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Hydrogen production from alcohol solution by microwave discharge in liquid

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ABSTRACT

Hydrogen, as an attractive energy carrier, is regarded as one of the best environmentally-friendly energy sources in the future. In the paper, it was reported that hydrogen was produced by 2.45 GHz microwave discharge in low carbon alcohol (methanol and ethanol) solution. The effects of microwave input power and concentration of alcohol solution on hydrogen production were studied. All results corresponded to the non-equilibrium plasma at reduced pressure (3000Pa). The gaseous products of microwave discharge in alcohol solution mainly included hydrogen, carbon monoxide, acetylene and carbon dioxide. The flow rates of total gaseous products and hydrogen increased with the increasing of power, while that increased firstly and then decreased with the increasing of concentration of alcohol solution. The percentage concentrations of hydrogen and carbon monoxide increased with the increasing of power, and when the concentration of alcohol solution was 8% v/v, the percentage concentrations of hydrogen and carbon monoxide reached a maximum value. As the power increased, the energy efficiency of hydrogen production improved significantly, and the energy efficiency of hydrogen produced from ethanol solution was higher than that from methanol solution with the same power. The energy efficiency of hydrogen production increased firstly and then decreased with the increasing of concentration of alcohol solution. In the paper, the best results of flow rate of hydrogen, percentage concentration of hydrogen and energy efficiency were 401.00 mL/min, 64.55% and 137.63 NL/kWh, respectively.

Introduction

Nowadays, the pollution problem and shortage of energy have become more and more prominent during last decade due to human demand for energy, therefore, the development of clean energy is extremely urgent. As the most potential energy carrier, hydrogen is regarded as one of the best environmentally-friendly energy sources in the future. To date, multiple methods to produce hydrogen have been studied by many experts and researchers at home and abroad.

The traditional method of production hydrogen is catalytic steam reforming that depends on fossil fuels, which is also contribution to the environmental pollution. Besides, catalytic steam reforming generally requires high temperature, high

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pressure and heavy equipment investment, which limits the large-scale application of hydrogen production [1–3]. Although bio-hydrogen production is an environment friendly method, the yield of hydrogen is low and unstable [4–7]. High purity hydrogen can be got by water electrolysis, however, the energy consumption is twice as much as that of catalytic steam reforming, which means that the further development of hydrogen production by water electrolysis encounters a “bottleneck” recently [8–12].

Hydrogen production by non-thermal discharge has opened up a new way for development and utilization of hydrogen energy. At present, many scholars have tried to produce hydrogen using gliding arc discharge [13,14], corona discharge [15], dielectric barrier discharge [16,17], glow discharge [18], microwave discharge in gas [19–23] and so on. In general, the non-thermal discharge mentioned above need to consume a large number of external energy to vaporizing alcohol or set a series of carrier gases as plasma is generated in gas phase. Besides, the rate of hydrogen production and energy efficiency are low because of low density of plasma generated in gas. Thus, discharge in liquid directly is expected to resolve the problem above in the future.

Microwave discharge in alcohol solution is a new non-thermal discharge technology [24–27], which make up the shortcoming of low density plasma generated in gas as plasma can be generated directly in alcohol solution. Therefore, it is reasonable to think that microwave discharge in alcohol solution provides an effective method for hydrogen production.

In the paper, hydrogen was produced by 2.45 GHz microwave discharge in alcohol solution. The effects of microwave input power and concentration of alcohol solution on hydrogen production were studied. In addition, the mechanism of hydrogen production by microwave discharge in alcohol solution was analyzed preliminarily to lay the foundation for further development of hydrogen production technology.

Experimental

System of microwave discharge in alcohol solution

Fig. 1 was the schematic of the plasma reactor and vertical profile of the electrode. The height and diameter of the reactor were 16 cm, 15 cm respectively. The electrode of microwave discharge in alcohol solution included the inner electrode which was made of tungsten, the insulating material, the outer electrode which was made of stainless steel, sealing block and fixed plate with mounting hole. The height and diameter of the inner electrode were 63 mm, 2 mm respectively, and the height and diameter of outer electrode were 56 mm, 8 mm respectively. The insulating material between the inner electrode and outer electrode included ceramic tube and silicone. In the experiment, 2450 MHz microwave generated by microwave generator were transmitted into the inner electrode through waveguide and coaxial cable. The plasma was generated on the top of the inner electrode in alcohol solution in which the solvent is water. The method of ignition is self-ignition. The initial solution temperature measured by two thermocouples was 20 °C which was same with the room temperature. The internal pressure of reactor was controlled at 3000 Pa using dry vacuum pump. Different concentration gradients of methanol and ethanol solutions were designed respectively in the reactor, and the solution volume of single experiment was 2 L which was 70.75% of reactor volume. And the volume of space between the liquid surface and the pump was 0.827 L, which meant that the distance between the liquid surface and the pump was 4.68 cm. The standing-wave ratio (SWR) was measured by Agilent network analyzer, and the initial SWR was 1.512 which meant the reflection coefficient was 20.4%.

Analysis techniques

Fig. 2 showed the schematic diagram of hydrogen generated by microwave discharge in alcohol solution. A flow rate meter was connected with the outlet of dry vacuum pump to monitor the flow rate of the gas produced by microwave discharge in alcohol solution. The gas from the reactor was collected and injected into mass spectrometer (HIDEN QIC20) and gas chromatograph with thermal conductivity detector (TCD) (SHIMADZU GC-2014C) for qualitative and quantitative analysis. A pressure maintaining valve was set between the flow rate meter and the mass spectrometer to keep sample injection stable and realize the on-line monitoring. Besides, the emission spectrometer (PMA-11, HAMAMATSU co.) was used to monitor the emission spectra of all kinds of particles generated by microwave discharge in alcohol solution. A probe fixed at constant distance from the quartz window of reactor was connected to monochromator with optical fiber, and the distance between the probe and the inner electrode was 130 mm. The exposure time of emission spectrometer was 30 ms. The number of elements and wavelength accuracy of the emission spectrometer were 1024ch and ±0.75 nm, respectively. In the experiment, each value was the average of three replicates.

In the paper, the percentage concentrations of hydrogen, carbon monoxide and other produced gases were defined in this work as:

$$\text{Percentage concentration}(\%) = \frac{\text{the flow rate of hydrogen, carbon monoxide or other gases}}{\text{the flow rate of total gases}} \times 100 \quad (1)$$

In addition, 3D High Frequency Structure Simulation (HFSS) was also used to simulate the electric field to analyze the process of microwave discharge in alcohol solution.

Results and discussion

Discharge process and phenomenon

Fig. 3 presented the electric fields of HFSS simulation with bubble and without bubble. In the process of microwave discharge in alcohol solution, many bubbles will be generated on the tip of the inner electrode [25]. Then, a large number of