



Short communication

A high performance anion exchange membrane-type ammonia borane fuel cell

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ABSTRACT

The electrochemical behavior of the novel fuel cell directly using aqueous ammonia borane (NH_3BH_3) as the fuel has been systematically investigated. The cell consists of an oxygen cathode and an ammonia borane solution fed anode, where the catalyst layers are made of Vulcan XC-72 with 46.6 wt.% Pt. An anion exchange membrane is employed as the electrolyte. It is found that the concentrations of NH_3BH_3 solution and temperatures significantly affect the open circuit potentials of the anode as well as the cell performance. Although the cell voltages decrease with the increase of current densities, the cell is capable of discharging at a current density of 185 mA cm^{-2} with the cell potential larger than 0.6 V. The obtained high energy densities indicate that the direct ammonia borane fuel cell holds potential applications for portable devices.

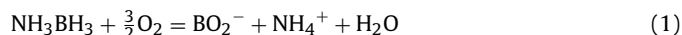
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1. Introduction

In the past decades, much attention has been paid to fuel cells because they could offer an attractive electricity generation technology that directly converts chemical energy into electricity with high efficiency [1,2]. Nowadays, proton exchange membrane fuel cells (PEMFCs) represent the most advanced fuel cell technology and are produced for vehicles and stationary application on a large scale [3]. Although pure H_2 is an ideal fuel for PEMFCs system, hydrogen storage technologies are still on the way to match practical requirements [4]. It is now well admitted that using other liquid fuels to replace hydrogen for feeding fuel cell anodes would have many advantages in terms of fuel cell system simplicity, high mass and volume densities, as well as safety reasons [5], which are mandatory for portable electronic devices. Many liquid fuels, such as methanol [6–8], ethanol [9,10], and ethylene glycol [11,12], have been employed as a substitute to hydrogen for low-temperature fuel cells. However, their electro-oxidation is generally slow. On this background, ammonia borane (NH_3BH_3), which is a safe, non-toxic, chemically stable, easy to transport in its dry state and is highly soluble in water [13–19], is emerging as a potential fuel for fuel cells.

A novel fuel cell using the aqueous ammonia borane solution as the fuel has been proposed [20,21]. It possesses high capacity

(5.2 Ah g^{-1}) and energy density (8.4 Wh g^{-1} at 1.62 V) according to the following cell reaction:



It should be noted that the used fuel (BO_2^-) can be reverted to BH_4^- through a reaction with a saline hydride (MgH) [22]. The resultant BH_4^- can then be converted into NH_3BH_3 via a reaction in diethyl ether at room temperature [23].

In this paper, considering the reaction mechanism of direct ammonia borane fuel cell (DABFC), that is, OH^- is produced at the cathode side and should be able to pass through the membrane to support the anode reaction, an anion exchange membrane is employed as the electrolyte. The performance of DABFC at different ammonia borane concentrations and temperatures was systematically investigated, and the obtained high energy densities provide us the promising prospect of DABFC to be used for portable devices.

2. Experimental

2.1. Reagents

Ammonia borane (NH_3BH_3 , Aldrich, purity 90.0%), sodium hydroxide (NaOH, Sigma–Aldrich, purity 97.0%), carbon supported platinum catalyst (Pt/C, TEC10V50E, Tanaka Kikinzo Kogyo, 46.6 wt.% Pt), ionomer solution of anion exchange resin (Tokuyama Corp., 5.0 wt.% resin, anion exchange capacity 2.0 mmol g^{-1}), and 2-ethoxyethanol ($\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$, Wako Pure Chemical Industries, Ltd., 98.0 wt.%) were used as received.

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2.2. Electrode preparation

Considering the special aspects in electricity generation and ion transfer mechanism of our fuel cells, we prepared a membrane electrode assembly (MEA) structure electrode for the fuel cell performance tests. Carbon supported platinum catalyst was used as both the anode and cathode catalysts. The catalyst was mixed with the ionomer solution of anion exchange resin and 2-ethoxyethanol, and then the mixture was laid on a polytetrafluoroethylene (PTFE) sheet and made into a thin layer (ca. 100 μm). Two pieces of the prepared catalyst layers were placed on both sides of anion exchange membrane (AEM, Tokuyama Corp., thickness 28 μm , anion exchange capacity 1.8 mmol g^{-1}) and then hot-pressed with the carbon cloth (used as porous packing layers) at 403 K to form the MEA. The Pt loadings were ca. 0.76 and 0.93 mg cm^{-2} for the anode and cathode, respectively. The MEA was sandwiched by two carbon plates with slits for fuel and air. Ammonia borane solution was pumped to the anode side and O_2 flow was introduced to the cathode.

2.3. Electrochemical characterization

To test the open circuit potentials (OCPs) of the anode side, an Hg/HgO reference electrode was placed in the fuel reservoir. The data were recorded until the potential became stable. The potentials of the cathode side were deduced from the potential values of the single cell and the anode side.

Evaluations of the cell performance were conducted using a single cell. The cell polarization was measured using a PLZ664WA electronic load (Kikusui electronics Corp., Japan) by applying a constant current for 10 s at each point. Power densities were calculated from the voltages and applied currents. The aqueous NH_3BH_3 fuel in 2 M NaOH was pumped into the cell at a flow rate of about 50 mL min^{-1} . The cell temperature was controlled through heating the fuel cell stack to 298, 308, or 318 K for the polarization measurements. The oxygen (humidified by bubbling through water or un-humidified) was supplied at the corresponding temperatures at a flow rate of about 120 mL min^{-1} . The cell stability tests were conducted using a current of 50 or 120 mA at room temperature.

2.4. Energy dispersive X-ray spectrometry (EDX) measurements

A fuel cell was assembled to verify the fuel crossover during cell operation. After operating at a current of 5 mA cm^{-2} for 2 h, the cathodes were subjected to a qualitative analysis of the N distribution by scanning electron microscopy and energy-dispersive X-ray analysis (SEM-EDX). The fluorescence of the atoms excited by the electron beam employed in the SEM measurements allowed the elemental identification of the samples using $\text{N K}\alpha^1$ line (0.392 keV).

3. Results and discussion

3.1. Open-circuit potential

As shown in Fig. 1, it can be easily found that the OCPs are strongly dependent on the concentrations of NH_3BH_3 solution. Although the OCP for the anode/anolyte system monotonously becomes more negative with the increase in the NH_3BH_3 concentration, the change in OCP includes three parts as follows: at the first stage where the NH_3BH_3 concentration is very low, the change in potential with the logarithm of the concentration is very slow; at the second stage, where the concentration increases to a certain level (about 0.05 M), the change in potential with the increase in the NH_3BH_3 concentration becomes much quicker. We suppose

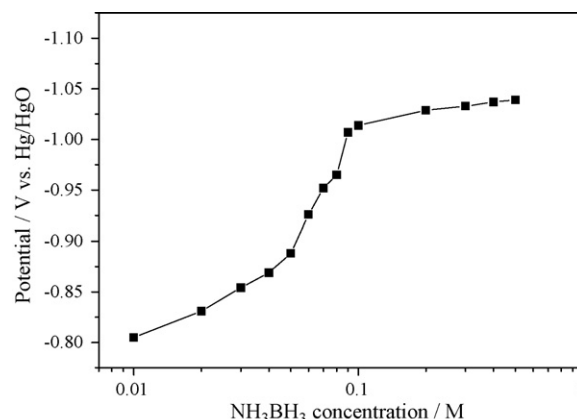
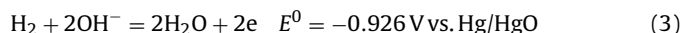
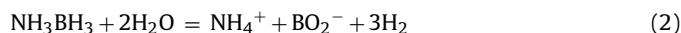


Fig. 1. The dependence of the open circuit potentials of anode side in direct ammonia borane fuel cell on the NH_3BH_3 concentration at 298 K.

that the difference in change tendency is related to a variation of the electrode surface. At low concentrations of NH_3BH_3 , the electrode surface is supposed to be in a passive state. When the NH_3BH_3 concentration increases to a certain level, the surface oxide or hydroxide may be chemically reduced by NH_3BH_3 and the surface changes to an active state; at the third stage, with the further increase in NH_3BH_3 concentration, the potential change becomes slow and the linear relation of the potential with the logarithm of NH_3BH_3 concentrations suggests that the potential corresponds to a reaction involving NH_3BH_3 . It has been reported that the standard potential of the expected anodic reaction is -1.216 V vs. NHE ($-1.314 \text{ V vs. Hg/HgO}$) [20]. The potentials observed here were less negative than this value, which may be partially established among NH_3BH_3 and other partially oxidized intermediates, especially molecular hydrogen derived from the following unwanted reactions:



Although the observed OCPs are less negative than the theoretical value, they are apparently higher than the hydrogen potential in the alkaline environment as shown above in Reaction (3), providing further evidence for a direct electro-oxidation of NH_3BH_3 .

Fig. 2 shows temperature dependence of OCPs. It is found that the potential becomes more negative with increasing temperature. This is consistent with the observations for other fuel cells, such as direct borohydride fuel cell [24].

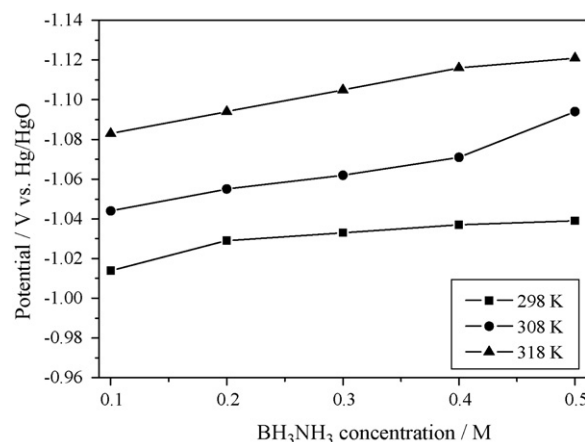


Fig. 2. The dependence of open circuit potentials of the anode side in direct ammonia borane fuel cell on the temperature and NH_3BH_3 concentration.

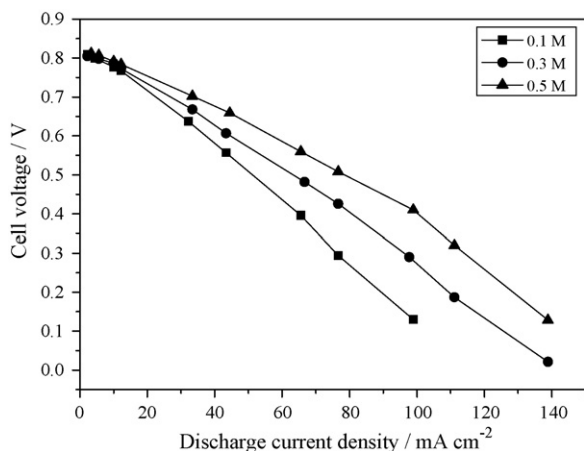


Fig. 3. Cell polarization of the DABFC with different NH_3BH_3 concentrations at 298 K. Anode: $0.76 \text{ mg Pt cm}^{-2}$, NH_3BH_3 solutions with different concentrations in 2 M NaOH at a flow rate of 50 mL min^{-1} . Cathode: $0.93 \text{ mg Pt cm}^{-2}$, humidified O_2 at 120 mL min^{-1} (1.2 atm).

3.2. Discharge performance

The dependences of discharge performance of the fuel cell on NH_3BH_3 concentration and working temperature are shown in Figs. 3 and 4, respectively. It can be seen that the increase in NH_3BH_3 concentration can significantly improve the cell performance, especially at higher current densities. This is because that the polarization is strongly dependent on the concentration of NH_3BH_3 at the electrode surface domain. Higher concentration can alleviate the fuel exhaustion within the electrode surface area and thus improve the cell performance. Moreover, the surface activity of the electrode, influenced by the NH_3BH_3 concentration as discussed above, may also affect the cell performance.

Fig. 4 shows the performances of the single cell at 298, 308, and 318 K. It is found that the temperature also strongly affects the discharge performance of the fuel cell. Like other low-temperature fuel cells, increasing the operation temperature leads to the improvement of the cell performance. This may be attributed to the improved catalytic activities of the anode and cathode at elevated temperatures. At the current density of 185 mA cm^{-2} and potential of 0.6 V, the power density $>110 \text{ mW cm}^{-2}$ has been obtained at 318 K. Considering the obtained high energy densities, we can expect the application of DABFC to portable devices.

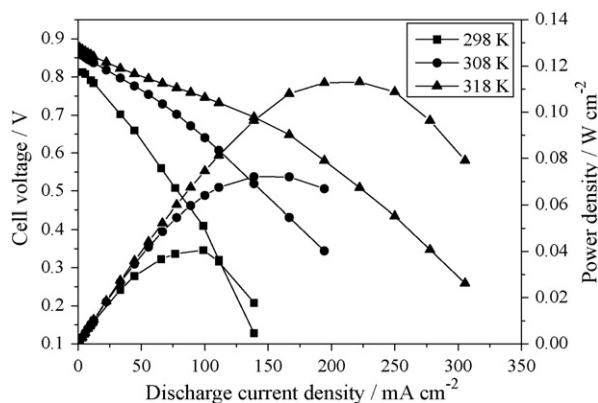


Fig. 4. Cell polarization and power densities for the DABFC at 298, 308, and 318 K. Anode: $0.76 \text{ mg Pt cm}^{-2}$, 0.5 M NH_3BH_3 in 2 M NaOH at a flow rate of 50 mL min^{-1} . Cathode: $0.93 \text{ mg Pt cm}^{-2}$, humidified O_2 at 120 mL min^{-1} (1.2 atm).

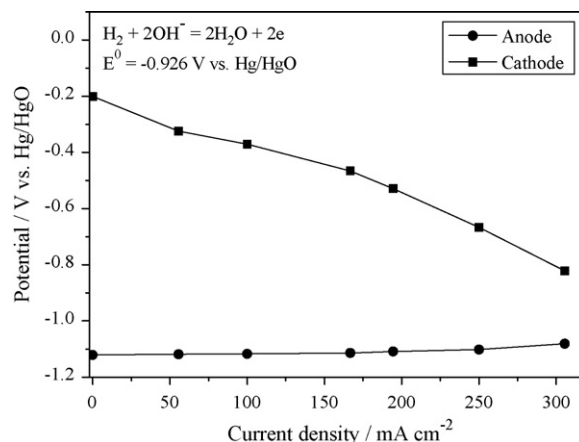


Fig. 5. Polarization curves for the DABFC at 318 K. Anode: $0.76 \text{ mg Pt cm}^{-2}$, 0.5 M NH_3BH_3 in 2 M NaOH at a flow rate of 50 mL min^{-1} . Cathode: $0.93 \text{ mg Pt cm}^{-2}$, humidified O_2 at 120 mL min^{-1} (1.2 atm).

Furthermore, to find out the reasons responsible for the dramatic potential drop of the single cell at high current densities, the potentials of both anode and cathode sides during the cell operation are given in Fig. 5. Interestingly, with the increase in current density the potential of the anode is kept unchanged, while the cathode is subject to a larger potential drop. The results observed here is similar to other fuel cells such as the direct borohydride fuel cell (DBFC), the PEMFC, the DMFC, and the AFC [24]. So the dramatic potential drop of the single cell comes from the large potential drop of cathode.

It is expected that AEM as the electrolyte inhibits the cation (NH_4^+) migration from the anode side to the cathode compartment. As a result, mainly anion (BO_2^- , OH^-) or neutral particles (H_2O , NH_3BH_3) can penetrate the membrane during operation. If NH_3BH_3 molecules, which may be accompanied with water, can pass through the membrane, thus fuel crossover happened and will seriously decrease the potential of cathode. To verify this assumption,

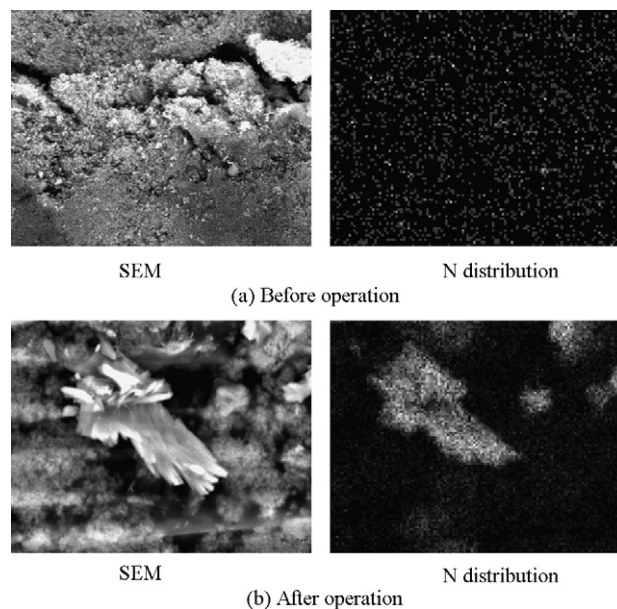


Fig. 6. Scanning electron microscopy picture and N distribution on the cathode catalyst (a) before and (b) after operation at the current density of 5 mA cm^{-2} for 2 h. Anode: $0.76 \text{ mg Pt cm}^{-2}$, 0.5 M NH_3BH_3 in 2 M NaOH at a flow rate of 50 mL min^{-1} . Cathode: $0.93 \text{ mg Pt cm}^{-2}$, humidified O_2 at 120 mL min^{-1} (1.2 atm).

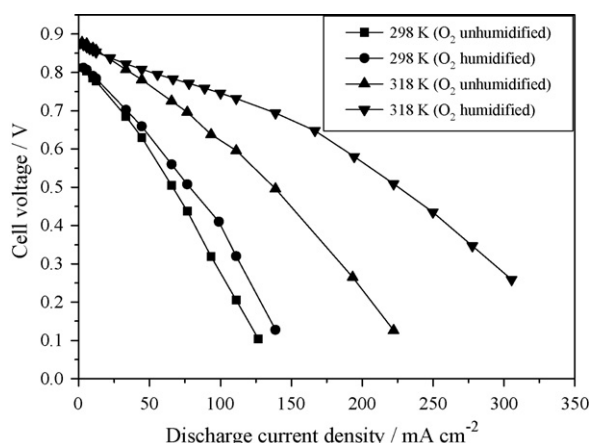


Fig. 7. Polarization curves for the DABFC using unhumidified and humidified O_2 at 298 and 318 K. Anode: $0.76 \text{ mg Pt cm}^{-2}$, $0.5 \text{ M NH}_3\text{BH}_3$ in 2 M NaOH at a flow rate of 50 mL min^{-1} . Cathode: $0.93 \text{ mg Pt cm}^{-2}$, unhumidified and humidified O_2 at 120 mL min^{-1} (1.2 atm).

EDX measurements were performed (Fig. 6). It is found that, after fuel cell operation, there is a mass of N (white spot) in the cathode. Considering that much lower amount of N is found at this electrode prior to electrochemical cell operation, we can reasonably conclude that NH_3BH_3 migrates from the anode side to the cathode compartment through the anion membrane and is thereafter oxidized at the cathode side. This will degrade the cell performance during the operation. We need develop high performance membranes to suppress the fuel crossover and thus improve cell performance of DABFC.

It is well known that the O_2 humidification should be considered in other fuel cell systems, such as PEMFCs. In our system, the influence of O_2 humidification on the cell performance is shown in Fig. 7. It is found that humidified O_2 can improve the cell performance because the water is involved in the cathode reaction. Moreover, this effect is more significant at higher temperature. This may be because that, at higher temperature, the electrodes are more active and thus more H_2O should be rapidly transfer to the cathode surface. In this case, the penetration of water from the anode side to the cathode side is not quick enough to support the rapid reaction. As a result, humidified O_2 can provide the cell with high open circuit potential and improved performance at high current densities.

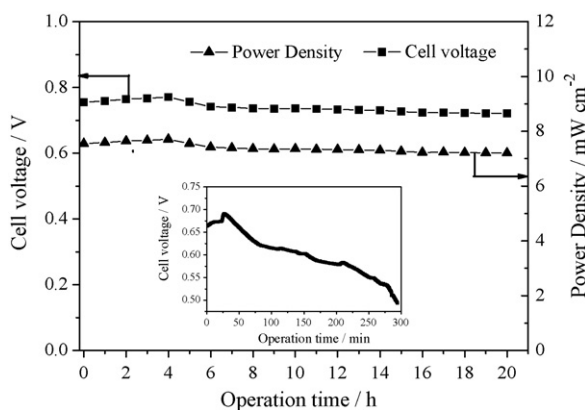


Fig. 8. Cell performance stability of the cell at 50 mA (120 mA for inset) at 298 K. Anode: $0.9 \text{ mg Pt cm}^{-2}$, $0.5 \text{ M NH}_3\text{BH}_3$ in 2 M NaOH at a flow rate of 50 mL min^{-1} . Cathode: $1.3 \text{ mg Pt cm}^{-2}$, humidified O_2 at 120 mL min^{-1} (1.2 atm).

3.3. Cell stability

Cell stability is very important from the viewpoint of practical application. We investigated the cell stability of our fuel cell at currents of 50 and 120 mA (Fig. 8). It can be seen that the cell can endure gradual performance degradation at the low current (50 mA), while the cell suffers from a significant loss of performance at the high current (120 mA). After waiting for a few minutes, the cell potential can recover to its initial value (before cell performance stability). The significant voltage decay at high current density suggests the deficiency of fuel and/or water at the catalyst surfaces at the anode and the cathode sides, respectively. Further efforts to improve the cell stability are in progress.

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. The cell consists of an oxygen cathode and an aqueous ammonia borane solution fed anode, where the catalyst layers are made of Vulcan XC-72 with 46.6 wt.% Pt. An anion exchange membrane is employed as the electrolyte. It is found that the open circuit potential of anode is strongly dependent of the NH_3BH_3 concentration and temperature. At the current density of 185 mA cm^{-2} and potential of 0.6 V, power density $>110 \text{ mW cm}^{-2}$ has been obtained at 318 K.

The above-obtained high energy densities provide us a high potential of application of aqueous NH_3BH_3 as the fuel for portable fuel cells. However, there still exist several problems with the present system. Hydrogen gas evolution lowers the efficiency and makes the system complicated. We hope to overcome these problems by system design and careful selection of anode catalyst materials and membranes.

Acknowledgments

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