

# Ethanol electrooxidation on PdIr/C electrocatalysts in alkaline media: electrochemical and fuel cell studies

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**Abstract** PdIr/C electrocatalysts in different atomic ratios (Pd:Ir 90:10, 70:30, and 50:50), Pd/C and Ir/C supported on Vulcan XC 72 carbon were tested for ethanol electrooxidation in alkaline media. The electrocatalysts were prepared by borohydride reduction method. The electrocatalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), cyclic voltammetry (CV), and chronoamperometry (CA). The XRD measurements suggested the PdIr alloy formation. EDS analyses showed the real atomic ratios similar to the nominal ones. TEM showed the average particle diameter between 4.6 and 5.8 nm for all compositions prepared. The catalytic activity for ethanol electrooxidation in alkaline medium investigated by CV and CA at room temperature showed that PdIr/C (90:10) exhibited higher performance for ethanol oxidation in comparison with others PdIr/C compositions, Pd/C and Ir/C, while the experiments on a single direct ethanol alkaline fuel cell at 70 °C showed higher performance for PtIr (70:30). The best results obtained using PdIr/C electrocatalysts may be associated to the electronic effect between Pd and Ir that might cause a decrease of poisoning on catalyst and the occurrence of bifunctional mechanism.

**Keywords** Direct ethanol alkaline fuel cell · PdIr/C · Electrocatalysts

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## Introduction

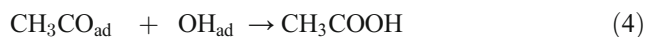
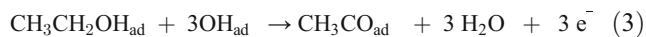
Alkaline fuel cells have recently attracted worldwide attention since it is low-cost, low corrosive, and is promising to be a clean and efficient energy production technology [1, 2]. Direct alkaline alcohol fuel cells (DAAFCs) could offer an excellent alternative solution to the current energy generation problems and could confer major improvements in the prospects for an economy based on renewable energy sources [3]. Furthermore, DAAFCs have some advantages in comparison with proton exchange membrane fuel cells (PEMFC), since the kinetics of the oxygen reduction reaction (ORR) is more facile and the less corrosive nature of an alkaline environment ensures a potential greater longevity [4–6].

Among the alcohols used as fuels, ethanol has been recognized as the most promising since it has a high energy density (8.0 kWh kg<sup>-1</sup>), rather low toxicity and can be obtained from biomass [7–9]. However, the high efficiency of the ethanol oxidation reaction (EOR) is still a significant goal because the cleavage of C–C bonds for the complete oxidation of ethanol to CO<sub>2</sub> (yielding 12 e<sup>-</sup> per ethanol molecule) requires the use of more active and selective anode catalysts [8, 10–13]. Thus, the main product of this reaction is acetaldehyde and acetate [14, 15].

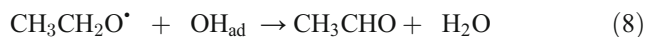
The ethanol oxidation reactions in alkaline media could be performed by parallel pathways that produces acetate (steps 1, 2, 3, 4, and 5) [16], acetaldehyde (steps 6, 7, and 8) [17], or CO<sub>2</sub> (9). However, the last pathway involves the reaction of poisoning species CO<sub>ad</sub> with OH<sub>ad</sub>/OH<sup>-</sup> species that in alkaline media produces carbonate [16]; additionally, the steps involving C–C break bond to produce CO<sub>2</sub> in alkaline media are not well established in the literature.

Path to acetate:

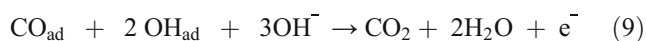




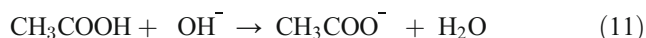
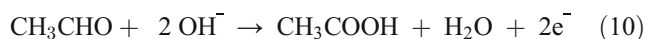
Path to acetaldehyde:



Path to  $\text{CO}_2$ :



However, it is also proposed that acetaldehyde is a key reaction to form acetic acid which exists as an acetate anion in alkaline media (steps 10 and 11) [17].



Palladium is recognized as the most efficient material for the EOR in alkaline media; moreover, Pd is more abundant in nature than Pt, and thus the catalyst cost can be substantially reduced [18]. Conversely to ethanol oxidation in acid media, in alkaline media the EOR activity of Pd is remarkably higher than that of Pt [6]. Nevertheless, both the catalytic activity and stability of Pd for the EOR in alkaline media need to be further enhanced [18]. Therefore, in order to improve the electrocatalytic activity and stability of Pd for EOR, some binary

electrocatalysts such as PdAu/C, PdSn/C, PdRu/C, PdIr/C, and others have been proposed [15, 18, 19].

Taking into account the EOR, iridium is recognized as an element that improves the stability and the electrocatalytic activity when combined to binary and ternary platinum-based catalysts [7, 8, 20]. The addition of Ir to Pd improves the ethanol oxidation reaction in alkaline media. The onset potential on the PdIr/C catalysts is much more negative for the mentioned reaction in alkaline media with respect to that on Pd/C [18]. Additionally, Ir addition can significantly improve the ethanol oxidation kinetics on Pd in alkaline media as reported by Shen et al. [18].

Aiming the improvement of direct ethanol fuel cells in alkaline media, this work contemplates a study considering electrochemical (cyclic voltammetry and chronoamperometry) and also fuel cells experiments using PdIr/C electrocatalysts prepared in different atomic ratios as work electrodes/anodes of a single fuel cell. The PdIr/C materials were prepared by the borohydride reduction process and supported on Vulcan XC 72 carbon.

## Material and methods

Pd/C and PdIr/C electrocatalysts (20 wt% of metals loading and Pd:Ir atomic ratios of 90:10, 70:30, and 50:50) were prepared by borohydride reduction using  $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (Fluka) and  $\text{IrCl}_3$  (Sigma-Aldrich) as metal sources, Vulcan XC72 as support, and sodium borohydride as reducing agent. In this method, the Vulcan XC72 was firstly dispersed in an isopropyl alcohol/water solution (50/50, v/v), after the mixture, the resulting solution was homogenized under stirring and then the metal sources were added and put on an ultrasonic bath for 5 min; finally, a solution of sodium borohydride into  $0.1 \text{ mol L}^{-1}$  KOH was added in one portion under stirring at room temperature and the resulting solution was maintained under stirring for 15 min more. Afterwards, the final mixture was filtered and the solids washed with water and then dried at  $70^\circ\text{C}$  for 2 h.

PdIr/C electrocatalysts were characterized by XRD analyses using a Rigaku diffractometer model Miniflex II using  $\text{CuK}\alpha$  radiation source ( $\lambda=0.15406 \text{ nm}$ ). The diffractograms were recorded from  $2\theta=20^\circ$  to  $90^\circ$  with a step size of  $0.05^\circ$  and a scan time of 2 s per step. The atomic ratios of Pd and Ir in the synthesized materials were measured by energy dispersive spectroscopy (EDS) by using a JEOL JSM6010 LA equipment and TEM analysis were carried out using a JEOL JEM-2100 electron microscope operated at 200 kV, where the morphology, distribution, and size of the nanoparticles in the support were determined. The mean particle sizes were determined by counting more than 100 particles from different regions of each sample [21].

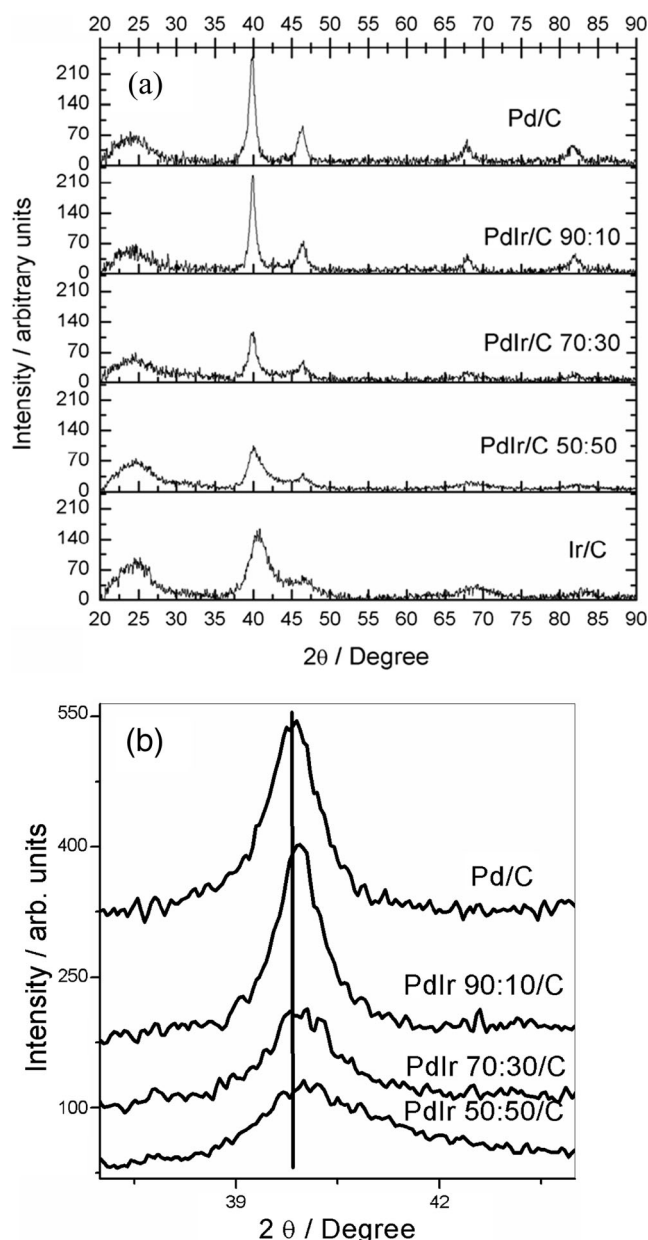
A Potentiostat/galvanostat PGSTAT 30 was employed for the electrochemical measurements, where a conventional three-electrode electrochemical cell was used. In this cell, a platinum electrode and an Ag/AgCl (3 mol L<sup>-1</sup> KCl) were used as the counter and reference electrodes, respectively. The work electrodes (geometric area of 0.5 cm<sup>2</sup> with a depth of 0.3 mm) were prepared using the thin porous coating technique [22]. The initial characterizations were made using CV, being these experiments conducted at a scan rate of 10 mV s<sup>-1</sup> in 1 mol L<sup>-1</sup> KOH aqueous solution in the presence and absence of 1 mol L<sup>-1</sup> ethanol. The amperometric curves (I-T) were recorded in the same electrolyte containing ethanol at -0.35 V for 1800 s.

The direct ethanol alkaline fuel cell took place in a single cell with an area of 5 cm<sup>2</sup>. The temperature was set to 70 °C for the fuel cell and 85 °C for the oxygen humidifier. All electrodes contained 2 mg of metal per cm<sup>2</sup> in the anode or in the cathode. In all experiments, Pt/C BASF was used as cathode. The electro catalyst was painted over carbon cloth in the form of a homogeneous dispersion prepared using Nafion<sup>®</sup> solution (5 wt%, Aldrich). After the preparation, the electrodes were hot pressed on both sides of a Nafion<sup>®</sup> 117 membrane at 125 °C for 3 min under a pressure of 247 kgf cm<sup>-2</sup>. Prior to use, the membranes were exposed to KOH 6 mol L<sup>-1</sup> for 24 h as already mentioned before [23]. The direct ethanol alkaline fuel cell experiments were realized in the presence of 2.0 mol L<sup>-1</sup> C<sub>2</sub>H<sub>5</sub>OH and 2.0 mol L<sup>-1</sup> KOH. The fuel was delivered at 1.0 mL min<sup>-1</sup> and the oxygen flow was regulated at 150 mL min<sup>-1</sup>. Polarization curves were obtained by using a potentiostat/galvanostat PGSTAT 302 N Autolab.

## Results and discussion

The XRD patterns of the PdIr/C, Pd/C, and Ir/C electrocatalysts are shown in Fig. 1a. The diffraction peaks at about 2θ=40, 46, 68, and 82° on the Pd/C patterns are attributed to Pd (111), (200), (220), (311), crystalline planes, respectively, indicating a typical face-centered cubic (fcc) crystalline structure of Pd [24]. The diffraction peaks at around 2θ=40, 47, 68, and 82° on Ir/C are ascribed to Ir (111), (200), (220), and (311) crystalline planes, respectively, representing the characteristic diffraction of fcc crystalline structure of Ir [7]. It is also possible to be observed in all diffractograms a broad peak at about 25° associated with Vulcan XC72 support [25].

The diffraction peaks of binary PdIr/C materials are slightly shifted toward higher 2θ values with respect to those of Pd/C, indicating that some Ir atoms entered into Pd lattice and substitute Pd atoms, suggesting the PdIr alloy formation [18]. For clear observation, the magnified (111) peaks of the catalysts are shown in Fig. 1b. The characteristic peaks of IrO<sub>2</sub>



**Fig. 1** a X-ray diffraction patterns for the Pd/C, Ir/C, and PdIr/C electrocatalysts. b Magnified (111) peaks

at 2θ=34.5 and 54° [8] were not observed in all XRD patterns. However, the presence of IrO<sub>2</sub> in the amorphous oxides form cannot be discarded.

The real compositions of all PdIr/C materials obtained using the EDS analysis are in Table 1. As can be seen, the real atomic ratios of each PdIr/C catalysts in all compositions are close to nominal values in all cases.

TEM micrographs and histograms of particle mean diameter distribution for the Pd/C, PdIr/C, and Ir/C electrocatalysts are shown in Fig. 2. All electrocatalysts prepared showed particles well dispersed on carbon support. Only Ir/C and PtIr/C (70:30) electrocatalysts showed a small percentage of particles higher than 10 nm, with a maximum mean diameter

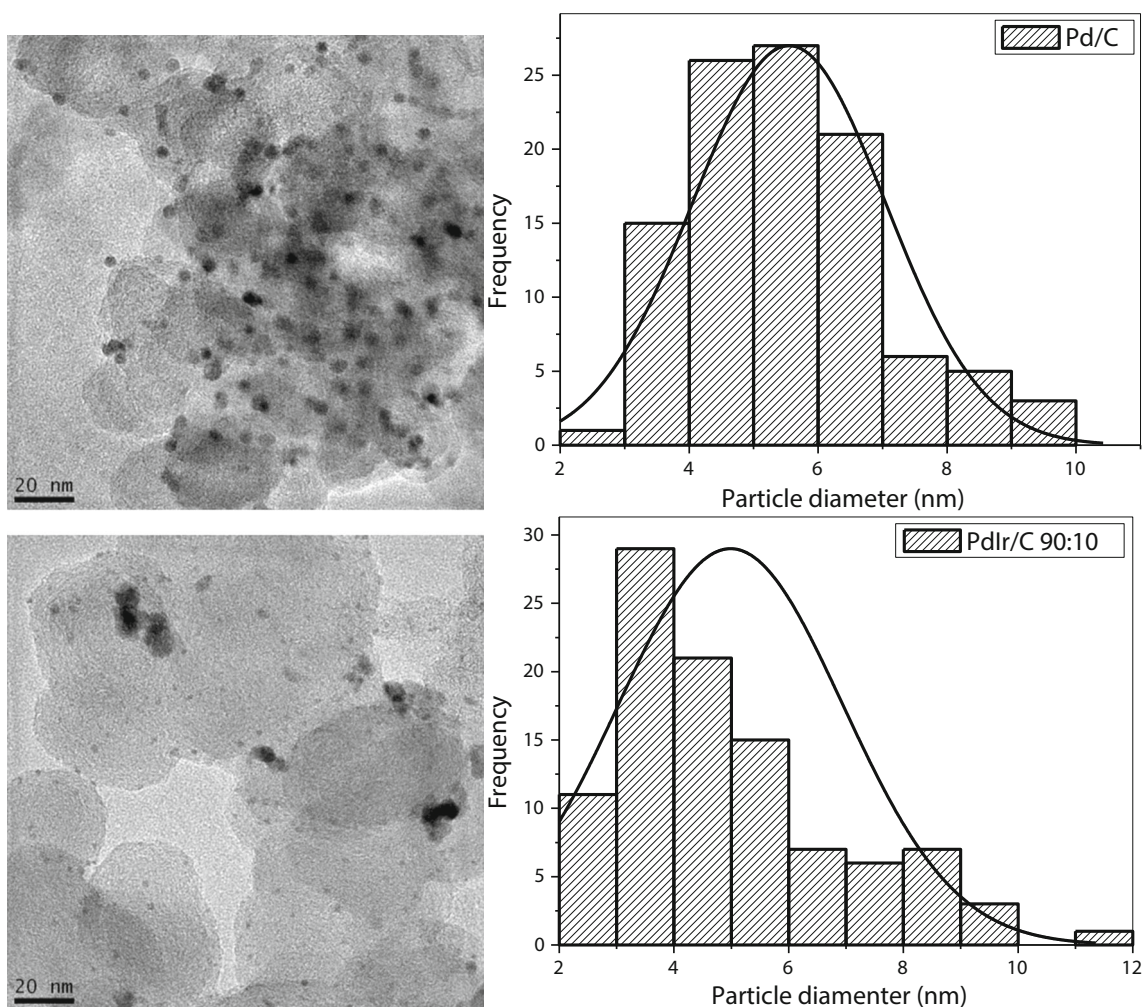
**Table 1** Atomic ratio of Pd:Ir and nanoparticles size

Catalyst	Nominal atomic composition (%)	EDS (%)	Mean particle size obtained with TEM
Pd/C	–	–	5.6
Pd <sub>9</sub> Ir <sub>1</sub> /C	90:10	91:09	5.3
Pd <sub>7</sub> Ir <sub>3</sub> /C	70:30	67:33	5.1
Pd <sub>5</sub> Ir <sub>5</sub> /C	50:50	52:48	4.6
Ir/C	–	–	5.8

of 20 and 16 nm, respectively. The mean particle sizes of the electrocatalysts are shown in Table 1.

The cyclic voltammograms of Pd/C, PdIr/C 90:10, PdIr/C 70:30, PdIr/C 50:50, and Ir/C in the presence of 1.0 mol L<sup>-1</sup> KOH solution are shown in Fig. 3. It is possible to observe the typical CV shape of Pd/C in alkaline media [15, 26]. The potential region from -0.85 to -0.50 is associated with hydrogen adsorption/desorption on the Pd surface [15]; in this region, it is possible to observe a small peak at about -0.53 V that is related to the OH adsorption in the hydrogen desorption region [26]. The potential region from -0.40 to 0.05 V is

related with the formation of palladium (II) oxide layer on the palladium surface [15]. During the reverse scan, a broad peak at about -0.344 V represents the reduction of palladium oxide layer [27]. The introduction of Ir into Pd/C leads to an increase in the voltammetric charge; this phenomena could be related to the reversible metal-oxide layers formed on Ir electrocatalysts surface during the anodic process [20]. Although in the XRD analyses the iridium oxides was not observed, its presence in small amounts and amorphous forms cannot be discarded, which can contribute to increasing of the double-layer charge of the catalysts.



**Fig. 2** TEM micrographs and histograms of the particle size distribution of Pd/C, PdIr/C (90:10), PdIr/C (70:30), PdIr/C (50:50), and Ir/C



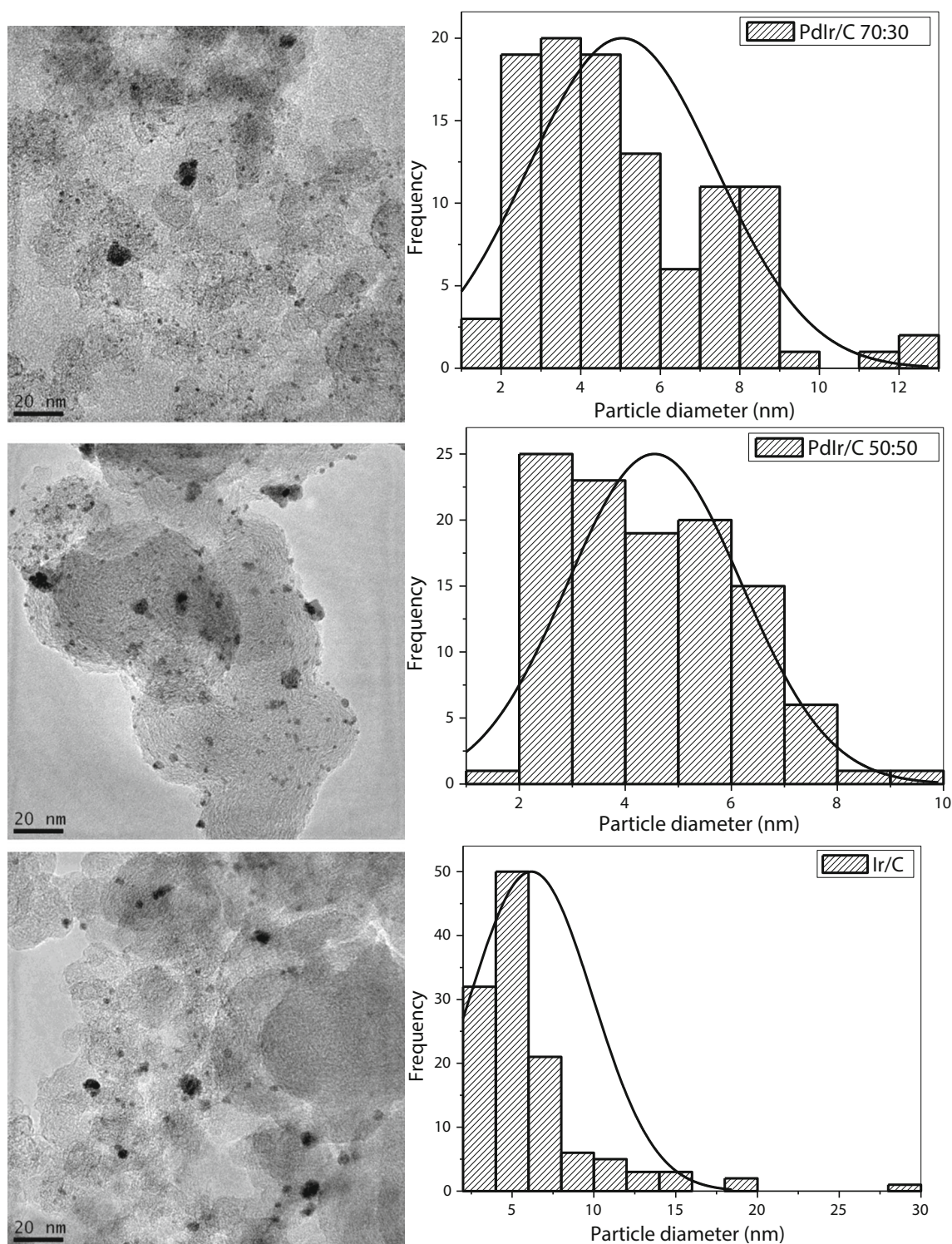
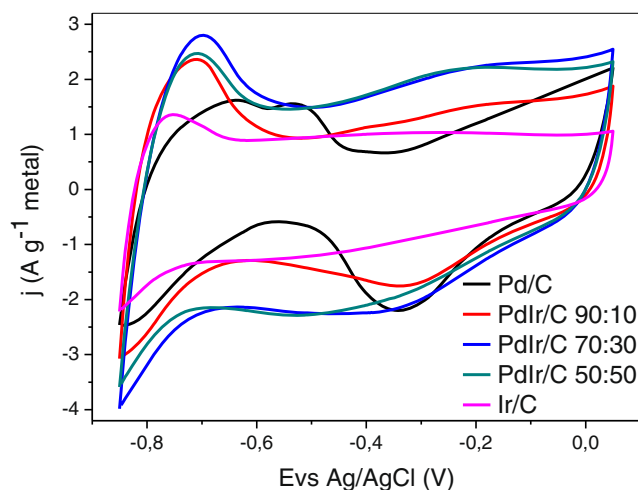


Fig. 2 (continued)

Figure 4 shows the CV of Pd/C, PdIr/C (90:10), PdIr/C (70:30), PdIr/C (50:50), and Ir/C in the presence of  $1.0 \text{ mol L}^{-1}$  of ethanol and in  $1.0 \text{ mol L}^{-1}$  KOH with a sweep rate of  $10 \text{ mV s}^{-1}$ . The CVs were normalized by the amount of metal in the electrocatalysts. PdIr/C (50:50) and PdIr/C (70:30) showed a better onset potential of  $-0.76 \text{ V}$  than

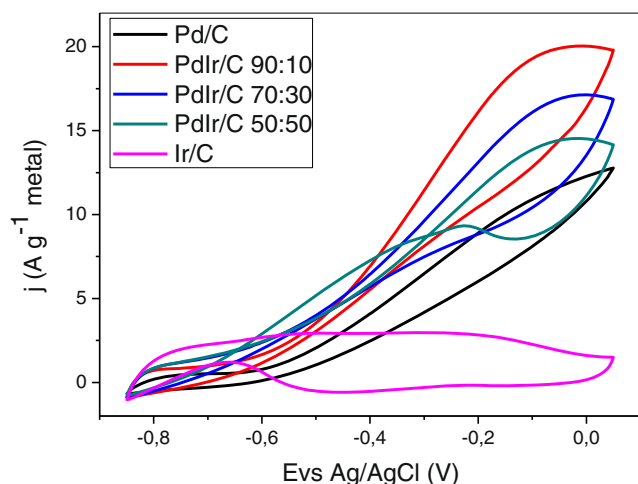
PdIr/C (90:10) and Pd/C ( $-0.69$  and  $-0.61 \text{ V}$ , respectively), while Ir/C electrocatalyst was virtually inactive toward ethanol oxidation. Shen et al. [18] showed that the introduction of Ir leads to an increase in the electroactivity of the binary electrocatalysts (PdIr) compared to pure Pd. This effect was explained by the activation of interfacial water molecules at



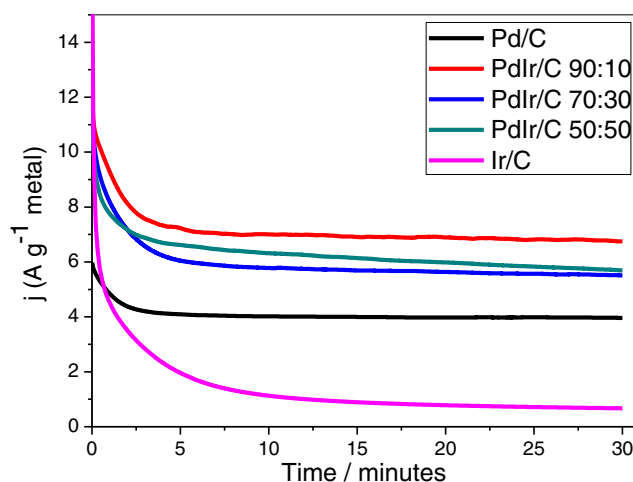
**Fig. 3** Cyclic voltammograms of Pd/C, PdIr/C (90:10), PdIr/C (70:30), PdIr/C (50:50), and Ir/C in 1.0 mol L<sup>-1</sup> KOH with a sweep rate of 10 mV s<sup>-1</sup>

lower potentials than in the case of pure Pd due to the presence of preferential sites for OH<sub>ads</sub> adsorption, where the presence of OH<sub>ads</sub> species is necessary for the complete oxidation of poisoning intermediates adsorbed, as the electronic modification of Pd might be another possible reasons for the enhanced activity.

The chronoamperometry curves for ethanol oxidation reaction on Pd/C, PdIr/C (90:10, 70:30, and 50:50), and Ir/C at potential of -0.35 V during 30 min are shown in Fig. 5. The highest current density measured for EOR was obtained using PdIr/C (90:10). The obtained final current density using PdIr/C (90:10) was about 18, 36, and 41 % higher than those obtained using PdIr/C (70:30), PdIr/C (50:50), and Pd/C, respectively. For CV experiments, Ir/C shows almost inactive toward ethanol oxidation. In all chronoamperometric curves, the current decreases continuously within the first minutes, and after some time, the fall is less pronounced. The current



**Fig. 4** Cyclic voltammograms of Pd/C, PdIr/C (90:10), PdIr/C (70:30), PdIr/C (50:50), and Ir/C in presence of 1.0 mol L<sup>-1</sup> KOH and 1.0 mol L<sup>-1</sup> ethanol with a sweep rate of 10 mV s<sup>-1</sup>

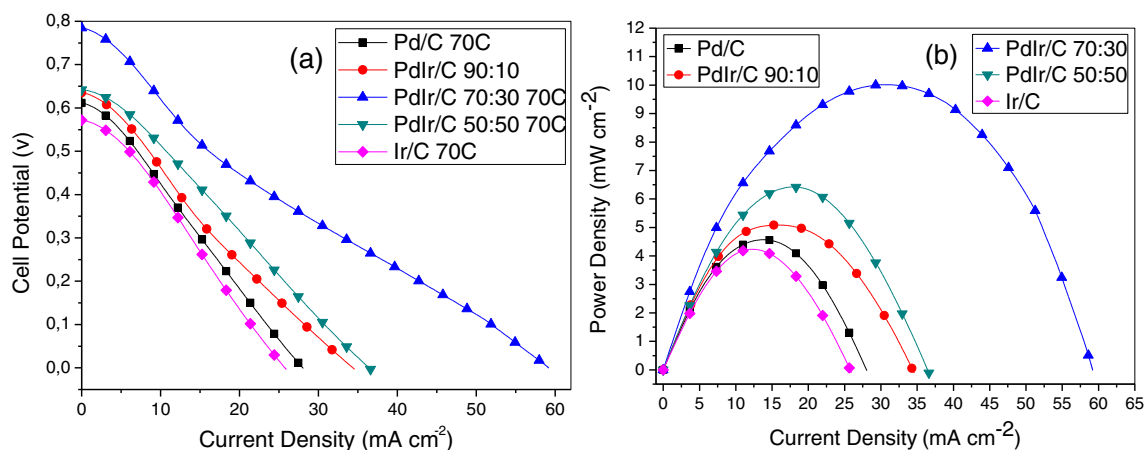


**Fig. 5** Current-time curves at -0.35 V in 1 mol L<sup>-1</sup> ethanol solution in presence of 1.0 mol L<sup>-1</sup> KOH for Pd/C, PdIr/C (90:10), PdIr/C (70:30), PdIr/C (50:50), and Ir/C at 25 °C

value may decay due to poisoning of surface active sites and instability of catalyst particles [8]. These effects decrease slowly the number of active sites and are responsible for the continuous and slow current time decay [8]. These results indicated an optimal composition between Pd and Ir. The optimal composition is commonly attributed as requires for the bifunctional mechanism occurrence and the electronic effect. Additionally, the optimal composition depends on of the electrocatalysts preparation method [8]. This occurs because there are differences between shapes, phases, dispersions, morphologies, and superficial phases, and these parameters can contribute either high or low coverage of the adsorption sites within the oxide [28, 29].

Shen et al. [18] showed that Pd<sub>7</sub>Ir/C catalyst had a lower polarization potential than Pd/C and with the increase in time, the potential difference becomes larger, indicating that Ir addition to Pd could facilitate the removal of the adsorbed ethoxi intermediates, hence releasing more active Pd sites for the EOR, and making it more resistant to poisoning. The best results obtained on chronoamperometry measurements using PdIr/C electrocatalysts compared to Pd/C might be associated to a disturbance at the Pd orbital symmetries caused by iridium atoms, thereby affecting the ethanol adsorption and, consequently, the electrooxidation rate, additionally promoting a lower poisoning of adsorbed species, as recently proposed for PtIr/C and IrPtSn/C in the case of ethanol oxidation in acid medium [7, 8, 20].

Figure 6 shows the performances of a single DAAFC operating at 70 °C with Pd/C, PdIr/C (90:10), PdIr/C (70:30), PdIr/C (50:50), and Ir/C as anode electrocatalysts and Pt/C BASF as cathode in all experiments. From this figure, it is possible to be observed that the open circuit voltage of the fuel cell for Pd/C, PdIr/C (90:10), PdIr/C (70:30), PdIr/C (50:50), and Ir/C were 0.61, 0.63, 0.78, 0.64, and 0.57 V, respectively. Furthermore, PdIr/C (70:30) showed



**Fig. 6**  $I$ - $V$  curves (a) and the power density (b) at 70 °C of a 5 cm<sup>2</sup> DAAFC using Pd/C, PdIr/C (90:10), PdIr/C (70:30), PdIr/C (50:50), and Ir/C electrocatalysts

higher values of maximum power density (10.0 mW cm<sup>-2</sup>), in comparison with PdIr/C (50:50, 6.4 mW cm<sup>-2</sup>), PdIr/C (90:10, 5.1 mW cm<sup>-2</sup>), Pd/C (4.6 mW cm<sup>-2</sup>), and Ir/C (4.2 mW cm<sup>-2</sup>). Moreover, the power density obtained using PdIr/C (70:30) electrocatalyst was about two times higher than the obtained using Pd/C.

The results on single DAAFC show the PdIr/C (70:30) as the best material toward ethanol oxidation reaction. This result do not means with that one obtained in electrochemical experiments which indicate the PdIr/C (90:10) as the best material. Despite the higher activity of PdIr/C (90:10) as observed at chronoamperometry experiments carried out at room temperature, the same behavior is not confirmed in the experiments realized under real operational conditions at 70 °C. The disagreement of electrochemical experiments results with direct ethanol fuel cell results were also reported in other works in the literature [15, 20, 30]. This probably could be associated to the different temperature of the experiments, since the ethanol energy activation changes with temperature, and these changes are not the same for deferent electrocatalysts compositions [31]. Additionally, the fuel cell experiments are quite different from electrochemical experiments, such as diffusion through the catalytic layer and durative constant flux.

The better results obtained using PdIr/C binary composition compared to Pd/C and Ir/C might be associated with the electronic effect generated between Pd and Ir. The electronic effect might be associated with the effect generated between two metals in close contact (alloy), since upon contact of two metals of different work functions, charge will be transported from one metal to another until the Fermi level of electrons at the interface is equilibrated [25, 32]. The work function of Pd is 5.2 eV and the Ir is 5.1 eV [25], thereby charge is transported from Ir to Pd. The changes in the electron state of Pd when

alloyed with Ir might causes weakening metal-CO<sub>ad</sub> bond strength leading to a decrease on the electro catalyst surface poisoning.

Additionally, the bifunctional mechanism could be contributing for the ethanol electrooxidation. This mechanism can be explained by the activation of the interfacial water molecules at lower potential on Ir surface than on Pd surface (as proposed to PtIr) due the preferential sites for -OH adsorption on Ir [20]. The presence of -OH species in large amounts is necessary for the complete oxidation of poisoning intermediates species like CO<sub>ad</sub> [20]. Therefore, the ethanol electrooxidation occurs at lower potential values [33].

## Conclusion

Borohydride process showed to be an efficient method to prepare PdIr/C electrocatalysts for ethanol electrooxidation in alkaline media. PdIr/C diffractograms showed four peaks in  $2\theta=40, 47, 68,$  and  $82^\circ$ , which are associated with the (111), (200), (220), and (311) planes, characteristic of Pd fcc and the formation of an alloy between Pd and Ir. Using PdIr/C (70:30) electrocatalyst as anode in the direct ethanol fuel cell, the highest power density (10.0 mW cm<sup>-2</sup>) and open circuit voltage (0.78 V) were obtained. While in the electrochemistry experiments, PdIr/C (90:10) showed the best electrocatalytic activity. The best results obtained using PtIr/C may be associated to the electronic effect between Pd and Ir that might cause a decrease of poisoning on catalyst and the bifunctional mechanism. Further studies are necessary to elucidate the mechanism of ethanol electrooxidation on the surface electrode using these electrocatalysts and also to improve the electrocatalytic activity toward ethanol electrooxidation. Thus, new experiments will be carried out using anionic membranes from Fumatech.



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