A direct methanol–hydrogen peroxide fuel cell with a Prussian Blue cathode

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A B S T R A C T

In this work, a direct methanol–hydrogen peroxide fuel cell is developed and tested. Theoretically, it is shown that the use of hydrogen peroxide in a direct methanol fuel cell (DMFC) not only increases the cell's voltage from 1.21 V to 1.76 V, but also reduces the activation loss of the reduction reaction as a result of two-electron transfer. Experimentally, it is demonstrated that the fuel cell with the use of an inexpensive carbon nanotube supported Prussian Blue catalyst, exhibits a peak power density of 125 mW cm$^{-2}$ at 60 °C, which is comparable to that of conventional DMFCs with platinum-based catalysts.

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Introduction

Direct methanol fuel cell is an electrochemical energy conversion technology, which can directly convert the chemical energy stored in methanol into usable electricity [1–3]. Its many striking advantages, including compact structure, high-specific energy, facile fuel storage and transportation as well as environmental friendliness, have garnered increasing attentions in recent studies. Although promising, the widespread commercialization of this technology is hindered by several technical issues [4–7]. For practical purposes, the inferior kinetics of the oxygen reduction reaction (ORR) requires the use of platinum (Pt) catalyst, which is expensive (~$45 g$^{-1}, the highest Pt price in 25 years) and scarce (37 p.p.b. in the Earth's crust) [8], making the system cost-ineffective. Also, the DMFC experiences methanol crossover, where methanol permeates from the anode to the cathode and is oxidized to form carbon dioxide. Any remaining methanol is incompletely oxidized and would form the intermediate products (e.g. CO, CHOH, CHO), which deactivates the activity of the catalyst in a process known as catalyst poisoning [9]. Hence, it is necessary to develop a highly active, cost-effective and methanol tolerable catalyst for cathodic reduction reaction.

Recent demonstrations show that the issues of high cost and catalyst poisoning might be addressed by employing hydrogen peroxide as the oxidant [10–14]. Since hydrogen peroxide exhibits superior kinetics during the reduction reaction and allows the use of non-platinum catalysts. Meanwhile, non-platinum catalysts are inactive to MOR and tolerable of methanol; thus, it could avoid the harmful effect caused by methanol crossover. In this work, we propose a direct methanol–hydrogen peroxide fuel cell fitted with a carbon nanotube (CNT) supported Prussian Blue (PB) cathode.

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It has been shown that PB, a hexacyano-Fe complex material, is unaffected by MOR [15,16] and exhibits a superior catalytic activity towards the reduction reaction of hydrogen peroxide owing to its zeolitic nature, which enables the diffusion of H$_2$O$_2$ molecules through the crystal lattice. Karyakin [17] reported that the catalytic activity of PB for the H$_2$O$_2$ reduction to be about 100 times higher than that for O$_2$. Furthermore, preparation of PB is simple and cost-effective, and PB itself shows high stability in acidic media. For these reasons, PB has found numerous electrochemical applications such as electrochromism [18], ion selective electrodes [19], charge storage devices [20] and electrocatalysis [21,22]. Here, PB supported on CNT is used as the cathodic catalyst for the proposed fuel cell. In addition, this fuel cell system offers two additional advantages: i) it is operable in oxygen-free environment, and ii) it can achieve a high theoretical voltage (1.76 V), providing plenty of room for the improvement of the cell performance. The schematic of this fuel cell system is shown in Fig. 1.

Experimental

**Preparation of carbon nanotube supported Prussian Blue**

The chemical route of PB synthesis was reported elsewhere [23,24]. In brief, carbon nanotubes were suspended in 0.1 M HCl solution and stirred in an ultrasonic water bath to form slurry. Next, the required amount of 0.5 M K$_3$[Fe(CN)$_6$] in 0.1 M HCl solution was added into the slurry drop-by-drop, followed by 0.5 M FeCl$_3$ in 0.1 M HCl. The mass ratio of Prussian Blue to CNT was controlled to be 2:1 to ensure high electric conductivity. The resulting mixture was stirred for 1 h and the entire process was maintained at room temperature. The resulting slurry (PB/CNT) was collected by filtration and washed with 0.1 M HCl until the washing solution became colorless. After that, it was dried at 100 °C for 3 h and then stored in darkness in a desiccator.

**Preparation of membrane electrode assembly**

With an active area of 2.0 cm $\times$ 2.0 cm, the membrane electrode assembly (MEA) was comprised of a pretreated Nafion® 115 membrane sandwiched between a commercially available anode from Johnson Matthey® and a cathode by hot-pressing at 135 °C under 4.0 MPa for 3 min. A SGL® carbon paper with 5 wt.% polytetrafluoroethylene (PTFE) treatment and a MPL coated as the anode diffusion layer. The anode catalyst layer consists of carbon supported PtRu (50% Pt, 25% Ru) with a loading of 4.0 mg cm$^{-2}$. The carbon cloth (ETEK, Type A) was used as the cathode diffusion layer. The cathode catalyst layer (CL) was made of the prepared PB/CNT with a loading of 20.0 mg cm$^{-2}$ and the mass ratio of Nafion ionomer in the cathode CL was 20 wt.%. For comparison, a typical cathode CL of the conventional DMFC was also fabricated, in which the catalyst was carbon supported Pt (60 wt. % Pt) with a loading of 2.0 mg cm$^{-2}$.

The fabricated electrodes were characterized by powder X-ray diffraction (XRD), cyclic voltammetry (CV), scanning electron microscope (SEM), transmission electron microscopy (TEM), and polarization curves.

**Single cell test**

An Arbin BT2000 electrical load was used to control the discharging condition and to record the data. For each discharging current point, it took about 60s for the voltage to become stable. The single cell tests were performed at 60 °C supplied with 2.0 M methanol solution at a flow rate of 2.5 mL min$^{-1}$. For the cathode of the conventional DMFC, oxygen/air was supplied at a flow rate of 100/500 sccm. For the cathode of the proposed direct methanol—hydrogen peroxide fuel cell, it was fed with the aqueous solution including 4.0 M H$_2$O$_2$ and 1.0 M H$_2$SO$_4$ at a flow rate of 2.5 mL min$^{-1}$. The difference in the flow rates of different oxidants is to confirm the equivalent stoichiometry.

**Results and discussion**

Powder X-ray diffraction (XRD) patterns for the CNT, PB and synthesized PB/CNT are shown in Fig. 2. For the PB/CNT, the peak at 2θ = 26.2 corresponds to the supporting material since it matches well with the XRD pattern of CNT. The other pronounced peaks at 2θ = 17.4 (2 0 0), 2θ = 24.6 (2 2 0), 2θ = 35.2 (4 0 0), 2θ = 39.4 (4 2 0) and 2θ = 43.4 (4 2 2) correspond to Fe$_6$[Fe(CN)$_6$]$_3$$\cdot$ xH$_2$O [25]. As proven by the XRD patterns, Prussian Blue was successfully synthesized and loaded onto the CNT.

The electrochemical reduction of hydrogen peroxide over CNT and PB/CNT was examined in a three-electrode cell with a rotating ring-disk glassy carbon electrode with the supporting electrolyte 0.1 M H$_2$SO$_4$ containing 1.0 M H$_2$O$_2$. Fig. 3 shows that the onset potential for H$_2$O$_2$ reduction reaction over PB/CNT is at about 0.5 V (vs. SCE); while, the value over CNT is about -0.25 V (vs. SCE). It indicates that the PB owns much better catalytic ability for electrochemical reduction of hydrogen peroxide than CNT does; it also proves that the PB was successfully loaded onto CNT, otherwise, the continuous electron pathway could not form. In addition, the reduction reaction current density is in the range of tens of milliampere per square centimeter, indicating that PB/CNT exhibits rather high catalytic activity to the reduction reaction of H$_2$O$_2$.

Fig. 4 depicts the surface morphology of the PB-based catalyst layer at different magnifications. It can be observed from Fig. 4a that the surface morphology is quiet smooth with few cracks. This is due to the fact that the supporting material, CNT, is able to offer a better interaction to form the crack-free catalyst layer owing to its one-dimensional nature [26]. More importantly, it is apparent in the high-magnification image that PB was uniformly distributed on the CNT, enabling the catalyst to have excellent electric-conductivity. As shown in the TEM image, the particle size of PB is roughly tens of nanometers.

Fig. 5 displays a comparison in the performances of the conventional DMFCs using pure oxygen and air. It is apparent that the use of pure oxygen receives a superior performance than the use of air. The peak power density achieved with O$_2$ is 105 mW cm$^{-2}$, which is twice the value of that with the use of air. The difference in performance is attributed to the fact that the partial pressure of oxygen is lower in air, causing a slower rate of oxygen transfer from the bulk to the reaction site of the cathode.
Fig. 5 also shows the polarization curve of the present direct methanol–hydrogen peroxide fuel cell. It is demonstrated that the change from oxygen to hydrogen peroxide increases the OCV from 0.62 V to 0.74 V. It should be noted, however, that the actual OCV (0.74 V) is much lower than the theoretical voltage (1.76 V). This phenomenon can be explained as follows. The cathodic reaction is the reduction reaction of hydrogen peroxide (HPRR) where the potential is theoretically as high as 1.78 V:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O; \quad E_0 = 1.78 \text{ V}$$ (1)

However, hydrogen peroxide oxidation reaction (HPOR) easily takes place at such a high potential, releasing oxygen, electrons and protons as shown below.

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-; \quad E_0 = 0.69 \text{ V}$$ (2)

Additionally, since $O_2$ is generated from the above reaction, the oxygen reduction reaction (ORR) may also occur:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O_2; \quad E_0 = 1.23 \text{ V}$$ (3)

The simultaneous reduction reactions and oxidation reaction taking place on one electrode results in a mixed potential, which significantly lowers the voltage of the fuel cell.

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Fig. 1 – Schematic description of (a) the direct methanol–hydrogen peroxide fuel cell and (b) crystal structure of Prussian Blue.

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That being said, the peak power density of the methanol–hydrogen peroxide fuel cell is able to reach 125 mW cm\(^{-2}\), a value 20% and 150% larger than that of the conventional DMFC with oxygen and air, respectively. This high performance can be attributed to the fact that direct methanol–hydrogen peroxide fuel cell has a higher theoretical voltage, and much faster kinetics of the reduction reaction which can be confirmed by the low activation loss at small current densities. In addition, there is no obvious difference between the internal resistances of the methanol–hydrogen peroxide fuel cell and the conventional DMFC (235 mΩ cm\(^{-2}\) vs. 216 mΩ cm\(^{-2}\)). Fig. 5 shows that the direct methanol–hydrogen peroxide fuel cell is outperformed by the conventional DMFC at high current regions (e.g. above 500 mA cm\(^{-2}\)). This is because when stoichiometries using different oxidants are kept constant, the gaseous oxygen has a much higher flow rate as a result of the lower density, enhancing mass transport at the high current density region. To confirm the catalytic activity of the PB, the CL fabricated with the CNT only was also prepared and tested. This cell shows a peak power density of 8 mW cm\(^{-2}\), indicating that the high performance of the present direct methanol–hydrogen peroxide fuel cell is mainly attributed to the PB rather than the supporting material CNT. The constant current discharging behavior of the direct methanol–hydrogen peroxide fuel cell is shown in Fig. 6. It can be seen that the present fuel cell runs stably at continuous operation.

**Conclusion**

In this work, we proposed a methanol–hydrogen peroxide fuel cell fitted with a Prussian Blue cathode and prepared PB/CNT as the catalyst. The synthesized PB/CNT possesses high conductivity due to an efficient electron transfer network offered by the CNT and superior catalytic activity from the PB. This fuel cell exhibits a peak power density of 125 mW cm\(^{-2}\) at

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**Fig. 2** – X-ray diffraction (XRD) patterns of CNT, PB and PB/CNT.

**Fig. 3** – Cyclic voltammogram of the HPRR on CNT and PB/CNT in 0.1 M H\(_2\)SO\(_4\) + 1.0 M H\(_2\)O\(_2\) (scan rate: 20 mV s\(^{-1}\)).

**Fig. 4** – SEM image of the PB based catalyst layer: (a) low magnification, (b) high magnification and (c) TEM image of the PB/CNT catalyst.
The striking advantage of this fuel cell lies in the fact that a non-precious metal catalyst, PB, is used to replace Pt, lowering the system cost but obtaining a comparable performance. In future studies of this type of fuel cell, focus should be given to solving issues such as the electrochemical decomposition of hydrogen peroxide.

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