Confirmation of anomalous hydrogen generation by plasma electrolysis

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Abstract: Direct decomposition of water is very difficult in normal conditions. Hydrogen gas is usually obtained by the electrolysis. Pyrolysis decomposition of water occurs at high temperatures, starting at ~3000°C. As we have already reported, anomalous hydrogen is sometimes generated during plasma electrolysis. Excess hydrogen usually appears once certain difficult conditions during high temperature glow discharge electrolysis are met. Here, we show that anomalous amounts of hydrogen and oxygen gas are generated during plasma electrolysis excess gas generation, presumably from pyrolysis. This is indirect proof that exceptionally high temperatures have been achieved. (Direct measurement of the reaction temperature has proved difficult.) Continuous generation of hydrogen above levels predicted by Faraday's law is observed when temperature, current density, input voltage and electrode surface meet certain conditions. Although only a few observations of excess hydrogen gas production have been made, production is sometimes 80 times higher than normal Faradic electrolysis gas production.

Key word: plasma electrolysis, hydrogen generation, current efficiency

1. Introduction

We previously reported anomalous hydrogen generation during plasma electrolysis [1,2]. Some researchers have attempted to replicate the phenomenon, but it is difficult to generate large excess hydrogen. Usually, the plasma state can be achieved fairly easily when voltage is increased to at least 140V at a high electrolyte temperature. Several researcher have tried to replicate tend to raise input voltage very high, to several hundred volts. But they have observed no excess hydrogen even at such high voltage, because they have not achieved the other conditions we specify.

During plasma electrolysis, so much vapor and the hydrogen gas are released from the cell that it becomes difficult to determine the heat balance. Measuring the enthalpy of the effluent gas is particularly difficult and complicated, and it has not been done heretofore.

It is even more challenging to measure enthalpy removed from the system in excess gas, but it is important to measure the power balance, to be sure one have replicated excess hydrogen, because without it one cannot expect excess hydrogen.

The amount of hydrogen and the oxygen generated by electrolysis is based on Faraday's law. The volumes of these gases are 0.116 cc/C for hydrogen and 0.0581 cc/C for oxygen at standard conditions [3,4]. The yield might exceed Faraday's law at very high temperatures, exceeding 3000°C, when direct pyrolysis can occur. However, the estimated temperature of ordinary glow discharge plasma at 100V is lower than this. Glow discharge occurs when electrolysis is performed at high input voltage (100V or more) in an aqueous solution [5,6,7,8]. A plasma forms, and a mixture of free hydrogen, oxygen and steam are formed on the surface of the cathode electrode. The generation of hydrogen at levels exceeding Faraday's law is observed when the conditions such as temperature, current density, input voltage and electrode surface are suitable [9,10,11,12]. The precise conditions are still not known, and controlling these conditions is difficult, so only a few observations of excess hydrogen have been made [13,14,15].

2. Experiment

2.1 Electrolysis cell

Figure 1 shows the schematic outline of the cell and measurement system [1,2]. The cell, made of Pyrex glass, is 10 cm diameter and 17 cm in height, and 1000 cc in capacity. The cap is Teflon rubber, 7 cm diameter. The cap has several holes, three for platinum RTDs (Resistance Temperature Detectors) to measure electrolyte temperature, two for a coolant water tube inlet and outlet (described below), one to vent the oxygen from the anode, and a dome to capture hydrogen gas from the cathode (described below).

2.2 Capture and measurement of hydrogen gas

The electrodes are isolated in separate

partitions within the cell, to prevent oxygen from mixing with hydrogen. A dome or funnel-like quartz glass dome surrounds the cathode, extending below it. It is 5 cm in diameter, 12 cm in length. The effluent gas from the cathode — a mixture of hydrogen from electrolysis, hydrogen and oxygen from pyrolysis, and water vapor from the intense heat — is captured inside the funnel as it rises up to the surface of the electrolyte. Oxygen from electrolysis is generated at the anode, outside the funnel. The anode is a platinum mesh wrapped around the funnel. Bubbles of oxygen rise from the anode to the surface and leave the cell through a separate vent hole.
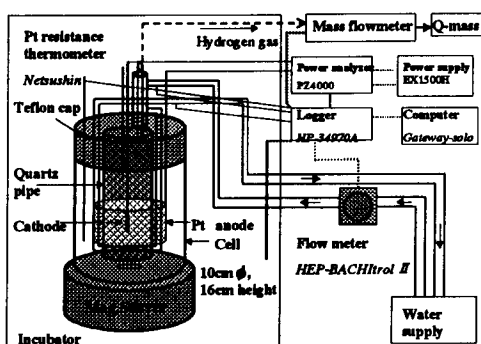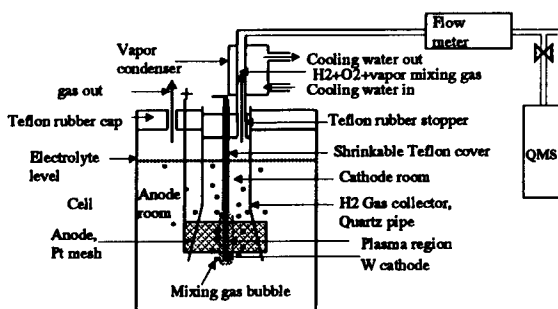

Fig.1: Detail of experimental set up.

Fig.2: Detail for gas measurement system.

After the gas rises to the top of the funnel, it passes through a Teflon sleeve into a condenser. The water vapor condenses and falls back into the cell, and the hydrogen and oxygen continues through an 8-mm diameter Tigon tube and a gas flow meter (Kofloc Corp., model 3100, controller model CR-700). This is a

thermal flow meter; the flow detection element is a heated tube. The minimum detectable flow rate is 0.001 cc/s, and the resolution is within 1%. The gas flow measurement system is interfaced to a data logger, which is attached to the computer.

After passing through the flow meter, part of the gas stream is diverted into a quadra pole mass spectrometer. A small, constant volume of the gas, typically 0.001 cc/s, passes through a needle valve and is analyzed by a mass spectrometer.

2.3 Power efficiency measurement

Two methods of power efficiency are performed simultaneously: flow and isoperibolic. Flow calorimetry is performed by circulating cooling water through a complicated circuit. The cooling water is tap water that begins by passing through a coiled copper tube immersed in a constant temperature bath. The cooling water then passes through a turbine flow meter (HEP-BATCHItrol II), and past the inlet temperature sensor RTD. From there, water goes through the outer chamber of the condenser above the cell. (Effluent gas from the cathode passes through the inner chamber. The water condenses and falls back into the cell, and the hydrogen gas continues on.) The cooling water tube then enters the cell to remove heat from the electrolyte solution. It is wound in a coil around the anode mesh and the funnel. The tube exits the cell, passes through the outlet temperature sensor RTD, and from there, it goes to the drain. Heat from both the condenser and the electrolyte is measured by comparing the inlet and outlet temperatures.

Isoperibolic calorimetry is performed by monitoring the temperature of the electrolyte solution with three RTDs, which are widely separated and placed at different levels in the solution. The solution is mixed with a magnetic stirrer.

The amount of the heat generation is estimated by combining the flow and isoperibolic data compared with the input electric power. The heat balance is still being investigated, and it will be described in a future paper.

2.4 Electrode and solution

The electrode was tungsten wire, 1.5 mm in diameter and 15 cm in length, the upper 13 cm of the wire covered with shrinkable Teflon, and the bottom 2 cm acted as the electrode. The

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light water solution was made from high purity K_2CO_3 reagent at 0.2M concentration.

2.5 Power supply

The power supply was a Takasago model EH1500H. Input power was calibrated for each five seconds and measured with a Yokogawa PZ4000 meter. The sampling time was 40μs, during which 100 kb of data is collected.

2.6 Data collection

All data, including the flow rate of the cooling water, the temperature of the coolant at the inlet and outlet, the temperature at three locations in the cell and one location in the thermostatic chamber, the input voltage, current, and the amount of the hydrogen gas generation were recorded by a data logger (Agilent Corp., 34970A), and a computer for each 5s.

3. Results

A calibration is shown in fig.3. The temperature, input voltage and current were shown in fig.3A; the input voltage was 100 and 80V, the current was increased from 2.5 to 3.5A and the temperature stayed 80°C. Figure 3B shows the change in the amount of the hydrogen gas measured directly from hydrogen gas flow meter and the expected hydrogen flow from the electric current, based on Faraday's law. Over the entire 1000-seconds run, the value obtained from flow meter and the Q-mass system, i.e. the current efficiency, was same with expected amount calculated according to Faraday's law for the measured current.

The changes in current efficiency are calculated above for a two-value ratio (ε) of the hydrogen gas amount of flow meter and the input current, and in addition, the ratios of heat output to input electric power (power efficiency) are shown in Figure 3C. The power efficiency shows a small fluctuation of 93% ~ 103%, and the ε is 0.98~1.1 in this electrolysis condition. In the generated oxygen and vapor had not been detected and calculated in the measurement for the heat, other word, some of the heat may escape from the system. On the other hand, here, the larger value of ε as 1.1 comparing the theoretical one can be considered that some oxygen gas goes into the hydrogen collecting tube. One of the reasons of the leakage is caused from the structure of the open part of the bottom side; some of hydrogen
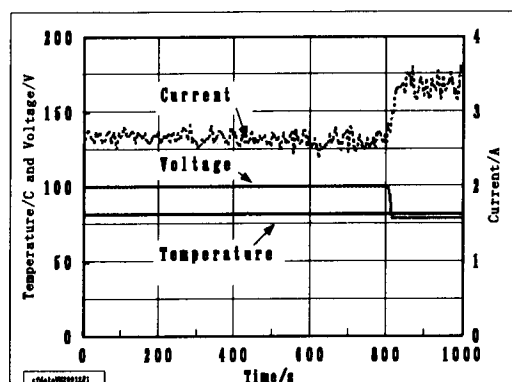

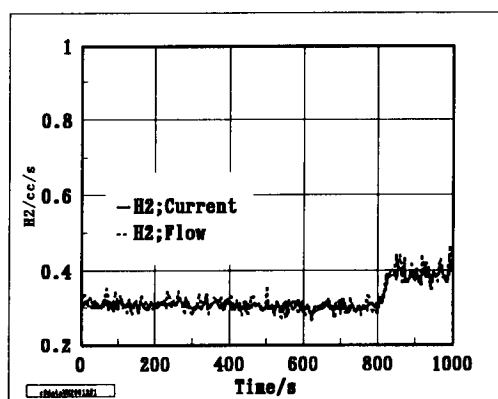Fig.3A: Changes of input voltage, current and cell temperature for the calibration measurement.

Fig.3B: Two rates of hydrogen generation measured by flow meter and estimation from current during normal electrolysis in fig.3A
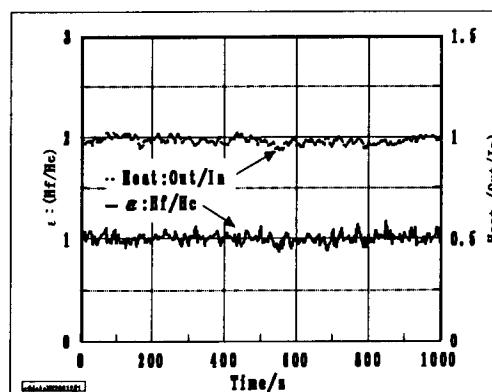

Fig.3C: Current and power efficiencies under fig.3A conditions

gas escaped from the cathode room, on the other hand, oxygen gas does into the cathode room where the capturing pipe surrounding the

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cathode electrode and refuse into anode room of the cell caused from strong stirring by the magnetic element. It is understood that the recovery changes by the generation rate of gas and stirring because if the stirring was ceased then the value of recoverystayed at 100%.
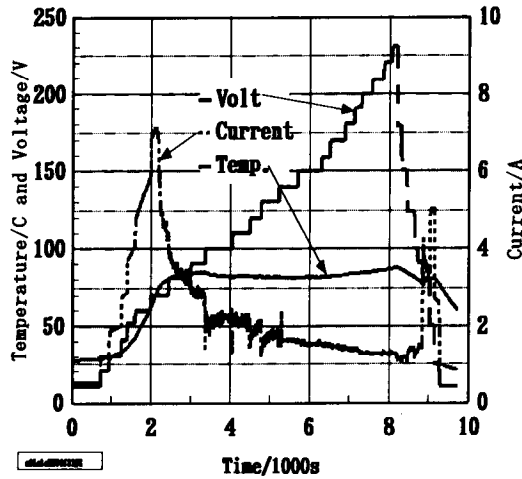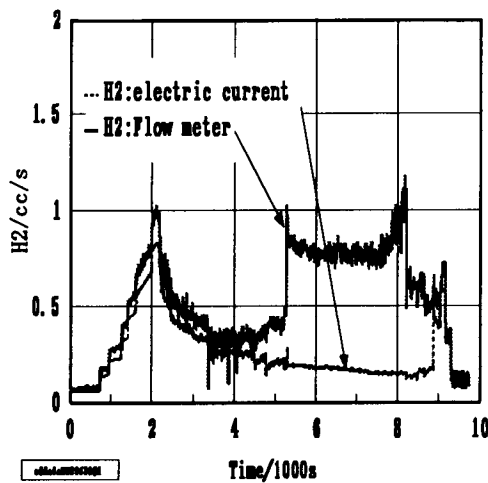

Fig.4A: Input changes for electrolysis.

Fig.4B: Change in hydrogen generation.

A typical result exceeding Faraday's law is shown in Figure 4. In this case, the plasma electrolysis occurred at 2A/cm^2 of input current at 120V and 80°C in electrolyte temperature, as shown in Figure 4A. The rate ε is shown in Figure 4B. Here, ε exceeded unity when the plasma electrolysis started; the gas generation much increased with the input voltage.

The power efficiency graphs (Figure 4B) show almost 100%. However, in the experiment, heat

recovery for oxygen evolution was not measured. So, we can only conclude that partial power efficiency was close to 100%. In same graph, the current efficiency of hydrogen gas generation are shown; the efficiency reached 8 (that is, 800% of the expected Faradic value), and it continued during plasma electrolysis at 230 V. Faraday's law predicts that 2440 cc should have been produced during the entire test run, but 5100 cc was measured (2662 cc excess). When we consider only hydrogen produced during periods when plasma formed, Faraday's law predicts 905 cc, and the measured amount was 3240 cc (2335 cc excess; 2.6 times the predicted value).
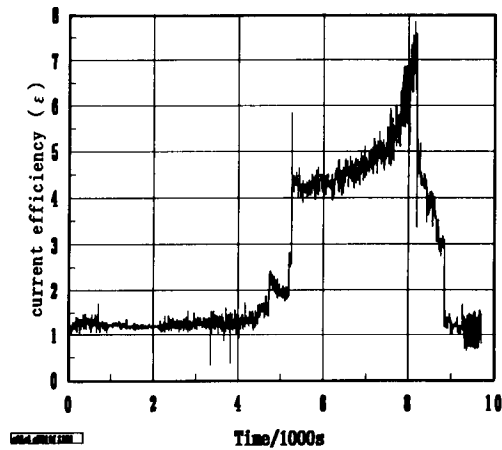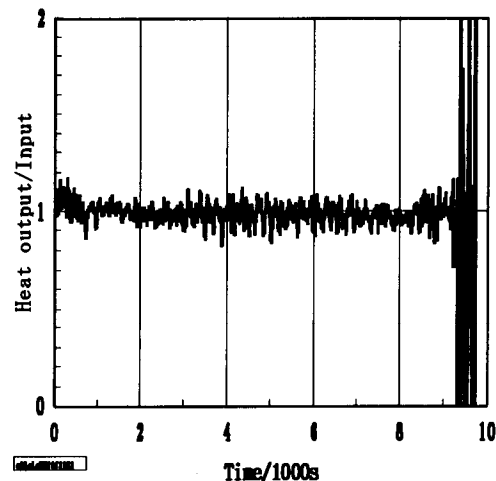

Fig.4C: Change of current efficiency(ε).

Fig.4D: Change in power efficiency.

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The relationship between current efficiency of hydrogen gas generation (ε) to voltage is shown in figure 5. Here, we can see that efficiency is strongly dependent on input voltage. Other parameters such as input current, duration time of the hydrogen generation and cell temperature do not show any strong correlation to ε.

4. Conclusions

It is difficult to determine the exact relationship between the current efficiency, ε and other factors. However, the data strongly suggests that one of the key factors is the input voltage, as shown in Figure 5 of the ε and V relationship. Here, it can be understand that the ε has a tendency of increase with input voltage. One point of ε value in the figure shows up to twice of the theoretical value of unity; the point was obtained by the result of plasma electrolysis. On the other hand, the ε is remaining at unity for all of the other normal electrolysis. It can be predicted that that if the input voltage were increased to several hundred volts, then the ε would far exceed unity.
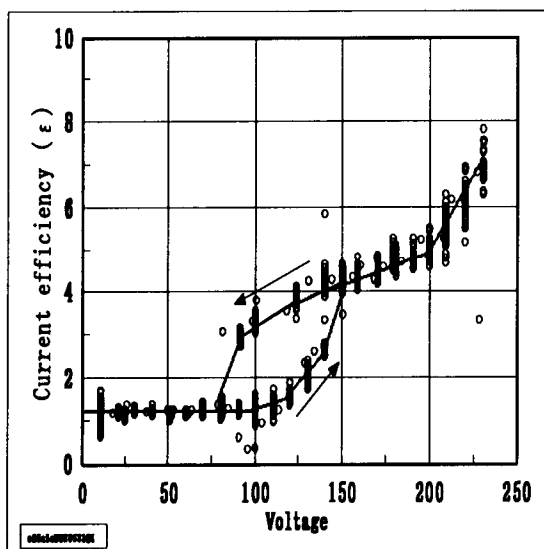

Fig.5: Voltage dependency for efficiency.

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