



Estimating the energy density of direct borohydride–hydrogen peroxide fuel cell systems for air-independent propulsion applications



Taek Hyun Oh ^a, Bosun Jang ^b, Sejin Kwon ^{b,*}

^a Launcher Thermal & Aerodynamics Team, Launcher Technology Development Division, KSLV-II R&D Program Executive Office, Korea Aerospace Research Institute (KARI), 169-84 Gwahak-ro, Yuseong-gu, Daejeon 305-806, Republic of Korea

^b Division of Aerospace Engineering, School of Mechanical, Aerospace and Systems Engineering, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon 305-338, Republic of Korea

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ABSTRACT

The energy density of DBPFCs (direct borohydride–hydrogen peroxide fuel cells) is estimated for air-independent propulsion applications. The performance of DBPFCs containing heat-treated electrocatalysts supported on multiwalled carbon nanotubes is evaluated. The open circuit voltage and the maximum power density are 1.44 V and 243 mW/cm², respectively, whereas the voltage efficiency is 17.9% at the maximum power density. Based on experimental results, the energy density is estimated to be 63.2 Wh/kg (87.1 Wh/L), which is much lower than those of other power sources. The degree of influence of various parameters on the energy density is ranked in the following order: fuel utilization efficiency > voltage efficiency > H₂O₂ (hydrogen peroxide) concentration > NaBH₄ (sodium borohydride) concentration > maximum power density. Performance targets comprising of fuel utilization efficiency of 90%, voltage efficiency of 40%, H₂O₂ concentration of 50 wt%, NaBH₄ concentration of 20 wt%, and maximum power density of 650 mW/cm², have been determined. Under these conditions, the energy density and fuel volume are expected to be 378.5 Wh/kg (541.4 Wh/L) and 1.57 L, respectively, which would allow them to be used widely as power sources for air-independent propulsion.

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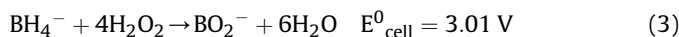
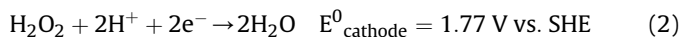
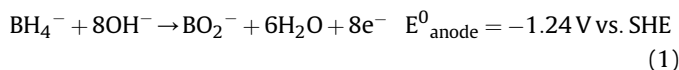
1. Introduction

DBPFCs (direct borohydride–hydrogen peroxide fuel cells) are attractive for applications in AIP (air-independent propulsion) systems. Research groups in India [1–7], the USA [8–17], China [18–30], the UK [31,32], and Portugal [33,34] have studied DBPFCs. Researchers at the Indian Institute of Science first developed a unit cell [1] and a 40 W DBPFC system [7], with a maximum power density of 352 mW/cm² at 70 °C [1]. Following this, researchers at Illinois University developed high performance electrodes [9] and a 500 W DBPFC [8], with a maximum power density of 680 mW/cm² at 60 °C [9], which is the highest value that has been achieved so far. Recently, scientists at Maryland University have developed models for DBPFCs [16,17]. In addition, research groups at Ohio University, Harbin Engineering University, Nanjing

University, Tsinghua University, Xiangtan University, Southampton University, and Instituto Superior Técnico have mainly focused on the development of high-performance electrocatalysts. However, the maximum power densities of their fuel cells are lower than that achieved at Illinois University.

Eqs. (1)–(3) present the reactions that take place in DBPFCs. Since liquid fuels (NaBH₄ (sodium borohydride) and H₂O₂ (hydrogen peroxide) solutions) are used instead of gaseous fuels in DBPFCs, they have many advantages over existing power sources for mobile applications. The advantages of DBPFCs include 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) [35], high maximum power density (DBPFCs: 680 mW/cm², DMFCs (direct methanol fuel cells): 30–100 mW/cm², PEMFCs (proton exchange membrane fuel cells): 300–1000 mW/cm²), high energy densities (DBPFCs (predicted): 1000 Wh/kg, lithium batteries: 250 Wh/kg) [8], easy cooling capability, easy refueling capability, fuel storability, environmentally-benign properties, fast-response characteristics, and simplicity of the system.

* Corresponding author. Tel.: +82 42 350 3721; fax: +82 42 350 3710.
E-mail address: trumpet@kaist.ac.kr (S. Kwon).



Although DBPFCs have been widely studied because of their advantages, they also exhibit some problems that need to be resolved. The primary problem is fuel-decomposition, which decreases the energy density of DBPFC systems and increases the total cost. While many research groups have developed various electrocatalysts to minimize the fuel-decomposition reaction and maximize the electrochemical reaction, the performance of such electrocatalysts needs to be further improved. Since the energy density of power sources determines the mission capability of a mobile system, it is an important parameter in the evaluation of DBPFCs. However, the energy density of DBPFC systems is rarely estimated, unlike other fuel cell systems [36–39].

We previously developed electrocatalysts and heat-treated electrodes with high performance for DBPFCs [40–42]. The optimum operating conditions of a unit cell were also investigated [40]. The energy density and performance targets that need to be met for the application of DBPFCs in AIP systems have been investigated in this study. The performance of a unit cell has been evaluated, and the energy density of a DBPFC system has been estimated based on the experimental results of the unit cell. Further, the effects of maximum power density, voltage efficiency, NaBH_4 concentration, H_2O_2 concentration, and fuel utilization efficiency on the energy density of a DBPFC system have been investigated. Finally, performance targets that need to be met in order to allow DBPFC systems to compete with existing power sources [43–48] have been determined.

2. Experimental

2.1. Electrode preparation

Heat-treated electrodes were prepared using the sputtering method unlike our previous studies which used NaBH_4 or NaH_2PO_2 reduction method [40,41]. First, carbon cloths (Fuel Cell Earth, USA) containing 5 mg/cm^2 of MWCNTs (multiwalled carbon nanotubes, Carbon Nano-material Technology, Korea) were prepared with dimensions of 3.3 cm (width) \times 3.3 cm (length) \times 0.04 cm (thickness). A MWCNTs slurry was prepared by mixing the MWCNTs, a solution containing 5 wt% Nafion (D521, DuPont, USA), and isopropyl alcohol ($(\text{CH}_3)_2\text{CHOH}$, Dongwoo Fine-chem, Korea) (MWCNTs/Nafion ionomer/isopropyl alcohol = 2.5:1:40). The slurry was homogenized

with a magnetic stirrer at 300 rpm for 12 h using a hot-plate (RET Control-VISC C, IKA, Germany), following which it was coated on carbon cloths using a spray gun (Airbrush, Sprayworks, USA). The carbon cloths were held at $100 \text{ }^\circ\text{C}$ on a hot-plate for drying.

The electrodes were manufactured at room temperature using sputtering (SPS-TG series, Ultech, Korea) developed in our previous study [42]. Pd (anode) and Au (cathode) were deposited on carbon cloths containing MWCNTs at a current of 30 mA. The electrodes containing 0.1 mg/cm^2 of electrocatalysts were treated with 0.5 M sulfuric acid (H_2SO_4 , Samchun Chemical, Korea) for 30 min. The electrodes were then washed with distilled water (H_2O , OCI, Korea), and dried at $80 \text{ }^\circ\text{C}$ for 30 min. Finally, the prepared electrodes were heated to $400 \text{ }^\circ\text{C}$ at a rate of $2 \text{ }^\circ\text{C/min}$ and held at that temperature for 30 min, in order to impart hydrophilic characteristics to the electrode surface. After heat-treatment, they were slowly cooled to room temperature in a furnace. The surface morphology of the electrodes was analyzed using scanning electron microscopy (SEM, Magellan 400, FEI, USA), and the composition of the electrodes was determined by energy dispersive spectroscopy (EDS, Magellan 400, FEI, USA).

2.2. Fuel cell assembly

A schematic illustration of a unit cell is shown in Fig. 1. A Nafion 212 membrane (DuPont, USA) was used in this study. The membrane was cleaned in a solution composed of 3 wt% H_2O_2 (Samchun Chemical, Korea), 3 wt% H_2SO_4 , and 94 wt% H_2O , in order to remove any impurities. The membrane was heated to and maintained at $80 \text{ }^\circ\text{C}$ for 1 h. The cleaned membrane was stored in deionized water at room temperature. Immediately before the performance test, the membrane was activated by soaking in a 0.5 M H_2SO_4 solution for 1 h. An MEA (membrane electrode assembly) was prepared using the activated Nafion 212 membrane and the Pd and Au-based electrodes (described in Section 2.1). Graphite bipolar plates with serpentine flow channels that were 1 mm in width and depth were used. Two silicon gaskets (thickness: 0.25 mm, Fuel Cell Earth, USA) were placed between the bipolar plates and the MEA to prevent fuel leakage, and two gold-coated aluminum plates (to increase conductivity) were used as current collectors. In addition, two stainless steel plates were used as end plates, in order to allow all the components to be assembled. Two K-type thermocouples were inserted into the end plates to measure the fuel cell temperature. The fuel cell was tightened with a clamping pressure of 20 kgf cm using a torque wrench (30 QL, Tohnichi, Japan).

2.3. Fuel cell test

The experimental setup for the fuel cell test was presented in our previous study [40,41]. Fuel concentration was 10 wt%

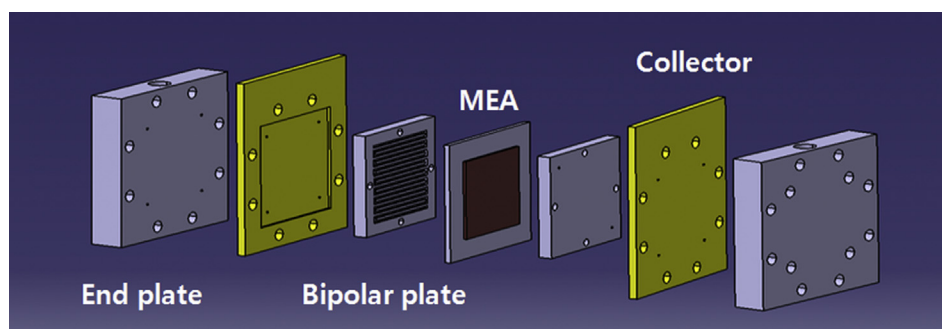


Fig. 1. Fuel cell components for fuel cell testing.

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