High Temperature Electrolysis for Hydrogen Production using Solid Oxide Electrolyte Tubular Cells Assembly Unit

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ABSTRACT

Toshiba has been developing the steam electrolysis system with tubular cells using solid-oxide electrolyte for hydrogen production over a temperature range of 800 to 900 degree C. Fifteen tubular electrolysis cells assembly unit, which 15 cells are installed in a casing and divided into three blocks of every five for electric supply individually to each block and parallel connection of all the cells was carried out, has been manufactured. Each cell is set on a pedestal via glass, which works for seal between hydrogen side and oxygen side and also works for electrical isolation. Experimental results were obtained from the unit. The measured open-cell potential, OCV, of the unit at 800 degrees C was mostly in agreement by 3 blocks, and further in agreement also with the theoretical value. Moreover, the area-specific resistance, ASR, was almost as same for every block. It was confirmed that there was almost no performance variation during a block. And the measured hydrogen production rate was mostly in agreement with the theoretical value, which was predicted from the current density. The hydrogen production rate of the unit of 130 Nl/h was checked to design value 100 Nl/h. It was confirmed that the unit, which consisted cells, seals, electrical isolations, electric supplies and so on, worked well from the result.

This paper describes the development of the solid oxide electrolyte tubular cell for steam electrolysis, and the performance of single tubular cell and 15 electrolysis cells assembly unit.

INTRODUCTION

Hydrogen society, which will use hydrogen as energy source and hardly discharges carbon dioxide to environment, is proposed as one of the measures against global warming. At the present time, almost all hydrogen is used as raw materials for chemical industry. In the near future, it is estimated that the hydrogen demand will increase several times larger than the present, because fuel cells must become popular. The Japanese government has a plan to reduce CO_2 emission by replacing 5 million gasoline-powered vehicles with fuel cell powered vehicles by 2020. Then, it is estimated that the demand for hydrogen will increase 40 billion Nm^3 a year more than the present. Large amount of

hydrogen is commercially produced with steam reforming, using methane, natural gas or LPG originated in fossil fuels. This does not help to work against global warming, for the process emits large amounts of CO_2.

High temperature steam electrolysis with solid oxide electrolyte cells is one of the most promising methods for hydrogen production, which has the potential to be high efficiency. Combining to the nuclear energy, the hydrogen production process emits no carbon dioxide. Its most parts consist of environmentally sound and common materials. This paper describes the development of the solid oxide electrolyte tubular cell for steam electrolysis, and the performance of 15 electrolysis cells assembly unit, which has hydrogen production capacity of 100 Nl/h.

PRINCIPLE OF HIGH TEMPERATURE ELECTROLYSIS

Figure 1 shows a principle of high temperature electrolysis(HTE). An electrolysis cell consists of three-layer structures which make electrolyte layer middle and have cathode (hydrogen electrode) and anode (oxygen electrode) in the both sides. The electrolyte is solid oxide with oxygen ion conductivity. Supplied steam is decomposed into hydrogen and oxygen ion on the cathode, then oxygen ion conducts the inside of the electrolyte to the anode, and releases an electron on the anode, and become to oxygen. Hydrogen is produced from supplied steam at cathode as described on equation (1), and oxygen is released at anode as described on equation (2). As a whole, water, which is steam here, is decomposed into hydrogen and oxygen as described on equation (3).

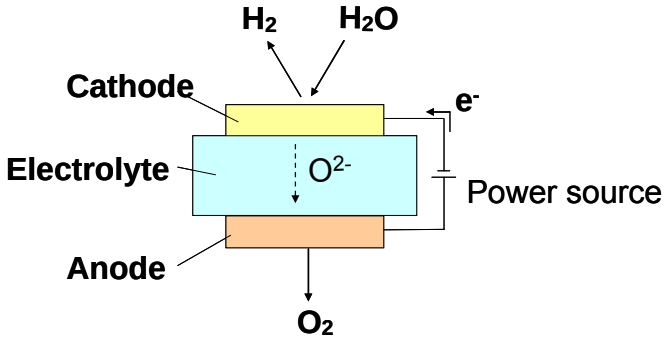


Figure 1 Principle of high temperature electrolysis

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

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

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

Required energy for water decomposition is given by:

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

where ΔH is the enthalpy change which is equal to negative of the hydrogen combustion heat, ΔG is Gibbs free energy change, ΔS is the entropy change in the reaction described on equation (3), and T is the reaction temperature. In electrolysis, ΔG is given with electric energy and $T\Delta S$ is given with thermal energy. Figure 2 shows required energy for electrolysis. As shown in Figure 2, ΔG decreases with temperature, although ΔH hardly changes with temperature. HTE is operated effectively at 800 to 900 degree C. So, the HTE basically requires less electric energy compared to other electrolysis operated in lower temperature.

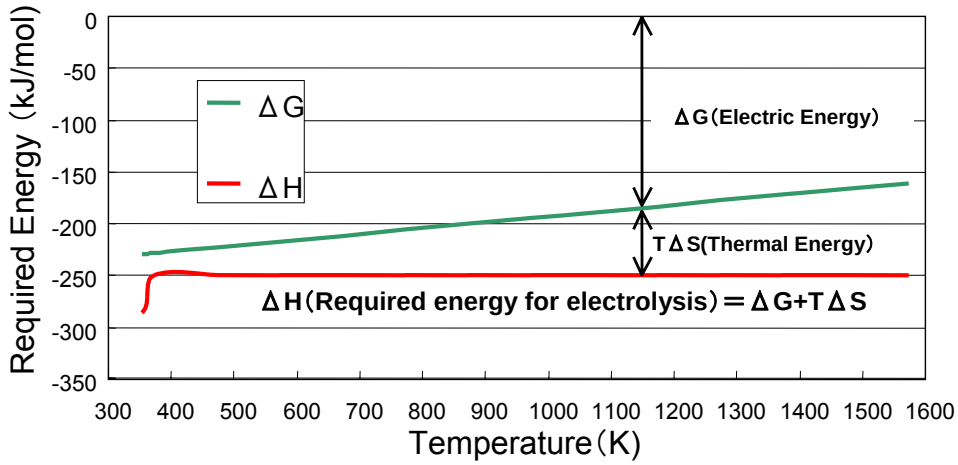


Figure 2 Required Energy for Electrolysis

TUBULAR ELECTROLYSIS CELL

For large-scale hydrogen production, design of multiple HTE cell stack is important, to secure high hydrogen productivity and purity. High temperature steam electrolysis cell also has to have thermal, chemical and mechanical stability to endure long-term operation at high temperature in red/ox atmosphere, or minimal movement for installation or maintenance. We selected tubular cells because they are good to achieve high leak-tightness.

The structure of tubular electrolysis cell is shown in Figure 3. The electrolysis cell manufactured is hydrogen electrode-supported, with yttrium-stabilized zirconia (YSZ) electrolytes, nickel-YSZ cermet steam/hydrogen electrodes, and mixed oxide of lanthanum, strontium and cobalt oxygen electrodes. Steam/hydrogen mixed gas is supplied to the hydrogen electrodes via steam induction pipe which is equipped inside the electrolysis cell,

oxygen/nitrogen mixed gas is supplied to the oxygen electrodes. Supplied steam is decomposed into hydrogen and oxygen ion on the cathode, then oxygen ion conducts the inside of the electrolyte to the anode, and releases an electron on the anode, and become to oxygen. Figure 4 shows the proto-type tubular single cell for lab-scale test. The outer diameter of the cell is 12mm. In this cell shown in figure 4, the electrolyte is 13 μm in thickness, the oxygen electrode is 25 μm in thickness, and the hydrogen electrode is 7 μm in thickess.

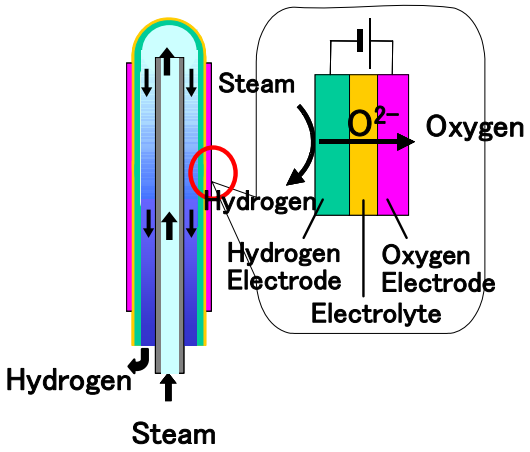


Figure 3　Structure of Tubular Electrolysis Cell

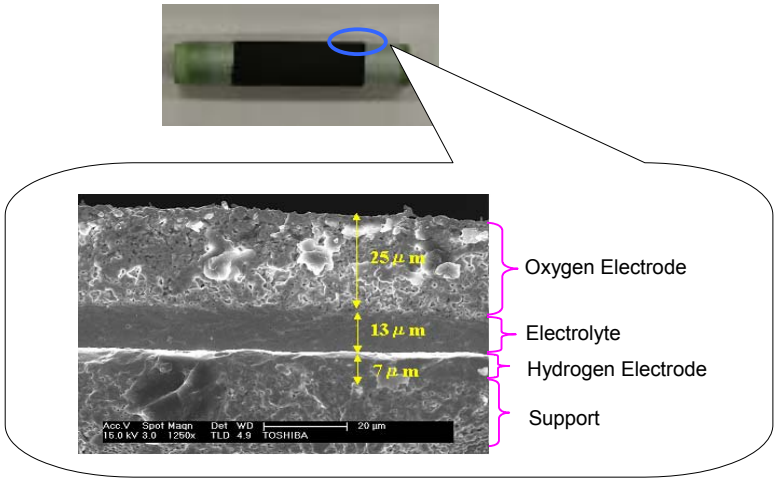
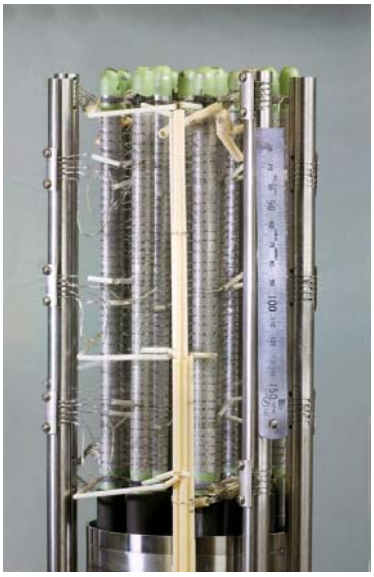


Figure 4　Proto-type Tubular Single Cell

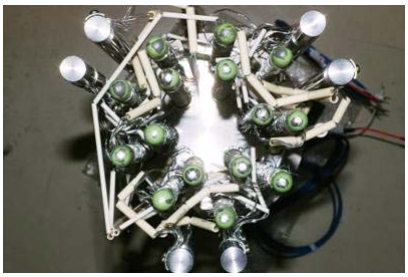
MULTI ELECTROLYSIS CELLS ASSEMBLY UNIT

Fifteen cells assembly unit, which the design value of the hydrogen production rate is 100 Nl/h, has been developed for the first step demonstration of large-scale hydrogen

production. Figure 5 shows internal structures of the unit where fifteen tubular electrolysis cells, which are 12mm in outer diameter and 75 cm^2 in active area, are installed. Each cell is set on a pedestal via glass, which works for seal between hydrogen side and oxygen side and also works for electrical isolation. These are installed in the casing when tested. Fifteen cells are installed in a casing and divided into three blocks of every five for electric supply individually to each block and parallel connection of all the cells was carried out. Electric power is supplied to each three blocks individually. The electricity supplies to the hydrogen electrode from the both ends of the cell. The electricity supplies to the oxygen electrode via silver expanded metal which covers the oxygen electrode. The electricity supply lines to the oxygen electrode attached in three places of silver expanded metal, the upper part, the central part, and the lower part.



Side view



Top view

Figure 5 Internal Structures of Fifteen Cells Assembly Unit

The steam / hydrogen gas mixture is entering the inlet manifold on the bottom in the photograph of side view, and flowing into steam induction pipe equipped inside the electrolysis cell, then exiting through the outlet hydrogen manifold, also on the bottom in the photograph of side view. Air flow enters into the space between the internal structures shown in Figure 5 and casing, and exits from another pipe installed in the space. Unit operating voltages are measured using wires that are attached on the hydrogen electrode and the oxygen electrode of one of five cells of each three blocks.

APPARATUS

A schematic of the unit-testing apparatus is shown in Figure 6. Primary system components include gas supply cylinders, gas mass-flow controllers, temperature and pressure measurement, high temperature furnace, and a solid oxide electrolysis unit. The flow rates of oxygen, nitrogen and hydrogen are measured with mass-flow controllers. Water is supplied to an evaporator and changes to steam. Steam flow rate is determined as the flow rate of water supplied to the evaporator with the metering pump. Nitrogen is used as an inert carrier gas. By using the inert carrier gas, it becomes possible to vary independently the partial pressures and the flow rates of the steam, hydrogen and oxygen gases while continuing to operate at atmospheric pressure. The electrolysis unit is installed in the electric furnace and test temperature condition is controlled by adjusting a heater output.

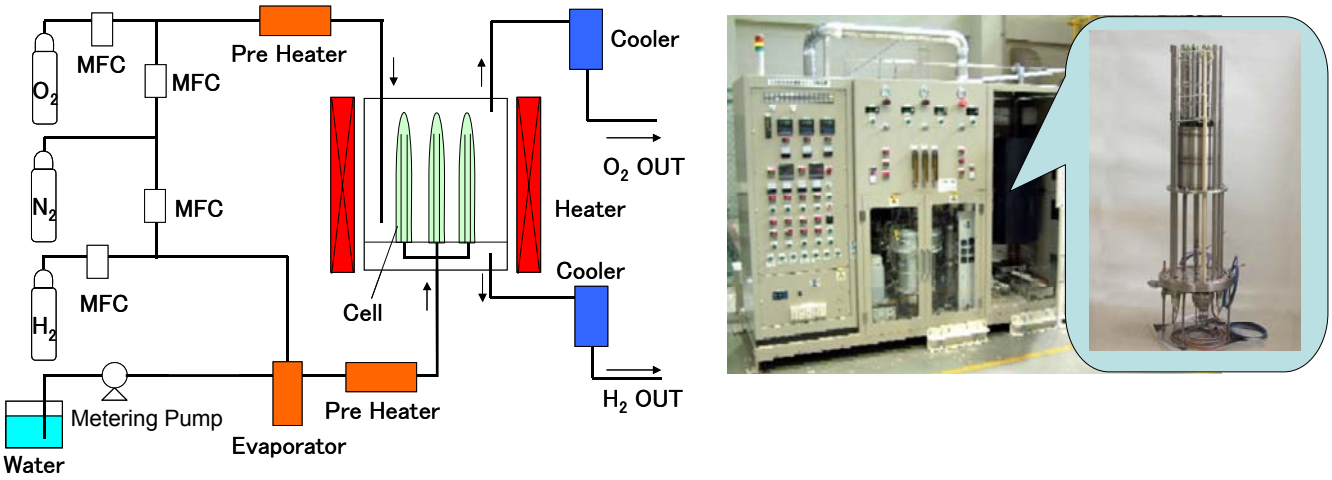


Figure 6　Schematic of the unit-testing apparatus

Steam is supplied to the hydrogen electrode. Hydrogen is included in the inlet flow to the hydrogen electrode as a reducing gas in order to prevent oxidation of the nickel cermet electrode material. The hydrogen gas is supplied to the water evaporator and mixed with the steam then the steam / hydrogen mixed gas is supplied to the hydrogen electrode through a preheater. In case the partial pressure of the steam contained is varied, the nitrogen gas is mixed. The supply gas to the oxygen electrode is oxygen and nitrogen mixed gas. The oxygen partial pressure is able to vary. In order to examine by air composition fundamentally, it may become 20% of oxygen, and 80% of nitrogen. The outlet gas of the hydrogen electrode is introduced into cooler and separated surplus moisture there, and gas flow rate is measured with a soap film flow meter. The hydrogen production rate is determined by subtracting the supplied gas flow rate to the hydrogen electrode from the measured gas flow rate with the soap film flow meter. The outlet gas of the oxygen electrode is also cooled through the cooler then measured the flow rate.

TEST RESULTS AND DISCUSSIONS

First, using single cells, the current-voltage characteristic was evaluated. Figure 7 shows the current-voltage characteristic of 15 cm^2 cell. The measured open-cell potential (E_{OCV}), which is the operating voltage in case current density is 0, of 15 cm^2 was 0.94V at 800 degrees C and 0.91V at 900 degrees C. The open-cell potential can also be predicted from test conditions using the Nernst equation (5).

$$E_{OCV} = -\Delta G_f/2F$$
$$= E^0 - (RT/2F)\ln(P_{H2O}/P_{H2}P_{O2}^{1/2}) \qquad (5)$$

where ΔG_f is Gibbs free energy change for water decomposition described as equation (3), E^0 is standard electromotive force, F is Faraday constant, 96500 C/mol, R is the gas constant, 8.314 J/mol/K, T is Temperature, and P_{H2O}, P_{H2}, and P_{O2} are the partial pressure of water, hydrogen, and oxygen, respectively.
Here, the test conditions were P_{H2O} =0.5 atm, P_{H2}=0.5 atm, and P_{O2}=0.2 atm. Standard electromotive force is 0.978V at 800 degrees C and 0.949V at 900 degrees C. So, the theoretical E_{OCV} value predicted from the Nernst equation is 0.941V at 800 degrees C and 0.908V at 900 degrees C. According to the above mentioned, the measured values were mostly in agreement with the theoretical value predicted from the Nernst equation.

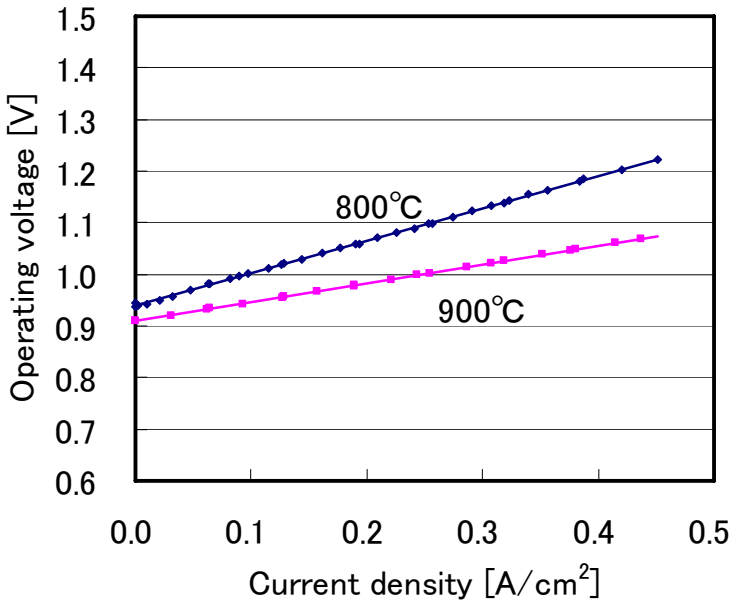


Figure 7 Current-voltage characteristic of 15 cm^2 cell

The area-specific resistance (ASR) defined by equation (6) was 0.63 ohm cm^2 for 800 degrees C and 0.37 ohm cm^2 for 900 degrees C.

$$ASR = (E - E_{OCV}) / I \qquad (6)$$

where E is operating voltage, and I is current density.
It is considered that ASR is the sum total of activation loss, gas diffusion loss and internal resistance on each electrode. The magnitude of those losses depends on the characteristics of the cell components. These losses become smaller with higher temperature. As expected, ASR became smaller as temperature was high. It was estimated that more than 0.45 A/cm^2 of current density was obtained at the thermal neutral voltage of 1.3V at 800 degree C, since the current density was 0.45 A/cm^2 when the operating voltage was 1.23V.

Next, the current-voltage characteristic of single 75 cm^2 cell was evaluated. Figure 8 shows the current-voltage characteristic of 75 cm^2 cell. The 75 cm^2 cell is 3 times longer than the 15 cm^2 cell. The influence of the cell length on the current-voltage characteristic was measured. The current-voltage characteristic, which attaches an electric supply system to the hydrogen electrode from the both ends of a cell or from one end of a cell, was compared. In the electric supply to the hydrogen electrode from cell one end, electrolysis voltage increased rapidly with current density, and it was observed that resistance of the length direction of the hydrogen electrode itself couldn't be disregarded. P_{H2O}, P_{H2}, and P_{O2} are as same as the 15 cm^2 cell test mentioned above. The measured open-cell potentials of 75 cm^2 at 800 degrees C were 0.92V for one end electric supply and 0.92V for both-ends electric supply, and these values were mostly in agreement with the theoretical value. On the other hand, the area-specific resistance (ASR) defined by equation (6) was 3.3 ohm cm^2 for one end electric supply and 1.2 ohm cm^2 for both-ends electric supply; the influence of an electric supply system and cell length was remarkable.

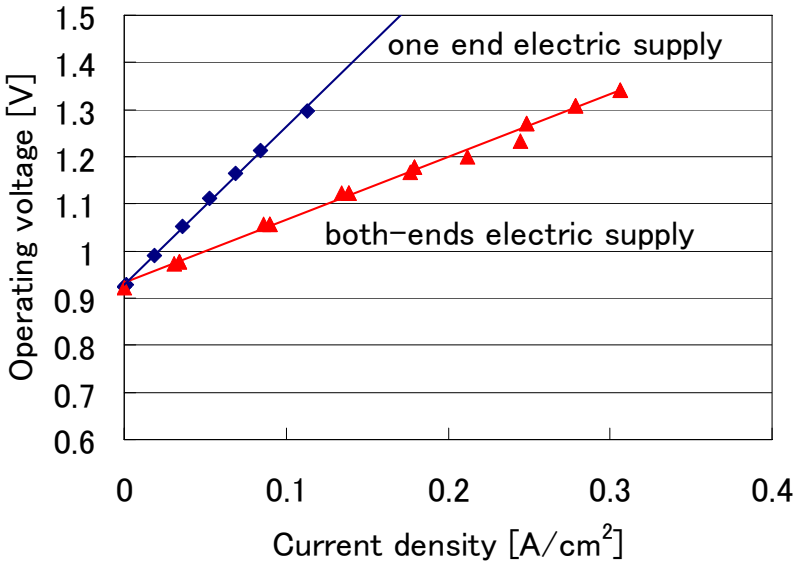


Figure 8 Current-voltage characteristic of 75 cm^2 cell

The hydrogen production rate was measured during the current-voltage characteristic measurement. It was confirmed that the observed hydrogen production rate was mostly in agreement with the theoretical value, which was predicted from the current density.

Figure 9 shows the current-voltage characteristic of fifteen 75 cm^2 cells assembly unit. P_{H2O}, P_{H2}, and P_{O2} are as same as the 15 cm^2 cell test and the single 75 cm^2 cell test mentioned above. The measured open-cell potential of the unit at 800 degrees C was 0.93V for each block, and these values were mostly in agreement with the theoretical value. Moreover, ASR was observed as 1.9 ohm cm^2, 1.9 ohm cm^2, and 2.0 ohm cm^2 for every block, and there was almost no performance variation during a block. The hydrogen production rate was measured. Figure 10 shows hydrogen production test result.

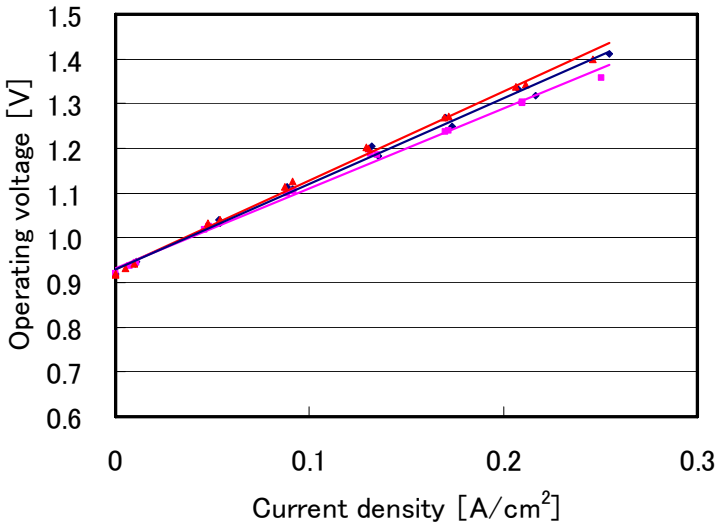


Figure 9 Current-voltage characteristic of fifteen 75 cm^2 cells assembly unit

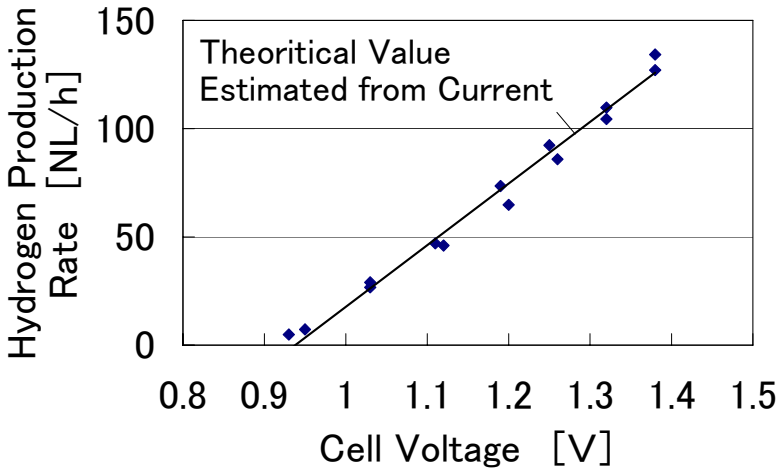


Figure 10 Hydrogen production test result of fifteen 75 cm^2 cells assembly unit

It was confirmed that the observed hydrogen production rate was mostly in agreement with the theoretical value, which was predicted from the current density. The hydrogen production rate of the unit of 130 Nl/h was checked to design value 100 Nl/h. It was confirmed that the unit, which consisted cells, seals, electrical isolations, electric supplies and so on, worked well from the result.

SUMMARY AND CONCLUSIONS

Toshiba has been developing the steam electrolysis system with tubular cells using solid-oxide electrolyte for hydrogen production over a temperature range of 800 to 900 degree C. Fifteen tubular electrolysis cells assembly unit, which 15 cells are installed in a casing and divided into three blocks of every five for electric supply individually to each block and parallel connection of all the cells was carried out, has been manufactured. Each cell is set on a pedestal via glass, which works for seal between hydrogen side and oxygen side and also works for electrical isolation. Experimental results were obtained from the unit. The measured open-cell potential, OCV, of the unit at 800 degrees C was mostly in agreement by 3 blocks, and further in agreement also with the theoretical value. Moreover, the area-specific resistance, ASR, was almost as same for every block. It was confirmed that there was almost no performance variation during a block. And the measured hydrogen production rate was mostly in agreement with the theoretical value, which was predicted from the current density. The hydrogen production rate of the unit of 130 Nl/h was checked to design value 100 Nl/h. It was confirmed that the unit, which consisted cells, seals, electrical isolations, electric supplies and so on, worked well from the result.

From now on, the influence on the characteristic with the passage of time and temperature, and steam consumption efficiency is examined to carry out prolonged operation of the 100 Nl/h unit. And the 1Nm^3/h unit is due to be developed using this result.

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