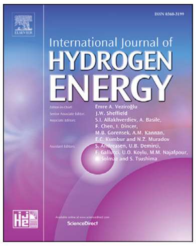
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 43 (2018) 4305–4310

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Effect of catalytic electrode and plate for methanol decomposition by in-liquid plasma

Ryoya Shiraishi[*], *Shinfuku Nomura*, *Shinobu Mukasa*, *Ryuya Nakano*, *Ryo Kamatoko*

Graduate School of Science and Engineering, Ehime University, Japan

ARTICLE INFO

Article history:
Received 8 November 2017
Received in revised form
5 January 2018
Accepted 11 January 2018
Available online 15 February 2018

Keywords:
Hydrogen
Catalyst
In-liquid plasma
Methanol

ABSTRACT

To enhance hydrogen production efficiency by in-liquid plasma, the method inserting catalytic metal into in-liquid plasma reaction field was considered. To retain a bubble at the tip of in-liquid plasma electrode, a plate is fixed over the electrode. That plate and electrode are composed of a catalytic metal. Methanol is decomposed by in-liquid plasma, and the gas generation rate and composition rate are measured. The gas is composed of 67% H_2, 30% CO, and 3% other. This rate is independent of the material of the electrode or plate. The plate enhances the hydrogen production rate. When the plate and electrode are composed of Ni (0.37 Nm^3/kWh), the maximum hydrogen production rate is obtained.

Introduction

In-liquid plasma is the technology that generates a plasma of several thousand K in a liquid which can decompose water, alcohol, oil and almost anything [1–7]. With this method everything is converted to gas by thermal decomposition within the in-liquid plasma. Therefore, should the target material contain hydrogen, hydrogen gas can be obtained by in-liquid plasma method. A particularly attractive target product for this is waste oil, because this method disposes of the waste oil while generating hydrogen gas at the same time. By using in-liquid plasma, hydrogen can be generated from various material not currently used such as waste oil. And this method does not need big and complicated facilities such as commercial methane steam reforming plant. Furthermore, there is big room for improvement in efficiency. So hydrogen production by in-liquid plasma is potentially economical. However, at present, hydrogen production efficiency using in-liquid plasma is lower than that for water electrolysis. For practical purposes, efficiency enhancement, optimization of various condition and simultaneous synthesis of valuables being researched [8–11].

Commercial production of hydrogen gas is conducted using the methane steam reforming method [12–14]. To enhance reforming efficiency, various catalysts have been researched, with nickel and cobalt catalysis typically used [15–19]. Additional research has been conducted regarding hydrogen production using biomass steam reforming with nickel or platinum catalysts [20–24]. On the other hand, the plasma decomposition method can decompose biomass directly with a one-step hydrogen production method. The plasma decomposition reaction may be enhanced when a catalyst is inserted in plasma reaction field, but little research investigating the catalytic effect on plasma reaction can be found. Nozaki et al., has conducted research about inserting a catalyst into the

---

[*] *Corresponding author.*
E-mail address: shiraishi.ryoya.kg@ehime-u.ac.jp (R. Shiraishi).

https://doi.org/10.1016/j.ijhydene.2018.01.060

plasma reaction field [25,26]. In this research, discharge was conducted on a methane decomposition reaction field with a nickel catalyst inserted, resulting in an enhanced hydrogen yield, with the decomposition reaction occurring at a lower temperature than with the nickel catalyst alone. Enhancement of the hydrogen production rate is expected when a catalyst is inserted to in-liquid plasma reaction field as well.

In this research, a method to insert catalysts into plasma reaction field is considered. Because in-liquid plasma is generated inside bubbles in liquid, catalytic metal particles cannot enter to the bubble when catalytic metal particles are dispersed in the liquid [4]. Rather, the method of fixing a plate over the electrode both composed of a catalytic metal is considered. Because the effectiveness of nickel-based catalysts for methanol decomposition is well known [27–31], in-liquid plasma methanol decomposition is conducted using a nickel electrode and plate. Then, to evaluate the nickel catalytic effect on in-liquid plasma methanol decomposition, comparison of other materials used for plate and electrode was conducted regarding gas generation rates.

Experimental method

The schematic image of the experimental setup is shown in Fig. 1. A 3 mm diameter electrode is inserted from bottom of reactor vessel and a 25 × 10 × 2 mm plate is fixed from 3 to 5 mm from the top of the electrode. Plasma heat generates bubbles around the top of the electrode. These bubble are retained by the plate, thus the in-liquid plasma is stabilized [32]. A volume of 100 mL of methanol was injected into the reactor vessel completely immersing the electrode. The reactor vessel pressure is reduced to 0.01 MPa by an aspirator. Electric current of 200 W, 27.12 MHz was supplied via matching box then plasma is generated at top of the electrode. After the stability of the plasma is confirmed, the valve in front of the aspirator is closed allowing the reactor vessel inner pressure return to atmospheric pressure. Once plasma is generated, the methanol is rapidly decomposed and converted to gas. This gas is collected by water replacement, and the time it takes to collect 150 mL of gas is measured. The gas composition rate is measured by gas chromatograph. And the temperature of the reverse side of the plate is measured by a K-type thermocouple.

In this experiment, copper and nickel are used for the electrode, and the plate was composed of solid copper, solid nickel, porous ceramics, porous bronze and porous nickel. To investigate the effect of the nickel catalyst, gas generation rates for each combination of plate and electrode are compared. Combinations of plates and electrodes are shown in Table 1.

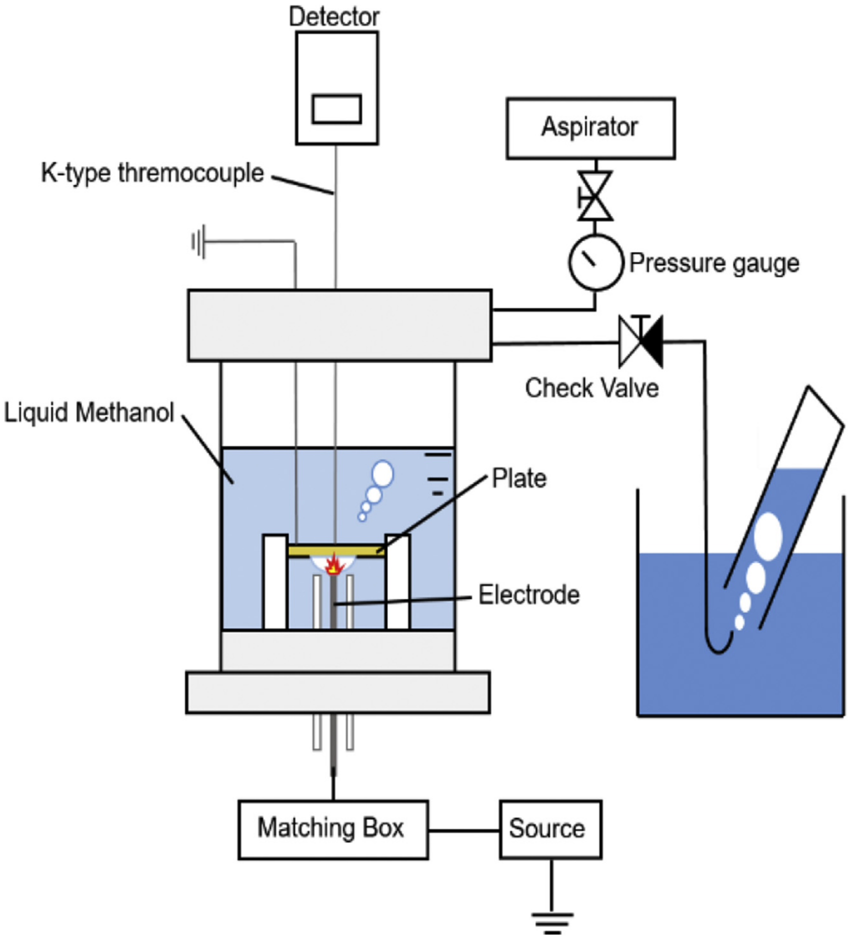


Fig. 1 – Schematic image of experimental set up.