



Short communication

Effects of NaOH addition on performance of the direct hydrazine fuel cell

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ABSTRACT

In this work, we suggested a figuration of the direct hydrazine fuel cell (DHFC) using non-precious metals as the anode catalyst, ion exchange membranes as the electrolyte and alkaline hydrazine solutions as the fuel. NaOH addition in the anolyte effectively improved the open circuit voltage and the performance of the DHFC. A power density of 84 mW cm^{-2} has been achieved when operating the cell at room temperature. It was found that the cell performance was mainly influenced by anode polarization when using alkaline N_2H_4 solutions with low NaOH concentrations. However, when using alkaline N_2H_4 solutions with high NaOH concentrations as the fuel, the cell performance was mainly influenced by cathode polarization.

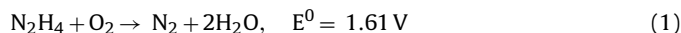
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1. Introduction

Fuel cell is an energy conversion device with high efficiency. Many kinds of fuel cells have been developed. Among them, the proton exchange membrane fuel cell (PEMFC) has been widely studied because of its operation easiness and high performance. The PEMFCs require pure hydrogen as the fuel. However, hydrogen storage technologies are still on the way to be developed especially for mobile applications. Compared with gaseous hydrogen, liquid fuels have advantages of high energy density and easy handling in fuel supplying. Methanol [1] and borohydride solutions [2] are considered to be potential fuels to power fuel cells for mobile applications. However, many problems remain to be solved in the development of the direct methanol fuel cell (DMFC) and the direct borohydride fuel cell (DBFC), such as the low performance and methanol crossover in the DMFC [1] and hydrogen evolution in the DBFC [3]. Besides, when methanol is used as a fuel to power the DMFC, green house gas (CO_2) will be generated. When borohydride solutions are used to power the DBFC, borates will leave in the spent fuel. A spent fuel treatment is necessary after operation.

Hydrazine (N_2H_4) is a compound with high hydrogen content (12.5 wt.%). Its hydrogen storage capability is higher than that of sodium borohydride (10.6 wt.%) and equivalent to that of methanol. The direct hydrazine fuel cell (DHFC) demonstrates a higher electric motive force (EMF) of 1.61 V which is close to that of the DBFC

(1.64 V) and higher than that of the DMFC (1.21 V). When hydrazine is used as a fuel to power the DHFC, only nitrogen and water will be formed as shown in the following reaction:



Nitrogen and water can be directly released to air without any harm to environment. Therefore, the fuel cell system design of the DHFC would be simple. On the other hand, nitrogen as the raw material for hydrazine synthesis can be easily obtained from air anywhere. However, a specific attention should be paid when using N_2H_4 solution as a fuel for the DHFC because N_2H_4 is a toxic compound.

The DHFC concept was first suggested in the 1960s [4]. Very few researches on the DHFC development have been done [5–7]. It is considered that more attentions should be paid to develop the DHFC technology due to the merits mentioned above.

It is known that hydrazine hydrolysis occurs when hydrazine is dissolved in water [8], as showed in the following reaction,



When N_2H_5^+ ions transferred from anode side to cathode side during operation of the DHFC, the crossover of N_2H_5^+ ions occurred. It was reported that the crossover of N_2H_5^+ ions decreased the DHFC performance [5]. How to suppress the crossover of N_2H_5^+ ions would be one of the key points to improve the performance of the DHFC.

It was considered that adding NaOH into hydrazine solution would be a resolution to depress hydrazine hydrolysis according to reaction (2). Here we suggested a figuration of the DHFC using

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alkaline hydrazine solution as the fuel and ion exchange membranes as the electrolyte. Based on test cells, the effects of alkali concentration on the cell performance were investigated.

2. Experiment details

Test cells were assembled with an anode using Zr–Ni alloy as the anode catalyst, a cathode using carbon supported Pt as the cathode catalyst and Nafion-117 (from DuPont Inco.) or anion exchange membrane (from Asahi Kasei Corporation) as the electrolyte. The Nafion-117 was pretreated by boiling in 3 wt.% of H_2O_2 solution for 1 h and then boiling in de-ionized water for 1 h. The preparation of anode, anode catalyst [9] and cell figuration [10] was the same as what described in our previous works. A saturated calomel electrode was applied as the reference electrode.

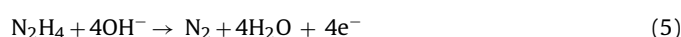
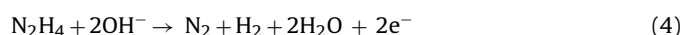
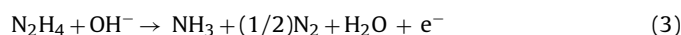
Alkaline hydrazine solutions were prepared by dissolving NaOH in hydrate hydrazine. Test cells were operated at a fuel flow rate of 5 ml min^{-1} and an oxygen flow rate of 150 ml min^{-1} at room temperature.

The generated gas during operation was introduced into a gas washing bottle in which phenolphthalein solution was added to identify the NH_3 existence. After drying with CaO, the generated gas was subjected to gas chromatography (GC). The volume of generated gas was transformed to the value in standard temperature and pressure (STP).

3. Results and discussion

3.1. Hydrazine electro-oxidation

It was considered hydrazine would be electro-oxidized in alkaline solution by following supposed reactions.



For convenience, these supposed anodic hydrazine electro-oxidation reactions are named 1-electron-reaction, 2-electron-reaction, and 4-electron-reaction, respectively. As shown in reactions above, the gas evolution amount has certain linear relation with the number of transfer electron according to the Faraday's law. Relations of each supposed reaction between operation currents and gas generation rates are drawn in Fig. 1.

During operation of the test cell using alkaline hydrazine solution ($2 \text{ M N}_2\text{H}_4$) as the fuel, it was found that some gas was generated as shown in Fig. 1. After operation, the phenolphthalein solution in the gas washing bottle was transparent. It indicated that no NH_3 was formed during operation. Through identification with gas chromatography, the generated gas was nitrogen. From Fig. 1, it can be seen that the nitrogen generation rates vs. operation currents well agreed with the 4-electron-reaction. Based on these experimental results, it can be concluded that N_2H_4 was electro-oxidized through reaction (5) when operation the DHFC at room temperature. This result was coincidence with that obtained by Burke and O'Dwyer [6].

3.2. Membrane as the electrolyte

Yamada et al. reported that the cell using anion exchange membrane (AEM) was superior in performance comparing the cell using cation exchange membrane (CEM) because AEMs could impede the crossover of N_2H_5^+ ions [5]. We followed their

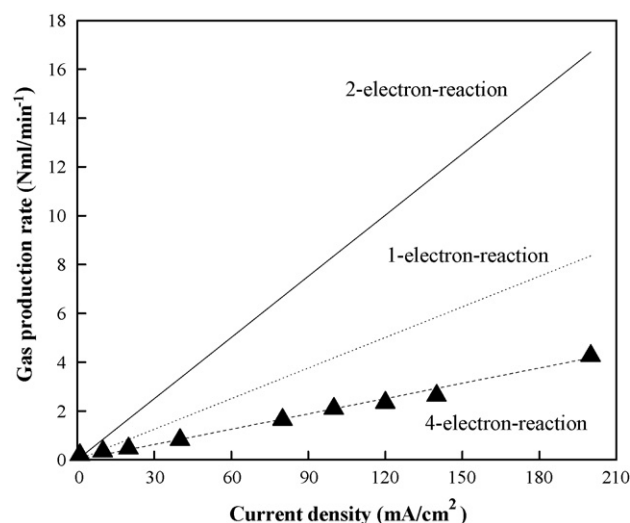


Fig. 1. Relation of gas evolution rates with operation current during operation of an alkaline DHFC.

researches. Power density of the cell using AEM reached to 14.9 mW cm^{-2} that was higher than that of the cell using Nafion 117 (2.3 mW cm^{-2}) when aqueous N_2H_4 solution was as the fuel (in Fig. 2).

It is known that N_2H_4 demonstrates a stronger reactivity in alkaline medium compared with in acid medium. N_2H_4 would be more reactive in an alkaline anolyte. Furthermore, NaOH addition in the anolyte would improve the ion conductivity of the anolyte. Therefore, we tried to use alkaline N_2H_4 solutions instead of aqueous N_2H_4 solution as the fuel. It was found that the cells using alkaline hydrazine solution demonstrated high power densities of 84 and 73.9 mW cm^{-2} when using AEM and CEM as the electrolyte, respectively as shown in Fig. 2. NaOH addition in N_2H_4 solution significantly improved the open circuit voltage and cell performance when using CEM as the electrolyte. It implied that the crossover of N_2H_5^+ ions was suppressed due to depression of N_2H_4 hydrolysis when NaOH was added into the anolyte. In order to better understand the effects of NaOH addition, we investigated the open circuit voltage and cell performance when increasing the NaOH content in the anolyte.

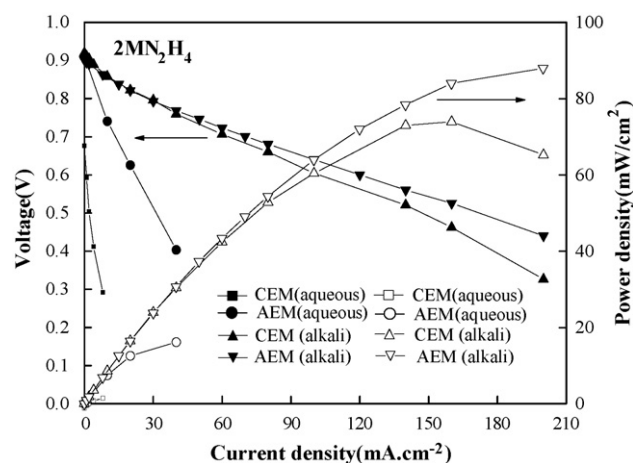


Fig. 2. Effect of NaOH addition in aqueous hydrazine solution on the performance of the DHFC at room temperature. Anolyte: $2 \text{ M N}_2\text{H}_4$ or $2 \text{ M N}_2\text{H}_4 + 4 \text{ M NaOH}$. Fuel flux: 5 ml min^{-1} , O_2 flux: 150 ml min^{-1} (0.1 MPa).

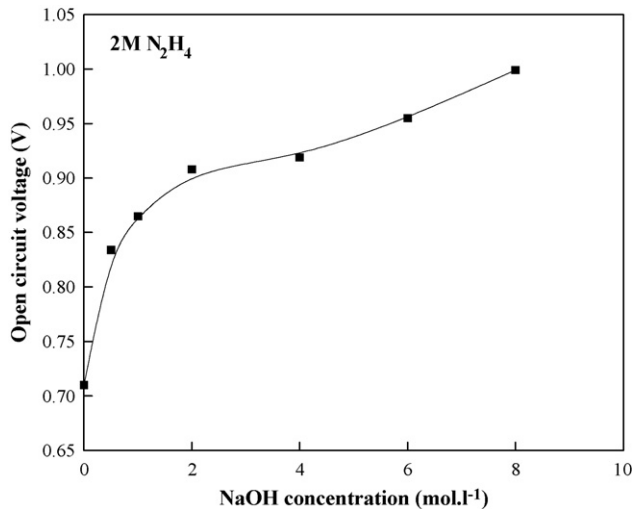


Fig. 3. Relation of NaOH concentration with the open circuit voltage of the DHFC at room temperature. Hydrazine concentration: 2 M.

3.3. Effects of NaOH addition

Fig. 3 shows the influence of NaOH concentration in the alkaline hydrazine solutions on the open circuit voltage of the DHFC. It was found that open circuit voltage was increased with increasing the NaOH concentration in the anolyte. It implied that NaOH addition in the anolyte effectively suppressed the crossover of N₂H₅⁺ ions due to depression of the hydrazine hydrolysis.

It was found that the cell performance demonstrated an interesting tendency when increasing NaOH content in the anolyte as shown in Fig. 4. With increasing NaOH concentration in the anolyte, cell operation voltage increased when NaOH concentration <4M, but decreased when NaOH concentration >6M.

As NaOH addition in the anolyte can improve the ion conductivity of the anolyte and suppress the crossover of N₂H₅⁺ ions, it is understandable that cell operation voltage increased with increasing NaOH concentration in the anolyte when NaOH concentration <4M.

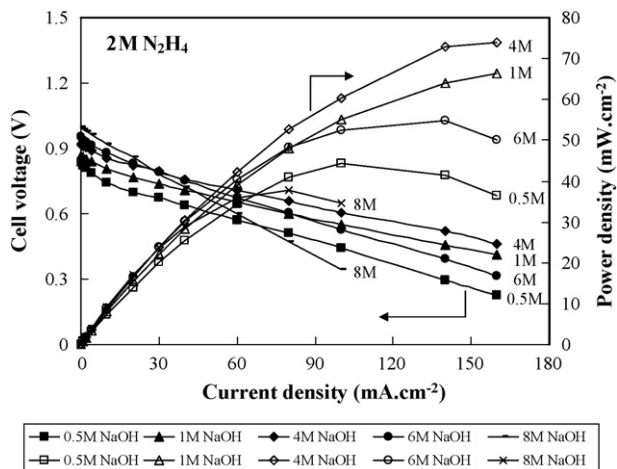


Fig. 4. Effect of NaOH concentration in anolyte on the cell performance when operation at room temperature. Anolyte contained 2 M N₂H₄. Fuel flux: 5 ml min⁻¹, O₂ flux: 150 ml min⁻¹.

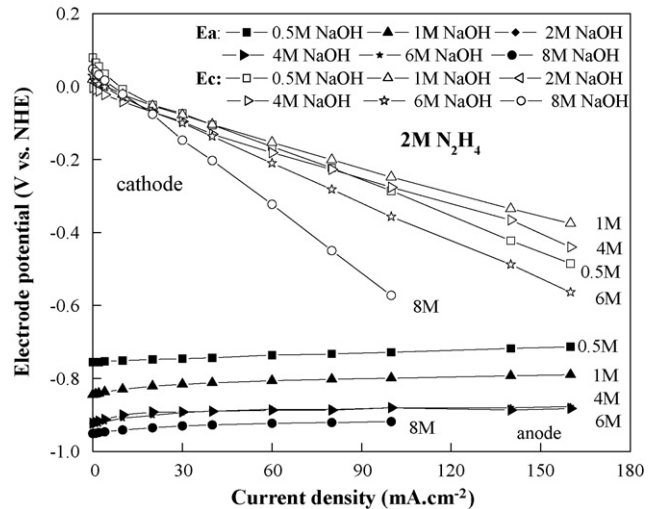


Fig. 5. Polarization curves of anode and cathode when using alkaline N₂H₄ solutions with different NaOH concentrations.

According to reaction (5), stoichiometric mole ratio of N₂H₄ to NaOH in the anolyte is 1:4. However, the test cell demonstrated the highest performance when using the alkaline solution with 2 M N₂H₄ and 4 M NaOH. In order to find out the reason why stoichiometric NaOH concentration was not a benefit of the cell operation, polarization behaviors of anode and cathode were investigated as shown in Fig. 5.

From polarization curves, it was found that anode potentials shifted to minus value further with increasing the NaOH concentration in the anolyte. It agreed with Nernst's equation based on reaction (5). Based on the cathode reaction (6), the decrease of cathode potential also agreed with the Nernst's equation in tendency:



However, it can be seen that the decrease of cathode potential is larger than the shift value of anode potential to minus. NaOH concentration in the anolyte showed a bigger influence on the cathode polarization than that on the anode polarization. It implied

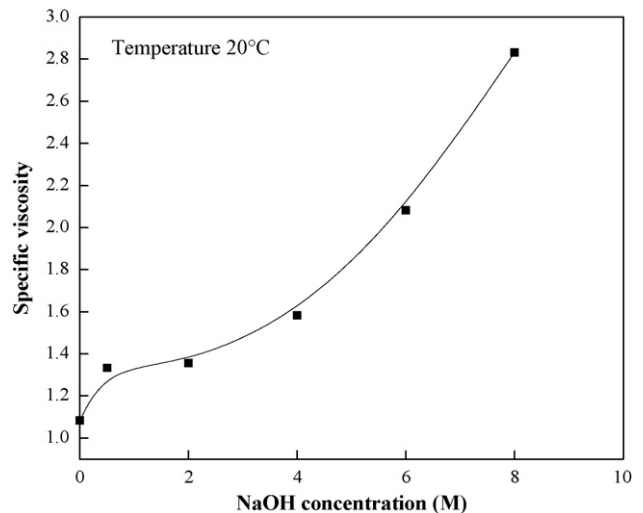


Fig. 6. Relation between specific viscosity of the anolyte and NaOH concentration.

that some mass transportation factors would influence the cathode polarization. We measured the specific viscosity of the used alkaline N_2H_4 solutions. It was found that the specific viscosity of the anolyte started to increase significantly from NaOH concentration >4 M as shown in Fig. 6. It was known that the increase of the anolyte viscosity would decrease the movability of charge carrier in the anolyte. Increase of the anolyte viscosity led to decrease the cell performance [11]. Therefore, it was considered that the higher viscosity of the alkaline N_2H_4 solution with high NaOH concentrations would be a factor to decrease the cathode potential in our test cell.

4. Conclusions

A figuration of the DHFC using ion exchange membranes as the electrolyte and alkaline hydrazine solution as the fuel was suggested. NaOH addition in anolyte can effectively improve the open circuit voltage and performance of the DHFC. A high power density of 84 mW cm^{-2} has been achieved when operating the cell at room temperature.

Acknowledgements

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