

Hydrogen Evolution by Plasma Electrolysis in Aqueous Solution

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Hydrogen has recently attracted attention as a possible solution to environmental and energy problems. If hydrogen should be considered an energy storage medium rather than a natural resource. However, free hydrogen does not exist on earth. Many techniques for obtaining hydrogen have been proposed. It can be reformulated from conventional hydrocarbon fuels, or obtained directly from water by electrolysis or high-temperature pyrolysis with a heat source such as a nuclear reactor. However, the efficiencies of these methods are low. The direct heating of water to sufficiently high temperatures for sustaining pyrolysis is very difficult. Pyrolysis occurs when the temperature exceeds 4000°C. Thus plasma electrolysis may be a better alternative, it is not only easier to achieve than direct heating, but also appears to produce more hydrogen than ordinary electrolysis, as predicted by Faraday's laws, which is indirect evidence that it produces very high temperatures. We also observed large amounts of free oxygen generated at the cathode, which is further evidence of direct decomposition, rather than electrolytic decomposition. To achieve the continuous generation of hydrogen with efficiencies exceeding Faraday efficiency, it is necessary to control the surface conditions of the electrode, plasma electrolysis temperature, current density and input voltage. The minimum input voltage required induce the plasma state depends on the density and temperature of the solution, it was estimated as 120 V in this study. The lowest electrolyte temperature at which plasma forms is ~75°C. We have observed as much as 80 times more hydrogen generated by plasma electrolysis than by conventional electrolysis at 300 V. [DOI: 10.1143/JJAP.44.396]

KEYWORDS: plasma electrolysis, hydrogen generation, current efficiency, pyrolysis

1. Introduction

The amounts of hydrogen and oxygen generated by electrolysis are predicted by Faraday's law. Under standard conditions of 298 K, and 1.013×10^5 Pa, $0.116 \text{ cm}^3\text{C}^{-1}$ hydrogen and $0.0581 \text{ cm}^3\text{C}^{-1}$ oxygen are produced. If the temperature exceeds 4000°C, pyrolysis may occur, and the amount of hydrogen generated will exceed the amount predicted by Faraday's law.^{1,2)}

Glow discharge reaction occurs when electrolysis is performed in a solution at a high input voltage (100 V or more).^{3–9)} Plasma is formed on the surface of the electrode. A layer of mixed hydrogen, oxygen, and steam is formed on the cathode surface. If the temperature and current density are right, hydrogen generation in excess of that predicted by Faraday's law can be observed. However, even when these conditions are met, the control of the amount of the hydrogen generated is still very difficult.

We have developed a method of efficient hydrogen generation. We reported anomalous hydrogen generation and the products of plasma electrolysis. When a voltage higher than 140 V was applied to interelectrodes in an electrolyte at high temperatures, the plasma state was easily achieved. Many researchers have confirmed the generation of various chemicals by plasma electrolysis.^{10,11)} There has been extensive discussion about the generation mechanism of the products.^{12,13)} It has been reported that the temperature reaches 9000 K, and the pressure reaches 4000 atm when plasma forms at several hundred volts.¹⁴⁾

It is necessary to estimate heat balance to determine the current efficiency of hydrogen generation. However, input

voltage and current fluctuate considerably, and it is difficult to measure the output heat balance during plasma electrolysis. The measurements of heat loss from the cell and fluid temperature are relatively simple, but that of the enthalpy of the effluent gas, which is a mixture of hydrogen, oxygen, and steam, is very difficult. An accurate measurement had not been performed heretofore. The measurement is complicated by the fact that the amount of gas generated cannot be estimated from input current (as it can with ordinary electrolysis), because the portion produced by pyrolysis must be included. To determine enthalpy, it is necessary to accurately measure the actual amount of hydrogen mixed in a gas stream.

2. Experiment

2.1 Electrolysis cell

Figure 1 shows a schematic of the cell and measurement system. The cell is made of Pyrex glass, and is of diameter 10 cm, 17 cm height, and 1 liter capacity. The cap of the cell is made of Teflon rubber, 7 cm in diameter and with several holes. The largest hole is in the center, where a glass funnel covering the cathode is inserted. There are also a vent for the effluent gas from the anode, inlet and outlet holes for a Tygon tube that carries cooling fluid through the cell, a hole to admit the anode lead wire, and three other holes for platinum resistance temperature detectors (RTDs). The RTDs measure electrolyte temperature. They are placed 3 cm from the cell wall, reaching depths of 3, 6 and 9 cm, to measure temperature at different points in the solution. Temperatures at three depths were continuously measured. No significant temperature difference between the three locations was observed because the solution is well mixed during electrolysis using a magnetic stirrer.

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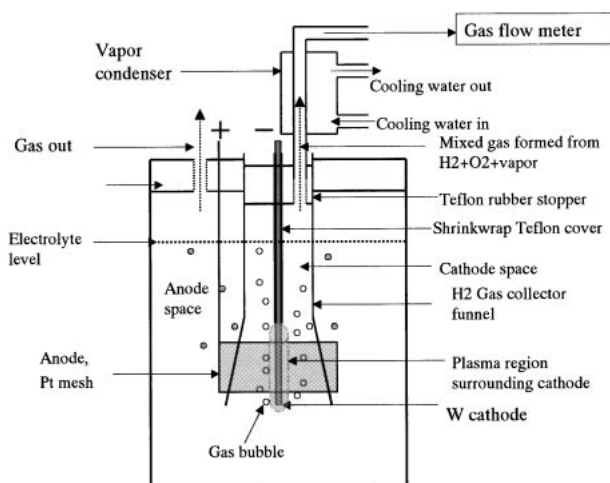


Fig. 1. Schematic of cell and measurement system.

As noted above, the cathode is separated from the anode, RTDs and other components by an inverted quartz glass funnel. After electric power input begins, it takes a few seconds for the heat and hot electrolyte to diffuse from under the funnel to reach the RTDs.

2.2 Capture and measurement of hydrogen gas

Since the cathode and anode are separated by a funnel, oxygen from the anode does not reach the cathode, and during normal electrolysis, oxygen and hydrogen do not mix. A funnel captures effluent gas from the cathode (but not from the anode). The lower part of the funnel is 5 cm in diameter, and 12 cm in length. As noted above, the narrow, upper portion of the funnel protrudes through a hole in the cell cap.

The top of the funnel protrudes approximately 1 cm on top of the cell. It is plugged with another, smaller Teflon rubber stopper, 2 cm in diameter. This smaller stopper has two holes: one for inserting the cathode lead wire, and one with an 8 mm Tygon tube for capturing effluent gas from the cathode. The gas is a mixture of hydrogen from electrolysis, hydrogen and oxygen from pyrolysis, and steam from the hot electrolyte. This gas rises from the surface of the electrolyte, goes through the hole in the funnel plug, and into the Tygon tube that goes through a cooler. The cooler condenses the water vapor, which returns to the electrolyte solution. The remaining hydrogen and oxygen gas in the Tygon tube passes through a gas flowmeter (Kofloc Co. Ltd, model 3100; controller model CR-700). The minimum detectable flow rate is $0.001 \text{ cm}^3/\text{s}$. Flowmeter data is captured by a data logger (Agilent 34970A) and then recorded on a computer (Gateway Solo).

To determine the amount of hydrogen in the mixed gas stream after the stream passes through the flowmeter, a constant amount of the gas ($0.01 \text{ cm}^3/\text{s}$) passes through a needle valve and is led to a quadrupole mass spectrometer (QMS). The remaining gas is released to the atmosphere. The ratio of hydrogen to oxygen is continuously recorded by the mass spectrometer.

Oxygen gas from the anode is released outside the funnel in the cell. The anode is a Pt mesh wrapped around the funnel, and is $50 \times 150 \text{ mm}$ with a surface area of 200 cm^2 .

To induce plasma electrolysis, the anode surface area has to be three times larger than the cathode surface area. The oxygen gas generated from the anode rises to the surface of the solution, and exits through the vent to the atmosphere.

Water flows through a Teflon tube immersed in the electrolyte. The water does not mix with the electrolyte; it acts as calorimeter fluid and cooling fluid, and maintains the electrolyte from boiling. The electrolyte is mixed with the magnetic stirrer, which keeps temperature fluctuations within 0.1°C .

The calorimeter fluid flow rate was continuously measured with a turbine meter (Japan Flow Control Ltd., model T-1965B). The minimum detectable flow rate is $0.01 \text{ cm}^3/\text{s}$. The fluid passes through the turbine meter and past an inlet temperature RTD sensor. It then passes the cooler above the funnel that condenses steam out of the cathode effluent gas stream. From there, it passes through the Teflon tube immersed in the electrolyte. Then the temperature is measured again with the outlet RTD sensor. Output power was measured based on flow rate and the temperature difference between the outlet and inlet.

The cell was set up in a constant-temperature air-cooled chamber kept at 20°C . The chamber is 60 cm wide, 50 cm deep, and 50 cm high. Chamber's air temperature was measured with an RTD placed 20 cm away from the cell.

2.3 Electrode and solution

The electrode is a tungsten wire of 1.5 mm diameter. This is cut into 15-cm long segments, and 13 cm of the upper part is covered with a shrink-wrap Teflon tube. The remaining exposed part of the wire acts as the electrode. This exposed area is 0.95 cm^2 . The electrolyte solution was prepared with 0.2 M analytical-grade K_2CO_3 .

2.4 Heat balance measurement

Electrolysis was performed using a stable power supply (Takasago model EH1500H). Input electric power was measured with a precision electric power meter (Yokokawa PZ4000). This meter measures voltage and current every $40 \mu\text{s}$, and accumulates 100,000 data points in 4 s. The average values are sent to the data logger every 5 s. The data logger also records eight other values at 5 s intervals: the flow rate of the calorimeter fluid; the calorimeter fluid temperatures at the inlet and outlet; the electrolyte temperature measured at three places in the cell; the temperature of the constant-temperature chamber; and the amounts of hydrogen and oxygen in the cathode effluent gas measured by the spectrometer.

3. Results

Figure 2 shows a typical result. Figure 2(a) shows the changes in input voltage, input current (b), and temperature of the electrolyte (c). Voltage gradually and smoothly changed from 80 V up to 300 V. Above 300 V, voltage had to be adjusted rapidly and repeatedly to control the condition of plasma. It was finally decreased to 300 V. Current density increases with voltage during normal electrolysis, but when plasma forms it decreases. It seems that the boundary voltage of electrolysis and normal plasma electrolysis is approximately 100 V. The current density just before plasma forms is $4 \text{ A}/\text{cm}^2$ at 80 V. In the example shown in Fig. 2,

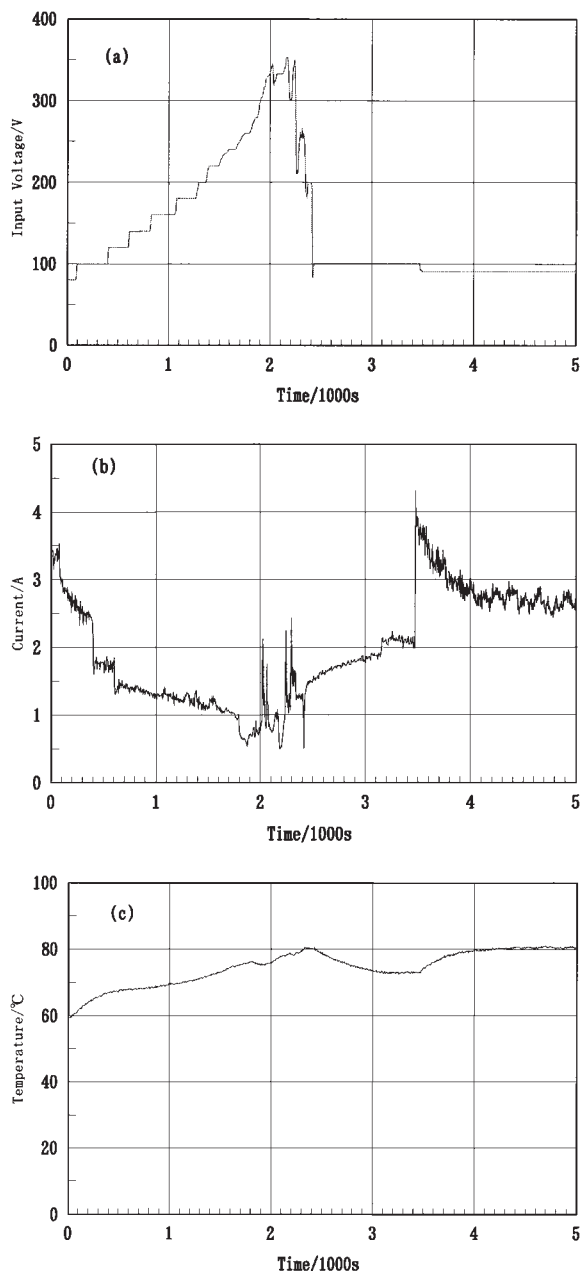


Fig. 2. (a) Changes in input voltage, (b) current change and (c) temperature change during normal and plasma electrolysis.

the temperature of the solution increased and current density fell to 3 A/cm^2 . Plasma formed when the voltage was increased to 120 V, and the current density fell to 2 A/cm^2 .

Four discrete, different plasma states were observed, at different voltages. They are shown in photographs in Fig. 3. Photograph (a) shows the plasma state immediately after plasma appears, at 100 V. The tungsten electrode begins to glow red. Excess hydrogen is not generated and plasma is close to the electrode surface.

Photograph (b) shows the state of the plasma at 200 V. Pyrolysis is observed; generation of excess hydrogen and oxygen has already begun. The plasma region is enlarged, at a distance of 5 mm from the cathode surface.

Photograph (c) shows the plasma at 250 V. The range of plasma has extended to a distance of 10 mm in the electrode. However, plasma is unstable at voltages above 250 V, and the size of the plasma envelope fluctuates rapidly. The

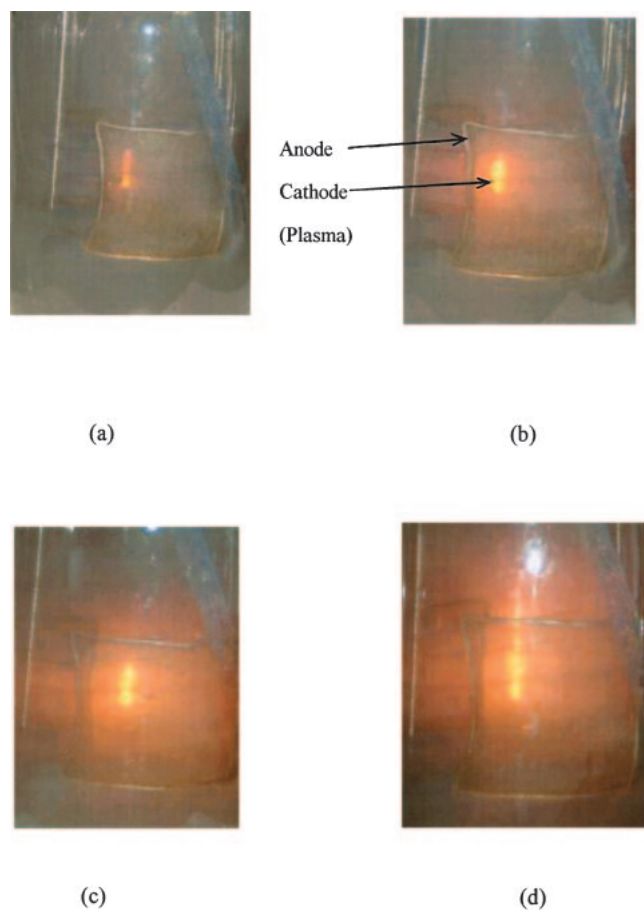


Fig. 3. Photograph of plasma electrolysis at (a) 100 V, (b) 200 V, (c) 250 V and (d) 350 V.

amount of excess hydrogen increases exponentially, and the free gas causes occasional electrical discharge arcs from the electrode surface.

Photograph (d) shows plasma at 350 V. The electrical discharge of the arc occurs continually, and plasma enters an extremely unstable state. The plasma envelope extended 5–7 cm from the electrode. Even though the current density is low, a large amount of gas is generated. Sometimes large bursts of hydrogen generation occur. Plasma extends to the entire region of the gas emitted from the cathode, and the tungsten electrode begins to disintegrate considerably. The shrink-wrap Teflon covering electrode is abraded. It becomes very difficult to maintain the plasma. For these reasons, it is impossible to keep plasma in this condition for more than a few minutes.

In the experiment shown in Fig. 2, the maintenance of a stable voltage became difficult after 2300 s, when remarkable, violent fluctuations in the current set in. For this reason, 350 V is the upper limit of this measurement, with this equipment. At 2400 s, voltage decreased to 100 V. Current density once again increased to 2 A/cm^2 , and then stabilized. At 3500 s, voltage decreased to 90 V, the plasma disappeared, and normal electrolysis hydrogen generation resumed. A large voltage change occurred in a thin layer on the surface of the cathode when voltage was increased, and the electric power was consumed mainly in this layer. This heats the layer to a high temperature, and forms plasma in the mixture of steam, hydrogen, and oxygen above the

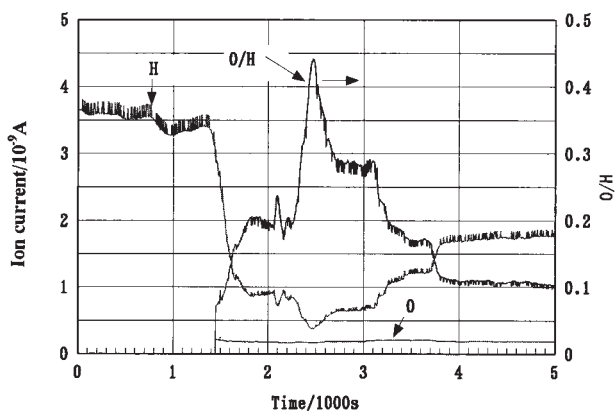


Fig. 4. Changes in ion current for hydrogen, oxygen gas and O/H ratio during the experiment shown in Fig. 2.

cathode surface. At this stage, electrical discharge rate is the limiting factor controlling the overall reaction rate, and even if input voltage was increased, the plasma layer only becomes thicker; overall reaction rate does not increase. Current density stays almost constant. However, the extent of heat generation increases as input is increased. It does not depend on voltage in the plasma electrolysis, even though the relationship between voltage and current density is linear during conventional electrochemical hydrogen generation. During conventional electrolysis, the amount of hydrogen is proportional only to input current. However, because the pyrolysis reaction takes place directly during plasma electrolysis, hydrogen generation is complicated.

The volume of the effluent gas can be easily being measured with a flow meter, but to measure enthalpy it is necessary to determine the composition of the gas. To accomplish this, after the gas passed through the gas flow meter, a constant volume of the gas was diverted into the QMS, where it was continuously analyzed. We analyzed mass numbers from 1 to 40. It was shown that hydrogen and oxygen were the main elements of the gas. The changes in ion current for O_2 (mass number 32) and H_2 (mass number 2) are shown in Fig. 4.

Six peaks were measured during the electrolysis, for the mass number range from 2 to 40, as shown in Fig. 4. They are $2(H_2^+)$, $3(HD^+)$, $4(D_2^+)$, $18(H_2O^+)$, $28(N_2^+)$ and $32(O_2^+)$. Before and after the run, when a sample of the effluent gas was not presented to the QMS, the background ions in samples of air were measured at 1.50×10^{-11} , 1.52×10^{-13} , 1.45×10^{-13} , 5.30×10^{-11} , 2.73×10^{-10} and 5.38×10^{-11} A, respectively. Fluctuations in these ionization currents were 5% or less. In a vacuum, smaller but similar peaks were observed, due to leakage and the entry of residual gas from outside. There were large peaks for molecules with atomic weights of 28(N_2) and 18(H_2O). When electrolysis began, and a sample of gas was diverted into the mass spectrometer, the ionization currents changed to 3.74×10^{-9} , 1.5×10^{-11} , 1.1×10^{-12} , 1.8×10^{-10} , 1.65×10^{-10} , and 5.46×10^{-11} A. The peaks for H_2 and O_2 were stable during normal electrolysis, as shown in Fig. 4. However, when plasma electrolysis began, the peak for hydrogen decreased while the peak for oxygen increased rapidly. The proportion of oxygen increased as current decreased, until it reached 2.46×10^{-10} A.

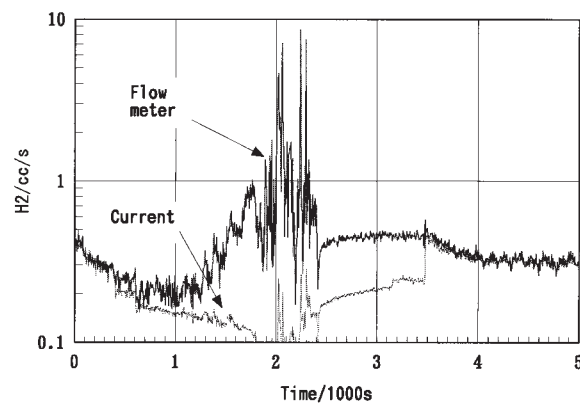


Fig. 5. Changes in amount of the hydrogen gas measured by H_2 gas flowmeter versus the amount expected from current.

The peak for hydrogen decreased with the increase in input voltage. After electrolysis, the ionization current of H_2O was minimum at an input voltage of 350 V, at 2500 s. On the other hand, the ionization current of O_2 after plasma electrolysis appears to be constant. A typical ratio of oxygen to hydrogen atom (O/H) is $2.46/37.4 = 0.066$ during conventional electrolysis. Figure 4 shows the change in the ion current ratio of hydrogen to oxygen. The ratio increased up to 0.45 during plasma electrolysis at 350 V. When the plasma electrolysis stops, the ratio decreases.

Figure 5 shows the change in the amount of the hydrogen gas measured by the flowmeter and QMS, and the value calculated based on input current. The value calculated from input current and measured by the flowmeter during conventional electrolysis are in accordance with Faraday's law, up to approximately 400 s. After 400 s, the amount of hydrogen measured by the flowmeter was clearly larger than Faraday's law prediction. Moreover, both values again agreed with those obtained when normal electrolysis was restarted at 3500 s.

Current efficiency ε is defined as the ratio of the amount of hydrogen actually generated to that of hydrogen predicted from input electric charge, based on Faraday's law. Its value is unity during normal electrolysis. The change in ε during the experiment is shown in Fig. 6. When input voltage increases, ε exceeded unity though plasma electrolysis starts at 400 s. ε was greater than ten when plasma electrolysis occurred at 300 V at 2000 s. It increased to 60 or 70 within a

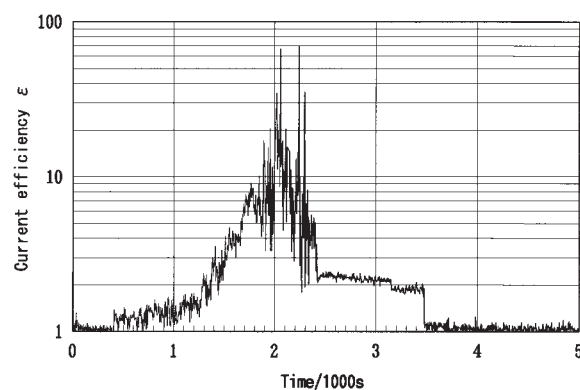


Fig. 6. Changes in current efficiency calculated from amount of hydrogen gas measured by flowmeter and that expected from input current.

few seconds. However, this is an extremely unstable phenomenon.

A steady hydrogen generation reaction with ε of ~ 2 continues when input voltage was decreased to 100 V and plasma was maintained, from 2400 s to 3500 s. When voltage was reduced to 90 V at 3500 s, the plasma disappeared and ε returned to unity.

During this experiment, 1140 cm³ of hydrogen should have been generated according to Faraday's law. The amount actually measured was 2200 cm³, which was 1060 cm³ in excess. All this excess was produced during plasma electrolysis, when the total electric charge should have produced 460 cm³ of hydrogen according to Faraday's law. The amount of hydrogen the measured was 1470 cm³, and the amount of excess hydrogen reached 1010 cm³, which was 3.2 times larger than that calculated value from electric charge. This includes all hydrogen, including hydrogen produced when voltage was manually increased, thus it may not be physically significant.

Current efficiency ε is strongly dependent upon input voltage, as shown in Fig. 7. In this case, data was obtained during the input voltage change shown in Fig. 2. The change in efficiency was large. It became unstable above 260 V, because at such high voltages it became difficult to control and maintain plasma. Instability in the high-voltage domain is normal in these experiments.

Figure 8 shows the voltage dependence of power effi-

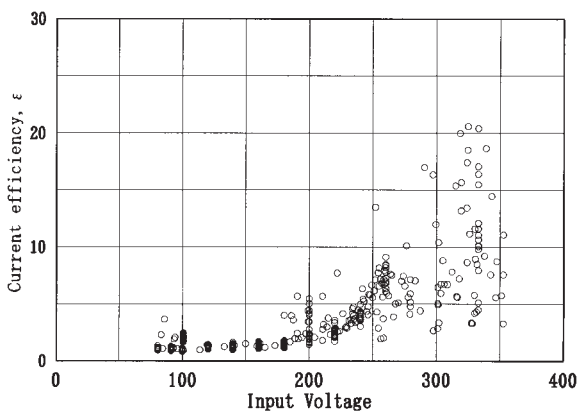


Fig. 7. Relationship between current efficiency of hydrogen gas generation and input voltage.

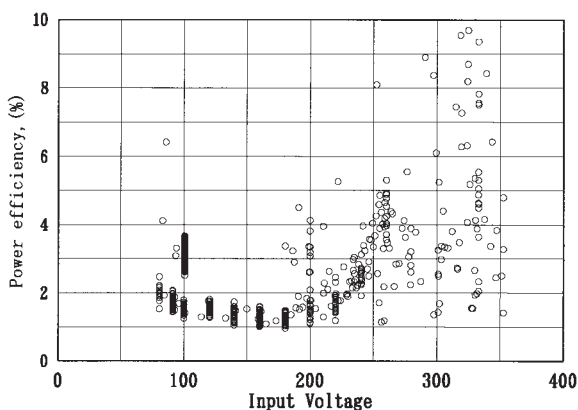


Fig. 8. Input voltage correlation with power efficiency.

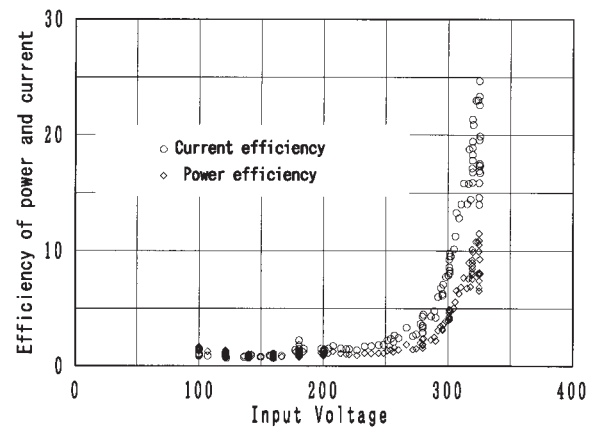


Fig. 9. Correlation of current and power efficiency with input voltage in 0.05 M K₂CO₃ electrolyte.

ciency in term of the amount of hydrogen generated. Here, power efficiency denotes the ratio of the amount of hydrogen generated to input electric power. It was less than 1% in conventional electrolysis, as shown at 100 V. When the plasma electrolysis starts, power efficiency increases because of an increase in input voltage. However, electric power efficiency is also very unstable above 260 V. This was caused by the disintegration of the electrode.

Figure 9 shows the result for a low-concentration (0.05 M) K₂CO₃ electrolyte. Current efficiency and electric power efficiency are shown. The current efficiency is low in the region below 260 V compared with the case of using the same electrolyte at 0.2 M concentration (Fig. 7). Above 260 V, current efficiency increased smoothly, reaching 25 at 320 V.

The change in stability is caused by changes in plasma state. It is difficult to maintain steady plasma in a high-density electrolyte solution. Current density increases rapidly with increasing electrolyte concentration. On the other hand, when the concentration is too low, it becomes difficult to generate plasma, and plasma only forms at high temperatures; thus, balancing these two factors and selecting an effective concentration are challenging.

Figure 10 shows the current efficiency dependence on electrolyte temperature during plasma electrolysis. This shows a typical relationship in a solution of 0.2 M K₂CO₃ at

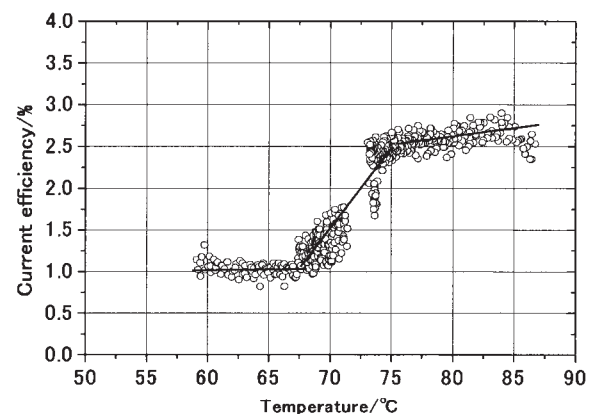


Fig. 10. Temperature dependence on current efficiency for 120 V electrolysis.

12 V. These data points were obtained from 20 experiments. The measurements were started after plasma formed. Voltage was decreased and temperature gradually decreased. Data points were collected until plasma finally disappeared. While the temperature remains higher than 68°C, plasma can be maintained at 120 V of input voltage. The current efficiency of hydrogen is unity from 60 to 68°C. It increases rapidly to 2.5 above 68°C up to 75°C. Above 75°C, the increase continues, but at a lower rate.

4. Conclusion

It is still difficult to accurately determine the correlation of ε and other factors. However, the data strongly suggests that input voltage is the key factors to generate excess hydrogen, as shown in Figs. 6 and 8. The current efficiency apparently exceeded unity, because the direct pyrolysis decomposition of water obviously occurred. Most of the voltage drop occurred in the layer of the cathode surface, when a cathode smaller than an anode was used. It is assumed that the rest of the voltage drop was due to the anode surface, and the electrical resistance of the solution is one order of magnitude smaller. When a sufficient amount of current passes through the cell, and the voltage in the gas layer on the surface of the cathode is sufficiently high enough, a large amount of hydrogen gas is generated. Furthermore, to pass sufficient current, voltage must be increased. Since the impedance of the gas layer above the cathode surface is high, heat is generated at that location. When temperature becomes sufficiently high sufficient heat is generated, and the gas is sufficiently heated, it enters the plasma state. Current density does not increase, but stays constant. The generation of heat is due to the voltage increase. Direct pyrolysis then occurs.

The minimum input power to trigger the plasma state depends on the density and temperature of the solution. It was estimated as 200 W/cm² in this study. The lowest electrolyte temperature in which plasma forms is ~75°C.

Electric power efficiency increased with input voltage. It reached 10% at 325 V, which is the highest voltage reached in the present experiment. Efficiency may continuously improve at input voltages of more than 325 V. However, a uniform electrical discharge becomes very difficult to maintain as voltage increases, and arc discharge may occur. The disintegration of the electrode intensifies rapidly at high input voltages.

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