



Short communication

Effects of hydrazine addition on gas evolution and performance of the direct borohydride fuel cell

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ABSTRACT

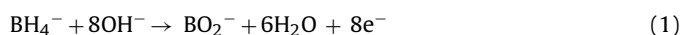
A fuel cell configuration using alkaline $\text{NaBH}_4\text{-N}_2\text{H}_4$ solutions as the fuel is suggested. Gas evolution behaviors and cell performances of alkaline $\text{NaBH}_4\text{-N}_2\text{H}_4$ solutions on different catalysts have been studied. It is found that gas evolution behaviors are influenced by the applied anodic catalysts and the concentration of NaBH_4 and N_2H_4 . NaBH_4 is mainly electro-oxidized on Pd but N_2H_4 is mainly electro-oxidized on Ni and surface-treated Zr–Ni alloy when using $\text{NaBH}_4\text{-N}_2\text{H}_4$ solutions as the fuel and a composite of Pd, Ni and surface-treated Zr–Ni alloy as the anodic catalyst. The cyclic voltammetry results show that electrochemical oxidation potential of NaBH_4 is higher than that of N_2H_4 . Adding hydrazine into alkaline sodium borohydride solutions can suppress gas evolution and improve the cell performance of the DBFC. The performances of fuel cells using $\text{NaBH}_4\text{-N}_2\text{H}_4$ solutions are comparable to that of fuel cell using N_2H_4 solution.

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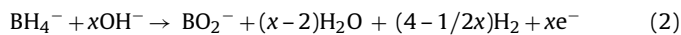
1. Introduction

Compared with the direct methanol fuel cell (DMFC), the direct borohydride fuel cell (DBFC) demonstrates high electromotive force (emf) of 1.64 V and high capacity of 5.67 Ah g^{-1} [1–5].

Theoretically, one BH_4^- can generate eight electrons through following anodic reaction:



However, in practical, the generated electrons are usually less than eight. In general, the anodic oxidation of BH_4^- can be described as [6,7]:



Here, x represents the actual number of the electrons released by each BH_4^- and it is called coulombic number in following paragraphs. The coulombic number depends on applied anode catalyst and fuel composition.

Many studies have been carried out aiming at clarifying the anodic oxidation mechanism of BH_4^- at many catalysts [8–15]. The anodic reaction of BH_4^- on Ni electrode is a 4e reaction (corresponding to $x=4$) [6,10,11]. Liu reported a 4e reaction of BH_4^- occurred on AB_2 or AB_5 hydrogen storage alloys when using

high concentrated borohydride solutions [12,13]. Higher coulombic number can be achieved at Pd/C or Pt/C electrode when using borohydride solutions with relatively low concentrations [7,11,14]. Gyenge et al. reported that Pt–Ni and Pt–Ir exhibited higher electro-catalytic activity than Pt [15]. Adding a carbon supported Pd into the Ni anode not only depressed the hydrogen evolution but also improved the DBFC performance [16]. Therefore, a composite catalyst prepared by mixing Ni, Pd/C and surface-treated Zr–Ni alloy was used as anode catalyst in this work.

The hydrogen evolution occurs during operation if the coulombic number is less than 8, which results in decreasing of the fuel utilization and the cell performance. How to restrain hydrogen evolution is one of the critical issues in the development of the DBFC technology [5,16]. It is considered that hydrogen evolution could be suppressed by optimizing fuel composition through adding some components that could inhibit hydrogen generation. Gyenge reported that thiourea was an effective inhibitor of the catalytic hydrolysis associated with BH_4^- electro-oxidation on Pt [17]. The BH_4^- utilization efficiency and coulombic efficiency of DBFC were improved by adding thiourea into the alkaline NaBH_4 solutions.

It is considered that hydrazine (N_2H_4) is alkaline and could stabilize borohydride because borohydrides are stable only in alkaline media. Furthermore, N_2H_4 itself can be used as a fuel in the direct hydrazine fuel cell (DHFC) [21]. In this work, we tried to add N_2H_4 into the alkaline NaBH_4 solution to stabilize BH_4^- and to improve the cell performance. The cell performance and gas evo-

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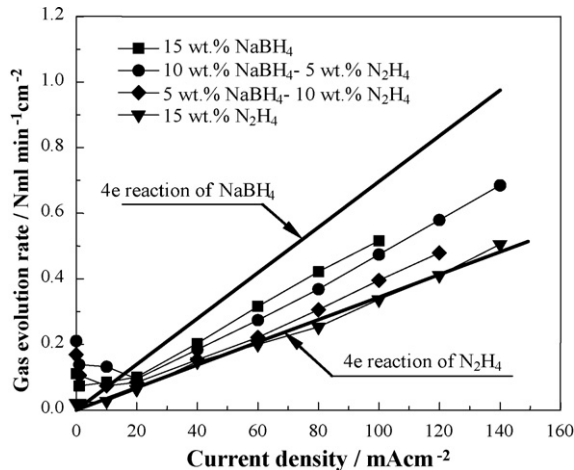


Fig. 1. Gas evolution rates of alkaline NaBH₄-N₂H₄ solutions on the catalyst composite of Pd/C, Ni and surface-treated Zr-Ni alloy. NaOH concentration: 10 wt.%.

lution behavior were investigated and the functions of the N₂H₄ addition were discussed.

2. Experimental details

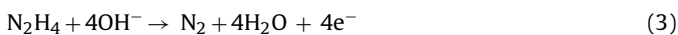
Anode electrodes were prepared by brushed anode catalyst paste into a piece of Ni foam with a catalyst loading of 10 mg cm⁻². The paste was composed of Nafion solution (5 wt.%) and anode catalysts. We tested the hydrogen evolution at Ni powder (INCO 210), surface-treated Zr-Ni alloy [19], Pd/C (10% Pd on Vulcan XC-72, E-Tek Co.) and their composite catalyst during operation. The composite catalyst was prepared by mixing Ni powder, surface-treated Zr-Ni alloy and Pd/C with a mass ratio of 0.75:0.75:0.6. Cathodes were commercially available with a catalyst loading of Pt 1 mg cm⁻² (Pt 30 wt.% on Vulcan XC-72, E-Tek Co.). Nafion N117 membrane was used to separate cathode and anode. The flow field area of end plates was 6 cm². The test cell structure was described in our previous paper [9]. Alkaline NaBH₄ and N₂H₄ solutions containing 10 wt.% of NaOH were used as the fuel. Polarizations of the alkaline NaBH₄ and N₂H₄ solutions were determined by cyclic voltammetry (CV) measurement. Cell performances were measured at a fuel flow rate of 10 ml min⁻¹ and an oxygen flow rate of 0.15 L min⁻¹ at ambient conditions. The amount of generated gas from the anode was determined by water displacement method.

The gas evolution rates of alkaline NaBH₄ and N₂H₄ solutions on Ni, Pd, surface-treated Zr-Ni alloy and composite catalyst were measured in a three-electrode system as described in our previous paper [7]. All experiments were performed at ambient conditions.

3. Results and discussion

3.1. Gas evolution

One of the critical disadvantages of the DBFC is the hydrogen evolution during operation because hydrogen evolution will significantly reduce fuel efficiency and lower the cell performance [20]. It has been reported that N₂H₄ could be electro-oxidized by following reaction [21]:



The gas evolution rates of the 4e reaction of NaBH₄ and the 4e reaction of N₂H₄ are given in Fig. 1. We studied the effect of N₂H₄ addition on the gas evolution behavior on the composite cat-

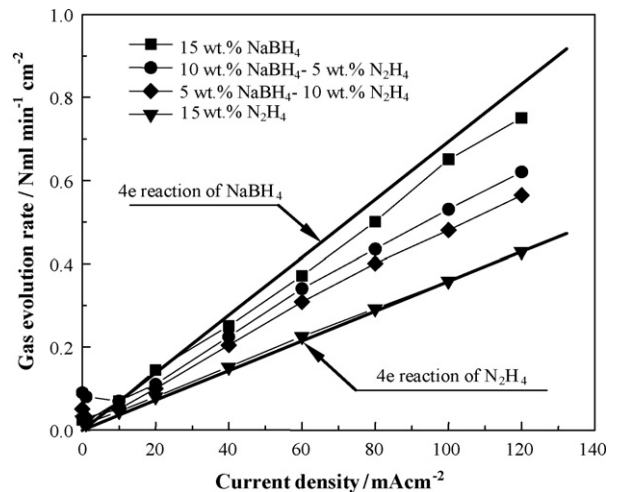


Fig. 2. Gas evolution rates of alkaline NaBH₄-N₂H₄ solutions on the Pd/C catalyst. NaOH concentration: 10 wt.%.

alyst of Ni, Pd and surface-treated Zr-Ni alloy when using alkaline NaBH₄-N₂H₄ solutions.

As shown in Fig. 1, it can be seen that the gas evolution rate of the alkaline N₂H₄ solution agreed well with the stoichiometric relation of the 4e reaction of N₂H₄ according to Eq. (3). However, alkaline NaBH₄-N₂H₄ solutions demonstrated interesting behaviors. When cells were operated at lower currents, the gas evolution rates of the alkaline NaBH₄-N₂H₄ solutions were first decreased slightly and then increased linearly with increasing the current density. This result can be attributed to the competition between the hydrolysis reaction of BH₄⁻, electro-oxidation of H₂ and their anode reactions [6]. When operating cells at large currents, the gas evolution rates of the alkaline NaBH₄-N₂H₄ solutions showed certain linear relations but located between 4e reactions of NaBH₄ and N₂H₄. The gas evolution rate was decreased with increasing the N₂H₄ portion in the alkaline NaBH₄-N₂H₄ solutions. These results implied that NaBH₄ and N₂H₄ would be oxidized on different catalysts during operation.

In order to understand the reaction mechanism of the alkaline NaBH₄-N₂H₄ solutions on the composite catalyst, the gas evolution behaviors of the alkaline NaBH₄-N₂H₄ solutions on Pd, Ni and surface-treated alloy were studied individually. Experimental results are shown in Figs. 2–4. It was found that gas evolution rates of the alkaline NaBH₄ solution and alkaline N₂H₄ solution agreed with their stoichiometric relations of the 4e reaction on Pd, Ni and surface-treated alloy respectively. However, the gas evolution of the alkaline NaBH₄-N₂H₄ solutions on these electro-catalysts demonstrated different behaviors. The gas evolution behaviors of the alkaline NaBH₄-N₂H₄ solutions on Pd catalyst were close to that of alkaline NaBH₄ solution, which indicated that NaBH₄ would be mainly oxidized on Pd catalyst.

From our previous results, it was known that BH₄⁻ would be electro-oxidized on Ni or surface-treated Zr-Ni alloy through the 4e reaction [6,7]. However, the gas evolution behaviors of the alkaline NaBH₄-N₂H₄ solutions on Ni or surface-treated Zr-Ni alloy catalyst were close to that of alkaline N₂H₄ solution, which implied that N₂H₄ would be mainly oxidized on Ni or surface-treated Zr-Ni alloy catalyst when using alkaline NaBH₄-N₂H₄ solutions as the fuel.

Based on the results and discussion mentioned above, the decrease of gas evolution rate when using alkaline NaBH₄-N₂H₄ solutions as the fuel, can be attributed to that N₂H₄ would occupy some catalyst sites to be oxidized. As a result, less gas was generated during operation, due to that the anodic reaction of N₂H₄

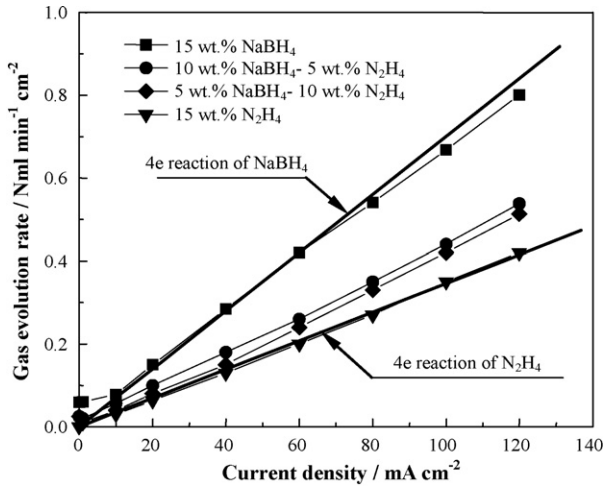


Fig. 3. Gas evolution rates of alkaline NaBH₄-N₂H₄ solutions on the Ni catalyst. NaOH concentration: 10 wt.%.

generated less gas (1 mol of N₂) compared with the anodic reaction of NaBH₄ (2 mol of H₂).

It was noted that the gas evolution rate of the alkaline NaBH₄ solution at composite catalyst was lower than the stoichiometric relation of the 4e reaction of NaBH₄ according to Eq. (2). This implied that the generated electrons of the alkaline NaBH₄ solution on the composite catalyst were more than 4 electrons. However, the Ni and surface-treated Zr-Ni alloy gave a 4e H₂ stoichiometry except of Pd/C as shown in Figs. 2–4. It seems to be a discrepancy between Fig. 1 and Figs. 2–4.

Since the potential of BH₄⁻ at Ni catalyst was more negative than that of BH₄⁻ at Pd catalyst, it was considered that Ni was more active than Pd in borohydride solutions [7]. We supposed that borohydride reacted on Ni and surface-treated Zr-Ni alloy prior to Pd/C in the composite catalyst during operation, so that the actual concentration of borohydride on Pd/C surface in anode was decreased. It favored for improving the generated electrons of BH₄⁻ on Pd/C to be six or eight, which increased the coulombic efficiency of BH₄⁻. As a result, the gas evolution rate of the alkaline NaBH₄ solution at composite catalyst was lower than the stoichiometric relation of the 4e reaction of BH₄⁻.

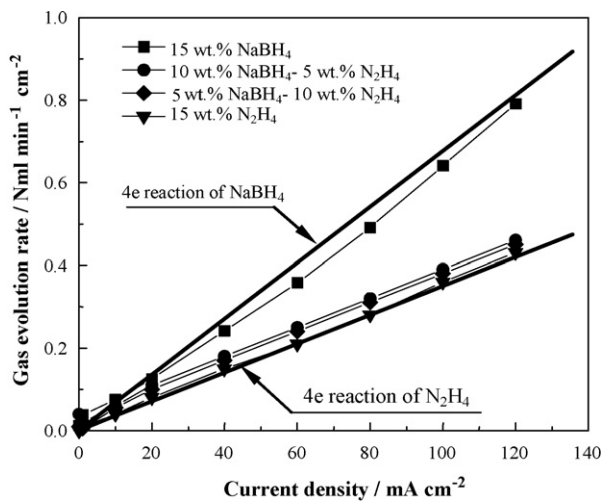


Fig. 4. Gas evolution rates of alkaline NaBH₄-N₂H₄ solutions on the surface-treated Zr-Ni alloy catalyst. NaOH concentration: 10 wt.%.

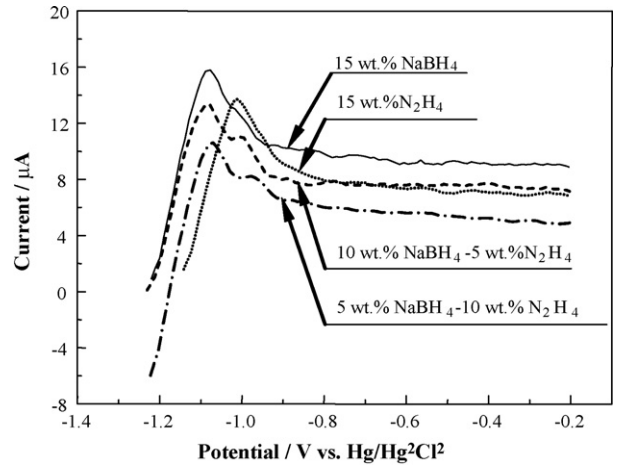


Fig. 5. Cyclic voltammograms of the alkaline NaBH₄-N₂H₄ solutions at a scan rate of 5 mV s⁻¹. NaOH concentration: 10 wt.%.

3.2. Cell performance

In order to understand more details about the electro-oxidation mechanism of the alkaline NaBH₄-N₂H₄ solutions, the cyclic voltammetry curves of the NaBH₄-N₂H₄ solutions were measured and shown in Fig. 5. The potential of NaBH₄ was more negative than that of N₂H₄ at anodic maximum current. It indicated that both NaBH₄ and N₂H₄ could be electro-oxidized in the alkaline NaBH₄-N₂H₄ solutions and BH₄⁻ was more active than N₂H₄. It implied that BH₄⁻ would be oxidized prior to N₂H₄ when operating the DBFC using an alkaline NaBH₄-N₂H₄ solution as the fuel.

It was known that cell performance would be decreased when using high concentrated borohydride solutions as the fuel for the DBFC [18]. Here, we investigated the effect of N₂H₄ replacement for NaBH₄ on the cell performance. Fig. 6 shows the cell performances when using alkaline NaBH₄-N₂H₄ solutions as the fuel. It was found that N₂H₄ addition in alkaline NaBH₄ solution would not influence the open-circuit voltage (OCV) of the DBFC. The OCVs of the DBFC using alkaline NaBH₄-N₂H₄ solutions were higher than that of the DHFC, but there was no significant differ-

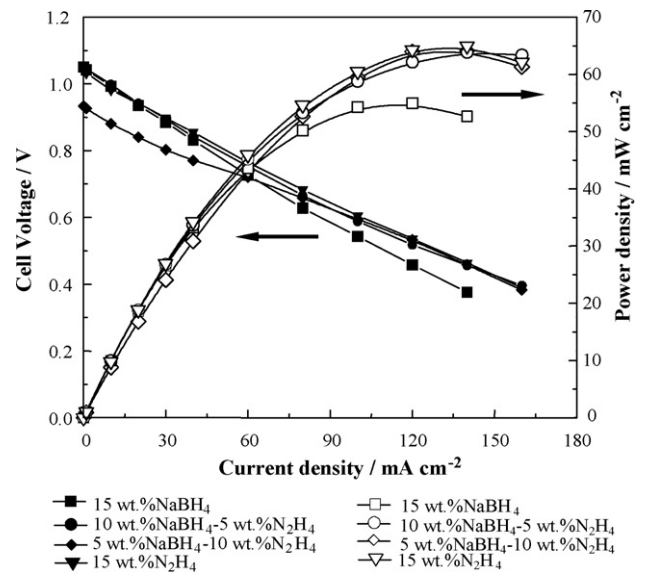


Fig. 6. Cell performances when using alkaline NaBH₄-N₂H₄ solutions as the fuel. NaOH concentration: 10 wt.%.

ence between the performance of DHFC and DBFC using alkaline $\text{NaBH}_4\text{-N}_2\text{H}_4$ solutions. For the DBFC, N_2H_4 addition in alkaline NaBH_4 solution improved the cell performance. A maximum power density of 64 mW cm^{-2} has been achieved when using the alkaline $\text{NaBH}_4\text{-N}_2\text{H}_4$ solution containing 5 wt.% of NaBH_4 , 10 wt.% of N_2H_4 and 10 wt.% of NaOH . It may be attributed to that the depression of gas evolution decreased the cell resistance during operation [20]. For the DHFC, adding sodium borohydride into alkaline hydrazine solutions can improve fuel capacity because the capacity of NaBH_4 (5.67 Ah g^{-1}) is higher than that of N_2H_4 (3.35 Ah g^{-1}).

It is known that N_2H_5^+ would be formed due to N_2H_4 hydrolysis [21]. It is considered that an ion complex of $\text{N}_2\text{H}_5^+\cdot\text{BH}_4^-$ would be formed in the alkaline $\text{NaBH}_4\text{-N}_2\text{H}_4$ solutions so that the crossover of N_2H_5^+ ions would be suppressed. As a result, OCVs of the DBFC using alkaline $\text{NaBH}_4\text{-N}_2\text{H}_4$ solutions were higher than that of the DHFC using alkaline hydrazine solution as the fuel. More efforts should be made to prove the existence of the $\text{N}_2\text{H}_5^+\cdot\text{BH}_4^-$ ion complex.

4. Conclusions

The addition of N_2H_4 in alkaline borohydride solutions can suppress the gas evolution of the DBFC during operation. NaBH_4 would be mainly oxidized on Pd whereas N_2H_4 would be mainly oxidized on Ni or surface-treated Zr–Ni alloy catalyst when using alkaline $\text{NaBH}_4\text{-N}_2\text{H}_4$ solutions as the fuel and a composite of Pd, Ni and surface-treated Zr–Ni alloy as the anodic catalyst.

The DBFC performance was improved by adding N_2H_4 into the alkaline NaBH_4 solutions and its performance was comparable to that of DHFC in this study. A maximum power density of 64 mW cm^{-2} was achieved when operating the cell at ambient con-

ditions. The alkaline $\text{NaBH}_4\text{-N}_2\text{H}_4$ solution is suitable for both DBFC and DHFC.

Acknowledgements

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