



Ceria promoted Pd/C catalysts for glucose electrooxidation in alkaline media



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ABSTRACT

Carbon support materials are modified by CeO₂ through a microwave decomposition method, and then CeO₂-C supported Pd catalysts are synthesized by a pulse microwave assisted polyol method. The content of CeO₂ is appropriately adjusted and Pd/CeO₂-C catalysts with different Pd:CeO₂ molar ratios are obtained and investigated for the reaction of glucose electrooxidation in alkaline media.

It is found that the introduction of CeO₂ onto the surface of the carbon support can significantly decrease the particle size of Pd with respect to the Pd/C case, generating sufficient OH_{ads} at lower potentials. Accordingly, the catalytic activity of Pd for glucose electrooxidation can be improved as a result of its high dispersion and the synergistic effect. It is also found that, among the Pd/CeO₂-C catalysts, the one with Pd:CeO₂ molar ratio of 3:1 exhibits the best performance for glucose electrooxidation, ~30% higher than that of Pd/C. Moreover, the optimized catalyst presents the advantages of rapid response, high sensitivity and good tolerance to the interfering agents co-existing in the human blood with glucose.

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1. Introduction

Ceria (CeO₂), possessing unique properties of oxygen storage property, surface basicity, electrochemical redox reaction between Ce⁴⁺ and Ce³⁺ in cerium oxide lattice, and the ability as an oxygen buffer [1,2], has been adopted as the promoter for Pt or Pd toward alcohol electrooxidation [3–7]. The enhanced electrode performance (reaction activity and poison resistance) for alcohols electrooxidation was attributed to the synergistic effect of CeO₂ by supplying sufficient OH_{ads} at lower potentials, which is necessary to eliminate the poisoning species adsorbed on Pt or Pd active sites [4,5]. Moreover, the promoting effect of CeO₂ can also be due to its oxygen storage capacity at low temperature, higher reducibility

in the presence of Pt, high dispersion of Pt on CeO₂ and prevention of agglomeration of Pt metal particles [8]. Moreover, CeO₂ can increase the dispersion of the active metal on the support surface [9], and in this way increase the metal utilization coefficient and its specific activity.

Glucose electrooxidation reaction (GOR) has recently received a great attention mainly due to its potential applications in both control and treatment of diabetes through an electrochemical glucose sensor, and the implantable direct glucose fuel cells for artificial hearts and heart pacer [10–13]. Among the different tentative candidates as the electrocatalysts for glucose electrooxidation, Pd based catalysts exhibited high activity, desirable stability, and high selectivity [14–19]. On the other hand, the poison problem still exists with Pd alone as the catalyst. Furthermore, the supported Pd catalysts, not like Pt, have a poor dispersion, with much bigger particle size than that of Pt with the similar catalyst preparation process [19,20]. Ammonia adjustment for Pd preparation through glycol reduction method can decrease the Pd particle size a little [17,21], but its dispersion needs further improvement for exploring

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its capability for glucose electrooxidation. In order to take advantage of both the electrocatalytic property of Pd toward glucose electrooxidation and the synergistic function of CeO₂ and its possible role in catalyst preparation for decreasing metal particle size, before Pd deposition, CeO₂ is designed to be firstly decorate the carbon supporting materials.

In the present investigation, the promoting effect of CeO₂ on Pd catalyst toward glucose electrooxidation in alkaline media and the optimization of CeO₂ content in the catalyst were investigated. The composite catalysts were prepared by firstly depositing CeO₂ onto Vulcan XC-72R carbon black by a microwave deposition process and then depositing Pd through a pulse microwave assisted polyol method. Glucose electrooxidation on the as-prepared Pd/CeO₂-C series catalyst was evaluated by cyclic voltammetry and chronoamperometry in alkaline media.

2. Experimental

2.1. Materials

Glucose (Guangzhou Chemical Reagent Corp., AR), NH₃·H₂O (Guangzhou Chemical Reagent Corp., 25 wt%), Ce(NO₃)₃·6H₂O, carbon black (Vulcan XC-72R, Cabot Corp.), PdCl₂ (Guiyanboye Corp., AR), ethylene glycol (Shanghai Lingfeng Corp., AR), Nafion solution (DuPont Company, 5 wt%) were used without further purification. All the other used chemicals were of analytical reagent grade. Deionized water with specific resistance more than 18.0 MΩ cm⁻¹ was obtained by a water purification system.

2.2. Preparation of Pd/CeO₂-C catalysts

Vulcan XC-72 R carbon black was modified by CeO₂ via the precipitation method. For a typical preparation process, according to the pre-calculated feeding weight ratio, Ce(NO₃)₃·6H₂O was dissolved in the mixed solution containing 15.0 mL distilled water and 15.0 mL isopropanol. After carbon black was well dispersed into the above solution, NH₃·H₂O was added drop by drop until the pH value was more than 9.0. The precipitation was aged in the mother solution for 3 h, followed by filtering, washing, and then drying at 80 °C in a vacuum oven for 12 h. The obtained powder was microwave-heated (Nanjinghuiyan Corp., MZG800S) for 3 min continuously to obtain CeO₂-C with different CeO₂ content.

The Pd/CeO₂-C catalysts with different Pd/CeO₂ molar ratios were prepared by a pulse microwave assisted polyol method [19]. The as-prepared CeO₂-C as the supporting materials (120.0 mg) was well mixed with ethylene glycol (EG) in an ultrasonic bath and then 2.50 mL of 12.0 mg mL⁻¹ Pd²⁺/EG solution was added into the mixture. After the pH value of the above mixture was adjusted to more than 10 by introducing 1.0 mol L⁻¹ NaOH/EG solution drop by drop, a well-dispersed slurry was obtained with magnetic stirring for another 1 h. Then, the slurry was heated in a microwave oven (Nanjinghuiyan Corp., MZG800S) in the pulse form of 10 s-ON/10 s-OFF for several times. After reaction, 1.0 mol L⁻¹ HCl solution was added to accelerate the deposition process. Finally, the resulting sample was filtered, washed with copious hot water (≥80 °C) until no chloride anion was detected in the filtrate by 1.0 mol L⁻¹ AgNO₃ solution and then dried at 90 °C overnight in a vacuum oven. In all the catalysts, the theoretical Pd loading was 20 wt%. The molar ratios of Pd to CeO₂ in the Pd/CeO₂-C-x samples were controlled to be 1–5, and the corresponding samples were denoted as Pd/CeO₂-C-1, Pd/CeO₂-C-2, Pd/CeO₂-C-3, Pd/CeO₂-C-4, and Pd/CeO₂-C-5, respectively. For the sake of one-to-one correspondence to the support materials, the corresponding used CeO₂-C samples were denoted as CeO₂-C-1, CeO₂-C-2, CeO₂-C-3, CeO₂-C-4 and CeO₂-C-5, respectively. In CeO₂-C-x samples, their

respective CeO₂ weight percentage were 35.86 wt% for CeO₂-C-1, 17.93 wt% for CeO₂-C-2, 11.95 wt% for CeO₂-C-3, 8.96 wt% for CeO₂-C-4 and 7.17 wt% for CeO₂-C-5.

2.3. Physico-chemical and electrochemical characterization

The samples were characterized by X-ray powder diffraction (XRD) (Rigaku Co., Japan) with Cu Kα radiation (40 kV, 40 mA). The chemical composition of the obtained products was determined by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) (JEOL JSM-6330F). For the determination of metal content in the catalysts, thermogravimetric (TG) experiments were carried out by the aid of a Netzsch TG-209 analyzer in air with a flow rate of 50 mL min⁻¹ and a temperature ramp of 10 °C min⁻¹.

Electrochemical measurements were carried out using an AUT84480 instrument in a three-electrode electrochemical cell at 36.5 °C. Hg/HgO electrode (0.1 mol L⁻¹ KOH) and platinum foil (1.0 cm × 1.0 cm) were adopted as the reference and the counter electrodes, respectively. The working electrode was prepared by dispersing 5.0 mg of the as-prepared catalyst powder in 1.80 mL ethanol and 0.20 mL Nafion solution. The suspension was sonicated and stirred for ca. 30 min. Then, 10 μL of this ink was transferred onto the surface of the glassy carbon electrode with a diameter of 0.5 cm, and then the electrode was dried by an infrared lamp. The electrochemical tests of cyclic voltammetry (CV) and chronoamperometry (CA) were performed in an aqueous solution containing 0.1 mol L⁻¹ NaOH and 20.0 mmol L⁻¹ glucose. Before measurements, the electrolyte solution was saturated with high-purity N₂ gas to remove the dissolved oxygen and provide an inert atmosphere. It should be noted that without specification, all the potentials are referred to Hg/HgO (0.1 mol L⁻¹ KOH) reference electrode.

3. Results and discussion

The XRD patterns of CeO₂-C samples with different CeO₂ content are schematically shown in Fig. 1. Five diffraction peaks (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (3 3 1) are observed, corresponding to about 28°, 33°, 47°, 56° and 79°, respectively. This result indicates that CeO₂ exists in the form of cubic fluorite structure, which is in good agreement with the reported values [22,23]. Moreover, with the content of CeO₂ increasing in the composite samples, the inten-

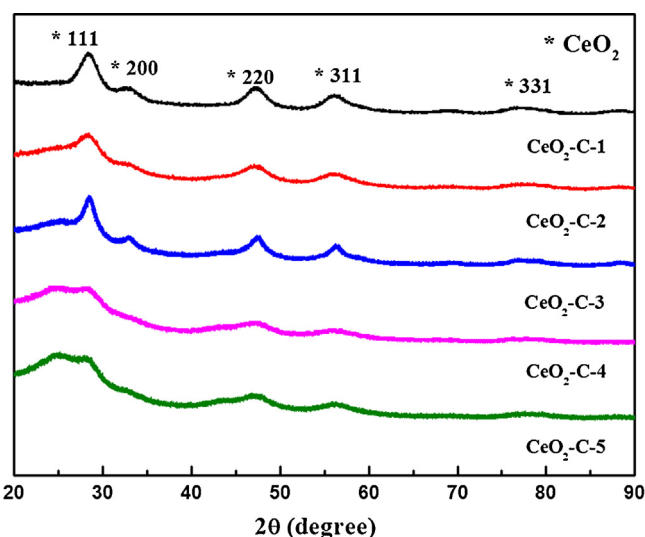


Fig. 1. XRD patterns for CeO₂-C samples. 2θ scanning range: 20–90° at a scan rate of 10° min⁻¹.

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