Fuel Cells

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A Platinum-Free Zero-Carbon-Emission Easy Fuelling Direct Hydrazine Fuel Cell for Vehicles**

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The two major barriers regarding the use of fuel cell vehicles (FCVs) are the expense associated with platinum catalysts and the many restrictions associated with the filling and storage of hydrogen. The highly acidic nature of proton (H^+) exchange membranes requires a corrosion-proof platinum catalyst and expensive bipolar plate. Here we have developed a new platinum-free fuel cell, from the reverse concept, by using a solid hydroxide anion (OH^-) exchange polymer membrane and by changing the fuel source from hydrogen to liquid hydrazine (N_2H_4). This platinum-free, direct hydrazine fuel cell (DHFC), comprising cobalt or nickel for the anode and cobalt or silver for the cathode, exhibits a maximum power generation performance of 0.5 $\mathrm{W\,cm^{-2}}$, which is comparable to a hydrogen fuel cell. The DHFC system achieves zero emission and does not produce any carbon dioxide. Although hydrazine is mutagenic, a detoxification technique was developed which safely fixed hydrazine to the carbonyl groups in the polymer and then released hydrazine through a solvent at the time of power generation. The onboard readsorption of hydrazine is possible, and the hydrazine supply in a filling stand can also be attained without returning to a factory. The direct hydrazine fuel cell points to the future of fuel cell vehicles.

A fuel cell can transform chemical energy into electrical energy efficiently. In various fuel cells, a solid polymer electrolyte fuel cell (PEFC) has been recognized as a future power source for vehicles. In particular, hydrogen FCVs may improve air quality, health, and climate significantly as they exhaust neither a toxic substance nor carbon dioxide (global warming).[1] However, the socioeconomic problem associated with Pt catalysts and the many restrictions associated with the filling and storage of H_2 are two major barriers regarding the wide-ranging spread of fuel cell vehicles. The first problem is an extensive use of Pt as an electrode catalyst in present fuel cell systems. Pt is a limited resource, and it is not only expensive but cannot respond to the demands of the automobile market. Development of Pt substitutes has been studied hard, but the further improvement of output performance is still required for practical use.[2]

One of the main reasons for requiring Pt is the highly acidic nature of proton-exchange membranes. Any base-metal catalysts cannot be used for the long period of time under such severe conditions. Here, in order to solve this problem, the development of a new Pt-free fuel cell was attempted by replacing the acidic membrane with an alkaline anion-exchange membrane. In past research,[3] the power densities of anion-type fuel cells have been shown to be very poor (about 0.055 $\mathrm{W\,cm^{-2}}$), even using Pt catalysts with H_2 and O_2. Though Ag, Co, and Ni could be used for cathode catalysts, no other anode catalysts than Pt, including Ni or Pd, generated a current (although minute) in our previous research of anion-type fuel cells with hydrogen. For realization of the Pt-free fuel cell with the potential of practical use, examination of the fuel is required also.

The second problem regarding fuel cells for vehicles is that the cruising range is restricted, as low-energy-density H_2 is used as the fuel source.[4] Although the emissions from H_2–O_2 fuel cells are clean, a high volume density and safe storing method have not been developed, with the current handling method restricted to storing at very high pressures. Pressurizing with a high-pressure pump is required at the time of filling, resulting in large energy losses through the generation of heat. Moreover, the high-pressure H_2-storing method has associated problems with regards to handling and safety.

We reinvestigated hydrazine, which was used for alkaline fuel cells in the past,[5] as a promising fuel for vehicles. As hydrazine is a liquid at ordinary temperatures at ordinary pressures, it can be transferred easily. In addition, the volume of the hydrazine storage tank is reducible as the energy density of hydrazine (anhydrous 5.5 $\mathrm{Wh\,cm^{-3}}$, or as a hydrate 3.5 $\mathrm{Wh\,cm^{-3}}$) is higher than that of high-pressure hydrogen (1.3 $\mathrm{Wh\,cm^{-3}}$ at 70 MPa) and that of liquid hydrogen (2.3 $\mathrm{Wh\,cm^{-3}}$). The hydrazine-O_2 fuel cell exhibits a high open-circuit voltage (about 1.61 V), and the theoretical energy-conversion efficiency ($e = \Delta G/\Delta H$) of hydrazine to

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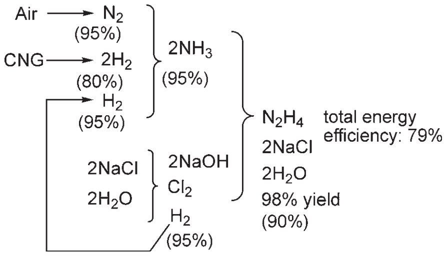
nitrogen and water is 100 %. The well-to-wheels (WTW) energy consumption is estimated by referring to the Japan Hydrogen and Fuel Cell Demonstration Project (JHFC)'s future data[6] (Table 1). The input primary energy for 1 km driving of hydrazine FCVs (1.01 MJ km^{-1}) is lower than that of hydrogen FCVs (1.08 MJ km^{-1}) because hydrazine FCVs show lower well-to-tank (WTT) energy consumption. WTT can be divided into two steps: the first step is fuel production, and the second step is transport and refilling. First, in comparison to the energy efficiency for producing each fuel, hydrogen is usually produced from the steam reforming of natural gas with approximately 80 % energy efficiency. Hydrazine can be generated by the process shown in Scheme 1, and the total energy efficiency is 79 %. Secondly, the transportation and refilling energy efficiency of hydrazine (99 %) is higher than hydrogen (91 %) because of the extra energy required to compress hydrogen.

Table 1: Input primary energy for 1 km driving of FCVs (MJ km^{-1}).[a]

Type	WTT	TTW	WTW
Hydrazine FCVs	0.22	0.79	1.01
Hydrogen FCVs	0.29	0.79	1.08

[a] WTT: well-to-tank; TTW: tank-to-wheel; WTW: well-to-wheel.



Scheme 1. The production of hydrazine and the energy efficiency (given as percentages in parentheses) at each step. CNG = compressed natural gas.

Moreover, as the products of the reaction are only nitrogen and water, the hydrazine-O_2 fuel cell is also a zero-emission system. Thus, it can be said that hydrazine would be an excellent fuel for vehicles.

The anode catalysts were examined by using a potentiostat with a rotating disk electrode (RDE) to perform the electrochemical measurements (potentials given versus the reversible hydrogen electrode (RHE)). The results indicated that the oxidation performance for hydrazine of Co (−0.18 V vs RHE) and of Ni (0 V vs RHE) exceeded that of Pt (0.0618 V vs RHE). The possibilities of direct electro-oxidation and hydrogen generation through the catalytic decomposition of hydrazine are suggested,[7] as the potential of the Co catalyst for hydrazine oxidation was lower than the potential of the RHE.

The performances of the direct hydrazine fuel cells and other direct fuel cells are shown in Figure 1 (see also Table 2). An Ag/C catalyst was used for the cathode in the hydrazine fuel cell, as the performance decrement of this catalyst in the crossover of hydrazine through the membrane is small. This is a result of the high reduction activity of Ag/C in the presence of oxygen versus the low oxidation activity of hydrazine. The Ag/C catalyst exhibited equivalent power generation characteristics to the Pt/C catalyst (see Figure S1 in the Supporting Information).

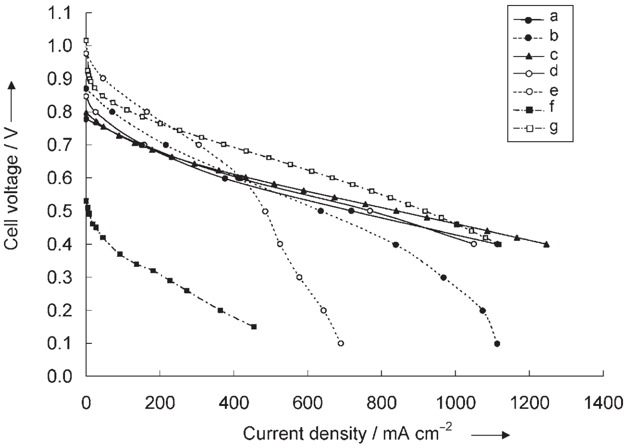


Figure 1. Current–voltage performance of direct fuel PEFCs (cell temperature: 80 °C). Hydrazine was dissolved (0.67 M) in 1 M KOH aqueous solution and supplied at 2 mL min^{-1}. a–e) Hydrazine (+20 kPa); f) methanol (+100 kPa); g) hydrogen (+20 kPa). See Table 2 for details of samples.

Table 2: Configuration of samples.[a]

Sample	Anode	Cathode	Polymer electrolyte
a	Ni	Ag/C	Anion A
b	Ni	Ag/C	Anion B
c	Ni	Co-PPY-C	Anion A
d	Co	Ag/C	Anion A
e	Co	Ag/C	Anion B
f	PtRu/C	Pt/C	Nafion
g	Pt/C	Pt/C	Nafion

[a] PPY: polypyrrol.

Two types of anion-exchange polymer electrolytes, both containing tetraalkylammonium cation groups as pendant groups with a polyolefin main chain, were used for the DHFCs. The chemical constitution of electrolyte A is homogeneous and that of electrolyte B is heterogeneous. The output characteristics of the DHFCs using any electrolyte were comparable to the H_2–O_2 PEFC and far exceeded the direct methanol fuel cell (DMFC), which is a typical liquid fuel cell. Here, DHFCs show a possibility of being applicable to various uses by appropriate selection of the electrolytes and catalysts. As a large current is required, electrolyte A is more suitable for vehicle applications. On the other hand, the performance of the DHFC with a combination of electrolyte B and Co catalyst exceeds that of conventional hydrogen PEFCs in the low-current-density region. The application to various electric devices is expected. Moreover, the performance of the Co-PPY-C composite cathode, as used in previous research by Zelanay and Bashyam,[2a] has also been remarkably improved by applying our DHFC technology. The high output performance is demonstrated only with base-metal catalysts, without using platinum and silver.

In the continuous power-generation experiment, the performance with the Co anode catalyst decreased after 40 h. In comparison, the performance with the Ni anode catalyst exhibited excellent stability over a long period of time (Figure 2).

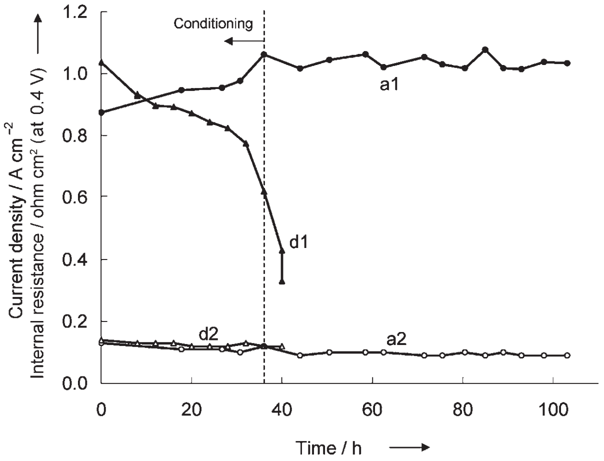


Figure 2. Durability test of direct hydrazine anion-exchange PEFCs. Hydrazine was dissolved (0.67 M) in 1 M KOH aqueous solution and supplied at 2 mL min^{-1}; O_2 was supplied at 500 mL min^{-1}; cell temperature: 80 °C. Current density: a1, d1; internal resistance: a2, d2 (a corresponds to the Ni anode catalyst; d corresponds to the Co anode catalyst; see Table 2).

Powder X-ray diffraction (XRD) measurements demonstrated that the Ni catalyst was still in a metallic state after the continuous power-generation experiment, while the Co catalyst had converted into cobalt hydroxide. In the conventional alkali-type fuel cell, the generation of carbonate from CO_2 results in a drop in the power-generation performance.[8] In the DHFC, the output slightly declined as a result of the presence of CO_2—about 50 times higher concentration than in the atmosphere. As the performance recovered shortly after CO_2 removal, it is clearly indicated that the DHFC is resistant to CO_2 (Figure 3). This behavior is believed to be a benefit of the fixed tetraalkylammonium cations as the ion-exchange groups of the polymer.

To deal with the mutagenicity of hydrazine,[9] a detoxification technique was examined in which carbonyl (> C=O) or amide (-CO-NH$_2$) groups are substituted onto hydrazine in the polymer to form a hydrazone (> C=N-NH$_2$) or hydrazide (-CO-NH-NH$_2$), respectively. When required, a solvent can be used to release the hydrazine once again. Both hydrazone and hydrazide gave negative results in a mutagenicity test (Table 3). Thus, a storage material was designed in which the readsorption of hydrazine was made possible by using a carbonyl compound. It was found that repetitious adsorption, desorption, and readsorption of hydrazine was possible for the polymer consisting of carbonyl groups. In using the hydrazide compound, readsorption of hydrazine was difficult after desorbing hydrazine, as the hydrazide was converted into carboxylic groups (-CO-OH).

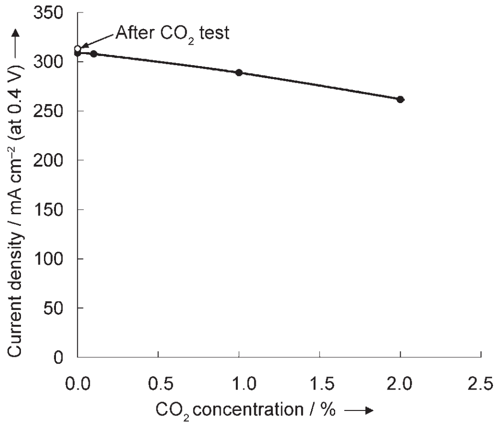


Figure 3. Influence test on carbon dioxide poisoning of anion-exchange PEFC sample d. Hydrazine was dissolved (0.67 M) in 1 M KOH aqueous solution and supplied at 2 mL min^{-1}; air + CO_2 was supplied at 500 mL min^{-1}; cell temperature: 80 °C. The test was conducted with increasing CO_2 concentration.

Table 3: Mutagenicity and toxicity of hydrazine and derivatives.

Derivatives	Mutagenicity (Ames test)	Toxicity LD$_{50}$ [mg kg^{-1} (mouse)]
Benzophenone hydrazone	negative	–
Polyacryl hydrazide	negative	3800
Hydrazine hydrate	positive[9]	83[9]

Through the adsorption of hydrazine, carbonyl groups tend to form cross-links between main chains of the polymer. It then causes the hardening of the polymer, therefore the difficulty of hydrazine desorption is increased. A sufficiently hydrophilic nature is necessary for the polymer to avoid hardening. In this study, sodium 4-vinylbenzene sulfonate was adopted and copolymerized with methyl vinyl ketone to increase the hydrophilicity of the polymer.

An adsorption-desorption-readsorption study was carried out (see Table S1 in the Supporting Information). This hydrazine-fixing material, with the polymer consisting of sodium 4-vinylbenzene sulfonate and methyl vinyl ketone, allowed the adsorption of hydrazine up to 108.2 % (substitutional ratio to the carbonyl groups). After desorption, the substitutional ratio of fixed hydrazine decreased to 27.9 % at room temperature and to 16.1 % at 80 °C. It means that 92.1 % of hydrazine desorbed from the carbonyl group at 80 °C. The substitutional ratio of hydrazine increased to 78.7 % as a result of the readsorption at room temperature. Although the development of efficient adsorption polymers should be aimed at industrially, we show here one scientific solution of adsorbing hydrazine as a harmless hydrazone and releasing it as hydrazine again.

In summary, we succeeded in developing a Pt-free fuel cell that exhibits a high output by replacing hydrogen with hydrazine and replacing the proton-exchange-type electrolyte with an anion-exchange type. This development will help to open the fuel cell age for vehicles with further technical improvements.

Experimental Section

For the adsorption-desorption-readsorption study, the hydrazine-fixing polymer consisted of sodium 4-vinylbenzene sulfonate and methyl vinyl ketone mixed in 1:1 molar ratio and cross-linked by methylene(bis)acrylamide. Full experimental details are provided in the Supporting Information.

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[1] M. Z. Jacobson, W. G. Colella, D. M. Golden, *Science* **2005**, *308*, 1901 – 1905.

[2] a) R. Bashyam, P. Zelenay, *Nature* **2006**, *443*, 63 – 66; b) T. Matsumoto, Y. Nagashima, T. Yamazaki, J. Nakamura, *Electrochem. Solid-State Lett.* **2006**, *9*, A160 – A162.

[3] J. R. Varcoe, R. C. T. Slade, E. L. H. Yee, *Chem. Commun.* **2006**, 1428 – 1429; E. H. Yu, K. Scott, *J. Appl. Electrochem.* **2005**, *35*, 91 – 96; K. Yamada, K. Yasuda, N. Fujiwara, Z. Siroma, H. Tanaka, Y. Miyazaki, T. Kobayashi, *Electrochem. Commun.* **2003**, *5*, 892 – 896.

[4] L. Schlapbach, A. Züttel, *Nature* **2001**, *414*, 353 – 358.

[5] G. E. Evans, K. V. Kordesch, *Science* **1967**, *158*, 1148 – 1152; S. G. Meibuhr, *J. Electrochem. Soc.* **1974**, *121*, 1264 – 1270.

[6] http://www.jhfc.jp/e/data/data/h17/06h17seminar_e.pdf

[7] K. Yamada, K. Yasuda, H. Tanaka, Y. Miyazaki, T. Kobayashi, *J. Power Sources* **2003**, *122*, 132 – 137.

[8] E. Gülzow, M. Schulze, *J. Power Sources* **2004**, *127*, 243 – 251.

[9] R. F. Kimball, *Mutat. Res.* **1977**, *39*, 111 – 126; B. Y. Ekshtat, *Hyg. Sanit.* **1965**, *30*, 191 – 197.