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물-수증기 계면을 통한 전기방전에 의한 수소 제조*

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Hydrogen Generation by Electrical Discharge across Water-Vapor Interface*

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Abstract

Generation of hydrogen and oxygen gas from water is mostly accomplished by electrolysis. In this report, a scheme is presented regarding the gas generation based on plasmolysis. Unlike electrolysis water dissociation by electrical discharge (plasmolysis) requires a high voltage to cause either electron emission or electron capture, and subsequent ionization of involved molecular species. When electrical discharge is initiated between electrodes separated by

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water-vapor interface, a very large electric field(~100kV/cm) is developed at the tip of the electrode placed in the vapor phase. It is found that the efficiency of plasmolysis depends on the polarity of the electrode placed in the vapor phase. Also presented is the scheme of hydrogen and oxygen generation by such electrical discharge.

1. Introduction

The method for hydrogen generation based on application of electrical discharge to reactive metal/water system has been reported for applications in fast hydrogen generator[1),2),3),4)].

The electrodes configuration can take a typical point-to-plane discharge type with a consumable fuel metal electrode as the cathode and a planar electrode as the anode, both placed in water. There are two steps involved with sustaining a plasma channel between the electrodes. First, there should occur the dielectric breakdown. If the power supply for the discharge has double modes, a high voltage/low current mode and a low voltage/high current mode, a high current flow after the breakdown can activate the tip of the fuel electrode. The temperature rise along the channel due to the joule heat dissipation and the exothermic heat from metal/water reaction vaporizes the electrode tip to initiate electrochemical combustion of the metal clusters with water oxidizer. This type of combustion helps sustain the electrical discharge. However, in liquid water medium such scheme is extremely difficult to be realized. The difficulty is attributed to abrupt change of the resistance between the electrodes due to various causes. For example, in order to initiate the electrical discharge, the gap between the electrodes placed in liquid water should be reduced to a very small value to create a large electric field. Also the fuel electrode needs to be fed into the plasma reaction zone at a speed precisely controlled by the current density. Otherwise, the discharge is very likely to be extinguished due to electrical short or abrupt rise in the resistance.

When the electrical discharge is made across water vapor-liquid interface, such problems can be eliminated. This is attributed to the large difference in dielectric constants between liquid water and its vapor. This is illustrated in Fig. 1 The gap between the electrodes and the voltage drop are $x+y$ and V, respectively. Then

$$V = E_l \cdot y + E_v \cdot x \quad (1)$$

where E_l and E_v denote the electric field in liquid and vapor phase, respectively.

The electric fields also have the relationship

$$\varepsilon_l \cdot E_l = \varepsilon_v \cdot E_v \quad (2)$$

where ε_l and ε_v denote the dielectric constant of liquid water and its vapor, respectively. Then

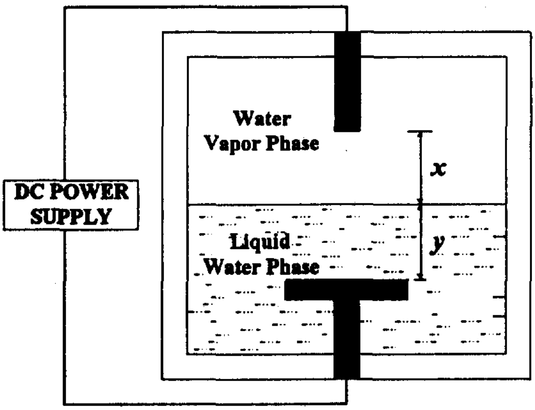


Fig. 1 Electrical discharge across water-vapor interface.

$$E_v = V/[x + (\varepsilon_v/\varepsilon_l)y] \quad (3)$$

Therefore as one electrode is pulled away from liquid water into vapor phase, x becomes almost zero and E_v is expressed as

$$E_v = (\varepsilon_l/\varepsilon_v) \cdot (V/y) \quad (4)$$

When V=3kV, $\varepsilon_l/\varepsilon_v$=50, y=1cm, E_v=150 kV/cm which is large enough to either electron emission or ionization of water molecular. Depending on the polarity of the electrode in the vapor phase, the nature of plasmolysis is vastly different.

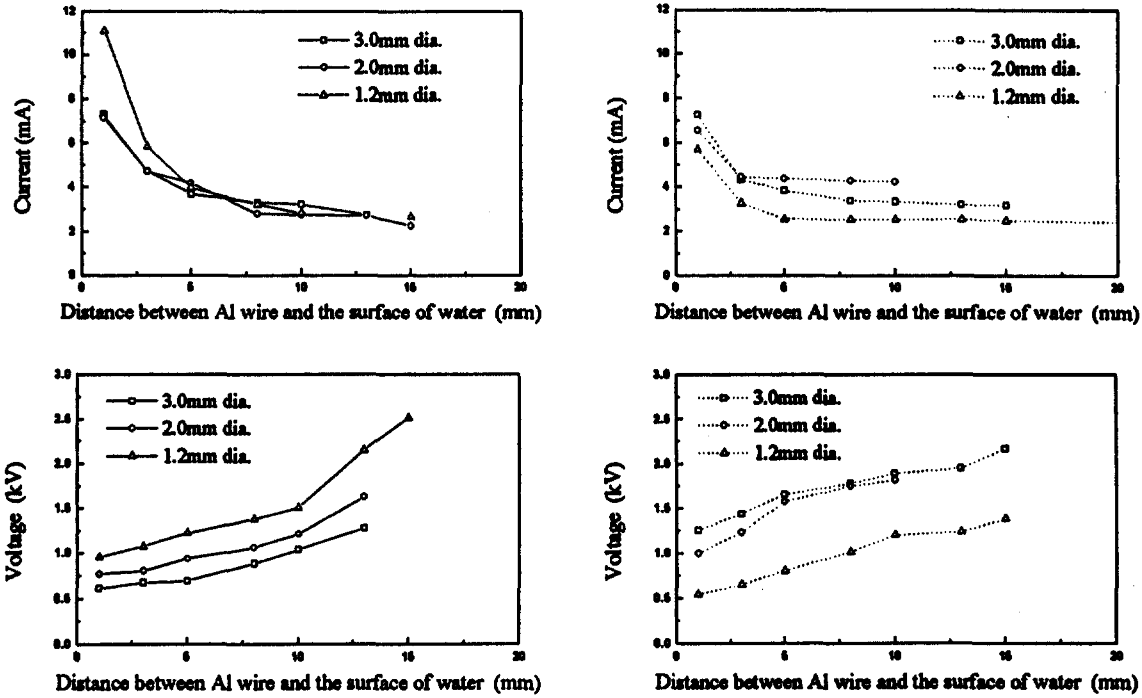
In this report some results regarding this type of plasmolysis are presented.

2. Experimental

The experimental setup basically consists of three parts; the DC power source, the reaction chamber and the measuring device. The air in the reaction chamber was removed before the onset of the discharge. The gaseous phase inside the reaction chamber consists only of water vapor before the onset of the discharge. Aluminum or nickel wire whose diameter ranges from 1.2 to 3 mm was used as the fuel electrode which is placed in the vapor phase. A nickel planar electrode was used as the electrode placed in liquid water. After the electrical discharge the product gas was analyzed by gas chromatography (HP 5890 II) or volume measurements based on water replacement. The voltage across the electrodes and the discharge current were measured using the usual voltage divider and current viewing resistor, respectively. The water was deionized by three-step water purifier incorporating ion-exchange and microfilter columns(18.2MΩ · cm). The temperature of the vapor and liquid phase was also measured using thermocouples.

3. Results and Discussions

The voltage drop between the two electrodes and the current are plotted in Fig. 2 as a function of the distance x shown in Fig. 1. The distance y was fixed to be 1cm which is the optimized value from the curve showing the relationship between the amount of generated gas and the distance. Another variables of the experiment were the diameter of the fuel electrode and the polarity of the electrode. Fig. 2 (a) and (b) show the results in which the electrodes placed in the vapor phase were used as the cathode or the



(a) (b)

Fig. 2 The voltage and current profiles of the electrical discharge.
(a) The electrode in the vapor phase is used as the cathode.
(b) The electrode in the vapor phase is used as the anode.

anode, respectively.

As expected, regardless of the polarity of the electrode, the electrical discharge was easily triggered as one of the electrodes was pulled away from the liquid across the interface. Once the stable discharge is established, the electrode can be pulled away a few centimeters from the interface. This is due to the fact that once the channel is established, the electrical energy dissipation makes it easy to maintain the stability of the plasma channel. Fig. 2 also shows that the current decreases as the gap x increases. It is seen that the stable discharge is terminated as the distance x is extended over 1.5cm. The electrode tip does not engage in heavy vaporization during the discharge because of a low current density.

When the electrode in the vapor phase is used as the cathode, electrons are readily emitted and transported to the interface forming a virtual electrode where hydrogen is generated. If the electrode is used as the anode, water molecules contacting the electrode will lose electron to become species like H_2O^+. These H_2O^+ ions

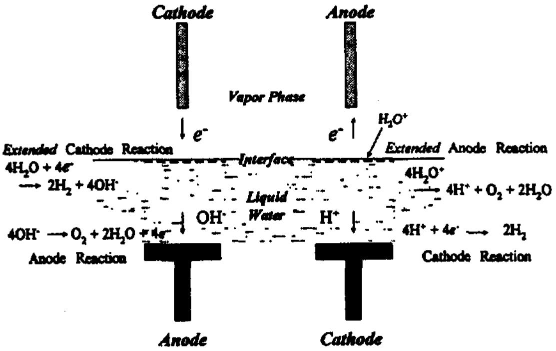


Fig. 3 Plasmamolysis across water-vapor interface.

also form a virtual anode where oxygen is generated. In such case, hydrogen is generated at the electrode placed in liquid water. One possible scenario of the movement of the charged particles during plasmolysis is presented in Fig. 3.

The results of the plasmolysis are summarized in Table 1. As seen in the Table, the efficiency of the water dissociation clearly depends on the polarity of the point electrode placed in the vapor phase. The point electrode used as the anode yields hydrogen gas with the efficiency over three times higher than the case in which the electrode is used as the cathode. But a puzzling result is that for both cases the produced gas volume is lower than that predicted by the Faraday law. We are still investigating this aspect.

The temperature of the vapor and the liquid phase monitored right after the completion of the discharge is shown in Fig. 4 (a) and (b). The results clearly indicate that the temperature of the vapor phase is much higher when the electrode of the vapor phase is the cathode whereas the trend is reversed for the case of temperature measurements in the liquid phase. When the vapor phase electrode is used as the cathode, the major current carrier in the vapor phase is electrons. Electrons should have lager conductivity than the ions which become the major current carrier for the other case. Thus, for the case of the point electrode used as the cathode, the electrical energy is mostly dissipated along the vapor phase conduction path, lowering the efficiency of the gas generation.

When the point electrode is used as the anode, water molecules are ionized generating ionic species such as H_2O^+. Such species migrate into the interface where they react

Table 1 The results of the plasmolysis

	Polarity of the electrode placed in the vapor phase*	
	Anode	Cathode
X (mm)	10	10
Y (mm)	10	10
Current (mA)	5.6	7.0
Voltage (kV)	1.0	0.8
Power (W)	5.6	5.6
Resistance (M)	0.18	0.11
Energy** (kJ)	1.0	1.0
Rate (ml/min)	47	14

* The electrode placed in water was used Ni (24135, 25mm dia.) and the one placed in vapor phase was used Ni wire (24135, 1.0mm dia.).
** Total discharge time is three minutes.

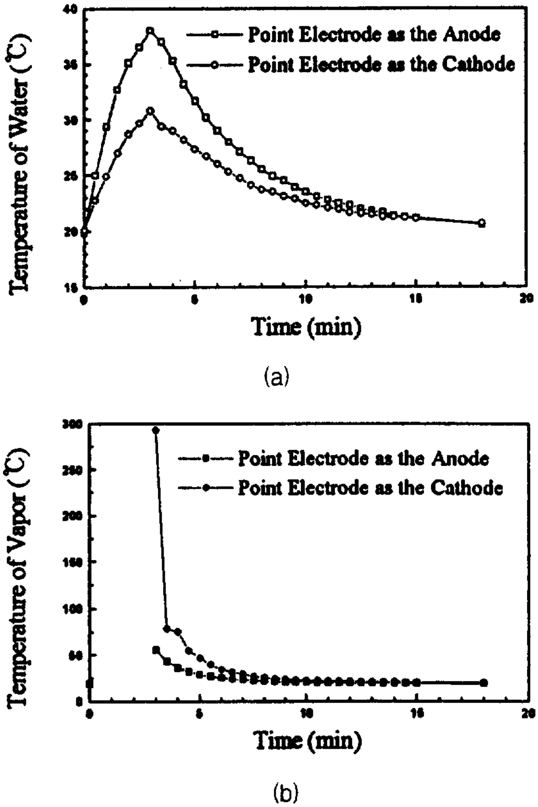


Fig. 4 The temperature of liquid(a) and the vapor phase (b).

Table 2 Hydrogen gas produced by the discharge method.

Electrode placed in the vapor phase	H_2 : O_2	Rate (ml/min)	Power(w)
cathode	2.2 : 1	7.5	5
anode	2.2 : 1	12.0	4

with OH^- ions in the liquid phase, liberating oxygen gas. Such reaction could be a source of electrical energy dissipation which in turn raises the water temperature.

The results of the gas generation is summarized in Table 2 for one particular set of experiments. It shows that the efficiency of the water dissociation based on this scheme is about 30% the theoretical value. But the results of the gas analysis seem to vary depending on the duration of the discharge. Further work is necessary to clarity this type of variation.

4. Conclusions

Plasmolysis(dissociation of water under plasma discharge) is the major route of hydrogen generation in electrical discharge across water vapor-liquid interface. With a small voltage drop (<4kV) between the electrodes, a very large electric field (~100kV/cm) is generated near the electrode placed in the vapor phase. The efficiency of water dissociation depends on the polarity of the electrodes. The point electrode used as the anode yields hydrogen gas with the efficiency over three times higher than the case in which the electrode is used as the cathode.

References

1. W. M. Lee, J. Appl. Phys., 69, 6945 (1991)
2. Y. M. Choi, G. J. Kang, S. Y. Cha and W. M. Lee, J. Kor. Hyd. Energy Soc., 7, 3 (1996)
3. Y. M. Choi, G. J. Kang, S. Y. Cha and W. M. Lee, Energy Eng. J., 5, 198 (1996)
4. G. J. Kang, Y. M. Choi and W. M. Lee, p57 in Proceedings of the Spring Annual Meeting 97 of the Korean Hydrogen Energy Society.