

Short communication

## A preliminary study of direct borazane fuel cell

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### Abstract

Borazane ( $\text{BH}_3\text{NH}_3$ ) is a stable and low-toxic crystalline solid with possibly the highest hydrogen content (19.5 wt.%) in chemical compounds. In this communication, we report for the first time the electrooxidation of borazane and a novel direct fuel cell using alkaline borazane solution as alternative fuel. Of particular importance in this work is that non-platinum catalysts were applied for both the anode and the cathode. After a screening of a number of candidates (including Pt, Au, Ni, Cu, etc.), Ag was found to be a highly efficient catalyst for anodic oxidation of borazane, and  $\text{MnO}_2$  turned out to be a good cathode catalyst showing borazane-tolerance. The energy density of the fuel released by such a preliminary direct fuel cell was ca.  $2000 \text{ mAh g}^{-1}$  at  $1 \text{ mA cm}^{-2}$  and  $0.9 \text{ V}$  at room temperature.

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Polymer electrolyte membrane fuel cells (PEMFC) have been now successfully developed to demonstrate a variety of applications from portable electronics to electric vehicles. [1] However, there still exist several economic and technical obstacles to the commercialization of fuel cells. One of the main problems is the high cost arising from the use of expensive noble metal catalysts and perfluorosulfonic polymer electrolyte. In addition, the present hydrogen storage technology cannot meet the application requirement of  $\text{H}_2$ -fueled PEMFC; [2] on the other hand, the sluggish anodic kinetics and the methanol crossover still remain to be major problems for further development of methanol-powered PEMFC. [3] These difficulties relate to, at least in part, the use of  $\text{H}_2$  and methanol as fuels. To solve these problems, the search for alternative fuels has received considerable attentions in recent years.

$\text{NaBH}_4$  is one of the most attractive alternative fuels. The advantage of direct borohydride fuel cells (DBFC) is the high theoretical voltage, high energy density, and fast anodic kinetics in comparison with direct methanol fuel cells. [4] A severe problem encountered in developing DBFC is the simultaneous hydrolysis of  $\text{BH}_4^-$  ions at the anode surface along with their electrochemical oxidation.

Borazane ( $\text{BH}_3\text{NH}_3$ ) is a stable and low-toxic crystalline solid with possibly the highest hydrogen content (19.5 wt.%) in chemical compounds. It has been shown [5] that borazane can thermally decompose in the temperature range of 350–410 K to release approximately  $2.2 \text{ mol H}_2 \text{ mol}^{-1} \text{ BH}_3\text{NH}_3$ . This corresponds to a remarkable hydrogen storage density of 14.3 wt.%, higher than that of  $\text{NaBH}_4$ . In addition, borazane is stable in water at ambient temperatures. Both the high energy density and the moderate decomposition temperature make borazane a very attractive hydrogen source for fuel cells [5,6].

We report herein, for the first time, the electrooxidation of borazane and a novel direct fuel cell using alkaline borazane solution as alternative fuel. Of particular importance in this work is that non-platinum catalysts were applied for both the anode and the cathode. After a screening of a number of candidates (including Pt, Au, Ni, Cu, etc.), Ag was found to be a highly efficient catalyst for anodic oxidation of borazane, and  $\text{MnO}_2$  turned out to be a good cathode catalyst showing borazane-tolerance.

The borazane used in this work was prepared from chemical reactions of ammonium carbonate and sodium borohydride in a tetrahydrofuran solution according to the synthetic method reported in Ref. [7]. The final product of borazane was characterized with powder X-ray diffraction (XRD), infrared spectroscopy (IR), and elemental analysis, and compared with the commercial product. The purity of borazane thus prepared was proved to be higher than 95%.

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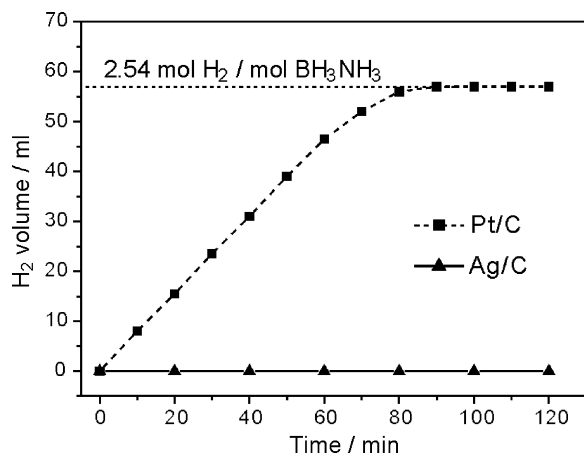
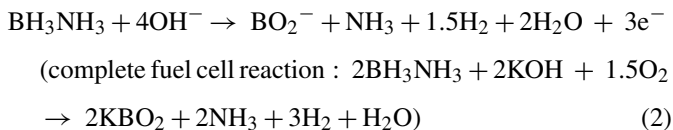
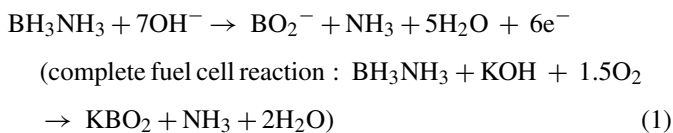
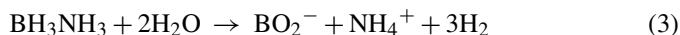


Fig. 1. A comparison of hydrolysis rate of  $\text{BH}_3\text{NH}_3$  (50 ml 0.02 M) on Ag and Pt at room temperature.

Considering the sluggish kinetics of the electrooxidation of molecular ammonia under current experimental conditions, the possible anodic reactions of borazane were proposed to be as follows:



Using the thermodynamic data of borazane ( $\Delta S = 96.34 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $\Delta H = -178 \text{ kJ mol}^{-1}$ ), [6b] the free energy ( $\Delta G$ ) of borazane was calculated to be  $-206.7 \text{ kJ mol}^{-1}$ , and the equilibrium electrode potentials for Reactions (1) and (2) were calculated to be  $-1.11$  and  $-1.3 \text{ V}$  (versus Hg/HgO at pH 14), respectively. These potentials are more negative than the standard electrode potential of hydrogen ( $-0.93 \text{ V}$ , versus Hg/HgO at pH 14), implying that the hydrolyzation of borazane will be thermodynamically spontaneous [8]:



For this reason, we have to choose an anode catalyst not only active for the electrochemical oxidation of borazane, but also inert to the chemical hydrolysis of borazane. Pt turned out to be inadequate for this application, because the hydrolyzation of borazane is overwhelming on Pt. After testing a number of metals and alloys, we found that Ag is the best candidate. A comparison of hydrolysis rate on Ag and Pt is shown in Fig. 1.

Fig. 2 shows the polarization curves of the Ag/C electrode in a  $2 \text{ mol L}^{-1}$  KOH solution containing  $0.1 \text{ mol L}^{-1}$  borazane. The anodic current starts from  $-1.15 \text{ V}$ , and then reaches its limiting current at ca.  $-0.6 \text{ V}$ , representing a well-defined diffusion-controlled electrooxidation behavior. Also presented in Fig. 2 is a flat baseline given by the carbon support in alkaline borazane solution, showing no contribution to the anodic current obtained

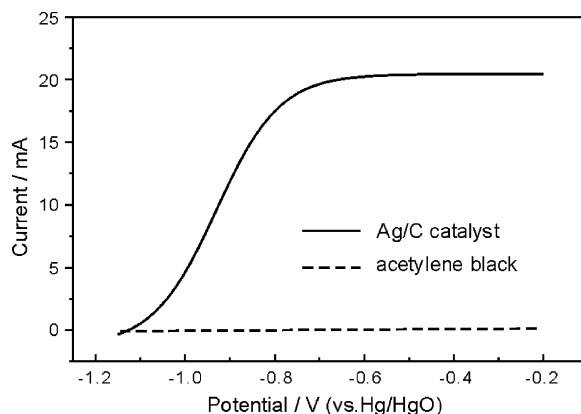


Fig. 2. Polarization curves of the Ag/C electrode (metal loading = 30 wt.%,  $1 \text{ cm}^2$ ) in  $2 \text{ mol L}^{-1}$  KOH +  $0.1 \text{ mol L}^{-1}$   $\text{BH}_3\text{NH}_3$ . ( $5 \text{ mV s}^{-1}$ , room temperature).

on Ag/C. A particularly valuable feature of the result in Fig. 2 is that the anodic oxidation of borazane starts at the potential negative than that of hydrogen evolution, which clearly indicates that the anodic current is not due to the oxidation of hydrogen produced from the possible chemical hydrolysis of borazane, and, more importantly, higher cell voltage should be obtainable in a direct borazane fuel cell with respect to those fuel cells using borazane as a hydrogen source.

To construct a direct borazane fuel cell, we also need a borazane-tolerant cathode. In our previous work, [9] we demonstrated that  $\text{MnO}_2$ , as an air cathode catalyst, showed not only a sufficient activity for oxygen reduction, but also a strong chemical resistance to the attack of strongly reducing borohydride ions in alkaline solutions. Thus, we examined the electrocatalytic activity and stability of the  $\text{MnO}_2$ -catalyzed cathode for the oxygen reduction in alkaline borazane solution.

Fig. 3 compares the polarization curves of the  $\text{MnO}_2$ -catalyzed air cathode in alkaline solutions with and without borazane. It can be seen that borazane did not cause a decrease in the cathodic current. Besides, no performance degradation was observed in prolonged time. Therefore, the existence of borazane has no negative influences on the discharge performance of the

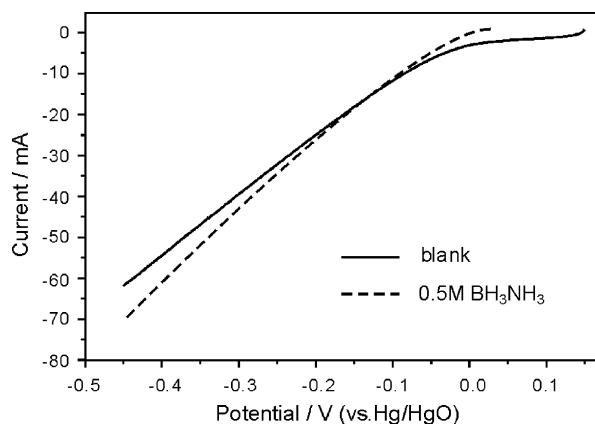


Fig. 3. Polarization curves of a  $\text{MnO}_2$ -catalyzed air cathode ( $1 \text{ cm}^2$ ) in a  $6 \text{ mol L}^{-1}$  KOH solution with/without  $0.5 \text{ mol L}^{-1}$   $\text{BH}_3\text{NH}_3$ . ( $1 \text{ mV s}^{-1}$ , room temperature).

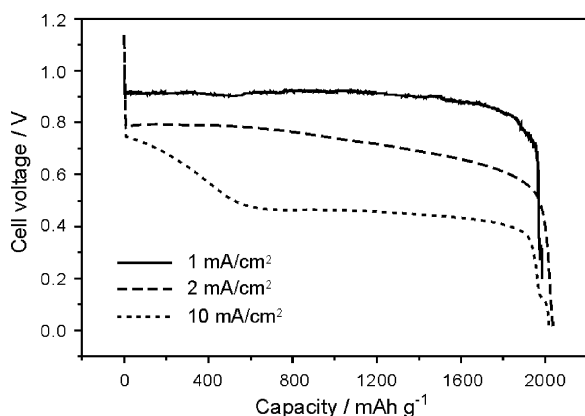


Fig. 4. Discharge curves of the borazane cells at different discharge rate. (10 ml  $0.5 \text{ mol L}^{-1} \text{ BH}_3\text{NH}_3$ ,  $S_{\text{anode}} = 5 \text{ cm}^2$ ,  $S_{\text{cathode}} = 7 \text{ cm}^2$ , room temperature).

$\text{MnO}_2$ -catalyzed air cathode. In addition, an iodometric titration of  $\text{BH}_3\text{NH}_3$  in solution after 48 h also revealed that the total amount of  $\text{BH}_3\text{NH}_3$  almost kept unchanged, which means no obvious hydrolysis of borazane taking place at  $\text{MnO}_2$  cathode. All these results make it possible to construct a direct borazane fuel cell without the need for a separator to prevent the deleterious effects of the fuel to the cathode.

To estimate the electron number involved in the anodic oxidation of borazane, we run a direct borazane fuel cell with a  $\text{MnO}_2$ -catalyzed air cathode and an Ag-catalyzed anode in a primary battery mode, i.e., discharging all the borazane in the solution and measuring the released amount of electricity. The open-circuit voltage of the cells is ca. 1.15 V, higher than that of hydrogen or methanol fuel cells as expected. As shown in Fig. 4, the discharge capacity of these cells is about  $2000 \text{ mAh g}^{-1}$  for the fuel, equivalent to a hydrogen storage density of 5 wt.%. Under low current density, the cell showed quite a high operating voltage plateau (0.8–0.9 V). However, when the current density increased to  $10 \text{ mA cm}^{-2}$ , the cell voltage plateau decreased to 0.45 V. This voltage loss could be ascribed to the relatively slow kinetics of electrode reactions and the premature electrode structure adopted in this preliminary work. Considering the low operating temperature and non-Pt catalysts adopted, the preliminary results are encouraging.

According to Eqs. (1) and (2), there are two possible reaction pathways, i.e., the 6e and 3e pathways. The maximum discharge capacity released by these two reactions will be 5206 and  $2603 \text{ mAh g}^{-1}$ , respectively. Now that we got a discharge

capacity of ca.  $2000 \text{ mAh g}^{-1}$ , it is more likely that the discharge reaction is predominated by the 3e pathway, with a slight capacity loss from chemical hydrolysis. Therefore, in order to improve the capacity utilization of borazane, further works are needed to unravel the fundamental mechanism of relevant electrode reactions and to explore the higher efficient anode catalyst.

Nevertheless, the results given above indicate that borazane is a promising alternative fuel for direct fuel cells. In addition to the high energy density of borazane, employing non-Pt catalysts is another important feature of such a direct borazane fuel cell. In our lab, a parallel effort has been devoted for years to developing alkaline polymer electrolytes with the aim of replacing the liquid alkaline solution. Hopefully, a direct borazane fuel cell based on alkaline polymer electrolyte will be tested in near future.

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