Hydrogen generation by glow discharge plasma electrolysis of ethanol solutions

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Abstract

Glow discharge plasma electrolysis (GDPE) of ethanol solutions for hydrogen generation was investigated in terms of discharged voltage, discharged polarity and ethanol concentration. H_2 and acetaldehyde are the dominant products of ethanol decomposition during GDPE. Discharged polarity, discharged voltage and ethanol concentration have important influences on the energy consumption, concentration and output of hydrogen and acetaldehyde. The hydrogen yield ($G(H_2)$) by cathodic GDPE is higher than that of anodic GDPE. The energy consumption (W_r) was $5.12\,kJ\,L^{-1}$ when the applied voltage of cathodic GDPE was 1000 V. The hydrogen concentration of cathodic GDPE in gases keeps above 80%. The experiments indicate that GDPE of ethanol solutions is an effective technology producing hydrogen and acetaldehyde simultaneously with low CO_2 emission.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Hydrogen is expected to be a secure and accessible energy supply for the sustainable development of modern societies, concerning air pollution, energy security and climate change. At the same time, hydrogen is an important reactant. The most economical route for production of hydrogen is hydrocarbon feedstock by steam reforming. Concerning possible climate change and reductions in greenhouse gas emissions, the methods producing hydrogen without emitting CO_2 will be in great demand. These requirements present a challenge and necessitate the development of new types of hydrogen production method [1–3].

Glow discharge plasma electrolysis (GDPE) is a hybrid of conventional electrolysis and atmospheric plasma process and has been a hot research field for many years. An important feature of GDPE is that around the glow discharge electrode its chemical yield is much higher than that calculated from the Faraday law. Another feature is that the products are always different from conventional electrolysis. During GDPE, the charged species in the plasma are accelerated by the sharp potential gradient and have enough kinetic energy to induce unique chemical changes in aqueous solutions [4]. Recently, GDPE has been regarded as a most promising technology and has been widely investigated in terms of the chemical effects caused by either inorganic or organic substances, e.g. electrical discharge machining, synthesis of bioorganic compounds, synthesis of diamond-like carbon films, water treatment, surface engineering [5–13].

The experiments reported by Chaffin and his colleagues showed that plasma electrolysis in aqueous solutions might provide a new method of hydrogen production [14]. Our earlier research on GDPE of methanol solutions revealed a promising hydrogen generation method with high efficiency and low CO_2 emission [15–17]. Ethanol, another important lower alcohol, produced by fermentation with renewable raw materials, will play an important role in the energy supply system. In this work our attention is focused on the hydrogen yield, hydrogen productivity and energy consumption in GDPE of ethanol solutions.

2. Experimental

A schematic of the experimental set-up used in this work is shown in figure 1. The reactor was similar to that used in our previous paper [16], and the outline of the reactor assembly is shown in figure 2. The volume of the internal cell of the reactor was 250 ml and the discharged electrode was tungsten. The qualitative analysis of the liquid after plasma electrolysis was conducted with GC-MS (SHIMADZU, QP2010). GC-MS conditions were as follows: column: DB-5MS capillary; carrier gas: He; ion source temperature: 523.15 K; m/z scan range: 10–250. The compositions of gas and liquid were

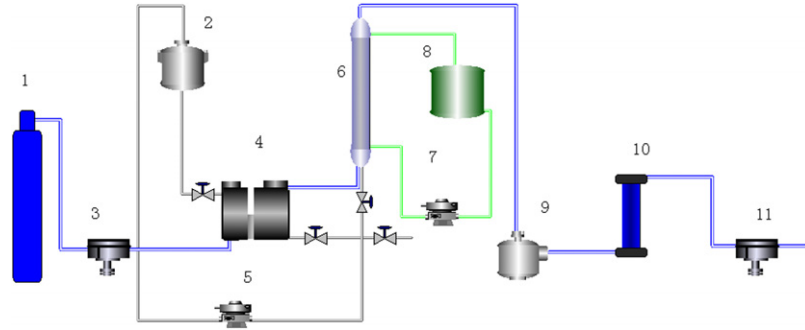J. Phys. D: Appl. Phys. **41** (2008) 155205

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Figure 1. Scheme of experiment flow chart: 1—carrier gas, 2—balance tank, 3—mass flow meter, 4—reactor, 5—micro-pump, 6—condenser, 7—ice water pump, 8—ice water tank, 9—formaldehyde absorbing tower, 10—desiccator, 11—mass flow meter.
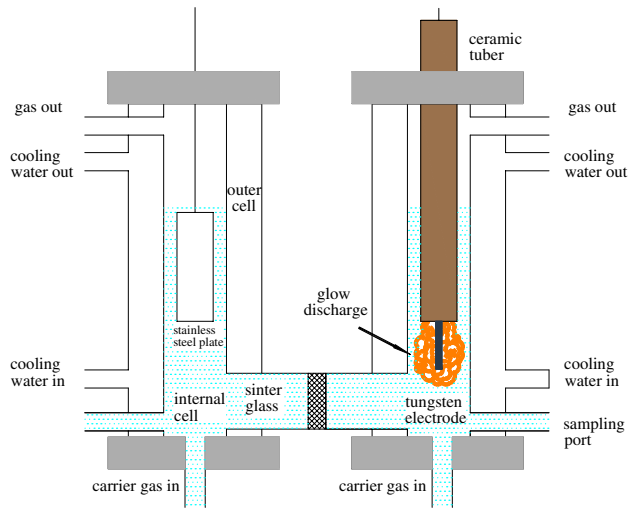

Figure 2. Outline of the experiment reactor assembly.

determined by a gas chromatograph (Model GC950). A TDX-01 packed column and a GDX-401 packed column were used for the composition analysis of gas and liquid, respectively. The GC conditions for gas analysis were as follows: the carrier gas was Ar; the detector was TCD; the column temperature was 303.15 K and the detector temperature was 353.15 K. The gas sample was injected by a six-way valve, and the volume of the gas sample injected was 1 ml. The GC conditions for liquid composition analysis were as follows: the carrier gas was H_2; the detector was TCD; the column temperature was 413.15 K and the detector temperature was 418.15 K. Ar was used as the carrier gas to wash out the air in the reactor prior to GDPE with a flow rate of 150 ml min^{-1} and maintained at this flow rate to carry out the gases produced by GDPE. The volume of gases released from the discharged electrode was measured with a mass flow meter (Model Sevenstar D07) after cooling and drying. The reactor was cooled with recycling water to keep the reaction system at a constant temperature of 303 ± 0.5 K. Current and voltage were measured with a lab card (PCI-1713), and the sampling rate was 100 k s^{-1}. The current and the consumed power were calculated by the software monitoring the lab card. The power supply was a home-made dc power unit providing voltages of 0–1500 V and a current of 0–5 A. The supporting electrolyte was NaOH and the conductivity of the ethanol solution was 5.6 mS cm^{-1}.

The volume of ethanol solution fed into the reactor for plasma electrolysis was 150 ml. The reaction time was 15 min. The residual ethanol solution in the reactor was collected and the volume measured. The liquid composition analysis was conducted before and after plasma electrolysis.

$G(H_2)$ is defined as the mole number of hydrogen divided by the Faradaic stipulated yield by passing the given electricity between the two electrodes. In our experiments the $G(H_2)$ calculation has been done by using the equation below:

$$G(H_2) = \frac{V_{gas}/22.4}{Q/2F} = \frac{V_{gas}F}{11.2Q} \text{ mol mol}^{-1} \quad (1)$$

where Q, F, V_{gas} denote the passed electric charge, Faraday constant and the hydrogen volume.

W_r of hydrogen is defined as the power depleted divided by the hydrogen volume. W_r is calculated by the equation

$$W_r = \frac{VQ}{V_{gas}} \text{kJ L}^{-1} \quad (2)$$

where V, Q, V_{gas} denote the voltage across the circuit, the passed electric charge and the hydrogen volume.

Hydrogen productivity (Y_{H_2}) is defined as

$$Y_{H_2} = \frac{n_{H_2}}{3n_{CH_3CH_2OH}} \times 100\%, \quad (3)$$

where n_{H_2} is the hydrogen molar number and $n_{CH_3CH_2OH}$ is the converted ethanol molar number. $n_{CH_3CH_2OH}$ is calculated by the original ethanol molar number minus the residual ethanol molar number.

Acetaldehyde productivity (Y_{CH_3CHO}) is defined as

$$Y_{CH_3CHO} = \frac{n_{CH_3CHO}}{n_{CH_3CH_2OH}} \times 100\%, \quad (4)$$

where n_{CH_3CHO} is the acetaldehyde molar number and $n_{CH_3CH_2OH}$ is the converted ethanol molar number.

3. Results and discussion

3.1. Characteristics of GDPE of ethanol solutions

Big volume and steady glow discharge plasmas were produced during GDPE of ethanol solutions. The current–voltage (I–V) curve of GDPE of lower alcohol solutions was similar to that of GDPE of aqueous solutions. The I–V curve observed

in the course of GDPE of 99.5% ethanol solutions is shown in figure 3. The curve typically has several distinct stages similar to aqueous solutions indicating the formation process of plasma electrolysis. The discharge plasma is generated in the gas envelope between the electrode and the surface of the solution. The formation of the gas envelope around the discharged electrode has a significant effect on the I–V curve. Ethanol is easier to vaporize than water. So the gas envelope around the discharged electrode is easier to form and tends to be of bigger volume in the course of plasma electrolysis in ethanol solutions than in aqueous solutions. The breakdown voltage (V_B), where the gas envelope around the discharged electrode becomes continuous, of 99.5% ethanol solutions is lower than that of aqueous solutions. And the gas envelope around the discharged electrode in ethanol solutions is thicker than that of aqueous solutions, so the midpoint voltage (V_D), at which the glow discharge around the electrode becomes full, is higher than that of the aqueous solution. In 99.5% ethanol solutions, V_D is about 540 V and 505 V for anodic GDPE (AGDPE) and cathodic GDPE (CGDPE), respectively.

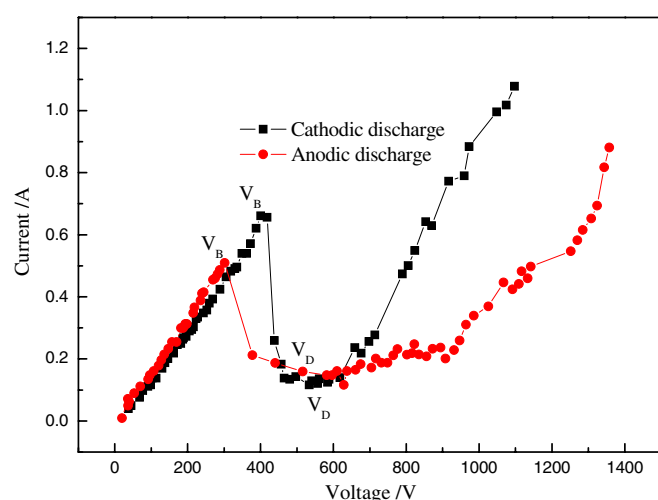The cathode fall occurred on the solution side during AGDPE whereas the cathode fall occurred on the surface of the electrode during CGDPE. In the course of the gas discharge, the energy is primarily dissipated in the cathode fall section. An analogous situation probably exists in the course of plasma electrolysis. When the cathode fall occurred on the solution side, the energy dissipated in the cathode fall section could be consumed primarily in solution vaporization. And then it is easy to get a thicker and bigger volume continuous gas envelope around the discharged electrode during AGDPE than in CGDPE. As figure 3 shows, V_B during AGDPE is lower than in CGDPE. When the thickness of the gas envelope is high, to develop a full glow discharge during GDPE is difficult and needs higher voltage. So V_D of AGDPE is higher than that of CGDPE.

3.2. Products of GDPE of ethanol solutions

Almubarak and Wood studied the chemical reaction in dilute aqueous ethanol solutions of anodic glow discharge electrolysis with ethanol concentration in the range 0–0.9 mol L^{-1} [18]. In their studies, CH$_3$CHO, butan-2,3-diol, hydrogen peroxide and acetic acid were the main products. And the yields of these products were found to vary substantially in the presence or absence of oxygen. In general, GDPE of aqueous solutions is regarded as an electrochemical process of water molecules decomposition and produces OH, OH$^-$, e$_{aq}^-$ species. So ethanol underwent mainly oxidation reactions. In our experiments, formaldehyde, hydrogen, acetaldehyde, carbon monoxide, methane, ethane and propane were the products of GDPE of ethanol solutions (shown in table 1). The 2,3-butanediol could be detected only in the solution when the ethanol concentration was 99.5%. This phenomenon is similar to GDPE of methanol solutions. The discharged polarity has no distinct difference in the variety of the GDPE products of ethanol solutions. CO$_2$ can be detected when the ethanol concentration is lower than 40%. The difference in chemical yields between Almubarak's work and our experiments shows a different reaction mechanism of ethanol molecules in different discharged conditions. Electrons were demonstrated as the most important particles to initiate the reactions of lower alcohols during GDPE in a high lower alcohol concentration. Molecules of lower alcohols

Figure 3. The I–V curve of GPDE of 99.5% ethanol solutions. Temperature = 303.15 K, conductivity = 5.6 mS cm^{-1}.

Table 1. Products of GDPE of ethanol aqueous solutions. Temperature = 303.15 K, conductivity = 5.6 mS cm^{-1}.

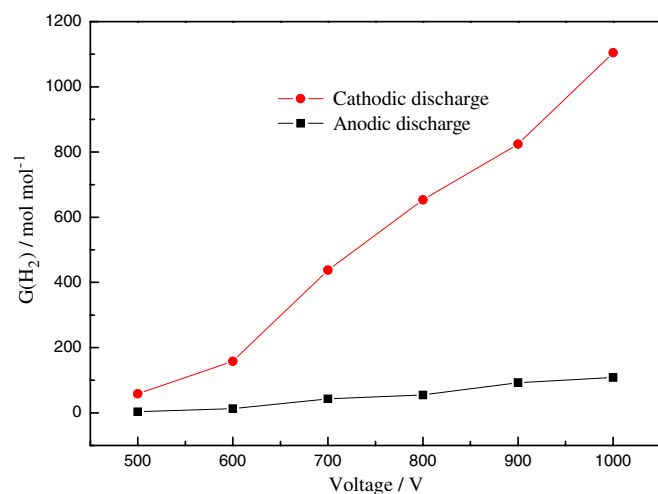| Ethanol concentration (W%)	Discharged voltage (V)	Discharged polarity	Products
99.5	1000	Anodic	C;HCHO; CH$_3$CHO; (CH$_3$CHOH)$_2$; CH$_3$COOH; H$_2$;C$_2$H$_6$; CH$_4$;CO; C$_3$H$_8$; C$_4$H$_{10}$
75	1000	Anodic	C;HCHO; CH$_3$CHO; H$_2$O;HCOOH; CH$_3$COOH;C$_5$H$_{12}$;H$_2$;C$_2$H$_6$; CH$_4$;CO; C$_3$H$_8$; C$_4$H$_{10}$
40	1000	Anodic	HCHO; CH$_3$CHO; H$_2$O;HCOOH; CH$_3$COOH;C$_5$H$_{12}$;H$_2$;C$_2$H$_6$; CH$_4$;CO$_2$ CO; C$_3$H$_8$; C$_4$H$_{10}$
99.5	1000	Cathodic	C;HCHO; CH$_3$CHO; H$_2$O; (CH$_3$CHOH)$_2$; CH$_3$COOH;C$_5$H$_{12}$;H$_2$;C$_2$H$_6$; CH$_4$ CO; C$_3$H$_8$; C$_4$H$_{10}$
75	1000	Cathodic	C;HCHO; CH$_3$CHO; H$_2$O;HCOOH; CH$_3$COOH;C$_5$H$_{12}$;H$_2$;C$_2$H$_6$; CH$_4$; CO; C$_3$H$_8$; C$_4$H$_{10}$
40	1000	Cathodic	HCHO; CH$_3$CHO; H$_2$O;HCOOH; CH$_3$COOH;C$_5$H$_{12}$;H$_2$;C$_2$H$_6$; CH$_4$;CO$_2$ CO; C$_3$H$_8$; C$_4$H$_{10}$

Figure 4. Effect of voltage on $G(H_2)$ of 99.5% ethanol solutions. Temperature $= 303.15$ K, conductivity $= 5.6$ mS cm^{-1}.

excited in glow discharge plasmas and at the interface between plasmas and solutions produced a lot of active radicals [17].

3.3. Hydrogen generation of GDPE of ethanol solutions

3.3.1. Discharged voltage effects. The plasma density of the glow discharge has a strong dependence on the magnitude of the applied voltage. The increase in the discharged power causes an increase in the electron density, enhancing the electron impact excitation processes and hence ethanol decomposition and causing more gas to liberate from the discharged electrode. We can understand that the potential gradient, the discharge extent and the quantity of high-energy electrons within the plasma increase with the applied voltage. And the glow discharge plasma volume can increase with the discharged voltage. So the path of the high-energy electrons within the glow discharge plasma increases, and electrons have more possibility of colliding with ethanol molecules and other radicals. The hydrogen yields, $G(H_2)$, sharply increased with the applied voltage (figure 4). When the applied voltage was 500 V, the system was just in a partial glow discharge and $G(H_2)$ of CGDPE was only 58.51 mol mol^{-1}. When the applied voltage was 1000 V and higher than V_D, the system reached a full glow discharge and $G(H_2)$ of CGDPE was 1104.33 mol mol^{-1}.

W_r decreased with the increase in the applied voltage (figure 5). W_r was 5.12 kJ L^{-1} when the applied voltage was 1000 V of CGDPE. The result is very significant and clearly indicates that hydrogen generation with GDPE is an energy saving technique. This value is just half of the theoretical energy of conventional electrolysis of water to produce hydrogen. W_r was 64.45 kJ L^{-1} when the applied voltage was 1000 V of AGDPE. The variation of W_r with the applied voltage implies that the efficiency of high-energy electrons to decompose ethanol molecules improves in the course of increase in the applied voltage. But the applied voltage cannot be increased without limitation. The discharged electrode will melt if the experiments are performed at a very high voltage.
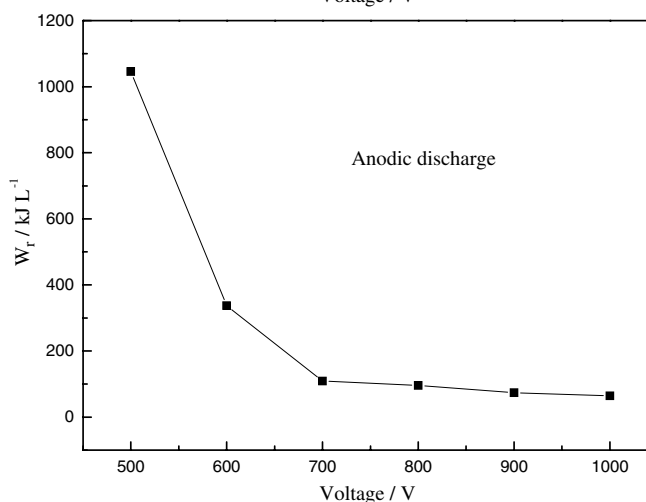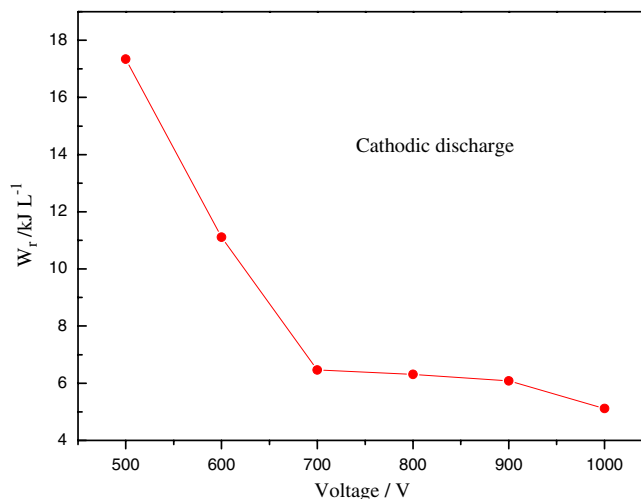

Figure 5. Effects of discharged voltage on W_r of 99.5% ethanol solutions. Temperature $= 303.15$ K, conductivity $= 5.6$ mS cm^{-1}.

The bonds of ethanol molecules have different binding energies. When the energy level of the electrons to initiate the ethanol decomposition increases, the reaction pathways of ethanol molecules might be more complex. The yields of different products vary with the variation of the reactions. The hydrogen concentration of releasing gases via CGDPE kept above 80% after the separation of HCHO when the applied voltage was above 500 V (table 2). The hydrogen concentration of releasing gases via AGDPE kept above 70% under similar conditions (table 3) and was lower than that of CGDPE by 8–9%. The binding energy of the C–C bond in ethanol molecule is low, only 364.8 kJ mol^{-1}, and is easily broken by high-energy species. The cleavage of the C–C bond of ethanol molecules can produce CH$_3^{\bullet}$ radicals and then produce CH$_4$ and other paraffin gases. So the paraffin gas concentration of CGDPE liberating gases was very high and reached higher than 13% and displayed a tendency to decrease with the discharged voltage.

The productivity of hydrogen and acetaldehyde is determined by the ethanol decomposition process. The productivity data show that H$_2$ and CH$_3$CHO are the dominant products of the ethanol decomposition under the collision of high-energy electrons in GDPE. In general, Y_{CH_3CHO} and Y_{H_2} increase with the applied voltage in the course of CGDPE, as

Table 2. Composition of CGDPE liberated gas with different discharged voltages. Temperature = 303.15 K, ethanol concentration = 99.5%, conductivity = 5.6 mS cm^{-1}.

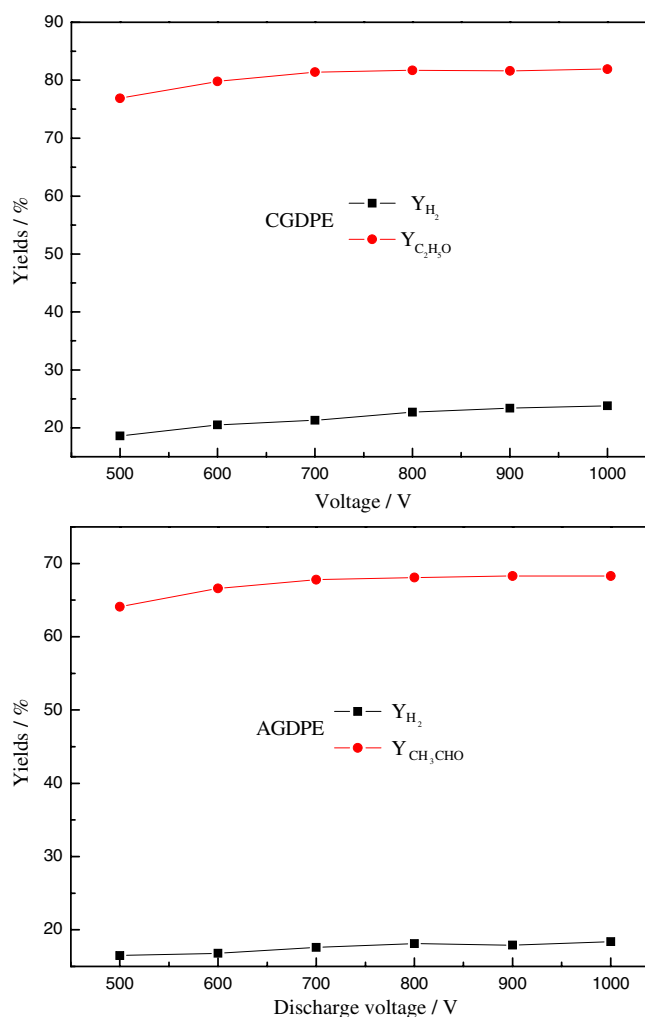| Discharged voltage (V)	H_2 (mol%)	CO (mol%)	CH_4 (mol%)	C_2H_6 (mol%)	C_3H_8 (mol%)	C_4H_{10} (mol%)
500	80.84	4.77	4.74	1.81	6.19	1.65
600	80.96	4.88	5.49	2.46	4.87	1.34
700	81.28	4.68	5.29	2.06	5.23	1.46
800	81.92	5.04	5.15	2.43	4.42	1.04
900	82.81	4.01	5.28	2.48	4.24	1.18
1000	82.67	4.17	5.22	2.65	4.08	1.21

Table 3. Composition of AGDPE liberated gas with different discharged voltages. Temperature = 303.15 K, ethanol concentration = 99.5%, conductivity = 5.6 mS cm^{-1}.

Discharged voltage (V)	H_2 (mol%)	CO (mol%)	CH_4 (mol%)	C_2H_6 (mol%)	C_3H_8 (mol%)	C_4H_{10} (mol%)
500	71.37	3.97	12.13	3.31	7.43	1.79
600	72.11	4.86	8.87	4.91	6.79	2.46
700	73.04	4.91	8.53	4.22	6.80	2.50
800	73.33	4.79	8.42	4.08	6.83	2.55
900	73.50	4.84	7.93	4.35	6.77	2.61
1000	74.16	5.02	6.98	4.64	6.52	2.68

Figure 6. Effects of discharged voltage on Y_{H_2}, Y_{CH_3CHO} of GDPE of 99.5% ethanol solutions. Temperature = 303.15 K, conductivity = 5.6 mS cm^{-1}.

shown in figure 6. Y_{CH_3CHO} and Y_{H_2} reach a maximum value when the discharged voltage is 1000 V. Under this condition, Y_{H_2} is 23.8% and Y_{CH_3CHO} is 81.9%.

3.3.2. Discharged polarity effects. The major positive ions produced by ethanol molecule ionization include H^+, $CH_3CH_2OH^+$, $CH_3CH_2^+$, $CH_2CH_2OH^+$, CH_3OH^+, CH_2OH^+. As we know, the charge/mass ratio of the positive ions is low. In contrast, the charge/mass ratio of electrons is high. The electrons tend to get a far higher accelerated kinetic energy than positive particles within the same cathode fall section. So the probability of initiating excitation collisions between positive ions and ethanol molecules is far less than for electrons and ethanol molecules. It is reasonable to pay more attention to the electrons to analyse the decomposition of ethanol in the course of GDPE.

The quantity of high-energy electrons is an important factor needed to consider to analyse the difference in $G(H_2)$ between AGDPE and CGDPE. Firstly, the capability of the cathode material to emit secondary electrons should be considered. During CGDPE, the cathode is tungsten. Meanwhile, during AGDPE, the cathode is ethanol solution. As we know, the capability of emitting secondary electrons of the metal material is stronger than that of the ethanol solution. Secondly, the moving directions of positive ions, which can lead to the cathode to emit secondary electrons, are different under different discharged polarities. When AGDPE is conducted, positive ions move from the tungsten anode to the ethanol solution cathode. As mentioned above, the capability of emitting secondary electrons of the solution is far weaker than that of the tungsten cathode. In contrast, positive ions move from the ethanol solution to the tungsten cathode during CGDPE and trigger the emission of secondary electrons on

the cathode surface when the positive ions reach the cathode. Positive ions can also lead to the ethanol molecules to ionize in the cathode fall region at the same time. So the number of high-energy electrons of CGDPE is far higher than that of AGDPE.

The moving direction of high-energy electrons is probably another important factor to cause $G(H_2)$ of CGDPE to be higher than that of AGDPE. During CGDPE, the cathode fall occurs on the surface of the electrode and the discharged energy is primarily dissipated in the cathode fall section. The electrons were accelerated and got high kinetic energy within the cathode fall region near the discharged electrode. In the course of moving to the plasma/solution interface, the high-energy electrons have more probability of colliding with ethanol molecules and other radicals. Meanwhile, electrons move from the plasma/solution interface towards the discharged anode during AGDPE. The cathode fall occurred on the solution side and most of the energy dissipated in the cathode fall section was consumed in the continuous vaporization of the ethanol solution. This led the interface of the plasma/solution to be in a unsteady state. Under this condition, the accelerated kinetic energy of the electrons

got in the cathode fall section is significant lower. Then the probability of electrons initiating excitation collisions among ethanol molecules and other radicals was less. And the contribution of high-energy electrons to induce a plasma reaction became less and less.

$G(H_2)$ of CGDPE was far higher than that of AGDPE, as shown in figure 4. The ratio of $G(H_2)$s between CGDPE and AGDPE was 10.2 when the discharged voltage was 1000 V. W_r of CGDPE is much less than that of AGDPE. For CGDPE, W_r was 5.12 kJ L^{-1} when the discharged voltage was 1000 V. Under the same condition, W_r was 64.45 kJ L^{-1} for AGDPE. The ratio of W_r between CGDPE and AGDPE was 12.6. The effects of discharged polarity on the chemical yields demonstrated by the experiments confirm that the high-energy electrons are the most important particles to induce the decomposition of ethanol molecules.

The plasma density and the energy level of electrons of AGDPE are lower than those of CGDPE when CGDPE and AGDPE were conducted at the same voltage. The C–C bonds tend to break first when the electron energy is low. Therefore, the concentration of paraffin in the liberating gas during AGDPE was higher than that of CGDPE by 10–13% and the hydrogen concentration of the CGDPE liberating gas was higher than that of the AGDPE liberating gas by 8–9% (as shown in tables 2 and 3). When the probability of producing paraffin gas is high, the probability of producing acetaldehyde tends to lower values. So productivities of hydrogen and acetaldehyde of CGDPE were higher than that of AGDPE (figure 6).

3.3.3. Ethanol concentration effects. CGDPE of ethanol aqueous solutions with various substrate concentrations is conducted to investigate the influence of the ethanol concentration on the hydrogen generation process. These experiments were conducted with a 700 V discharged voltage. The binding energy of O–H in H_2O is higher than that of any bond of ethanol molecule. And ethanol molecules have more H atoms than H_2O molecules. In the course of GDPE, the discharged electrode is enveloped by the vapour of the solutions. The composition of vapour around the discharged electrode depends on the composition of the solution. The saturated vapour pressure of ethanol is higher than that of water. When the concentration of ethanol in the solution is 40.0%, the concentration of ethanol of the gas envelope around the discharged electrode can reach 61.4%. At the same time, the volume of the gas envelopes increases with the ethanol concentration. These factors mentioned above ensure the rapid increase in $G(H_2)$ with the ethanol concentration (figure 7) as well as the decrease in W_r with the ethanol concentration (figure 8).

The composition of the liberated gas of the discharged electrode is shown in table 4. If the ethanol concentration of the solution decreases, the water concentration of the gas envelope would increase. Then the probability of water molecules excited to decompose increased in the plasma sheath. The decomposition of water molecules would contribute more hydrogen atoms to the production of hydrogen. So the hydrogen concentration increased with the
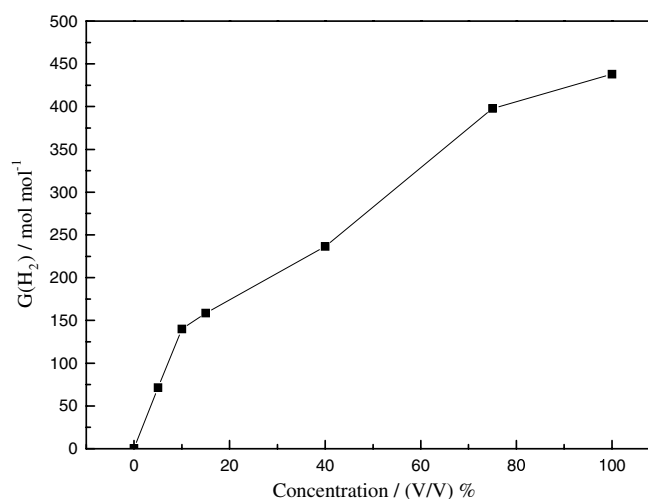

Figure 7. Effect of ethanol concentration on $G(H_2)$. Temperature = 303.15 K, conductivity = 5.6 mS cm^{-1}, discharged voltage = 1000 V.
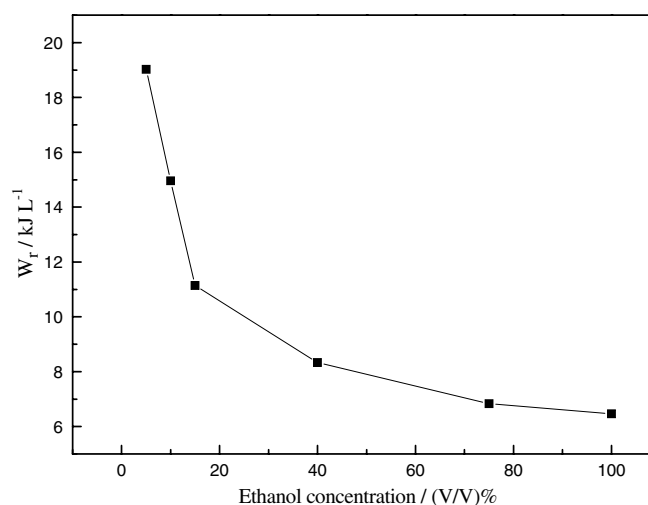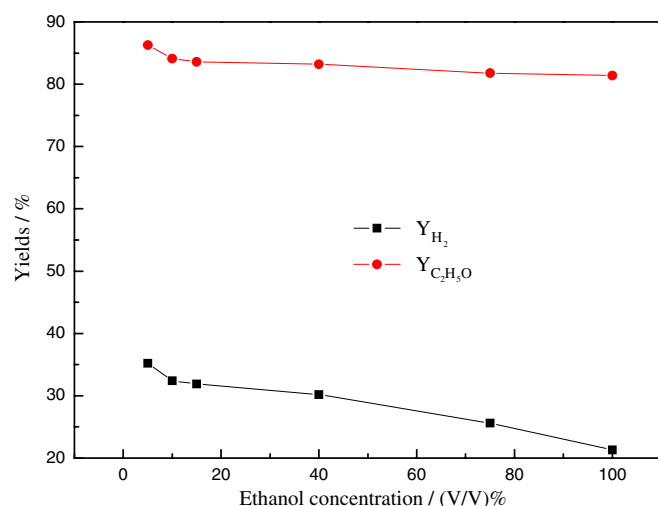

Figure 8. Effects of ethanol concentration on W_r. Temperature = 303.15 K, conductivity = 5.6 mS cm^{-1}, discharged voltage = 1000 V.

ethanol concentration of the solutions and the paraffin gas concentration increased with the ethanol concentration. CO_2 was detected when the ethanol concentration was lower than 40% and the CO_2 concentration increased with the decrease in the ethanol concentration. This meant CO_2 comes from the oxide compounds of ethanol by OH radicals. One thing that should be pointed out is that the concentration of carbon dioxide of the liberating gas is very low. Even when the ethanol concentration of the solution was 5%, the CO_2 concentration of the liberating gas was 3.23% by molar fraction. That is to say, to produce one volume hydrogen just requires 0.063 volume CO_2 emission. Based on this, hydrogen production by ethanol decomposition with GDPE can be regarded as a green technology.

Ethanol oxidized by OH$^\bullet$ radicals can produce CH_3CHO. The quantity of OH$^\bullet$ radicals increased with the decrease in ethanol concentration. So Y_{CH_3CHO} increased with the water concentration (figure 8). H atoms produced by the water decomposition process recombined with each other and

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Table 4. Composition of CGDPE liberated gas with different ethanol concentrations. Temperature = 303.15 K, discharged voltage = 1000 V, conductivity = 5.6 mS cm^{-1}.

Ethanol concentration (V%)	H_2 (mol%)	CO (mol%)	CH_4 (mol%)	C_2H_6 (mol%)	C_3H_8 (mol%)	CO_2 (mol%)	C_4H_{10} (mol%)
99.5	81.28	4.68	5.29	2.06	5.23	0.00	1.46
75	81.76	5.03	4.21	2.70	4.85	0.00	1.45
40	83.13	5.20	4.06	2.98	2.90	0.69	1.04
15	84.02	5.61	3.41	3.10	1.30	1.65	0.91
10	85.22	5.74	3.32	2.48	0.54	2.07	0.63
5	85.32	6.03	2.59	2.17	0.20	3.23	0.46

Figure 9. Effects of ethanol concentration on Y_{H_2}, Y_{CH_3CHO}. Temperature = 303.15 K, conductivity = 5.6 mS cm^{-1}, discharged voltage = 1000 V.

generated hydrogen gases. Therefore, Y_{H_2} decreased with the increase in the ethanol concentration. When the ethanol concentration was 5% by volume fraction, Y_{H_2} was 35.2%. Under this condition, 1 mol ethanol produced 1.05 mol H_2. If hydrogen was the main product, ethanol aqueous solutions were optimum raw materials. But the energy depleted during GDPE is high (figure 9).

4. Conclusions

This work shows that GDPE of the ethanol solutions is a promising technique for H_2 production. Hydrogen and acetaldehyde are the dominant products of ethanol decomposition of GDPE. High-energy electrons are species for inducing the decomposition reactions of ethanol in GDPE. Discharged polarity, discharged voltage and ethanol concentration have important influences on the hydrogen yield, energy consumption, hydrogen concentration and productivity of hydrogen and acetaldehyde in GDPE.

The hydrogen yield of CGDPE is higher than that of AGDPE and the energy consumption of CGDPE is much less than that of AGDPE. $G(H_2)$ of CGDPE is 10.2 times that of AGDPE when the discharged voltage was 1000 V. Under this condition, W_r of CGDPE was 5.12 kJ L^{-1}, and the ratio of W_r between CGDPE and AGDPE was 12.6.

$G(H_2)$ increased with the applied voltage. W_r decreased with the applied voltage. $G(H_2)$ increased with the ethanol concentration as well as lower W_r and hydrogen productivity.

The experiments indicate that GDPE of ethanol solutions is a highly efficient technology to produce hydrogen and formaldehyde simultaneously with low emission of CO_2. The recovery of acetaldehyde could effectively reduce the cost of hydrogen generation.

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