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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 Pd^{2+} . 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], C_{60} [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

A glassy carbon (GC) electrode (3 mm in diameter) was polished with 0.05 μm alumina (Al_2O_3) to a mirror finish and washed with triple-distilled water prior to each experiment. Subsequently, 6 mg portion of the catalyst was added to a mixture of 0.3 mL deionized water and 0.3 mL ethanol and the mixture was ultrasonically agitated for 30 min to obtain an ink. Following this, 20 μL (4 $\mu\text{L} \times 5$ aliquots) of this mixture was dropped by micropipette onto the surface of the GC electrode. The deposited ink was allowed to dry in air and was then covered with 4 μL of a Nafion solution (5 wt%) and again dried at room temperature. The as-prepared catalyst-modified GC electrode was employed as the working electrode in our experiments.

2.4. Physical characterization

X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance instrument (Bruker, Germany) with $\text{Cu } K\alpha$ radiation at $\lambda = 0.15406$ nm. Scanning electron microscopy (SEM) images were obtained with a Hitachi SU-70 microscope. The morphology of each product was assessed by transmission electron microscopy (TEM, JEOL JEM-1011) at an acceleration voltage of 200 kV. High-resolution transmission electron microscopy (HR-TEM) was carried out with a JEOL JEM 2100. Raman spectra were recorded on a JY HR800 multi-channel confocal microspectrometer (HORIBA Jobin Yvon, Paris, France) with 514 nm laser excitation. X-ray photoelectron spectroscopy (XPS) was performed with a Kratos XSAM-800 spectrometer with $\text{Mg } K\alpha$ radiation. Catalyst compositions were determined via inductively coupled plasma-atom emission spectrometry (ICP-AES, iCAP7000 series).

2.5. Electrochemical measurements

The electrochemical measurements were performed with a CHI832B electrochemical workstation (CH Instruments, Austin, Texas) and a conventional three-electrode cell at room temperature. The three-electrode cell consisted of a carbon-rod serving as the counter electrode, a $\text{Hg}/\text{Hg}_2\text{SO}_4$ (saturated K_2SO_4) electrode serving as the reference electrode and a GC electrode (3 mm in diameter) coated with the catalyst, serving as the working electrode. All the potentials in this paper are reported with respect to a reversible hydrogen electrode (RHE). Cyclic voltammetry curves were acquired in 0.5 mol L^{-1} H_2SO_4 at a scan rate of 10 mV s^{-1} . Linear sweep voltammetry (LSV) plots and chronoamperometry data were obtained in a solution of 0.5 mol L^{-1} HCOOH in 0.5 mol L^{-1} H_2SO_4 at a scan rate of 10 mV s^{-1} . All electrolyte solutions were deaerated with bubbling N_2 for more than 20 min just prior to use and maintained under a N_2 atmosphere throughout the entire experimental procedure.

3. Results and discussion

3.1. Characterization of Pd/Gr-C and Pd/C catalysts

The actual Pd concentrations in the various samples were

evaluated by ICP-AES analysis, and the Pd/C, Pd/Gr, 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 found to have metal loadings of 20.22, 20.35, 20.12, 20.12, 20.10, and 20.06 wt%, respectively. The Pd loading of each catalyst was therefore approximately 20%. The crystal structure of each sample was determined by XRD, and Fig. 1 presents their XRD patterns. The peaks at approximately 25° are assigned to the C(002) plane [45]. The four peaks at $2\theta = 40^\circ$, 46° , 68° and 82° are characteristic of a face-centered-cubic (fcc) structure, corresponding to the (111), (200), (220) and (311) crystalline planes of Pd [46], respectively. Compared with the Pd/C pattern, the characteristic Pd(220) peaks in the Pd/Gr-C and Pd/Gr patterns are shifted to higher 2θ values, indicating decreased lattice constants and shrinkage of the Pd lattices [47]. Nearly all XRD peaks generated by the Pd/Gr-C can be attributed to Pd/Gr. An examination of XRD data in various publications [34,48–51] demonstrated that almost all the XRD peaks of catalysts supported on hybrids made of graphene and other materials (such as Pd/GNS-CNTs [34], Pd/NS-G [48] and Pd/rGO-MWCNTs [49]) matched those generated by our Pd/Gr catalyst. However, it is difficult to explain this phenomenon. The Gr is known to undergo significant metal-support interactions [52], thus we speculate that it has a greater effect on the Pd lattice constant than the C in the Gr-C hybrids. The XPS data also confirmed interactions between the Pd and the binary Gr-C support, as discussed further on. The lattice constant (a) of the Pd nanoparticles was calculated from the diffraction peak position (θ_{max}) using the Eq. (1) [42]:

$$a = \frac{\sqrt{2}\lambda}{\sin \theta_{\text{max}}} \quad (1)$$

The Pd(220) peak was chosen for the calculation of lattice constants because it appears at approximately 68° and thus is far from the background signal of the C support in the XRD patterns [53]. The Pd lattice constants were found to be approximately 0.391 nm for the Pd/Gr-C and Pd/Gr catalysts and 0.398 nm for the Pd/C. Huang et al. [53] have demonstrated that the lattice constants of Pd nanoparticles have an obvious effect on the catalytic performance during FAO. The crystallite sizes of the Pd nanoparticles in the direction perpendicular to the lattice planes were also calculated from the Pd(220) dif-

Fig. 1. XRD patterns of Pd/C (1), Pd/Gr (2), Pd/Gr_{0.1}C_{0.9} (3), Pd/Gr_{0.3}C_{0.7} (4), Pd/Gr_{0.5}C_{0.5} (5), and Pd/Gr_{0.7}C_{0.3} (6) catalysts.

fraction peaks using Scherrer's equation [54], and were determined to be 5.5, 4.6, 3.8, 4.1, 4.3 and 4.1 nm for the Pd/C, Pd/Gr, 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, respectively.

From the SEM image of the Pd/Gr_{0.3}C_{0.7} catalyst in Fig. 2, it is evident that the spherical C particles accumulated on the wrinkled surface of the Gr to form a C cluster/Gr hybrid with a 3D structure. It has been reported that reduced Gr sheets tend to form irreversible agglomerates through van der Waals interactions and can even restack to form graphite [34,55]. As can be seen, the C clusters effectively hinder the restacking of the Gr layers, thus retaining the outstanding single-layer electric properties of the material. The C clusters also prevent the wrinkled/curved surfaces of neighboring Gr sheets from forming enclosed spaces, which facilitates the movement of reactant/product molecules. The lateral resolution of SEM is typically on the order of 3 nm, and so it is difficult to observe Pd nanoparticles directly in the SEM image, although these nanoparticles can readily be identified with TEM (Fig. 3).

Fig. 3 presents TEM images and particle size distribution histograms for the Pd/C, Pd/Gr and Pd/Gr_{0.3}C_{0.7} catalysts. Fig. 3(d) provides the standard deviation (SD) error bars associated with the histograms that indicate the mean particle size deviations. The Pd/Gr_{0.3}C_{0.7} catalyst was selected for these analyses because it exhibited the best performance during FAO, as discussed further on. As shown in Fig. 3(C), the dispersion of the Pd nanoparticles on the surface of the Gr_{0.3}C_{0.7} binary support was slightly more uniform than that on the Pd/C and Pd/Gr catalysts. The average diameters of the particles in the Pd/C, Pd/Gr and Pd/Gr_{0.3}C_{0.7} catalysts as determined from the TEM images were 5.6, 4.7, and 4.0 nm, respectively, and these values are consistent with the XRD results. Furthermore, the HR-TEM image of the Pd/Gr_{0.3}C_{0.7} catalyst in Fig. 3(D) shows well-resolved lattice fringes with spacing of 0.222, 0.138 and 0.188 nm, which correspond to the (111), (220) and (200) planes of Pd crystals [56], respectively.

Fig. 4 shows the Raman spectra of the Pd/Gr and Pd/Gr_{0.3}C_{0.7} specimens. The two prominent peaks seen in these spectra, D (1330 cm⁻¹) and G (1590 cm⁻¹), are normally attributed to the presence of defects or edge areas and in-plane sp² hybridized carbon atoms [57], respectively. It is worth noting that the intensity ratio (*I*_D/*I*_G) in the Pd/Gr_{0.3}C_{0.7} spectrum is smaller than that in the Pd/Gr spectrum, indicating an increased degree of crystallinity in the Gr [42], which can be ascribed to the steric effect of the C clusters. Because of their sin-

Fig. 2. SEM image of the Pd/Gr_{0.3}C_{0.7} catalyst.

Fig. 3. TEM images of Pd/C (A), Pd/Gr (B) and Pd/Gr_{0.3}C_{0.7} (C), and an HR-TEM image (D) of Pd/Gr_{0.3}C_{0.7}. Particle size distribution histograms of Pd/C (a), Pd/Gr (b) and Pd/Gr_{0.3}C_{0.7} (c), and a histogram of average particle sizes with standard deviation (SD) error bars (d).

gle-atom-thick structure, Gr nanosheets have a tendency to undergo irreversible agglomeration via overlapping as a result of π - π stacking and van der Waals forces, even to the extent of

Fig. 4. Raman spectra of the Pd/Gr (1) and Pd/Gr_{0.3}C_{0.7} (2).

restacking to form graphite [34,58]. This effect can severely restrict the usefulness of this material as a catalyst support. As noted, the C clusters inhibited the stacking of the Gr nanosheets. Consequently, a greater quantity of oxygen-containing functional groups could be removed by chemical reduction to form a more orderly crystal structure, which is consistent with the XPS results discussed below.

The surface elemental compositions of the Pd/C, Pd/Gr and Pd/Gr_{0.3}C_{0.7} composites were determined by XPS, with the results provided in Fig. 5. All the XPS profiles were fitted by the Gaussian-Lorentzian (20% Gaussian) method after background subtraction using Shirley's method [59]. The survey spectra of the Pd/C, Pd/Gr and Pd/Gr_{0.3}C_{0.7} displayed in Fig. 5(A) all show three peaks located at approximately 284, 338 and 531 eV, corresponding to C 1s, Pd 3d and O 1s. Fig. 5(B) presents the C 1s spectra of Pd/Gr and Pd/Gr_{0.3}C_{0.7} samples. The C 1s binding energy is further separated into five peaks at 284.7, 286.1, 287.8, 289.1 and 291.1 eV, corresponding to the C–C, C–O, C=O, O–C=O and $\pi\rightarrow\pi^*$ groups [60,61], respectively. Density functional theory (DFT) calculations confirmed that the presence of both defects and oxygen-containing species on the graphene surface could play important roles in improving the catalyst's stability [62]. The relative percentages of the various carbon species obtained from the peak areas are summarized in Table 1. The concentrations of oxygen-containing functional group atoms in the Pd/Gr and Pd/Gr_{0.3}C_{0.7} composites were 29.81% and 22.88%, respectively. Due to the intercalation of the C between the Gr layers in the Pd/Gr_{0.3}C_{0.7}, the oxygen group content was reduced in comparison with that in the Pd/Gr catalyst. The Pd 3d XPS (Fig. 5(C)) spectra can be deconvoluted into two sets of peaks corresponding to Pd 3d_{5/2} (~335.8 eV) and Pd 3d_{3/2} (~341.0 eV). The peaks at relatively lower binding energy values (at approximately 335.6 and 340.8 eV) are attributed to metallic Pd (Pd⁰) while the other set of double peaks (at approximately 337.2 and 342.6 eV) results from Pd(II)O. It should be noted that the Pd 3d_{5/2} binding energy of the Pd/Gr_{0.3}C_{0.7} (336.08 eV) was significantly shifted in the positive direction (by approximately 0.23 and 0.30 eV) relative to the values for

Table 1

The relative percentages of the various carbon species as determined from C 1s spectra.

Catalyst	C specie	Atom %
Pd/Gr	C–C	61.2
	C–O	15.86
	C=O	5.87
	O–C=O	8.08
	$\pi\rightarrow\pi^*$	8.99
Pd/Gr _{0.3} C _{0.7}	C–C	74.1
	C–O	12.96
	C=O	4.96
	O–C=O	4.96
	$\pi\rightarrow\pi^*$	3.03

the Pd/Gr (335.85 eV) and Pd/C (335.78 eV) catalysts. This positive shift suggests a decrease in the 3d electron density of the Pd [33], which can be attributed to the strong interaction between the Pd nanocrystals and the support [60]. Pd having a lower 3d electron density does not bind to the COOH intermediates as readily, such that the surface (COOH)_{ads} coverage is decreased. For this reason, the FAO reaction would be expected to proceed primarily via the direct pathway [63] on the as-prepared Pd/Gr-C catalysts. The finding that the Pd 3d binding energy of the Pd/Gr_{0.3}C_{0.7} was more positive than those of the Pd/Gr and the Pd/C confirms the interaction between the Pd metal and the binary Gr-C support. Based on the relative peak areas, the Pd⁰:PdO ratio in the Pd/Gr_{0.3}C_{0.7} catalyst was estimated to be 1.44, indicating that the Pd surfaces were partially oxidized, presumably as the result of exposure to ambient air. It is known that nano-sized Pd particles are readily oxidized in ambient atmospheres.

3.2. Electrochemical analysis of Pd/Gr-C and Pd/C catalysts

Cyclic voltammetry (CV) was used to estimate the electrochemical active surface areas (ECSAs) of the Pd catalysts. Fig. 6 shows the cyclic voltammograms of Pd/C, Pd/Gr, Pd/Gr_{0.1}C_{0.9},

Fig. 5. XPS spectra of the Pd/C, Pd/Gr and Pd/Gr_{0.3}C_{0.7} catalysts.

Fig. 6. The CV curves of the Pd/C (1), Pd/Gr (2), Pd/Gr_{0.1}C_{0.9} (3), Pd/Gr_{0.3}C_{0.7} (4), Pd/Gr_{0.5}C_{0.5} (5), and Pd/Gr_{0.7}C_{0.3} (6) catalysts in 0.5 mol L⁻¹ H₂SO₄ at a scan rate of 10 mV s⁻¹.

Pd/Gr_{0.3}C_{0.7}, Pd/Gr_{0.5}C_{0.5} and Pd/Gr_{0.7}C_{0.3} catalysts acquired at a scan rate of 10 mV s⁻¹ in a H₂SO₄ solution (0.5 mol L⁻¹). Because of the ability of bulk Pd to absorb hydrogen, it is difficult to calculate the ECSA due to the presence of a monolayer of adsorbed hydrogen. Therefore, the ECSA of the Pd electrode was calculated by determining the coulombic charge associated with the reduction of Pd(II) oxide [64]. The peak in the potential range from 0.5 to 0.8 V is assigned to the reduction of Pd(II) oxide. The ECSA value of each electrocatalyst was found using the Eq. (2) [6]:

$$ECSA = Q_R / Q_{MR} \quad (2)$$

where Q_R is the coulombic charge associated with the peak due to the reduction of Pd(II) oxide, and Q_{MR} is the charge (0.424 mC cm⁻²) associated with the reduction of a Pd(II) oxide monolayer. The resulting ECSA values are provided in Table 2. It is evident that the Pd/Gr-C catalysts had larger ECSAs than the Pd/C and Pd/Gr electrocatalysts.

Fig. 7 compares the FAO performance of the Pd/C, Pd/Gr and Pd/Gr-C catalysts, as assessed by LSV in 0.5 mol L⁻¹ H₂SO₄ + 0.5 mol L⁻¹ HCOOH. The main peak at approximately 0.2 to 0.5 V is attributed to FAO via the direct pathway, while the small shoulder near 0.8 V is ascribed to the oxidation of adsorbed CO via the indirect pathway. The peak potentials of the Pd/Gr-C electrocatalysts during FAO are initially negatively shifted and subsequently positively shifted with increases in the C content (inset in Fig. 7) in the mixture of GO and C prior to NaBH₄ reduction. The peak potential of the Pd/Gr_{0.3}C_{0.7} is 120 and 70 mV more negative than those of the Pd/C and Pd/Gr catalysts (Table 2). At a peak potential of 0.23 V, the current density of the Pd/Gr_{0.3}C_{0.7} catalyst was 102.14 mA mg_{Pd}⁻¹, a value that is approximately 3 and 2.6 times those generated by the Pd/C (34.40 mA mg_{Pd}⁻¹) and Pd/Gr (38.50 mA mg_{Pd}⁻¹), in-

Fig. 7. The LSV curves of the Pd/C (1), Pd/Gr (2), Pd/Gr_{0.1}C_{0.9} (3), Pd/Gr_{0.3}C_{0.7} (4), Pd/Gr_{0.5}C_{0.5} (5), and Pd/Gr_{0.7}C_{0.3} (6) catalysts in 0.5 mol L⁻¹ HCOOH + 0.5 mol L⁻¹ H₂SO₄ at a scan rate of 10 mV s⁻¹.

Fig. 8. The LSV curves of Pd/Gr_{0.3}C_{0.7} and physically mixed Pd/Gr and Pd/C catalysts in 0.5 mol L⁻¹ HCOOH + 0.5 mol L⁻¹ H₂SO₄ at a scan rate of 10 mV s⁻¹.

dicating higher catalytic activity during FAO (Table 2). The Pd/Gr_{0.3}C_{0.7} peak is also much sharper than those of the other catalysts, suggesting that more active sites were accessible [65]. The SEM image in Fig. 2 demonstrated that the binary Gr-C support formed a 3D nanostructure, which assists in loading the Pd nanoparticles. As noted, the more extensive 3D distribution of Pd allowed reactant molecules to more easily reach the active sites on the Pd surface, thus improving the catalytic performance. The XPS analysis described earlier also supports the enhanced catalytic activity of the Pd/Gr_{0.3}C_{0.7} catalyst.

For comparison purposes, the performance of physically mixed Pd/Gr and Pd/C catalysts (made at Pd/support mass ratios of 3:7) is provided in Fig. 8. It can be seen that the

Table 2

Electrochemical data for the Pd/C, Pd/Gr, 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.

Catalyst	Pd/C	Pd/Gr	Pd/Gr _{0.1} C _{0.9}	Pd/Gr _{0.3} C _{0.7}	Pd/Gr _{0.5} C _{0.5}	Pd/Gr _{0.7} C _{0.3}
ECSA (cm ²)	5.04	6.37	8.24	13.24	8.53	11.06
Peak potential (E/V)	0.35	0.30	0.27	0.23	0.24	0.25
Peak current density (j_p /mA mg _{Pd} ⁻¹)	34.40	38.50	57.38	102.14	82.84	63.12
CA terminal current (mA mg _{Pd} ⁻¹)	5.80	11.20	—	16.50	—	—

Fig. 9. The chronoamperometric curves of the Pd/C (1), Pd/Gr (2) and Pd/Gr_{0.3}C_{0.7} (3) in 0.5 mol L⁻¹ HCOOH + 0.5 mol L⁻¹ H₂SO₄ at 0.3 V (vs. RHE).

Pd/Gr_{0.3}C_{0.7} catalyst had a more negative peak potential and a larger current density than the mixture, demonstrating superior catalytic activity.

To evaluate the stability of the Pd/Gr_{0.3}C_{0.7} catalyst, chronoamperometry (CA) experiments were carried out at 0.3 V vs. RHE for 3600 s. Fig. 9 shows the chronoamperometric curves for the Pd/C, Pd/Gr and Pd/Gr_{0.3}C_{0.7} catalysts in 0.5 mol L⁻¹ H₂SO₄ + 0.5 mol L⁻¹ HCOOH. The current density decreased rapidly in the initial stage, possibly due to deactivation of the Pd electrocatalyst by adsorption of CO or CO-like intermediates during the FAO process [66]. The current density subsequently stabilized, and the stable current density generated by the Pd/Gr_{0.3}C_{0.7} catalyst was higher than those of the Pd/C and Pd/Gr (Table 2). Thus, the Pd/Gr_{0.3}C_{0.7} catalyst was more stable than either the Pd/C or Pd/Gr.

The Fig. 10(a) shows the LSV data obtained in 0.5 mol L⁻¹ H₂SO₄ + 0.5 mol L⁻¹ HCOOH for the Pd/Gr_{0.3}C_{0.7} electrode at different scan rates during FAO. The relationship between the peak current density (j_p) and the square root of the scan rate ($v^{1/2}$) at the Pd/Gr_{0.3}C_{0.7} electrode is plotted in Fig. 10(b). These data demonstrate that the oxidation potential and j_p were both increased with increasing scan rates. This result suggests that the rate-determining step of FAO on the Pd/Gr_{0.3}C_{0.7} electrode is an irreversible electrode process. In addition, a linear relationship is evident between j_p and $v^{1/2}$, further confirming that

the FAO is an irreversible electrode process [67].

4. Conclusions

This work demonstrated the successful fabrication of binary Gr-C supports for Pd nanoparticles by a one-pot chemical reduction method. The resulting Pd/Gr-C catalysts exhibit improved electrocatalytic performance compared with Pd/C and Pd/Gr catalysts during FAO. The superior performance of the Pd/Gr-C can be attributed to its intrinsic 3D nanostructure, in which C clusters effectively hinder the restacking of Gr, thus retaining the outstanding single-layer electric properties of Gr and facilitating the movement of reactant/product molecules. Furthermore, the strong interaction between the Pd nanoparticles and binary Gr-C support reduce the Pd 3d electron density. As a result, the Pd does not readily bind COOH intermediates, and FAO proceeds largely via the direct pathway. The as-prepared Pd/Gr_{0.3}C_{0.7} catalyst shows the highest activity and good stability, and so binary Gr-C appears to be a promising candidate as a support material for noble metal-based catalysts.

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Fig. 10. LSV curves (a) acquired during FAO on the Pd/Gr_{0.3}C_{0.7} electrode in 0.5 mol L⁻¹ HCOOH + 0.5 mol L⁻¹ H₂SO₄ at different scan rates. The peak current density as a function of the square root of the scan rate (b).

Graphical Abstract

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

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Composite catalysts consisting of Pd loaded on binary graphene/carbon black supports were synthesized by a reduction method. These materials exhibit better electrocatalytic performance than either Pd/carbon black or Pd/graphene catalysts, suggesting a new approach to binary carbon supports for noble metal-based catalysts with fuel cell applications.

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利用石墨烯-炭黑组成的二元碳载体增强甲酸在钯催化剂上电化学氧化的活性

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摘要: 本文采用“一锅法”将氧化石墨烯(GO)、炭黑(C)和钯离子用 NaBH_4 共还原, 制备了石墨烯-炭黑二元载体(Gr-C)负载的钯催化剂(20% Pd/Gr-C), 用于催化甲酸的电氧化反应。电化学测试结果表明, 前驱体GO和C的质量比为3:7的Pd/Gr_{0.3}C_{0.7}催化剂催化活性最好, 它的峰电流密度($102.14 \text{ mA mg}_{\text{Pd}}^{-1}$)约为Pd/C催化剂($34.40 \text{ mA mg}_{\text{Pd}}^{-1}$)的3倍, 为钯/石墨烯催化剂(Pd/Gr, $38.50 \text{ mA mg}_{\text{Pd}}^{-1}$)的2.6倍。甲酸在Pd/Gr_{0.3}C_{0.7}催化剂电极直接氧化时的峰电位比Pd/C催化剂的峰电位负移约120 mV, 比Pd/Gr催化剂的峰电位负移约70 mV。采用透射电子显微镜(TEM)、扫描电子显微镜(SEM)、X射线衍射(XRD)、X射线光电子能谱(XPS)、拉曼光谱、电感耦合等离子体发射光谱(ICP-AES)等手段对催化剂进行了表征。从SEM图像可以观察到, 球形的炭黑团簇聚集在具有褶皱的石墨烯面上, 形成了炭黑团簇/石墨烯三维立体结构, 有效地抑制了相邻石墨烯层在范德华力作用下的吸引聚集和堆叠造成的石墨烯表面积减小, 减小了单层石墨烯叠合成为多层石墨烯所造成的导电性损失, 避免了相邻石墨烯片叠合形成封闭空间, 有助于反应物和产物分子的运动。载体的三维结构使反应物分子更容易到达钯纳米粒子, 有利于催化性能的提高。XPS结果也证实了二元Gr-C载体对Pd催化的促进作用。Pd/Gr_{0.3}C_{0.7}催化剂的Pd $3d_{5/2}$ 峰发生了右移, 表明Pd $3d$ 电子结合能正移, Pd $3d$ 电子云密度降低。具有较低的 $3d$ 电子云密度的Pd不易与甲酸氧化过程中吸附的中间体 $(\text{COOH})_{\text{ads}}$ 结合, 钯催化剂上 $(\text{COOH})_{\text{ads}}$ 表面覆盖率降低, 从而使甲酸更容易直接脱氢氧化生成 CO_2 , 有利于甲酸通过直接途径进行电化学氧化。

与Pd/C, Pd/Gr相比, Pd/Gr_{0.3}C_{0.7}催化剂对甲酸电氧化有最好的催化活性。Pd/Gr_{0.3}C_{0.7}催化剂优异的催化活性可归因于其内在的三维纳米结构: 炭黑团簇有效地抑制了石墨烯纳米片的聚集, 保持了其大的比表面积和高导电性, 促进了反应物和产物分子的运动。此外, Pd纳米粒子与二元载体之间的强相互作用降低了Pd的 $3d$ 电子云密度, 使甲酸氧化主要经直接途径进行。本文证实了钯金属和石墨烯-炭黑二元载体之间的强相互作用, 提供了简单和高性价比的方法以提高钯基催化剂的活性, 有利于工业化的应用。

关键词: 二元碳载体; 钯; 石墨烯; 炭黑; 甲酸氧化; 燃料电池

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