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# Synthesis and performance of a novel PdCuPb/C nanocatalyst for ethanol electrooxidation in alkaline medium

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## ABSTRACT

This work presents fabrication of a novel ternary PdCuPb/C nanocatalyst via reducing  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions on carbon surface followed by  $\text{Pd}^{2+}$  ion substitution. X-ray power diffraction, transmission electron microscope, X-ray photoelectron spectroscopy, cyclic voltammogram, constant potential and linear current sweep tests were used to characterize the catalyst. More Cu relative to Pb was substituted by  $\text{Pd}^{2+}$  ions to form the PdCuPb/C catalyst. The three metals were uniformly dispersed on carbon surface. The PdCuPb/C catalyst can produce abundant oxygenated species on its surface for oxidative removal of poisonous intermediates at a low potential. Owing to the promoting effects of the factors above, the PdCuPb/C nanocatalyst exhibited excellent activity for ethanol electrooxidation in alkaline medium. The catalytic stability and anti-poisoning ability were also greatly improved.

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## 1. Introduction

As a kind of promising energy conversion device for portable electronics, direct alcohol fuel cells (DAFCs) have attracted much attention owing to their high efficiency and low or zero emission [1–3]. So far, methanol is the most widely used organic matter in direct fuel cells (DFCs). However, methanol

is a toxic chemical and has the issue of cross-over through proton exchange membranes (PEMs) as used in DFCs [4]. Compared with methanol, ethanol is considered as a better fuel because it is less toxic and has a higher energy density (8 vs. 6 kWh kg<sup>-1</sup>). Besides, ethanol can be easily produced in large quantities by the fermentation of biomass from agriculture and the organic fraction of municipal solid wastes, without breaking the natural balance of carbon dioxide in the

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atmosphere [5,6]. The big challenge in development of direct ethanol fuel cells (DEFCs) is preparing highly active catalysts which can completely oxidize ethanol to carbon dioxide. This oxidation process involves cleavage of the C–C bond and release of twelve electrons. However, the C–C bond cleavage is difficult to be implemented at low temperature [7,8]. To address this issue, lots of research was devoted to electrochemical oxidation of alcohol in alkaline medium because of the faster oxidation kinetics in alkaline medium relative to in acid medium [9,10]. Recently, some new alkaline anion-exchange membranes (AEMs) were developed, making DAFCs operated in alkaline medium more attractive and realistic [11–14].

Pd catalyst is considered as an excellent alternative for the application of alkaline ethanol fuel cells on the basis of the following two reasons: one is that Pd is at least fifty times more abundant than Pt on the earth [15], which makes Pd less expensive compared to Pt; the other is that Pd gives the higher electro-catalytic activity and the less poisoning effect compared to Pt for ethanol oxidation in alkaline medium [15–18]. To fulfill the commercial application of Pd catalyst in AFCs, however, its performance needs to be further improved. Lots of research was devoted to the performance improvement of Pd catalyst via introducing other one or more elements. For example, a series of Pd catalysts promoted by metal oxides ( $\text{Co}_3\text{O}_4$ ,  $\text{CeO}_2$ ,  $\text{Mn}_3\text{O}_4$  and  $\text{NiO}$ ) were prepared via an intermittent microwave heating (IMH) approach [18]. Compared with Pt, these catalysts exhibited higher activity and stability for ethanol electrooxidation in alkaline media [18]. Other efforts to enhance the activity of Pd catalyst by combining Pd with other metals or metal carbides were also reported [19–21].

More than forty possible derivatives including  $\text{CH}_3\text{CO}$ ,  $\text{CH}_x$ ,  $\text{CH}_3\text{COH}$  and  $\text{CO}$  can be produced during ethanol electrooxidation [22]. The strongly adsorbed intermediates such as  $\text{CO}$  and  $\text{CHCO}$  on catalyst surface prevent further adsorption and electrooxidation of ethanol molecules in solution, leading to a decrease in the catalyst efficiency. It was reported that Pb in Pt-based catalysts can promote their tolerance towards  $\text{CO}$ -like specie poisoning by weakening the bond energy of Pt– $\text{CO}$  or enhancing electrooxidation of  $\text{CO}$ -like species [23]. These promoting effects are defined as the electronic effect, the geometric effect and the bifunctional mechanism [23,24], which may also occur on Pd-based catalysts. Wang et al. reported that Pb had a promoting effect in ethanol electrooxidation on Pd catalyst in a potassium hydroxide solution [25]. In their work, the ethanol oxidation peak current of PdPb/C increased by ca. 25% compared to that of Pd/C [25]. Since Pb is more active than Pd, we may obtain a PdPb catalyst via a substitution synthesis between  $\text{Pd}^{2+}$  ions and Pb particles. However, Pd is hard to directly deposit on Pb particle surfaces via a simple substitution reaction in ambient air due to very easy oxidation of Pb. Introducing another sacrificial element which has better stability than Pb in air and can be substituted by  $\text{Pd}^{2+}$  ions, is an effective approach to address this issue. Cu can be readily substituted by  $\text{Pt}^{4+}$  ions [26]; Cu was found to have a promoting effect in ethanol electrooxidation [27–29] recently. In this work CuPb nanoparticles were first prepared by  $\text{NaBH}_4$  reduction. The subsequent substitution reaction between CuPb nanoparticles and  $\text{Pd}^{2+}$

ions was used to prepare a high performance PdCuPb/C catalyst. Ethanol oxidation reaction (EOR) in alkaline medium and various physical tests were used to characterize this catalyst. The origin of high performance of the catalyst was analyzed.

## 2. Experimental

### 2.1. Synthesis of catalysts

Active carbon from Vulcan XC-72R was first pretreated with 6 M  $\text{HNO}_3$  at 120 °C for 2 h. The PdCuPb/C catalyst was synthesized as follows: 160 mg of pretreated Vulcan XC-72R carbon, 100.5 mg of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 139.1 mg of  $\text{Pb}(\text{NO}_3)_2$  were mixed with 50 ml of double-distilled water in a flask under ultrasonic stirring. Then, 50 mg of  $\text{NaBH}_4$  was dissolved in 50 ml of water and this solution was added dropwise into the suspension above to reduce  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions. This redox reaction was conducted for 1 h. Then the suspension was filtered, washed with double-distilled water and dried in a vacuum oven overnight to obtain the CuPb/C composite. 147.8 mg of CuPb/C was dispersed in a mixture of 30 ml of ethylene glycol (EG) and 30 ml of water under ultrasonic stirring for 30 min. 3.96 ml of 37.8 mM  $\text{H}_2\text{PdCl}_4$  aqueous solution was added very slowly into the suspension under vigorous stirring. Afterwards the stirring was kept for another 1 h to ensure the substitution reaction proceeded completely. The resultant suspension was filtered, washed and dried overnight to obtain the PdCuPb/C catalyst. The Pd/C catalyst was prepared by the direct reduction of  $\text{NaBH}_4$  for comparison.

### 2.2. Physical and electrochemical characterization

The Pd loadings and atomic ratios in the samples were determined using an Ultima2 inductively coupled plasma OES spectrometer (ICP-OES, Jobin Yvon). Before the tests, carbon in the samples was removed at 700 °C; then the residue was dissolved in a mixed solution containing 5 ml HF, 4 ml  $\text{HNO}_3$  and a few drops of  $\text{HClO}_4$ . This process was repeated twice after acid evaporation. Finally, the residue was dissolved in chloroazotic acid and the mixture was heated until dryness.

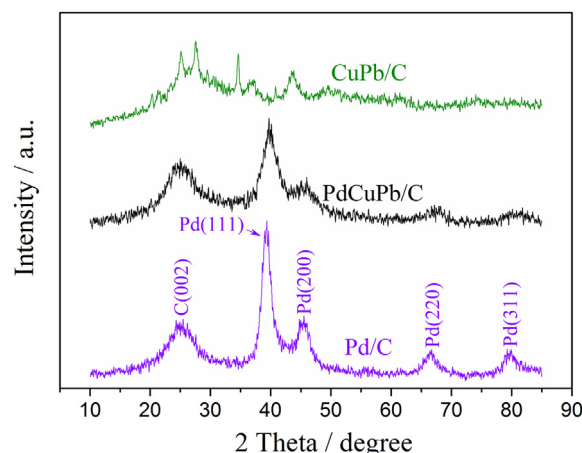


Fig. 1 – XRD patterns of CuPb/C, PdCuPb/C and Pd/C.

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