



Studies of electrochemical performance of carbon supported Pt–Cu nanoparticles as anode catalysts for direct borohydride–hydrogen peroxide fuel cell

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ABSTRACT

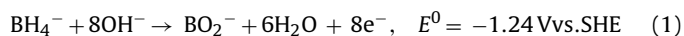
Carbon supported Pt–Cu bimetallic nanoparticles are prepared by a modified NaBH_4 reduction method in aqueous solution and used as the anode electrocatalyst of direct borohydride–hydrogen peroxide fuel cell (DBHFC). The physical and electrochemical properties of the as-prepared electrocatalysts are investigated by transmission electron microscopy (TEM), X-ray diffraction (XRD), cyclic voltammetry (CV), chronoamperometry (CA), chronopotentiometry (CP) and fuel cell test. The results show that the carbon supported Pt–Cu bimetallic catalysts have much higher catalytic activity for the direct oxidation of BH_4^- than the carbon supported pure nanosized Pt catalyst, especially the $\text{Pt}_{50}\text{Cu}_{50}/\text{C}$ catalyst presents the highest catalytic activity among all as-prepared catalysts, and the DBHFC using $\text{Pt}_{50}\text{Cu}_{50}/\text{C}$ as anode electrocatalyst and Pt/C as cathode electrocatalyst shows as high as 71.6 mW cm^{-2} power density at a discharge current density of 54.7 mA cm^{-2} at 25°C .

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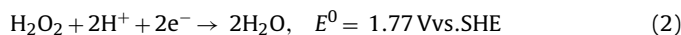
1. Introduction

Fuels cells are actively investigated as an attractive alternative to conventional fossil fuel combustion engines for cleaner power generations [1,2]. Compared with a hydrogen combustion engine, a hydrogen fuel cell can directly change chemical energy into electrical energy with higher efficiency and requires gaseous hydrogen as fuel. However, there still remain some problems for transportation and storage of hydrogen. Direct borohydride–hydrogen peroxide fuel cell (DBHFC), especially using sodium borohydride (NaBH_4) aqueous solution as fuel, has been intensively studied [3–6]. Sodium borohydride (NaBH_4) contains high hydrogen content (weight content of 10.6%) and a high capacity (5.7 Ah g^{-1}). Moreover, sodium borohydride is non-toxic, rather safe, chemically stable, easy to store and transport in its dry state. Thus, sodium borohydride has been considered to be an attractive hydrogen source for DBHFCs.

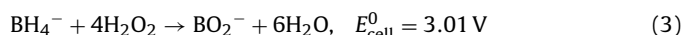
The anode reaction of DBHFC in an aqueous alkaline medium according to an eight-electron mechanism is described as follows [7]:



With the oxidation of NaBH_4 at the anode, the hydrogen peroxide in an acid electrolyte instead of oxygen as an oxidant can yield higher cell potential and energy density:



In combination with the reduction of hydrogen peroxide, DBHFC can give a theoretical cell voltage of 3.01 V and presents a high energy density. Overall cell reaction is as follows:



The anode electrocatalyst is one of the key components in fuel cell. In the past years, different metals have been studied as the anode electrocatalyst for DBHFC, such as Pt [8–10], Au [9–11], Os [12,13], Pd [14], Ag [15], Ni [16], Zn [17] and hydrogen storage alloys [18]. Among these metals, Pt, Au and Os are more attractive than other metals as anode catalyst for DBHFC. However, although it has been reported that the electrooxidation of BH_4^- on Au particles is an approximate eight-electron process [9,11], Chatenet et al. [19,20] recently find that Au does in fact show catalytic activity for hydrolysis of borohydride to some extent. Moreover, slow electrode kinetics of BH_4^- on Au anode results in low current and power output, and thus degrades the electrochemical performance of the DBHFC [21–23]. Gyenge et al. [12,13] investigated the DBFC using carbon supported Os and Os–alloys (Os–Sn, Os–Mo and Os–V) as anode catalysts, and found that Os could be a promising electrocatalyst for BH_4^- oxidation, but Os–alloys were not a good candidate due to their high positive overpotentials [13].

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Up to now, platinum has been intensively studied on anode electrocatalyst of DBFC [8–10,24], but Pt is a noble metal and will result in a high cost. Many efforts have been made to lower the cost of catalyst; one way is to alloy Pt with transition metals such as Co [25], Ni [26], Sn [27], Fe [28] and Cr [29]. It has been reported that the Pt-based alloys have demonstrated similar or even higher electrocatalytic activities than the simplex Pt catalyst [25–29]. Wang et al. [30] investigated Pt–Ni/C as anode electrocatalyst for the DBFC, and found that the addition of Ni to Pt/C results in the improvement of the electrocatalytic activity. Gyenge et al. [31] studied the DBFC using carbon supported Pt and Pt–alloys (Pt–Ir/C, Pt–Ni/C, and Pt–Au/C) as anode catalyst, and found that Pt–Ir/C and Pt–Ni/C gave the higher cell voltage at a given superficial current density than Pt/C and Pt–Au/C. However, Cu is relatively inexpensive metal, to the best of our knowledge, Pt–Cu bimetallic nanoparticles supported on carbon as anodic catalyst for BH_4^- electro-oxidation were barely studied. In this work, a series of Pt–Cu bimetallic nanoparticles supported on carbon black XC-72R (Pt–Cu/C) were prepared by a modified NaBH_4 reduction method in aqueous solution and used as the anode catalyst for BH_4^- electro-oxidation. The electrochemical evaluations of catalytic activity for the as-prepared catalysts were carried out by cyclic voltammetry (CV) chronoamperometry (CA) and chronopotentiometry (CP). Moreover, the performances of the DBHFC employing Pt–Cu/C as the anode catalyst and Pt/C as the cathode catalyst were studied in detail.

2. Experimental methods

All chemical reagents were of analytical grade: sodium borohydride (AlfaAesar, 98%), hexachloroplatinic acid (Sigma–Aldrich), cupric sulfate (Sigma–Aldrich), polyvinylpyrrolidone (Sigma–Aldrich), Vulcan XC-72R carbon (Cabot Corp., $240 \text{ m}^2 \text{ g}^{-1}$) and Nafion solution (Dupont, 5%).

2.1. Preparation of Pt–Cu/C catalysts

$\text{HPtCl}_6 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were used as precursors of Pt–Cu bimetallic catalysts. XC-72R carbon black and NaBH_4 were used as a support and reducing agent, respectively. Polyvinylpyrrolidone (PVP) was used to prevent nanoparticles from aggregating in the solution. A brief description of the preparation method is as follows: the required amounts of HPtCl_6 , CuSO_4 , carbon and PVP were added to 100 ml deionized (DI) water under vigorous stirring, and then it was kept to stir for 30 min. The pH of the mixed solution was adjusted to 10 by adding 3 M NaOH solution, and 1 ml of 1 M NaBH_4 was added dropwise. After an additional 24 h stirring, the resulting catalyst was filtered and washed with deionized water until no Cl^- was detected, finally dried for 12 h at 80°C in vacuum to obtain Pt–Cu/C catalysts. The atomic ratios of Pt/Cu which contained in the impregnation solutions were 100:0, 67:33, 50:50 and 33:67. The prepared four catalysts were denoted as Pt/C, $\text{Pt}_{67}\text{Cu}_{33}/\text{C}$, $\text{Pt}_{50}\text{Cu}_{50}/\text{C}$ and $\text{Pt}_{33}\text{Cu}_{67}/\text{C}$, respectively. For each catalyst, the amount of metal is 20 wt.% of total catalyst weight.

2.2. Physical characterization of Pt–Cu/C electrocatalysts

The structure and morphology of the prepared electrocatalyst were examined by transmission electron microscopy (TEM), using a Jeol 3010 microscope at 300 kV. For TEM analyses, samples were prepared by placing one or two drops of nanoparticles solution onto the carbon-coated copper grid and drying it in air at room temperature.

X-ray diffractometer (D/MAX-3C) was employed with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) and a graphite monochromator at 50 kV, 100 mA to obtain X-ray diffraction (XRD) patterns of the samples.

The 2θ angular regions between 10° and 80° were explored at a scan rate of 5° min^{-1} .

2.3. Electrochemical performance of anode catalysts

Electrochemical measurements were performed using CHI660A Electrochemistry Workstation and a typical three-electrode one-compartment electrolysis cell. The Pt–Cu/C or Pt/C was used as working electrode, a Ni foam mesh with $3 \text{ cm} \times 5 \text{ cm}$ as counter electrode and an Ag/AgCl, KCl_{std} as the reference electrode. The electrolyte was 0.1 M $\text{NaBH}_4 + 3.0 \text{ M NaOH}$. The working electrode was prepared as follows: 10 mg of Pt–Cu/C or Pt/C powder was dispersed by ultrasonic for 2 h in 1 ml blend solution of 0.25 ml 5 wt.% Nafion solution and 0.75 ml de-ionized water. Then $5 \mu\text{l}$ of slurry was pasted on the surface of the glassy carbon (GC) electrode (3 mm in diameter) which was polished to mirror by $0.5 \mu\text{m}$ alumina and sonicated 5 min prior to use. The dispersed catalyst on the GC surface was dried for 5 h at room temperature. The loading mass of catalyst was 0.7 mg cm^{-2} and actual metal loading mass on electrode is 0.14 mg cm^{-2} .

2.4. Fuel cell test

The catalyst ink was made by mixing isopropyl alcohol with 7 wt.% of Nafion solution and carbon supported catalysts. Then the ink was coated onto a stainless steel gauze resulting in a 4.5 mg cm^{-2} catalyst loading, and actual metal loading mass on electrode is 0.9 mg cm^{-2} . The catalyst electrodes were pressed at 10 MPa for 1 min to ensure a good electric contact, then dried at 50°C for 8 h in vacuum.

The cell performance was tested against a Pt/C cathode and a Pt–Cu/C or Pt/C anode. A schematic diagram of the experimental set-up was shown in our previous studies [32]. A Nafion 117 membrane was used to separate the anolyte and catholyte. Anolyte is composed of 1 M $\text{NaBH}_4 + 3 \text{ M NaOH}$, and the catholyte is composed of 2 M $\text{H}_2\text{O}_2 + 0.5 \text{ M H}_2\text{SO}_4$. The fresh anolyte and catholyte were continuously supplied and withdrawn from the cell at a rate of 0.7 ml min^{-1} , respectively. The load was applied in steps of 5 mA within the range of 0–90 mA. Each step lasted 2 min and the current was continuously applied from one value to next without disconnecting the cell. The cell testing was performed using a battery testing system (Xinwei, Shenzhen, China). Power densities were calculated from the applied current and steady state potential.

3. Results and discussion

3.1. Physical characterization

Fig. 1(a) and (b) is the TEM and HR-TEM images of the $\text{Pt}_{50}\text{Cu}_{50}/\text{C}$ catalysts. It can be clearly seen that the metal nanoparticles with a narrow particle size distribution are uniformly dispersed on the surface of carbon. The morphologies of the metal nanoparticles are generally spherical, and the mean diameter is approximately 3 nm. Fig. 2 shows the XRD patterns of the Pt/C, $\text{Pt}_{67}\text{Cu}_{33}/\text{C}$, $\text{Pt}_{50}\text{Cu}_{50}/\text{C}$ and $\text{Pt}_{33}\text{Cu}_{67}/\text{C}$. The wide diffraction peak located at a 2θ value of about 25.0° is attributed to carbon (002) crystal face, which matches well with the standard C peak (JCPDS No. 75-1621). The diffraction peaks positioned at $2\theta = 39^\circ, 46^\circ, 67^\circ$ could be indexed to the (111), (200), (220) planes of face-centered cubic (fcc) Pt, which match well with the standard Pt peaks (JCPDS No. 88-2343). The diffraction peaks positioned at $2\theta = 35.4^\circ$ and 38.7° on the XRD pattern of $\text{Pt}_{33}\text{Cu}_{67}/\text{C}$ are attributed to (002) and (111) planes of end-centered monoclinic CuO, which match well with the standard CuO peaks (JCPDS No. 80-1917). However, no diffraction peaks of Cu or its oxides are observed for $\text{Pt}_{67}\text{Cu}_{33}/\text{C}$ and $\text{Pt}_{50}\text{Cu}_{50}/\text{C}$, indicating that Pt metal and Cu metal are alloyed well. And the XRD

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