



Performance evaluation of direct borohydride–hydrogen peroxide fuel cells with electrocatalysts supported on multiwalled carbon nanotubes



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ABSTRACT

The performance of direct borohydride–hydrogen peroxide fuel cells with electrocatalysts supported on multiwalled carbon nanotubes is evaluated under various conditions. Electrocatalysts are reduced on multiwalled carbon nanotubes by NaH_2PO_2 and electrodes are investigated using scanning electron microscopy, energy dispersive spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and fuel cell testing. The maximum power density decreases with increasing NaBH_4 concentration, likely owing to increases in NaBH_4 decomposition and crossover rates and to production of increasing amounts of NaBO_2 . In contrast, the maximum power density increases with increasing H_2O_2 concentration, likely owing to increases in reactant concentrations. Moreover, increased operating temperatures improve decomposition and electrochemical reaction rates. A thin membrane increases fuel crossover, whereas a thick membrane decreases the maximum power density; consequently, the Nafion 212 membrane is the optimal thickness for use in fuel cells such as those studied here. Under selected conditions, the maximum power density is 101.9 mW/cm^2 . As operation time increases, fuel cell performance is degraded by oxidation and Na deposition.

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1. Introduction

Energy is critical in the mission ability of aerospace systems [1,2]. Particularly, power sources with higher energy density are required, yet existing examples of such power sources have some limitations. For example, internal combustion engines are inefficient, batteries typically have low gravimetric energy density, atomic batteries are hazardous, and solar cells cannot be used in the dark. Although DMFCs (direct methanol fuel cells) [3,4] and PEMFCs (proton exchange membrane fuel cells) [5–7] can be used for mobile systems, they also have some disadvantages. In particular, DMFCs have low power density ($30\text{--}100 \text{ mW/cm}^2$) and limited power range ($0\text{--}1 \text{ kW}$), whereas PEMFC (proton exchange membrane fuel cell) systems that use gaseous hydrogen and oxygen as fuels have low volumetric energy density. Conversely, PEMFC systems that use liquid hydrogen and oxygen are complex, and the storage period of liquid hydrogen is short owing to boil-off

losses. Accordingly, DBPFCs (direct borohydride–hydrogen peroxide fuel cells) have attracted considerable attention for use as AIP (air-independent propulsion) systems thanks to their many advantages over existing power sources.

In contrast to PEMFCs, which use gaseous hydrogen and oxygen as fuels, DBPFCs use NaBH_4 (sodium borohydride) and H_2O_2 (hydrogen peroxide) solutions as fuels. As shown in Eqs. (1) and (2), the NaBH_4 solution in DBPFCs is oxidized directly by an anode catalyst, whereas the H_2O_2 solution is reduced directly by a cathode catalyst.

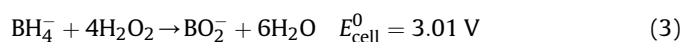
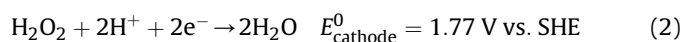
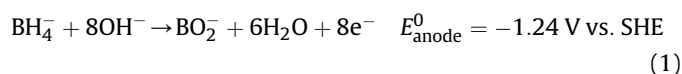


Table 1 presents information regarding previous studies by DBPFC (direct borohydride–hydrogen peroxide fuel cell) research

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Table 1
Activities of various DBPFC research groups.

Groups	USA		India	China				UK	Portugal
	Illinois University	Ohio University	Indian Institute of Science	Harbin Engineering University	Xiangtan University	Tsinghua University	Nanjing University	Southampton University	Instituto Superior Técnico
Component System	0	0	0	0	0	0	0	0	0
Power	1 kW		40 W						
Maximum power density (mW/cm ²)	680 (60 °C)	665 (60 °C)	352 (70 °C)	345 (55 °C)	92 (25 °C)	130 (80 °C)	400 (80 °C)	78 (42 °C)	206 (65 °C)

groups and demonstrates that the USA [8–15], India [16–22], China [23–35], the UK [36,37], and Portugal [38] (all of which possess advanced technology in the field of aerospace engineering) have conducted various studies to investigate the use of DBPFCs as new power sources for aerospace systems. The USA has produced particularly outstanding results, having developed a 1 kW fuel cell stack with a maximum power density of 680 mW/cm² (60 °C) [9]; this density is the highest achieved by any of these research groups. The first DBPFC research was performed in India [16], and they produced a 40 W fuel cell system [22]. China has conducted research primarily on electrocatalysts to improve energy efficiency, although four universities have performed DBPFC research, and the UK and Portugal have also studied DBPFC components.

The maximum power density obtained for DBPFCs to date (i.e., 680 mW/cm²) [9] is much higher than that of DMFCs (30–100 mW/cm²) but comparable to that of PEMFCs (300–1000 mW/cm²). Moreover, the predicted energy density of DBPFCs (1000 Wh/kg) is much higher than that of lithium batteries (250 Wh/kg) [8]. DBPFCs offer many other advantages, including high theoretical voltage (CH₃OH/O₂: 1.19 V, H₂/O₂: 1.23 V, HCOOH/O₂: 1.45 V, N₂H₄/O₂: 1.56 V, NaBH₄/O₂: 1.64 V, and NaBH₄/H₂O₂: 3.01 V), easy cooling, storability, and fast response characteristics. Furthermore, NaBH₄ and H₂O₂ are environmentally benign and are used widely in aerospace systems [39–44].

Although extensive and thorough research has been conducted regarding DBPFCs, knowledge of their behavior and use remains far from perfect. In particular, issues remain regarding fuel decomposition, which decreases energy efficiency and increases costs. Accordingly, many research groups have developed various electrocatalysts to minimize fuel decomposition reactions while maximizing electrochemical reactions. However, their performance still remains low owing to low electrochemical performance. In our previous study, we showed that DBPFC electrocatalysts prepared by MWCNTs (multiwalled carbon nanotubes) had improved performance over conventional ones prepared by VC-72 [45,46]. This was owing to a higher electrical conductivity of MWCNTs. Catalyst supports with higher electrical conductivity are required for DBPFC since liquid reactants serve as electric resistance.

Various conditions, including electrocatalyst choice, can affect fuel decomposition, fuel cell performance, and energy density. The optimum operating conditions may vary depending on the preparation methods of the electrocatalyst [26,47]. In the present study, the performance of DBPFCs with electrocatalysts supported on MWCNTs was evaluated under various conditions. Electrocatalysts were reduced on MWCNTs by NaH₂PO₂ (sodium phosphinate) and were then investigated using various analyses. The effects of fuel concentration, operating temperature, membrane thickness, and operation time on fuel decomposition and fuel cell performance were also investigated to determine optimum conditions for high energy density.

2. Experimental

2.1. Electrode preparation

Anode and cathode electrocatalysts were manufactured based on our previous results [45]: the anode and cathode catalysts were Pd (palladium) and Au (gold), respectively. Palladium chloride (PdCl₂, Alfa Aesar, USA) and gold chloride (AuCl₃, Alfa Aesar, USA) were used as catalyst precursors. The catalyst solution was composed of catalyst precursor and 20 g of distilled water (H₂O, OCI, Korea). Sodium citrate (C₆H₅Na₃O₇, Junsei Chemical, Japan) was also dissolved in the catalyst solution to improve catalyst dispersion. The mole ratio of sodium citrate to catalyst was 1:1. Before catalyst manufacture, MWCNTs (Carbon Nano-material Technology, Korea) were heated at 400 °C for 4 h to remove contaminants. The heat-treated MWCNTs were added to the catalyst solution at a mass ratio of 5:1 (MWCNTs to catalyst), and the MWCNTs in the solution were dispersed by placing in an ultrasonic bath (JAC-1505, Kodo Technical Research, Korea) for 30 min. Then, the catalyst was reduced on MWCNTs using 20 g of a NaH₂PO₂ solution. NaBH₄ was used as a reducing agent in a previous study [45]; however, NaH₂PO₂ (Junsei Chemical, Japan) was adopted as a reducing agent in the present study. The mole ratio of NaH₂PO₂ to catalyst was 10:1. A NaH₂PO₂ solution was added to the catalyst solution over the course of 1 h using a syringe pump (KDS 100, Kd Scientific, USA). Then, the catalyst solution was agitated with a magnetic stirrer at 100 rpm for 5 h using a hot plate (RET Control-VISC C, IKA, Germany). The metal/MWCNT catalyst was filtered and washed with H₂O and then dried at 100 °C for 2 h.

The electrode was constructed with catalyst slurry and carbon cloth (Fuel Cell Earth, USA) [9]. The catalyst slurry was composed of the metal/MWCNT catalyst, a 5 wt% Nafion solution (D521, DuPont, USA), and methanol (CH₃OH, OCI, Korea) at a mass ratio of 1:1:20. The catalyst slurry was dispersed by placing in an ultrasonic bath for 30 min and was then coated on 3.2 cm (width) × 3.2 cm (length) × 0.04 cm (thickness) carbon cloth. The electrode was dried at 80 °C for 20 min, then treated with sulfuric acid (H₂SO₄, Samchun Chemical, Korea) for 30 s and washed with H₂O. The electrode was again dried at 80 °C for 1 h, after which it was stored in a sealed plastic bag until the experiment.

2.2. Membrane pretreatment

Nafion 211, 212, 115, and 117 membranes (DuPont, USA) were heated in a cleaning solution at 80 °C for 1 h to remove impurities. The cleaning solution was composed of 3 wt% H₂O₂ (Samchun Chemical, Korea), 3 wt% H₂SO₄, and 94 wt% H₂O. Additionally, the membranes were heated in 200 g of DI (deionized water) at 80 °C for 1 h. The cleaned membranes were stored in DI water at room temperature. Before performance testing, the membranes were immersed in a 0.5 M H₂SO₄ solution for 2 h and washed with DI water.

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