Treatment of low concentration hydrogen by electrochemical pump or proton exchange membrane fuel cell

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ABSTRACT

Proton exchange membrane fuel cell (PEMFC) can produce electricity through electrochemical reaction of hydrogen with oxygen with the use of a membrane and electrode assembly (MEA). In other words, the hydrogen pressure difference between the anode and cathode can produce electricity via an electrochemical process. Conversely, when we supply electricity to MEA from an external power source, we can pump up or separate hydrogen from the low-pressure anode to the high-pressure cathode, according to the principle of "concentration cell". By the way, PEMFC cannot use the fuel completely, because a cell potential decreases and electrode material may corrode when most of the fuel is consumed. Therefore the fuel released from PEMFC should be treated safely. The depleted hydrogen from PEMFC can be recovered by the electrochemical hydrogen pump, or further can be used as a fuel for the power generation by PEMFC, even though the cell voltage might be low. In this study we preliminarily measured the voltage–current characteristics of hydrogen pump and PEMFC changing the hydrogen concentration from 99.99% to 1%, as another option to platinum catalytic combustion of low concentration hydrogen. Moreover we could successfully treat the low concentration hydrogen by electrochemical pump or PEMFC, for the widely changing hydrogen concentration and mixture flow rate. The gas chromatography confirmed the hydrogen concentration of the treated gas to be 1000 ppm at most.

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1. Introduction

In proton exchange membrane fuel cell (PEMFC) hydrogen and oxygen flow on opposite sides of a proton exchange membrane (PEM) to react electrochemically for producing electricity directly at the external load. Conversely, if hydrogen is made to flow at anode supplying electricity externally, the electrochemical hydrogen pump can transport hydrogen selectively to cathode through PEM. Hydrogen becomes protons at the anode of the membrane and electrode assembly (MEA), and the protons move through PEM, and at the cathode of MEA, where no air or oxygen is flowing, protons return to the higher-pressure hydrogen than at anode by combining with electrons via the external load.

Two applications of the hydrogen pump were proposed [1,2]. The first is a hydrogen separation pump that functions mainly to selectively separate and recover hydrogen only [1–3]. This pump can decrease the amount of hydrogen discharged from PEMFC in places where discharge is difficult, such as underground tunnel, deep sea, or space. Moreover, the recovered hydrogen can be recy-

cled to the intake of PEMFC and raise the fuel utilization ratio at fuel cell [1–3]. The other application is a hydrogen compressor [1–5] that functions mainly to pressurize low-pressure hydrogen at anode to high-pressure hydrogen at cathode. An electrochemical cell or stack similar to PEMFC was reported to work as a compressor to pump up atmospheric hydrogen at anode to high-pressure hydrogen of 5.4 MPa at cathode [5]. The isothermal compression power required by the electrochemical pump is smaller than the adiabatic compression power by ordinary mechanical compressor, which means that the electrochemical pump is more efficient than ordinary mechanical compressor [2].

Usually fuel cell cannot use hydrogen fuel completely, because the Nernst potential decreases and the electrode material of carbon corrodes when most of the fuel is consumed. Therefore the usual fuel utilization ratio is limited to near 80% in order to keep the cell voltage appropriate and to avoid the electrode corrosion. The depleted fuel is utilized as the heating fuel to reform fuel, such as methane or kerosene, to hydrogen, or released to atmosphere without any use. The National Fire Protection Association regulates the hydrogen concentration of released gas to be less than 1%. So the released hydrogen must be treated safely when the concentration exceeds the regulated value. The platinum catalytic combustor is suitable to burn the low concentration hydrogen with oxidant of air. But here we propose the electrochemical pump or PEMFC to recover the depleted hydrogen, which performance is not known

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Nomenclature

F	Faraday constant ($C\,mol^{-1}$)
i	current density ($A\,cm^{-2}$)
i_{ave}	average current density ($A\,cm^{-2}$)
P_i	pressure or partial pressure of element i (Pa)
r	membrane resistance per unit area ($\Omega\,cm^2$)
R	gas constant ($J/K/mol^{-1}$)
T	operating temperature (K)
V_{cell}	cell voltage (V)

Greek letter

η_{cur}	current efficiency (%)

Subscripts

a	anode
c	cathode
H_2	hydrogen

well. When the low concentration hydrogen is treated by the hydrogen pump or PEMFC, we must pay the same attention with PEMFC to the carbon corrosion by fuel starvation due to the non-uniform distribution of fuel in PEMFC stack [6].

In this paper we measured both the power consumption characteristics of hydrogen pump and the power generation characteristics of PEMFC, changing the hydrogen concentration from 1% to 99.99% to make clear merits and demerits of both PEMFC and hydrogen pump from an energetic point of view. As will be described later when the hydrogen recovered at 0.2 V at hydrogen pump can be used as fuel for PEMFC to produce 0.6 V cell voltage, it means that energy of 0.4 V, the difference between 0.6 and 0.2 V, can be gained even when the depleted hydrogen concentration is low such as 1% in hydrogen pump.

There are not so many papers as PEMFC which report the electrochemical hydrogen pump. In our previous experiment [1,2] the measurement error was 2%, therefore in some cases we could not confirm the released hydrogen concentration of less than 2%. And the fuel was diluted by N_2 in our previous study. The reformed gas of hydrocarbon contains CO_2 and its concentration increases when hydrogen is consumed along the flow channel of fuel cell. Further our previous reports have studied only the steady state of constant hydrogen concentration or constant flow rate. Domestic fuel cell systems and fuel cell vehicles are usually operated following the load change, therefore the hydrogen pump or PEMFC for treating low concentration hydrogen is preferred to work under the load following condition, i.e., under changing hydrogen concentration and/or changing depleted gas flow rate. To make sure these unsolved items this paper will describe in the following the voltage–current characteristics of hydrogen pump and PEMFC, changing hydrogen concentration from 1% to 99.99% in dilution by N_2 or CO_2 in order to confirm the low limit of hydrogen concentration of depleted fuel. Also these two hydrogen treatment methods are checked under the varying conditions of hydrogen concentration and depleted gas flow rate to make sure their load following performance.

2. Experimental equipment and condition

2.1. Experimental equipment

Fig. 1 shows the schematic diagram of the electrochemical hydrogen pump and PEMFC. In a case of hydrogen pump, hydrogen (including mixture of N_2 or CO_2) is supplied to the anode inlet, and nothing is supplied to the cathode inlet. After a mass flow controller
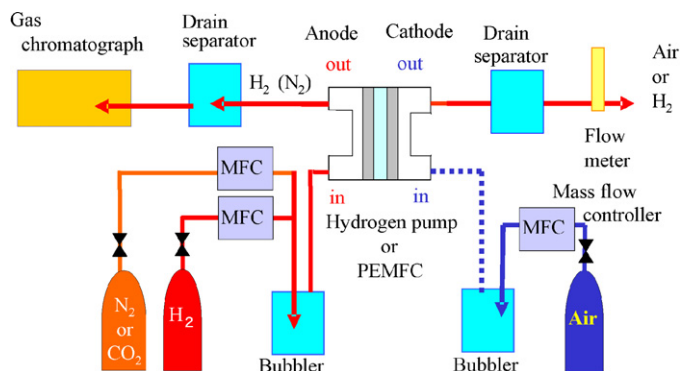

Fig. 1. Schematic diagram of experimental apparatus of hydrogen pump and PEMFC.

(MFC) regulates the hydrogen flow rate, hydrogen is humidified through a bubbler and fed to the anode of hydrogen pump cell. With a constant flow rate the voltage–current characteristics ($V_{cell}-i_{ave}$) are measured changing i_{ave}. Moisture of hydrogen transferred to cathode is trapped through a drain separator, and the flow rate of dry hydrogen is measured by a soap film flow meter. The flow rate is compared with one given by current according to the Faraday law, and the ratio of the former to the later is obtained as the current efficiency. A LCR meter measures the PEM film resistance with a frequency of 1 kHz including its contact resistance. In this measurement the phase difference is always kept below 5°. The purity of hydrogen used in this experiment is an industrial grade of over 99.99%. In a case of PEMFC experiment, hydrogen is fed to the anode in a similar way to hydrogen pump, and air is fed to cathode as shown by the dotted line in Fig. 1.

The cell constitution of hydrogen pump is almost the same as that of fuel cell, and the gas feed grooves for both cells are of a single serpentine. In experiments the MEA plane is set vertically so that gas can flow from the top to the bottom to reduce the water flooding inside the cell (conversely shown in Fig. 1). Several kinds of MEA, such as for water electrolysis, reversible cell and PEMFC, were tested for hydrogen pump. As the MEA for PEMFC has given the best performance, it was adopted in this experiment. The dry thickness of MEA is 80 μm, and the effective electrode area is 10 cm². At both sides of MEA a sheet of carbon paper of 200 μm thickness is placed as a gas diffusion layer (GDL), and the periphery of GDL is sealed by silicon rubber sheet not to leak hydrogen to the surroundings [2]. These MEA, GDLs and silicon sheets are sandwiched by separators grooved by gas flow channel. The separators are heated up by circulating the constant-temperature water to keep the cell temperature a pre-decided one.

2.2. Experimental condition

Experimental condition is shown in Table 1. The constant hydrogen flow rate of 3.8 cm³ min⁻¹ (at 25 °C and 101.3 kPa) is fed to both hydrogen pump and PEMFC with the hydrogen concentration of 1–99.99% diluted by N_2 or CO_2. The cell temperature is set to 60 °C,

Table 1
Experimental condition.

Items	Operating condition
Cell temperature (°C)	60
Anode gas flow rate (cm³ min⁻¹)	H_2:3.8 or 38 + N_2 or CO_2
Anode hydrogen concentration (%)	1–99.99
Dew point temperature (°C)	59
Cathode air flow rate (cm³ min⁻¹) (only for PEMFC)	200 or 300
Current density (A cm⁻²)	0–0.05 or 0.5
Hydrogen treatment ratio (%)	0–100

and the dew point temperature is set to 59–60 °C, keeping the operating pressure at both anode and cathode atmospheric. Since in the real application the flow rate and concentration of depleted hydrogen from PEMFC are supposed to vary widely, the treatment tests of such varying depleted hydrogen were performed under applying the constant voltage, which value was decided from the V–i characteristics of pump or PEMFC measured at constant flow rate. At these constant voltage tests, the hydrogen concentration was switched between 1 and 10% alternatively every 10 min with a constant hydrogen flow rate of 3.8 cm^3 min^{-1}, and the gas flow rate was switched between 3.8 and 38 cm^3 min^{-1} with a constant hydrogen concentration of 10%. Under these varying conditions we measured the current response to the switched concentration or flow rate.

3. Treatment of low concentration hydrogen by hydrogen pump

3.1. Voltage–current characteristics of hydrogen pump

The V–i characteristics of hydrogen pump is shown in Fig. 2 where the hydrogen concentration was changed parametrically to be 99.99, 10 and 1% in dilution of N_2. Since the hydrogen flow rate was fixed at 3.8 cm^3 min^{-1}, 0.05 A cm^{-2} at the right end of abscissa corresponds to a hydrogen treatment ratio of 100%. At a region where the hydrogen concentration is high and the current density i_{ave} is low, the relation between V_{cell} and i_{ave} is linear, but at a region of high i_{ave} and low hydrogen concentration V_{cell} becomes larger than the linear line. The lower the hydrogen concentration becomes, the higher V_{cell} was obtained including the open-circuit voltage. This voltage increase is due to the following Nernst potential E_{Nernst},

$$E_{Nernst} = \frac{RT}{2F} \ln \frac{P_{cH_2}}{P_{aH_2}}, \qquad (1)$$

where F is the Faraday constant, R is the gas constant, T is temperature, P_{aH_2} is hydrogen partial pressure at anode, and P_{cH_2} is hydrogen partial pressure at cathode. The open-circuit voltage E_{Nernst} was calculated to be 33.4 mV for hydrogen concentration of 10%, and 66.4 mV for 1% concentration. The calculated values agree well with the measured. The reason why V_{cell} increases rapidly from the linear line at a high i_{ave} region is thought to be due to the decreasing E_{Nernst} at downstream of anode where hydrogen concentration is decreasing. When hydrogen concentration is 1%, V_{cell} increases up to 126.9 mV at $i_{ave} = 0.049$ A cm^{-2}. At this time the measured ir loss (resistance overpotential) as described in Section 2.1
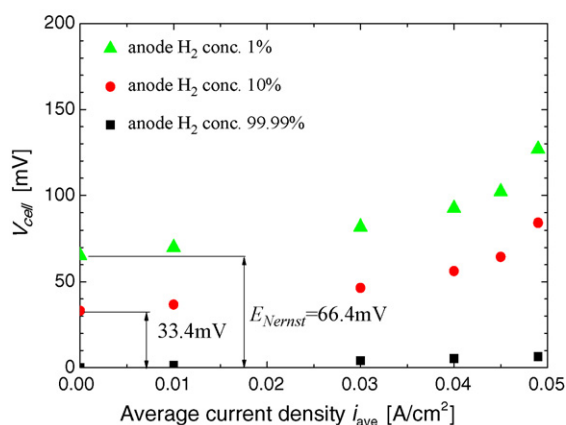

Fig. 2. Change of V_{cell}–i_{ave} characteristics by H_2 concentration of hydrogen pump mixed with N_2.
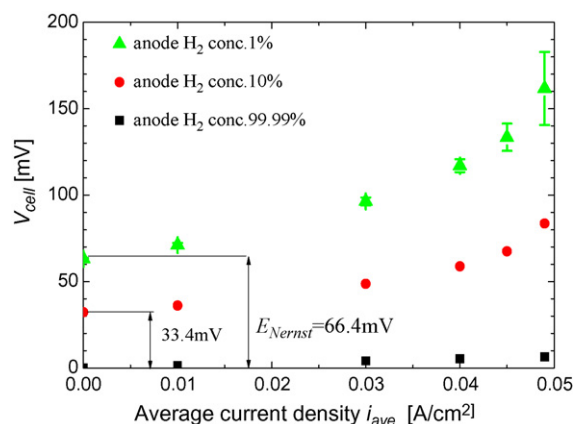

Fig. 3. Change of V_{cell}–i_{ave} characteristics by H_2 concentration of hydrogen pump mixed with CO_2.

was independent from the changing concentration, and was proportional to i_{ave}. The flow rate of hydrogen transported to cathode followed the Faraday law independently from the changing concentration. Therefore the current efficiency η_{cur} obtained from the transported flow rate was almost 100%.

Next the V–i characteristics of hydrogen pump for CO_2 mixture gas were measured as a case for reformed gas. They are shown in Fig. 3 with parametric change of hydrogen concentration. At a region where the hydrogen concentration is high and the current density is low, the relation between V_{cell} and i_{ave} is linear similarly to N_2 mixture, while at a region of high i_{ave} and low hydrogen concentration V_{cell} becomes larger than the linear line. Further V_{cell} for 1% hydrogen concentration was larger than that for N_2 mixture, and the data reproducibility became worse than N_2 mixture case. In Fig. 3 the average value and its standard deviation are shown for 5 times measurement. The ir loss measured at 1 kHz was almost the same as the N_2 mixture case. One of the reasons for the worse performance might be the reverse shift reaction between CO_2 and H_2 at anode, or partial oxidation of carbon by CO_2, producing CO to poison the anode and to reduce the catalyst activity. In case of CO_2 mixture the hydrogen flow rate transported to cathode also followed the Faraday law independently from the changing concentration, and η_{cur} obtained from the transported flow rate was almost 100%.

3.2. Current response to change of hydrogen concentration and flow rate at constant voltage applied hydrogen pump

Since PEMFC is usually operated to follow the load change, the hydrogen concentration and flow rate of the depleted gas is not constant. Therefore in order to simulate the changeable depleted gas the following experiment was performed to confirm the hydrogen pump capability under changing conditions of hydrogen concentration and gas flow rate of feed mixture.

When current i_{ave} is set near a region of high treatment ratio, i.e., the right-side region of Figs. 2 and 3, a small change of current may produce too large cell voltage to corrode electrode carbon by fuel starvation. Therefore we propose here to set V_{cell}, instead of i_{ave}, a little higher than the selected voltage from V–i characteristics. For example, in a case of hydrogen concentration of 1%, cell voltage of 126.9 mV is a rigid value corresponding to $i_{ave} = 0.049$ A cm^{-2} for hydrogen treatment ratio of 0.98 as shown in Fig. 2. Therefore if the constant voltage of 150 mV is applied to the hydrogen pump, i.e., a little higher voltage than 126.9 mV with a margin, the pump may recover hydrogen more than 98% in suppressing the carbon corrosion.
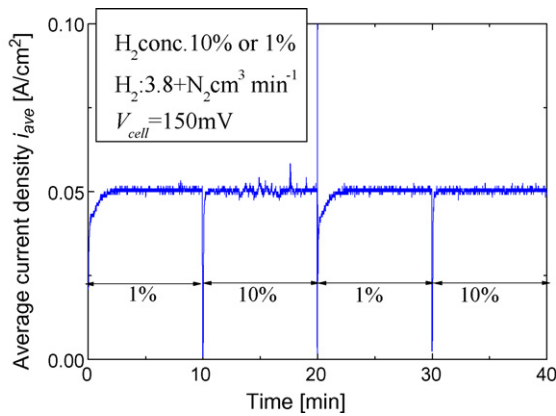
Fig. 4. Current density response for H_2 concentration change at hydrogen pump mixed with N_2.

Fig. 4 shows the current response to the concentration change of feed hydrogen mixture under the constant cell voltage of 150 mV. It can be seen that the responding current density i_{ave} is constant 0.05 mA cm^{-2} for both the hydrogen concentration of 1% and 10%. This constant current corresponds to the constant flow rate of hydrogen diluted by N_2, and i_{ave} of 0.05 A cm^{-2} means 100% of hydrogen treatment ratio. Fig. 4 shows the rapid response and sufficient performance of hydrogen pump. The further details of hydrogen treatment ratio will be discussed in a following section. The sudden increase or decrease of current, vertical lines like hairs in Fig. 4, may be due to the sudden gas stop or gas pressure increase by the manual valve switching to change the hydrogen concentration.

The concentration change test was also performed for CO_2 mixture gas. i_{ave} was set to 250 mV, a little higher voltage than 150 mV for N_2 mixture, because the cell voltage in Fig. 3 was a little higher than in Fig. 2 for N_2 mixture. Since the responding current to concentration change was almost the same as the N_2 mixture case, it is not shown here for saving space.

Next Fig. 5 shows the current response to the flow rate change of N_2 mixture gas under a constant hydrogen concentration of 10%. V_{cell} was set to 300 mV. For hydrogen flow rate of 38 cm^3 min^{-1} i_{ave} was saturated to 0.5 A cm^{-2}, and for hydrogen flow rate of 3.8 cm^3 min^{-1} i_{ave} was saturated to 0.05 A cm^{-2}. These current densities correspond to 100% of hydrogen treatment ratio. At the flow rate change test of CO_2 mixture gas V_{cell} was set to 350 mV. In the CO_2 mixture case the current response was almost the same as the N_2 mixture case.
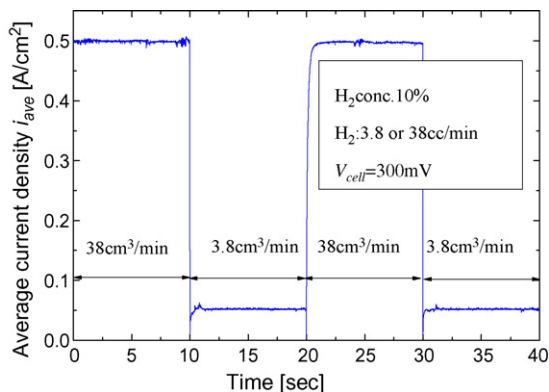

Fig. 5. Current density response for flow rate change at hydrogen pump mixed with N_2.

Table 2
H_2 concentration of released anode gas for H_2 concentration change of feed mixture at H_2 pump.

Items	H_2 conc. 1%	H_2 conc. 10%
Total flow rate (cm^3 min^{-1})	380	38
Current density (A cm^{-2})	0.05	0.05
Treatment ratio at H_2 pump (%)	100 ± 2	100 ± 2
Total treatment ratio (%)	100 ± 0.02	100 ± 0.2
H_2 concentration of released anode gas for N_2 mixture (ppm)	Under 50	Under 50
H_2 concentration of released anode gas for CO_2 mixture (ppm)	70–90	Under 50

3.3. Hydrogen concentration of anode gas released from hydrogen pump

As described in previous section the hydrogen treatment ratio, (hydrogen flow rate corresponding to the measured i_{ave})/(hydrogen flow rate feed to anode), became almost 100%, when the cell voltage was set a little higher than the maximum voltage of V–i characteristics. However when the measurement error is taken into account, the treatment ratio might not be 100% precisely. Further we should consider the hydrogen cross leak from cathode to anode . Therefore we checked the hydrogen concentration of released anode gas using gas chromatography (GS, Science GC-323).

Table 2 shows the measured hydrogen concentration of released anode gas when the concentration was switched to change. The measurement error of hydrogen pump is totally 2%, adding 1% error of flow rate measurement and 1% error of current measurement. The measured hydrogen concentration of released anode gas was below 50 ppm for N_2 mixture gas of either 1% or 10% of hydrogen concentration. Here 50 ppm is the guaranteed accuracy limit of the gas chromatography used here. All of the measured concentrations were below 50 ppm. Therefore the released hydrogen concentration could be decreased below 50 ppm for N_2 mixture gas. For CO_2 mixture gas of 10% hydrogen concentration the released hydrogen concentration was below 50 ppm similarly to N_2 mixture gas, but for CO_2 mixture gas of 1% hydrogen concentration the released hydrogen concentration was a little high of 70–90 ppm, and not stable when compared to N_2 mixture gas.

Table 3 shows the measured hydrogen concentration of released anode gas when the flow rate was switched to change. In a case of N_2 mixture the hydrogen concentration of released anode gas was under 50 ppm similarly to the hydrogen concentration change test either for the hydrogen flow rate of 3.8 or 38 cm^3 min^{-1}. In a case of CO_2 mixture the hydrogen concentration of released anode gas was also under 50 ppm similarly to the N_2 mixture case for the hydrogen flow rate of 3.8 cm^3 min^{-1}, but the released hydrogen concentration became 100–300 ppm for the hydrogen flow rate of 38 cm^3 min^{-1}. This might be due to higher and less stable V_{cell} in CO_2 mixture case than in N_2 mixture case as shown in their V–i characteristics of Figs. 2 and 3. But the maximum concentration was still 300 ppm

Table 3
H_2 concentration of released anode gas for H_2 flow rate change at H_2 pump.

Items	H_2: 38 cm^3 min^{-1}	H_2: 3.8 cm^3 min^{-1}
Hydrogen concentration (%)	10	10
Total flow rate (cm^3 min^{-1})	380	38
Current density (A cm^{-2})	0.5	0.05
Treatment ratio at H_2 pump (%)	100 ± 2	100 ± 2
Total treatment ratio (%)	100 ± 0.2	100 ± 0.2
H_2 concentration of released anode gas for N_2 mixture (ppm)	Under 50	Under 50
H_2 concentration of released anode gas for CO_2 mixture (ppm)	100–300	Under 50

at all of the tested conditions of single cell, and it is sufficiently low when compared to the explosion limit of 4% at room temperature. Therefore the hydrogen pump seems to be useful in engineering application.

Most of fuel cells for industrial use are stacks consisting of many single cells to produce a certain power with an appropriate output voltage. In such stacks fuel must be supplied evenly to each cell to avoid the corrosion of electrode carbon due to the fuel starvation. In order to attain a high fuel utilization ratio, some special stack constitutions are adopted such as the series fuel supply through some grouped stacks or the fuel re-circulation. When we extend the hydrogen pump cell described here to the hydrogen pump stacks, a similar attention must be paid to get a high hydrogen treatment ratio, which is a future issue of development.

4. Treatment of low concentration hydrogen by proton exchange membrane fuel cell

4.1. Voltage–current characteristics of PEMFC

Fig. 6 shows the $V–i$ characteristics of PEMFC in change of the hydrogen concentration of N_2 mixture gas. The flow rates of hydrogen and air were set to 3.8 and 200 $cm^3 min^{-1}$, respectively. PEMFC worked stably till fuel utilization ratio of 98% in cases of 10% and 99.99% hydrogen concentration, and till fuel utilization ratio of 96% in case of 1% hydrogen concentration. At the region over the above-mentioned ratio the performance of PEMFC was unstable with widely oscillating V_{cell}. The reason why the maximum fuel utilization ratio in case of 1% hydrogen concentration was lower than those for 10 and 99.99% hydrogen concentration might be due to the decreasing Nernst potential and the increasing concentration overpotential along channel flow. Also the fuel starvation at down stream of anode channel is anticipated due to the experimental error of test condition. Nevertheless it could be confirmed that PEMFC has operated stably till such high fuel utilization as 96% for anode gas of such low hydrogen concentration as 1%.

Next Fig. 7 shows the $V–i$ characteristics of PEMFC in change of hydrogen concentration of CO_2 mixture gas. Similarly to N_2 mixture gas PEMFC worked normally till fuel utilization ratio of 98% in cases of 10% and 99.99% hydrogen concentration, and till fuel utilization ratio of 96% in case of 1% hydrogen concentration. But similarly to hydrogen pump in case of 1% hydrogen concentration V_{cell} became smaller and showed less reproducible data than in N_2 mixture case. However V_{cell} was still 541 mV for $i_{ave} = 0.048$ $A cm^{-2}$ for 1% hydrogen anode fuel, and this cell voltage may be usable in real applications.
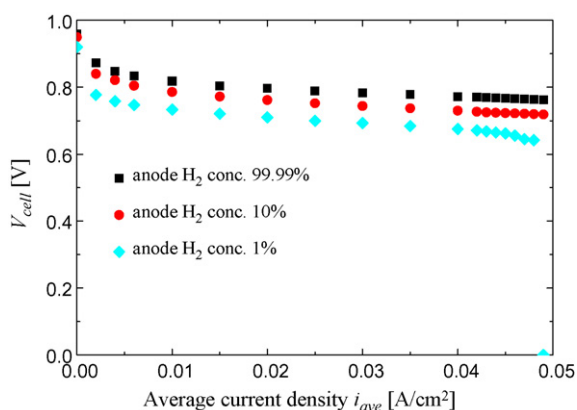

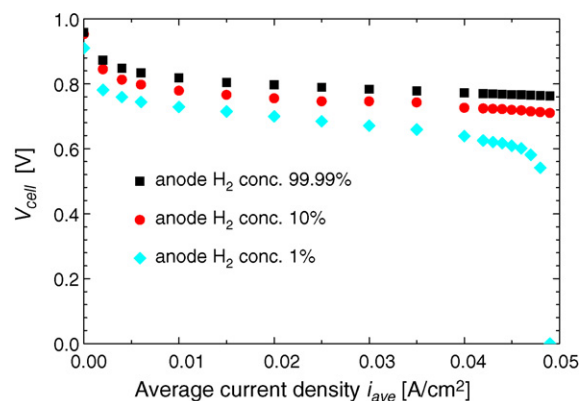**Fig. 7.** Change of $V_{cell}–i_{ave}$ characteristics by H_2 concentration of PEMFC mixed with CO_2.

4.2. Current response to change of hydrogen concentration and flow rate at constant voltage applied PEMFC

In order to correspond to the load following operation described in Section 3.2, PEMFC for hydrogen treatment application was operated under lower cell voltage than the minimum V_{cell} shown in Fig. 6, in a similar way to hydrogen pump. Fig. 8 shows the current response to the hydrogen concentration change of N_2 mixture with a constant flow rate of hydrogen. V_{cell} was set to 0.6 V. While i_{ave} was 0.049 $A cm^{-2}$ for 1% hydrogen mixture, i_{ave} was 0.05 $A cm^{-2}$ for 10% hydrogen mixture. Since $i_{ave} = 0.05$ $A cm^{-2}$ means hydrogen treatment ratio = 1, Fig. 8 shows that 100% of hydrogen was treated in case of 10% hydrogen mixture, and that 98% of hydrogen was treated in 1% hydrogen mixture. The reason why the hydrogen treatment ratio of 100% could not be attained for 1% hydrogen mixture might be due to the concentration overpotential along anode channel and the fuel starvation in anode.

In the hydrogen concentration change test of CO_2 mixture V_{cell} was set to lower voltage of 0.4 V than 0.6 V for N_2 mixture, expecting that much hydrogen might be treated by reducing V_{cell} less than the minimum V_{cell} in Fig. 7. The measured current was almost the same as Fig. 8 for N_2 mixture case, so the figure of measured i_{ave} for CO_2 mixture is omitted here.

Under constant hydrogen concentration of 10% the current response to sudden change of flow rate is shown in Fig. 9 for N_2 mixture. V_{cell} was set to 0.4 V constant too. For hydrogen flow rate of 38 $cm^3 min^{-1}$ i_{ave} became 0.49 $A cm^{-2}$, which corresponds to hydrogen treatment ratio of 98%, and for hydrogen flow rate

Fig. 6. Change of $V_{cell}–i_{ave}$ characteristics by H_2 concentration of PEMFC mixed with N_2.
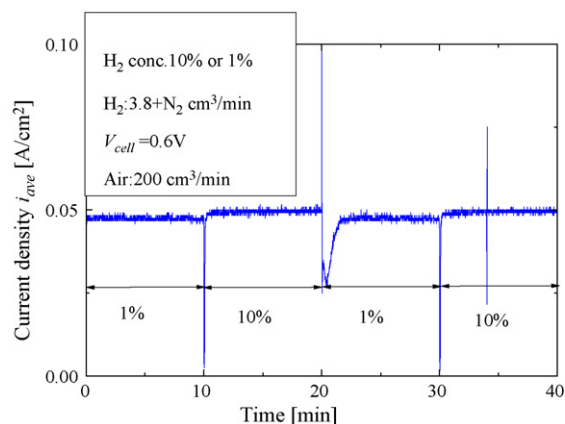

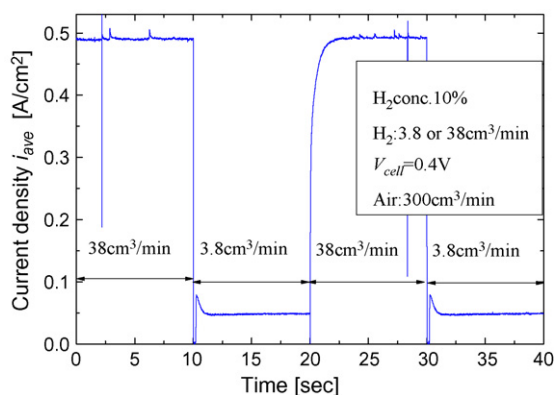**Fig. 8.** Current density response to H_2 concentration change at PEMFC mixed with N_2.

Fig. 9. Current density response for flow rate change at PEMFC mixed with N_2.

Table 4
H_2 concentration of released anode gas for H_2 concentration change of feed mixture at PEMFC.

Items	H_2 conc. 1%	H_2 conc. 10%
Total flow rate ($cm^3 min^{-1}$)	380	38
Current density ($A cm^{-2}$)	0.049	0.05
Treatment ratio at PEMFC (%)	98 ± 2	100 ± 2
Total treatment ratio (%)	99.98 ± 0.02	100 ± 0.2
H_2 concentration of released anode gas for N_2 mixture (ppm)	80–90	Under 50
H_2 concentration of released anode gas for CO_2 mixture (ppm)	60–100	Under 50

of $3.8 cm^3 min^{-1}$ i_{ave} became $0.05 A cm^{-2}$, which corresponds to hydrogen treatment ratio of 100%. In flow rate change test of CO_2 mixture V_{cell} was set to lower voltage of 0.3 V than 0.4 V for N_2 mixture. Since the current response was almost the same as N_2 mixture case the figure of responding i_{ave} is not shown here.

4.3. Hydrogen concentration of anode gas released from PEMFC

The hydrogen concentration of anode gas released from PEMFC was checked by gas chromatography similarly to hydrogen pump. Table 4 shows the measured hydrogen concentration of released gas when the hydrogen concentration of anode mixture gas was changed. The measured hydrogen concentration of released gas was below 50 ppm when the N_2 mixture gas of 10% hydrogen concentration was supplied. The measured hydrogen concentration was 80–90 ppm when 1% hydrogen mixture was supplied. When the CO_2 mixture gas of 10% hydrogen concentration was supplied, the measured hydrogen concentration of released gas was below 50 ppm similarly to N_2 mixture. The measured hydrogen concentration increased to a little high value of 60–100 ppm when 1% hydrogen mixture gas was supplied. Thus

Table 5
H_2 concentration of released anode gas for H_2 flow rate change at PEMFC.

Items	H_2: 38 $cm^3 min^{-1}$	H_2: 3.8 $cm^3 min^{-1}$
Hydrogen concentration (%)	10	10
Total flow rate ($cm^3 min^{-1}$)	380	38
Current density ($A cm^{-2}$)	0.49	0.05
Treatment ratio at PEMFC	98 ± 2	100 ± 2
Total treatment ratio (%)	99.8 ± 0.2	100 ± 0.2
H_2 concentration of released anode gas for N_2 mixture (ppm)	900–1000	Under 50
H_2 concentration of released anode gas for CO_2 mixture (ppm)	600–1000	Under 50

almost the same concentration was obtained for either N_2 or CO_2 mixture independently from the feeding hydrogen concentration.

Table 5 shows the measured hydrogen concentration of released anode gas when the flow rate was changed. In case of N_2 mixture the hydrogen concentration of released anode gas was under 50 ppm for the hydrogen flow rate of $3.8 cm^3 min^{-1}$, and the hydrogen concentration became 900–1000 ppm for the hydrogen flow rate of $38 cm^3 min^{-1}$. In case of CO_2 mixture the hydrogen concentration of released anode gas was under 50 ppm for the hydrogen flow rate of $3.8 cm^3 min^{-1}$, and the hydrogen concentration became 600–1000 ppm for the hydrogen flow rate of $38 cm^3 min^{-1}$. Almost the same concentration was obtained for either N_2 or CO_2 mixture similarly to hydrogen concentration change test. The maximum concentration was still 1000 ppm at all of the tested conditions of single cell, and it is sufficiently low when compared to the National Fire Protection Association limit of less than 1%.

However as described in above section of hydrogen pump, fuel must be supplied evenly to each cell of fuel cell stack to avoid the electrode carbon corrosion due to fuel starvation. Special stack constitutions, such as the series fuel supply through some grouped stacks or the fuel re-circulation, are required to attain the high fuel utilization, which are future development issues of high hydrogen treatment stack.

5. Conclusion

The experiment of electrochemical hydrogen pump and proton exchange membrane fuel cell (PEMFC) was performed to treat low concentration hydrogen, and it was confirmed that we could decrease the hydrogen concentration of depleted anode gas either for N_2 or CO_2 mixture gas. In case of hydrogen pump where an applied cell voltage was selected appropriately from its voltage–current characteristics, nearly 100% of hydrogen could be separated and recovered even when the hydrogen concentration of anode gas was changed or the flow rate of anode mixture gas with constant hydrogen concentration was changed. The measurement by gas chromatography confirmed that the hydrogen concentration of the anode gas released from hydrogen pump was below 50 ppm in most cases, and 300 ppm at most in CO_2 mixture case. In case of PEMFC the released hydrogen concentration increased slightly, and 1000 ppm at most in CO_2 mixture case, with a slight decrease of hydrogen treatment ratio. Thus we could confirm to treat hydrogen in mixture gas at wide ranges of hydrogen concentration and gas flow rate, and to make the hydrogen concentration of released gas well below the National Fire Protection Association limit of less than 1%. When we compare the treatment test by N_2 or CO_2 mixture gas, the cell voltage for CO_2 mixture became unstable, less reproducible and increased much in hydrogen pump case, and decreased less in PEMFC case than cases for N_2 mixture. Hydrogen pump may be selected as hydrogen treatment equipment when much low hydrogen concentration is desirable to be released to ambient, despite of its unavoidable power consumption. When much net output from fuel cell system is required, PEMFC may be another selection despite of its lower treatment ratio. There are still many remained development items, such as the hydrogen treatment stack of pump or PEMFC, because high hydrogen treatment ratio is difficult to be attained at stack level. Also the performance comparison is required between the high hydrogen treatment stack and the platinum catalytic combustor.

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