Short communication

A development of direct hydrazine/hydrogen peroxide fuel cell

Shao Jiang Lao[a], Hai Ying Qin[a], Li Qiang Ye[a], Bin Hong Liu[b], Zhou Peng Li[a,*]

[a] Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, PR China
[b] Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

ABSTRACT

A direct hydrazine fuel cell using H_2O_2 as the oxidizer has been developed. The N_2H_4/H_2O_2 fuel cell is assembled by using Ni–Pt/C composite catalyst as the anode catalyst, Au/C as the cathode catalyst, and Nafion membrane as the electrolyte. Both anolyte and catholyte show significant influences on cell voltage and cell performance. The open-circuit voltage of the N_2H_4/H_2O_2 fuel cell reaches up to 1.75 V when using alkaline N_2H_4 solution as the anolyte and acidic H_2O_2 solution as the catholyte. A maximum power density of 1.02 W cm^{-2} has been achieved at operation temperature of 80 °C. The number of electrons exchanged in the H_2O_2 reduction reaction on Au/C catalyst is 2.

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1. Introduction

Direct liquid-feed fuel cells are considered to be suitable power sources for mobile appliances due to their high energy densities and easy handling in fuel supplying. Hydrazine (N_2H_4) is a powerful fuel for fuel cells due to its high hydrogen content (12.5 wt.%) and rather negative eletrooxidation potential (-1.21 V vs. SHE). The electromotive force (EMF) of the direct hydrazine fuel cell (DHFC) is as high as 1.61 V, which is much higher than that of the direct methanol fuel cell (1.21 V), so that the DHFC is considered to be a potential mobile power source [1–3].

Yamada et al. [1] suggested a DHFC configuration using Nafion membrane as the electrolyte. It was found that this DHFC configuration was suffered from $N_2H_5^+$ crossover when using aqueous N_2H_4 solutions as the fuel because Nafion membrane could not stop migration of $N_2H_5^+$ ions from anolyte to the cathode [1]. In our previous work [2], it was found that increase of OH$^-$ concentration in the anolyte could effectively suppress the crossover of $N_2H_5^+$. A power density as high as 617 mW cm^{-2} has been reported when alkaline N_2H_4 solution is used as the fuel [3]. However, the slow kinetics of oxygen reduction reaction is considered to be a critical problem to improve the DHFC performance.

Hydrogen peroxide (H_2O_2) is a powerful oxidizer. H_2O_2 has high electrochemical reactivity. Choudhury et al. [4] suggested a fuel cell

configuration using hydrogen peroxide as the oxidizer and alkaline borohydride solution as the fuel. Miley et al. [5] experimentally proved that the direct utilization of H_2O_2 as the oxidizer for fuel cell could improve the cell performance. A power density of 1.5 W cm^{-2} was achieved at 65 °C when using alkaline borohydride solutions as the fuel and H_2O_2 as the oxidizer [6].

It is considered that borate crystallization is a troublesome problem when using alkaline borohydride solutions as the fuel [7]. When N_2H_4 is employed as the fuel to power a DHFC, no such kind problem would appear because only nitrogen and water would be generated as shown in following reaction:

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O \quad E^o_{cell} = 1.61 \text{ V vs. SHE} \tag{1}$$
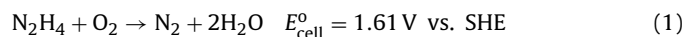
Neither CO-like poisoning species, environmentally harmful materials such as CO_2 from the direct methanol fuel cell [8] nor solid species will be generated.

When N_2H_4 is used as the fuel, and H_2O_2 is used as the oxidizer, the total reaction of N_2H_4/H_2O_2 fuel cell can be described as

$$N_2H_4 + 2H_2O_2 \rightarrow N_2 + 4H_2O \quad E^o_{cell} = 2.13 \text{ V vs. SHE} \tag{2}$$
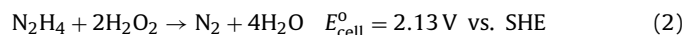
It means that the DHFC using H_2O_2 as the oxidizer can provide higher EMF than that using oxygen as the oxidizer. In addition, both N_2H_4 and H_2O_2 are used in aqueous form which makes the fuel cell system more compact.

In this work, we attempted to use H_2O_2 as the oxidizer to develop a new type of DHFCs. The carbon-supported Au (Au/C) was fabricated and used as the catalyst for H_2O_2 electroreduction reaction. The influences of anolyte and catholyte on cell voltage
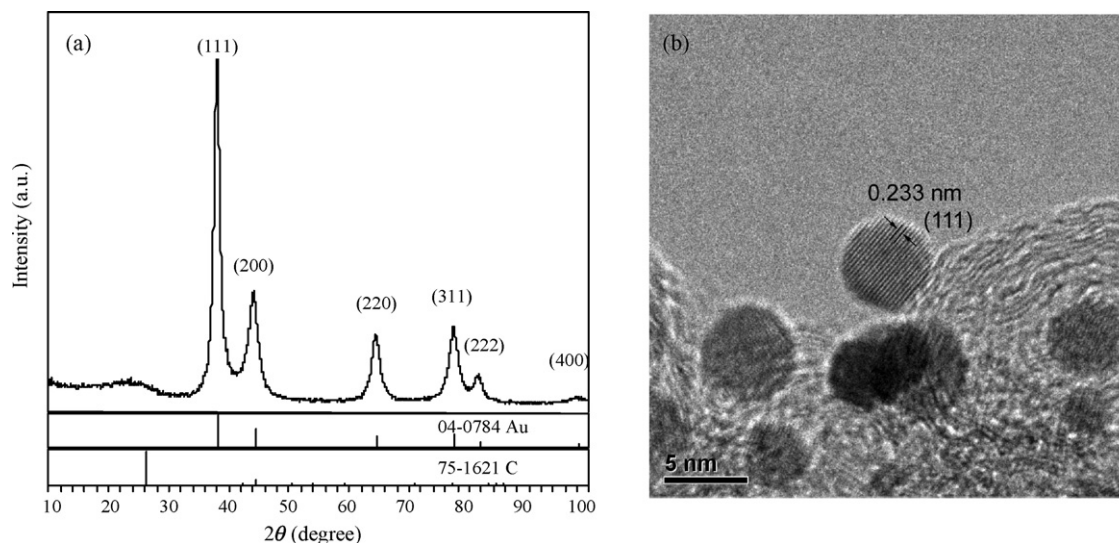
Fig. 1. (a) XRD pattern and (b) TEM image of the prepared Au/C catalyst.

and cell performance were studied. The temperature effects on cell performance and the electrode polarization were evaluated.

2. Experimental

The Au/C catalyst was synthesized by loading Au particles on BP2000 carbon through the method as described elsewhere [9]. The synthesized catalyst was characterized by powder X-ray diffraction (XRD) with a Rigaku-D/MAX-2550PC diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5406\,\text{Å}$). The catalyst morphology was observed with a JEM-2010 transmission electron microscope operated at 200 kV.

Cyclic voltammetry (CV) and RDE measurements were performed with Zahner IM6 analyzer in one compartment cell from -1.0 to -0.6 V for N_2H_4 electrooxidation and from 0 to 1.0 V for H_2O_2 electroreduction at a scan rate of $50\,\text{mV s}^{-1}$. The electrolytes were bubbled with pure Ar for 30 min to remove dissolved oxygen before each measurement, and then H_2O_2 was added into the electrolyte to reach a desired concentration. All measurements were conducted at room temperature ($25 \pm 1\,^\circ\text{C}$). Electrode potentials were converted to the values vs. standard hydrogen electrode (SHE).

Test cells were assembled by using Nafion 112 membrane as the electrolyte to separate the catholyte from the anolyte. The cathode was prepared by coating the cathode ink onto a piece of nickel foam (from INCO, porosity: 85%, thickness: 1.6 mm) with Au loading of $1\,\text{mg cm}^{-2}$. The cathode ink was prepared by mixing Au/C, de-ionized water, Nafion solution (5 wt.%), and anhydrous ethanol in a mass ratio of 1:3:7:3 in an agate mortar for 20 min. A composite catalyst (Ni–Pt/C) was used as the anode catalyst for N_2H_4 electrooxidation. The anode electrode was prepared by coating the anode ink onto a piece of nickel foam with a catalyst loading of $10\,\text{mg cm}^{-2}$. The anode ink was prepared by mixing Ni powder (INCO.210), Pt/C (5% Pt on Vulcan XC-72, E-Tek Co.) and Nafion solution (5 wt.%) in a mass ratio of 5:2:20 in an agate mortar for 20 min. Both cathode and anode were dried in air at $50\,^\circ\text{C}$ for 3 h. Nafion 112 membrane was pretreated by boiling in 3% H_2O_2 solution and then in de-ionized water for 1 h, respectively. The flow field area of end plates was $6\,\text{cm}^2$.

Two peristaltic pumps were equipped to circulate anolyte and catholyte at a flow rate of $50\,\text{mL min}^{-1}$. Cell performance and electrode polarization curves were measured in a cell test system as described in our previous work [10]. A saturated Ag/AgCl electrode

was used as the reference electrode placed in the anolyte side for polarization measurements.

Rotating disk electrode (RDE) technique was used to evaluate the number of electrons exchanged in the H_2O_2 reduction reaction. Au/C-modified glassy carbon (Au/C–GC) electrode was prepared as follows: 8 mg of Au/C catalyst was dispersed into a mixture of Nafion solution (5 wt.%, 0.1 mL) and anhydrous ethanol (1.5 mL) to make the dispersion. The dispersion was ultrasonically mixed for 30 min to make the cathode ink. 20 μL of the ink was pipetted onto the polished GC disk electrode and then dried at room temperature. A platinum wire and a saturated Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively.

3. Results and discussion

Fig. 1 shows the XRD pattern and the TEM image of the prepared Au/C catalyst. The diffraction profile of sample matches the JCPDS (PDF-04-0784) file, identifying the existence of Au with an fcc structure. The average crystallite size is smaller than 10 nm according to the TEM image and the estimation through Scherrer's equation from the full width half maximum (FWHM) of the diffraction peaks.

Fig. 2 illustrates the influence of the applied anolytes on the electrooxidation of N_2H_4 at the composite catalyst of Ni–Pt/C. It can
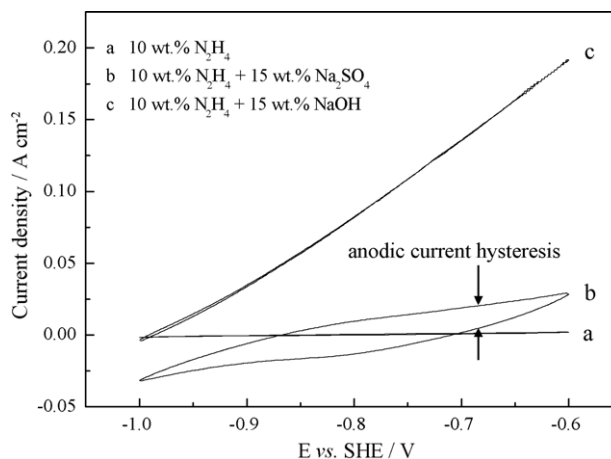

Fig. 2. Cyclic voltammograms of N_2H_4 in (a) 10 wt.% N_2H_4, (b) 10 wt.% N_2H_4 + 15 wt.% Na_2SO_4 and (c) 10 wt.% N_2H_4 + 15 wt.% NaOH, on Ni–Pt/C catalyst. Scan rate: $50\,\text{mV s}^{-1}$.
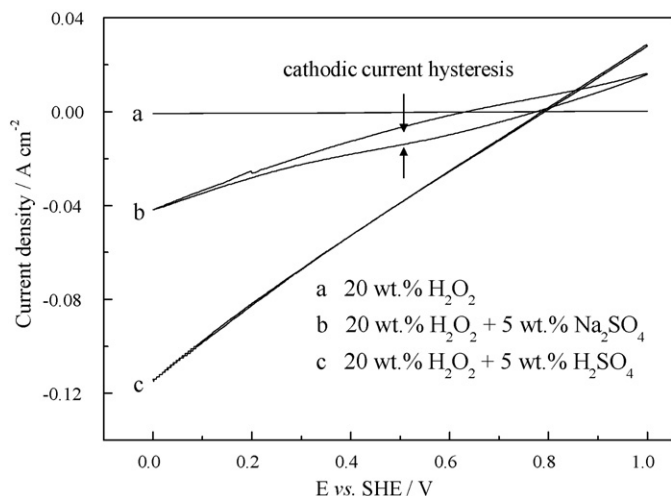
Fig. 3. Cyclic voltammograms of H_2O_2 in (a) 20 wt.% H_2O_2, (b) 20 wt.% H_2O_2 + 5 wt.% Na_2SO_4 and (c) 20 wt.% H_2O_2 + 5 wt.% H_2SO_4, on Au/C catalyst. Scan rate: 50 mV s^{-1}.

Fig. 4. Cell performance of the direct N_2H_4/H_2O_2 fuel cell operated at 30, 60 and 80 °C. Fuel: 10 wt.% N_2H_4 in 15 wt.% NaOH solution. Oxidizer: 20 wt.% H_2O_2 in 5 wt.% H_2SO_4 solution. Membrane: N 112.

be seen that N_2H_4 has higher electrochemical reactivity in NaOH added anolyte than that in other anolytes. It is known that only a little amount of OH$^-$ exists in aqueous N_2H_4 solution or Na_2SO_4 added N_2H_4 solution. When a large oxidation current was applied, the OH$^-$ concentration around the catalyst would be decreased according to the anode reaction:

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^- \qquad (3)$$
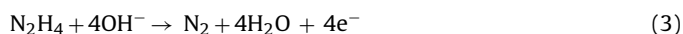
leading to an OH$^-$ concentration polarization, so that a large oxidation current hysteresis could be observed for the Na_2SO_4 added N_2H_4 solution compared with alkaline N_2H_4 solution. As for the aqueous N_2H_4 solution, the oxidation current hysteresis disappeared because the oxidation current was too small to be observed compared with alkaline N_2H_4 solution. Similarly, on the catholyte side, it can be seen that H_2O_2 demonstrates higher electrochemical reactivity in the H_2SO_4 added catholyte than that in other catholytes as shown in Fig. 3. The smaller reduction current hysteresis in the cyclic voltammogram loop can be attributed to that acidic H_2O_2 solution contains more H$^+$ than the Na_2SO_4 added H_2O_2 solution. Considering the cell configuration similar to the direct borohydride fuel cell [11], Na$^+$ ions from anolyte would migrate to catholyte during operation. It is considered that the H_2SO_4 addition in the catholyte could not only improve the electrochemical reactivity of H_2O_2, but also increase the Na$^+$ concentration gradient so that Na$^+$ migration in Nafion membrane could be improved. As a result, the performance of the direct N_2H_4/H_2O_2 fuel cell is improved. However, more detailed studies are needed to prove this hypothesis.

From above results, it can be known that OH$^-$ is important to N_2H_4 electrooxidation, and H$^+$ is important to H_2O_2 electroreduction. In order to evaluate the influence of anolyte and catholyte on the DHFC performance, DHFCs using Ni–Pt/C as the anode catalyst and Au/C as the cathode catalyst were assembled. The
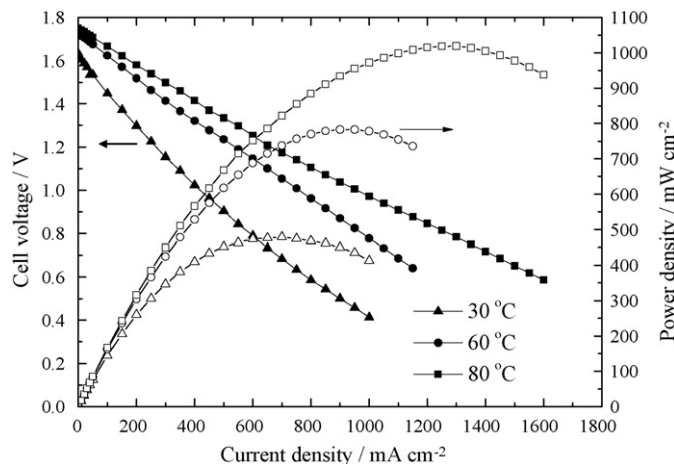
open-circuit voltages (OCVs) and cell performances when using different anolytes and catholytes were tabulated in Table 1. It was found that OCV and the cell performance were improved significantly when adding Na_2SO_4 or NaOH into the aqueous N_2H_4 solution, and they were further improved when adding Na_2SO_4 or H_2SO_4 into the aqueous H_2O_2 solution. The cell showed a voltage of 0.314 V when using the anolyte of NaOH solution without N_2H_4 and the catholyte of H_2SO_4 solution without H_2O_2, but no stable operation voltage was observed even at a very small current density such as 1 mA cm^{-2}. Therefore, it is considered that NaOH addition in anolyte and H_2SO_4 addition in catholyte are beneficial to improvement of the DHFC performance.

The temperature effect on the cell performance is illustrated in Fig. 4. Maximum power densities of 0.47, 0.78, and 1.02 W cm^{-2}, were achieved when the cell was operated at 30, 60 and 80 °C, respectively. These values are much higher than those obtained from conventional N_2H_4/O_2 fuel cells operated at the same temperatures [1–3].

The anode and cathode polarization curves at 30, 60 and 80 °C were plotted in Fig. 5. It can be seen that the cathode polarization was obviously improved with elevating the operation temperature, but operation temperature shows little effects on the anode performance.

Considering the possibility of H_2O_2 decomposition to O_2 and H_2O during operation to decrease the coulombic efficiency of H_2O_2, the RDE voltammetry was performed to evaluate the number of electrons for H_2O_2 reduction on Au/C. Fig. 6 shows the RDE voltammograms of H_2O_2 on the Au/C–GC electrode at various rotation rates of 400, 900, 1600 and 2500 rpm. The number (n) of electrons for H_2O_2 reduction on Au/C can be estimated from Koutecky–Levich (K–L) plots as follows [12]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{0.62nFC_{H_2O_2}D_{H_2O_2}^{2/3}\upsilon^{-1/6}\omega^{1/2}} \qquad (4)$$

Table 1
Cell voltages and performances of DHFCs using different anolytes and catholytes.

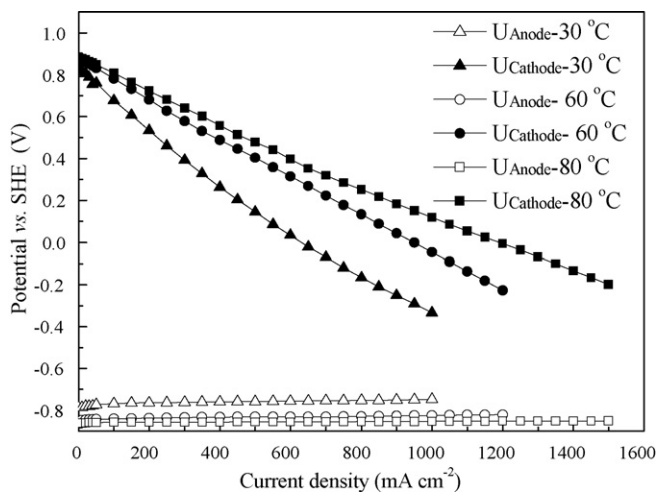| Sample	Anolyte (solution)	Catholyte (solution)	OCV (V)	Maximum power density (mW cm^{-2})
1	10 wt.% N_2H_4	20 wt.% H_2O_2	0.509	1.46
2	10 wt.% N_2H_4 + 15 wt.% Na_2SO_4	20 wt.% H_2O_2	0.610	14.8
3	10 wt.% N_2H_4 + 15 wt.% NaOH	20 wt.% H_2O_2	1.13	74.6
4	10 wt.% N_2H_4	20 wt.% H_2O_2 + 5 wt.% H_2SO_4	0.868	8.20
5	10 wt.% N_2H_4 + 15 wt.% Na_2SO_4	20 wt.% H_2O_2 + 5 wt.% H_2SO_4	1.09	96.0
6	10 wt.% N_2H_4 + 15 wt.% NaOH	20 wt.% H_2O_2 + 5 wt.% H_2SO_4	1.63	479
7	15 wt.% NaOH	5 wt.% H_2SO_4	0.314	Null

Fig. 5. Anode and cathode polarization behavior of the direct N_2H_4/H_2O_2 fuel cell at 30, 60 and 80 °C. Fuel: 10 wt.% N_2H_4 in 15 wt.% NaOH solution. Oxidizer: 20 wt.% H_2O_2 in 5 wt.% H_2SO_4 solution.
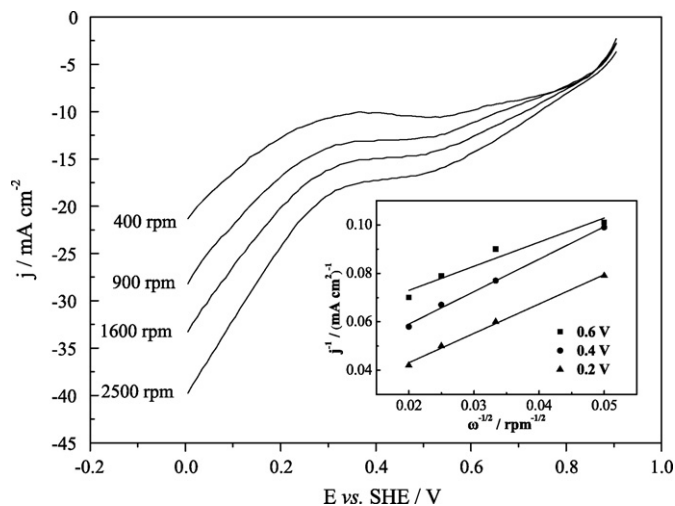

Fig. 6. RDE voltammograms obtained from Au/C + 0.1 M H_2SO_4 + 20 mM H_2O_2 in Ar-purged atmosphere. Scan rate: 50 mV s^{-1}. The inset shows Koutechy–Levich plots obtained at 0.2, 0.4 and 0.6 V.

where j is the measured current density, j_k is the kinetic current density, n is the number of electrons transferred per H_2O_2 molecule, F is the Faraday constant. $C_{H_2O_2}$ is the concentration of H_2O_2 in the solution (0.02 M), υ is the kinematic viscosity of the solution (0.009 cm^2 s^{-1}), $D_{H_2O_2}$ is the diffusion coefficient of H_2O_2 in the solution (1.3×10^{-5} m^2 s^{-1}) [12], ω stands for the rotation rate (rad s^{-1}).

By using the limiting currents at 0.6, 0.4 and 0.2 V, the K–L plots obtained from RDE voltammograms are shown in the inset figure of Fig. 6. From the slopes of the K–L plots, the values of n for H_2O_2 electroreduction on the Au/C–GC electrode are estimated to be 2.1, 1.6, 1.8 at 0.6, 0.4 and 0.2 V, respectively. It is considered that the number of electrons exchanged in the H_2O_2 reduction reaction on Au/C catalyst is 2. This result reveals that the H_2O_2 can be electroreduced completely on Au/C catalyst.

4. Conclusions

In the present work, a new type of DHFC using H_2O_2 as the oxidizer is explored. Both anolyte and catholyte show significant influences on cell voltage and cell performance. Alkaline anolyte and acidic catholyte are beneficial to improvement of the DHFC performance. A maximum power density of 1.02 W cm^{-2} has been achieved by using alkaline N_2H_4 solution as the fuel and acidic H_2O_2 solution as the oxidizer at 80 °C. The number of electrons exchanged in the H_2O_2 reduction reaction on Au/C catalyst is 2, which reveals that the H_2O_2 can be electroreduced completely on Au/C catalyst.

Acknowledgements

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