Short communication

A novel high power density borohydride-air cell

Steven C. Amendola, Per Onnerud, Michael T. Kelly, Phillip J. Petillo,
Stefanie L. Sharp-Goldman, Michael Binder *

*Millennium Cell, 1 Industrial Way West Buiding K, Eatontown, NJ 07724, USA*

Abstract

The electrochemistry of an alkaline, aqueous cell based on sodium borohydride, $NaBH_4$, oxidation has been studied. Cell performance has been elucidated in 3.6 cm^2 laboratory cells constructed with an air cathode and an anode current collector made of highly dispersed gold/platinum particles supported on high-surface area carbon silk. The number of electrons utilized per molecule of BH_4^- oxidized (~ 6.9 out of a possible 8) implies efficient utilization of the BH_4^- oxidation. Specific energies > 180 W h/kg (based on total fuel weight) and power densities > 20 mW/cm^2 at room temperature and > 60 mW/cm^2 at 70°C have been obtained. © 1999 Elsevier Science S.A. All rights reserved.
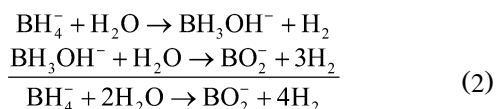
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1. Introduction

Providing power for portable consumer products and electric vehicles requires high current densities. This note continues the work of Amendola [1], in describing an environmentally friendly, aqueous power source based on sodium borohydride oxidation. Sodium borohydride, $NaBH_4$, (sodium tetrahydridoborate), a water-soluble, reducing agent, oxidizes in aqueous alkaline media, to BO_2^- (metaborate) and water.

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad E° = 1.24 \text{ V.} \tag{1}$$
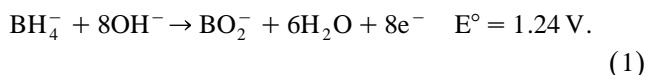
Effective utilization of the BH_4^- faradaic capacity requires that electrochemical oxidation rates be high compared to the rate of competitive side reactions. Hydrolysis, an unwanted reaction, occurring to some extent in all BH_4^- solutions (especially at pH < 7 or at elevated temperatures), liberates hydrogen gas.

$$\frac{\begin{array}{l} BH_4^- + H_2O \rightarrow BH_3OH^- + H_2 \\ BH_3OH^- + H_2O \rightarrow BO_2^- + 3H_2 \end{array}}{BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2} \tag{2}$$

To minimize hydrolysis, BH_4^- solutions are kept alkaline ([OH^-] > 5 M). When using BH_4^- as an oxidation fuel, side reactions (e.g., reaction (2)) which produce hydrogen are undesirable because they deplete BH_4^- and rob useful energy. For every molecule of hydrogen formed, two electrons are no longer available to provide electrical energy. Competition between BH_4^- oxidation (reaction (1)) and hydrogen formation is a function of electrode material, electrolyte composition and applied potential.

In BH_4^- oxidation, the required eight OH^- can originate either from excess hydroxide initially present, or from a coupled redox reaction that provides OH^-. Amendola [1] has shown that BH_4^- oxidation (reaction (1)), coupled with oxygen reduction

$$2O_2 + 4H_2O + 8e^- \rightarrow 8OH^- \quad E° = 0.40 \text{ V} \tag{3}$$

provide eight OH^- necessary for BH_4^- oxidation and yield the cell reaction:

$$BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O \quad E° = 1.64 \text{ V.} \tag{4}$$
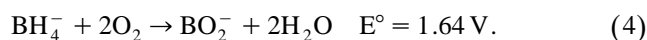
A borohydride/air cell consists of a $NaBH_4$ solution as an anode, an oxygen fed cathode, and an anionically conducting separator membrane. When electrodes are connected through an external circuit, BH_4^- oxidizes to BO_2^- while O_2 reduction at the cathode generates OH^-. Oxygen

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* Corresponding author. Tel.: +1-732-524-4000; fax: +1-732-542-4010; E-mail: steven@amendola.com

does not pose a weight penalty since it is present in ambient air and diffuses into the cell as needed. During cell discharge, OH^- generated at the cathode diffuses through the separator to provide the anode with OH^- necessary for oxidation. The 1.64 V cell potential and low equivalent weight for $NaBH_4$ yields a theoretical specific energy for the overall reaction:

$$\frac{(1.64\,\mathrm{V})(96{,}500\,\mathrm{C/F})(1000\,\mathrm{g/kG})}{(37.83\,\mathrm{g/8\,F})(3600\,\mathrm{s/h})} = 9296\,\mathrm{W\,h/kg}.$$

The combined advantages (i.e., $NaBH_4$ is chemically stable, not very expensive, readily available, and discharge products that are water-soluble and environmentally safe) make the borohydride-air cell an extremely attractive power source. It is noteworthy that although BH_4^- oxidation and hydrolysis reactions have been extensively investigated [2–5], its use as an 8-electron oxidation fuel has been generally overlooked. For this reason, we studied borohydride-air cells and showed its viability as a primary power source.

2. Experimental

2.1. Cell configuration

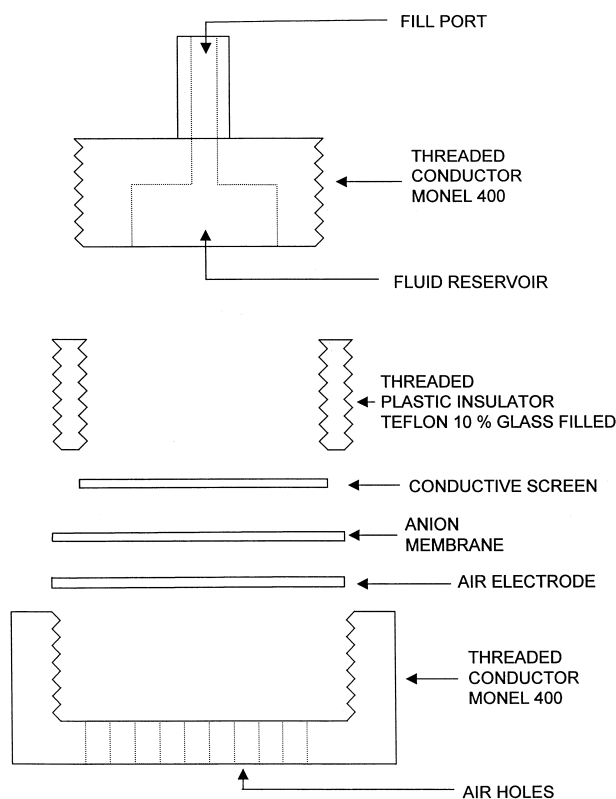Fig. 1 schematically shows the 3.6 cm^2 laboratory cell used. The cell consisted of three cylindrical sections (ap-
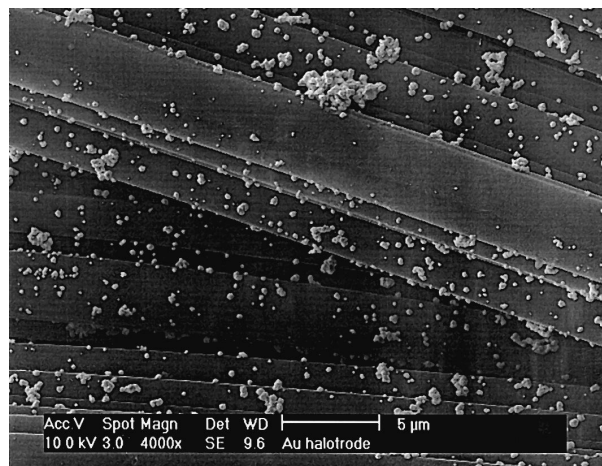
Fig. 2. Low magnification scanning electron micrographs of a gold-coated carbon silk surface.

proximately 2″ in length when totally assembled) that could be rapidly screwed together for cell fabrication or disassembled for cleaning and interchanging test electrodes and membranes. The three cylinders consisted of a stainless steel cylinder with the inside threaded; a smaller Teflon (1 7/16″ diameter) cylinder with both inside and outside threaded; and a smaller stainless steel (13/16″ diameter) with only the outside threaded. An air electrode (1 1/16″ diameter) punched from a commercial gas diffusion electrode sheet (Johnson-Matthey, Ward Hill, MA) was placed on the bottom of the largest stainless steel cylinder with the Teflon coated side of the air electrode facing outwards. An anion conducting polymer membrane (2259-60 Pall RAI, Hauppauge, NY) was placed on top of the air electrode. The Teflon cylinder was then screwed into the cylinder so that the anion conducting membrane was firmly and smoothly pressed against the air electrode. The Teflon cylinder insulated the inner and outer stainless steel cylinders and prevented fuel from leaking from the cell. A (13/16′ diameter) gold or gold/platinum coated carbon silk and gold screen current collector was then placed on top of the anion conducting membrane. The smallest stainless steel cylinder was then screwed into the Teflon cylinder and tightened to apply stack pressure to the entire assembly. This ensured good electrical contact between the gold/carbon anode current collector, anion conducting polymer membrane and air electrode, and minimized overall cell resistance. The smallest cylinder had a thin tube extending out of the top for adding fuel. This fill port was the anode terminal; the outer stainless cylinder the cathode. All measurements were made between these two electrodes. Best performing laboratory cells had internal resistances of 0.5–1.0 Ω as measured by current interrupt techniques.

2.2. Electrodes

Gold is an effective catalyst for BH_4^- oxidation [5,6] but not for BH_4^- hydrolysis while platinum is a good

Fig. 1. Schematic of the borohydride-air cell.

Labels in Fig. 1: FILL PORT; THREADED CONDUCTOR MONEL 400; FLUID RESERVOIR; THREADED PLASTIC INSULATOR TEFLON 10 % GLASS FILLED; CONDUCTIVE SCREEN; ANION MEMBRANE; AIR ELECTRODE; THREADED CONDUCTOR MONEL 400; AIR HOLES

Table 1
Current/power of a borohydride-air cell at room temperature and 70°C for different applied cell potentials

Cell potential, V	Room temperature		70°C	
	Steady state		Steady state	
	Current density mA/cm^2	Power density mW/cm^2	Current density mA/cm^2	Power density mW/cm^2
0.9	2.5	2.3	12.8	11.5
0.8	7.8	6.2	32.2	25.8
0.7	15.3	10.7	59.7	41.8
0.6	25.8	15.5	90.3	54.2
0.5	38.3	19.2	123.9	61.9
0.4	50.0	20.0	157.8	63.1
0.3	59.7	17.9	191.7	57.5
0.2	63.8	12.8	226.4	45.3
0.1	68.1	6.8	260.0	26.0
Short Circuit	152		277	

catalyst for both BH_4^- oxidation and hydrolysis. Soft, high surface area, conductive carbon silk cloth (Actitex, PICA, Columbus, OH) was used as anode current collector substrates because it would not puncture anion conducting membranes during cell assembly. Optimum energy densities were obtained with anode current collectors containing finely divided Au particles. Optimum power densities were obtained with anode current collectors containing finely divided 97% Au/3% Pt particles.

Au particles, either alone, or with 3% Pt, were electrochemically deposited on carbon cloths. Carbon cloths were supported in a stainless steel frame and suspended in an ultrasonically agitated aqueous plating solution containing $AuCl_4^-$ and chloroplatinic acid. Constant cathodic current was applied to the frame.

Fig. 2 shows a low magnification SEM of gold-coated carbon silk. Gold particles are fairly identical and uniformly distributed. When adhesive tape was pressed on gold or gold/platinum coated carbon silk surfaces and rapidly removed, no metal particles were observed on the removed tape. This indicated that deposited metal particles were adhering very well to the carbon surface.

2.3. Power measurements

The power density data in Table 1 were obtained by applying constant potentials (from −0.9 V to −0.1 V in 0.1 V steps) for one min across the 3.6 cm^2 borohydride-air cell. Cell potentials were then stepped to the next value and the procedure repeated. Power densities were calculated from steady state currents and applied potentials.

3. Results and discussions

3.1. Discharge capacity

Theoretical ampere–hour capacities of galvanostatically discharged borohydride-air laboratory cells were calculated

based on known weights of $NaBH_4$ in the cell and applied constant currents:

$$\frac{\text{grams NaBH}_4}{37.83 \text{ g/mole}} = \frac{(8e^-/BH_4^-) * I(A) * t(s)}{96,500 \text{ F/C} * 3600 \text{ s/h}}.$$

Comparing experimentally obtained ampere–hour capacity (current × time) to theoretical capacity (assuming all eight electrons per BH_4^- provide current), indicates cell reaction efficiency. The closer to eight electrons/BH_4^- obtained, the more efficient the BH_4^- oxidation. For our cells, we measured > 7 electrons (ampere–hours) utilized per BH_4^- initially present in the fuel; implying efficient utilization of BH_4^- oxidation.

With gold particles deposited on carbon cloth as an anode current collector, at 5 mA/cm^2 constant current discharge, we obtained specific energies (cell capacities) of 184 W h/kg of BH_4^- fuel (245 mA h/kg fuel). Higher specific energies could be obtained if a paste form of the fuel (mostly $NaBH_4$; less NaOH and water) were used. Since the air electrode would be providing the required eight OH^- ions per BH_4^- oxidized, OH^- would not have to be carried in the fuel and specific energies would increase.

Choosing proper anion conducting membranes to allow OH^- transport from the air cathode to the BH_4^- anode is crucial. Membranes for the borohydride-air cell must not only be stable in caustic environments, resistant to reduction, have reasonable mechanical stability, and be electrically insulating, but must also function as a selective anion transporter. Although OH^- transport is necessary for cell performance, BH_4^- transport is undesirable since it results in BH_4^- fuel being oxidized without generating electrical power. Thus, membranes for BH_4^- cells must allow efficient OH^- transport while simultaneously blocking BH_4^- transport.

3.2. Current/power

Representative current/power for a 3.6 cm^2 borohydride-air cell constructed with 97% Au/3% Pt on a con-
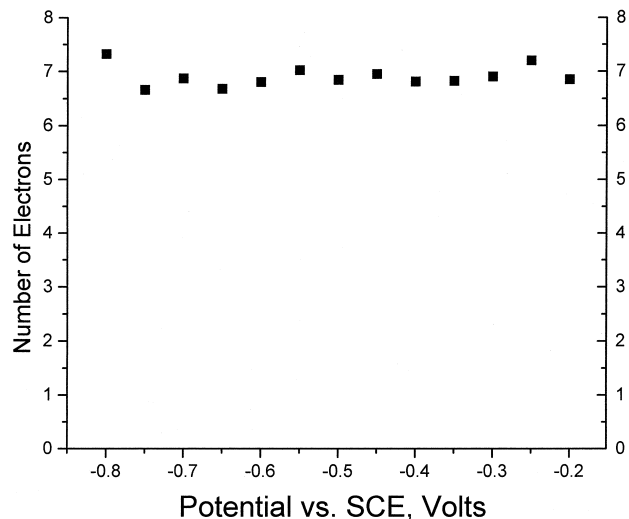
Fig. 3. The number of electrons utilized during BH_4^- oxidation (out of a maximum of eight) as a function of applied cell potential.

ductive, carbon silk anode current collector is shown in Table 1. These cells delivered 20 mW/cm^2 at room temperature and > 60 mW/cm^2 at 70°C.

3.3. The number of utilized electrons

Hydrogen generation, either through hydrolysis or oxidation of BH_4^- intermediates, limits the number of electrons that can be effectively utilized. The number of electrons contributing to (useful) oxidation and (unwanted) hydrogen generation reactions was determined as follows. Constant potential electrolysis were performed for fixed times in a sealed cell containing 5% NaBH$_4$ in 25% NaOH solution, a gold/carbon working electrode, and a Saturated Calomel Electrode (SCE) reference. Hydrogen gas, formed during the reaction, was collected in an inverted burette filled with water and its volume was measured. From this gas volume, and number of coulombs, the effective number of electrons (out of a possible eight) available for useful electrochemical work was obtained. This number, plotted for different applied potentials, is shown in Fig. 3. The gold electrode open circuit potential is approximately

-1.1 V relative to SCE. Over most of the potential range, the number of electrons available to provide useable energy/power is ~ 6.9. This value, in good agreement with the value > 7 obtained in discharge experiments above, indicates quite efficient BH_4^- oxidation.

4. Summary

Borohydride-air cells are an attractive, environmentally friendly, high energy/power source for consumer electronics and electromotive applications. With Au on carbon as a current collector, 6.9 out of a total of eight electrons can be utilized. Further performance enhancements are anticipated through improved oxidation catalysts (e.g., ternary metals) and improved OH$^-$ transporting (and BH_4^- rejecting) membranes.

Acknowledgements

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