

Short communication

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

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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.

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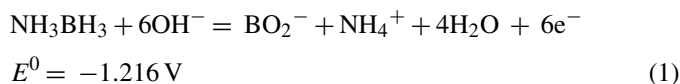
Keywords: Ammonia-borane; Fuel cells; Direct oxidation; Cyclic voltammetry; Electrocatalysis

1. Introduction

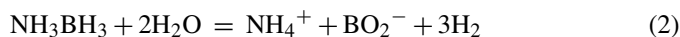
Because of their high hydrogen densities, ammonia-borane (NH_3BH_3) and the related amine borane compounds are now being intensely investigated to release their hydrogen via hydrolysis [1,2] or pyrolysis [3,4] routes. The obtained hydrogen gas can then be used to feed the fuel cells. Along these pathways, 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:



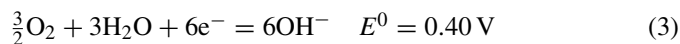
This potential is comparable with that of direct borohydride fuel cell proposed by Amendola et al. [5]. In the above reaction, each NH_3BH_3 releases six electrons. At 298 K, from the standard enthalpies [6–8] of -178 kJ mol^{-1} (NH_3BH_3), $-1380.144\text{ kJ mol}^{-1}$ (6OH^-), $-772.366\text{ kJ mol}^{-1}$ (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:



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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:



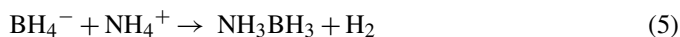
provide six OH^- necessary for NH_3BH_3 oxidation and yield the cell reaction:



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

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