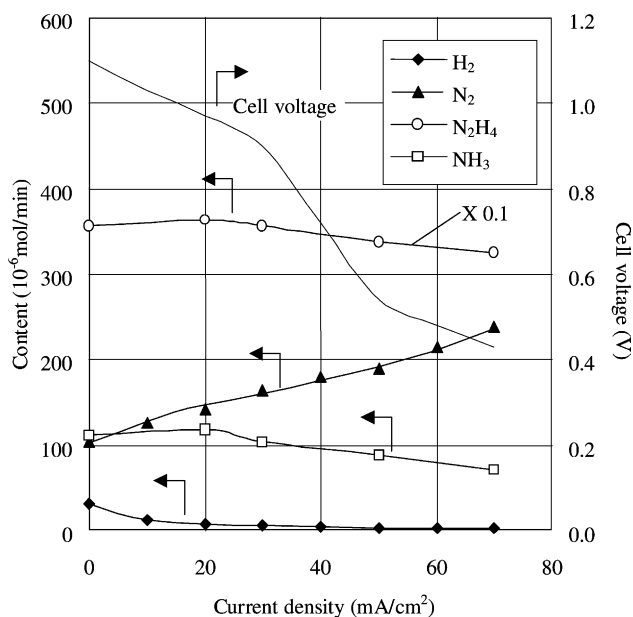


Fig. 8. Dependence of the content of exhaust materials from the anode on the current density. Conditions as in Fig. 7.

(left side of Fig. 7), the large amount of unreacted hydrazine was exhausted and a small amount of nitrogen, ammonia and almost no hydrogen was detected, when Pt(LSSA) was used. Electro-oxidation was clearly dominant in Pt(LSSA). On the other hand, when Pt(HSSA) was used, the ratio of unreacted hydrazine was very low, and instead there was large generation of nitrogen, hydrogen and ammonia, which indicates that most of the supplied hydrazine was catalytically decomposed on the anode by side reactions as shown in Eqs. (3) and (4). This catalytic decomposition not only decreases the fuel utilization but also seems to cause the lowering of the cell voltage because the hydrogen that was generated by decomposition reaction contributes to the anode reaction:



Nitrogen and ammonia were also detected from the exhaust of the cathode side (right side of Fig. 7). Concerning the anode exhaust measurement of each electrocatalyst, it seems that nitrogen was produced at the cathode by oxidation of the hydrazine that permeated through the membrane to the cathode, and the ammonia is regarded as being formed in the anode and having permeated through the membrane. The loss of cell voltage by the formation of mixed potential at the cathode due to the hydrazine permeation seems to be larger when Pt(LSSA) was used, because the content of nitrogen in the cathode exhaust is high. Because of hydrazine decomposition on the anode side, the crossover rate of hydrazine was low in DHFC with the Pt(HSSA) anode. Although ammonia is also easily transported through the membrane, it seems not to be reactive at the cathode.

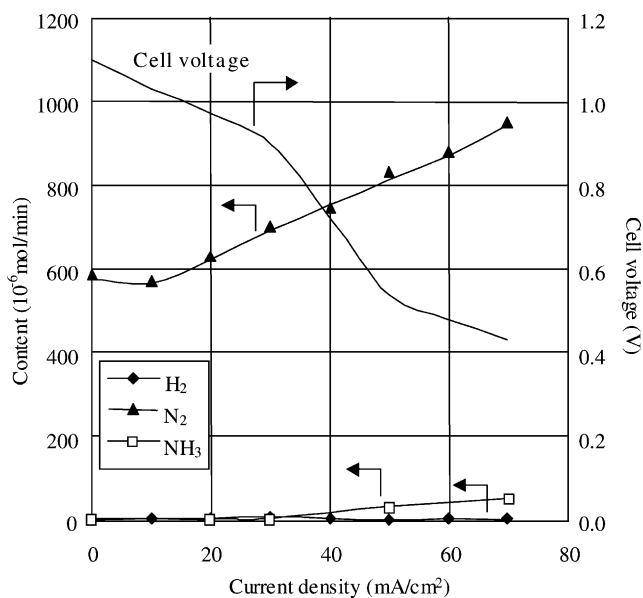


Fig. 9. Dependence of the content of exhaust materials from the cathode on the current density. Conditions as in Fig. 7.

The change of the exhaust composition with the current density in using the Pt(LSSA) catalyst was measured. Fig. 8 shows the anode side exhaust and Fig. 9 the cathode side exhaust. On the anode side, the catalytic decomposition products such as hydrogen and ammonia decreased with the increase of current density since the electro-oxidation rate increased. As indicated in Fig. 9, although the crossover of hydrazine is suppressed in the low-current density (20 mA/cm² or less), the increase of the current density increases the crossover quantity. Rapid lowering of the cell voltage with increase of current density is considered to be correlated with this increase of crossover, but further examination is necessary to elucidate the mechanism.

Though the performance of DHFC is not sufficient yet, it is expected to improve to the new practical fuel cell. Reduction of the hydrazine permeation through the membrane is important for improving the performance of DHFC. Cation exchange membranes such as Nafion[®] are now widely used in PEMFC due to their high ionic conductivity and durability. However, cation exchange membranes are not always suitable electrolyte membranes in DHFC because the fuel hydrazine is alkaline liquid and hydrazinium cation easily penetrates into the cation exchange membrane by ion exchange. This phenomenon is supposed to cause the increase of internal resistance and hydrazine crossover. Therefore, the development of anion exchange membrane with low hydrazine permeation is one of the solutions, which would increase the faradic efficiency and lead to rise of the cell voltage of DHFC at high current density. The development of the more effective catalysts, which promote the electrochemical reaction and suppress the side reaction like decomposition to hydrogen or ammonium, is also one of the solutions.

4. Conclusions

This study has demonstrated for the first time that it is possible to run a direct hydrazine fuel cell using a Nafion[®] membrane.

- Hydrazine generates a higher cell voltage than methanol in direct-liquid-fueled fuel cell using PEM as the electrolyte.
- High voltage over 1 V was obtained in the low-current density region when using Pt black having a low surface area as the anode electrode catalyst.
- The catalytic activity for hydrazine catalytic decomposition tends to occur more dominantly than the electro-oxidation reaction by increasing the specific surface area of the Pt black used for the anode electrocatalyst. The open circuit voltage was lowered by the effect of decomposition products such as the hydrogen.
- The permeation of hydrazine and ammonia through the membrane was observed. Moreover, crossover of hydrazine seems to be a factor of the deterioration of cathode potential. Reduction of this crossover is an important task.

Acknowledgements

The authors thank Dr. T. Akita (National Institute of Advanced Industrial Science and Technology) for his measurement of transmission electron microscope.

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