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# Enhanced Formic Acid Electro-Oxidation on PdIr Nanoparticles Prepared by Ethylene Glycol-Assisted NaBH<sub>4</sub> Reduction Process

Jinwei Chen, Gang Wang, Xueqin Wang, Jing Tian, Shifu Zhu, and Ruilin Wang\*

College of Materials Science and Engineering, Sichuan University, Chengdu 610065, China

The carbon supported PdIr nanoparticles were synthesized by an ethylene glycol-assisted NaBH<sub>4</sub> reduction method, and the mass ratio of Pd to Ir was optimized. Then, their performances for formic acid electro-oxidation (FAEO) were investigated. The XRD and TEM characterizations show that the prepared PdIr/C catalysts have small mean size and good dispersion of PdIr nanoparticles. The electrochemical measurements demonstrate that the PdIr/C catalysts have greatly enhanced performance for FAEO compared with the Pd/C catalyst. The PdIr/C catalysts show higher current density and more than 50 mV negative shift of onset and peak potential than that of the Pd/C catalyst. With the optimal mass ratio of Pd to Ir, the PdIr/C-5 catalyst presents the highest catalytic activity for FAEO.

Keywords: Direct Formic Acid Fuel Cell, Electro-Oxidation, Palladium, Iridium, Nanoparticles.

## **1. INTRODUCTION**

Electro-oxidation of formic acid has attracted increasing attention due to the development of direct formic acid fuel cell (DFAFC),<sup>1-8</sup> which is particularly suitable for portable devices because of its high theoretical open circuit voltage, superior performance and small fuel crossover relative to direct methanol fuel cells (DMFCs).9-11 As we know, Pt-based catalysts have been frequently employed for small organic compounds electro-oxidation.<sup>12</sup> However, lower oxidation activity toward formic acid and higher cost of Pt-based catalysts are the major drawbacks to hinder the practical application of DFAFC. Generally, it is accepted that formic acid electro-oxidation (FAEO) on Pt catalyst is mainly via an indirect pathway and the catalyst is easily poisoned by the adsorbed CO-like intermediate at low potential. Recently, Pd-based catalysts have attracted increasing attention for small organic molecules electro-oxidation.<sup>13-16</sup> It is generally accepted that the electro-oxidation of formic acid on Pd catalyst can proceed through a direct dehydrogenation reaction mechanism<sup>17</sup> to form carbon dioxide with less CO-like poisoning species generated.

Recent efforts in FAEO have been focused on increasing catalyst activity and stability through various strategies. It has been demonstrated that combination of a second

Copyright: American S component (such as Pt,<sup>18</sup> Au,<sup>4</sup> Co,<sup>19</sup> Cu,<sup>5</sup> and Ni<sup>20</sup>) with Pd is an effective approach to further enhance its performance. In this work, we report an ethylene glycol (EG)-assisted NaBH<sub>4</sub> reduction method to synthesize the PdIr/C catalyst, and optimize the mass ratio of Pd to Ir. The structural properties of the catalysts were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The electrochemical properties were characterized by the cyclic voltammetry (CV) and linear sweeping voltammetry (LSV). The results demonstrated that the prepared PdIr/C catalyst with optimized mass ratio exhibited excellent catalytic activity for FAEO.

#### 2. EXPERIMENTAL DETAILS

#### 2.1. Synthesis of Catalysts

Vulcan XC-72R carbon black was obtained from Cabot Company (Boston, USA). At first, the 400 mg carbon black was pretreated with 40 ml 8 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> and 40 ml 8 mol  $L^{-1}$  HNO<sub>3</sub> mixture under refluxing condition at 90 °C for 3 hours to import oxygen-containing functional groups onto carbon black. Palladium chloride (PdCl<sub>2</sub>) and hexachloroiridate acid (H<sub>2</sub>IrCl<sub>6</sub> · 6H<sub>2</sub>O) was purchased from Shenyang Research Institute of Nonferrous Metals (Shenyang, China). All other reagents were of analytical grade and used as received without further treatment.

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<sup>\*</sup>Author to whom correspondence should be addressed.

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The Pd/C and Pd–Ir/C (20 wt.% of metals loading; the mass ratio of Pd to Ir was 7:1, 5:1 and 3:1, respectively) catalysts were synthesized by the following route. The 40 mg of pretreated carbon black and appropriate PdCl<sub>2</sub> and H<sub>2</sub>IrCl<sub>6</sub> aqueous solution were dispersed in 20 ml EG with sonication for 30 min, and then stirred for 2 hours. A freshly prepared NaBH<sub>4</sub> in EG solution (the molar ratio of NaBH<sub>4</sub> to metal was 125:1) was added dropwise into the above solution at 20 °C and the resulting suspension was stirred for 3 hours. The mixture was filtered, washed, and dried in a vacuum oven at 75 °C for 10 hours. The prepared PdIr/C catalysts with Pd:Ir mass ratio of 7:1, 5:1 and 3:1 were designated as PdIr/C-7, PdIr/C-5, PdIr/C-3, respectively.

#### 2.2. Characterization of the Catalysts

The X-ray diffraction (XRD) analyses were carried out on a DX-2000 X-ray diffractometer (DX-2000, Dandong Ltd., China). TEM images were obtained using a FEI, TECNAI  $G^2$  microscope (USA).

All electrochemical measurements were carried out in a conventional three-electrode electrochemical cell at 25 °C using LSV and CV techniques on a CHI 760B. The counter electrode was a graphite electrode and the reference electrode was a saturated calomel electrode (SCE). All potentials reported in this paper were referred to the SCE. A glassy-carbon working electrode ( $\phi$ 3, surface area  $7.0 \text{ mm}^2$ ) was used as substrate. A 5.0 mg sample of the prepared catalyst was dispersed in a solution containing 1.0 mL of deionized water, 1.0 mL of isopropanol, and 50 µL of a 5 wt% Nafion solution using 30 min of ultrasonification to form a uniform suspension. A 5  $\mu$ L sample of the dispersed catalyst suspension was pipetted onto the glassy-carbon substrate. The calculated loading of metal was 35  $\mu$ g cm<sup>-2</sup>. The LSV and CV were carried out in  $0.5 \text{ mol } L^{-1} \text{ HCOOH} + 0.5 \text{ mol } L^{-1} \text{ H}_2 \text{SO}_4$  solution deaerated by ultra-pure argon for 20 min before measurements.

## 3. RESULTS AND DISCUSSION

The crystalline structure of the prepared catalysts is confirmed by the XRD technique and the results are shown in Figure 1. All diffraction patterns show the typical signals of the face centered cubic (fcc) structure of Pd (PDF 87-0643). And the ratio of the diffraction peak intensity of metal to that of carbon indicates that the relative crystallinity of PdIr nanoparticles (NPs) is higher than that of Pd NPs. Moreover, the mean crystallite size can be calculated using Scherrer's equation.<sup>21, 22</sup> For that, the (220) peak of the Pd fcc structure was used because the broad carbon peak does not interfere in this region. Although, the lower diffraction peak intensity of Pd/C catalyst makes it look broader, the crystallite sizes of Pd/C, PdIr/C-7, PdIr/C-5, PdIr/C-3 catalysts are 3.3, 2.8, 2.7 and 2.5 nm,

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Fig. 1. XRD patterns of the (a) Pd/C, (b) PdIr/C-7, (c) PdIr/C-5 and (d) PdIr/C-3 catalysts.

respectively. For all PdIr/C catalysts the diffraction signals are slightly shifted toward smaller 2 theta values compared to the Pd/C sample, indicating that Ir atoms entered into Pd lattice and substituted Pd atoms forming PdIr solid solution. In addition, no peak related to IrO<sub>2</sub> and Ir phases, which indicated the absence of metallic Ir and the presence of unalloyed Ir most probably in amorphous oxides states. Figure 2 shows TEM images of the prepared PdIr/C-5 catalysts and its corresponding particle size distribution histograms. The 20-30 nm spherical particles are carbon blacks and the dark dots are PdIr-NPs supported on the carbon blacks. It is observed from Figure 2(a) that the PdIr NPs of the PdIr/C-5 catalyst prepared by the EGassisted NaBH<sub>4</sub> reduction method are highly dispersed on the carbon support. According to distribution histogram of catalysts, the PdIr NPs have a mean size of 2.6 nm with a narrow size distribution. These features are consistent with the results of XRD analyses.

Figure 3 presents the cyclic voltammograms of 0.5 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> solution at different catalyst electrodes. It can be observed that the peaks of the adsorption/desorption of hydrogen around 0 V are obvious at the Pd/C catalyst electrode, while there are not observed on PdIr/C catalysts. This result also indicates the formation of PdIr solid solution, as Ir has poor ability for the adsorption/desorption of hydrogen. Moreover, the onset potential of the Pd oxidation for all the Pd/C and PdIr/C catalysts are at around



**Fig. 2.** TEM images of the PdIr/C-5 catalyst and the corresponding histogram of size distribution of the PdIr nanoparticles.



Fig. 3. Cyclic votammograms of the prepared Pd/C and PdIr/C catalysts in an Ar-saturated solution of 0.5 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> at a scan rate of 50 mV s<sup>-1</sup> at 25 °C.

0.55 V and the reduction peak are located at about 0.5 V (the PdIr/C catalysts have slightly negative shift peaks), while the current of Pd oxidation and reduction at PdIr/C are larger than that of Pd/C because of the smaller size of PdIr-NPs or the oxidation of Ir.

The catalytic activities of the prepared catalysts for formic acid electro-oxidation were evaluated in deaerated 0.5 mol L<sup>-1</sup> HCOOH + 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> by LSV with a scan rate of 50 mV s<sup>-1</sup> at 25 °C, as shown in Figure 4. It can be observed that the onset oxidation potential of formic acid on Pd/C catalyst is about -0.12 V, and there is a main anodic peak located at about 0.22 V. However, the onset oxidation potentials of formic acid on PdIr/C catalysts are almost the same, -0.17 V, which is about 50 mV more negative than that at the Pd/C catalyst. And the anodic peaks of PdIr/C-7, PdIr/C-5 and PdIr/C-3 are located at 0.17 V, 0.14 V and 0.135 V, which are about 50 mV, 80 mV and 85 mV more negative than that at the Pd/C catalyst, respectively. Moreover, the PdIr/C catalysts show higher FAEO current densities than that of the Pd/C catalyst. The FAEO current densities (mass activity of PdIr, in Fig. 4(a)) at 0.14 V of Pd/C, PdIr/C-7, PdIr/C-5, PdIr/C-3 catalysts are 1189, 1317, 1628 and 1470 mA  $mg_{PdIr}^{-1}$ , respectively. The utilization of Pd in each prepared catalysts was also calculated and presented in Figure 4(b). It can be observed that the mass activities of Pd at 0.14 V of Pd/C, PdIr/C-7, PdIr/C-5, PdIr/C-3 catalysts are 1189, 1505, 1954 and 1911 mA  $mg_{Pd}^{-1}$ , respectively. The enhanced FAEO on PdIr/C catalysts can be explained by the small particle size with good dispersion of PdIr NPs and the addition of Ir. Although the main pathway of FAEO on Pd is through direct oxidation to  $CO_2$ , trace amount of CO intermediates may still be generated through dehydration pathway (HCOOH<sub>ads(Pd)</sub>  $\rightarrow$  $CO_{ads(Pd)} + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$ ) and then poison the catalysts.<sup>23</sup> And the CO-stripping CVs of Pd/C, Ir/C and PdIr/C reported by Wang et al.24 showed that CO could not be adsorbed on the Ir surface and small amount of Ir in the Pd lattice could significantly decrease the adsorption strength of CO on Pd. So, Ir can promote



**Fig. 4.** Linear sweeping votammograms of the prepared Pd/C and PdIr/C catalysts in an Ar-saturated solution of 0.5 mol  $L^{-1}$  H<sub>2</sub>SO<sub>4</sub> containing 0.5 mol  $L^{-1}$  HCOOH at a scan rate of 50 mV s<sup>-1</sup> at 25 °C.

the oxidation of formic acid on Pd because Ir can modify the electronic structure of Pd and decrease the adsorption strength of CO. In addition, the PdIr/C-5 catalyst showed the highest catalytic activity, even to the PdIr/C-7 and PdIr/C-3 catalysts. The PdIr/C-7 catalyst has low content of Ir, resulting in low promotion of Ir to Pd. The PdIr/C-3 catalyst has high content of Ir, while the catalytic activity is decreased. So, the suitable amount of Ir in PdIr/C catalyst is very important, and the optimized mass ratio of Pd to Ir from our experiments is 5:1.

### 4. CONCLUSIONS

In summary, we showed that the PdIr/C catalysts with small mean size and good dispersion of PdIr NPs were synthesized by a novel and facile chemical reduction method. The PdIr/C catalysts present lower onset and peak potentials and higher current densities of FAEO than that of the Pd/C catalyst. It can be attributed to that Ir could promote the FAEO on the Pd catalyst through the direct pathway. Moreover, with the optimal mass ratio of Pd to Ir, the PdIr/C-5 catalyst exhibits the best catalytic activity for FAEO. The lower cost and higher performance of PdIr/C catalyst make it a good choice for future DFAFC.

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