Energy 51 (2013) 230–236

Contents lists available at SciVerse ScienceDirect

Energy

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

Hydrogen generator system using Ru catalyst for PEMFC (proton exchange membrane fuel cell) applications

Zhen-Ming Huang [a], Ay Su [a,*], Ying-Chieh Liu [b]

[a] Department of Mechanical Engineering, Yuan Ze University, Chung-Li 32003, Taiwan, ROC
[b] The Fuel Cell Center, Yuan Ze University, Chung-Li 32003, Taiwan, ROC

ARTICLE INFO

Article history:
Received 17 August 2012
Received in revised form
28 December 2012
Accepted 5 January 2013
Available online 4 February 2013

Keywords:
Sodium borohydride
Hydrogen generation
Ru catalyst
PEMFC (proton exchange membrane fuel cell)

ABSTRACT

High purity hydrogen produced by hydrolysis of sodium borohydride can be used directly in (proton exchange membrane) PEM fuel cells for portable devices and automotive applications. The advantages of high storage capacity, quickly start, controllable reaction and mild condition, hydrogen generation by catalytic hydrolysis of chemical hydride, such as sodium borohydride, has attracted much attention for development recently.

Development and optimal design of a hydrogen generator based on (sodium borohydride) $NaBH_4$ using Ru catalyst are reported in the present study. A multi-layer coating process of Ru on Ni foam was employed to enhance its capability for hydrogen generation cycles. The optimal deposition density of Ru particles on Ni foam was confirmed by the SEM (scanning electron microscopy) morphology. The cycling generation for the steady state reaction can be maintained at least 10 times. The activity of Ru catalyst during a hydrogen generation process was examined in a continuous flow reactor. In general, $NaBH_4$ solution cannot be fully utilized through the hydrogen generator, as a result, the effluent from the generator may continue to dissociate, which turns into hydrogen leakage. A secondary reactor was therefore installed after the primary generator to collect the remaining hydrogen. The reactant solution containing 20 wt.% $NaBH_4$ and 3 wt.% NaOH was introduced into the structured catalyst at a constant flow rate using a liquid pump, and H_2 rate of 1.72 L min^{-1} (0.43 L (H_2) min^{-1} g^{-1} catalyst). The conversion of $NaBH_4$ from flow rates of hydrogen was about 92.2%.

The present hydrogen generator was later integrated with a 100 W PEM fuel cell and the performance of the integrated system was investigated. The hydrogen produced from $NaBH_4$ has high purity and saturated humidity; therefore, it can be directly used as the fuel for PEMFCs (proton exchange membrane fuel cells), which in general require humidified hydrogen. It is found that for cell voltage above 0.6 V, the performance of cell using $NaBH_4$ hydrogen is 103.45 W, versus 99.9 W with cylinder hydrogen. The cell performance using the hydrogen from $NaBH_4$ is 3.6% higher than that using cylinder hydrogen.

1. Introduction

Hydrogen is known to be an ideal fuel that provides zero-emission energy. The chemical energy of hydrogen can be directly converted into electric energy by a (proton exchange membrane) PEM fuel cell with water as the only byproduct [1–3]. Hydrogen possesses merits of being non-toxic, high energy per unit mass, and the energy produced being free of greenhouse gases and air pollutants such as CO and NO_x. Hydrogen fuel cells have advantages of high power density and long range, which make them particularly suitable for portable devices and automobiles. The (membrane electrode assembly) MEA is the core of PEMFC (proton exchange membrane fuel cell) stack for generating electrical and thermal energy [4–6]. An MEA consists of anode and cathode catalyst layers, (proton exchange membrane) PEM and electrode backing/(gas diffusion layers) GDL [7]. A fuel cell power sources have three major components: (A) fuel supply, (B) fuel cell, and (C) control and power conditioning electronics. Storage of hydrogen has been recognized as a key technical challenge for the commercialization of portable fuel cell systems. Currently some existing methods for storing hydrogen, e.g. high pressure tanks, activated carbon and nanoscale materials, are not viable means for long-term hydrogen storage. Micro-reformers, which convert hydrocarbon fuels into hydrogen-rich mixtures, are rather problematic because of a number of technical issues. A reformer system is a complex device, which includes vaporizer, heater, reactor,

---

* Corresponding author. Tel.: +886 3 4638800x2460; fax: +886 3 4555574.
E-mail address: meaysu@saturn.yzu.edu.tw (A. Su).

0360-5442/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.energy.2013.01.020

combustor, heat-exchanger, and CO remover. These make it difficult to reduce the total weight and dimensions of the system [8]. Hydrogen produced by reforming hydrocarbon fuels often contains CO, which causes severe poisoning of the catalysts in a fuel cell.

Hydrogen generation/storage constitutes a significant portion of weight of a fuel cell system. Therefore, it is important to choose an appropriate hydrogen source. In recent years, chemical hydrides have emerged as a promising option for hydrogen generation/storage because of their high energy density. Chemical hydrides ($NaAlH_4$, $NaBH_4$, $LiBH_4$, LiH, $LiAlH_4$, NaH, KBH_4, etc.) are good candidates of hydrogen generation materials at room temperature [9,10] and they have received much attention lately [11,12]. $NaBH_4$ alkaline solution is stable, nonflammable, non-toxic, and has high hydrogen capacity (10.8 wt.%). From a system management perspective, it is easy to control hydrogen generation rate by catalytic hydrolysis. At present, the borohydrides have been proven an ideal carrier to provide stable, high purity hydrogen. Hydrogen generation by hydrolysis of (sodium borohydride) $NaBH_4$ has been demonstrated for PEM fuel cells [13,14]. Because of its high hydrogen storage capacity, controllable reaction and mild operating conditions, hydrogen generation via catalytic hydrolysis of $NaBH_4$ has attracted much attention recently. $NaBH_4$ solutions, which have a high pH value, generate a significant amount of hydrogen under ambient conditions when they are in contact with specific catalysts [15,16]; when the catalyst is removed from the $NaBH_4$ solution, hydrogen generation ceases. It is easy to control hydrogen generation rate by the hydrolysis reaction:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \tag{1}$$

At room temperatures, the rate of hydrolysis reaction (1) is slow without the presence of catalysts. Various catalysts such as Ru catalysts [17–20], Pt–$LiCoO_2$ catalysts [21,22], Co–B catalysts [23–26], CoB/alginate beads [27], Ni-based catalyst [28], Co–W–B catalysts [29], Ru/G catalysts [30], Co–P–B catalysts [31] have been tested as the catalysts for $NaBH_4$ hydrolysis. Since the hydrolysis of $NaBH_4$ is highly exothermic, the reactor temperature often exceeds 100 °C, especially when the reactor is operated at a continuous flow mode [32]. The catalysts in the hydrolysis of $NaBH_4$ are exposed to a hot and caustic environment; therefore, durability of these catalysts is crucial for practical applications.

Based on previous studies using various metal salts, Ru and Rh have been identified to have high capability of hydrogen generation from $NaBH_4$ solutions [21]. Ru in general has lower cost and higher hydrogen generation rate than metallic Rh. In the present study, Ni foam was chosen as the substrate supporting the catalysts because of its high thermal capacity and chemical stability in the reaction environment. In the present study, Ru catalyst was coated by chemical plating on Ni foam substrates. A PEM fuel cell was connected with such hydrogen generation device, and its performance was compared to hydrogen from a gas cylinder. Our experimental results show that Ru catalyst yields high catalytic performance and good durability for the hydrolysis reaction of $NaBH_4$. The present hydrogen generator was later integrated with a 100 W PEM fuel cell and the optimum performance of the integrated system was investigated.

2. Experimental setup

2.1. Ru catalyst preparation on Ni foam

In the present study, Ru catalyst was coated on Ni foam using the electroless plating method. The composition of Ru catalyst used in this work and the conditions of the bath solution are shown in Table 1. Ni foam was chosen to be the catalyst support material because of its porous structure, low density, high thermal conductivity and chemical stability under the hydrolysis conditions. The Ni foam has open pore structure with an area density approximately 500 g/m^2 and average pore size of 0.2–0.5 mm. The size of the plate-type Ni foam used in the present study is 20 mm (*L*) × 30 mm (*W*) × 1.4 mm (*H*), and weighs 300 ± 10 mg per piece. Before combining with Ru catalyst, the Ni foam was cleaned by an ultrasonic cleanser in ethanol bath for 60 min, thereafter it was immersed in a 0.01 mol/L HCl solution for 30 min. The Ni foam was then dipped into $RuCl_3$ solution maintained at 120 °C for 30 min for complete replacement reaction. The chemical reaction of the electroless plating process is:

Table 1
Ru catalyst composition and operating conditions of the bath.

Chemicals	Concentration (g/mL)
CH_3CH_2OH	20
H_2O	80
$RuCl_3 \cdot \times H_2O$	0.5
Ni foam	300 ± 10 mg
pH value (adjusted using $NH_3 \cdot\ H_2O$)	8
Bath temperature (°C)	100–120
Plating time (h)	0.5

$$3Ni + 2Ru^{3+} \rightarrow 2Ru + 3Ni^{2+} \tag{2}$$

This process was repeated several cycles to reach the desired Ru loading by microscopic analysis. The Ni/Ru foam was then dried under vacuum at 100 °C for 2 h. The morphology and physical properties of catalyst adhesion were characterized by several analytical methods. (Field-Emission Scanning Electron Microscopy) FE-SEM and (energy dispersive X-ray) EDS were employed to identify catalyst surface and composition, respectively. The loading of Ru on Ni support was measured by (inductivity coupled plasma optical emission spectrometer) ICP/OES. For this analysis, a small amount of the sample was dissolved by strong acid (HNO_3) and then diluted by the analyzer.

2.2. Hydrogen production system

The activity of Ru catalyst during the hydrogen generation process was examined in a continuous flow reactor. The hydrogen generation system consisted of a fuel tank, fuel feeding pump, hydrogen generation reactor, byproduct tank, gas coolant, and mass flow meter. Fig. 1 shows a schematic diagram of the experimental setup. The catalyst plate (70 mm × 46 mm × 20 mm) was arranged

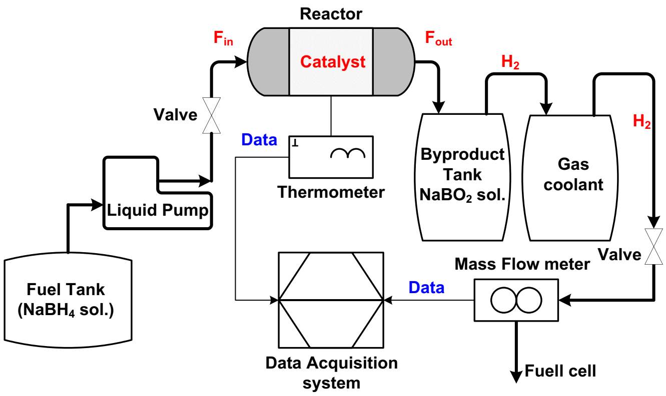

Fig. 1. Schematic diagram of experimental setup for measuring hydrogen generation rate.