

Use of PtAu/C electrocatalysts toward formate oxidation: electrochemical and fuel cell considerations

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Abstract This study reports the use of PtAu/C electrocatalysts with different atomic ratios (90:10, 70:30 and 50:50) supported on Vulcan XC 72 carbon and prepared by the sodium borohydride method toward formate electrooxidation in alkaline media. The materials were characterized by X-ray diffraction, showing peaks characteristics of Pt and Au face-centered-cubic structures, and also by transmission electron micrographs that show the nanoparticles well dispersed on carbon and a mean particle size between 4 and 5 nm for all electrocatalysts. Electrochemical experiments show PtAu/C as promising catalysts toward formate oxidation, while single cell experiments reveal PtAu/C 90:10 as the best material since it provides a power density higher than Pt/C. The incorporation of Au could increase formate oxidation for more than one reason: (i) a facilitated rupture of C–H bond; (ii) the Au/oxide interface or (iii) by regenerating active sites.

Keywords Direct formate fuel cell · PtAu/C electrocatalysts · Borohydride process, formate oxidation

Introduction

The increasing in the atmospheric CO₂ is attributed to the burning of fossil fuels for our energy needs. The present need for power for an average US lifestyle is ~11 kW/person while a good guess appears to be a world average no less than 4 kW/person [1–3]. The excess of CO₂ in atmosphere causes environmental pollution, green house effect and it is found to be a major cause for the global warming process. In order to address these issues, different strategies are being considered and most of them involve a deep change in the current energy supply. Thus, the development of high-efficiency and renewable energy conversion systems are the main issue [4–7].

Therefore, carbon capture such as storage technologies and CO₂ valorization are in the interest of many researchers and one promising way of CO₂ valorization is the conversion of CO₂ in valuable products (such as formic acid and formate) and its use as fuels in direct liquid fuel cells (DLFC) [8, 9]. DLFCs convert chemical energy into electricity and have been recognized as one of the most attractive alternative when compared to the H₂-proton exchange membrane fuel cell (PEMFC), since DLFC shows obvious advantages in terms of fuel storage, simple configuration, easy operation, safety, and transportation [2, 3, 10, 11].

Actually, numerous organic, inorganic and bioorganic fuels have been studied for using in DLFC such as methanol, ethanol, glycerol, formic acid, formate, sodium borohydride, hydrazine, ascorbic acid and glucose. Nevertheless, among these fuels, formic acid have being considered the best one considering its theoretical electromotive force, less toxicity and low crossover [10, 12–14], Pt being the most active catalysts for its decomposition [15]. However, DLFC using formic acid has

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several engineering challenges such as: (i) the oxidation reactions are kinetically sluggish in acid media; (ii) the catalysts are susceptible to be poisoned and (iii) the environment of the fuel cell is corrosive [12, 16].

In order to improve the use of formic acid, the use of formate in alkaline solutions has been intensely studied for fuel cell applications [3, 11, 17–20]. The change from the acid media to the alkaline can dramatically improve kinetics of the oxygen reduction reaction (ORR) and also formate oxidation. Additionally, lower overpotential is required to oxidize the fuel in alkaline environment and the anode catalyst does not poison during formate oxidation as it does during oxidation of formic acid. Furthermore, formate salts are stable, have low toxicity, are easily handled and relatively inexpensive and is a carbon-neutral fuel which can be produced from reduction of carbon dioxide [18, 19, 21–23]. Moreover, Del Castillo et al. [4] affirmed that electrochemical conversion of CO₂ into formate is the most promising reaction to be used at commercial scale.

Following the literature, there has been only a handful of studies of HCOO[−] oxidation on Pt. To the best of our knowledge, the earliest report of HCOO[−] oxidation on Pt was proposed in 1962 by Buck and Griffith [24]. More recently, Jiang et al. [19] proposed a triple-path mechanism of formate oxidation on Pt electrode in alkaline media while John et al. [25] propose a dual mechanism which shows that mechanistic details of HCOO[−] oxidation are still very much lacking in the literature.

Studies show that in alkaline media formate is relatively stable on Pt and itself cannot be oxidized at mild conditions and this stability was attributed to the poor absorbability of formate on Pt [19, 26, 27]. Nevertheless, Günther and Wetzl [28, 29] investigated HCOO[−] electro-oxidation on Pt in pH range of 10–13.5 and low current densities were obtained for this process, but they observed an enhancement of the electro-oxidation rate when the pH goes below 12.5 [25].

In the past few years, formate oxidation has been taken upon the metallic Pt or Pd moieties [23]. For example, Noborikawa et al. [22] used PdCu/C and Pd/C electrocatalysts toward formate oxidation and found that the bimetallic material was better than just Pd/C. Moreover, Hsu et al. [30] used Au/Pd core-shell nanoparticles toward formate-based solutions, showing superior catalytic activities.

Considering fuel cell experiments, within the past year there have been at least two demonstrations of direct formate fuel cell, using dissolved potassium formate as fuel. Thus, formate has been proved to be readily oxidized in alkaline media as successfully demonstrated by Jiang and Wieckowski [31, 32] and Bartrom and Hann [33].

As already mentioned above, the scientific-technological communities of modern society are looking intensively for

alternative sources of energy which could contribute also to reduction of greenhouse emissions. Considering the existent technologies, direct liquid fuel cell is a promising one and among the fuels, formate has been proved to be the best choice.

According to the literature, formate oxidation catalysis are limited and the main catalysts are still Pt and Pd-based ones [9, 25]. Thus, the catalytic properties of Pt-containing nanostructures are strongly dependent on their morphology and compositions and in accordance with Zhang et al [34] combining Pt with other metal element(s) to form bi or multimetallic nanostructures could be efficient to tune the structure and catalytic activity of Pt. Moreover, the creation of a hetero-(metal-metal) bond in well-defined Pt surfaces may induce significant changes in the electronic structure and catalytic property of Pt. Thus, this paper describes the use of PtAu/C electrocatalysts with different atomic ratios (90:10, 70:30, and 50:50) aiming that Au could increase the formate adsorption [35] and also because theoretically Au nanoparticles would show enhanced electron density near Fermi level, narrowed d-band and higher lying d-band center relative to bulk Au [34].

Experimental

PtAu/C electrocatalysts with different atomic ratios (Pt:Au: 90:10, 70:30, and 50:50) and with 20 wt% of metal loading were prepared by the sodium borohydride reduction method [36–39] using H₂PtCl₆·6H₂O (Aldrich) and HAuCl₄·3H₂O (Aldrich), as metallic precursors and Vulcan XC72 (Cabot) as support. Firstly the support was dispersed in an isopropyl alcohol/water solution (50/50, v/v) and put on stirring. After the metal sources were added and the resultant solution was put on an ultrasonic bath for 10 min and afterward, a solution of NaBH₄ in 0.01 mol L^{−1} NaOH was added (in one portion) and maintained on stirring for 30 min. The final mixture was filtered, the solids washed with distilled water and then dried at 70 °C for 2 h.

The X-ray diffraction (XRD) patterns were recorded in the range of 2θ = 20°–90° with a step size of 0.05° and a scan time of 2 s per step using a Rigaku diffractometer model Miniflex II with a Cu Kα radiation source (0.15406 nm) while transmission electron microscopy (TEM) images were obtained using a JEOL transmission electron microscope model JEM-2100 operated at 200 kV. The atomic ratios of Pt and Au were taken by energy dispersive spectroscopy (EDS) using a JEOL—JSM6010 LA equipment.

Electrochemical measurements were conducted at room temperature using a potentiostat/galvanostat PGSTAT 302N Autolab and a three-electrode electrochemical cell. A

platinum electrode and an Ag/AgCl (3.0 mol L^{-1} KCl) electrode were used as the counter and reference electrodes, respectively. The work electrodes (geometric area of 0.5 cm^2 with a depth of 0.3 mm) were prepared using the thin porous coating technique [40–42]. Characterizations were made using cyclic voltammetry conducted at a rate of 10 mV s^{-1} in 2 mol L^{-1} NaOH aqueous solution in presence and absence of 1 mol L^{-1} sodium formate and the amperometric $i-t$ curves were recorded in the same electrolyte containing sodium formate at -0.55 V for 1800 s .

Direct formate fuel cell experiments, or in other words, experiments considering real conditions were taken using a single cell with 5 cm^2 of area. The membrane electrode assemblies (MEA) were prepared by hot pressing the anode and the cathode to a pre-treated Nafion[®] 117 membrane at 125 °C for 3 min under a pressure of 247 kgf cm^{-2} . Prior to use, the membranes were exposed to 6 mol L^{-1} KOH for 24 h as already proposed in our previous studies [42, 43]. The catalytic ink, used as anode and cathode was formulated in a way that Nafion[®] comprised about 35 % wt\% of the total solid in the ink and this was applied to a carbon cloth. All the cathodes and anodes were prepared using 2 mg of metal per cm^2 . Fuel cell performances were determined with polarization and power density curves using a potentiostat/galvanostat PGSTAT 302N Autolab. In all experiments the fuel cell was maintained at 60 °C and the oxygen humidifier maintained at 85 °C with a flow of 150 mL min^{-1} . The fuel, 1.0 mol L^{-1} formate and 2.0 mol L^{-1} NaOH was delivered at 1 mL min^{-1} , based on the results of Bartrom et al. [33]. Moreover, a commercial Pt/C (BASF) was used as cathode in all tests.

Results and discussion

Figure 1 shows the XRD patterns of the PtAu/C electrocatalysts. All XRD patterns showed a broad peak at 2θ about 25° assigned to the (022) reflection of the hexagonal structure of Vulcan XC 72 carbon [44, 45]. The face-centered cubic systems of Pt were observed by five main peaks at $2\theta = 39^\circ, 46^\circ, 67^\circ, 81^\circ$ and 86° which, respectively, corresponds to (111), (200), (220), (311) and (222) planes, accordingly to JCPDF # 04 802 and JCPDF # 88 2334, respectively, and as already observed before [40, 41, 46]. Au/C electrocatalysts showed diffraction peaks at about $38^\circ, 44^\circ, 65^\circ, 78^\circ$ and 82° , attributed to the (111), (200), (220), (311) and (222) planes, characteristics of the fcc structure of Au [21, 43, 47, 48]. The PtAu/C electrocatalysts showed diffractograms peaks shifted to lower 2θ values when compared to Pt/C, suggesting the PtAu alloy formation as already observed before [49–51]. Zhou et al.

[52] attributed the downshift of XRD patterns to the lattice parameter expansion on the PtAu electrocatalysts.

Figure 2 shows TEM micrographs and histograms with mean diameter distribution for the different PtAu/C electrocatalysts in study and also for Pt/C. The mean average size was determined by counting 100 particles at different regions of the different electrocatalysts [49, 53] and was achieved in the range of about $4\text{--}5 \text{ nm}$ for all PtAu/C and Pt/C catalysts. In all images the nanoparticles are well dispersed on the substrate although some agglomerates can also be observed. The mean diameter of the nanoparticles is also shown in Table 1. The narrow size distribution obtained could be attributed to the sodium borohydride method of preparation [54].

Figure 3 shows the cyclic voltammetry of PtAu/C, Au/C and Pt/C electrocatalysts measured in 2.0 mol L^{-1} NaOH solution normalized by gram of metal. With reducing Pt content there was also a reduction in the hydrogen adsorption/desorption, characteristic region of Pt [55].

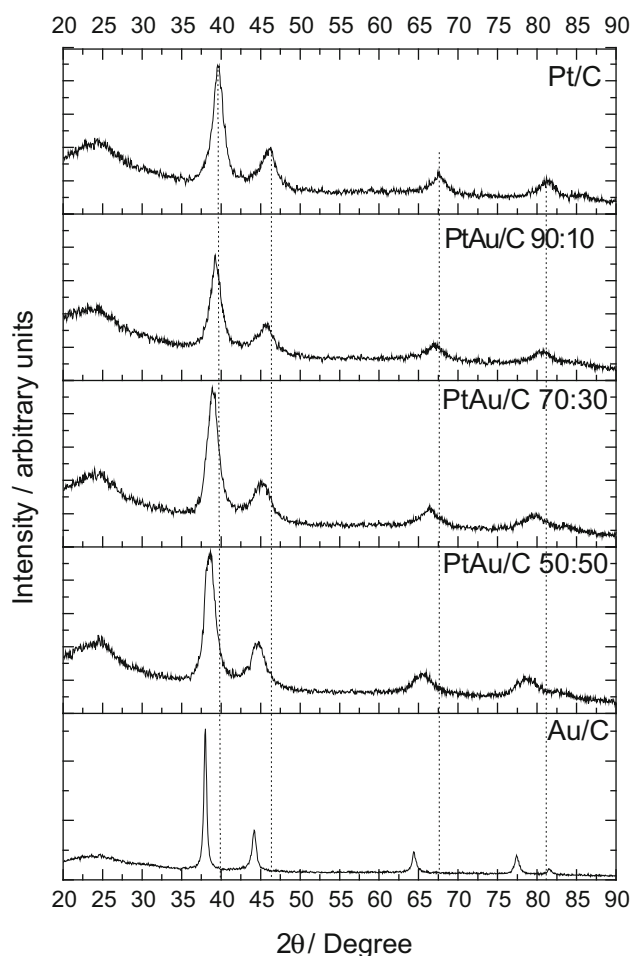


Fig. 1 X-ray diffraction patterns for the Pt/C, PtAu/C and Au/C electrocatalysts

Fig. 2 TEM micrographs and histograms of PtAu/C and Pt/C electrocatalysts

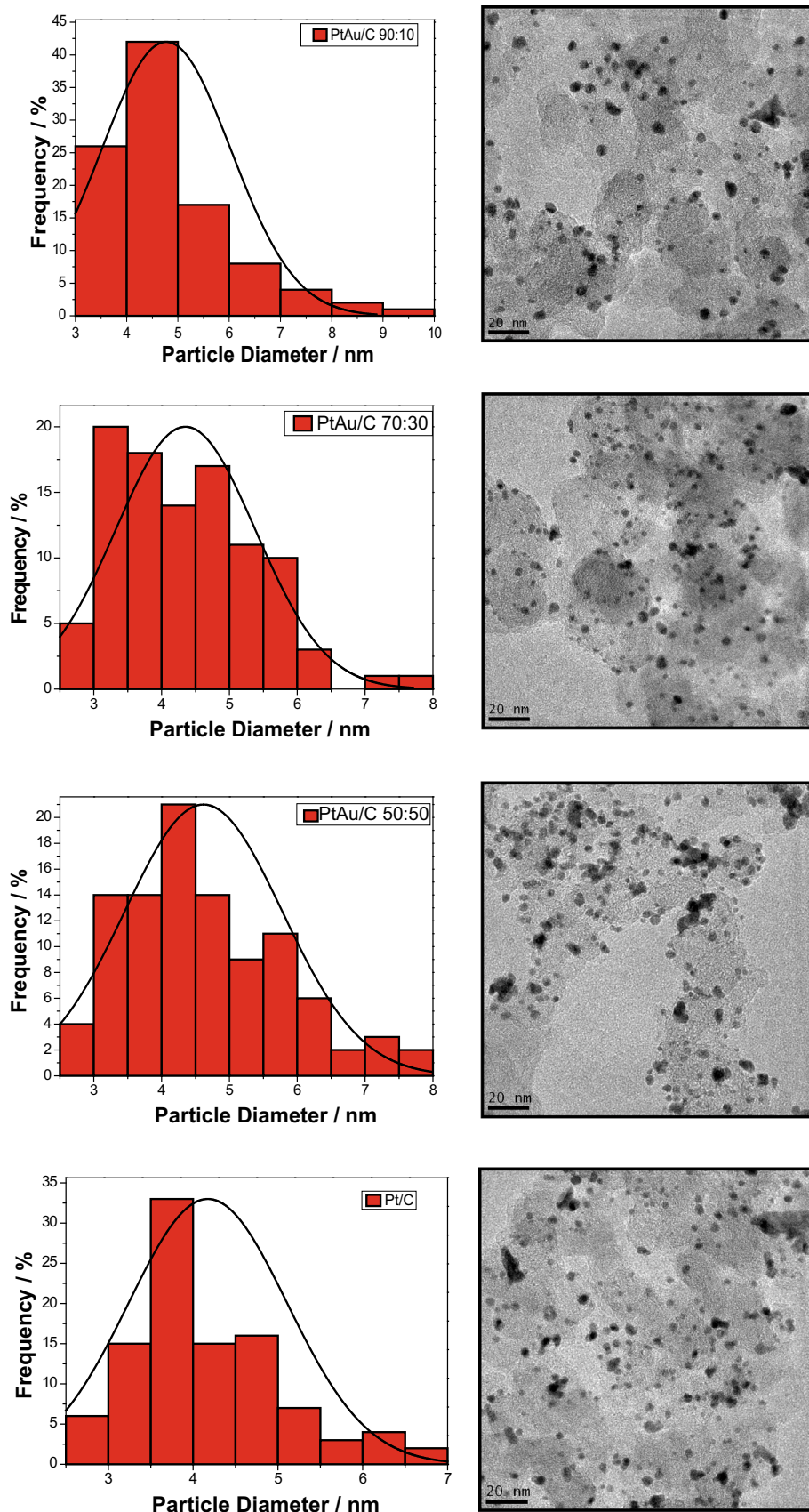


Table 1 PtAu/C mean diameter sizes obtained by TEM images

Pt: Au	TEM <i>d</i> (nm)
100:0	4.2
90:10	4.8
70:30	4.3
50:50	4.6

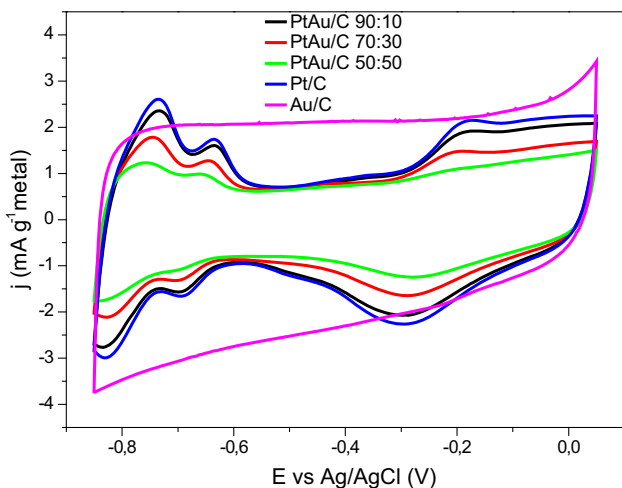
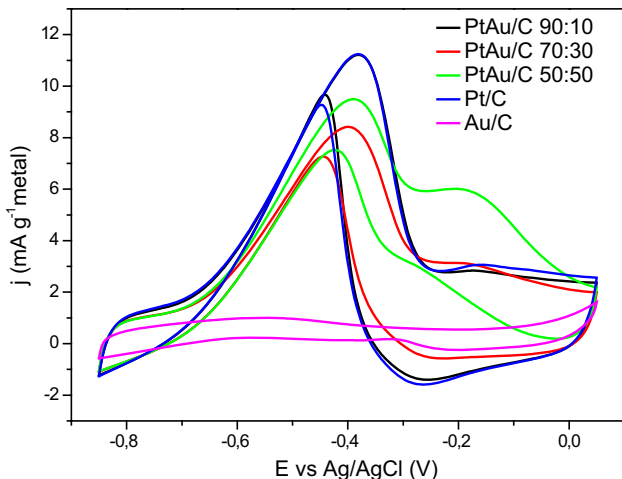
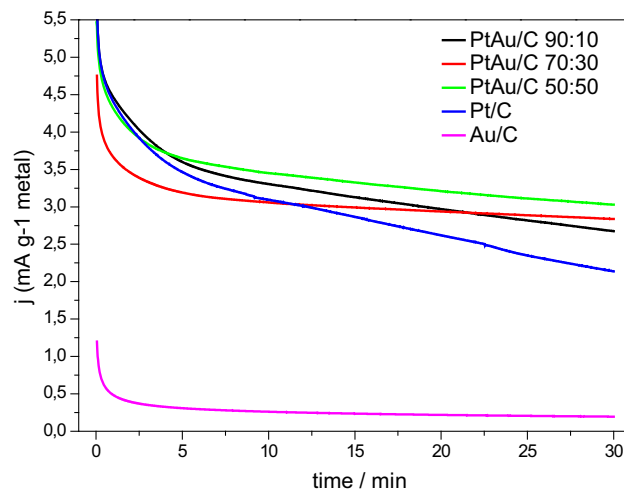
**Fig. 3** Cyclic voltammograms of Pt/C and PtAu/C electrocatalysts in 2.0 mol L⁻¹ NaOH at $v = 10 \text{ mV s}^{-1}$ at room temperature**Fig. 4** Cyclic voltammograms of Pt/C and PtAu/C electrocatalysts in 2.0 mol L⁻¹ NaOH + 1.0 mol L⁻¹ sodium formate at $v = 10 \text{ mV s}^{-1}$ at room temperature

Figure 4 shows the cyclic voltammetry of PtAu/C, Au/C and Pt/C electrocatalysts in presence of 1.0 mol L⁻¹ sodium formate. During positive scan the curves were split into two peaks while negative scan shows only one sharp peak. It is considered that the peaks during positive scan correspond to an oxidative pathway (which do not involve CO_{ads}) and the oxidation of CO_{ads} accompanied by an

**Fig. 5** Chronoamperometric measurements at -0.55 V vs Ag/AgCl for Pt/C and PtAu/C electrocatalysts in 2.0 mol L⁻¹ NaOH + 1.0 mol L⁻¹ sodium formate at room temperature

indirect pathway of formate oxidation. Besides, during negative scan, the higher currents are due to the quicker electro-oxidation of formate on the CO_{ads}-free surface [18]. From Fig. 4, the oxidation current of formate starts at about -0.7 V for all electrocatalysts except Au/C. However, considering just this figure Pt/C seems to be the best material toward formate oxidation in alkaline solution because of the highest peak current at about -0.4 V . However, seeing chronoamperometric curves (Fig. 5), it is possible to observe that PtAu/C 50:50 presents better stability than Pt/C and also a current density of about 50 % higher than Pt/C. Such as PtAu/C 50:50, PtAu/C 70:30 and PtAu/C 90:10 also show good stabilities and current densities higher than Pt/C. Thus, considering electrochemical experiments PtAu/C electrocatalysts seems to be promising materials for direct formate fuel cells.

In order to verify the results obtained in electrochemical experiments the real single cell measurements were done. Figure 6 shows the polarization and power density curves using 1.0 mol L⁻¹ sodium formate and 2 mol L⁻¹ NaOH as fuel. For these measurements Pt/C, Au/C and PtAu/C in different atomic ratios were used as anodes and Pt/C Basf was used as cathode. The summarized results are shown in Table 2, showing the open circuit potential (OCV) and also the maximum power density (MPD). Among all the electrocatalysts in study the PtAu/C 90:10 showed the best result, 8.3 mW cm⁻² while Pt/C showed a power density of 7.8 mW cm⁻². The Au/C electrocatalyst showed almost no activity toward formate oxidation. Considering the experiments using single cell, it is possible to affirm that increasing the Au content into the materials there is also a decrease of power density as already observed in previous studies using PdAu/C electrocatalysts [43]. However, in lower proportions, such as 90:10 Au proves to be a good

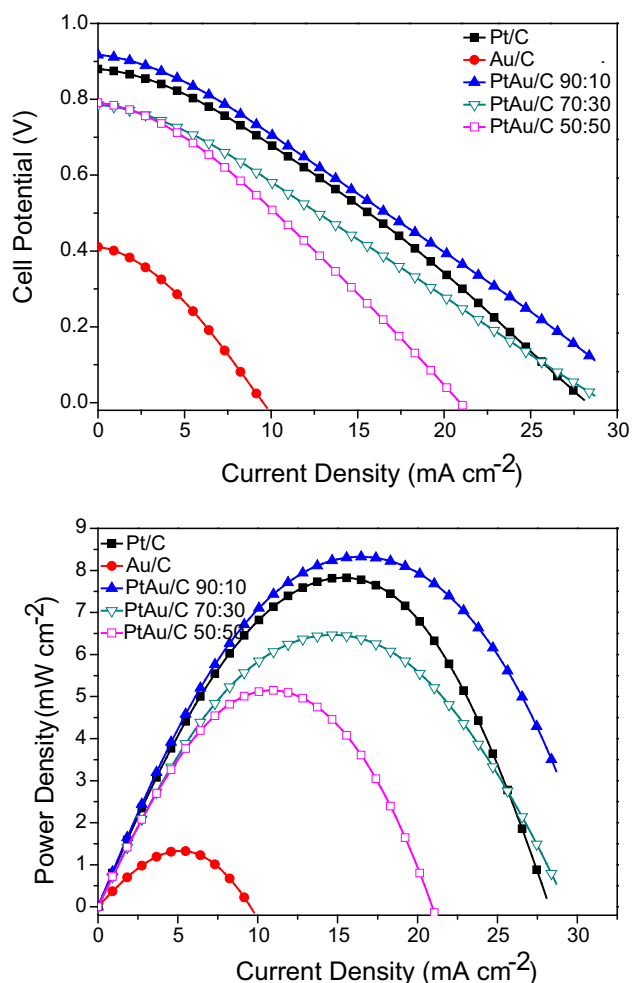


Fig. 6 Polarization and power density curves of a 5 cm² direct formate fuel cell with 2 mg metal cm⁻² in both anode and cathode at 60 °C and using 1.0 mol L⁻¹ sodium formate and 2.0 mol L⁻¹ NaOH

Table 2 Main results obtained using PtAu/C catalysts using a direct formate fuel cell: open circuit potential (OCV) and maximum power density (MPD)

Catalyst	OCV (V)	MPD (mW cm ⁻²)
Au/C	0.41	1.3
Pt/C	0.88	7.8
PtAu/C 50:50	0.79	5.1
PtAu/C 70:30	0.79	6.5
PtAu/C 90:10	0.92	8.3

option as second metal in Pt and Pd binary compositions [21, 43].

As already mentioned before, studies showed that formate is relatively stable on Pt and itself cannot be oxidized at mild conditions and this stability was attributed to the poor absorbability of formate on Pt [19, 26, 27]. Nevertheless, Beden et al. [56] showed the activity of gold and

platinum for the oxidation of formate. Additionally, according to Hsu et al. [30], the impact of sodium formate on Pd-based materials in formic acid would be different to what has been discovered on Pt/C based on the studies of Guo et al. [57] and Gao et al. [10].

Furthermore, Hsu et al. [58] working with Au/Pd nanoparticles toward formic acid oxidation observed that the comparison between the Au/Pd NPs and Pd black suggests higher formate coverage on the Au/Pd nanoparticles, especially at higher potentials. Considering that Pt and Pd show similar properties [26], the information revealed by Hsu shows that Au could contribute to the absorbability of formate on PtAu/C electrocatalysts and consequently increase its oxidation. In addition, Hsu et al. [30] affirm that the catalytic efficiency of formate oxidation depends on the rate of removing reaction intermediates from the catalyst surface (regenerating more active sites) and using simulation studies they suggested that Pd oxidation has been retarded and formatted consuming rate could have been boosted on Au/Pd nanoparticles.

Additionally, Gazsi et al. [35], working with the decomposition of formic acid and methyl formate on TiO₂ doped with N and promoted with Au observed, using infrared spectroscopic measurements, that formate does exist on Au particles. Thus, they affirm that Au nanoparticles are very active catalysts of the decomposition of formic acid at elevated temperature and this is attributed to the facilitation of the rupture of a C–H bond in the formate species adsorbed on the Au or the Au/oxide interface.

Moreover, the creation of a hetero-(metal–metal) bond in well-defined Pt surfaces could induce significant changes in the electronic structure and catalytic property of Pt and Au nanoparticles could show enhanced electron density near Fermi level, narrowed d-band and higher lying d-band center [34].

As a result, considering the discussion above and also the results obtained, Au, in small quantities, contributes to the formate absorbability and consequently to its oxidation. Thus, the use of Au could increase formate oxidation by more than one reason: (i) a facilitated rupture of C–H bond; (ii) the Au/oxide interface or (iii) by regenerating active sites.

Conclusions

The use of the sodium borohydride process for PtAu/C electrocatalysts yields materials with mean particle size between 4 and 5 nm. PtAu/C showed to be good alternative for Pt/C toward formate oxidation since they increase the formate absorbability and also its oxidation. Considering fuel cell experiments, PtAu/C 90:10 showed the highest

power density. By the results, the use of Au could increase formate oxidation by facilitating the rupture of C–H bond, the Au/oxide interface or by regenerating active sites.

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