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Design specifications of direct borohydride–hydrogen peroxide fuel cell system for space missions

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ABSTRACT

The design specifications of a direct borohydride–hydrogen peroxide fuel cell (DBPFC) system for space missions were determined based on the energy density. A unit cell test of the DBPFC with electrocatalysts supported on multiwalled carbon nanotubes was conducted to evaluate the DBPFC performance. A relationship between the current density and voltage was obtained from the test results to estimate the total mass and energy density of the DBPFC system. The effects of changing the voltage efficiency and fuel concentrations on the total mass of the DBPFC system were investigated to determine the appropriate design specifications for space missions. When the voltage efficiency was 35%, the system mass was the lowest, regardless of the fuel concentrations. Finally, the energy density of the DBPFC system operating at the optimum voltage efficiency was calculated at various fuel concentrations. When the $NaBH_4$ and H_2O_2 concentrations are higher than 20 and 65 wt%, respectively, the energy density (>400 Wh/kg) of the DBPFC system is higher than those of other power sources and the DBPFC system can be widely used for space missions.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been widely used as power sources for mobile applications [1–14] owing to their advantages such as high efficiency, high energy density, fast response characteristics, and low noise. However, PEMFCs are not suitable for space missions because of hydrogen storage problems. Although liquid hydrogen has high gravimetric and volumetric energy densities, boil-off problems limit the mission duration. Gaseous hydrogen and metal hydrides, on the other hand, have low gravimetric and volumetric energy densities.

In countries with advanced aerospace technology, various institutes (the Indian Institute of Science [15–21], University of Southampton [22,23], University of Illinois [24–29], Harbin Engineering University [30,31], Xiangtan University [32–42], Tsinghua University [43], Ohio State University [44,45], Instituto Superior Téchnico [46–48], Nanjing University [49], University of Maryland [50,51], KAIST [52–56], and Taiyuan University of Technology [57–59]) have developed direct borohydride–hydrogen peroxide fuel cells (DBPFCs) to solve the problems associated with PEMFCs. DBPFCs use liquid fuels instead of gaseous fuels. Electricity is generated by direct electrochemical reactions of sodium borohydride ($NaBH_4$) and hydrogen peroxide (H_2O_2) solutions, as shown in Eqs. (1)–(3).

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad E^0_{anode} = -1.24\ \text{V vs. SHE} \tag{1}$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E^0_{cathode} = 1.77\ \text{V vs. SHE} \tag{2}$$

$$BH_4^- + 4H_2O_2 \rightarrow BO_2^- + 6H_2O \quad E^0_{cell} = 3.01\ \text{V} \tag{3}$$

DBPFCs can be used for space missions owing to their advantages. For example, solar cells can only be used in an environment with sunlight, but DBPFCs can be used in any environment. Batteries have low gravimetric energy density, but DBPFCs have high gravimetric energy density. Atomic batteries have some safety issues, but DBPFCs use liquid fuels that are environmentally friendly. Furthermore, DBPFCs are simple systems that have high theoretical voltage, high maximum power density, fast response characteristics, easy cooling, easy refueling, and easy fuel storage. In addition, fuel storage systems for fuel cell and propulsion systems can be integrated because H_2O_2 is widely used for space propulsion such as in monopropellant thrusters [60–63], bipropellant thrusters [64–66], and hybrid rockets [67].

However, the performance of the DBPFCs is still inferior to that of PEMFCs because of fuel decomposition, fuel crossover, and de-

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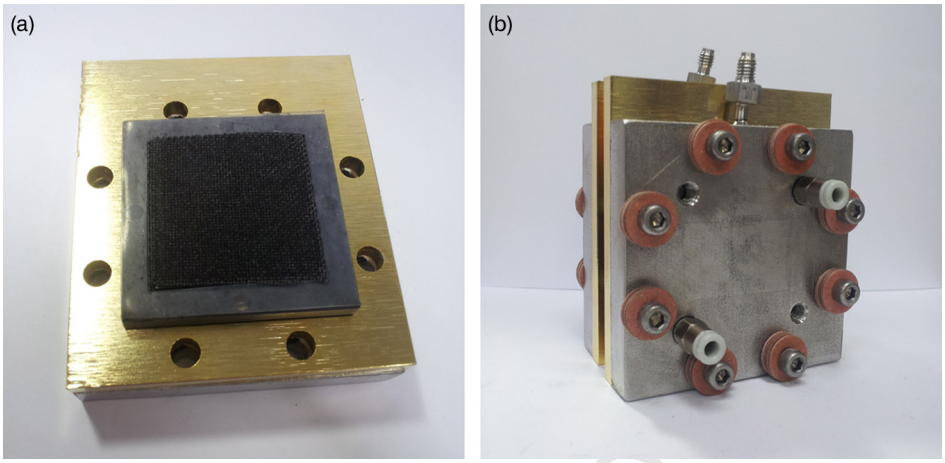

Fig. 1. Unit cell for fuel cell test: (a) components and (b) unit cell.

position of the reaction product on the electrocatalysts [52]. The performance of DBPFCs should be further improved to compete with other power sources for space missions. Research on the electrocatalysts, bipolar plates, fuel cell stack, and DBPFC system has been conducted by many research groups, but the design specifications of the DBPFC system have rarely been investigated.

Because a higher energy density of the power sources implies better mission capability, energy density is an important performance parameter for space missions. As a result, the design specifications of the DPBFC system for space missions were determined based on the energy density. First, the performance of a DBPFC with electrocatalysts supported on multiwalled carbon nanotubes (MWNCTs) was evaluated to obtain a relationship between current density and voltage. Second, the total mass of the DBPFC system was calculated at various voltage efficiencies and fuel concentrations to investigate the effect of those parameters on the system mass. Finally, the energy density of a DBPFC system operating at the optimum voltage efficiency was estimated at various fuel concentrations. The design specifications of the DPBFC system were determined, and the energy density of the DBPFC system was compared with other power sources.

2. Experimental

2.1. Electrode preparation

MWCNTs (Carbon Nano-material Technology, Korea) were heated at 400 °C for 4 h to remove impurities. Electrocatalysts were supported on MWCNTs using our previous procedure [53]. Each catalyst solution for the anode and cathode catalysts was prepared with a metal salt and sodium citrate ($C_6H_5Na_3O_7$, Junsei Chemical, Japan). The metal salts for the anode and cathode catalysts were palladium chloride ($PdCl_2$, Alfa Aesar, USA) and gold chloride ($AuCl_3$, Alfa Aesar, USA), respectively. Sodium citrate was used to disperse the catalyst. The MWCNTs were immersed in the catalyst solution, and then agitated in an ultrasonic bath (JAC-1505, Kodo Technical Research, Korea) for 30 min. The catalyst was reduced on the MWCNTs using 20 mL of $NaBH_4$ (Samchun Chemical, Korea) solution. A syringe pump (KDS 100, KD Scientific, USA) supplied the $NaBH_4$ solution to the catalyst solution for 1 h, after which it was agitated with a magnetic stirrer at 100 rpm for 5 h. The electrocatalyst supported on MWCNTs was washed with distilled water (H_2O, OCI, Korea) and dried at 100 °C for 2 h in a convection oven.

Each electrode (anode and cathode) was manufactured using a catalyst slurry and carbon cloth [53]. The catalyst slurry was composed of the catalyst, 5 wt% Nafion solution (D521, DuPont, USA), and methanol (CH_3OH, OCI, Korea) (catalyst:Nafion solution:methanol = 1:1:20). The slurry was dispersed in an ultrasonic bath for 30 min, after which it was coated on carbon cloth (Fuel Cell Earth, USA). The piece of carbon cloth was 3.2 cm (width) × 3.2 cm (length) × 0.04 cm (thickness) and the catalyst loading for the carbon cloth was 1 mg/cm^2. The electrode was then dried by heating in a convection oven at 80 °C for 20 min. The dried electrode was immersed in a sulfuric acid solution (H_2SO_4, Samchun Chemical, Korea) for 30 s. Finally, the electrode was washed with copious amounts of H_2O and dried at 80 °C for 1 h in a convection oven.

2.2. Electrode characterization

The electrode was investigated by various analyses. Transmission electron microscopy (TEM, Tecnai F20, Philips, Netherlands) was used to analyze the catalyst distribution on MWCNTs. Scanning electron microscopy (SEM, Nova 230, FEI, USA) and energy dispersive spectroscopy (EDS, Nova 230, FEI, USA) were used to investigate the surface morphology and composition, respectively, of the electrode. X-ray diffraction (XRD, D/MAX-2500, RIGAKU, Japan) was used to determine the microstructure of the electrode.

2.3. Unit cell for fuel cell test

Fig. 1 shows a unit cell for the fuel cell test. The unit cell consists of a Nafion 212 membrane (DuPont, USA), two electrodes (anode and cathode), two silicon gaskets (thickness: 0.25 mm, Fuel Cell Earth, USA), two bipolar plates, two collectors, and two end plates. The membrane was cleaned to remove organic contaminants by immersing it in 200 g of a solution composed of 3 wt% H_2O_2 (Samchun Chemical, Korea), 3 wt% H_2SO_4, and 94 wt% H_2O and heating at 80 °C for 1 h. The membrane was then heated in 200 g of deionized water at 80 °C for 1 h. The cleaned membrane was activated in a 0.5 mol/kg H_2SO_4 aqueous solution for 2 h before the fuel cell test. The activated membrane was placed between the two electrodes. The silicon gaskets were used to prevent fuel leakage between the membrane and bipolar plates. The graphite bipolar plates had serpentine flow channels that were 1 mm in width and depth. The Au-coated collectors were used to increase the electrical conductivity and the end plates were used to assemble the components. The unit cell was tightened with 20 kgf cm of clamping pressure by a torque wrench (30 QL, Tohnichi, Japan). Two K-type thermocouples (±1.0 °C accuracy) in the end plates measured the anode and cathode temperatures.

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