

전기방전에 의한 수소제조방법의 전압-전류특성

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Voltage-Current Characteristics of Electrical Discharge Method for Hydrogen Generation

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초 록

금속과 물의 혼합체에 전기방전을 야기시켜 수소를 제조하는 방법은 필요시에 즉시 수소를 제조할 수 있는 유용한 방법이다. 그러나 이 방법이 실제로 이용될 수 있기 위해서는 입력되는 전기에너지당 물과의 반응을 일으키는 금속의 양이 가능한한 큰 값을 가져야 한다. 이러한 에너지 효율을 높이기 위해서는 약한 전기방전이 화학반응을 지속시킬 수 있어야 된다. 이러한 효율에 직결되는 실험변수중에서 방전 전압-전류 곡선을 측정하여 토의하였다.

Abstract

Hydrogen generation by electrical discharge through metal/water system is a viable method for on-demand applications. But its success depends on high energy efficiency defined as the ratio of the amount of consumed metal for a complete reaction with water to the electrical energy input. To improve the energy efficiency the electrical discharge has to sustain the hydrogen generation reaction with a minimal energy dissipation. Some experimental results on the discharge voltage-current profiles are reported and discussed.

1. Introduction

Generation or storage of hydrogen molecules for the use in vehicular applications, as seen in fuel cells, imposes a very important but formidable technological challenge to solve. Traditional methods include a reformer which utilizes a hydrocarbon fuel, storage in the form of liquid or high pressured gas or of metal hydride. Technologically sound as each method may appear there are still many technical problems to be solved, particularly reducing size or weight of the generation or storage device, fast utilization, purification of the product gas.

The hydrogen generation based on electrical discharge through reactive metal/water system has been reported for such applications as a fast hydrogen generator⁽¹⁾ or a vehicular fuel source⁽²⁾. Most commonly used metal is aluminum. These methods are in principle very simple. It is well known that although aluminum has high oxidation potential, the passive oxide film prevents a further oxidation. By raising temperature or adding chemicals such as NaOH the oxidation reaction proceeds. The electrical discharge is, in a sense, a replacement of the chemical effect which breaks the oxide film. But besides that function, the electrical discharge method provides a "hot" reaction zone which could let the metal fuel react all the way with water. The major technical problem to be solved is to improve the electrical energy efficiency defined as the ratio of the metal consumed (measured in total enthalpy change in the metal-water reaction) to the electrical energy

input. For the fast generation method⁽¹⁾ in which the aluminum fuel is premixed with water, the energy efficiency already exceeds 100. One drawback of this method is the short reaction time (less than 1 msec) to produce high pressure and high temperature products which are often difficult to confine in a closed system.

In the method 2, the electrodes configuration can take a typical point-to-plane discharge type with the aluminum wire electrode as the cathode and a planar aluminum electrode as the anode, both placed in water. When an electrical discharge is induced between the electrodes, the wire-type fuel electrode which is activated by the Joule heat dissipation can undergo an electrochemical combustion with the surrounding water. But in order for this method to have practical value, it must have the high energy efficiency described previously. To have high energy efficiency the reaction needs to be sustained by the heat generated from the reaction itself⁽¹⁾. The electrical energy input should be maintained at such a low level as not to extinguish the combustion. The difficulty with the method 2 is ascribed to that a stable reaction zone is not easily established. The condition for the establishment is the coupling of the aluminum-water chemical reaction to the electrical discharge. Unless the reaction takes place continuously the discharge alone can not drive the metal/water reaction. Then the continuous reaction can be warranted only when many experimental variables such as the voltage-current shape and the metal feeding rate are optimized. In terms of the discharge

voltage-current profiles the voltage should be maintained at low value. If the medium restores high resistance, higher rate of electrical energy dissipation has to take place either by increasing the voltage to several KV or by forcing physical contacts of the two electrodes to establish the stable hot reaction zone again. The voltage-current profiles on different experimental conditions will be presented and discussed.

2. Experimental

The experimental setup shown in Fig. 1 basically consists of three parts; the DC power source, the reaction chamber and the measuring device. The DC power source provides two modes of power-high voltage/low current(0~6kV, 0~100mA) and low voltage/high current(0~750V, 0~10A). The high voltage source causes the electrical breakdown between the electrodes, which is about 2~3mm apart in low conductivity water(>18MΩcm). As the cathode, aluminum wire (AWS, ER4043 and ER5336 type, 0.8, 1.2, 2.0 mm dia.) was used whereas a plane electrode made of aluminum, stainless steel or nickel was used as the anode as shown in Fig. 2. The breakdown establishes a high electrical conduction path so that the electrical energy from the low voltage/high current mode activates the fuel metal electrode. A MIG-type power supply(KEMPOMAT Model 320) was also used as the DC power supply which provides voltage up to 50 V and current up to 150 A. The product gas was determined by

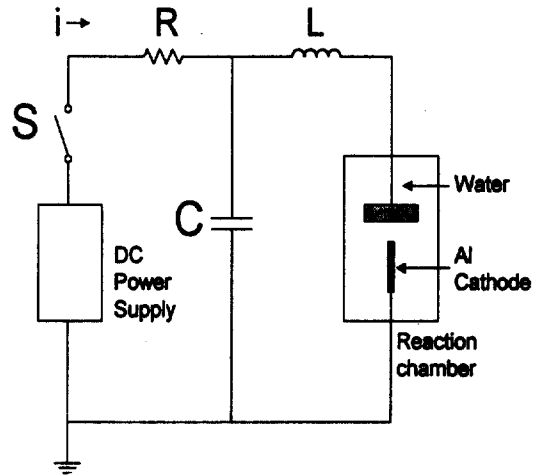


Fig. 1 Experimental set-up

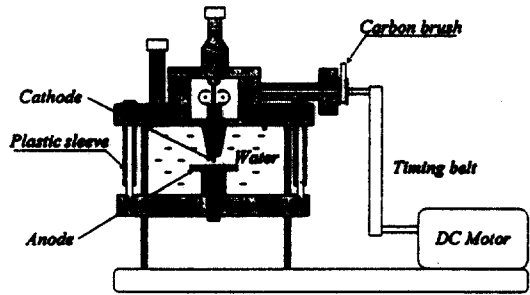


Fig. 2 The reaction chamber and the wire feeder consisting of brush, belt and a DC motor

pressure measurement, gas chromatography analysis or volume measurements based on Mohr buret method. The voltage across the electrodes and the discharge current were measured using the usual voltage divider and hall effect current probe, respectively. A DC motor was attached to the aluminum wire feeder to control the feeding rate. The water was deionized by three-step water purifier

incorporating ionexchange and microfilter columns. The anodization of Al wire electrodes was made by passing anodic currents through the wire electrode placed inside a circular cathode in dilute sulfuric acid.

3. Results and Discussion

Although the water used has very little electrical conductivity($R > 18 \text{ M}\Omega$), some degree of electrolysis can take place. In Fig. 3 the current due to electrolysis is plotted against the applied voltage across the electrodes. In the plot the distance between the electrodes and the surface condition of the wire electrode were also varied. The surface anodization on the wire surface suppressed the current density by about 70%, but it does not completely block the current leak through the side surface. Increasing the electrode gas does not affect the current density in any significant margin. This results suggests that unless the wire surface is completely insulated or shielded, the ignition of the reaction near the wire tip is hard to materialize. It was found that the shielded wire electrode does not pass any measurable electrolytic currents.

Two kinds of DC power supply were used to provide the electrical power necessary for ignition of and sustaining the reaction between aluminum wire and the surrounding water. One kind provides two modes of power and the other kind delivers a welding type of power as described in the experimental section. With the two-mode power supply the ignition occurs in

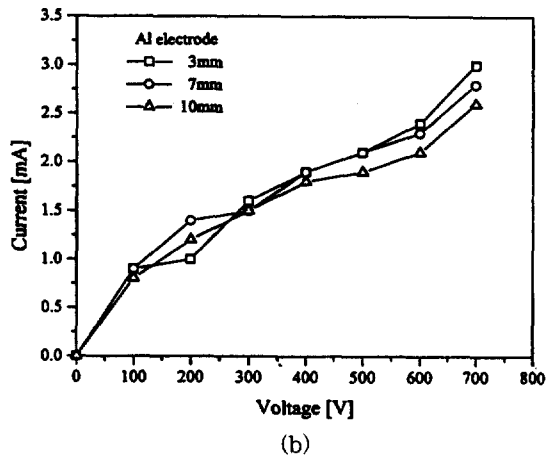
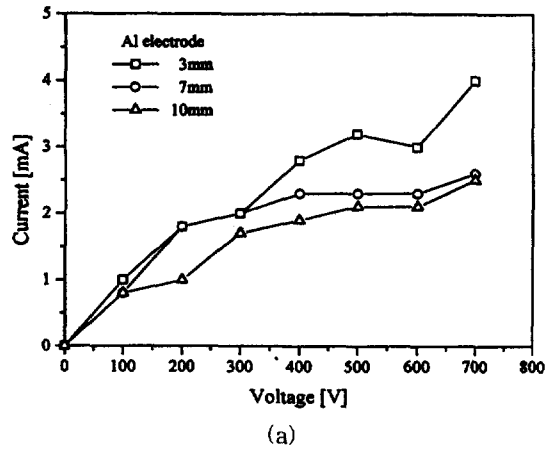


Fig. 3 The current-voltage profiles for the electrolysis ; (a) the wire electrode surface is not treated and (b) the surface is anodized.

the high voltage mode. At high voltage over 1 KV the electrical break-down occurs and a sudden surge of current over 10 A is observed. The appearance of negative current pulse seen in Fig. 4 is due to some electrical noise. The power delivered during this breakdown is order of 2~3 KW, which is dissipated mainly for activating the wire material. This activation

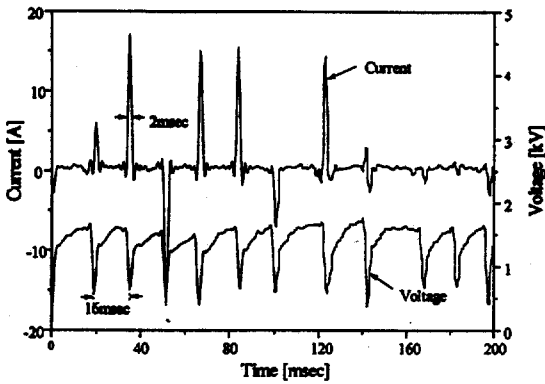


Fig. 4 The current-voltage profiles for the electrical discharge when the circuit does not have any extra RLC components.

often results in falling-off of the tip portion of the wire, some of it reacting with water. But as seen in Fig. 4, the low voltage-high current mode does not last over a few milli-seconds. The gas bubble formed in the electrical region shrinks eventually unless the continuous combustion reaction coupled to the electrical discharge takes place. Filling of the reaction region by the surrounding water restores a high ohmicity in the medium and the power source shifts back to the high voltage/low current mode again. In order for a stable reaction zone to be formed between the electrodes, the wire material has to be activated continuously in a physical form of atoms or clusters, although in small amount. Under the steady activation of aluminum cathode, electrical conductivity increases due to the low ionization potential of aluminum particles (order of 2~3 eV) and the dense population of the metal particles.

As a means to increase the discharge time in

the low current mode, extra RLC components were added to the discharge circuit outside the power supply. With these extra components the low voltage mode lasted even over 2~3 seconds, an increase of more than factor of 1,000 as seen in Fig. 5. This increase is attributed mainly to the inductive voltage, which provides the source for the extra dissipation. With the RLC components ($R=10\Omega$, $L=7mH$, $C=20nF$), almost 50% of the consumed fuel metal underwent the combustion reaction with water to generate hydrogen gas. But yet the energy efficiency, the amount of the thermal output from the Al/water reaction to the electrical energy input was below 5% of the desired value, which is about 100.

Without any extra components of R, L, C, the power source shifts back and forth between the two modes, with the time gap shorter than 0.1 second. Under such circumstance the energy efficiency is extremely low. By adding extra R,

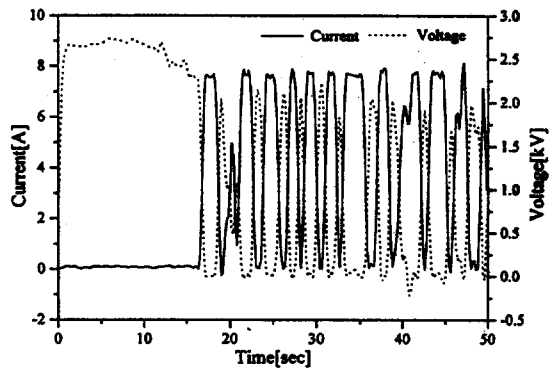


Fig. 5 The current-voltage profiles for the electrical discharge when the circuit has extra RLC components.

L, C components outside the DC power supply, the time duration of the low voltage/high current mode was extended sometimes to longer than 10 seconds(Fig. 5). Gas chromatography analysis of the product gas shows that the hydrogen generation is mainly(over 80%) due to the metal-water reaction rather than direct electrolysis. As mentioned previously the energy efficiency is approaching 5% of the desired value with the addition of extra circuit components.

To induce the ignition a MIG welding-type power supply was used instead of the aforementioned twomode power supply. This weldingtype power supply provides the power necessary for the ignition by forcing actual physical contact between the anode and the feeding wire electrode. This is equivalent to the high-voltage mode discharge with the two-mode power supply. When the actual contact is made, the large power dissipation activates the wire material, widening the electrode gap. As seen in Fig. 6, the contact lasts about 20 milli- seconds. After that the current almost dies off until the feeder pushes the wire back near to the anode. The power dissipated during the contact is around 3 KW, which suddenly drops to near zero as the gap widens. This implies that unless the feeding rate is well adjusted, the fluctuation of power delivery is extremely severe resulting in low efficient gas generation.

In establishing a sustained electrochemical combustion between the fuel metal and water, many more system variables need to be adjusted. These variables include besides the

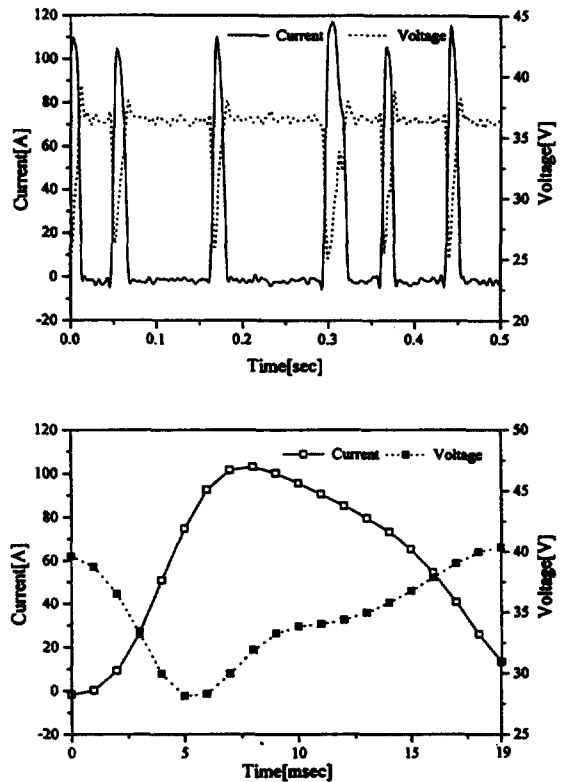


Fig. 6 The current-voltage profiles for the electrical discharge when a Mig-type power supply was used ; (a) second time scale and (b) milli-second time schedule

RLC values of the discharge circuit, the surface area of the metal wire on which electrolysis takes place, the feeding rate of the wire electrode, the water temperature, and agitation of the reaction region. The exposed surface area was minimized by encapsulating the wire with ceramic tubing. The feeding of the wire electrode was adjusted using a DC motor(see Fig. 2). Ideally the feeding rate should be a function of the discharge current density. But in

our experiment the rate was fixed. Also no agitation of the reaction medium was attempted in this experiment. With these variables optimized, the energy efficiency should increase and our research is presently aimed at optimizing these variables.

4. Conclusions

The discharge voltagecurrent profiles are reported for different experimental conditions. The extra addition of RLC components outside the DC power supply helps lengthen the electrochemical combustion time for hydrogen generation. However, the minimization of the electrical energy in achieving the sustained

reaction awaits the optimization of much wider experimental variables such as the feeding rate and agitation, and the reaction zone temperature.

Acknowledgment

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