Hydrogen Generation by Ark from Moisture

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1.Summary

Here, we can show the method for obtaining hydrogen gas during ark discharge in moisture. At the same time, the gas included H2 and O2. Gas generation was changed by the condition of ark discharge. It can be very useful to generate the hydrogen gas for the purpose to usage of the hydrogen.

2.Introduction

We have already reported the hydrogen generation during plasma discharge [1]. Usually, the Plasma discharge can be easily started if the input voltage had been increased at rather high temperature [2,3]. The amount of hydrogen and the other products generated by the reaction can be considered under the thermal equivalent law at the conventional conditions. The yield was changed in case of high temperature electrolysis due to the direct decomposition process. However, it cannot be occurred in the conventional electrolysis. The pyrolysis can only occurs at more than 4000℃.

The gas mixture of hydrogen and steam are formed on the surface of the cathode electrode when plasma is formed if electrolysis is taken by high input voltage up to 140V in aqueous solutions [4,5,6,7]. The generation of hydrogen and oxygen that exceeded the faradic law, and other gas were observed when the conditions such as temperature, current density, input Voltage and electrode surface are suitable. The condition of the over unity generation of hydrogen gas is easily replicates and can be controlled, and the report of claim of the observation for the generation the hydrogen and others is not so much.

The gas mixture of hydrogen and steam are formed on the surface of the electrodes when arc is formed if discharge is taken by high input voltage up to 10,000V in moisture. The generation of hydrogen and other gases, which changes the law, is observed when the conditions such as temperature, current density, input Voltage and electrode surface are suitable. The condition of the over unity generation of hydrogen gas is easily replicates and can be controlled, and the report of claim of the observation for the generation the hydrogen and others is not so much.

3.Experiment

3.1 Electrolysis cell

Figure 1 shows the experimental set up. We measure many parameters including sample surface temperature, neutron and x-ray emission, mass spectrum of gas, input and output power, and so on. Figure 2 shows the schematic sketch of the cell and measurement system [1-2]. The cell is made of the plastic 2.5 cm diameter and 10 cm in length and 100 cc in capacity. It is set in vessel that was closed with a Teflon rubber cap, 7 cm in diameter. The cap has several holes in it, three for platinum resistance temperature detectors (RTD) (Netsushin Co., Plamic Pt-100Ω), two for the inlet and outlet of the flowing coolant water, and one that captures the effluent gas from the cell. The tube is made of quartz glass. Gas leaves the tube and goes into a water-cooled condenser, which is connected to the tube with another tube.

We measured several parameters, rate of gas flow, electrolyte temperature, mass spectrum of gas and input power. Measurement system was described in elsewhere [1,4]. The moisture was composed pure water solution. The electrolyte for the plasma discharge included the several weight percents of K2CO3. Electrolysis was changed by input voltage up to 350V for the plasma discharge. The gas generated in ark and plasma electrolysis was continuously analyzed by the Quadra pole mass spectra system.

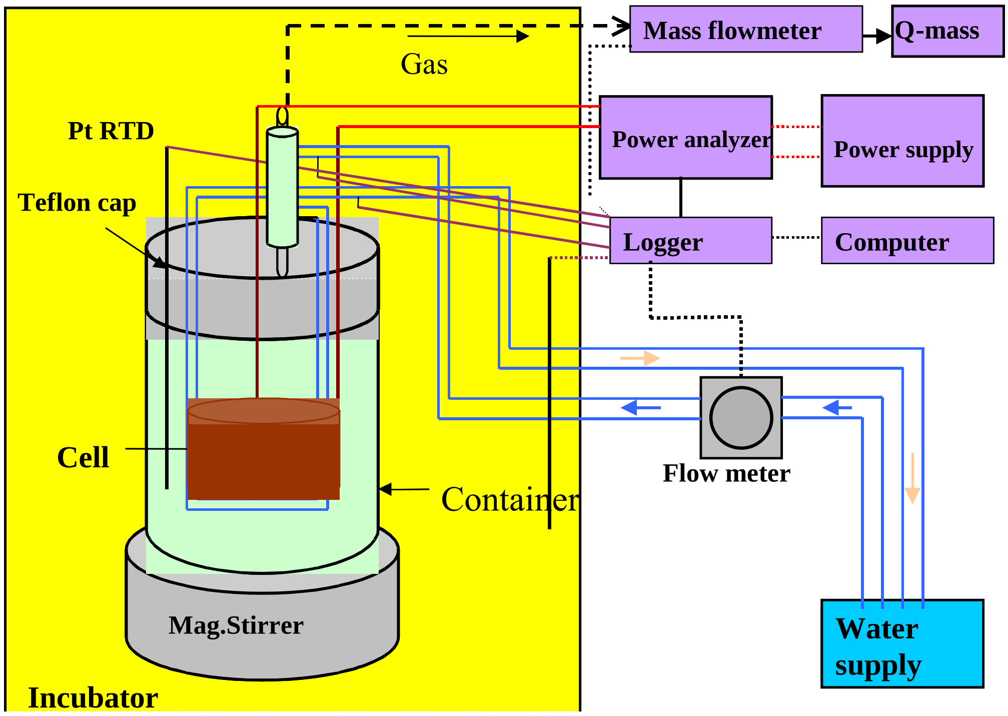


Fig.1 Experimental set up for power balance estimation.

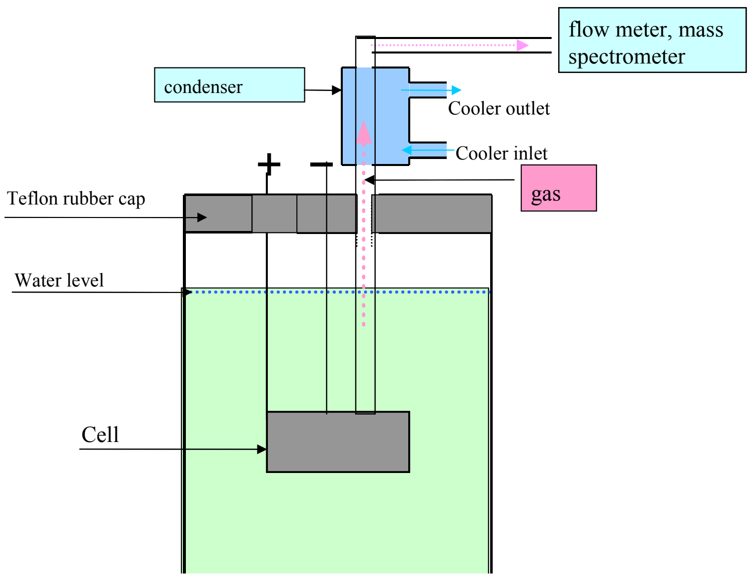


Fig. 2 Detail of gas calibration set up.

3.2 Measurement of hydrogen gas

A mixture of steam, hydrogen and oxygen (from pyrolysis) passes from the cell to the condenser. The steam condenses and falls back into the cell. An 8-mm diameter Tigon tube is coupled with the gas exit of the condenser, connecting it to a gas flow meter (Kofloc Co., model 3100, controller: Kofloc Co., model CR-700).

The flow to voltage transformer element is a heated tube of thermal flow meter system, the minimum detection rate of hydrogen gas flow is 0.001 cc/s, and the resolution is within 1%. The power output from the measurement system was led to the computer through a logger.

After path through the flow meter, the gas goes to a mass spectra analysis system. A small amount of constant volume of the gas such as 0.001 cc/s paths continuously through a needle valve and was analyzed by a quadruple mass analysis method.

The main composition of gas released from the cathode was then continuously analyzed by above-mentioned method.

3.3 Calorimetry

Temperature measurements were made with 1.5 mm diameter RTDs. Calorimetry was performed by combining the flow and isoperibolic method. Flow calorimetry is based on the temperature change of the cooling water. The cooling water is tap water flowing through Tigon tubing. It passes first through a constant temperature bath to keep the temperature constant. From there, it flows through the outer jacket of the condenser, and then through the coil of tubing wrapped around the funnel. (The outside of this cooling water coil is covered with the anode, a platinum mesh). The flow rate is measured with a turbine meter (Japan Flow Control Ltd., model T-1965B). The inlet temperature is measured before the cooling water enters the condenser, and outlet temperature is measured where it exits the cell. Heat from both condensation and glow discharge electrolysis are combined together. Isoperibolic calorimetry is performed by placing three other RTDs were in the cell electrolyte at different depths in the solution to measure the temperature. The solution is mixed with a magnetic stirrer.

Figure 3 shows the notional sketch for heat measurement. Heat out can be divided into several factors. These are energy for water decomposition, heat of electrolyte, heat bring by the coolant, heat releasing from the call wall and heat releasing with the vapor through the cell plug.

The heat balance is estimated by input and output formulas, input and output power is given in the following equations:

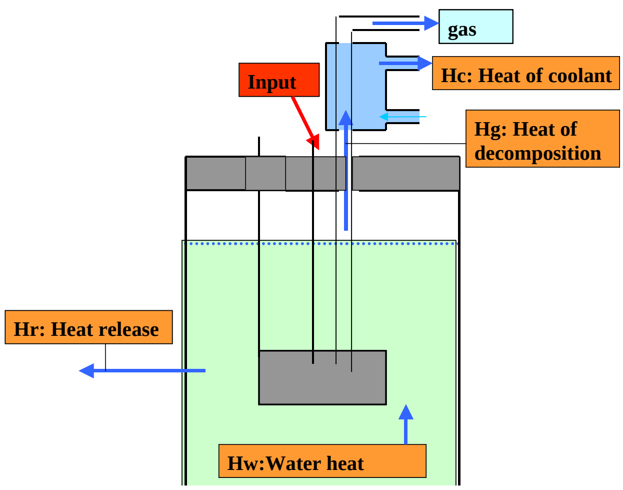
· **Input** (J) = **I** (current) ・ **V**(Volt) ・ **t(time),** · **Out** = Hg + Hw + HC + Hr, here,

Hg = Heat of decomposition = $\int$ 1.48 ・ d**I** ・ dt

Hw = Electrolyte heat = $\int$ Ww ・ Cw ・ δT; *Ww*:electrolyte weight, C*w*: heat capacity, δT:temperature difference

Hc = Heat of coolant = $\int$ Wc ・ Cc ・ δT; Wc:coolant weight, Cc:heat capacity, δT:temperature difference

· Hr = Heat release = $\int$ (Ww ・Cw + Wc ・ Cc)Tr; Tr*:* temperature change



· Fig. 3. Schematic representation of heat balance

The heat balance is calculated in straightforward. Input power is only from the electric power source. Output is divided into several parts. The first factor is heat of water decomposition (designated Hg). It is easily calculated from the total electric current. The second factor is electrolyte enthalpy (Hw). It is easily derived from the solution temperature difference. The third factor is heat removed by the coolant (Hc). This is measured from the temperature difference between the coolant inlet and outlet, and the coolant flow rate. The fourth factor is heat release from the cell (Hr). This is rather complicated and can be estimated with a semi-empirical equation. We have measured most of the heat in the condenser directly by monitoring the inlet and outlet temperature of the cooling water that passes through the condenser outer jacket.

If there were various gases, we have to measure the gas composition precisely, because even a small volume of gas generated, it may remove a large amount of enthalpy. This was done with the precision gas flow meter and mass analysis. The first factor, water decomposition (Hg) has a large effect on the rest of the equation.

3.4 Electrode and solution

The electrode is tungsten wire, 1.5 mm in diameter and 15 cm in length. The upper 13 cm of the wire is covered with shrink-wrap Teflon and the bottom 2 cm is exposed to the electrolyte and acts as an electrode. After the electrolysis, the sample wire was consumed. The electrolyte solution was made from high purity K_2CO_3 reagent at 0.2M concentration for plasma electrolysis. The moisture was formed by pure water.

3.5 Power supply

Power supply was used a model of EH1500H made by Takasago Co. Ltd.. The electric power was collected with a power meter (Yokogawa Co., model PZ4000) in every 5 seconds. And the electric power was measured in each 40μs and accumulated for 100k numbers during 5 seconds.

3.6 Data collection

All data, including the mass of cooling water flow from the flow calorie measurement, the temperature of coolant entrance and exit, electrolyte temperature measured by three RTDs, input voltage, current, electric power and the amount of the hydrogen gas generated were collected by a data logger (Agilent Co., model 34970A), and stored in a personal computer.

3.7 element analysis

The sample electrodes and the electrolyte were subjected to element detection by means of energy dispersion X-ray spectroscopy (EDX), Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS) and electron probe micro analyzer (EPMA).

3.8 Mass analysis

The generated gas was continuously analyzed a Quadra –pole mass analysis. Few amount of gas was once introduced into a differential evacuation system and then bring to the mass analysis measurement system. We used mass analysis of Ulvac Rega-201 that is a mass filter type of Quadra-pole mass analyzer. The analyzer can measure mass number from 2 to 400.

4.Results and Discussion

4.1 Ark discharge

The gas from the cell was changed by the Ark conditions and temperature of the moisture. Figure 1 shows the typical conditions for the ark discharge in water moisture. Input voltage was rose up to 30000V and supplied intermittently. Input current was changed between 0.37 and 4.3mA.

Figure 4 shows the rate of gas generation during ark discharge. Rate of gas measured by flow meter was higher as several hundreds times compared with the vale estimated from the current.

Figure 5 shows the ration between the values of amount of gas estimated from flow meter and current.

Figure 6 show the energy efficiency of H2 gas estimated from input power. The efficiency rose up several ten % of input power.

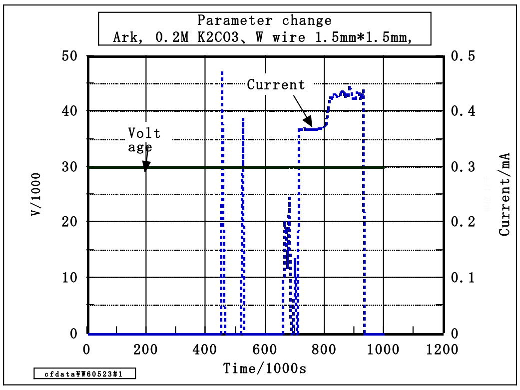


Fig.3 Typical input condition

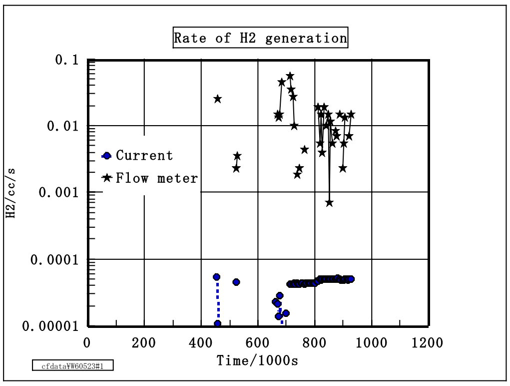


Fig.4 Rate of gas generation by ark discharge

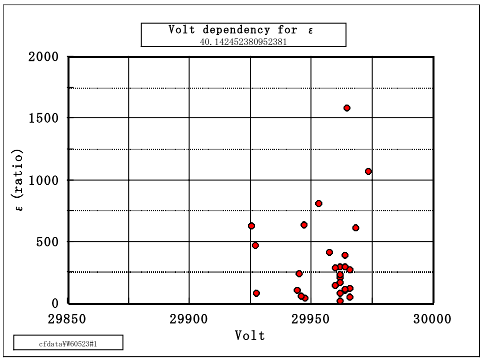


Fig.5 Current efficiency of H2 gas generation

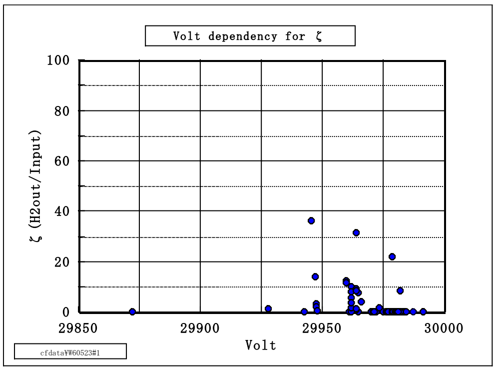


Fig.6 Power efficiency of H2 generation

Figure 7 show the time change of analysis of the mass number 2, 3 and four during ark discharge. They show stable after ark discharge start.

Figure 8 shows the mass spectrum for the ark discharge. The gases are mainly occupied with H_2 and O_2 for the moisture. Amount of hydrogen and oxygen gas were highly increased by ark voltage compared with the conventional electrolysis. This shows the direct water decomposition was occurred. The ratio of O/H stayed almost stable as 0.5.

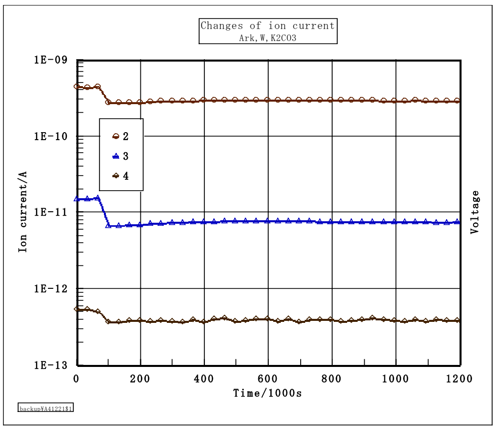


Fig.7 Mass analysis in ark discharge

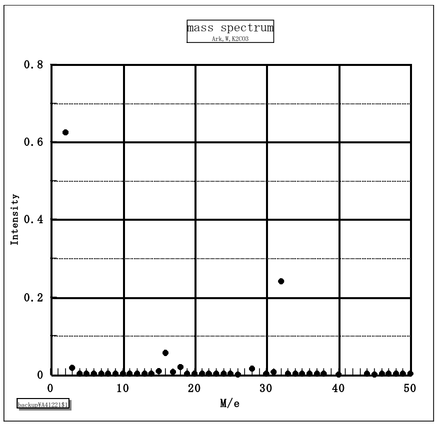


Fig.8 Mass spectrum in ark discharge

4.2 Plasma electrolysis in K_2CO_3 solution

The gas from the cell was changed by the electrolysis conditions and chemical compounds in the solution. The gases are mainly occupied with H_2 and O_2 for the electrolysis of K_2CO_3 solution. Amount of hydrogen and oxygen gas were steeply increased by input voltage compared with the Faradic law. This means that the direct water decomposition was occurred and the current efficiency was increased more than the theoretical value of unity. The ratio of O/H stayed almost stable as 0.5 at input voltage up to 350V.

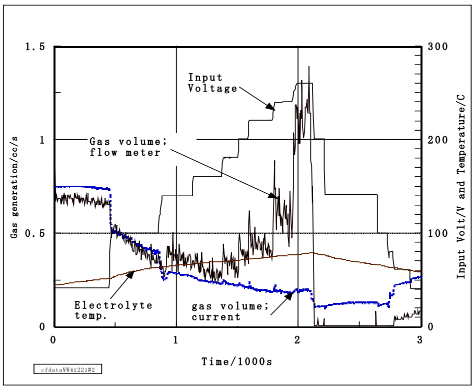


Fig.9 Change of gas, V and Temp. in plasma discharge.

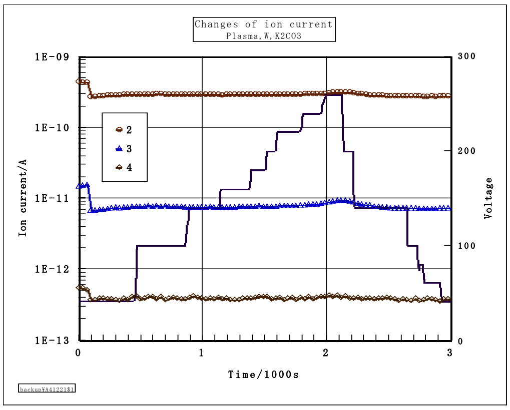


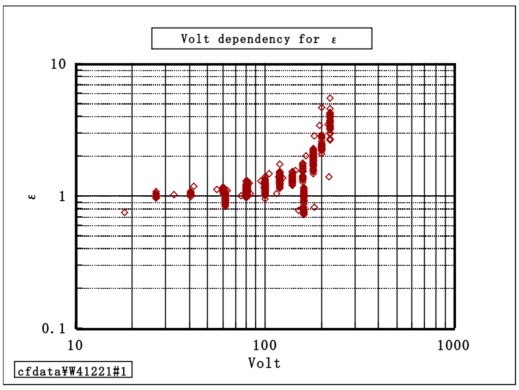
Fig.10 Changes of M/e = 2, 3 and 4

Figure 9 shows changes of input voltage, cell temperature and gas volumes estimated from current and flow meter. Input voltage was increased as stepwise from 40V to 260v and then decreased to 40V. The input current was 4.3A at 40V, but it decreased at 100V and once plasma started it again decreased to 1.6A at 140V. Generated gas that was estimated from the flow meter exceeded the value estimated from the current at once the plasma start. The deviation started from 800s where the plasma has occurred. The amount of gas estimated by the flow meter reached 5 times larger than the value of current estimation at 260V of input voltage.

The ion currents measured by the q-mass system are indicates for M/e 2,3 and 4 in fig.10. Here, the mass number of 2,3 and 4 stay constant during plasma electrolysis. We can say that there was no considerable increase of gas by the plasma electrolysis for the normal electrolyte.

The relationship between current efficiency of hydrogen gas generation (ε) to input Voltage is shown in Fig. 11. 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 .

The power efficiency is shown in Fig.12, it is 2% at 100V of normal electrolysis. It steeply increases with input voltage and the value is 10% around 300V. However, over 300V, it was very unstable because the electrode breakdown during high voltage plasma electrolysis.



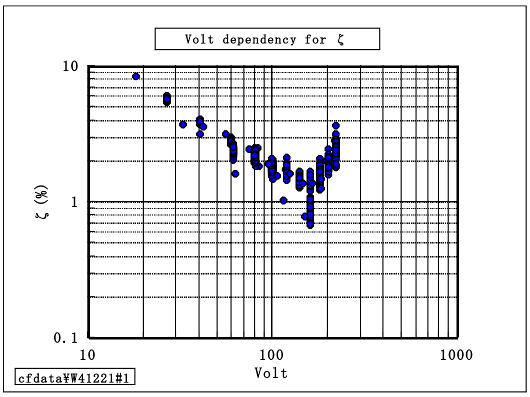


Fig.11 V dependence of current efficiency

Fig.12 V dependence of power efficiency.

Figure 13 shows the mass spectrum for the plasma discharge. The gases are mainly H_2 and O_2 as same as the case of the moisture. This plasma electrolysis shows the same direct water decomposition can be occurred. The ratio of O/H stayed stable as 0.5.

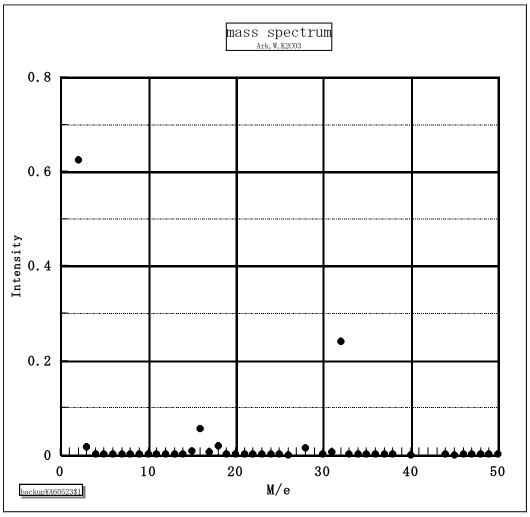


Fig.13 Mass spectrum of gas in plasma discharge.

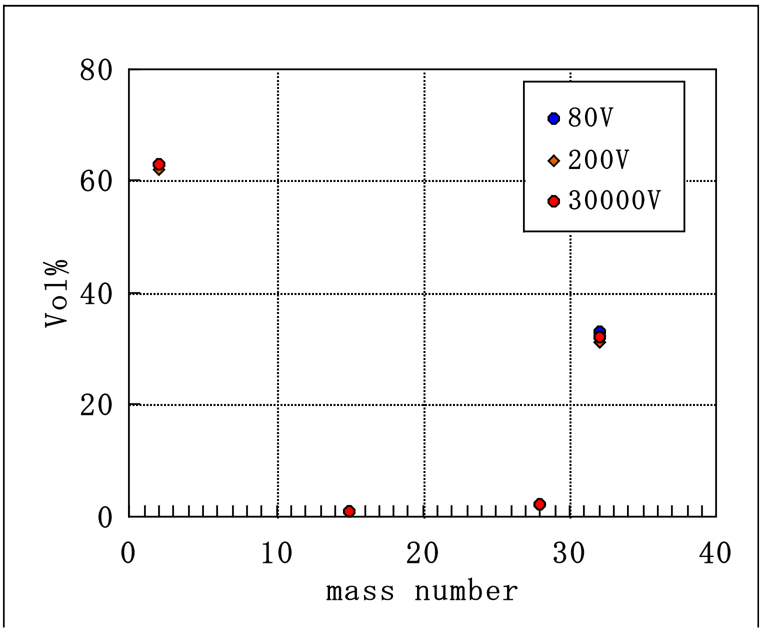


Fig. 14 Mass spectrum foe plasma, conventional electrolysis and ark discharge

Difference of generated gases in ark, conventional at 40V electrolysis and plasma electrolysis at 240V is shown in fig. 14. The graph does not show the amount of gas and it shows their intensity ratio. We can conclude that only hydrogen and oxygen gas have occupied in the case for all discharge method.

5.Conclusions

We can conclude that ark and plasma electrolysis of the solution generated H2 and O2 gas by direct pyrolysis reaction. The rate of the gases was depended on the input voltage. Typical constitutions for these gases are summarized in table 1.

Table 1 Constitution for the gas by various conditions; in percentage.

	Gas	H2	C	CH3	CO	O2	CO2
	Mass No.	2	12	15	28	32	44
Solution	Voltage						
K2CO3	80V	63				33	
	200V	62			2	31	
	30000V	63		1	2	32	

Gas constitution was little bit changed by the method. The number and the constitution for these gases were 2, 15, 16, 28, 32 and 44. The main constitution of these numbers was occupied by H2, CH3, CH4, CO, O2 and CO2.

We have obtained several conclusions as follows; (1). Current efficiency for the plasma electrolysis was 20 times higher than the conventional electrolysis of the inorganic solution. (2). Current efficiency for the ark discharge of the moisture was several hundred times higher than the conventional electrolysis. (3). In some cases, carbon oxides and hydrocarbons were observed.

6.Acknowledgement

We wish to express our thankful for the Thermal and Electric Energy Technology Foundation having given us the fund.

7.References:

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