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Hydrogen production from ethanol decomposition by pulsed discharge with needle-net configurations

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HIGHLIGHTS

- Hydrogen produced by pulsed discharge with needle-net configurations was studied.
- Hydrogen yield was affected little with the increase of discharge time.
- Nano carbon particles were discovered during the process of hydrogen production.
- Mechanism of hydrogen produced from ethanol/water by pulsed discharge was studied.

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ABSTRACT

Hydrogen produced from ethanol solution by pulsed discharge was investigated in this work. With needle-net configurations, hydrogen can be easily exported from the plasma reactor thereby preventing hydrogen from consuming by the oxidizing active substances generated from pulsed discharge. Both flow rate and percentage concentration of hydrogen were enhanced with the increase of energy density, but not much change with the increase of discharge time. Flow rate, percentage concentration, and energy consumption of hydrogen were achieved about 800 mL/min, 73.5%, and 0.9 kWh/m^3 H_2 respectively with energy density of 6.4 J/L. All products were analyzed, which were divided into main and secondary products guiding the mechanism analysis of hydrogen production. The main products contain H_2, CO, CH_3OH, and the secondary products include C_2H_2, CO_2, macromolecular compounds, nano carbon particles. The high hydrogen yield, emerged nano carbon, low ethanol and energy consumption make this method possess bright prospect in hydrogen production.

1. Introduction

As one of the most promising clean energy, hydrogen has drawn much attention in recent years. Hydrogen can be widely used in industrial manufacture, such as synthesis ammonia, metallurgical engineering, fertilizer production and high-energy fuel, which is owing to its high calorific value, light weight, non-toxicity, and no pollution emissions [1–3]. Additionally, on-board hydrogen production is a hot spot, which can directly provide hydrogen to hydrogen fuel cells avoiding the problems of hydrogen storage and transportation in automobiles [4–6]. Industrial hydrogen production was generally dependent on catalytic reforming from natural gas or water gas, which needs high temperature, high performance catalysts and non-renewable energy consumption [7–10]. Therefore, a more efficient and sustainable method of hydrogen production is needed.

Hydrogen production by discharge plasma in liquid is emphatically studied by some researchers these years. Discharge plasma in liquid can be categorized as discharges in bubbles in liquids, discharges in the gas phase with liquid electrode, and direct liquid phase discharges [11,12]. Hydrogen produced by discharges in bubbles in liquids needs a carrier gas such as N_2, Ar [13–16]. The carrier gas can lower the initial voltage, however, it also increases the cost and causes problems at separation between carrier gas and hydrogen. Zhang et al. [13] investigated aqueous discharge in argon bubbles reforming hydrocarbons for hydrogen production. The work achieved hydrogen percentage concentration of 75% and hydrogen flow rate of 4.3 mL/min. As the results show, hydrogen yield is too low to apply in industry by discharges in bubbles in liquids. Discharges in the gas phase with liquid electrode for hydrogen production was also researched by some scholars. Ihara et al. [17] studied hydrogen production from water by gas-liquid nanosecond pulsed discharge that the hydrogen yield and energy consumption were achieved 0.5 mL/min and 416.7 kWh/m^3 H_2, respectively. It shows that

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discharges in the gas phase with liquid electrode for hydrogen production is energy-intensive. Hydrogen produced by direct liquid phase discharges attracts more attention these year, which has no use for carrier gas. It can be further divided into microwave discharge (MD) [18,19], radio frequency discharge (RF) [20,21], and pulsed discharge (PD) [22–24]. Microwave and radio frequency discharge belong to high-frequency discharge, which need higher energy consumption for hydrogen production. Wang et al. [18] utilized microwave discharge in liquid for hydrogen production, and the energy consumption was about 7.3 kWh/m^3 H_2. Rahim et al. [19] achieved hydrogen production from methane hydrate by radio frequency in-liquid plasma, which needed 148.8 kWh for generating 1 m^3 hydrogen. Hydrogen production by pulsed discharge in liquid has great prospect, which can be achieved both high hydrogen yield and low energy consumption. Xin et al. [23] applied pulsed spark discharge in ethanol solution for hydrogen production. By optimizing the plasma reactor, hydrogen yield and energy consumption were achieved 1.5 L/min, 0.48 kWh/m^3 H_2 respectively.

The reactor type of pulsed discharge in liquid includes needle-plate, plate-plate, plate-pinhole-plate and so on [25]. The plate-plate configurations are difficult to form plasma in liquid owing to the uniform electric field distribution. With plate-pinhole-plate configurations, both sides of the pinhole can generate hydrogen affecting collection and transportation. The needle-plate configurations were used more in hydrogen production [3,13,22–24]. Hydrogen was mainly produced around plate electrode, and decreasing retention time of hydrogen can increase hydrogen yield [23]. Therefore, plate electrode designed near gas port is more favorable to hydrogen production. However, plate electrode can also affect transportation of gas production. As a result, improvement in plasma reactor for hydrogen production is eagerly needed.

Hydrogen produced by discharge plasma in liquid comes from hydrogen-containing substances, which mainly contain water [17], hydrocarbons [13,19,21,24], alcohols [14–16,18,22,23], carbohydrates [20]. Discharge plasma in water for hydrogen production exists the problem like low hydrogen yield and high energy consumption. Hydrocarbons are normally non-renewable and less eco-friendly. Additionally, hydrocarbons have restrictions such as narrower flammability limits, lower compression ratio and so on [26]. Alcohols and carbohydrates are renewable, which have high hydrogen contents. To increase percentage concentration of hydrogen and decrease the by-products, low-carbon alcohols and carbohydrates are optimized. Compared with other low-carbon materials, ethanol is more popular due to its nontoxicity and high hydrogen ratio. Besides, proper proportion of water mixed in ethanol can increase the hydrogen yield [3].

In this work, hydrogen production from ethanol solution by pulsed spark discharge plasma was investigated with needle-net configurations. The needle-net configurations can let gas production export reactor in time, which can effectively prevent hydrogen from consuming by the strong oxidizing substances generated from the plasma. The plasma reactor can be used in automobiles for on-board hydrogen production to hydrogen fuel cells. Both gas and liquid products were analyzed, and the mechanism of plasma reforming in ethanol solution was also deduced. Additionally, nano carbon particles were discovered during the reforming processes. The high yield of hydrogen and the presence of nano carbon make this method possess bright prospect.

2. Experimental setup and methods

Fig. 1 shows the schematic of experimental setup for pulsed spark discharge in ethanol solution for hydrogen production. The structure of the plasma reactor was the needle-net configurations. The needle electrode was made of platinum and shaped to have a sharp tip with a radius of curvature of approximately 0.2 mm at the end with high positive potential, while the ground net electrode with 2 mm × 2 mm mesh was made of stainless steel and its diameter was about 80 mm. The plasma reactor about 400 cm^3 was powered by a high voltage power supply (DGM-60, DaLian Power Supply Technology) equipped with a maximum allowable voltage of 60 kV and frequency of 300 Hz. An oscilloscope (TDS2024B, Tektronix) with a high voltage probe (P6015A, Tektronix) and a current probe (2878, Pearson Electronics) was used to analyze the variation of voltage and current in the discharge circuit. A rotor flow meter (LZB-3, ZhengXing) was used to measure the flow rate of gas production. The mass spectrometry (HALO201, Hiden) and gas chromatography (GC-2014C, SHIMADZU) were used to make qualitative and quantitative analysis of gas production. A CCD camera (HiSpec1 2G Color, Fastec Imaging) was fixed in front of quartz window to monitor the variation in the plasma reactor. In order to distinctly visualize the gas generated from spark discharge, a strong light source was set behind the reactor and projected a powerful beam of light through the electrode region in the camera direction, called shadowgraph method. The morphological features of carbon particles were identified by transmission electron microscopy, or TEM (JEM-2000EX, JEOL). The conductivity and pH of ethanol solution were detected by a conductivity meter (PHS-3C, Leici) and a pH meter (DDS-11A, Leici) respectively.

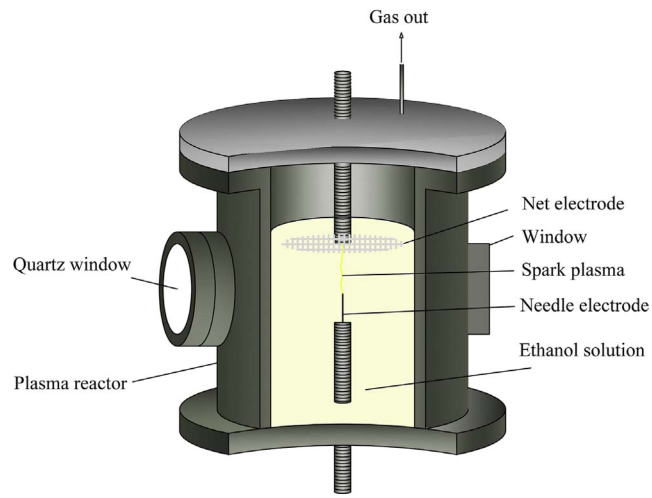

Fig. 1. Schematic diagram of experimental setup for pulsed spark discharge in ethanol solution for hydrogen production.

During the processes of discharge, plasma reactor was filled with ethanol solution that the plasma was indeed formed in the liquid. Flow rate of hydrogen can be acquired by combining the rotor flow meter and gas chromatography. Flow rate of total gas can be obtained by the rotor flow meter, and percentage concentration of hydrogen can be calculated by chromatographic analysis.

$$Q_{H_2} = \omega_{H_2} Q_{\text{total gas}} \tag{1}$$

where Q_{H2} refers to flow rate of hydrogen, ω_{H2} refers to percentage concentration of hydrogen, and $Q_{\text{total gas}}$ refers to flow rate of total gas.

Characteristics of spark discharge are important for analysis of hydrogen production. Energy density can be calculated by energy of single pulsed discharge and volume of ethanol solution, while energy of single pulsed discharge can be acquired by V-I derived from the oscilloscope.

$$\omega = \frac{W}{V} \tag{2}$$

$$W = \int v(t)i(t)dt \tag{3}$$

where ω refers to energy density, W refers to energy of single pulsed discharge, V refers to volume of ethanol solution, and v(t), i(t) refer to voltage and current respectively, both of them are in the function of time acquired by oscilloscope.

The rate constant of spark formation is the reciprocal value of duration of spark formation, shown in formula (4).

$$v = \frac{1}{t} \quad (4)$$

where v refers to rate constant of spark formation, and t refers to duration of spark formation.

Liquid products were analyzed by GC with flame ionization detector (FID). Chromatographic column RTX-1 was applied for product analysis and high purity nitrogen (> 99.999%) was used as carrier gas. The operational conditions were flow rate of nitrogen = 1 mL/min, flow rate of hydrogen = 40 mL/min, flow rate of air = 400 mL/min, split ratio = 50:1, temperature of the injection port = 200 °C, injection volume = 0.1 μL. Column temperature program was set as below: initial column temperature was set at 35 °C and maintained 5 min; then temperature was increased to 160 °C with the speed of 4 °C/min and kept 1 min; at last, temperature was further increased to 260 °C with the speed of 15 °C/min and retained 2 min.

In this work, every experiment was repeated 5 times. The errors mainly came from instantaneous instability of discharge. In addition, numerical reading and changing external environment may have also led to errors.

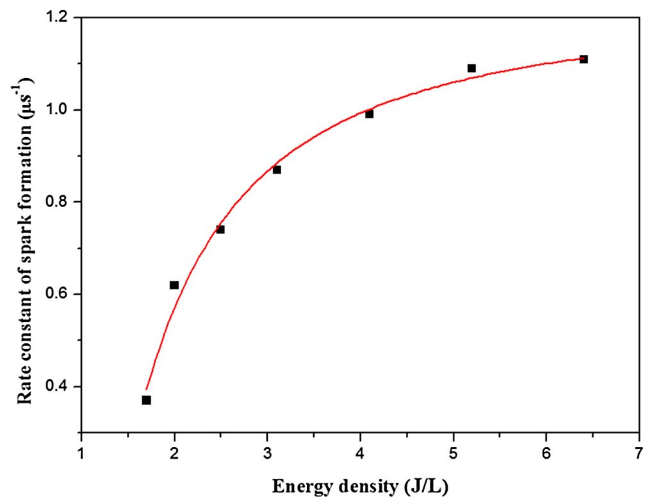

Fig. 3. Rate constant of spark formation as a function of energy density.

3. Results and discussion

3.1. Characteristics of pulsed discharge in ethanol solution

With the needle-net configurations, the typical current-voltage oscillogram of spark discharge in ethanol solution at peak voltage of 24 kV is shown in Fig. 2. It can be divided into two stages: propagation stage, and initiation stage. When the spark discharge is shaped, voltage declines sharply and a strong current forms at the same time. The current-voltage oscillogram shown in Fig. 2 is similar to the needle-plate configurations. It attributes to the parallel electric field distribution with dense mesh of the net electrode. Fig. 3 shows rate constant of spark formation as a function of energy density. Though the growth rate slows down, rate constant of spark formation raises with the increase of energy density. It means that large amount of high-energy electrons are formed in a shorter period of time when the injected energy is increased. Peak current density and electrons producing efficiency are higher, leading to generate more active substances for chemical reactions.

3.2. Characteristics of hydrogen production

Attributed to the characteristics of pulsed discharge in ethanol solution, hydrogen and some other substances can be generated. As shown in our previous work [3], gas production contained H_2, CO, C_2H_2, CO_2 detected by MS that H_2 and CO occupied the main position. Influence of energy density on hydrogen production was investigated by varying energy density from 1.7 J/L to 6.4 J/L. The operational conditions were discharge frequency = 30 Hz, initial ethanol concentration = 50%, electrode distance = 15 mm. The flow rate of gas as a function of energy density is presented in Fig. 4. It is observed that both of the curves of total gas and hydrogen have similar variations, which are continuous growth with the increased energy density. Fig. 5 shows percentage concentration of gas as a function of energy density. Percentage concentration of hydrogen increases with the rising energy density, carbon monoxide shows a slight growth and then declines, other gas decreases rapidly and stays around 0.6% at last. Both flow rate and percentage concentration of hydrogen rise with the increase of energy density, which are good messages for pulsed discharge for hydrogen production.

Further studies were performed at energy density = 6.4 J/L, discharge frequency = 30 Hz, electrode distance = 15 mm and initial ethanol concentration = 50% with discharge time ranging from 0 to 40 min. Fig. 6 presents the flow rate of gas as a function of discharge time. Both flow rate of total gas and hydrogen show almost invariable tendency. The flow rate of hydrogen maintains about 800 mL/min. Percentage concentration of gas as a function of discharge time is presented in Fig. 7. As similar with the flow rate of gas, percentage

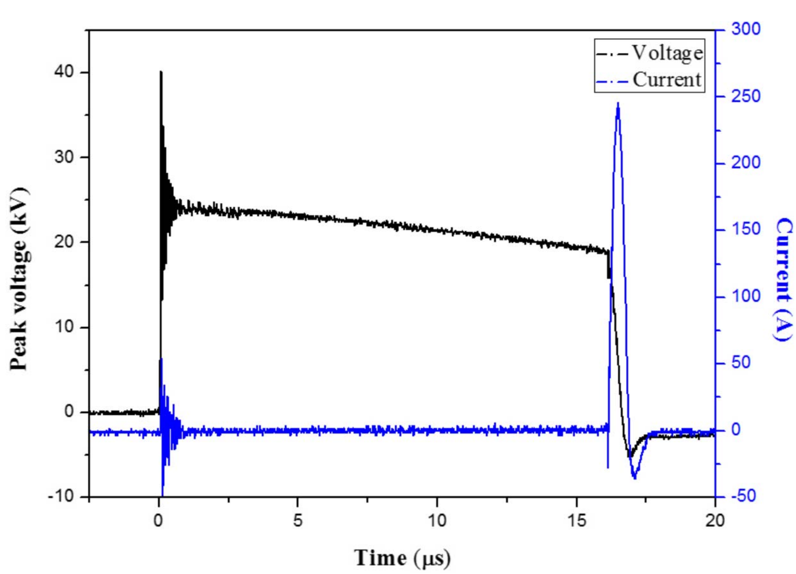

Fig. 2. The typical current-voltage oscillogram of spark discharge in ethanol solution.

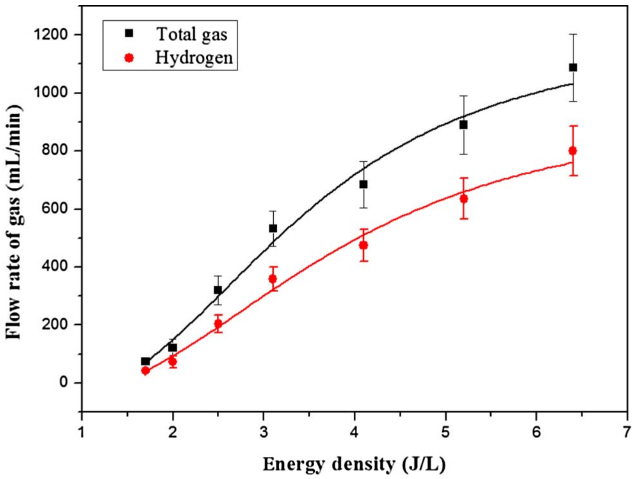

Fig. 4. Flow rate of gas as a function of energy density.

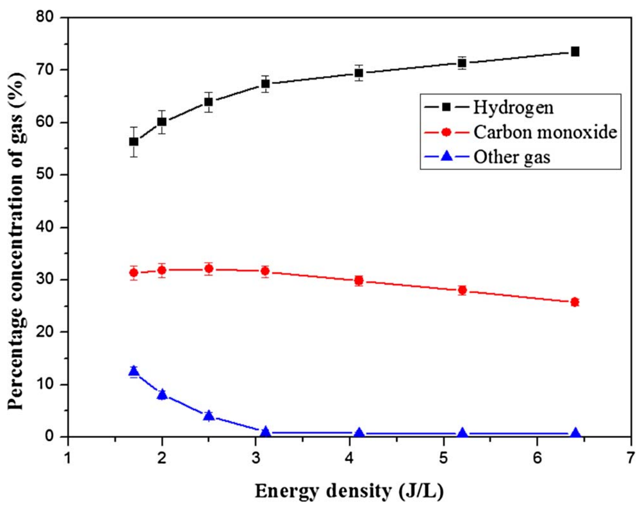

Fig. 5. Percentage concentration of gas as a function of energy density.

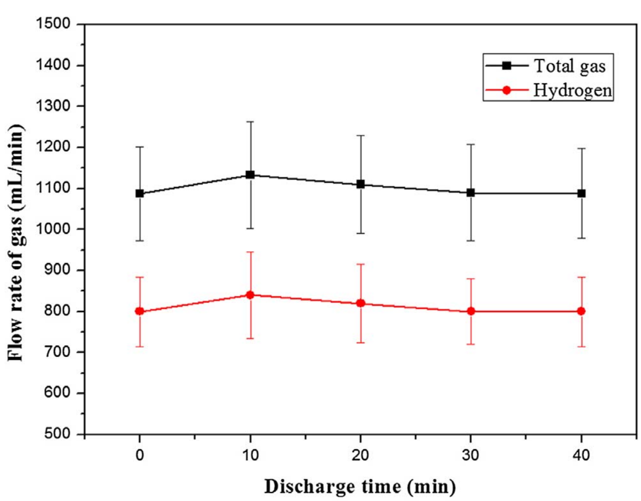

Fig. 6. Flow rate of gas as a function of discharge time.

concentration of gas almost keeps unchanged with the variation of discharge time. The results show that hydrogen production by pulsed discharge in liquid is not affected by discharge time, it does good to the application of this method for a long time.

In order to better realize the process of hydrogen production by

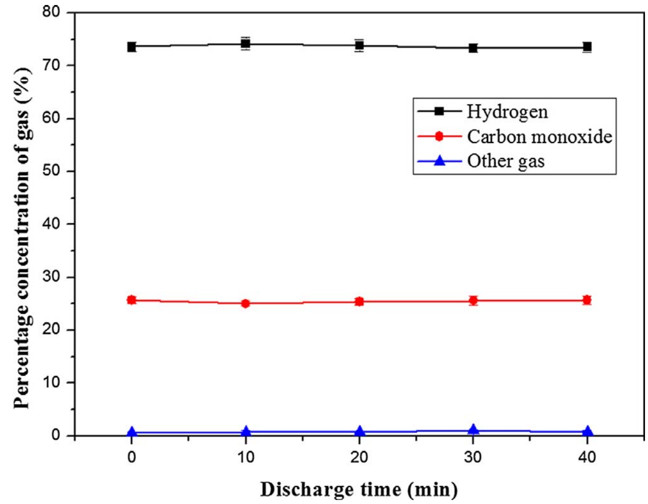

Fig. 7. Percentage concentration of gas as a function of discharge time.

pulsed discharge, a CCD camera combined with shadowgraph method was used. This method can be found in Stelmashuk's work [27,28]. Fig. 8 shows dynamic variation of pulsed spark discharge in ethanol solution for hydrogen production. Fig. 8a presents the original state in the plasma reactor, no plasma or gas is produced in this figure. Corona discharge is initiated and a small number of gas is produced around the electrodes shown in Fig. 8b. Spark discharge is formed with the increase of voltage, which is difficult to catch due to a huge dynamic range of light emitted by the discharge just like the image in Fig. 8c. After the spark discharge, a large amount of gas is generated around the net electrode and directly exported through the mesh of net electrode shown in Fig. 8d-f. As the figures show, gas production was easily extracted from the plasma reactor with needle-net configurations. It can effectively prevent hydrogen from consuming by the oxidizing active substances generated from the next pulsed discharge. This conclusion can be confirmed by the comparison with the needle-plate configurations. With needle-net configurations, the flow rate of hydrogen was achieved 800 mL/min with the energy density of 6.4 J/L. However, under the same conditions, the flow rate of hydrogen was only about 200 mL/min with needle-plate configurations. When the net electrode was replaced by the plate electrode with same size, most of gas production was blocked by plate electrode and only a small part of gas exported from the gap between plate electrode and wall of plasma reactor. The blocked gas can be rapidly consumed by the oxidizing active substances generated from the next pulsed discharge. Thus, the flow rate of hydrogen markedly decreases with needle-plate configurations.

3.3. Solid and liquid products

Besides various gas products, carbon particles in solid state were also found in this work. Fig. 9 shows TEM image of carbon particles produced by pulsed discharge in ethanol solution. The carbon particles are spherical and belong to nanoscale. Carbon nanospheres can be used in lithium battery materials [29], heavy metal adsorption [30], hydrogen storage [31], photocatalysis [32] and so on. Jarvid et al. [33] added carbon nanospheres in voltage stabilizers for power cable insulation, achieved an even higher improvement of 26% in high voltage resistance. Therefore, carbon nanospheres own wide application prospect. Further studies will be presented in our next work.

Liquid ingredient analysis after 40 min discharge detected by GC were shown in Fig. 10. The peaks of methanol, ethanol appear at 2.210 min, 2.361 min respectively. Macromolecular compounds (carbon number $>$ 3) turn up after 30 min, which can be confirmed in Refs. [34,35] with the similar experimental conditions in this work. However, as the figure shows, the proportion of ethanol accounts for

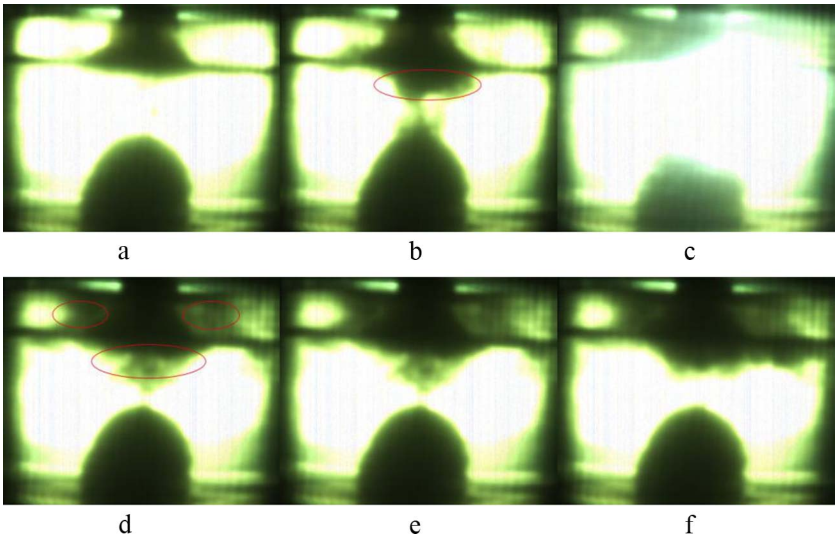

Fig. 8. Dynamic variation of pulsed spark discharge in ethanol solution for hydrogen production.

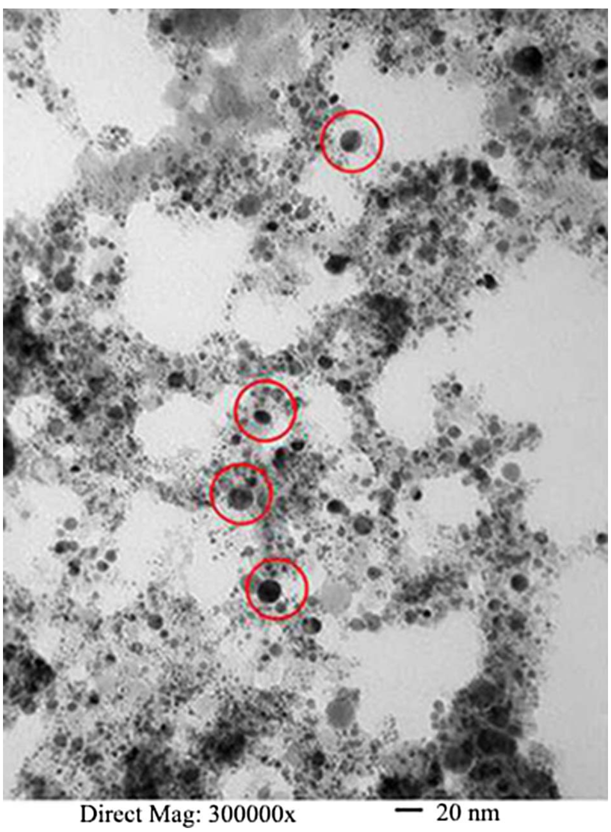

Fig. 9. TEM image of carbon particles produced by pulsed discharge in ethanol solution.

the major proportion. It illustrates that only a small number of ethanol was decomposed into other materials after 40 min discharge. By calibration analysis, only about 4% of ethanol was converted into other substances and the amount of methanol was about 0.38 mol. The volume of produced methanol accounted for over 90% in liquid products. It is a good signal to long-playing hydrogen production. Besides, macromolecular compounds (carbon number > 3) appeared in the liquid products. It indicates that not only decomposition reactions, but also polymerization reactions arise in this system.

3.4. Analysis of pulsed discharge in ethanol solution

To further clarify the process of hydrogen produced by pulsed spark discharge in ethanol solution, mechanism analysis was done in this section. Table 1 shows the variation in plasma reactor during 40 min discharge. The variation of pH and conductivity in ethanol solution indicate that acidic materials were formed after the discharge. Combined the results of liquid ingredient analysis shown in Fig. 10, macromolecular organic acid may be generated. The decrement of ethanol concentration was only about 1.5% after 40 min discharge, which conformed to the observation from Fig. 10. The ratio of percentage concentration of H_2 to CO approximated to 3:1, and the amount of hydrogen production in 40 min discharge was about 1.34 mol. The amount of carbon production was about 0.005 mol, which was far less than hydrogen production. Thus, the carbon was not the one of main products compared to H_2 and CO. The amount of methanol was about 0.38 mol, and the volume of produced methanol accounted for over 90% in consumed ethanol shown in Section 3.3. The molar ratio of H_2 to CH_3OH was close to 3:1. It illustrates that methanol was another main product. Except for methanol, the volume of other liquid products only occupied less than 10% revealed the truth that other liquid

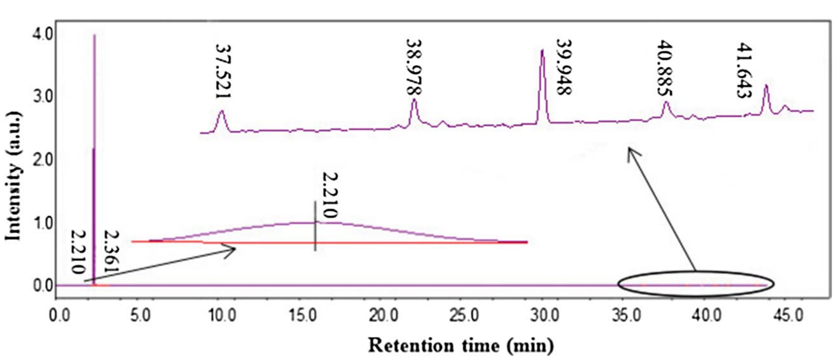

Fig. 10. Liquid ingredient analysis after 40 min discharge.

Table 1
The variation in plasma reactor during 40 min discharge.

Discharge time (min)	0	10	20	30	40
Flow rate of hydrogen (mL/min)	800	840	820	800	800
Percentage concentration of H_2 (%)	73.6	74.2	73.9	73.4	73.5
Percentage concentration of CO (%)	25.7	25	25.4	25.6	25.7
Amount of carbon production (mol)	0.005				
Variation of pH	7.76 → 5.53				
Variation of conductivity (μS/cm)	1.02 → 9.47				
Variation of ethanol concentration (%)	50 → 48.5				

products were not the main products. To sum up, H_2, CO, CH_3OH were the main products and C, C_2H_2, CO_2, macromolecular compounds were the secondary products. Considering the ratio among H_2, CO, CH_3OH, the main reaction occurred in ethanol solution was as below:

$$CH_3CH_2OH + 2H_2O \rightarrow 3H_2 + CO + CH_3OH \quad (5)$$

The produced methanol and some other macromolecular compounds can be further used for hydrogen production, which have been mentioned in some researches about hydrogen production by plasma reforming [36–40]. It is conducive to secondary hydrogen production and makes the raw material for hydrogen production last longer.

Pulsed discharge in liquid can form high-energy electrons thereby generating hydrated electrons and active substances, which can be used for material decomposition and formation [41–43]. By optical emission spectrographic analysis, $H^{\cdot}$, $O^{\cdot}$, $OH^{\cdot}$ can be found in ethanol solution by pulsed discharge presented in our previous work [22,23]. And the formation of $H^{\cdot}$ was regarded as an important step for hydrogen production. Fig. 11 shows the mechanism of hydrogen production from ethanol solution by pulsed spark discharge. High-energy electrons (e^{-*}) generated from pulsed spark discharge lead to decomposition of ethanol and water molecules. Hydrated electrons (e_{aq}^{-}) and many free radicals such as $H^{\cdot}$, $O^{\cdot}$, $OH^{\cdot}$ are formed, which result in the formation of various new substances. The main products contain H_2, CO, CH_3OH, and C, C_2H_2, CO_2, macromolecular compounds ($C_xH_yO_z$) can be also acquired.

3.5. Comparison with different methods of hydrogen production

Energy consumption is a main parameter for evaluating the methods of hydrogen production. Energy consumption of hydrogen production can be calculated by the output energy and hydrogen yield, the output energy can be gotten by Eq. (3) shown in Section 2. Table 2 shows the comparison with different methods of hydrogen production, which contains catalytic reforming (CR), water electrolysis (WE), arc discharge (AD), dielectric barrier discharge (DBD), microwave discharge (MD), glow discharge (GD), pulsed discharge (PD), micro arc discharge (MAD), and radio frequency discharge (RF). As the table shown, catalytic reforming, water electrolysis and discharge in gas for hydrogen production have relatively high energy consumption. Gas-liquid discharge is not suitable for hydrogen production owing to its low hydrogen yield and high energy consumption. High-frequency (≥kHz) discharge in liquid, such as RF, MD, presents high energy consumption. However, low-frequency (< kHz) discharge in liquid shows low energy consumption. Especially in our work, energy consumption of hydrogen production is only about 0.9 kWh/m^3, which is better than most existing methods. Flow rate of hydrogen is less than some work, so increasing the hydrogen yield is the target of further studies.

Table 2
The comparison with different methods of hydrogen production.

Methods	Material	Medium	Flow rate of hydrogen (L/min)	Energy consumption of hydrogen production (kWh/m^3 H_2)	References
CR	Methane	Gas	–	1.3–4.0	[44]
WE	Water	Liquid	–	2.7–6.3	[44]
AD	Ethanol	Gas	1.7	1.3	[45]
DBD	Methanol	Gas	0.01	27.2	[46]
MD	Ethanol	Gas	19.2	3.8	[47]
GD	Biomass	Gas	–	2.2	[48]
PD	Hydrocarbons	Gas-liquid	0.004	–	[13]
PD	Water	Gas-liquid	0.0005	416.7	[17]
GD	Methanol	Liquid	–	1.2	[15]
GD	Ethanol	Liquid	0.3	–	[16]
PD	Ethanol	Liquid	0.3	1.1	[44]
MAD	Ethanol	Liquid	1.1	18.5	[49]
RF	Glucose	Liquid	0.02	–	[20]
MD	Methane	Liquid	–	34.3	[19]
MD	Ethanol	Liquid	0.4	7.3	[18]
PD	Ethanol	Liquid	0.8	0.9	This work

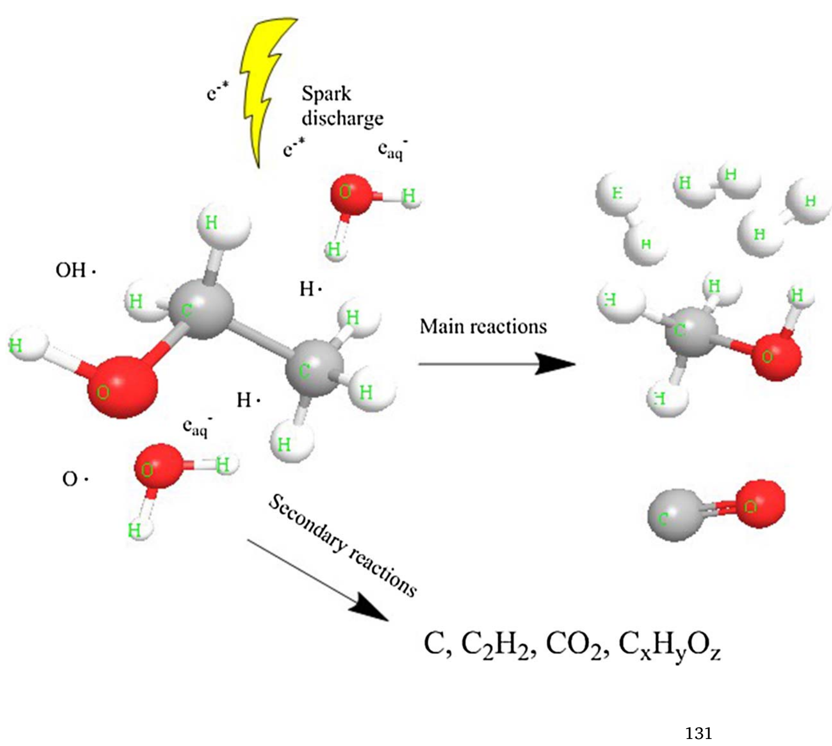

Fig. 11. The mechanism of hydrogen production from ethanol solution by pulsed spark discharge.

4. Conclusion

Hydrogen production from ethanol solution by pulsed spark discharge with needle-net configurations was studied in this work. A small-scale and high-efficiency plasma reactor was designed for hydrogen production, which is suitable for on-board hydrogen production to hydrogen fuel cells in automobiles. Characteristics of hydrogen production and discharge plasma were investigated. Besides hydrogen, other products were also researched by quantitative analysis. The main conclusions are as bellow:

(1) With needle-net configurations, hydrogen production can be easily exported from the plasma reactor thereby preventing hydrogen from consuming by the oxidizing active substances generated from pulsed discharge.
(2) Both flow rate and percentage concentration of hydrogen can be enhanced with the increase of energy density, but not much change with the increase of discharge time.
(3) The main products contain H_2, CO, CH_3OH, and the secondary products include C_2H_2, CO_2, macromolecular compounds, nano carbon particles.
(4) The mechanism of hydrogen production from ethanol solution by pulsed spark discharge was studied, which can be a good guidance for hydrogen production by plasma reforming.
(5) Energy consumption of hydrogen production by pulsed spark discharge in ethanol solution was only about 0.9 kWh/m^3 H_2, which is better than most existing methods.

In general, hydrogen production from ethanol solution by pulsed spark discharge with needle-net configurations possesses bright prospect owing to the high hydrogen yield, emerged nano carbon particles, low ethanol and energy consumption. However, some problems still need to be solved such as how to further enhance the hydrogen yield and how to utilize the produced nano carbon particles. Further researches will focus on these problems.

Acknowledgments

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