# Experimental Study of Plasma Under-liquid Electrolysis in Hydrogen Generation

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**Abstract**: The application and characteristics of relatively big volume plasma produced with cathodic glow discharges taking place across a gaseous envelope over the cathode which was dipped into electrolyte in hydrogen generation were studied. A critical investigation of the influence of methanol concentration and voltage across the circuit on the composition and power consumption per cubic meter of cathode liberating gas was carried out. The course of plasma under-liquid electrolysis has the typical characteristics of glow discharge electrolysis. The cathode liberating gas was in substantial excess of the Faraday law value. When the voltage across the circuit was equal to 550 V, the volume of cathodic gas with sodium carbonate solution was equal to 16.97 times the Faraday law value. The study showed that methanol molecules are more active than water molecules. The methanol molecules were decomposed at the plasma−catholyte interface by the radicals coming out the plasma mantle. Energy consumption per cubic meter of cathodic gases ($W_V$) decreased while methanol concentration of the electrolytes increased. When methanol concentration equaled 5% ($\varphi$), $W_V$ was $10.381\times10^3$ kJ/m$^3$, less than the corresponding theoretic value of conventional water electrolysis method. The cathodic liberating gas was a mixture of hydrogen, carbon dioxide and carbon monoxide with over 95% hydrogen, if methanol concentration was more than 15% ($\varphi$). The present research work revealed an innovative application of glow discharge and a new highly efficient hydrogen generation method, which depleted less resource and energy than normal electrolysis and is environmentally friendly.

**Key words**: hydrogen generation; plasma; glow discharge electrolysis; methanol

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## 1 INTRODUCTION

Plasmas are ionized gases which consist of positive, and negative ions, and electrons as well as neutral species. The plasma state is regarded as the fourth state of matter. In general, plasmas are classified into two kinds, thermal equilibrium plasma and non-thermal equilibrium plasma. Thermal equilibrium implies that the temperatures of all species, including electrons, ions and neutral species, are the same. On the other hand, non-thermal equilibrium means that the temperatures of the different plasma species are not the same. More precisely, the electrons are characterized by much higher temperatures than the heavy particles (ions, atoms, molecules)[1]. Non-thermal plasma can drive high-temperature chemistry at low ambient temperatures using input energy levels that are much lower than the energy required for driving an equilibrium reaction. The wide variety of chemical non-equilibrium conditions is possible in which parameters can easily be modified by external control, such as chemical input, pressure, electromagnetic field structure, discharge configuration and temporal behavior. Because of this multi-dimensional parameter space of the plasma conditions, plasmas are employed in a number of applications, such as plasma spectra-chemistry, cutting, spraying, welding, etching or deposition of thin layers and catalysis[2,3].

In recent years, the field of glow discharge plasma applications has rapidly expanded. Contact glow discharge electrolysis (CGDE) is a novel kind of electrochemical process in which plasma is sustained by DC or DC pulsed glow discharges between an electrode and the surface of surrounding electrolyte. The conventional normal electrolysis is developed into CGDE when the applied voltage is sufficiently high in aqueous media. A remarkable feature of CGDE is its high deviation of chemical yields at the glow discharge electrode from that expected on the basis of Faraday's law. The yields obtained at the glow discharge electrode are several times the faradaic value and the products novel for conventional electrolysis such as $H_2$ can be generated at the anode, $O_2$ at the cathode. According to the research findings of Susanta et al.[4], the yields of CGDE in a solution is origin of two separate reaction zones: the liquid near the plasma−electrolyte interface and the plasma around the electrode, and this happened

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through dissociation of solvent and solute molecules by appropriate energy transfer process[4]. There are a lot of radicals, ions and other active species produced via electron impact dissociation, excitation and ionization.

When the active species diffuse away from the initial positions to enter into the solution, the reaction zone may be considered as a single spur that is located in a fixed position and constantly renewed. In the reaction zone within the plasma around the electrode, gaseous $H_2O$ molecules were ionized or activated, and then bombarded each other to be broken up by charge transfer, with resultant production of free OH radicals and sometimes of H atoms. On the other hand, in the liquid-phase reaction zone near the plasma–electrode interface, some liquid $H_2O$ molecules are broken up into $H_2$, $H_2O_2$ and $O_2$, bombarded by $H^+$ from the electrode plasma. Polyakov et al.[5,6] studied the cathodic plasma chemical process, based on the comparison of the experimentally revealed features of water decomposition, combination and capture of primary radicals by scavengers under the action of atmospheric pressure glow discharges on electrolytic electrodes. The similarity of mechanisms of water decomposition was shown in the case of the electrolytic cathode for the stationary discharge over the surface and for the array of quasi-stationary micro-discharges on the valve electrode immersed in the solution[5,6]. The assumption that the generation of primary products of water decomposition in discharge systems with the electrolytic cathode occurs preferably via ionization in the liquid phase at the expense of the kinetic energy of accelerated particles entering the solution from the discharge is confirmed[7,8].

Hydrogen is regarded as a truly environmentally friendly fuel. And hydrogen production from methanol is an interesting and promising option for the energy supply of fuel cells and other applications. Compared with other hydrogen generation technologies, the plasma processes can provide technologically simple, economically cheap and environmentally friendly method for hydrogen generation[9]. During CGDE course the electrodes are immerged into the electrolyte, and plasma is sustained between the electrode and the interface of the electrolyte by DC or pulsed DC glow discharge. This kind of plasma is called plasma under-liquid. On this condition, the plasma is sustained around the electrode, which has fewer dimensions. And this plasma under-liquid can be used to induce some unusual chemical changes in the solution. The solvent molecules in the gas sheath around the electrode, which sustains glow discharge plasma, will be discomposed into smaller molecules when the plasma occurs[10]. When the solution is methanol–water mixture, water and methanol vaporize and a gaseous sheath forms around one electrode. When the potential between the electrodes is high enough, the gaseous sheath is break down, and glow discharge plasma will occur in this gaseous sheath. Water molecules and methanol molecules in the plasma sheath are decomposed to hydrogen, oxygen, carbon oxide and carbon dioxide[11]. We explored a hydrogen generation technology using cathodic glow discharge under-liquid as a non-thermal plasma source. This paper reports the results of the experiments of this technology.

## 2 EXPERIMENTAL

The apparatus is shown in Fig.1. The reactor was cylinder cell with one-liter capacity, and the electrodes were fixed in the reactor. The cathode, a tungsten cylinder of 5 mm diameter and 1 cm length, immersed into an aqueous solution by a depth of 5 cm, no insulation on the side dipped in the solution, was set in the center of cathodic chamber of the reactor. The anode was a stainless steel plate of 1.76 $cm^2$ area, placed in another chamber of the reactor, which was called anodic chamber. There was a membrane between the cathodic chamber and anodic chamber to prevent the yields of the two chambers to mix with each other. The current was supplied by a self-made high voltage DC (HVDC) and pulse DC power supply, which provided a maximum current of 5 A at voltage up to 1200 V. The frequency range of the power was 0~20 kHz. The current passing through the electrodes and the voltage across the circuit were measured by digital multi-meter. The cooler after the reactor had a valve to recycle the cooled solution carried out by the cathodic gas. And the volume of the cathodic gas was measured after cooling down and drying by a gas volume meter (Changchun Instrument Co. Ltd., LML-1, Changchun, China). The composition of the cathodic gas was determined online by a GC-950 chromatogram (Haixin Chromatography Co. Ltd., Shanghai, China). Electrolytes used in the experiments were varying aqueous constituents ($Na_2CO_3$, $H_2SO_4$, KOH) with the same conductivity (0.2 S/m). Pressure was atmospheric. And the reaction time was 5 min.

In the beginning several minutes, low voltage normal electrolysis was needed to lead to a gaseous sheath over cathode, then the applied voltage across the two electrodes was slowly increased. The

current–voltage (*I*–*V*) curve could be observed by recording the current passing through the electrodes corresponding to applied voltage. The curve typically has several distinct segments characterizing the transition from normal electrolysis with an unstable and partially grown glow discharge to the full glow discharge at the cathode, which is similar to the results given by Susanta et al.[4].

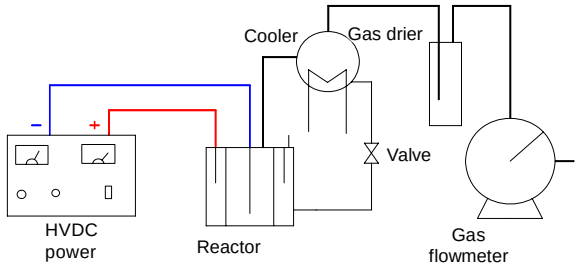


Fig.1 Schematic diagram of experimental apparatus

In the experiments a critical investigation on the influence of methanol concentration and voltage across the circuit on the output, composition of cathodic gas and power consumption of every cubic meter gas was carried out. The goal of this work was to get some data for the hydrogen generation by plasma under-liquid and testify the feasibility of this technology.

# 3 RESULTS AND DISCUSSION

## 3.1 The Characteristics of Glow Discharge Plasma Under-liquid

The current–voltage (*I*–*V*) curve observed (Fig.2) in the course of production of cathodic glow discharge plasma under-liquid of $Na_2CO_3$ solution at 80℃ is of the same standard type as that reported for contact glow discharge electrolysis (CGDE)[4]. And the curve typically has several distinct segments characterizing the formation process of plasma under-liquid. The mid-point voltage ($V_D$) is a critical voltage, and this

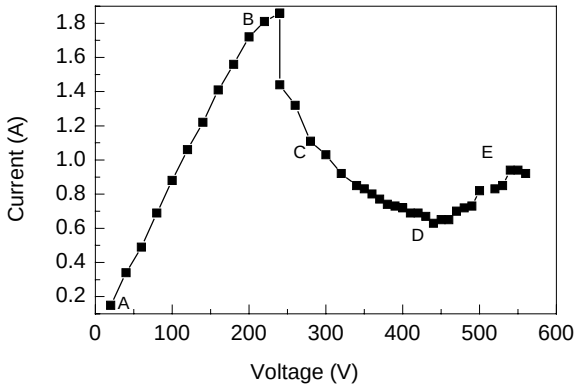


Fig.2 A typical current–voltage (*I*–*V*) curve characteristics of cathodic glow discharge plasma under-liquid

voltage is variable in our experiments depending on the constituents, conductivity and reaction temperature[4,8]. The glow discharge can be observed at mid-point. The color of glow discharge depends on the constituent of the electrolyte. When the electrolyte is $Na_2CO_3$, the emitting light is orange (Fig.3).

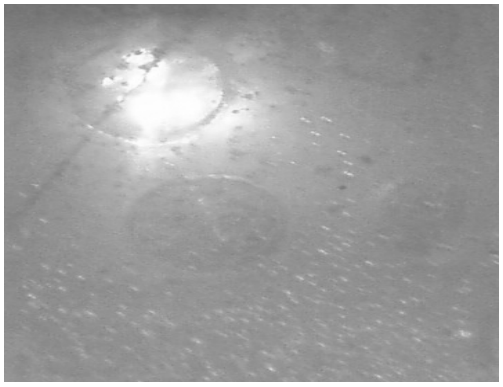

Fig.3 The color of cathodic glow discharge plasma under-liquid in a $Na_2CO_3$ solution

## 3.2 Effect of Voltage on the Cathodic Gas

3.2.1 Effect of voltage on composition of cathodic gas

The volume of gas liberating from the cathode was in substantial excess of the Faraday law value. Cathodic output increased with the discharge voltage. When the voltage across the circuit was equal to 550 V, the volume of cathodic gas with sodium carbonate solution was 16.97 times the Faraday law value. In sodium carbonate solution, the gas volume was 1.35 times of the potassium hydroxide solution and 2.97 times of the sulfuric acid solution, when the discharge voltage was 400 V under otherwise same conditions.

The cathode gas contained considerable percentage of $H_2$ (Fig.4). The cathodic liberating gases were consisted of 86.7% ($\varphi$) $H_2$ and 13.3% ($\varphi$) $O_2$ at the condition of 400 V voltage across the circuit with $Na_2CO_3$ solution, and the ratio of hydrogen and oxygen was noted decreasing the discharge voltage. The magnitude of deviation from the Faraday law value and the percentage of oxygen of the cathode gas depended on the voltage applied across the circuit heavy. In the reaction zone within the plasma over the cathode, $H_2O$ vapor molecules are fragmented into H· and OH· radicals. The cathode potential drop increased with the increase of voltage applied across the circuit. When the voltage applied across the circuit increased, the plasma intensity increased at the same time, as well as the cathode potential drop. Under this condition, more water molecules were fragmented and more oxygen was formed in the cathode gas. The mechanism of

decomposition of water vapor in electrical discharges was shown as follows[4]:

$$H_2O \rightarrow H\cdot+OH\cdot, \quad (1)$$

$$H\cdot+H\cdot \rightarrow H_2, \quad (2)$$

$$OH\cdot+OH\cdot \rightarrow H_2O+1/2O_2, \quad (3)$$

$$H\cdot+OH\cdot \rightarrow H_2O. \quad (4)$$

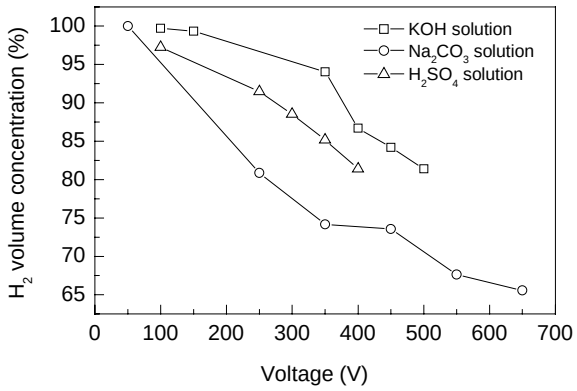


Fig.4 Effect of voltage across the circuit on hydrogen concentration of cathode

When the electrolyte is $Na_2CO_3$, carbon monoxide and carbon dioxide could be detected in the cathode liberating gas, after the plasma mantle formed over the cathode, and the percentages of these two gases increased with the increase of the voltage across the circuit (Fig.5). The reason for the formation of carbon monoxide and carbon dioxide in the cathode gas appeared to be the decomposing of $CO_3^{2-}$ at the interface of plasma phase and liquid phase by the excitation of active radicals produced in the plasma sheath. And the percentages of CO and $CO_2$, detected in the cathode gas, increased with the voltage across the circuit, which affected the plasma intensity and the energy level of active radicals in the plasma.

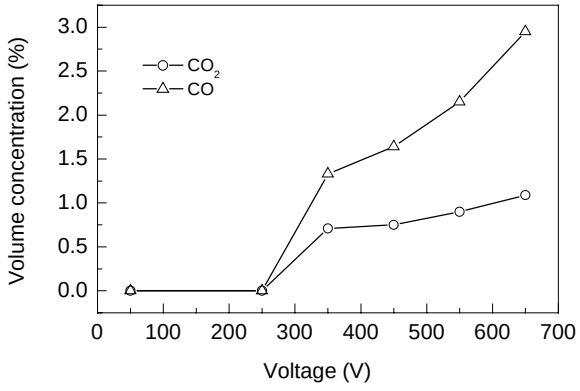


Fig.5 Effect of voltage across the circuit on CO and $CO_2$ concentration in $Na_2CO_3$ solution

3.2.2 Effect of voltage on the energy consumption of cathodic gas

By varying the voltage input, the intensity of cathode glow can be altered. And the intensity of plasma under-liquid grows with increase of the voltage. To study the energy consumption $W_V$ in the course of plasma under-liquid hydrogen generation, $Na_2CO_3$ solution was used as feed material. Because the voltage was high and the current efficiency of charge-transfer process of the normal electrolysis was very low, much power was depleted on the water vaporization over the cathode in this hydrogen generation process. $W_V$ was equal to the power input divided by the gas volume liberated by cathode plasma under-liquid electrolysis course. The net energy consumption per cubic meter of cathodic gases ($W_n$) was equal to the power input minus the energy depleted on the water vaporization course and then was divided by the gas volume.

According to the experimental results, $W_V$ decreased with the discharge voltage (Fig.6). $W_n$ equaled $9.130\times10^3$ kJ/m$^3$, under the condition of voltage across the circuit was 650 V in sodium carbonate solution, which is less than the theoretic value ($1.058\times10^4$ kJ/m$^3$) of normal water electrolysis method.

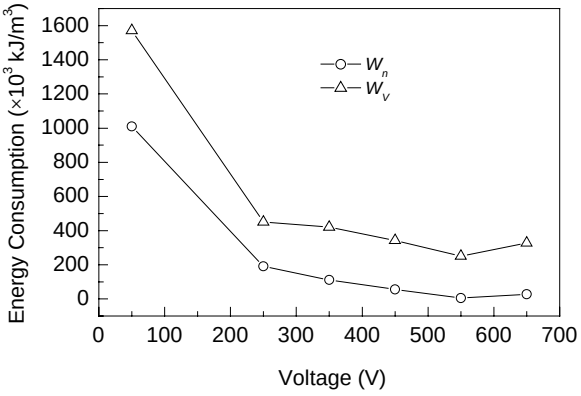


Fig.6 Effect of voltage across the circuit on energy consumption per cubic meter of cathode liberating gas in $Na_2CO_3$ solution

### 3.3 Effect of Methanol in the Solution on the Hydrogen Generation Process

In the present experiments, methanol was added into the aqueous solution to be subjected to the plasma under-liquid as the electrolyte. During cathode glow discharge plasma electrolysis, the cathode was isolated from the electrolytic solution by being sheathed in a mantle of plasma. This mantle was essentially composed of methanol and water vapors plus the ions, radicals and atoms produced by discharge through it. Electrons emitted from the cathode during its transition

through the plasma mantle collided with the water and methanol molecules therein. As a result of energy transfer following such collisions, each electron will activate one or more $H_2O$ and $CH_3OH$ molecules. These reactive species of ions and radicals produced in the mantle would interact with one another, giving $H_2$, $O_2$, CO and $CO_2$. After the action of dissociating methanol and water molecules by the process envisaged above, the radicals coming out of the plasma mantle collided with the bulk solution at the plasma–catholyte interface and excited methanol and water molecules of bulk solution, and interacted among them. Methanol molecules were the scavengers of the free OH radicals, which might interact with one other to form $H_2O_2$, $H_2O$ and $O_2$. The higher the methanol concentration in the electrolyte, the less the oxygen to be detected in the cathode librating gas, as shown in Fig.7. The concentration of hydrogen is more than 95% ($\varphi$) and the oxygen concentration is less than 0.5% ($\varphi$), when the methanol concentration is higher than 15% ($\varphi$).

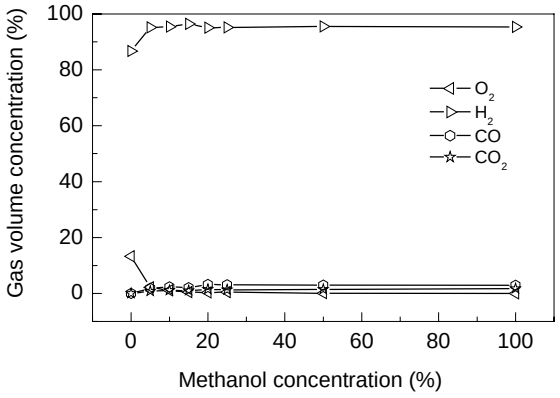


Fig.7 Effect of methanol concentration on the composition of cathode liberating gas

Viewing the glow process as above, it was thus known that the activity of methanol molecules was much higher than that of water molecules. So, the composition of cathode liberating gases with the methanol and water solution had great difference compared with electrolyte with the solution using water as solvent only. In the light of above mechanism, it was expected that the higher the concentration of methanol in the electrolyte was, the less the energy consumption of per cubic meter of the cathode liberating gas on the plasma electrolysis with methanol and water mixtures as feed materials would be. It is seen from Fig.8 that when the methanol concentration of the electrolytes equaled 5%, the cathodic output was 14.45 times that without methanol electrolyte. If the concentration of methanol reached 50% in the electrolytes, the cathodic output increased by 39.5 times the output of the electrolytes without methanol. The energy consumption per cubic meter hydrogen ($W_V$) was $10.381\times10^3$ kJ/m$^3$, when the methanol concentration of the electrolytes equaled 5%. This value is less than the corresponding theoretic value of conventional water electrolysis method. When the methanol concentration in water solution equaled 50% ($\varphi$), $W_V$ is $3.496\times10^3$ kJ/m$^3$, being 33% of the theoretic value of conventional water electrolysis method.

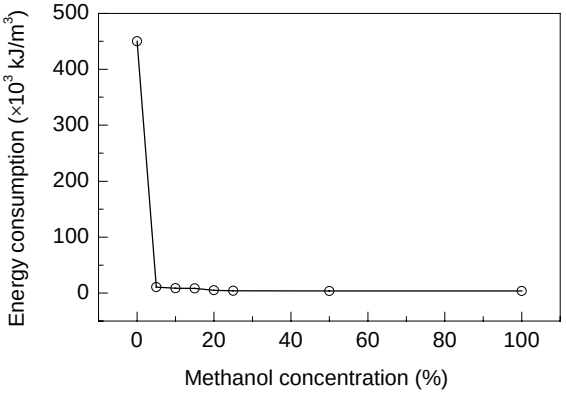


Fig.8 Effect of methanol concentration on energy consumption per cubic meter of cathode liberating gas

## 4 CONCLUSIONS

Based on the experimental results of cathode glow discharge plasma under-liquid electrolysis to generate hydrogen, the following conclusions can be drawn:

(1) Glow discharge plasma produced over the electrode which dipped into the electrolytes has similar characteristics to those of contact glow discharge.

(2) Cathodic plasma under-liquid electrolysis can be considered as a feasible technology in hydrogen generation, which is based on the non-faradaic law phenomenon.

(3) The present study shows that water molecules and methanol molecules are fragmented by the radicals of glow discharge plasma, and plasma under-liquid electrolysis course shows the typical characteristics of glow discharge electrolysis. Methanol molecules are more active when subjected to the plasma environment. The cathode liberating gas can maintain a high hydrogen percentage level with methanol water solution as electrolytes and the energy consumption per cubic meter gas can reach a very low level.

The present work reveals an innovative application of glow discharge and a new highly efficient hydrogen making method, which expenses less resource and energy than normal electrolysis in an environmentally friendly way.

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