Short communication

A 28-W portable direct borohydride–hydrogen peroxide fuel-cell stack

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Abstract

A 28-W direct borohydride–hydrogen peroxide fuel-cell stack operating at 25 °C is reported for contemporary portable applications. The fuel cell operates with the peak power-density of ca. 50 mW cm^{-2} at 1 V. This performance is superior to the anticipated power-density of 9 mW cm^{-2} for a methanol–hydrogen peroxide fuel cell. Taking the fuel efficiency of the sodium borohydride–hydrogen peroxide fuel cell as 24.5%, its specific energy is ca. 2 kWh kg^{-1}. High power-densities can be achieved in the sodium borohydride system because of its ability to provide a high concentration of reactants to the fuel cell.
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1. Introduction

Polymer electrolyte fuel cells employing hydrogen as fuel and oxygen from the air as oxidant are attractive electrochemical power systems for ambient-temperature operations. Hydrogen is, however, not available freely in the nature and hence needs to be generated from a readily available hydrogen-carrying fuel, such as natural gas through a catalytic reformer [1]. Such a process leads to generation of hydrogen with some carbon monoxide that, even at a miniscule level, is detrimental to its performance. Pure hydrogen can be generated through water electrolysis but it needs to be stored either as compressed or liquefied gas, which is expensive.

To obviate the aforesaid problem, certain hydrogen-carrying organic fuels, such as methanol, ethanol, propanol, ethylene glycol and diethyl ether, have been considered for fuelling polymer electrolyte fuel cells directly. Among these, methanol with a hydrogen content of 12.8 wt.% is the most attractive liquid fuel [2]. On the other hand, polymer electrolyte fuel cells fuelled directly with methanol suffer from methanol crossover from the anode to the cathode across the membrane electrolyte, and this affects cell performance. In addition, such fuel cells have the inherent limitations of low open-circuit potential and low electrochemical activity [3].

Given the above difficulty, the possibility of using sodium borohydride, which has a hydrogen content of about 11 wt.%, has been explored [4]. Two types of direct borohydride fuel cell have been reported in the literature, namely, direct borohydride–air fuel cells [5–7] and direct borohydride–hydrogen peroxide fuel cells [8–10]. Among these, the latter are potentially attractive for underwater and space applications where anaerobic situations prevail.

A direct borohydride–hydrogen peroxide fuel cell employs a misch-metal alloy as an anode and carbon-supported platinum (Pt/C) as a cathode with Nafion-117 membrane as separator-cum-electrolyte. Hydrogen peroxide has, however, been found to decompose on a Pt/C cathode [10]. It is noteworthy that Pt/C preferentially catalyses the four-electron reduction of oxygen to water in relation to the two-electron reduction of hydrogen peroxide to water [11].

In the literature [11], hydrogen peroxide reduction on iridium, osmium, platinum, palladium, and combinations of these are studied, but all of these exhibit decomposition of hydrogen peroxide into water and oxygen instead of the

direct reduction of hydrogen peroxide to water. Accordingly, efforts are being expended to replace these catalysts in direct borohydride–hydrogen peroxide fuel cells [8].

In this short communication, we report a 28-W portable direct borohydride–hydrogen peroxide fuel-cell stack that utilizes misch-metal alloy as the anode and gold-coated stainless-steel gauze as the cathode. The stack delivers a peak power-density of about $50\,mW\,cm^{-2}$ at 1 V, which is superior to the anticipated performance for a methanol–hydrogen peroxide fuel cell [12].

2. Experimental

In the direct borohydride fuel cell reported here, M_m (misch metal) $Ni_{3.6}Al_{0.4}Mn_{0.3}Co_{0.7}$ ($M_m = $ La-30 wt.%, Ce-50 wt.%, Nd-15 wt.%, Pr-5 wt.%) was used as the anode. The $M_mNi_{3.6}Al_{0.4}Mn_{0.3}Co_{0.7}$ alloy was prepared by arc-melting stoichiometric amounts of the constituent metals in a water-cooled copper crucible under an argon atmosphere. The alloy ingot thus obtained was mechanically pulverized to a fine powder.

The gold cathode was obtained by electroplating a gold layer of 1 μm thickness on to stainless-steel-316 gauze of 200 mesh. To examine the electrochemical activity of the electrode, a three-electrode glass cell was used for cyclic voltammetric experiments undertaken with an AutoLab PGSTAT-30 Potentiostat. The working electrode was a $1.5\,cm^2$ gold-coated 200-mesh stainless-steel gauze. The counter electrode was also made of gold-plated stainless-steel gauze. The working electrode was scanned between 0 and 1 V against a standard hydrogen electrode (SHE) at a scan rate of $10\,mV\,s^{-1}$.

For the electrochemical characterization of the direct borohydride fuel cell (DBFC), membrane electrode assemblies (MEAs) were obtained by sandwiching a Nafion-961 polymer electrolyte membrane between the anode and the cathode. The Nafion-961 membrane is a Teflon-fibre reinforced composite membrane with sulfonate (100 μm) and carboxylate (10 μm) polymer layers. Unlike Nafion-117, the Nafion-961 membrane mitigates alkali crossover from the anode to the cathode. Accordingly, Nafion-961 facilitates higher oxidant utilization at the cathode of the DBFC. To prepare the anode catalyst layer, a slurry of the alloy was obtained by ultra-sonicating the required amount of alloy with 5 wt.% Vulcan XC-72R carbon and 5 wt.% of Nafion® solution in isopropyl alcohol. The slurry was then pasted on to the carboxylate side of the membrane. The loading of the alloy catalyst was kept at $39\,mg\,cm^{-2}$. A gold-coated stainless-steel gauze, held on the sulfonate side of the membrane, acted as the cathode. The membrane electrode assembly is obtained by hot-pressing cathode and anode placed on either side of a Nafion-961 membrane at $60\,kg\,cm^{-2}$ at 125 °C for 3 min.

The anode catalyst layer in the MEA was supported on a stainless-steel mesh. Both the anode and the cathode were contacted on their back side with fluid-flow field plates that were machined from stainless-steel-316 blocks. Channels connecting the main tank were machined in the block to achieve minimum mass-polarization in the DBFC, as shown in Fig. 1. The ridges between the channels make electrical contact with the back of the electrode and assist the conduction of current to the external
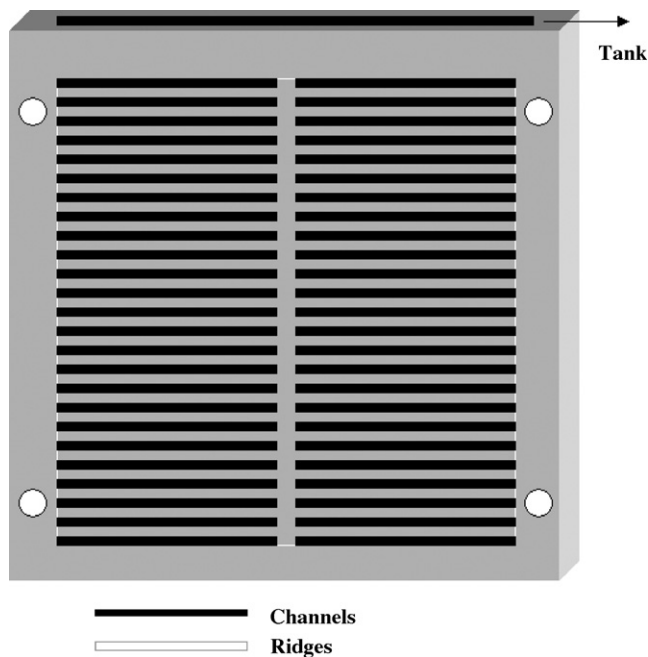

Fig. 1. Schematic diagram of $100\,cm^2$ flow-field pattern employed with a stack machined from stainless-steel block.

circuit. Two monopolar and five bipolar plates were machined to assemble a six-cell stack. The active geometrical area in each cell was $100\,cm^2$. The channels supply alkaline sodium borohydride solution to the anode and acidified hydrogen peroxide to the cathode. Aqueous sodium borohydride solution (4 wt.% $NaBH_4$ in 20 wt.% aqueous NaOH) was injected into the fuel tank and 2 M hydrogen peroxide solution in 1.5 M sulfuric acid and 0.1 M orthophosphoric acid mixture was injected into the oxidant tank. The stainless-steel blocks were also provided with electrical contacts. Such a DBFC stack is shown schematically in Fig. 2.

Galvanostatic-polarization data for single DBFCs at 25 °C are recorded by injecting 50 ml of alkaline $NaBH_4$ in their fuel tanks with a similar amount of acidic hydrogen peroxide in the oxidant tanks. The respective anode and cathode data determined
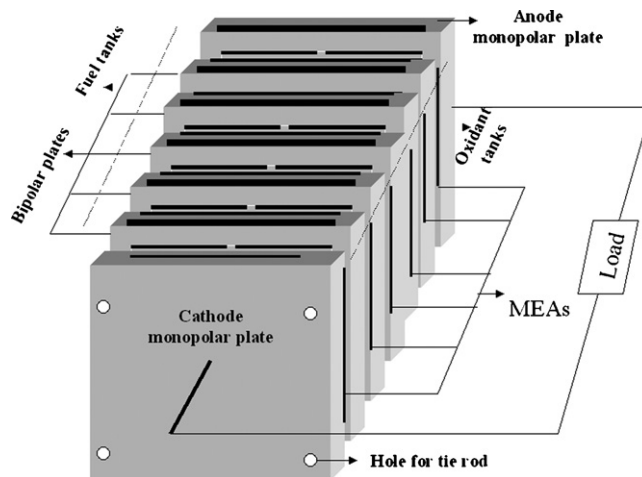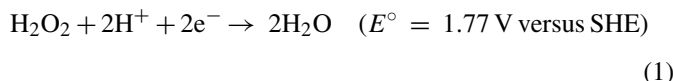

Fig. 2. Schematic diagram of six-cell stack along with its components.

against a Hg/HgO, OH⁻ reference electrode placed in the fuel tank and Hg/Hg$_2$SO$_4$/SO$_4$$^{2-}$ reference electrode placed in the oxidant tank. On the other hand, the polarization data obtained in an acidic medium are reported with respect to a standard hydrogen electrode.
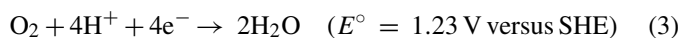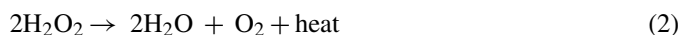
To obtain the faradaic efficiency for borohydride oxidation and hydrogen peroxide reduction in a stack of six cells in series, 50 ml of alkaline NaBH$_4$ is injected into each of the fuel tanks and 50 ml of acidic hydrogen peroxide is injected into each of the oxidant tanks. The stack is operated at a load current-density of 10 mA cm^{-2}. The fuel efficiency is calculated from the data collected during anode polarization up to the inflection point. In a similar fashion, oxidant efficiency is obtained from cathode polarization data at a load current-density of 10 mA cm^{-2}. The stack has higher utilization efficiency for hydrogen peroxide in relation to borohydride and hence needs to be replenished with borohydride fuel intermittently during its operation.

3. Results and discussion

The reduction of hydrogen peroxide can occur by two different reaction pathways [3], namely: (i) a direct two-electron pathway and (ii) a decomposition reaction followed by reduction to water by a four-electron pathway. In the acidic medium, reduction of hydrogen peroxide to water is possible through the following pathways [3].

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad (E^\circ = 1.77 \text{ V versus SHE})$$
(1)

or,

$$2H_2O_2 \rightarrow 2H_2O + O_2 + heat$$
(2)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (E^\circ = 1.23 \text{ V versus SHE})$$
(3)

Gold is a potential catalyst for the reduction of hydrogen peroxide [13,14]. Given this capability, gold or modified-gold surfaces used for immobilization of biomolecules are employed as sensors for quantitative detection of hydrogen peroxide in food, pharmaceuticals, chemicals, biochemicals, industrial and environmental analyses [14]. El-Deab and Ohsaka [13] have studied the catalytic reduction of oxygen and hydrogen peroxide in 0.5 M sulfuric acid and have found the reduction of hydrogen peroxide to be pH dependent. In an acidic medium, reduction of oxygen on a gold surface proceeds in two steps where first oxygen is reduced to peroxide and then the peroxide is reduced to water. Each step involves two electrons. It should be noted, however, that hydrogen peroxide reduction to water occurs with little decomposition of the former on the gold surface. Cyclic voltammograms for a gold electrode in a 1.5 M sulfuric acid and 0.1 M orthophosphoric acid mixture, with and without 2 M hydrogen peroxide, are shown in Fig. 3. The data indicate that the onset of hydrogen peroxide reduction on gold occurs at 0.9 V versus SHE.

A Nafion-961 membrane mitigates aqueous NaOH crossover from the anode to the cathode in a cell. Accordingly, the catholyte pH is kept below 1 and this helps to increase oxidant utilization
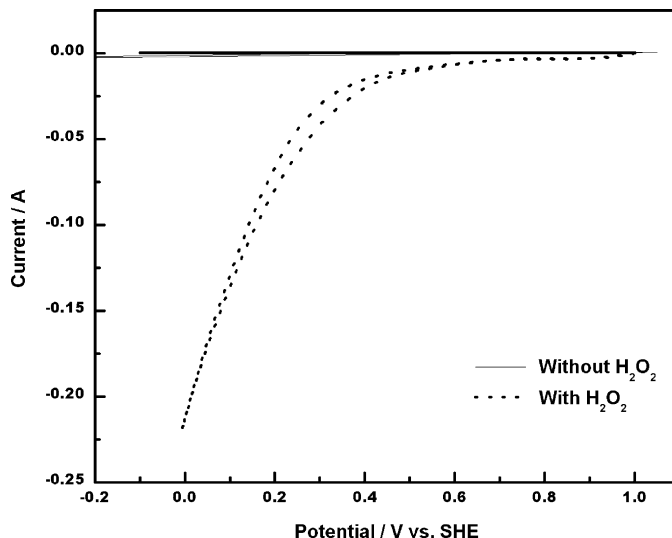

Fig. 3. Cyclic voltammograms for Au electrode in aqueous 1.5 M sulfuric acid and 0.1 M orthophosphoric acid mixture, with and without 2 M hydrogen peroxide.

with concomitant suppression of cathode polarization. It is noteworthy that reaction (1) reflects an increase in pH due to proton consumption as the reaction proceeds. Usage of a high concentration of hydrogen peroxide in alkaline medium over a gold cathode results in exacerbated decomposition of hydrogen peroxide into oxygen and water and thereby yields a poor utilization for hydrogen peroxide.

The cell performance data for the direct borohydride–hydrogen peroxide fuel cell along with its anode and cathode data are shown in Fig. 4. The polarization data are obtained in steps of 0.25 mA s^{-1} up to 100 mA and subsequently in steps of 5 mA s^{-1} until the end of the experiment. The individual electrode potentials exclude any drop across the membrane as these are measured by placing reference electrodes in the respective tanks. The polarization curve for the stack at 25 °C, along
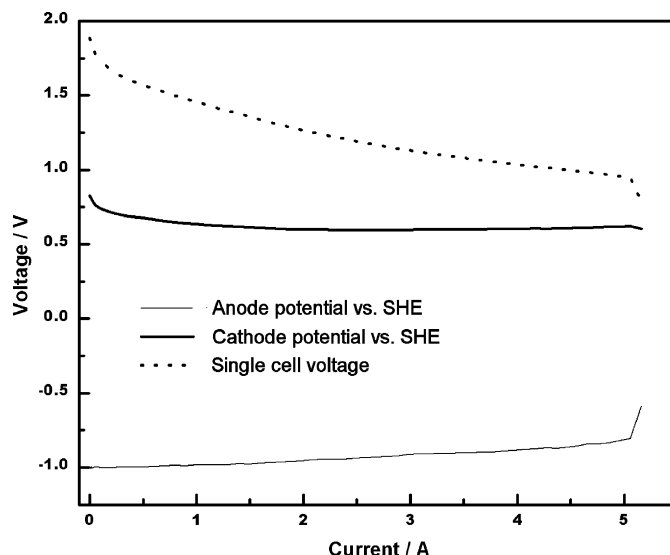

Fig. 4. Polarization data for single direct borohydride–hydrogen peroxide fuel cell and for the anode and cathode.
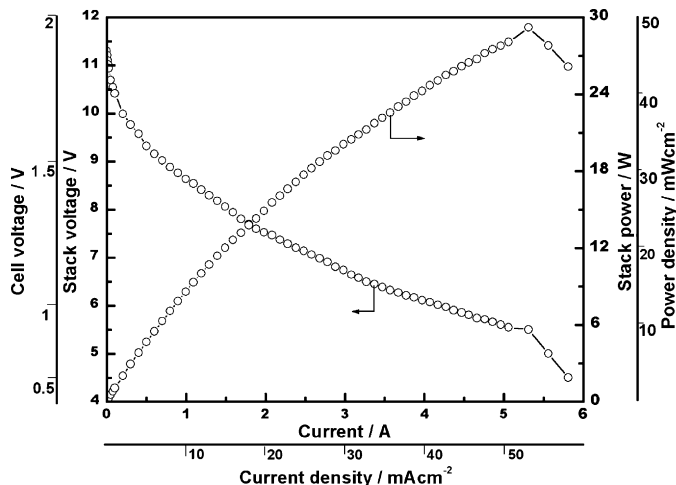
Fig. 5. Galvanostatic-polarization data for direct borohydride–hydrogen peroxide fuel-cell stack along with variation in power and power-density with varying load current-density.
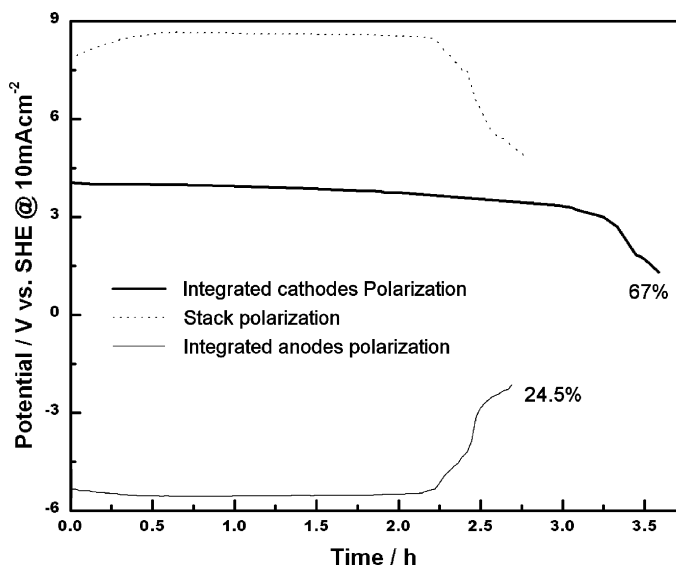

Fig. 6. Coulumbic efficiency data for sodium borohyride fuel on misch-metal hydride alloy anode and hydrogen peroxide oxidant on Au cathode in direct borohydride–hydrogen peroxide fuel-cell stack.

with its power-density data are presented in Fig. 5. A peak power of about 28 W (peak power-density $\sim 50\,\mathrm{mW\,cm^{-2}}$) is achieved at a stack voltage of about 5.5 V. Columbic efficiency values for borohydride oxidation on a metal hydride anode are obtained from anode polarization data at a load current-density of $10\,\mathrm{mA\,cm^{-2}}$, as shown in Fig. 6. Similarly, columbic efficiency values for hydrogen peroxide reduction on a gold cathode are obtained from cathode polarization data at a load current-density of $10\,\mathrm{mA\,cm^{-2}}$ as shown in Fig. 6. A comparison of the cell and stack polarization data reflects the reproducibility of the performance of the cells that constitute the stack.

It is noteworthy that the DBFC operates at an anode potential that is more negative to the standard potential for hydrogen evolution reaction in basic medium. Consequently, the hydrogen evolution reaction is inevitable and to evolution of hydrogen at the anode during oxidation of the borohydride. Accordingly, the utilization efficiency of borohydride falls to $\sim 25\%$ which corresponds to a two-electron oxidation reaction with a specific energy of ca. $2\,\mathrm{kWh\,kg^{-1}}$ on the misch-metal alloy at an operation voltage of 8.6 V, as against the theoretical value of ca. $12\,\mathrm{kWh\,kg^{-1}}$ obtained for a complete eight-electron borohydride oxidation [7]. Obviously, there is no reason to believe that the stack engineering is fully optimized, and further improvements are highly likely.

4. Conclusions

A 28-W direct borohydride–hydrogen peroxide fuel-cell stack operating at $25\,^\circ\mathrm{C}$ with a peak power-density of $50\,\mathrm{mW\,cm^{-2}}$ has been demonstrated. The fuel cell is amenable to operation where free-convection of air is limited and anaerobic conditions prevail, for example, in submersible and space applications.

Acknowledgements

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