Carbon-supported Pd-Ir nanoalloys as cathodic catalyst for oxygen reduction reaction

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Abstract
Pd as cathodic catalyst exhibits relatively low current density in mixing kinetic/diffusion controlled region. To improve catalytic activity of Pd, alloying Pd with another transition metal is an effective approach. Here, we prepared carbon-supported Pd-Ir nanoalloys (Pd-Ir/C) through impregnation method. Four types of Pd-Ir/C were designed and referred as Pd\textsubscript{19}Ir\textsubscript{1}, Pd\textsubscript{9}Ir\textsubscript{1}/C, Pd\textsubscript{3}Ir\textsubscript{1}/C, and PdIr/C using nominal Pd/Ir atomic ratios of 19:1, 9:1, 3:1, and 1:1, respectively. The results showed that Pd and Ir formed the nanoalloy structures and Pd-Ir/C exhibited significantly improved catalytic activity for oxygen reduction reaction than Pd/C, indicating that Ir had important effect on Pd-Ir nanoalloys.

1. Introduction
Proton exchange membrane fuel cell (PEMFC), as one type of clean and efficient power source, has some significant advantages such as carbon dioxide zero-emission, low corrosion, safe operation, and relatively high efficiency [1]. PEMFC has been widely adopted in distributed power station, portable power supply, new energy vehicles and others [2]. However, a lot of precious metal Pt (the state-of-the-art commercial catalyst) is used to overcome low energy conversion efficiency caused by sluggish kinetic of oxygen reduction reaction (ORR) and bad durability of the catalyst in the cathode of PEMFC, which severely limits its commercial application [3]. Therefore, improving the utilization of Pt or using non-Pt metals is a very important research field in fuel cells [4–9].

With respect to non-Pt electrocatalysts for ORR, one of the main alternatives seems to be Pd catalyst. Unfortunately, the binding of Pd and oxygen is too strong to effectively remove ORR intermediates [10]. However, oxygen binding energy is considered to be an important descriptor for ORR catalytic activity [11]. This may be why Pd exhibits low ORR current density and few peroxide in ORR mixing kinetic/diffusion controlled region [12]. In order to obtain superior electronic property or physical structure, alloying Pd with another transition metal is an effective way [13].

The transition metals in Pd-based alloys may not have catalytic activity, but Pd-based alloys usually show superior catalytic performance including the decrease of ORR overpotential, the increase of current density, and the enhancement of the stability owing to the electronic effect and the synergistic effect [14]. The electronic effect usually refers to the electron-electron interaction between Pd atoms and transition metal atoms [15]. This interaction causes the change of electron binding energy, thus leading to the improvement of catalytic performance. You et al used replacement method to obtain Pd-Cu alloys whose surface is modified by Ir. The authors expected that high ORR catalytic activity was attributable to electronic and structural change of Pd-Cu alloys caused by Ir atoms [16]. The synergistic effect typically refers to the introduction of an active element (such as Co) to promote the decomposition of O–O bond, and the generated Co-O\textsubscript{ads} species can be rapidly transferred to the active site on Pd to induce the electrochemical reduction occurrence immediately [17]. Pan et al deduced that the synergistic effect between Fe and Pd atoms lead to higher ORR catalytic activity and better methanol tolerance for Pd-Fe/C than those for Pd/C [18].

DFT calculations and experimental results show that oxygen binding energy increases at active sites with the increase of Ir content on the surface of Pd-Ir nanoalloys, thus decreasing ORR activity [19]. Yang et al reported
that Pd-Ir nanowires or nanodendrites with high Ir content (e.g., Pd1Ir2) and Ir-rich surface exhibit high catalytic activity and durability towards ORR due to altered surface electron structure and rough surface with many atomic steps/corners [20]. In fact, Pd-based bimetallic catalysts (e.g., Pd-Ir) were computationally evaluated for ORR and the results indicated Pd-rich surface [21]. It has been reported that Ir atom in Pd-Ir-Co [22], Pd-Ir-Fe [23], or Pd-Ir-Ni [24] induced Pd segregation at the surface and the modification of electronic structure, thus weakened the binding strength of oxygen-containing intermediates. Here, we explore catalytic activity and durability of Pd-Ir nanoalloys with high Pd content as ORR catalyst. Carbon-supported Pd-Ir nanoalloys (Pd-Ir/C) with different Pd/Ir atomic ratios were prepared by controlling the feed ratios. The nanostructures and properties of the as-prepared Pd-Ir/C were characterized by XRD, XPS, TEM, and electrochemical measurements.

2. Experimental

2.1. Materials

20 wt% Pt/C from Johnson-Matthey (JM) was used as the reference catalyst. H2IrCl6, 6H2O, PdCl2, HClO4, H2SO4 were purchased from National Pharmaceutical Group Chemical Reagent Co., Ltd (Shanghai, China). All chemicals are analytical grade and used directly without further purification.

2.2. Catalyst preparation

Carbon-supported Pd-Ir nanoalloys (Pd-Ir/C) with different Pd/Ir atomic ratios and the total metal loading of 20 wt% were synthesized through impregnation method. Typically, a mixture of H2IrCl6, PdCl2, and Vulcan carbon XC-72R in deionized water was uniformly dispersed using ultrasonic treatment and magnetic stirring. The mixture was dried at 40 °C overnight and then 100 °C for 1 h. Then, the powder was reduced by hydrogen at 60 °C for 2 h (Pd reduction) in electric resistance furnace and then heated up to 400 °C for 2 h (Ir reduction and inducing alloying). After cooled in argon atmosphere, the powder was collected. The catalysts were marked as Pd1Ir/C, Pd3Ir/C, Pd5Ir/C, and Pdlr/C derived from Pd/Ir atomic ratios. The Ir content values of the different alloys are determined by feed ratio, which are agreement with the result from ICP-AES. Using the similar procedure, Pd/C was obtained via hydrogen reduction of PdCl2 at 60 °C for 2 h.

2.3. Catalyst characterization

The x-ray diffraction (XRD) patterns of the catalyst powder were collected on a Shimadzu XRD-6000 x-ray diffractometer using a Cu Kα radiation source operated under a voltage of 40 kV and a current of 30 mA. Transmission electron microscopy (TEM) observations were conducted on a JEOL JEM-2010 instrument operated at an accelerating voltage of 200 kV. Particle size was calculated directly by measuring the diameters of nanoparticles from the corresponding TEM image and particle distribution was fitted by using Lorentz fit. X-ray photoelectron spectroscopy (XPS) spectra of catalysts were measured using a Kratos XSAM800 spectrometer with Mg Kα x-ray source. The data were fitted by using the software XPSPEAK41 with Shirley function as baseline and Gauss-Lorentzian linearity fitting. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on an IRIS Intrepid II XSP from Thermo Electron Corporation.

2.4. Electrochemical measurements

The electrochemical measurements were performed with a three electrode configuration. Electrochemical experiments were conducted on CHI-660 with a rotating disk electrode (RDE) system (Pine Research Instruments) at 25 °C. To prepare the working electrode, briefly, 5 mg of catalyst powder was dispersed ultrasonically in 1 ml of a Nafion (0.05 wt%) isopropyl alcohol solution. An aliquot (10 μl) of the resulting suspension was then pipetted onto a glassy carbon (GC) substrate (diameter: 5 mm) to form a thin catalyst film. The total loading of catalyst sample (metal + carbon) on GC electrode was ca. 255 μg cm−2. The counter electrode was a Pt foil, and the reference electrode was a saturated calomel electrode (SCE), which was separated from the working electrode by a Luggin capillary. However, all the potentials were referred to the reversible hydrogen electrode (RHE) in this work. The working electrolyte was 0.5 M H2SO4 aqueous solution.

3. Results and discussion

3.1. Catalyst characterization

Carbon-supported Pd-Ir nanoalloys (Pd-Ir/C) were prepared through impregnation method. In order to explore the effect of Pd/Ir atomic ratios on catalytic activity, four types of Pd-Ir compositions were designed and referred using nominal Pd/Ir atomic ratios of 19:1, 9:1, 3:1, and 1:1 as Pd19Ir/C, Pd9Ir/C, Pd3Ir/C, and Pdlr/C, respectively. The total loadings of Pd and Ir supported on Vulcan carbon XC-72R are 20 wt%.
Pd-Ir/C were characterized by XRD, XPS, and TEM. Figure 1(a) is the XRD patterns of Pd/C and Pd-Ir/C. Pd/C displays the diffraction peaks of face-centered cubic (fcc) Pd (111), (200), (220), and (311) at 2θ of 40.1°, 46.7°, 68.1°, 82.1°, respectively. The similar diffraction patterns of Pd-Ir/C and Pd/C suggest that Ir atoms enter the Pd lattice to form nanoalloys. The diffraction peaks of fcc Pd (220) for Pd/C, Pd_{19}Ir/C, Pd_{9}Ir/C, Pd_{3}Ir/C, PdIr/C are at 68.1°, 68.2°, 68.2°, 68.4°, 68.7°, respectively. It is found that the peaks of the (220) reflection shift to higher angles with increasing Ir content. Figure 1(b) shows the lattice constants determined by the diffraction angles of the (220) reflection peaks in the XRD patterns. The result clearly supports the formation of an alloy between Pd and Ir, and indicates that lattice contraction arising from the substitution of the smaller Ir for the larger Pd.

TEM images and the corresponding particle size distribution histograms of Pd/C and Pd-Ir/C are presented in figure 2. Pd and Pd-Ir nanoparticles uniformly disperse on the surface of Vulcan carbon XC-72R. The average sizes of Pd, Pd_{19}Ir, Pd_{9}Ir, Pd_{3}Ir, and PdIr are approximately 2.2, 5.9, 5.9, 6.3 and 6.0 nm, respectively. The alloying of Pd-Ir using high temperature treatment makes the particle size increase significantly.

Figure 3 is the XPS spectra of Pd_{19}Ir/C and Pd_{3}Ir/C in binding energy range of 3d orbitals of Pd and 4f orbitals of Ir. The black line is the original data; the red line is the fitted data; and the green line is the background. The fitted peaks are marked out in the figures. The valence and the metal content of the near-surface region in nanometer depth can be detected through XPS measurement. The Pd/Ir atomic ratios in near-surface region of Pd_{19}Ir/C, Pd_{9}Ir/C, Pd_{3}Ir/C, and PdIr/C are 11.2, 6.5, 1.8, and 0.6, respectively. The results are slightly lower than those in bulk, indicating that high temperature annealing does not result in Pd-rich surface to form Pd-skin. Interestingly, the characteristic peaks of Pd_{5d}^{3/2} in Pd-Ir/C negatively shift compared to Pd/C. In the XPS spectra of Pd_{19}Ir/C, the relatively lower binding energy set of double peaks (335.4 eV and 340.7 eV) derive from Pd_{0}^{3d}^{5/2} and Pd_{0}^{3d}^{3/2}, which reaspond of the nonoxidized state of the Pd. And the other set of double peaks (336.8 eV and 342.1 eV) belong to Pd_{2}^{3+}^{3d}^{5/2} and Pd_{2}^{3+}^{3d}^{3/2}, which represents the oxidation state of Pd which is most probably a result of the oxidation of surface Pd atoms in air. Similarly, the Ir^{4+} bond is predominantly in oxidized state of Ir. The peaks of Pd_{5d}^{3/2} in Pd/C centered at 335.9 eV and 337.4 eV are assigned to Pd^{0} and Pd^{2+}, which are in good agreement with previous reports [25]. The results suggest that the electronic structure of Pd in Pd-Ir nanoalloys undergo changes. In the XPS spectra of Pd_{5d}^{3/2} and Pd_{3d}^{3/2} of Pd_{19}Ir/C, the relatively lower binding energy compare with that peaks of pure Pd, it means Pd atoms probably obtain the extra electrons from Ir atoms to form rich electron structure [26]. Furthermore, the shift of the characteristic peaks of Pd_{3d} in Pd-Ir/C weakens with increasing Ir content and Pd_{19}Ir/C has the most obvious changes.
3.2. Electrochemical studies

The electrocatalytic performance of Pd-Ir/C was investigated by comparing the as-prepared Pd/C and 20 wt% Johnson-Matthey (JM) Pt/C (figure 4). The cyclic voltammetry (CV) curves of the catalysts in figure 4(a) show that both Pd/C and Pd-Ir/C have the reduction/oxidation peaks for hydrogen adsorption/desorption in potential region of 0.1 ~ 0.3 V and the reduction peak for removal of Pd surface oxides in potential region of 0.4 ~ 0.9 V. The oxygen desorption peak positions of Pd-Ir/C and Pd/C are at 0.71 V and 0.75 V, which implies that the oxygen species are more difficult to remove from Pd after the alloying of Pd-Ir. Figure 4(b) is ORR polarization curves of Pd-Ir/C with the less loadings, i.e., 30 μg and 20 μg. The similar results including the catalytic activities were obtained, indicating that lowering the loading of the catalysts is not beneficial to the test results, instead, may affect the roughness of the catalysts on GC electrode. In order to ensure the reliability of the data, three parallel samples are tested for each data.

Figure 3. XPS spectra of Pd₃Ir/C and Pd₉Ir/C. Black line: the measured XPS response; Red line: the superposition of the deconvoluted component spectra of Pd₃d₅/₂, Pd₃d₃/₂, Ir₄f₇/₂, Ir₄f₅/₂; Green line: the background.

Figure 4. CVs (a), ORR polarization curves (b), mass transport corrected Tafel plots (c), and the specific activites and mass activities at 0.85 V (d) of Pt/C (black), Pd/C (red), Pd₃Ir/C (green), Pd₉Ir/C (blue), Pd₃Ir (cyan) and PdIr/C (magenta) in 0.5 M H₂SO₄ electrolyte.
To deduce the effect of oxygen transport, the kinetic current ($I_k$) is calculated by Koutecky-Levich equation from ORR polarization curves: $1/1 = 1/I_d + 1/I_0$, where $I$ is the experimental data, $I_d$ is the limiting diffusion current, $I_k$ is the kinetic current. And the mass-transport corrected Tafel plots for ORR Pd/C, Pd-Ir/C, and JM Pt/C are shown in figure 4(c). $I_k$ of Pd-Ir/C decreases with increasing Ir content. In addition, for comparing the ORR electrode activity between catalysts, specific activity (SA) and mass activity (MA) at 0.85 V for Pd-Ir/C catalysts have been showed in figure 4(d). SA is obtained by normalizing $I_k$ to the electrochemical active surface area (ECSA) of Pd, represents the intrinsic catalytic activity of surface Pd atoms in each catalyst. The ECSA is calculated by integrating the peak related to the Pd-oxide reduction between 0.4 and 0.8 V Versus RHE. A charge of 405 mC cm$^{-2}$ for the reduction of a Pd-oxide monolayer is assumed according to the literature [27]. MA was calculated by normalizing $I_k$ to the mass of Pd on electrode reflects the ultimate utilization of Pd in a catalyst. Pd-Ir/C have the close SA and MA at 0.85 V, indicating the utilization of Pd is similar for the different components of the Pd-Ir alloys. Pd$_{19}$Ir/C is the cheapest in Pd-Ir/C because the price of Ir is much higher than Pd. The ORR activity of Pd$_{19}$Ir/C is twice as much as Pd/C, because the Ir atoms cause the lattice contraction and a rich electron structure of Pd. From figure 3, it is found that the binding energy peak of Pd$_{19}$Ir/C catalyst is 335.4 eV, while that of pure Pd/C is 335.9 eV. The characteristic peak of Pd$_{19}$Ir/C in the alloy shifts negatively to the direction of low binding energy by 0.5 eV, and that of Pd$_{19}$Ir/C shifts by 0.6 eV. Compressive strain leads to lowering of $d$-band center with respect to Fermi level. This will lead to decreased oxygen binding on the catalyst surface and hence higher ORR activity compared to the Pd/C catalyst. MA at 0.85 V of Pd-Ir catalysts in 0.5 M H$_2$SO$_4$ electrolyte is approximately 40 A g$^{-1}$, which is higher than that at 0.75 V of Pt-Ir catalysts in 0.1 M HClO$_4$ electrolyte reported to be 17.8 A g$^{-1}$ [28]. However, the surface area of the catalysts can be increased by selective corrosion of the oxides in the composite, which can significantly improve catalytic properties of the catalysts [28].

The Pt/C and Pd$_{19}$Ir/C catalysts were subject to accelerated durability tests of repeating potential cycles between 0.05 and 1.2 V in 0.5 M H$_2$SO$_4$ with a potential scanning rate of 50 mV s$^{-1}$. Figure 5 shows the changes in the CVs and ORR polarization curves before and after accelerated durability tests of 1,000 cycles. After 1,000 cycles, the Pt/C catalyst shows more than 35% loss in ESA and 23 mV negative shifts in the $E_{1/2}$ of ORR polarization. For Pd$_{19}$Ir/C, the measured degradations of ESCA and $E_{1/2}$ of ORR polarization were approximately 15% and 10 mV, demonstrating that Pd$_{19}$Ir/C has better durability than the commercial Pt/C. Pd-Ir/C possess high stability in acid medium because Ir has high oxidation/reduction potential, which is higher than the typical operating voltage of fuel cells. Therefore, Pd alloyed with Ir is a promising alternative to develop an efficient electrocatalyst for ORR.

### 4. Conclusions

In summary, carbon-supported Pd-Ir nanoalloys (Pd-Ir/C) were prepared through impregnation method. XRD data of Pd-Ir/C indicate the alloy formation of Pd and Ir. TEM images show that Pd-Ir nano nanoparticles are uniformly dispersed on the surface of carbon and the high temperature treatment makes the particle size increase significantly. The alloying causes lattice contraction and a rich electron structure of Pd, which is...
beneficial for ORR. Our work suggests that carbon-supported Pd-Ir nanooalloy via Pd alloyed with Ir is a promising alternative to develop an efficient electrocatalyst for ORR.

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