



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# Electrocatalysts supported on multiwalled carbon nanotubes for direct borohydride–hydrogen peroxide fuel cell

Taek Hyun Oh, Bosun Jang, Sejin Kwon\*

Division of Aerospace Engineering, School of Mechanical, Aerospace and Systems Engineering, KAIST, 335 Gwahangno, Yuseong-gu, Daejeon 305-701, Republic of Korea

## ARTICLE INFO

### Article history:

Received 6 December 2013

Received in revised form

21 January 2014

Accepted 19 February 2014

Available online 18 March 2014

### Keywords:

Sodium borohydride

Hydrogen peroxide

Electrocatalyst

Multiwalled carbon nanotubes

Direct borohydride–hydrogen

peroxide fuel cell

## ABSTRACT

Electrocatalysts of Rh, Ru, Pt, Au, Ag, Pd, Ni, and Cu supported on multiwalled carbon nanotubes for direct borohydride–hydrogen peroxide fuel cells are investigated. Metal/ $\gamma$ - $\text{Al}_2\text{O}_3$  catalysts for  $\text{NaBH}_4$  and  $\text{H}_2\text{O}_2$  decomposition tests are manufactured and their catalytic activities upon decomposition are compared. Also, the effects of XC-72 and multiwalled carbon nanotube (MWCNT) carbon supports on fuel cell performance are determined. The performance of the catalyst with MWCNTs is better than that of the catalyst with XC-72 owing to a large amount of reduced Pd and the good electrical conductivity of MWCNTs. Finally, the effect of electrodes with various catalysts on fuel cell performance is investigated. Based on test results, Pd (anode) and Au (cathode) are selected as catalysts for the electrodes. When Pd and Au are used together for electrodes, the maximum power density obtained is  $170.9 \text{ mW/cm}^2$  ( $25^\circ\text{C}$ ).

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

Research in support of space exploration has been widely conducted. Solar cells, batteries, and atomic batteries are used for unmanned systems such as exploration robots but these devices have some disadvantages. For example, solar cells cannot be used in an environment without sunlight, batteries have low gravimetric energy density, and atomic batteries have some safety problems.

In the aviation field, research on high-altitude long-endurance unmanned aerial vehicles (HALE UAVs) for surveillance and reconnaissance has been conducted. HALE UAVs require power sources with high energy density because

these UAVs are continuously operated at an altitude of 20 km over three days.

Although fuel cells in general have attracted attention as new power sources with high energy density for aerospace systems, proton exchange membrane fuel cells (PEMFCs) have some disadvantages. When gaseous hydrogen and oxygen are used as fuels for PEMFCs, the volumetric energy density of the fuel cell system decreases. When liquid hydrogen and oxygen are used, the system becomes complex owing to the need for a low storage temperature ( $-253^\circ\text{C}$ ) and mission duration is limited owing to boil-off. Countries with advanced technology in the field of aerospace engineering such as the USA [1–8], India [9–15], China [16–25], the UK [26,27], and Portugal [28] have performed many studies on the use of direct

\* Corresponding author. Tel.: +82 42 350 3721; fax: +82 42 350 3710.

E-mail address: [trumpet@kaist.ac.kr](mailto:trumpet@kaist.ac.kr) (S. Kwon).

<http://dx.doi.org/10.1016/j.ijhydene.2014.02.117>

0360-3199/Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

borohydride–hydrogen peroxide fuel cells (DBPFCs) to solve the problems of PEMFCs.

Power density ( $\text{mW}/\text{cm}^2$ ) and energy density ( $\text{Wh}/\text{kg}$  or  $\text{Wh}/\text{L}$ ) are criteria that represent the performance of a fuel cell system. It has been reported that the power density and energy density of DBPFC systems are good. Fuel cells for small mobile systems are direct methanol fuel cells (DMFCs) and PEMFCs. The maximum power density obtained with DBPFCs is  $680 \text{ mW}/\text{cm}^2$  [2], which is much higher than that of DMFCs ( $30\text{--}100 \text{ mW}/\text{cm}^2$ ) and comparable to that of PEMFCs ( $300\text{--}1000 \text{ mW}/\text{cm}^2$ ). Miley et al. [1] predicted a high energy density of  $1000 \text{ Wh}/\text{kg}$ , which is much higher than that of Li batteries ( $250 \text{ Wh}/\text{kg}$ ).

DBPFCs have many advantages. The theoretical voltage of DBPFCs is higher than that of other fuel cells ( $\text{CH}_3\text{OH}/\text{O}_2$ :  $1.19 \text{ V}$ ,  $\text{H}_2/\text{O}_2$ :  $1.23 \text{ V}$ ,  $\text{HCOOH}/\text{O}_2$ :  $1.45 \text{ V}$ ,  $\text{N}_2\text{H}_4/\text{O}_2$ :  $1.56 \text{ V}$ ,  $\text{NaBH}_4/\text{O}_2$ :  $1.64 \text{ V}$ , and  $\text{NaBH}_4/\text{H}_2\text{O}_2$ :  $3.01 \text{ V}$ ) [29]. Reformers are unnecessary because sodium borohydride ( $\text{NaBH}_4$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) are used directly. Cooling and storage are easy owing to the use of liquid fuel. DBPFCs also have good response characteristics because they are operated at low temperatures ( $20\text{--}80 \text{ }^\circ\text{C}$ ).  $\text{NaBH}_4$  and  $\text{H}_2\text{O}_2$  are environmental friendly, and the cost of  $\text{NaBH}_4$  and  $\text{H}_2\text{O}_2$  can be reduced through recycling and mass production.  $\text{H}_2\text{O}_2$  is widely used for aerospace systems [30,31]. Consequently, storage systems can be simplified through system integration.

However, DBPFCs also have some problems.  $\text{NaBH}_4$  and  $\text{H}_2\text{O}_2$  concentrations have to increase in order to improve the energy density of the fuel cell system. However, as the fuel concentration increases, the performance of the fuel cells decreases and the cost increases owing to the decomposition of  $\text{NaBH}_4$  and  $\text{H}_2\text{O}_2$  and fuel cross over. Also, products such as  $\text{NaBO}_2$  are precipitated on electrode catalysts and membranes. Although DBPFCs have some problems now, those problems will be solved through ongoing research [32–39].

Electrocatalysts supported on multiwalled carbon nanotubes (MWCNTs) for DBPFCs were investigated in this study. First, various metal/ $\gamma\text{-Al}_2\text{O}_3$  catalysts for  $\text{NaBH}_4$  and  $\text{H}_2\text{O}_2$  decomposition tests were manufactured in order to compare the effect of catalytic activity on fuel decomposition. Second, MWCNTs and XC-72 were used as catalyst supports for DBPFCs. The effect of MWCNTs and XC-72 on fuel cell performance was determined through performance tests and various analyses. Third, electrodes with various catalysts were manufactured in order to compare the effect of catalytic activity on direct  $\text{NaBH}_4$  oxidation and  $\text{H}_2\text{O}_2$  reduction. Optimum catalysts for anode and cathode electrodes were selected based on test results.

## 2. Experimental

### 2.1. Preparation of metal/ $\gamma\text{-Al}_2\text{O}_3$ catalysts

Various metal/ $\gamma\text{-Al}_2\text{O}_3$  catalysts for  $\text{NaBH}_4$  and  $\text{H}_2\text{O}_2$  decomposition tests were manufactured in order to compare the effect of catalytic activity on fuel decomposition. The incipient wetness method was used in this study [40]. First,  $\text{Al}_2\text{O}_3$  (Alfa Aesar, USA) was dried to eliminate any remaining water and hydroxyl groups. The  $\text{Al}_2\text{O}_3$  was heated at a rate of  $2 \text{ }^\circ\text{C}/\text{min}$  to

$300 \text{ }^\circ\text{C}$  and maintained at that temperature for 2 h. Rh, Ru, Pt, Au, Ag, Pd, Ni and Cu catalysts were used. The catalyst precursors used for catalyst manufacture were rhodium chloride ( $\text{RhCl}_3$ , Alfa Aesar, USA), ruthenium chloride ( $\text{RuCl}_3$ , PM Research, Korea), chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ , PM Research, Korea), gold chloride ( $\text{AuCl}_3$ , Alfa Aesar, USA), silver perchlorate ( $\text{AgClO}_4$ , Kanto Chemical, Japan), palladium chloride ( $\text{PdCl}_2$ , Alfa Aesar, USA), nickel chloride ( $\text{NiCl}_2$ , Alfa Aesar, USA), and copper chloride ( $\text{CuCl}$ , Alfa Aesar, USA). Each catalyst solution was made to manufacture 1 wt% catalysts. Each catalyst precursor was dissolved in 15 g of distilled water ( $\text{H}_2\text{O}$ , OCI, Korea).  $\text{Al}_2\text{O}_3$  5 g was immersed in each catalyst solution for 24 h to enable sufficient absorption of the solution. Then, the metal/ $\gamma\text{-Al}_2\text{O}_3$  catalysts were heated to  $150 \text{ }^\circ\text{C}$  at a rate of  $2 \text{ }^\circ\text{C}/\text{min}$  and held at  $150 \text{ }^\circ\text{C}$  for 12 h to evaporate any remaining water. After drying, calcination was performed to remove unnecessary components. The catalysts were then heated to  $500 \text{ }^\circ\text{C}$  at a rate of  $2 \text{ }^\circ\text{C}/\text{min}$  and maintained at  $500 \text{ }^\circ\text{C}$  for 3 h, after which they were slowly cooled to room temperature in a furnace. Reduction was also conducted after calcination. The catalysts were heated to  $500 \text{ }^\circ\text{C}$  at a rate of  $2 \text{ }^\circ\text{C}/\text{min}$  and maintained at  $500 \text{ }^\circ\text{C}$  for 3 h, after which they were slowly cooled to room temperature in a furnace. A mixed gas consisting of 4%  $\text{H}_2$  and 96%  $\text{N}_2$  was supplied to the furnace at a rate of  $200 \text{ mL}/\text{min}$  during the reduction process. The manufactured catalysts were stored in sealed plastic bags until the experiment.

### 2.2. Preparation of metal/MWCNTs and metal/XC-72 electrodes

Electrodes were manufactured with Rh, Ru, Pt, Au, Ag, Pd, Ni, and Cu catalysts and MWCNT (Carbon Nano-material Technology, Korea) and XC-72 carbon black (Vulcan, Fuel Cell Earth, USA) supports. Electrodes were manufactured under identical conditions in order to compare the effect of catalytic activity on  $\text{NaBH}_4$  oxidation and  $\text{H}_2\text{O}_2$  reduction.

First, catalysts were reduced on the carbon supports by a  $\text{NaBH}_4$  (Samchun Chemical, Korea) solution. The carbon supports were heated to  $400 \text{ }^\circ\text{C}$  at a rate of  $2 \text{ }^\circ\text{C}/\text{min}$  and maintained at  $400 \text{ }^\circ\text{C}$  for 4 h to remove impurities. The catalyst solutions were made to manufacture electrodes with  $1 \text{ mg}/\text{cm}^2$  catalyst. For each catalyst solution, the respective catalyst precursor was dissolved in 20 g of distilled water. Then, sodium citrate ( $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ , Junsei Chemical, Japan) was added to the catalyst solutions in a mole ratio of 1:1 in order to improve catalyst dispersion. The carbon supports were then added to the catalyst solutions at a weight ratio of 5 (carbon supports):1 (catalyst). The solutions were then immersed in an ultrasonic bath (JAC-1505, Kodo Technical Research, Korea) for 30 min to disperse the carbon supports. After agitation, the catalysts were reduced on the carbon supports by a  $\text{NaBH}_4$  solution, which was added to the catalyst solutions at a rate of  $20 \text{ mL}/\text{h}$  for 1 h using a syringe pump (KDS 100, Kd Scientific, USA). Twenty grams of a  $\text{NaBH}_4$  solution was made and the mole ratio of catalyst and  $\text{NaBH}_4$  was 1 (catalyst):10 ( $\text{NaBH}_4$ ). Then, the catalyst solutions were agitated with a magnetic stirrer at  $100 \text{ rpm}$  for 5 h to allow sufficient reduction of the respective catalyst. A hot plate (RET Control-VISC C, IKA, Germany) was used for agitation. The resulting catalysts were filtered and

Download English Version:

<https://daneshyari.com/en/article/1273452>

Download Persian Version:

<https://daneshyari.com/article/1273452>

[Daneshyari.com](https://daneshyari.com)