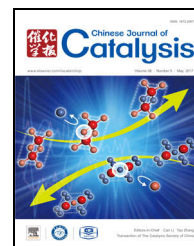


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Article

Enhancement of the formic acid electrooxidation activity of palladium using graphene/carbon black binary carbon supports



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ABSTRACT

Combinations of graphene (Gr) and carbon black (C) were employed as binary carbon supports to fabricate Pd-based electrocatalysts via one-pot co-reduction with Pd²⁺. The electrocatalytic performance of the resulting Pd/Gr-C catalysts during the electrooxidation of formic acid was assessed. A Pd/Gr_{0.3}C_{0.7} (Gr oxide:C = 3:7, based on the precursor mass ratio) electrocatalyst exhibited better catalytic performance than both Pd/C and Pd/Gr catalysts. The current density generated by the Pd/Gr_{0.3}C_{0.7} catalyst was as high as 102.14 mA mg_{Pd}⁻¹, a value that is approximately 3 times that obtained from the Pd/C (34.40 mA mg_{Pd}⁻¹) and 2.6 times that of the Pd/Gr material (38.50 mA mg_{Pd}⁻¹). The anodic peak potential of the Pd/Gr_{0.3}C_{0.7} was 120 mV more negative than that of the Pd/C and 70 mV more negative than that of the Pd/Gr. Scanning electron microscopy images indicated that the spherical C particles accumulated on the wrinkled graphene surfaces to form C cluster/Gr hybrids having three-dimensional nanostructures. X-ray photoelectron spectroscopy data confirmed the interaction between the Pd metal and the binary Gr-C support. The Pd/Gr_{0.3}C_{0.7} also exhibited high stability, and so is a promising candidate for the fabrication of anodes for direct formic acid fuel cells. This work demonstrates a simple and cost-effective method for improving the performance of Pd-based electrocatalysts, which should have potential industrial applications.

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1. Introduction

The electrooxidation of formic acid has been studied for more than half a century [1]. In recent years, direct formic acid fuel cells (DFAFCs) have been the subject of considerable research interest as clean power sources. Pd is currently considered a state-of-the-art electrocatalyst for DFAFCs [2] because it exhibits higher catalytic activity and lower CO poisoning than Pt during the anode oxidation of formic acid [3,4]. A drawback of Pd as an electrocatalyst for formic acid oxidation (FAO) is its instability [5]. In addition, the activity of Pd catalyst must be

improved. Various approaches to increasing the catalytic activity/stability of Pd-based electrocatalysts and reducing the required quantity of this metal have been examined, and are summarized in our previous report [6], which cites more than 90 literature publications. These methods include the use of bimetallic and trimetallic Pd-based catalysts [7,8] and nano-sized catalysts, such as the recently reported nano-complex structures [9]. Another effective means of enhancing the catalytic performance of electrocatalysts is the selection of appropriate support materials [10].

The materials used as supports for electrocatalysts include,

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but are not limited to, carbon-based materials [11–18], transition metal oxides [19–24], conducting polymers [25,26], carbon nitride [27], tungsten carbide [28,29] and silicon [30]. Carbon materials are being continuously developed, including carbon black (C) [11], carbon nanotubes [12], carbon nanofibers [13], mesoporous carbon [14], graphene (Gr) [15], diamond film [16], C₆₀ [17] and carbon aerogel [18]. Among these carbon supports, C is the most widely used [31,32] because of its high surface area, good electrical conductivity, stability and low cost. Investigations into improving the performance of Pd/C catalyst have primarily focused on tailoring the metal particles, such as by changing the alloy composition or nanostructure. We have reported carbon-supported binary Pd-Cr alloy [33] and ternary Pd-Cu-Fe composites, fabricated by the partial galvanic sacrifice of an alloy template [6], as electrocatalysts for FAO. Past studies have demonstrated that some Pd-based binary alloy or ternary metal composites exhibit better catalytic performance than unitary Pd catalysts. This raises the question: can the use of binary or ternary carbon supports obtained by combining different carbon materials improve the electrocatalytic performance relative to that obtained from a unitary carbon support?

Yang et al. [34] have reported that Pd nanoparticles supported on Gr nanosheets-multiwalled carbon nanotubes (Pd/GNS-CNTs) hybrid supports exhibit high electrocatalytic performance during FAO. We therefore anticipated that C could have advantages when combined with Gr to form a binary support, because spherical C particles are readily situated on two-dimensional planar graphene surfaces to form three-dimensional (3D) nanostructures. In contrast, one-dimensional carbon nanotubes tend to lie flat on the Gr plane. In addition, the cost of C is less than that of either carbon nanotubes or Gr, which is beneficial with regard to potential industrial applications. Thus, the concept of Pd catalysts loaded on binary carbon supports comprised of Gr and C (Pd/Gr-C) attracted our attention.

In the present study, C and Gr were used to fabricate binary carbon supports for Pd. Following the emergence of Gr as an ideal catalyst support material in 2009, it has become one of the most widely researched subjects in the field of fuel cells [35]. Many methods have been established for Gr synthesis, such as mechanical exfoliation [36], epitaxial growth [37], chemical vapor deposition (CVD) [38], reduction of Gr oxide (GO) [39], unzipping of carbon nanotubes [40] and intercalation [41]. However, most of these methods involve high costs and low yields. The reduction of GO is regarded as an effective means of producing Gr with high yields [42], and so we fabricated Pd/Gr-C electrocatalysts in this work via the one-pot reduction of a mixture of Pd, C and GO. Among the materials tested, the Pd/Gr_{0.3}C_{0.7} catalyst was found to exhibit the highest catalytic activity and stability during FAO. Compared with Pd/C, the anodic peak potential during FAO of the Pd/Gr_{0.3}C_{0.7} was shifted by 120 mV, while the current density of this new catalyst (102.14 mA mg_{Pd}⁻¹) was about three times that of the Pd/C (34.40 mA mg_{Pd}⁻¹). These results indicate superior electrocatalytic activity throughout the FAO reaction.

To the best of our knowledge, this paper represents the first

report of the application of binary Gr/C supports to the anode oxidation of formic acid. Huang and co-workers [43] demonstrated that C mixed with Pt loaded on reduced GO (Pt/rGO) greatly improved the electrocatalytic activity and stability during the oxygen reduction reaction. However, Pt is only supported on the rGO planes in this material, while there is no Pt on the C. The C is inserted between the rGO layers. In contrast, in the case of our Pd/Gr-C catalysts, Pd nanoparticles are loaded not only on the Gr but also on the C clusters, resulting in a 3D distribution. This more extensive 3D distribution of Pd nanoparticles allows the reactant molecules to more easily reach the active sites on the noble metal surfaces, thus improving the catalytic performance. Moreover, this study confirmed the presence of interactions between the Pd metal and the binary Gr-C support. This work therefore represents a simple and cost-effective approach to improving the performance of Pd-based electrocatalysts intended for industrial applications.

2. Experimental

2.1. Materials

Palladium (II) chloride (PdCl₂, Pd ≥ 59.0%) was purchased from the Sinopharm Chemical Reagent Co., Ltd., while Vulcan carbon powder (XC-72R) was obtained from the Cabot Corp. Graphite flakes (natural, -325 mesh, 99.8%) were purchased from Alfa Aesar (Tianjin, China) and Nafion (5 wt%) was purchased from the America Dupont Co. All other chemicals were analytical grade and were used as-received without further purification. Triple-distilled water was used throughout.

2.2. Synthesis of the Pd/Gr-C and Pd/C catalysts

The Pd/Gr-C catalysts were prepared by a one-pot NaBH₄ method. GO was synthesized from the graphite flakes according to an improved version of Hummers' method [44]. Following this, the required amount of Vulcan carbon black was added to a constantly stirred GO solution to obtain the desired mass ratio. Subsequently, the required amount of a PdCl₂ solution was added to the suspension. The Pd metal loading on the GO/C combination was 20 wt%. The pH of the suspension was adjusted to 10 by the dropwise addition of 1 mol L⁻¹ NaOH. After adding 10 mL of a NaBH₄ solution (5 wt%) to the suspension, the resulting reaction mixture was stirred for 6 h and then allowed to stand for 1 h. Following these procedures, the resulting Pd/Gr-C slurry was filtered, thoroughly washed with triple-distilled water, and finally dried in a vacuum oven at 50 °C for 10 h. It should be noted that Pd/Gr_{0.1}C_{0.9}, Pd/Gr_{0.3}C_{0.7}, Pd/Gr_{0.5}C_{0.5} and Pd/Gr_{0.7}C_{0.3} catalysts were obtained by using GO:C mass ratios of 1:9, 3:7, 5:5 and 7:3, respectively. These values were not necessarily the final mass ratios of the rGO and C since the accurate separation of Gr and C in the final Pd/Gr-C catalysts was difficult. For comparison purposes, Pd/Gr and Pd/C catalysts were prepared using the same reduction procedure.

2.3. Preparation of the working electrode

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