



Nanoporous carbon supported platinum-copper nanocomposites as anode catalysts for direct borohydride-hydrogen peroxide fuel cell



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ABSTRACT

Nanoporous carbon (NPC) supported Pt-Cu nanocomposites (Pt_xCu/NPC) with different Pt/Cu molar ratios have been successfully synthesized via NaBH₄ reduction method and used as anode catalysts for direct borohydride-hydrogen peroxide fuel cell (DBHFC). The as-synthesized Pt_xCu/NPC electrocatalysts are characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), cyclic voltammetry (CV), chronoamperometry (CA), rotating disc electrode (RDE) and fuel cell test. It has been found that the PtCu nanoparticles are uniformly dispersed on the surface of the NPC support with average size of about 2.3 nm. Besides, the Pt_xCu/NPC catalysts show higher activities for borohydride oxidation than that of monometallic Pt/NPC and Vulcan XC-72 carbon supported Pt₂Cu (Pt₂Cu/XC-72) catalysts. Especially, the DBHFC equipped with Pt₂Cu/NPC as anode catalyst shows the maximum power density of 89 mW cm⁻² at 25 °C.

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1. Introduction

Borohydrides is considered to be a promising fuel for fuel cells owing to a number of advantages, such as low toxicity, superior storage properties, large amounts of hydrogen (10.6 wt.% for NaBH₄), high theoretical capacity and specific energy density [1–3]. Therefore, direct borohydride-hydrogen peroxide fuel cell (DBHFC) has attracted particular attention in recent years as a means of converting borohydride ion and an oxidant directly into electricity with a high efficiency and low-emission [4,5]. However, the DBHFC has a long way to become commercially viable for applications, because it still suffers from inadequate performance and durability arising mainly from anode catalyst oxidation, as well as the high costs caused by the use of scarce precious metals (e.g., Pt, Au or Pd) as its primary catalysts [6–8]. Besides, the borohydride oxidation reaction (BOR) is a very complex process, involving many chemical (hydrolysis) or electrochemical steps and yielding a large number of intermediates, so the process always suffers from the possibility of catalyst poisoning, hindrance by bubbles formation and other related mass-transport issues [9–10]. In conclusion, the

optimization of anode catalyst plays an important role for the future DBHFC technology.

Recently, Pt is still regarded as one of the most active monometallic catalyst for fuel cells due to its fast electrode kinetics and good stability [11]. However, the sky-rocketing price of Pt greatly increases the total cost of catalysts and there is an urgent need to reduce its overall use. One strategy is to alloy Pt with cost-efficient transition metals, e.g. Cu, Ni, Co and Fe. Over the past decade, bimetallic catalysts have been demonstrated to be superior to the monometallic Pt catalyst [11–16]. For instance, Gyenge et al. [14] studied colloidal Pt and Pt-alloys electrocatalysts for BH₄⁻ oxidation. Interestingly, the higher cell voltages were obtained on both Pt-Ni/C and Pt-Ir/C alloys. Tegou et al. [16] also investigated the Pt-Ni and Pt-Co alloys for borohydride oxidation and found that the catalytic activity of the bimetallic catalysts in the kinetic and mixed control potential range was higher than that of pure Pt. The similar results have also been gained in our previous works related to Vulcan XC-72 carbon supported bimetallic catalysts, which present much better catalytic activity and stability for BH₄⁻ oxidation compared to Pt/C catalyst [17–19].

Another realistic strategy to improve the catalyst performance is to search new carbon support with excellent properties [20]. The nature of the support can substantially affect the properties of synthesized electrocatalysts, such as electrochemical active area,

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morphology of the metallic crystallites, stability, composition, etc. [21,22]. Currently, the supports for catalysts are usually graphene, graphite nanofibres, carbon xerogel and carbon nanotubes [23–25]. Among the above carbons, the porous carbon has many advantages, such as high surface area, bulk porosity, stable chemical/electrochemical properties and good conductivity, which are an attractive choice for catalysts. Recently, a remarkable progress has been made in the synthesis of nano-structured porous carbons using metal-organic frameworks (MOFs) template [26] which has permanent nanosized cavities and open channels offering congenial conditions for small molecules to access. And the yielded porous carbons show excellent property in gas adsorption, electrochemical capacitance and sensing [27–30]. As well known, the high specific surface area can not only be favorable to maximize the availability surface area of the catalytic particles, but also be benefit to facilitate mass transfer. In our previous work [31], a nanoporous carbon (NPC) has been prepared with a metal-organic framework-5 (MOF-5) template, and it showed a significantly large specific surface area up to $1123 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.896 \text{ cm}^3 \text{ g}^{-1}$ [32]. Moreover, it has been shown that the Pt/NPC exhibited a much higher activity for borohydride oxidation compared to that of the corresponding Vulcan XC-72R carbon supported Pt catalyst. Thus, the NPC might be a promising catalyst support for anode catalyst in DBHFC.

Take into account the above two strategies, the excellent support loaded noble metal-non-noble metal alloy electrocatalyst might be one of the best options for the economical catalyst. Thus, in this work the NPC supported Pt-Cu nanocomposites with different Pt/Cu molar ratios are synthesized and investigated as anode catalysts for borohydride oxidation. The single DBHFC performance with the as-synthesized catalyst as anode electrocatalyst is also studied.

2. Experimental

2.1. Synthesis of $\text{Pt}_x\text{Cu}/\text{NPC}$ electrocatalysts

The preparation method of the NPC was described in our previous work [31]. Briefly, the MOF-5 was prepared by solvothermal method with the optimal synthesis conditions according to the literature [33]. Then the as-prepared MOF-5 was degassed at 200°C for 24 h and the furfuryl alcohol (FA) was introduced into the pores of degassed MOF-5 via the incipient wetness technique. Subsequently, the FA/MOF-5 composite was placed in a tube furnace and heated with the treatment process as follows: polymerized at 80°C for 24 h, then carbonized at 150°C for 6 h followed by 900°C for 6 h. The resultant nanoporous carbon was denoted as NPC.

$\text{Pt}_x\text{Cu}/\text{NPC}$ electrocatalysts were prepared via NaBH_4 reduction method. Chloroplatinic acid and copper sulfate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) were used as metal precursors with controlled molar ratios. The total metal loading of all the as-prepared electrocatalysts is 20 wt%. For example, the $\text{Pt}_x\text{Cu}/\text{NPC}$ electrocatalyst with a Pt/Cu molar ratios of 1/1, denoted as PtCu/NPC, was prepared as follows: 0.5 mL of 0.1 M $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution, 0.5 mL of 0.1 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 51.8 mg of NPC and 0.28 mL of polyvinyl pyrrolidone (PVP, 1.1 wt%, K15) were added to 100 mL deionized water successively and the mixture was subjected to magnetic stirring for 30 min. Subsequently, the pH of the system was adjusted to 10 by adding the solution of 3 M NaOH, then 1 mL of 1 M NaBH_4 solution was dropwise added under vigorous stirring. After additional stirring for 24 h, the mixture was filtered and washed copiously with deionized water, followed by heat treatment at 80°C under vacuum for 12 h to obtain PtCu/NPC electrocatalyst. By adjusting the amount of the metal precursors and NPC, the other $\text{Pt}_x\text{Cu}/\text{NPC}$ nanocomposites with different Pt/Cu molar ratios (1:0,

3:1 and 2:1) were prepared via the same method and denoted as Pt/NPC, $\text{Pt}_3\text{Cu}/\text{NPC}$ and $\text{Pt}_2\text{Cu}/\text{NPC}$, respectively.

2.2. Physical characterization

The surface chemical state and bonding of the as-prepared catalysts were analyzed by XPS (K-Alpha 1063, Thermo Fisher Scientific). Transmission electron microscope JEOL JEM-2100F with accelerating voltage of 200 kV was used in order to obtain TEM images. XRD patterns were recorded on a D/Max-3C diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). Elemental analysis of the as-prepared catalysts was carried out by energy dispersive spectra (EDS) system, which was attached to the JEOL JSM-6360 scanning electron microscopy.

2.3. Electrochemical measurements

Electrochemical measurements were conducted with a VersaSTAT3 electrochemical workstation (Princeton, America), and the RDE was controlled by Jiangmen ATA-1B motor. A conventional three-electrode system was used to perform the electrochemical tests. The glassy carbon (GC, 3 mm in diameter) electrode coated with electrocatalyst ink was used as working electrodes; Ag/AgCl, KCl_{sat} was used as reference electrode; Ni foam mesh ($3 \times 5 \text{ cm}^2$) was used as counter electrode for CV, ESA, CA test, and Pt wire was used as counter electrode for RDE test. The electrocatalyst ink was prepared by mixing 5 mg electrocatalyst powder, 350 μL distilled water with 125 μL Nafion (5 wt% from Aldrich) and subsequently sonicating the mixture into a homogeneous slurry. Finally, 5 μL of electrocatalyst ink was pipetted on the GC surface for CV, ESA, CA test, and 1 μL of that for RDE test.

2.4. Fuel cell test

The schematic of the DBHFC has been showed in our previous work [17]. In the cell test system, the $\text{Pt}_x\text{Cu}/\text{NPC}$ and commercial Au/XC-72 electrocatalysts were used as anode and cathode catalysts, respectively. An alkaline NaBH_4 solution (1 M NaBH_4 + 3 M NaOH) was applied as the anolyte and the corresponding catholyte was composed of 2 M H_2O_2 + 0.5 M H_2SO_4 . The separator employed in this study was pretreated Nafion 117 membrane. The cell performances were measured by a battery testing system (BTS-51800, Neware Technology Co. Ltd. China) at 25°C . The load was applied in steps of 5 mA within the range of 0–120 mA. Each

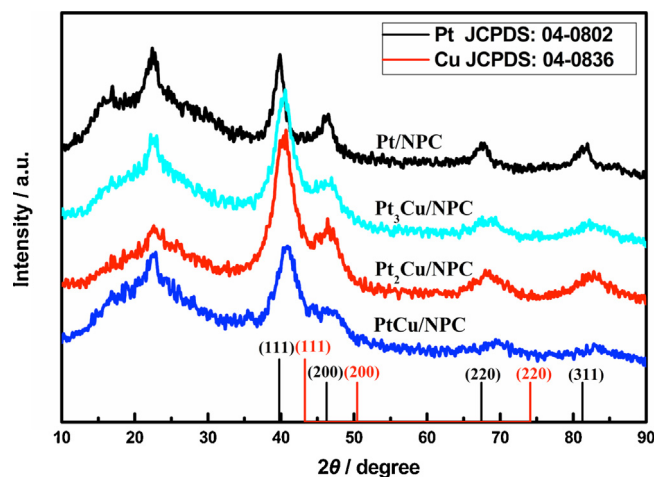


Fig. 1. XRD patterns of Pt/NPC and $\text{Pt}_x\text{Cu}/\text{NPC}$ catalysts.

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