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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 byproducts, 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.

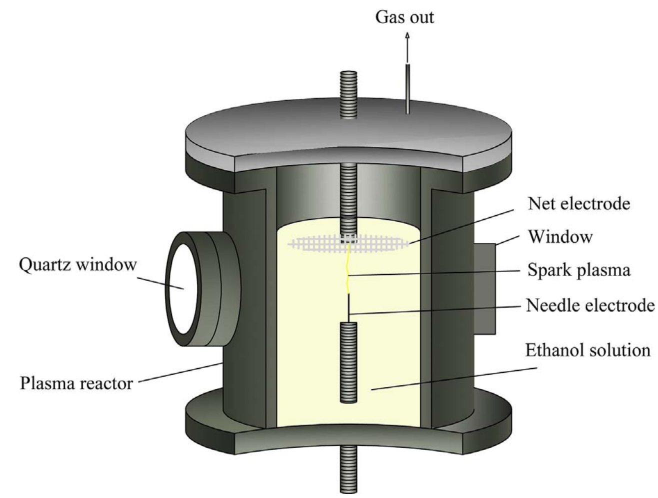

Fig. 1. Schematic diagram of experimental setup for pulsed spark discharge in ethanol solution for hydrogen production.

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).