

Short communication

A new fuel cell using aqueous ammonia-borane as the fuel

Xin-Bo Zhang, Song Han, Jun-Min Yan, Manish Chandra, Hiroshi Shioyama, Kazuaki Yasuda, Nobuhiro Kuriyama, Tetsuhiko Kobayashi, Qiang Xu*

National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Received 19 January 2007; received in revised form 1 March 2007; accepted 3 March 2007

Available online 12 March 2007

Abstract

Ammonia-borane (NH_3BH_3), as a source of protide (H^-), is initially proposed to release its energy through a fuel cell (direct ammonia-borane fuel cell, DABFC). Cell performance has been elucidated in a 25 cm^2 laboratory cell constructed with an oxygen cathode and an ammonia-borane solution fed anode, where the catalyst layers are made of Vulcan XC-72 with 30 wt.% Pt. The potential is 0.6 V at the current density of 24 mA cm^{-2} , corresponding to power density $>14\text{ mW cm}^{-2}$ at room temperature. The direct electron transfer from protide (H^-) in NH_3BH_3 to proton (H^+) has been further proved by the open circuit potential and the cyclic voltammetry results, which show the possibility of improvement in the performance of DABFC by, for example, exploring new electrode materials.

© 2007 Elsevier B.V. All rights reserved.

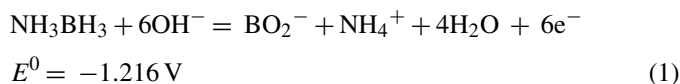
Keywords: Ammonia-borane; Fuel cells; Direct oxidation; Cyclic voltammetry; Electrocatalysis

1. Introduction

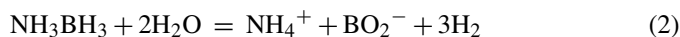
Because of their high hydrogen densities, ammonia-borane (NH_3BH_3) and the related amine borane compounds are now being intensely investigated to release their hydrogen via hydrolysis [1,2] or pyrolysis [3,4] routes. The obtained hydrogen gas can then be used to feed the fuel cells. Along these pathways, the protide (H^-) in NH_3BH_3 is firstly transformed into hydrogen gas (H^0) by the above mentioned dehydrogenation routes, and then the hydrogen gas is further transformed into water (H^+) by the electrochemical reaction in the fuel cell. It is obvious that if the direct electrochemical oxidation of ammonia-borane (H^- to H^+) occurs in a fuel cell, a more negative potential and more power than using hydrogen gas as the fuel (H^0 to H^+) can be obtained, which will also get rid of the problem of the safety and efficiency during storage and supply of the light and inflammable gas, H_2 .

Here, we, for the first time, propose a novel direct ammonia-borane fuel cell (DABFC) by combining the anodic oxidation of ammonia-borane and the cathodic reduction of O_2 . The anodic

oxidation of NH_3BH_3 is supposed to be as follows:



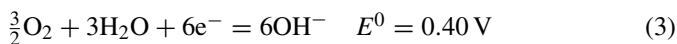
This potential is comparable with that of direct borohydride fuel cell proposed by Amendola et al. [5]. In the above reaction, each NH_3BH_3 releases six electrons. At 298 K, from the standard enthalpies [6–8] of -178 kJ mol^{-1} (NH_3BH_3), $-1380.144\text{ kJ mol}^{-1}$ (6OH^-), $-772.366\text{ kJ mol}^{-1}$ (BO_2^-), $-133.26\text{ kJ mol}^{-1}$ (NH_4^+), and $-1143.32\text{ kJ mol}^{-1}$ ($4\text{H}_2\text{O}$), and the standard entropies of $96.34\text{ J mol}^{-1}\text{K}^{-1}$ (NH_3BH_3), $-64.266\text{ J mol}^{-1}\text{K}^{-1}$ (6OH^-), $-37.238\text{ J mol}^{-1}\text{K}^{-1}$ (BO_2^-), $111.169\text{ J mol}^{-1}\text{K}^{-1}$ (NH_4^+) and $279.792\text{ J mol}^{-1}\text{K}^{-1}$ ($4\text{H}_2\text{O}$), the standard-state potential of the reaction (1) can be calculated to be -1.216 V (versus SHE), which is 0.388 V more negative than the hydrogen electrode in an alkaline medium. To effectively utilize the faradic capacity of NH_3BH_3 , the electrochemical oxidation rates should be higher than that of competitive side reactions. Hydrolysis as a main unwanted reaction, occurring to some extent in NH_3BH_3 solutions, generates hydrogen gas:



* Corresponding author. Tel.: +81 72 751 9652; fax: +81 72 751 9629.
E-mail address: q.xu@aist.go.jp (Q. Xu).

When one molecule of hydrogen is formed, two electrons are no longer available to provide electrical energy. Competition between NH_3BH_3 oxidation (reaction (1)) and hydrogen evolutions (reaction (2)) is a function of electrode material, electrolyte composition, applied potential, and so on. To minimize hydrolysis, we can increase the pH value of the solution and employ electrode materials inactive for hydrolysis.

For NH_3BH_3 oxidation, the required six OH^- can originate either from hydroxide initially present, or from a coupled oxygen reduction reaction that provides OH^- as follows:



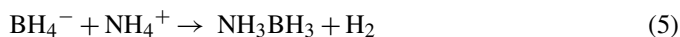
provide six OH^- necessary for NH_3BH_3 oxidation and yield the cell reaction:



An ammonia-borane/oxygen cell consists of a NH_3BH_3 -solution fed anode, the oxygen fed cathode, and an anion or cation permeable separator membrane. When electrodes are connected through an external circuit, NH_3BH_3 could be oxidized to BO_2^- whilst O_2 is reduced at the cathode to generate OH^- . Oxygen 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 1.616 V cell potential and low equivalent weight for NH_3BH_3 yield a high theoretical specific energy for the overall reaction:

$$\frac{(1.616 \text{ V})(96500 \text{ C F}^{-1})(1000 \text{ g kg}^{-1})}{(30.86 \text{ g} \cdot (6\text{F})^{-1})(3600 \text{ s h}^{-1})} = 8422.12 \text{ Wh kg}^{-1}$$

The combined advantages (i.e., NH_3BH_3 is chemically stable, not very expensive, readily available, and discharge products are water-soluble and environmentally safe) make the DABFC an extremely attractive power source. For this reason, we studied DABFC and show its viability as a primary power source. It should be noted that the used fuel (BO_2^-) can be reverted to BH_4^- through a reaction with a saline hydride (MgH) [9]. The resultant BH_4^- can then be converted into NH_3BH_3 via a reaction in diethyl ether at room temperature in accordance with the following equation [10]:



2. Experimental

2.1. Reagents

Ammonia-borane (NH_3BH_3 , Aldrich, ACS Reagent, purity 90%), sodium hydroxide (NaOH , Sigma–Aldrich, ACS Reagent, purity 97%), thiourea (TU , $\text{CH}_4\text{N}_2\text{S}$, Sigma–Aldrich, ACS Reagent, purity 100%), and polytetrafluoroethylene (POLYFLON PTFE, D-2CE, Daikin Industries, Ltd., PTFE content: 60 wt.%) were used without further purification.

2.2. Electrodes

An Au disk with 3 mm diameter (area of $7.07 \times 10^{-2} \text{ cm}^2$; BAS Inc.) was employed as the working electrode for CV tests. Before each CV experiment, the Au electrode was polished with $0.5 \mu\text{m}$ diamond paste (BAS Inc.). After the mechanical pre-treatment, the working electrodes were cleaned by sonication in distilled water and finally rinsed by distilled water.

Considering the special aspects in electricity generation and ion transfer mechanism of our cells, we prepared a membrane electrode assembly (MEA) structure electrode for the cell performance test. Vulcan XC-72 with 30 wt.% platinum was used for both of the anode and cathode catalysts. The electrocatalysts were made into a thin layer (ca. $100 \mu\text{m}$) by mixing with the 5 wt.% Nafion solution (Sigma–Aldrich). The Pt loadings were ca. 0.15 mg cm^{-2} for both of the anode and cathode. The electrode-coated polytetrafluoroethylene (PTFE) sheets were placed on both the sides of Nafion 117 membrane and then hot-pressed with the carbon cloth or carbon paper used as porous packing layers at 423 K to form the MEA. Evaluations of cell performance were conducted using a single cell with an activated area of 25 cm^2 . The cell temperature was RT. It should be pointed out that the carbon cloth at the cathode side is wet proofing whereas both carbon cloth and carbon paper employed at the anode side are no wet proofing.

2.3. Electrochemical characterization

The open circuit potential was measured by holding the electrodes in NH_3BH_3 solutions until the potential became stable. Potentials are measured versus SCE reference electrode.

In CV tests, the potential of the working electrode was controlled by a HZ-5000 automatic polarization system (Hokuto Denko Inc., Japan) carried out in a conventional three-electrode cell arrangement. The effective cell volume was 35 ml. The electrolyte was 2 M NaOH with 0.02 M NH_3BH_3 without/with 0.002 M TU. All experiments were performed at room temperature.

The cell polarization was carried out using a PLZ664WA electronic load (Kikusui electronics Corp., Japan) by applying constant currents for 10 s at each point. Power densities were calculated from the voltages and applied current. The fuel was 0.01 M NH_3BH_3 solutions in 2 M NaOH . It was pumped into the cell at a flow rate of about 5 ml min^{-1} .

3. Results and discussion

3.1. Performance of the single cell

To confirm whether the DABFC is feasible, we constructed a laboratory fuel cell and its performance at 298 K is shown in Fig. 1. It can be seen that the performance of the cell with carbon cloth is better than that with carbon paper. In the former case, the potential is 0.6 V at the current density of 24 mA cm^{-2} . It is found that hydrogen gas was evolved from the anode side whether in an open circuit condition or during operation. So, how to restrain the ammonia-borane hydrolysis is a key point to

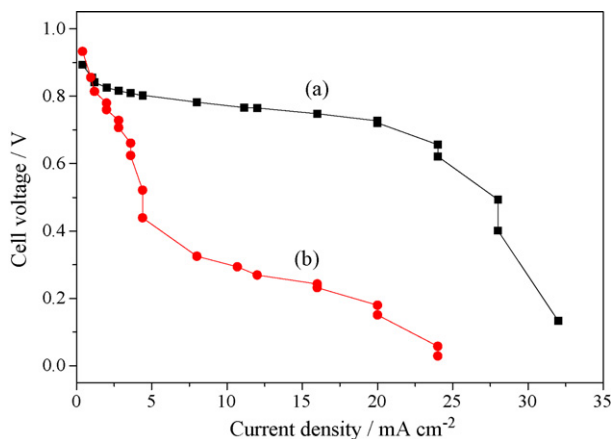


Fig. 1. Discharge curves of a single fuel cell using different carbon materials at anode side (fuel: 0.01 M NH_3BH_3 in 2 M NaOH): (a) carbon cloth and (b) carbon paper.

improve the coulombic efficiency of our cells. Using different electrode materials and surface treatment of these materials are considered to be the reasonable ways to restrain the hydrogen evolution.

3.2. Open circuit potential

Open circuit potential (OCP) is a very important indicating parameter for choosing suitable electrode materials for the NH_3BH_3 electrooxidation. Table 1 shows the OCPs of different electrodes in ammonia-borane solution with different concentrations. It is found that the OCPs are strongly dependent of the electrode materials and the concentration of BH_3NH_3 solution. In the case of Ni foam ($35\text{--}44\text{ cell in.}^{-1}$) and Ni mesh (100 mesh), their OCPs are different, indicating that the electrode morphology is another important effective factor. Moreover, excepting Ta rod and Pt plate, there is no linear relationship between the OCP and the BH_3NH_3 concentration, and the observed OCPs for all electrodes were less negative than their theoretical values, implying that the observed potentials are established among NH_3BH_3 and other partially oxidized intermediates, especially molecular hydrogen (reaction (2)). Although the observed OCPs are less negative than the theoretical values, in the case of Ta rod, Cu mesh and Pt plate, it is apparently higher than the hydrogen potential in the alkaline environment (-0.926 V versus Hg/HgO [11], corresponding to -1.070 V versus SCE), providing evidence for a direct electrochemical oxidation of NH_3BH_3 . Further investigation on seeking for new electrode materials, such as hydrogen storage alloy, or chemical modification of electrode surface,

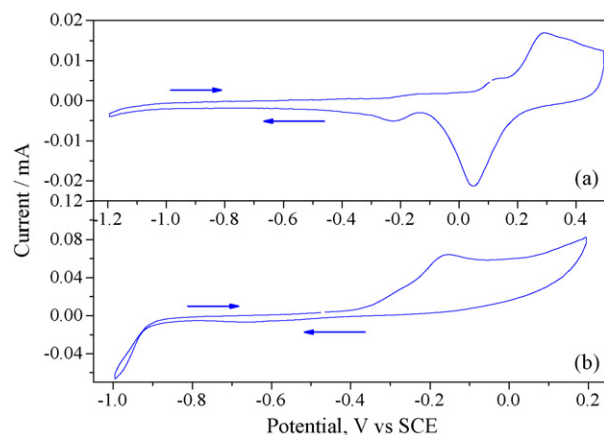


Fig. 2. Cyclic voltammogram recorded at a 3 mm diameter gold electrode in 2 M NaOH without (a) and with (b) 0.002 M $\text{CH}_4\text{N}_2\text{S}$ at 100 mV s^{-1} .

may push the OCP to its theoretical value. Moreover, like other middle-temperature fuel cell, the potential could become more negative when work under higher temperature.

3.3. CV results

Both of the Pt and Au electrodes are employed for the CV test to investigate whether there are peaks corresponding to direct electrochemical oxidation of NH_3BH_3 . However, in the case of Pt, there exists no peak that could be reasonably attributed to the direct electrooxidation of NH_3BH_3 (one strong oxidation peak at -0.751 V is observed). It is reported that, unlike the Pt electrode, the choice of Au electrode could eliminate hydrolysis and provide the most reliable way for studying the direct electrooxidation of BH_4^- [12]. We thus expect the Au electrode to be effective in NH_3BH_3 system and the following are the results. To check the background of the Au electrode in 2 M NaOH without (Fig. 2a) or with (Fig. 2b) 0.002 M TU, the typical behavior is observed in the CV recorded over the potential range $+0.2$ to -1.0 V versus SCE. The onset of monolayer oxide formation [13] is shown to occur above 0.05 V (Fig. 2a) with the corresponding oxide reduction peak on the reverse sweep. With the presence of TU in the electrolyte, there is an oxidation peak at -155.66 mV (Fig. 2b) which is due to the adsorption of TU on the Au electrode surface.

Fig. 3 shows the NH_3BH_3 cyclic voltammogram on the Au electrode. In the potential range of $+0.2$ to -1.0 V versus SCE, the electrochemical behavior of NH_3BH_3 is fairly complicated as characterized by a number of oxidation peaks. Scanning in the positive direction, at a rate of 0.1 V s^{-1} , the first oxidation peak occurs at -818.12 mV (p1), followed by a second anodic peak

Table 1
Open circuit potential of different electrodes in ammonia-borane solution with different concentrations

Concentration (M)	Open circuit potential (mV vs. SCE)					
	Ta rod	Au wire	Ni foam	Ni mesh	Cu mesh	Pt plate
0.01	-808	-782	-892	-883	-1291	-964
0.02	-942	-919	-987	-1055	-1216	-1094
0.03	-1115	-785	-964	-1037	-1164	-1140

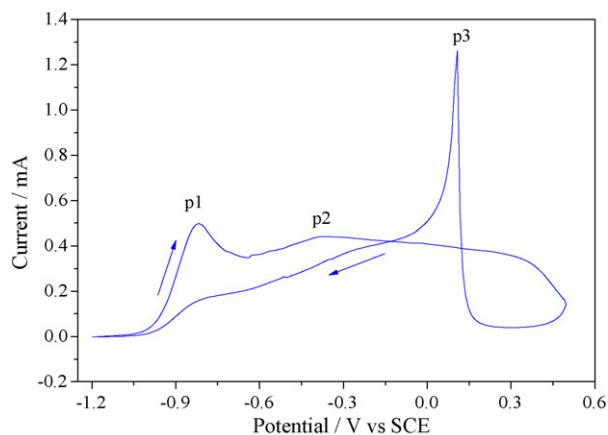


Fig. 3. Cyclic voltammogram of 0.02 M NH_3BH_3 in 2 M NaOH on Au electrode (3 mm diameter) at 100 mV s^{-1} .

at about -378.29 mV (p2). On the reverse scan, interestingly, an additional oxidation peak has been observed with a peak potential of 107.23 mV (p3). It is suggested that amine-boranes may be oxidized via the reactive intermediated hydroxytrihydroborane ion, BH_3OH^- [14]. Regarding the processes responsible for the peak p1, conclusions could be drawn based on the occurrence of H_2 bubble adsorbed on the gold electrode and comparison with the voltammogram obtained in the absence of NH_3BH_3 (Fig. 2a). Gyenge [12] reported that the electrooxidation of H_2 yielding from catalytic hydrolysis of BH_4^- is at the peak potentials between -0.7 and -0.9 V versus Ag/AgCl. Based on their similarity, the peak p1 as well as the oxidation peak in CV of Pt electrode could be attributed to the $\text{H}_2/\text{H}_2\text{O}$ couple in which H_2 may come from the catalytic hydrolysis (reaction (2)) or the following electrochemical hydrolysis:



It is reported that direct electrooxidation of BH_3OH^- is typically observed over a wide potential range between -0.3 and -0.67 V on Au in 0.2 M KOH [15]. In the present study, the peak p2 is located in the same potential region, indicating that the peak p2 may be due to the direct electrooxidation of NH_3BH_3 , probably via the intermediate BH_3OH^- , i.e., without the implication of H_2 electrooxidation. Regarding the peak p3, it could be attributed to the reaction intermediates of BH_3OH^- electrooxidation on Au surface.

Thiourea is chosen as an additive for the present system due to its inhibiting effect on the H_2 evolution reaction by retarding the Tafel process (i.e., $2\text{H}_{\text{ad}} \leftrightarrow \text{H}_2$) [16]. This effect is very important for BH_3OH^- electrooxidation, that is, by minimizing the H_2 evolution rate, the additives could potentially improve the coulombic efficiency of DABFC. Fig. 4 shows the effect of 0.002 M TU on the BH_3OH^- voltammogram on Au electrode in 2 M NaOH . Comparing Figs. 3 and 4, i.e., without and with TU respectively, reveals that TU considerably change the BH_3OH^- cyclic voltammogram by eliminating the peaks p1 and p3. In addition, in the presence of TU one new peak, p4 with E_p at -85.67 mV appears. Thus, taking into account the retardation of the Tafel step by TU, i.e., in the present system TU

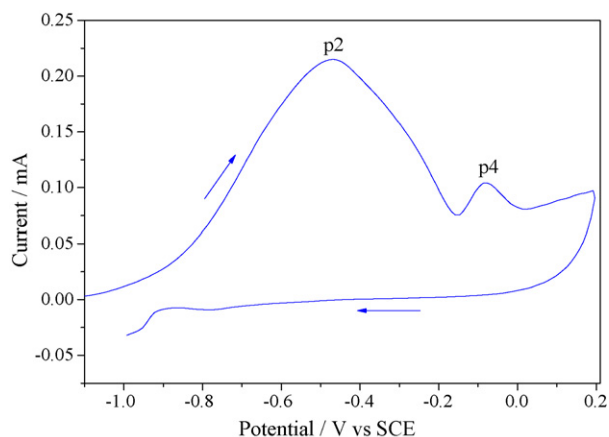


Fig. 4. CV recorded at a 3 mm diameter gold electrode for NH_3BH_3 (0.02 M) oxidation in 2 M NaOH in presence of $0.002 \text{ M CH}_4\text{N}_2\text{S}$ at 100 mV s^{-1} .

inhibits the H_2 evolution in conjunction with both the catalytic hydrolysis of BH_3OH^- (reaction (2)) and the electrooxidation of BH_3OH^- (reaction (6)) responsible for peak p1, and peak p2 could also be due to the direct electrooxidation of NH_3BH_3 , probably via the intermediate BH_3OH^- . Regarding p4, there is an obvious similarity between p4 and the oxidation peak in Fig. 2b, with the former shifted to a more positive potential, i.e., -87.67 versus -155.66 mV , respectively. This oxidation peak could be attributed to the adsorbed TU on Au electrode surface as well as the reaction intermediates of BH_3OH^- electrooxidation.

4. Summary

A fuel cell has been developed using the aqueous ammonia-borane solution as the fuel. We constructed a laboratory fuel cell using membrane electrode assembly. At the discharge current density of 24 mA cm^{-2} and potential of 0.6 V , power density $>14 \text{ mW cm}^{-2}$ has been obtained at room temperature. The results showed that the OCP is up to -1.291 V (versus SCE) which is about 221 mV more negative than the hydrogen potential in the alkaline solution, but less negative than the theoretical value ($E^0 = -1.216 \text{ V}$). The CV results give evidence of the direct electrooxidation of NH_3BH_3 . Further intensive investigations on improving the anode materials are needed to utilize the theoretical six electron transfer and thus increase the coulombic efficiency. Moreover, supplying the evolved hydrogen to an alkaline FC or a proton exchange membrane fuel cell (PEMFC) is another effective way to increase the coulombic efficiency from a system consideration. Our results will aid the search for other attractive, environmentally friendly, high energy density alternative fuel. Other amine borane compounds such as $\text{NH}_3\text{B}_3\text{H}_7$ and Me_2NHBH_3 are possible alternatives.

Acknowledgment

The present work is financially supported by NEDO and AIST. The authors thank Ms. Naoko Fujiwara for valuable discussion and help. Xin-Bo Zhang thanks JSPS for a fellowship.

References

- [1] M. Chandra, Q. Xu, *J. Power Sources* 156 (2006) 190.
- [2] Q. Xu, M. Chandra, *J. Power Sources* 163 (2006) 364.
- [3] A. Gutowska, L. Li, Y. Shin, C.M. Wang, X.S. Li, J.C. Linehan, R.S. Smith, B.D. Kay, B. Schmid, W. Shaw, M. Gutowski, T. Autrey, *Angew. Chem. Int. Ed.* 44 (2005) 3578.
- [4] G. Wolf, J. Baumann, F. Baitalow, F.P. Hoffmann, *Thermochim. Acta* 343 (2000) 19.
- [5] S.C. Amendola, P. Onnerud, M.T. Kelly, P.J. Petillo, S.L. Sharp-Goldman, M. Binder, *J. Power Sources* 84 (1999) 130.
- [6] T-Raissi, Proceedings of the (2002) U.S. DOE Hydrogen Program Review, <http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/32405b15.pdf>.
- [7] R.C. Weast, M.J. Astle, W.H. Beyer (Eds.), *CRC Handbook of Chemistry and Physics*, 67th ed., CRC Press, Florida, 1986–1987, p. D-163.
- [8] G. Wolf, WE-Heraeus-Seminar on Hydrogen Storage with Novel Nanomaterials (Germany), http://www.h-workshop.uni-konstanz.de/pdf/Wolf_Gert.pdf.
- [9] Z.P. Li, B.H. Liu, K. Arai, N. Morigazaki, S. Suda, *J. Alloys Compd.* 356–357 (2003) 469.
- [10] S.G. Shore, R.W. Parry, *J. Am. Chem. Soc.* 77 (1955) 6084.
- [11] B.H. Liu, Z.P. Li, S. Suda, *J. Electrochem. Soc.* 150 (2003) A398.
- [12] E. Gyenge, *Electrochim. Acta* 49 (2004) 965.
- [13] L.C. Nagle, J.F. Rohan, *Electrochem. Solid State Lett.* 8 (2005) C77.
- [14] A. Sargent, O.A. Sadik, L.J. Matienzo, *J. Electrochem. Soc.* 148 (2001) C257.
- [15] Y. Okinaka, *J. Electrochem. Soc.* 120 (1973) 739.
- [16] T. Maoka, M. Enyo, *Surf. Technol.* 9 (1979) 147.