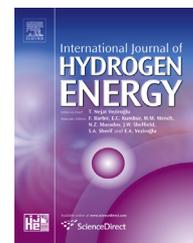




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A direct methanol–hydrogen peroxide fuel cell with a Prussian Blue cathode

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ABSTRACT

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 useable 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_2O_2 molecules through the crystal lattice. Karyakin [17] reported that the catalytic activity of PB for the H_2O_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 $\text{K}_3[\text{Fe}(\text{CN})_6]$ 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 × 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 was used 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_2O_2 and 1.0 M H_2SO_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 $2\theta = 26.2$ corresponds to the supporting material since it matches well with the XRD pattern of CNT. The other pronounced peaks at $2\theta = 17.4$ (2 0 0), $2\theta = 24.6$ (2 2 0), $2\theta = 35.2$ (4 0 0), $2\theta = 39.4$ (4 2 0) and $2\theta = 43.4$ (4 2 2) correspond to $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ [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_2SO_4 containing 1.0 M H_2O_2 . Fig. 3 shows that the onset potential for H_2O_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 milliamperes per square centimeter, indicating that PB/CNT exhibits rather high catalytic activity to the reduction reaction of H_2O_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.

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