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Anodic oxidation of formic acid on PdAuIr/C-Sb_2O_5·SnO_2 electrocatalysts prepared by borohydride reduction

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Abstract: PdAuIr/C-Sb_2O_5·SnO_2 electrocatalysts with Pd∶Au∶Ir molar ratios of 90∶5∶5, 70∶20∶10 and 50∶45∶5 were prepared by borohydride reduction method. These electrocatalysts were characterized by EDX, X-ray diffraction, transmission electron microscopy and the catalytic activity toward formic acid electro-oxidation in acid medium investigated by cyclic voltammetry (CV), chroamperometry (CA) and tests on direct formic acid fuel cell (DFAFC) at 100 ℃. X-ray diffractograms of PdAuIr/C-Sb_2O_5·SnO_2 electrocatalysts showed the presence of Pd fcc phase, Pd-Au fcc alloys, carbon and ATO phases, while Ir phases were not observed. TEM micrographs and histograms indicated that the nanoparticles were not well dispersed on the support and some agglomerates. The cyclic voltammetry and chroamperometry studies showed that PdAuIr/C-Sb_2O_5·SnO_2(50∶45∶5) had superior performance toward formic acid electro-oxidation at 25 ℃ compared to PdAuIr/C-Sb_2O_5·SnO_2(70∶20∶10), PdAuIr/C-Sb_2O_5·SnO_2(90∶5∶5) and Pd/C-Sb_2O_5·SnO_2 electrocatalysts. The experiments in a single DFAFC also showed that all PdAuIr/C-Sb_2O_5·SnO_2 electrocatalysts exhibited higher performance for formic acid oxidation in comparison with Pd/C-Sb_2O_5·SnO_2 electrocatalysts, however PdAuIr/C-Sb_2O_5·SnO_2(90∶5∶5) had superior performance. These results indicated that the addition of Au and Ir to Pd favor the electro-oxidation of formic acid, which could be attributed to the bifunctional mechanism (the presence of ATO, Au and Ir oxides species) associated to the electronic effect (Pd-Au fcc alloys).

Keywords: PdAuIr/C-Sb_2O_5·SnO_2 electrocatalysts; formic acid oxidation; fuel cell; borohydride reduction process
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Direct formic acid fuel cells (DFAFC) have been considered as promising power sources for portable electronic devices and electric vehicles in comparison with direct methanol fuel cell, since methanol is easy to penetrate through the Nafion® membrane causing the decrease in fuel cell performance and the use of methanol is not safe because it is a toxic, evaporable, and burnable compound. Furthermore, Pt, usually used as the anodic catalyst, is easily poisoned by CO[1,2].

Considering the electro-oxidation of formic acid, Pt and Pd electrocatalysts have commonly been used[3]. In the Pt electrocatalysts the formic acid oxidation occur mainly via an indirect path and the electrocatalyst is easily poisoned by the CO adsorbed at low potential. However, in the Pd electrocatalysts the oxidation happens via the direct pathway, where the formic acid is directly oxidized to CO_2[4,5]. By this way, the activity and durability of Pd catalysts still need substantially improvement. Consequently, the addition of co-catalysts such as Ir[6], Pb[7], Au[8], Co[9], P[10] and Ni[11] is yet necessary.

Chiou et al[12] showed that Au(10%)/[Pd/multi-walled carbon nanotube (MWCNTs) (1∶9)] catalyst had higher activity and better stability than Pd/MWCNTs electrocatalyst in formic acid electro-oxidation. This behavior was explained by a conversion of 100% of CO to CO_2. Nandenha et al[2] showed that a PdAu had better performance than that of Pd electrocatalyst toward formic acid electro-oxidation and this effect was explained by the electronic or alloying effects.

The Pd binary electrocatalysts has been suggested that the second atom could increase the adsorption of the active oxygen and the oxidation rate of the reaction. Thus, the use of PdIr electrocatalysts could be interesting since Ir has the ability of active oxygen and then increase the formic acid oxidation rate, which could be explained by the bifuntional mechanism[6].

Nandenha et al[4] showed that a PdIr/C-ATO (50∶50) electrocatalyst had superior performance toward formic acid electro-oxidation in comparison with Pd electrocatalyst. However, in this case, the highest catalytic activity of PdIr/C-ATO (50∶50) was related to the combination of the bifunctional mechanism and the electronic effect.

It is known from the literature that the addition of metal oxides such CeO_2, RuO_2, SnO_2 or ATO

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(antimony tin oxide-$Sb_2O_5 \cdot SnO_2$) into noble metal could also enhance the catalytic activity toward small organic molecule. Among the metal oxides, ATO exhibits a number of characteristics that make them interesting for catalytic studies such as the enhancement of electrical conductivity when compared to CeO_2, RuO_2 and SnO_2 oxides. The presence of ATO oxides in the electrocatalysts could favor the oxidation of CO_{ads} for CO_2 by the bifunctional mechanism[13~17].

Neto et al[18] showed that Pt nanoparticles supported on a physical mixture of carbon and ATO (Pt/C-ATO) were more active for ethanol electro-oxidation in acidic medium than Pt nanoparticles supported on ATO (Pt/ATO), carbon (Pt/C) or using physical mixtures of Pt/ATO plus Pt/C. The enhancement of activity of Pt/C-ATO electrocatalyst was attributed to Pt nanoparticles, ATO and carbon supports in close proximity.

Ayoub et al[19] showed a PtSn/C-ATO electrocatalysts more active for ethanol electro-oxidation than PtSn/C electrocatalyst. The experiments at 100 ℃ on a single DEFC showed that the power density of the cell using PtSn/C-ATO (90∶10) was nearly 100% higher than the one obtained using PtSn/C (50∶50). FT-IR measurements indicated that the addition of ATO to PtSn/C favors the formation of acetic acid as a product, while for PtSn/C acetaldehyde was the principal product formed. The aim of this work was to prepare PdAuIr/C-ATO electrocatalysts by the borohydride reduction process and to test these electrocatalysts for formic acid electro-oxidation in acidic medium by cyclic voltammetry, chronoamperometry and using a single DFAFC.

1 Experimental

PdAuIr/C-$Sb_2O_5 \cdot SnO_2$(20% of metals loading with Pd∶Au∶Ir atomic ratio of 90∶5∶5, 70∶20∶10 and 50∶45∶5) was prepared by borohydride reduction method using $HAuCl_4 \cdot 3H_2O$, $IrCl_3 \cdot 3H_2O$ and $Pd(NO_3)_2 \cdot 2H_2O$ as metal sources and sodium borohydride as reducing agent. As support a physical mixture of 85% Vulcan Carbon XC72 and 15% $Sb_2O_5 \cdot SnO_2$ was employed. Considering the borohydride process, the metal sources were dissolved in a mixture of water/2-propanol (50∶50, *V*/*V*), while the support of 85% Vulcan Carbon XC72 and 15% $Sb_2O_5 \cdot SnO_2$ was dispersed in the solution. The resulting mixture was submitted to an ultrasonic bath for 10 min after a solution of sodium borohydride was added under stirring in one portion at room temperature. Finally, the obtained solid was filtered, washed with water and dried at 70 ℃ for 2 h[20].

The electrocatalysts prepared were initially characterized by X-ray diffraction (XRD) analyses and these studies performed in a RigaKu Miniflex II diffractometer using Cu $K\alpha$ radiation source (λ = 0.154 06 nm). All diffractograms were recorded from $2\theta = 20°$ to 90° with a step size of 0.05° and a scan time of 2 s per step. After the XRD studies, the electrocatalysts were also characterized by Transmission Electron Microscopy (TEM) using a JEOL JEM-2100 electron microscope operated at 200 kV. Using this technique, the mean particle sizes were determined by counting more than 150 particles from different regions of each sample.

The cyclic voltammetry and chronoamperommetry measurements were carried out at room temperature using a Microquimica potentiostat. These studies were performed using working electrodes prepared by thin porous coating technique[2]. The reference electrode was a reversible hydrogen electrode (RHE) and the counter electrode was a Pt plate. The electrochemical measurements were realized in presence of 0.5 mol/L H_2SO_4 or 1.0 mol/L formic acid + 0.5 mol/L H_2SO_4 solutions saturated with N_2.

Direct formic acid fuel cell tests were performed using PdAuIr/C-$Sb_2O_5 \cdot SnO_2$ electrocatalysts as anode and Pt/C electrocatalysts as cathode with an area of 5 cm^2. A carbon-cloth teflon-treated was also used as gas diffusion layer and a Nafion 117® membrane as electrolyte. First to use, the prepared electrodes containing 1 mg (Pd)/cm^2 in the anode and 1 mg(Pt)/cm^2 in the cathode were hot pressed on both sides of a Nafion® 117 membrane at 100 ℃ for 2 min under a pressure of 22.06 MPa. The fuel cell temperature was set to 100 ℃ and the oxygen humidifier to 80 ℃. The formic acid aqueous solution in 8 mol/L was delivered at approximately 1 mL/min and the oxygen flow was set to 500 mL/min under 0.2 MPa of pressure.

2 Results and discussion

The X-ray diffractograms of Pd/C-ATO and PdAuIr/C-ATO electrocatalysts are shown in Figure 1. Pd/C-ATO and PdAuIr/C-ATO electrocatalysts show a broad peak at about $2\theta = 25°$ associated to the carbon support material. The peaks at about $2\theta = 40°$, 47°, 68° and 82° are characteristic of the face-centered cubic (fcc) structure of metallic Pd or Pd alloys and those at about $2\theta = 27°$, 34°, 38°, 52°, 55°, 62°, 65° and 66° are characteristic of ATO which is also used as support.

All PdAuIr/C-ATO electrocatalysts show a shift

to smaller angles of the peak associated to the (220) plane compared to Pd/C-ATO electrocatalyst with increasing Au content. This result is an indicative of the insertion of Au in the Pd structure. PdAuIr/C (70∶20∶10) and (50∶45∶5) electrocatalysts indicate separated Pd-rich (fcc) and Au-rich (fcc) phases about $2\theta = 38°$ and 40°, respectively. This result was also observed by Nandenha et al[2] for PdAu/C-ATO electrocatalysts prepared by borohydride reduction process.

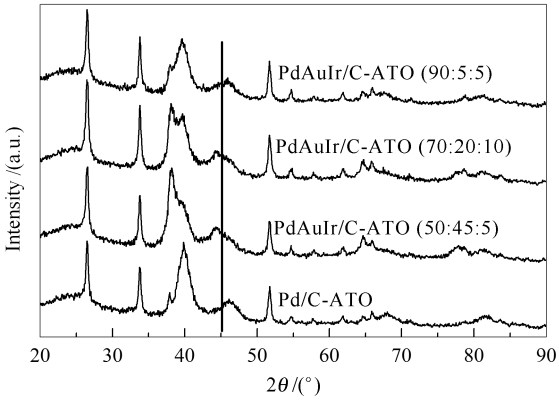

Figure 1　X-ray diffractograms of the Pd/C-ATO and PdAuIr/C-ATO electrocatalysts

For all PdAuIr/C-ATO materials, neither evidences of the insertion of Ir in the Pd structure nor peak related to Ir are observed. However, the presence of Ir oxides in small amounts and in amorphous forms cannot be discarded. Nandenha et al[4] showed that PdIr/C-ATO (50∶50) electrocatalyst had a shift to higher angles of the peak associated to the (220) plane compared to Pd/C-ATO, indicating the insertion of Ir in the Pd structure. However, for all PdIr/C-ATO no peak related to Ir was observed. The experimental compositions of all PdAuIr/C materials using the EDS analysis were 94∶3∶3 (nominal 90∶5∶5), 68∶25∶7 (nominal 70∶20∶10) and 59∶38∶3 (nominal 50∶45∶5). As can be seen these results confirmed a presence of iridium.

TEM micrographs and histograms of the particle size distributions of Pd/C-ATO and PdAuIr/C-ATO electrocatalysts are shown in Figure 2. All images indicate that the nanoparticles are not well dispersed on the support and some agglomerates are present. A monomodal is prepared for all electrocatalysts and relatively broad distribution of particle sizes are also observed for all electrocatalysts. The mean particle sizes of Pd/C-ATO, PdAuIr/C-ATO (90∶5∶5), PdAuIr/C-ATO (70∶20∶10) and PdAuIr/C-ATO (50∶45∶5) electrocatalysts are 6.40, 7.43, 8.26 and 8.53 nm, respectively. By these results, the increase of Au content in PdAuIr/C electrocatalysts results in an increase of the mean particle size, which is in accordance with the observation by Brandalise et al[21], who also observed an increase of the mean particle size with the increase of Au content in PdAu/C electrocatalysts. This effect is explained in the following manner: Au is nobler than Pd and it is reduced initially forming Au seeds with Pd growing epitaxially on its surface rather than forming a new nucleus[21,22].

The cyclic voltammograms of Pd/C-ATO and PdAuIr/C-ATO electrocatalysts in 0.5 mol/L H_2SO_4 solution are shown in Figure 3. All electrocatalysts prepared show a well-defined hydrogen adsorption-desorption region (peaks in the range of 0.05 to 0.35 V vs RHE). For PdAuIr/C-ATO electrocatalysts clear shifts of the peaks positions for the hydrogen adsorption-desorption are observed in comparison with Pd/C-ATO, which is an indication of the electronic modification of Pd atoms by Au. For PdAuIr/C-ATO (50∶45∶5) and PdAuIr/C-ATO (70∶20∶10) an increase in the current values in the double layer (0.4 ~ 0.8 V) is observed in comparison with Pd/C-ATO. This behavior has been related as characteristic of binary and ternary electrocatalysts[23]. The capacitance increase could also be explained by the presence of Au or Ir for providing OH and O species at less positive potential[24]. However, this effect is most pronounced at PdAuIr/C-ATO (50∶45∶5) due to the existence of a greater amount of adsorbed oxygen species related to the highest Au content.

Figure 4 indicates the cyclic voltammograms of Pd/C-ATO and PdAuIr/C-ATO electrocatalysts recorded at 25 ℃ in the presence of 1.0 mol/L formic acidic in 0.5 mol/L H_2SO_4. All PdAuIr/C-ATO electrocatalysts show higher current values in all potential range when compared with Pd/C-ATO. PdAuIr/C-ATO (50∶45∶5) electrocatalyst indicate the highest current values in all potential range in comparison with PdAuIr/C-ATO (70∶20∶10) and PdAuIr/C-ATO (90∶5∶5). The highest current values observed for PdAuIr/C-ATO electrocatalyst could be associated to the electronic effect due to the proximity of Au, Ir and Pd atoms on the surface of the C-ATO. The electro-oxidation of formic acid on PdAuIr/C-ATO electrocatalysts could also occur in the direct pathway, where formic acid is directly oxidized to CO_2.

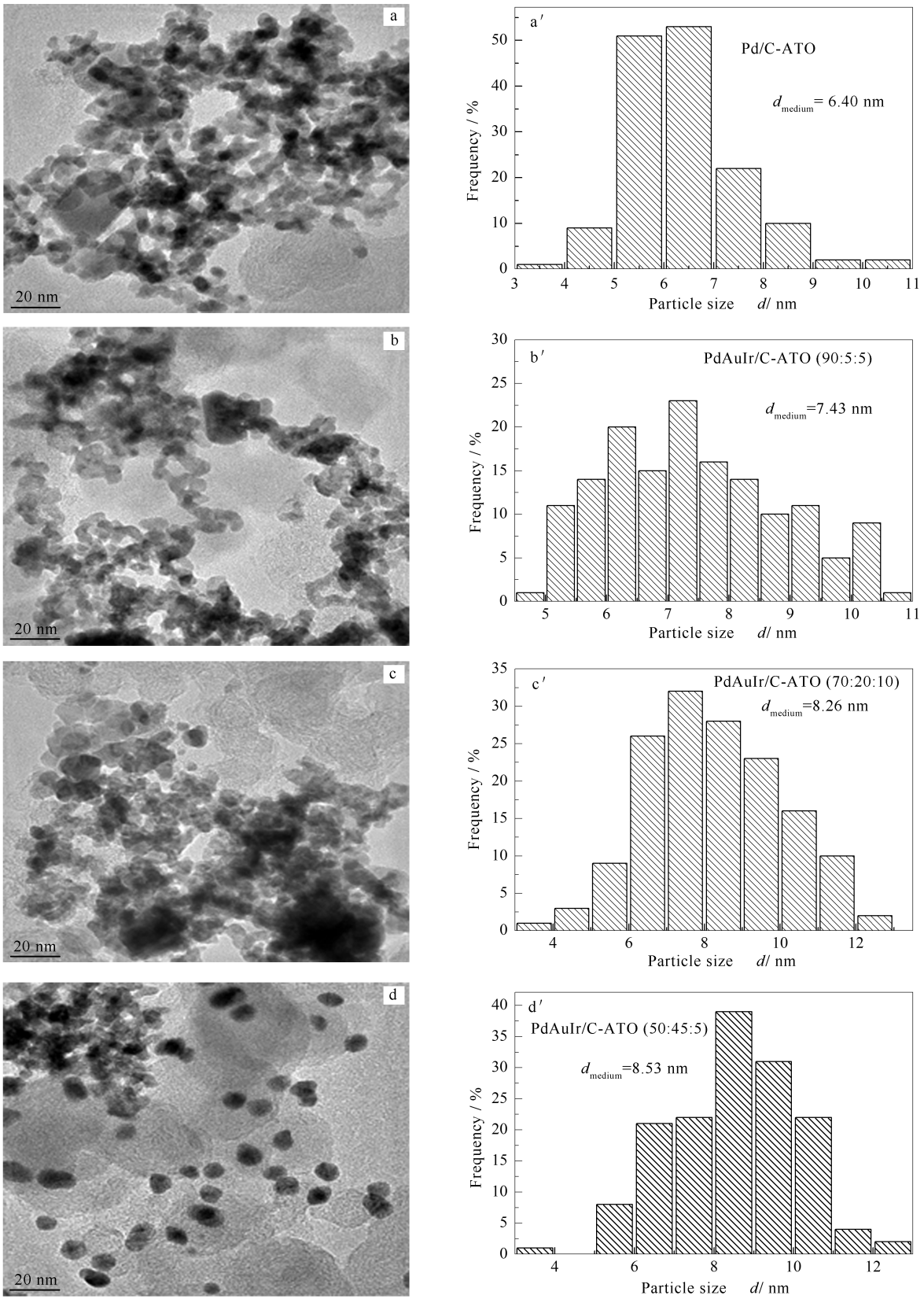

Figure 2 TEM micrographs and histograms of Pd/C-ATO (a,a′), PdAuIr/C-ATO (90∶5∶5) (b,b′), PdAuIr/C-ATO (70∶20∶10) (c,c′), and PdAuIr/C-ATO (50∶45∶5) (d,d′) electrocatalysts with the mean diameter and particle distribution

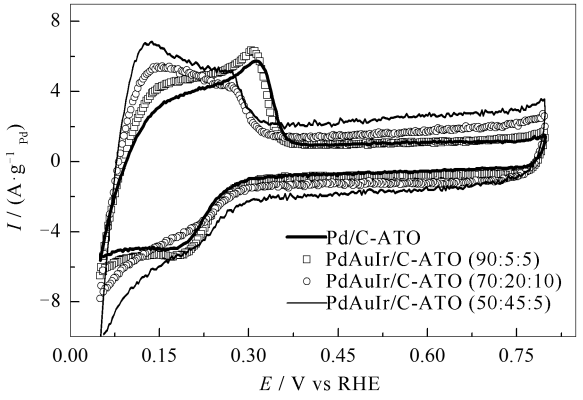

Figure 3　Cyclic voltammograms of Pd/C-ATO and PdAuIr/C-ATO electrocatalysts in 0.5 mol/L H_2SO_4 solution with a sweep rate of 10 mV/s

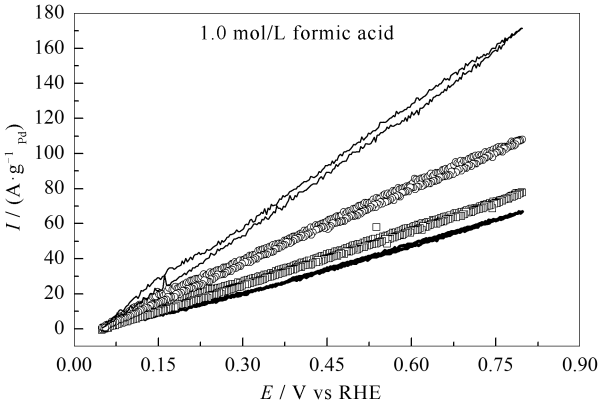

Figure 4　Cyclic voltammograms of the Pd/C-ATO and PdAuIr/C-ATO electrocatalysts in 1.0 mol/L formic acid solution and 0.5 mol/L H_2SO_4, solution with a sweep rate of 10 mV/s at 25 ℃
——: Pd/C-ATO; □: PdAuIr/C-ATO(90∶5∶5);
○: PdAuIr/C-ATO(70∶20∶10);
——: PdAuIr/C-ATO(50∶45∶5)

Figure 5 shows the current-time curves of formic acidic electro-oxidation for Pd/C-ATO and PdAuIr/C-ATO electrocatalysts at 25 ℃ in the potential of 0.5 V for 30 min. All electrocatalysts prepared disply a pronounced current decay in the first 1 min, which could be explained by the accumulation of poisonous intermediates. The final current values at 0.5 V (t= 25 ℃) increase in the following order: PdAuIr/C-ATO (50∶45∶5) > PdAuIr/C-ATO (70∶20∶10) > PdAuIr/C-ATO (90∶5∶5) > Pd/C-ATO. The activity of all PdAuIr/C-ATO electrocatalysts is higher than the Pd/C-ATO, confirming that the activity and stability of Pd could be improved due to the co-presence of Au and Ir. The electronic modification of Pd might be the possible reason for the enhanced activity, as the proximity of Au or Ir and Pd atoms on the surface of the C-ATO. However, the higher catalytic activity of PdAuIr/C-ATO electrocatalysts could be attributed to the synergism among the constituents of the electrocatalyst.

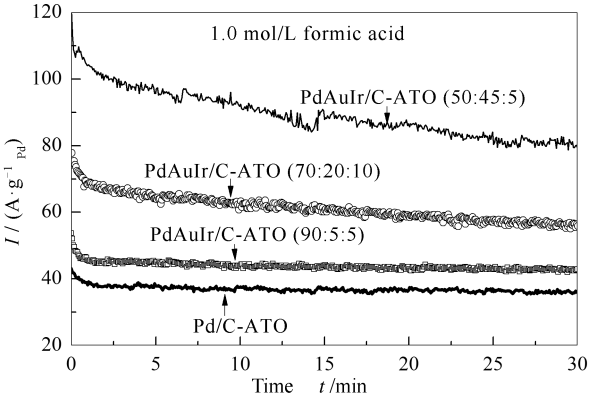

Figure 5　Current-time curves at 0.5 V in presence of 1.0 mol/L formic acid solution and 0.5 mol/L H_2SO_4 solution for Pd/C-ATO and PdAuIr/C-ATO electrocatalysts at 25 ℃

Figure 6 shows the performance of a single DFAFC using Pt/C, Pd/C-ATO and PdAuIr/C-ATO electrocatalysts as anode. PdAuIr/C-ATO (90∶5∶5) electrocatalyst indicates the highest value of maximum power density (94 mW/cm^2) in comparison with the other PdAuIr/C-ATO (50∶45∶5 and 70∶20∶10 with power density values of 67 mW/cm^2 and 63 mW/cm^2, respectively) and Pd/C-ATO (56 mW/cm^2).

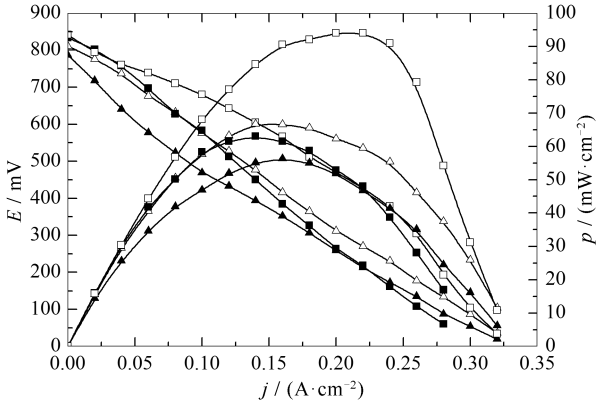

Figure 6　Curves (I-V) and the power density at 100 ℃ using Pd/C-ATO and PdAuIr/C-ATO electrocatalysts
▲: Pd/C-ATO; △: PdAuIr/C-ATO(50∶45∶5);
■: PdAuIr/C-ATO(70∶20∶10);
□: PdAuIr/C-ATO(90∶5∶5)

The experiments on single DFAFC show that the addition of Au and Ir into Pd/C-ATO electrocatalyst promotes the activity toward formic acidic electro-oxidation in accordance with electrochemistry experiments. Nandenha et al[2] showed for PdAu/C-ATO electrocatalysts a maximum power density of 61 mW/cm^2. However, for a Pt/C electrocatalyst

used for comparison, it showed a maximum power density of 30 mW/cm^2, indicating that the combination of palladium and C-ATO for formic acid electro-oxidation was more appropriated than pure platinum.

The highest catalytic activity of PdAuIr/C-ATO could be attributed to the synergism among the constituents of the electrocatalyst (metallic Pd, Au, Ir and ATO). In the presence of ATO, golden and iridium oxides could also enhance the formation of chemisorbed oxygen species, which promotes the oxidation of adsorbed carbon monoxide on the surface of Pd. However, the electronic effect of Au donating electrons to the *d*-band of Pd also should be considered[2,12].

3 Conclusions

The borohydride reduction method in single step was an efficient process to produce an activity PdAuIr/C-ATO electrocatalyst for formic acid electro-oxidation.

PdAuIr/C-ATO (70∶20∶10 and 50∶45∶5) electrocatalysts showed the presence of PdAu (fcc) alloys, a segregated fcc Pd-rich, Au-rich phases and ATO oxide phases. All PdAuIr/C-ATO prepared did not show peaks related to Ir, however, the presence of Ir was confirmed by EDX analysis.

All PdAuIr/C-ATO electrocatalysts exhibited superior performance toward formic acid electro-oxidation in comparison with Pd/C-ATO. The highest catalytic activity of PdAuIr/C-ATO seems to be related to the combination of the bifunctional mechanism and the electronic effect. Nevertheless, further work is now necessary to investigate the surface of these materials and the mechanism of formic acid electro-oxidation using these electrocatalysts.

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