Influence of Steam Conversion Rate and Cathode Gas Composition on Performance of High-Temperature Steam Electrolysis Cell

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ABSTRACT

High-temperature steam electrolysis is one of the most promising methods for producing hydrogen and has the potential do so with high efficiency. Additionally, this hydrogen production process, combined with nuclear energy, emits no carbon dioxide. Toshiba has been developing a high-temperature steam electrolysis system using solid-oxide cells for hydrogen production in a temperature range of 1073 to 1173K. A tubular cell was selected for development from the viewpoint of leak-tightness. The influence of the steam conversion rate and the cathode gas composition on the cell performance was examined. The effect of the steam conversion rate was examined for a cathode gas composition of 50% hydrogen and 50% steam. The cell performance was not affected by a steam conversion rate of up to 63% and gradually decreased as the conversion rate increased. The effect on the cell performance of cathode hydrogen concentrations from 50% to 0% was also examined for a steam conversion rate of 60%. The cell performance was not affected by hydrogen concentrations ranging from 50% to 5% but dropped when the hydrogen concentration was 0%. The cause of this deterioration is considered to be oxidation of nickel at the cathode surface when the nickel contacts steam. As a result, the hydrogen production efficiency is expected to reach a maximum of 53% at a steam conversion rate of 63% and a cathode hydrogen concentration of 5%. The hydrogen production efficiency of a high-temperature electrolysis (HTE) system, connected to a high-temperature gas reactor, should be greater than that of a conventional water electrolysis system. Based on our findings, the HTE system, combined with nuclear power, is one of the most promising methods of producing hydrogen.

INTRODUCTION

A so-called hydrogen society, where primarily hydrogen will be used as an energy source and carbon dioxide will be scarcely discharged to the environment, has been proposed as one of the best measures against global warming. At present, almost all of the available hydrogen is used as raw material in the chemical industry. It is estimated that the future hydrogen demand will be several times larger than at present because of the widespread adoption of fuel cells. The Japanese government plans to reduce CO_2 emission by replacing 5 million gasoline-powered vehicles with fuel-cell-powered vehicles by 2020. As a result, it is estimated that the demand for hydrogen will increase to 40 billion m^3 at 273K, 0.1MPa a year more than the current level. A large amount of hydrogen is commercially produced by steam reforming, using methane, natural gas or LPG, which originate from fossil fuels. This process, however, is not effective against global warming, because it emits large amounts of CO_2.

Hydrogen production based on High Temperature Electrolysis (HTE), using solid oxide fuel cell (SOFC) technology, in combination with nuclear energy emits no carbon dioxide. For the most part, it uses environmentally sound and commonly available materials. [1]

Toshiba has been developing a tubular solid oxide electrolysis cell (SOEC) that uses heat and electricity from a nuclear power plant as an energy source for hydrogen production. Tubular electrolysis cells have a number of advantages over planar-type cells, including sealing performance and thermal stress, and have been developed from both experimental and numerical approaches.[2,3,4]

An assembly unit consisting of fifteen tubular electrolysis cells was developed. The unit was designed to get the hydrogen production rate of 100L/h at 273K, 0.1MPa and 130L/h at 273K, 0.1MPa had been accomplished. [7] In the paper, it was confirmed that the unit, which consisted of cells, seals, electrical isolation, power supplies and so on, worked well. [5,6,7] However, when hydrogen is produced by HTE, it is important to determine how effectively the supplied thermal energy is used. This paper describes the influence of the steam conversion rate and the cathode gas composition on the performance of an HTE cell.

PRINCIPLE OF HIGH TEMPERATURE ELECTROLYSIS

Figure 1 shows the principle of high-temperature electrolysis (HTE). The electrolysis cell consists of an electrolyte layer between a cathode (hydrogen electrode) and an anode (oxygen electrode) on either side. The electrolyte is made of solid oxide with high oxygen ion conductivity. Supplied steam is decomposed into hydrogen and oxygen ions at the cathode. The oxygen ions then pass through the electrolyte to the anode, where they release electrons and become oxygen. Hydrogen is produced from the supplied steam at the cathode as described in Equation (1) below, and oxygen is released at the anode as described in Equation (2). As a whole, water, in the form of steam here, is decomposed into hydrogen and oxygen as described in Equation (3).

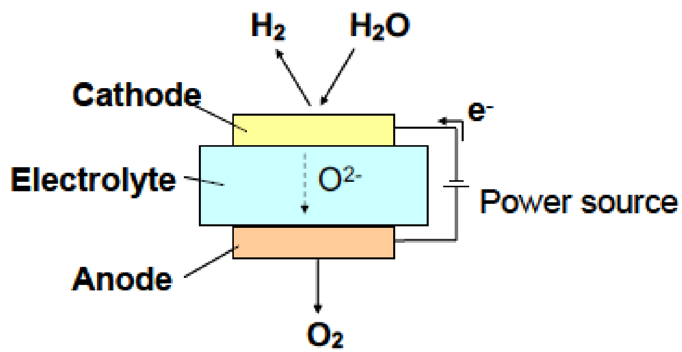

Figure 1 Principle of high-temperature electrolysis (HTE)

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \quad (1)$$

$$O^{2-} \rightarrow 1/2\ O_2 + 2e^- \quad (2)$$

$$H_2O \rightarrow H_2 + 1/2\ O_2 \quad (3)$$

The required energy for water decomposition is given by:

$$\Delta H = \Delta G + T\Delta S \quad (4)$$

where ΔH is the enthalpy change, which is equal in magnitude and opposite in sign to the hydrogen heat of combustion, ΔG is the Gibbs free energy change, ΔS is the entropy change in the reaction described in Equation (3), and T is the reaction temperature. In electrolysis, ΔG is given by electrical energy and $T\Delta S$ is given by thermal energy. Figure 2 shows the required energy for electrolysis as a function of temperature. As shown, ΔG decreases with temperature, whereas ΔH hardly changes with temperature. HTE operates effectively at 1073 to 1173 K. HTE basically requires less electrical energy compared with other electrolysis methods carried out at lower temperature.

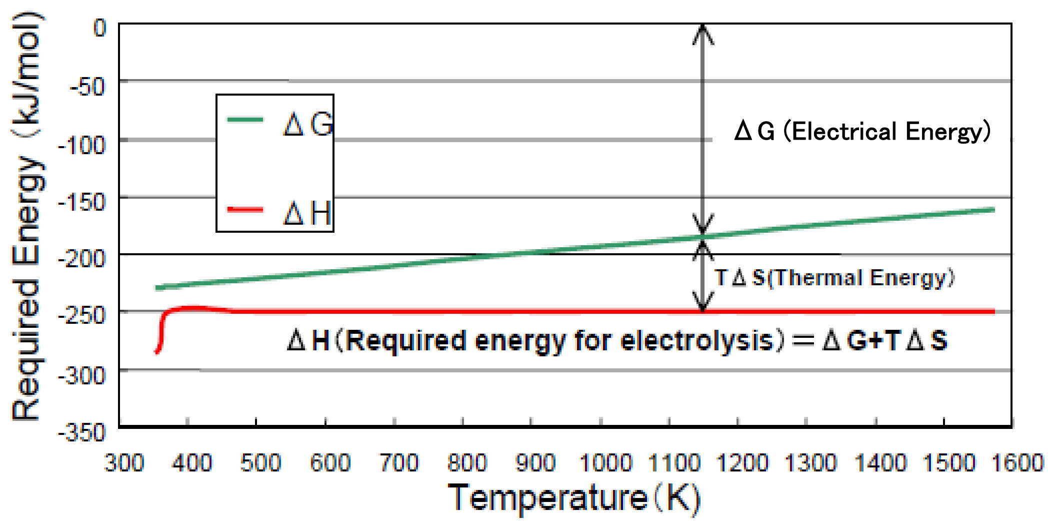

Figure 2 Required Energy for Electrolysis

TUBULAR ELECTROLYSIS CELL

A high-temperature steam electrolysis cell also needs to have thermal, chemical, and mechanical stability to endure long-term operation at high temperature in a red/ox atmosphere. Tubular cells were used because of their superior leak-tightness.

The structure of the tubular electrolysis cell is shown in Figure 3. The cell consists of three layers. The hydrogen electrode was made of nickel-yttrium-stabilized zirconia cermet (Ni-YSZ). The electrolytes was made of yttrium-stabilized zirconia (YSZ). The oxygen electrode was made of mixed oxide of lanthanum, strontium and cobalt. The electrolysis cell was supported by the hydrogen electrode. Steam mixed with hydrogen is supplied to the hydrogen electrodes through a steam introduction pipe provided inside the electrolysis cell, and oxygen mixed with nitrogen is supplied to the oxygen electrodes.

Figure 4 shows a prototype tubular single cell fabricated for lab-scale tests. The outer diameter of the cell is 12 mm. In this cell, the electrolyte is 13 μ m thick, the oxygen electrode is 25 μ m thick, and the hydrogen electrode is 7 μ m thick.

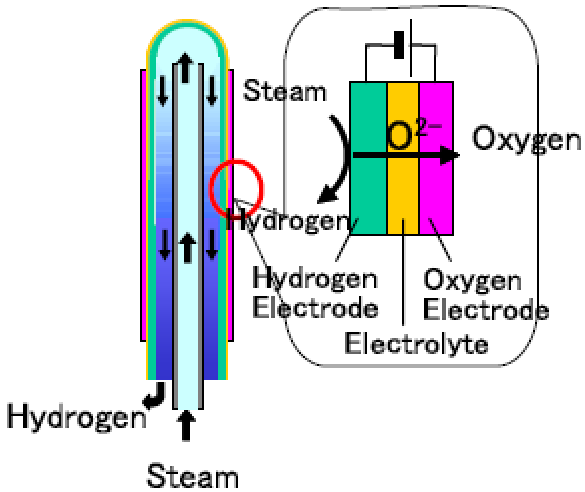

Figure 3 Structure of Tubular Electrolysis Cell

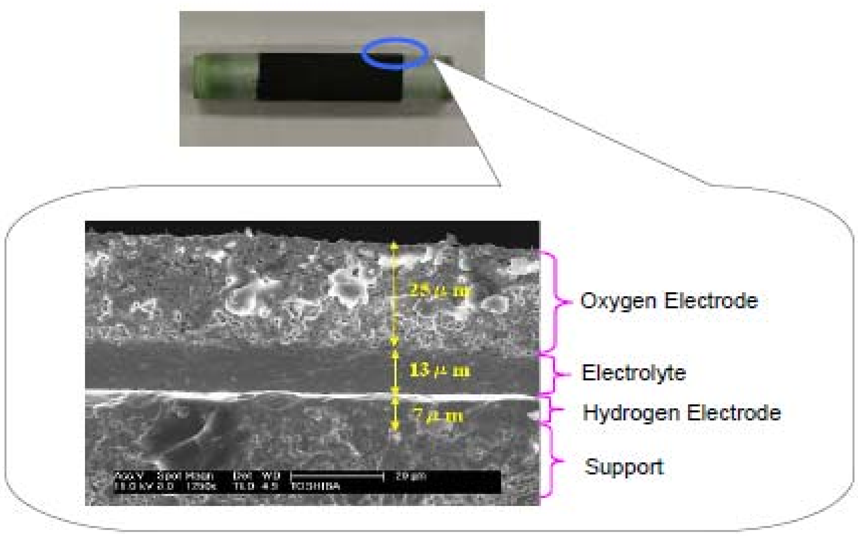

Figure 4 Prototype Tubular Single Cell

HYDROGEN PRODUCTION EFFICIENCY

An important parameter in the design of a hydrogen production system is the hydrogen production efficiency. The power generation efficiency of a High Temperature Gas Reactor (HTGR) is about 50%.[8] When water is electrolyzed with electricity generated by the HTGR, the hydrogen production efficiency is calculated by multiplying the power generation efficiency of the HTGR by the efficiency of the electrolysis. Thus, when the electrolysis efficiency of the water is assumed to be 80%[9], the hydrogen production efficiency is 40%. The hydrogen production efficiency using an HTE must be more than 40%.

An HTE-based hydrogen production system is shown in Figure 5. The inlet of this system is liquid water. The water is evaporated by and its temperature controlled by a preheater. The steam, that is, evaporated water, is fed along the surface of the cathode and decomposes to hydrogen and oxygen. In order to maintain high catalytic activity, the nickel on the surface of the cathode must be in a reduced state. A part of the produced hydrogen is mixed with the supplied steam and is consumed to keep the nickel reduced. The hydrogen production efficiency (ψ) of the HTE system is defined as shown in Equation (5). It is derived by dividing the higher heating value (HHV) of the produced hydrogen by the consumed energy, which is the total of thermal and electrical energy. The thermal energy consists of E_1 and E_2, where E_1 is the thermal energy supplied to the evaporator and E_2 is the thermal energy supplied to the preheater. E_1 is a function of the flow rate of supplied steam, Q_1, as defined in Equation (7). E_2 is a function of Q_1 and the flow rate of circulated hydrogen, Q_2, as defined in Equation (8). The steam conversion rate, α, is defined as the amount of steam converted into hydrogen divided by the flow rate of supplied steam, as given by Equation (6). Therefore, the steam conversion rate is a function of Q_1. The hydrogen concentration supplied to the cathode is a function of Q_2, as defined in Equation (9). Therefore, E_{th} is a function of the steam conversion rate and the hydrogen concentration supplied to the cathode. The hydrogen production efficiency (ψ) of the HTE system is thus a function of the steam conversion rate and the hydrogen concentration. The factors which have an influence on the hydrogen production efficiency are the steam conversion rate and the hydrogen concentration. When there is little supplied steam relative to the flow rate of hydrogen production, the steam conversion rate is high. The thermal energy (E_1) supplied to the evaporator and the thermal energy (E_2) supplied to the preheater decrease, and the total thermal energy (E_{th}) thus decreases. Therefore, the hydrogen production efficiency (ψ) becomes higher. Improving the steam conversion rate causes a decrease in the flow rate of waste of the steam. In addition, the thermal energy (E_{th}) decreases, and the hydrogen production efficiency improves. Once the flow rate of circulated hydrogen (Q_2) is decreased, the hydrogen concentration decreases. And then E_2 decreases, and finally E_{th} decreases. Therefore, the hydrogen production efficiency increases. The hydrogen concentration is defined as the flow rate of circulated hydrogen in the supplied steam.

$$\Psi = \frac{HHV}{(E_{el}/\eta)+E_{th}} \qquad (5)$$

$$\alpha=Q_4/Q_1 \qquad (6)$$

$$E_1=K_1Q_1 \qquad (7)$$

$$E_2=K_2Q_1+K_3Q_2 \qquad (8)$$

$$E_{th}=E_1+E_2$$

$$C=f(Q_2) \qquad (9)$$

$$\phi=F(\alpha,C)$$

ϕ (-):	Hydrogen production efficiency
HHV (kJ):	Higher heating value
E_{el} (kW/h):	Supplied electrical energy
η (-):	Generation efficiency
E_{th} (kJ):	Supplied thermal energy
E_1:	Supplied thermal energy to evaporator
E_2:	Supplied thermal energy to preheater
α:	Steam conversion rate
K_1, K_2, K_3:	Constants
Q_1:	Flow rate of supplied steam
Q_2:	Flow rate of circulated hydrogen
Q_3:	Flow rate of hydrogen produced
Q_4:	Flow rate of the steam converted into hydrogen

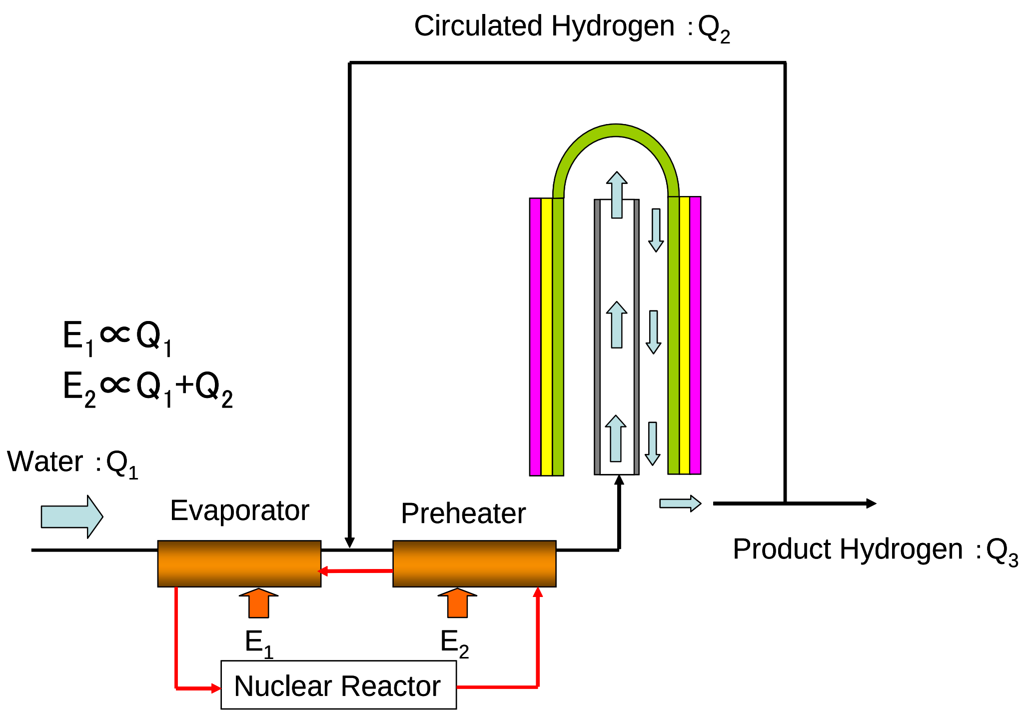

Figure 5 HTE System

APPARATUS

A schematic drawing of the apparatus is shown in Figure 6. The cell is installed inside an electric furnace to keep the cell at constant temperature. The outside of the cell is the anode, and the inside is the cathode. The flow rate of water is controlled with a pump. Water is supplied to the evaporator where it changes into steam, which is then supplied to the cathode. Hydrogen for reduction is supplied together with the steam so that the cathode is not oxidized. The flow rate of hydrogen is measured with a mass-flow controller (MFC). Oxygen and nitrogen are supplied to the anode. The flow rates of the oxygen and nitrogen are measured with MFCs. The flow rate of the exit gas of the cathode is measured with a soap film-type flowmeter, and the exit gas passes through a cooler to remove surplus water. The exit gas of the anode is exhausted after cooling in a cooler.

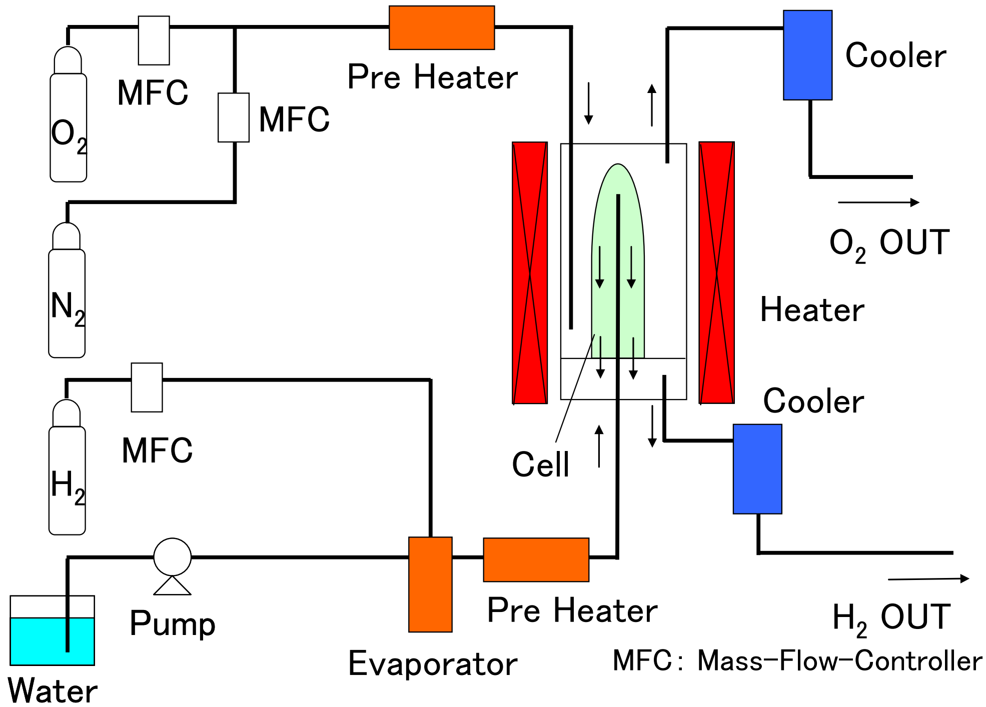

Figure 6 Test Apparatus

TEST CONDITIONS

The evaluation metric for the cell performance was the current density at a cell voltage of 1.3 V at 1073K. The current density was calculated by dividing the measured electric current by the surface area of the electrode. When the electric current supplied to the cell is constant, the hydrogen production rate must be constant. When the hydrogen production rate is constant, the steam consumption is constant. Therefore, the steam conversion rate changes according to the amount of supplied steam. The flow rate of the steam was set as a test parameter for the steam conversion rate. Table 1 shows the test conditions. The gas composition supplied to the cathode was 50% steam and 50% hydrogen. The test parameter was the flow rate of the total amount of gas supplied to the cathode, and the ratio of steam and hydrogen was constant The composition of the gas supplied to the anode was 20% oxygen and 80% nitrogen, and the flow rate of the total amount of gas supplied to the anode was the same as that for the cathode.

Table 1 Test conditions for Influence of steam conversion rate on cell performance

Cell Temp (K)	Cathode		Anode		Cell
	Steam (L/min) (at 273K, 0.1MPa)	Hydrogen (L/min) (at 273K, 0.1MPa)	Nitrogen (L/min) (at 273K, 0.1MPa)	Oxygen (L/min) (at 273K, 0.1MPa)	Voltage (V)
1073	0.09	0.09	0.14	0.03	1.3
1073	0.07	0.07	0.12	0.03	1.3
1073	0.06	0.06	0.10	0.02	1.3
1073	0.05	0.05	0.08	0.02	1.3
1073	0.04	0.04	0.06	0.01	1.3
1073	0.02	0.02	0.04	0.01	1.3

The influence of the hydrogen concentration for reduction on the performance of the cell was examined as follows. The test parameter was the hydrogen concentration supplied to the cathode. The test conditions are shown in Table 2. The steam conversion rate was 20% and 60%. The cathode gas composition was 50% to 100% steam and 50% to 0% hydrogen. The composition of the gas supplied to the anode was 20% oxygen and 80% nitrogen, and the flow rate was the same as that of the gas supplied to the cathode.

Table 2 Test conditions for hydrogen concentration supplied to the cathode

Cell Temp.	1073K
Cell Voltage	1.3 V
Steam conversion rate	20 %, 60 %
Cathode H_2/H_2O	0 %/100 % ~ 50 %/50 %
Anode O_2/N_2	20 % /80 %

RESULTS AND DISCUSSION

Figure 7 shows the test results for the influence of the steam conversion rate on cell performance. The vertical axis shows the normalized cell performance, and the horizontal axis shows steam conversion rate. The cell performance was normalized by the current density of the cell at a cell temperature of 1073K, a cell voltage of 1.3V, a steam conversion rate of 20%, and cathode gas composition of 50% steam and 50% hydrogen. The steam conversion rate was changed by varying the flow rate of the steam. The larger the flow rate is, the smaller the steam conversion rate is. With one cell, several cell performance values can be obtained by varying the steam conversion rate. From the results obtained from four cells, the measurement method is considered to be reproducible. According to the test results, the cell performance was not influenced by the steam conversion rate in the range of 20% to 65%. When the steam conversion rate was more than 65%, the cell performance was considered to deteriorate because of insufficient decomposed steam at the cathode surface.

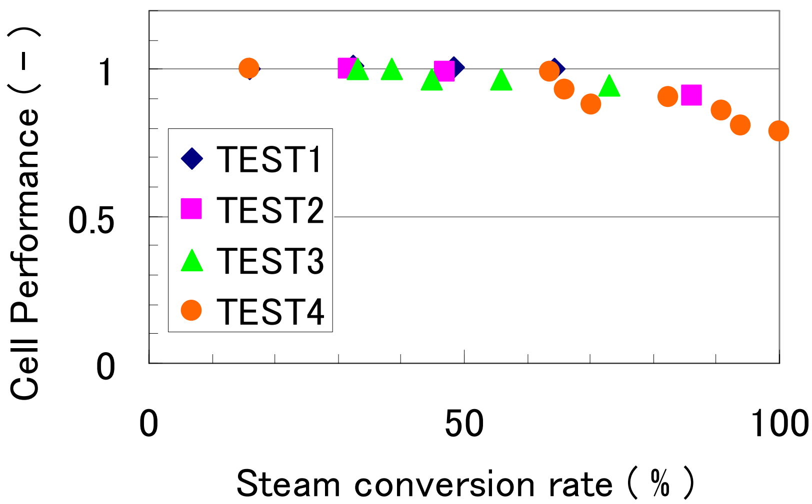

Figure 7 Influence of steam conversion rate on cell performance

Figure 8 shows the influence on cell performance of the concentration of hydrogen supplied to the cathode for keeping it reduced. The vertical axis shows the cell performance, and the horizontal axis shows the hydrogen concentration. The cell performance was not influenced by the hydrogen concentration in the range from 50% to 5%, but the cell performance dropped when the hydrogen concentration was 0%. The cause of this deterioration is considered to be the oxidation of nickel on the cathode surface when the nickel contacts the hydrogenless steam, which is a strong reductant.

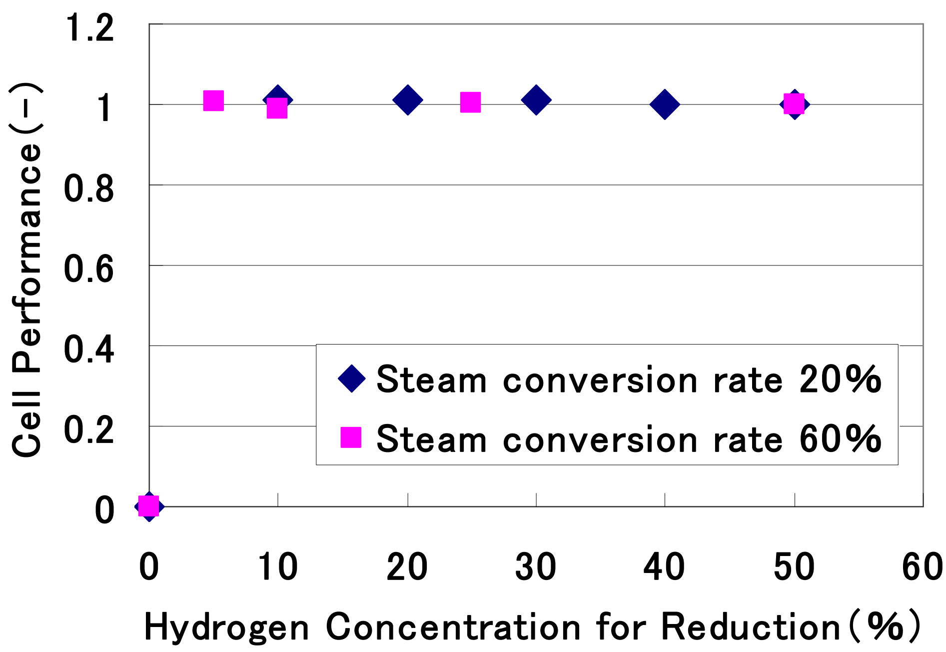

Figure 8 Influence of hydrogen concentration for reduction

The hydrogen concentration for reduction did not affect the cell performance when the hydrogen concentration was more than 5%. The hydrogen production efficiency, given by Equation (5), is the ratio of the higher heating value (HHV) of the product hydrogen to the supplied energy, which is the total of the supplied electrical and thermal energies. The electrical energy is the electrical energy supplied to the cell at a cell voltage of 1.3 V. The thermal energy is the total of the energy supplied to the evaporator and the preheater. The heat loss in the heat exchange was considered to be 0. Figure 9 shows the influence of the hydrogen concentration supplied to the cathode versus the hydrogen production efficiency. The solid lines are the theoretical hydrogen production efficiency given by Equation (5) at a current density of 0.3 A/cm^2. The points are the measured data.

Hydrogen production efficiency reached a maximum of 53% when the steam conversion rate was 60% and the hydrogen concentration was 5%. Steam containing more than 5% hydrogen must be supplied to prevent the cell from oxidizing.

The influence of the hydrogen concentration at the steam conversion rate of 60% was the same as that at the steam conversion rate of 20%. As a result, the hydrogen production efficiency is expected to be maximum at a steam conversion rate of 63% and a cathode hydrogen concentration of 5%.

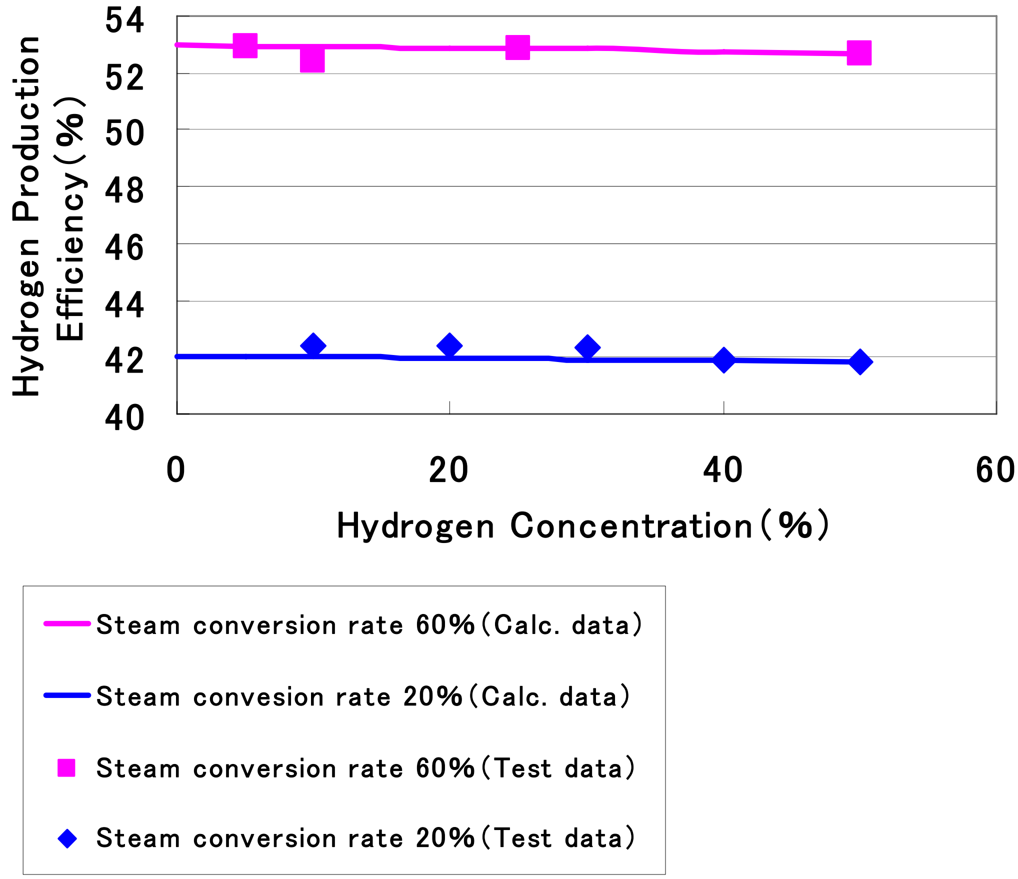

Figure 9 Hydrogen production efficiency

SUMMARY AND CONCLUSIONS

The influence of the steam conversion rate was tested, with the flow rate of the cathode gas as a test parameter. The cell performance was not influenced by the steam conversion rate in the range of 20% to 65%. The influence of the hydrogen concentration for reduction on cell performance was also tested, with the hydrogen concentration as a test parameter. The cell performance was not influenced by the hydrogen concentration supplied to the cathode in the range of 50% to 5%.

As a result, it is expected that the hydrogen production efficiency is maximized at a steam conversion rate of 63% and a cathode hydrogen concentration of 5%. The hydrogen production efficiency of an HTE system, connected to an HTGR, should be greater than that of a conventional water electrolysis system. Based on our findings, an HTE system, combined with nuclear power, appears to be one of the most promising methods of producing hydrogen.

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