Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–8

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Flower-like PdCu catalyst with high electrocatalytic properties for ethylene glycol oxidation

Zhulan Gu[a], Zhiping Xiong[a], Fangfang Ren[b,*], Shumin Li[a], Hui Xu[a], Bo Yan[a], Yukou Du[a,*]

[a] *College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China*
[b] *Analysis and Testing Center, Yancheng Teachers University, Yancheng 224051, PR China*

ARTICLE INFO

Article history:
Received 16 September 2017
Revised 19 October 2017
Accepted 8 December 2017
Available online xxx

Keywords:
Flower-like PdCu
Three-dimension structure
EG oxidation
Electrocatalyst
Fuel cells

ABSTRACT

A highly efficient PdCu alloy nanocatalyst has been designed and synthesized, which exhibited excellent selectivity and activity toward ethylene glycol (EG) oxidation reaction with a low loading of electrocatalyst. The results of characterization show that the atom ratio of 1:1 (Pd:Cu) as well as the addition of polyvinyl pyrrolidone (PVP) and potassium bromide (KBr) contributed to the unique morphology of the as-prepared PdCu catalyst. Owing to the flower-like nanostructure and the synergistic effect between Pd and Cu, PdCu electrocatalyst has distinct enhancement in electrocatalytic performance whose forward peak current density is almost 3.2 and 4.3 times higher than that of pure Pd and commercial Pd/C electrocatalysts. We put forward that the prepared PdCu catalyst may have promising and alternative applications in direct EG alkaline fuel cells.

1. Introduction

In recent decades, great efforts have been focused on fuel cells because of their advantages of high power efficiency, low environmental pollution, high specific energy, wide fuel range and so on [1–3]. In general, direct fuel cells can be divided into direct alkaline fuel cells and direct acidic fuel cells [4]. In Antolini's research, direct fuel cells which use methanol, ethanol, EG, and hydrazine are typical examples and it can be concluded that the kinetics for fuel oxidation in alkaline medium are much better than that in acidic medium [5]. To date, wide-spread attentions have been paid on direct methanol alkaline fuel cells and direct ethanol alkaline fuel cells, while the research system of electrocatalysts toward EG oxidation reaction has not been consummated completely. Direct ethylene glycol fuel cells (DEGFCs) in alkaline media can be a promising power source, which possess the merits of low toxicity, easy transportation and storage, high energy density and efficient energy conversion [6–10]. However, implementing the commercialization of DEGFCs may encounter lots of obstacles, like the relatively slow kinetics as compared with methanol and ethanol, inefficient oxidation of EG to CO_2 and the high cost of noble metal used in the preparation of catalysts [11–13]. Hence, it is significant to design and synthesize catalysts with superior electrocatalytic performance, such as Pd catalysts and Pt catalysts. Pd and Pt possess similar properties, due to the fact that they belong to the same group in the periodic table [14–16]. But Pd can take the place of Pt toward EG oxidation in an alkaline environment without worsening fuel cell performance which costs lower than Pt with 50 times more abundant than Pt on Earth [17].

At present, it is important to synthesize new catalysts with highly electrocatalytic activity but less usage of Pd. One typical strategy is to prepare highly active binary Pd-based electrocatalysts by adding a suitable metal like Au [18], Ru [19] or Ni [20]. For example, a series of Pd-based alloy electrocatalysts have been reported for improving their electrocatalytic activity considering the alloy effect. Xu et al. found that the as-prepared PdAu nanocatalyst presents the highest mass activity (11.85 A/mg), which is 7.5 times higher than commercial Pd/C (1.58 A/mg) [18]. Also, the verdict of Zhang et al.'s research is that the peak current density on the Pd_7/Ru_1 reaches the highest value (1150 mA/mg), which is about 3.0 times as large as that on commercial Pd/C (382.25 mA/mg) [19]. Among these catalysts, PdCu alloy catalysts may be a good research point toward EG oxidation in alkaline media. Additionally, to control the particle size and shape of Pd-based electrocatalysts is another common method [21–25], such as Pd–Pt core-shell nanoparticles with 80 nm Pd core and 15 nm Pt shell [26], Pd–Ag nanoparticles with the average particle size of 3.2 nm [27]. These catalysts with particular morphology and size all exhibited superior electrocatalytic performance. To this end, synthesizing PdCu alloy catalyst with special structure and particular size can provide abundant surface active sites in order to improve the electrocatalytic performance.

---

[*] Corresponding author.
E-mail addresses: fangfang7916@163.com (F. Ren), duyk@suda.edu.cn (Y. Du).

https://doi.org/10.1016/j.jtice.2017.12.010

Please cite this article as: Z. Gu et al., Flower-like PdCu catalyst with high electrocatalytic properties for ethylene glycol oxidation, Journal of the Taiwan Institute of Chemical Engineers (2017), https://doi.org/10.1016/j.jtice.2017.12.010

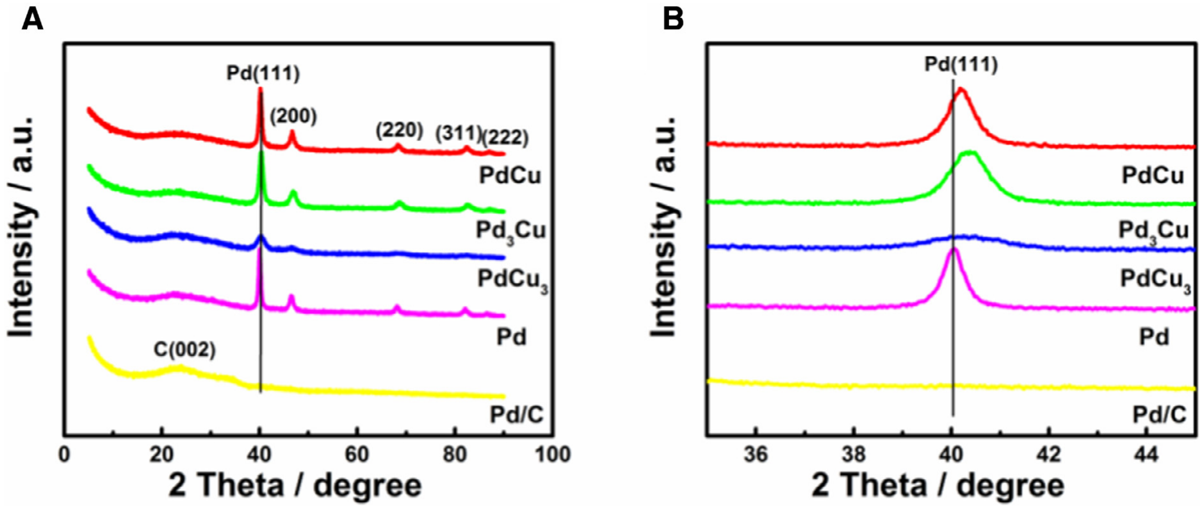

Fig. 1. (A) XRD patterns of PdCu, Pd_3Cu, $PdCu_3$, pure Pd and commercial Pd/C catalysts. (B) XRD patterns located from 35° to 45° of PdCu, Pd_3Cu, $PdCu_3$, pure Pd and commercial Pd/C catalysts.

Perfectly considering the above factors, we herein demonstrate a facile preparation of PdCu nanoflowers with the assistance of PVP (to prevent the agglomeration of nanoparticles), KBr (to direct the structure of nanoparticles) and AA (to be the reducing agent). Transmission electron microscopy (TEM), X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS) are employed to obtain the morphology and crystal structures of the as-prepared catalysts. Besides, the results of the electrochemical measurements showed the as-prepared PdCu (1:1) nanocatalysts exhibited the best electrocatalytic activity with the forward peak current densities of 7.15 A/mg and enhanced stability toward EG oxidation reaction in alkaline medium.

2. Experimental section

2.1. Chemicals

Palladium chloride ($PdCl_2$, 99%), copper nitrate trihydrate [$Cu(NO_3)_2{\cdot}3H_2O$], polyvinyl pyrrolidone (PVP), potassium bromide (KBr), ethylene glycol ($C_2H_8O_2$), ethanol (C_2H_5OH) and ascorbic acid (AA) were all of analytical grade and used without further purification, which were purchased from Sinopharm Chemicals Reagent Co., Ltd. Commercial Pd/C catalyst (JM 20% Pd) was obtained from Shanghai Hesen Electric Co., Ltd. Doubly distilled water was used throughout the work.

2.2. Apparatus

X-ray diffraction (XRD) patterns were performed with a PANalytical X'Pert PRO MRD X-ray diffractometer using CuKα as the radiation source ($\lambda = 1.54056$ Å) which operated at 40 kV and 30 mA, and the relative intensity was set in the scattering range (2θ) of 5–90°. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) was carried out using a TECNAI-G20 electron microscope and JEM-2100F high-resolution transmission electron microscope, respectively, both obtained with an accelerating voltage of 200 kV. X-ray photoelectron spectra (XPS) was performed on an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα X-ray radiation.

All electrochemical experiments were recorded with a CHI660 B electrochemical workstation (Shanghai Chenhua Instrument Plant, China) at ambient temperature. A glassy carbon electrode (GCE, 3 mm in diameter), a saturated calomel electrode (SCE) and a platinum wire were used as the working electrode; the reference electrode and the counter electrode, respectively. Before every measurement, the working electrode (GCE) was polished with alumina slurries on a polishing cloth and then was sonicated in distilled water for 30 s. After this, 10 µL of the composite catalyst solution was dropped on the surface of the GCE and then dried in an oven at 60 °C in order to test the electrocatalytic activity of all the catalysts. Furthermore, the Pd loading of our catalysts on the surface of electrodes is 1.6×10^{-6} mg.

2.3. Synthesis of PdCu catalyst

In the preparation process of PdCu nanoflowers, 0.44 mL H_2PdCl_4 (22.56 mM), 2.4 mg $Cu(NO_3)_2{\cdot}3H_2O$, 50 mg KBr, 20 mg PVP (a colloidal stabilizer) and 50 mg AA were dissolved in 10 mL EG and then placed in a flask. The mixture was stirred continuously for 6 h in an oil bath pan at 85 °C. The colloidal solution was centrifuged and washed repeatedly with ethanol and doubly distilled water to remove impurity and the obtained sample is denoted as PdCu (the atom ratio of 1:1). The Pd_3Cu, $PdCu_3$ and pure Pd catalysts were also prepared in the same procedure except that the adding mass of $Cu(NO_3)_2{\cdot}3H_2O$ (0.8 mg, 7.2 mg and 0 mg). Finally, the resulting sample sediment was dispersed in 10 mL distilled water and treated for 1 h in ultrasonic equipment.

3. Results and discussion

XRD patterns of as-prepared catalysts as well as Pd/C catalysts were used for analyzing their crystallization. As displayed in Fig. 1(A), the diffraction peaks of PdCu, Pd_3Cu, $PdCu_3$, pure Pd and Pd/C catalysts located at about 40.2°, 46.4°, 68.3°, 82.8° and 87.1° are indexed as the (111), (200), (220), (311) and (222) reflection facets of Pd face-centered cubic (*fcc*) lattice [JCPDS no. 46-1043] [28], respectively, while the first diffraction peak of commercial Pd/C catalyst at 23.8° correspond to the (002) plane of carbon support [29]. Furthermore, the Pd (111) peak position of PdCu, Pd_3Cu and $PdCu_3$ catalysts has a slightly shift compared to the same peak of pure Pd and Pd/C catalysts, as shown in Fig. 1(B), indicating the alloying of Pd atoms and Cu atoms because of the increased lattice constant [30]. Also, as shown Table S1, the lattice parameters of the PdCu, $PdCu_3$, Pd_3Cu and pure Pd were calculated using the Bragg equation and were found to be 3.887 Å, 3.882 Å, 3.871 Å and 3.901 Å. The reported lattice parameter of Cu is 3.61491 Å [31,32]. It is clear to see that the lattice constants of as-prepared PdCu electrocatalysts lie somewhere in between, whose behaviors could be

Please cite this article as: Z. Gu et al., Flower-like PdCu catalyst with high electrocatalytic properties for ethylene glycol oxidation, Journal of the Taiwan Institute of Chemical Engineers (2017), https://doi.org/10.1016/j.jtice.2017.12.010