

# PdAu/C Electrocatalysts as Anodes for Direct Formate Fuel Cell

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**Abstract** PdAu/C electrocatalysts in different atomic ratios (90:10, 80:20, 70:30, and 50:50) supported on Vulcan XC72 carbon were evaluated toward formate oxidation in alkaline media. The materials were prepared by the borohydride process. X-ray diffraction (XRD) patterns of PdAu materials showed peak characteristic of Pd and Au face-centered-cubic (fcc) structures while transmission electron micrographs (TEM) showed the nanoparticles with particle size between 4 and 10 nm for all electrocatalysts. Experiments considering single cell suggested the PdAu/C (90:10) and PdAu/C (80:20) as promisors for formate oxidation. The best result obtained was attributed to the presence of Au in small quantities that contributes to the formate adsorption.

**Keywords** Direct formate fuel cell · PdAu electrocatalysts · Borohydride process

## Introduction

Nowadays, the world-wide basis, considering electrical power, is coal-fired. However, in developed countries, an increasing part of energy consumption is being produced from renewable sources such as wind, biomass, and solar. The main propose of the shift from fossil fuel to renewable energy is to phase out fossil fuels in power production and in

the transport sector aiming the reduction of greenhouse gas emission, the major cause of climate change [1, 2].

Nevertheless, the change to renewable energy sources is slow. In 2010, fossil fuels represented 81.1 % of the total primary energy supply in the world while renewable energies only accounted for 13.2 % [3] Thus, predictions indicate that the world energy demand will still depend on fossil fuels for many years to come [1, 2]. In this context, different strategies are being considered to overcome the use of fossil fuels and among them, the direct liquid fuel cell (DLFC).

DLFC is a clean, highly efficient, and easy-operation energy conversion technology that has attracted much attention. DLFC possesses obvious advantages over hydrogen fuel cell in terms of fuel storage and transportation, and the most common liquid fuels are methanol, ethanol, formic acid, and formate [4, 5].

Among the most used liquid as fuel, formic acid is one of the promising fuels due to its facile oxidation kinetics, high theoretical cell potential, and low fuel crossover. On the other hand, formic acid is corrosive. Thus, its transportation, storage, and uses must be handled with care, and furthermore, it has also toxic effects [5, 6]. In order to overcome these challenges, formate salt (formic acid in alkaline media) is used. Formate is easily handled, stable, low toxic and low cost, and has a theoretical cell voltage of 1.45 V, which is greater than that DLFCs employing alcohol fuels [5, 7].

In fact, formate has been proved to be readily oxidized in alkaline media since recently the prospect of a direct formate fuel cell operated with alkaline potassium formate was successfully demonstrated by Jiang and Wieckowski [5, 6] and Bartrom and Hann [8].

According to Jiang et al. [6], in alkaline media, formate is relatively stable on Pt and it cannot be oxidized at mild conditions, and Munson [9] reported that the rate of the formate oxidation reaction is slow because of the poor absorbability of formate on Pt. Moreover, Takamura et al. [10] observed that

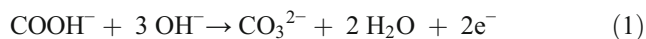
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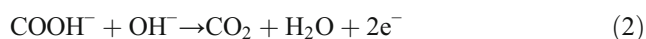
platinum is very active against the oxidation of formic acid in acid media, whereas it is rather inactive in alkaline media.

On the other hand, palladium has generally a similar catalytic activity to platinum but it has a particular affinity to hydrogen, so a specific catalytic behavior for formate is expected [10]. Thus, it is intended that facile formate oxidation was achieved on Pd and Pd-based catalysts.

Actually, formate has been proved to be readily oxidized on Pd catalysts in alkaline media [7, 11]:



Or



Considering a fundamental point of view, formate oxidation on Pd/C is generally considered to follow a mechanism as follow [11]:



At this point, it is important to stress that in this mechanism, there is no surface CO poisoning issue during the formate oxidation. However, the mechanism produces  $\text{CO}_2$ , which contributes to the greenhouse emissions. But the most advantage of using formate is that this fuel could be formatted from  $\text{CO}_2$ , and many studies contemplates interesting results in which the  $\text{CO}_2$  is converted in formic acid/formate [2, 7, 12–15].

Considering the great efforts in reducing the greenhouse emissions and also in renewable energy sources, this work describes the use of PdAu/C electrocatalysts in different atomic ratios toward the formate oxidation in alkaline media. This paper evaluates experiments using single cell, in other words, experiments in real conditions, using  $1 \text{ mol L}^{-1}$  sodium formate +  $2 \text{ mol L}^{-1}$  sodium hydroxide as fuel.

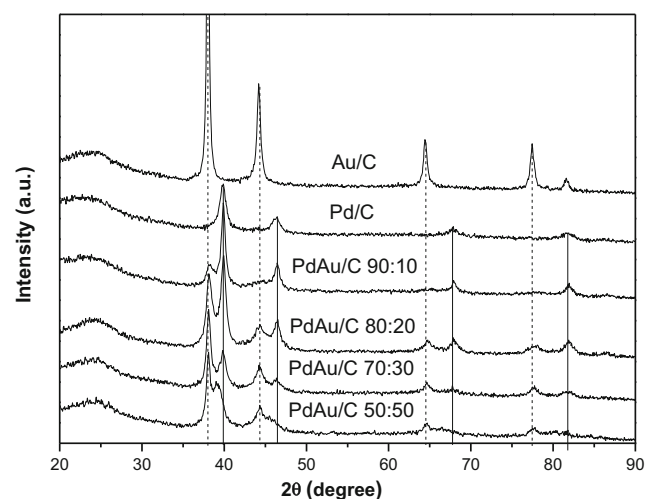
## Experimental

PdAu/C electrocatalysts (20 wt% of metal loading) with different Pd:Au molar ratios: PdAu/C 50:50, PdAu/C 70:30, PdAu/C 80:20, PdAu/C 90:10 Au/C and Pd/C were prepared by the borohydride reduction process [16, 17] using  $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (Aldrich) and  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (Aldrich), as metallic precursors and Vulcan XC72 (Cabot) as support in the following manner: Vulcan XC72 was dispersed in an isopropyl alcohol/water solution (50/50, v/v) and put on stirring. Then, the metal sources were added and the resultant solution was put on an ultrasonic bath for 10 min. After that, a solution of  $\text{NaBH}_4$  in  $0.01 \text{ mol L}^{-1}$  NaOH was added in one portion, under stirring, which was maintained for 30 min. The final

mixture was filtered, and the solids washed with distilled water and dried at  $70 \text{ }^\circ\text{C}$  for 2 h.

The X-ray diffraction (XRD) patterns were recorded using a Rigaku diffractometer model Miniflex II with a  $\text{Cu K}\alpha$  radiation source. Transmission electron microscopy (TEM) images were also obtained aiming to analyze the nanoparticle distribution on the carbon support and the nanoparticle mean distribution, using a JEOL transmission electron microscope model JEM-2100 operated at 200 kV. The atomic ratios of Pd and Au in the synthesized materials were also measured by energy dispersive spectroscopy (EDS) by using a JEOL-JSM6010 LA equipment.

Direct formate fuel cell tests were conducted in a single cell with  $5 \text{ cm}^2$  of area. The membrane electrode assemblies (MEA) were prepared by hot pressing the anode and the cathode to a pre-treated Nafion<sup>®</sup> 117 membrane at  $125 \text{ }^\circ\text{C}$  for 3 min under a pressure of  $247 \text{ kgf cm}^{-2}$ . Prior to use, the membranes were exposed to  $\text{KOH } 6 \text{ mol L}^{-1}$  for 24 h as already proposed by Hou et al. [17] and in previous studies [18]. For the anode and cathode preparation, a catalytic ink containing the catalysts and Nafion<sup>®</sup> solution was applied to a carbon cloth. The catalytic ink was formulated in a way that Nafion<sup>®</sup> comprised about 35 % wt% of the total solid in the ink. All the cathodes and anodes were prepared using  $2 \text{ mg}$  of metal per  $\text{cm}^2$ . Electrical performances were determined with polarization and power density curves by using a potentiostat/galvanostat PGSTAT 302N Autolab. For these experiments, the fuel cell was maintained at  $60 \text{ }^\circ\text{C}$  while the oxygen humidifier was maintained at  $85 \text{ }^\circ\text{C}$  with a flow of  $150 \text{ mL min}^{-1}$ . The fuel, formate  $1.0 \text{ mol L}^{-1}$  and NaOH  $2.0 \text{ mol L}^{-1}$ , was delivered at  $1 \text{ mL min}^{-1}$ , based on the results of Bartrom et al. [8]. For all experiments, a commercial Pt/C (BASF) was used as cathode.



**Fig. 1** X-ray diffraction patterns of the PdAu/C in different atomic ratios, Pd/C and Au/C electrocatalysts. Au/C peaks stressed in *dash lines* and Pd/C peaks stressed in *solid lines*

**Table 1** EDS results for the PdAu electrocatalysts

Sample	Nominal composition	EDS composition
PdAu/C	50:50	54:46
PdAu/C	70:30	73:27
PdAu/C	80:20	81:19
PdAu/C	90:10	90:10

## Results and Discussion

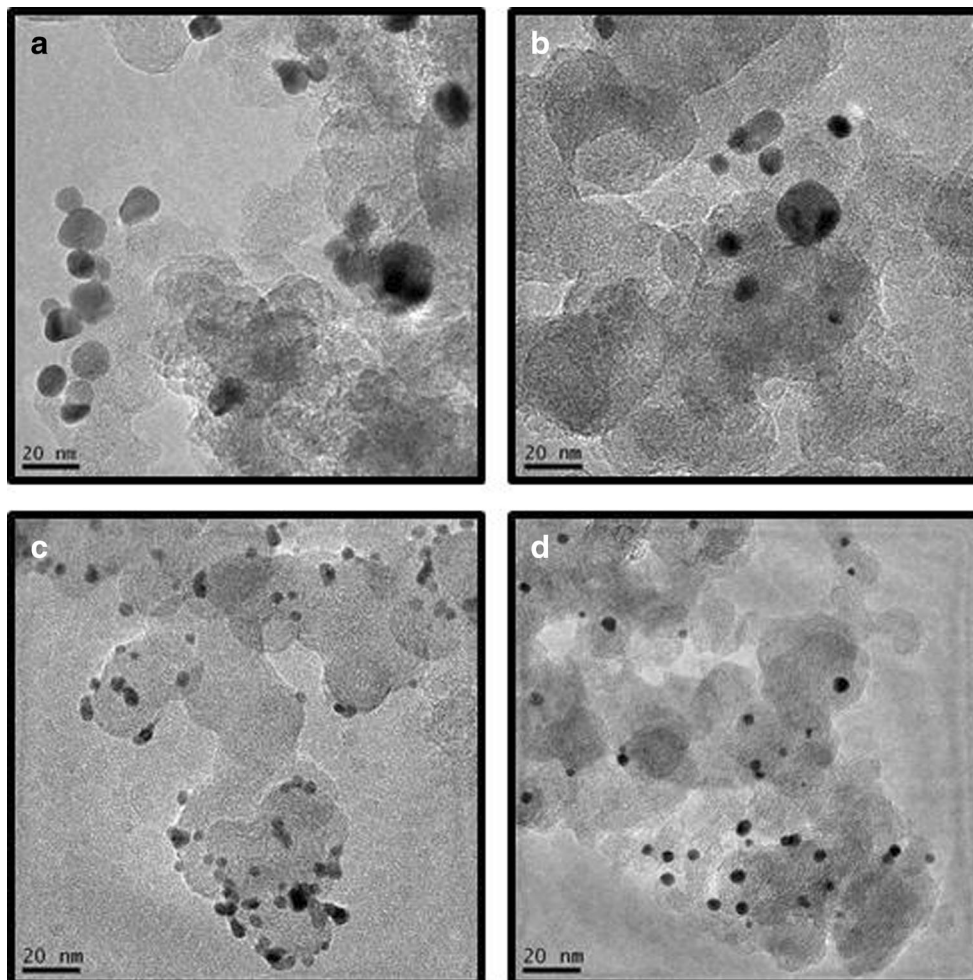
Figure 1 shows the XRD patterns of the PdAu/C prepared with different atomic ratios, Pd/C and Au/C catalysts prepared by the borohydride reduction process. In all XRD patterns, a broad peak at  $2\theta$  about  $25^\circ$  was observed and assigned to the (022) reflection of the hexagonal structure of Vulcan XC72 carbon [18, 19]. The face-centered cubic systems of Pd can also be observed by the peaks at  $2\theta=40^\circ$ ,  $46^\circ$ ,  $68^\circ$ , and  $82^\circ$ , which respectively corresponds to (111), (200), (220), and (311) reflections of Pd face-centered-cubic (fcc) according to JCPDF# 88-2335, as already observed before [18–22]. Au/C electrocatalysts show diffraction peaks

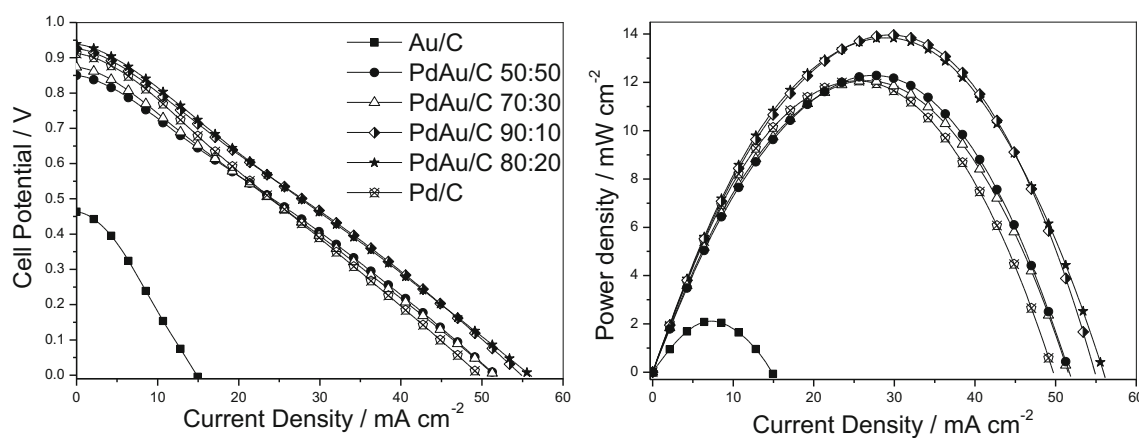
at about  $38^\circ$ ,  $44^\circ$ ,  $65^\circ$ ,  $78^\circ$ , and  $82^\circ$ , attributed to the (111), (200), (220), (311), and (222) planes, characteristics of the fcc structure of Au [22–24]. In all the diffractograms, there is no evidentially shifting of peaks suggesting no formation of PdAu alloy. This evidence was already observed before [23]. Lee et al. [24] working with PdAu electrocatalysts observed that the alloyed phase was formed by increasing the temperature. According to these authors, the PdAu intermixing was essentially complete by 573 K [24]. As in these experiments, there is no use of temperature; this could contribute to the no formation of alloyed phases.

The compositions of all PdAu/C materials were confirmed by using the EDS analysis. Table 1 shows the composition of each electrocatalyst in study. Considering these experiments, it is possible to confirm that all materials are in agreement with the theoretical composition.

Figure 2 shows the TEM images of each electrocatalyst in study. From these images, it is possible to affirm that the nanoparticles are well dispersed on the substrate although some agglomerates can be observed. The mean nanoparticle size obtained for the PdAu/C electrocatalysts is in the range of 4–10 nm for all materials. Larsen et al. [25] synthesized PdAu

**Fig. 2** TEM micrographs of **a** PdAu/C (90:10), **b** PdAu/C (80:20), **c** PdAu/C (70:30), and **d** PdAu/C (50:50)





**Fig 3** Polarization and power density curves of a direct formate fuel cell using PdAu/C in different atomic rations, Pd/C and Au/C electrocatalysts

nanoparticles by a metal chloride reduction process and observed that the Pd nanoparticles were typically 3–10 nm in size with few as large as 30 nm with some of the nanoparticles in agglomerates while the PdAu nanoparticles presented the same size but appear to be less agglomerated than the Pd on carbon. The same observation can be taken from Fig. 2. In the studied materials, PdAu electrocatalysts with more Au contents show the nanoparticles more dispersed on the support than the PdAu with more Pd content.

Figure 3 shows the polarization and power density curves using  $1.0 \text{ mol L}^{-1}$  formate and  $2 \text{ mol L}^{-1}$  KOH as fuel. Au/C, and PdAu/C catalysts were used as anodes in a direct formate fuel cell (DAFC) operated at  $60^\circ\text{C}$ , using also Pt/C BASF as cathode for all experiments. The results obtained in DAFC are summarized on Table 2, showing the open circuit potential (OCV) and also the maximum power density (MPD). Among all the electrocatalysts in study, the PdAu 90:10 and PdAu 80:20 showed the best results ( $\sim 14 \text{ mW cm}^{-2}$ ) while PdAu 70:30 and PdAu 50:50 ( $\sim 12 \text{ mW cm}^{-2}$ ) showed lower values of power density. The best PdAu/C electrocatalysts (PdAu/C 90:10) showed a power density about 15 % higher than the reference material (Pd/C) with the smallest addition of Au. The Au/C electrocatalyst showed almost no activity toward formate oxidation. By these results, it is possible to affirm that increasing the Au content, there is also a decrease of power density. However in lower proportions, such as 90:10 and

**Table 2** Main results obtained using a direct formate fuel cell: open circuit potential (OCV) and Maximum power density (MPD)

Catalyst	OCV/V	MPD/mW $\text{cm}^{-2}$
Au/C	0.46	2.1
Pd/C	0.91	12.6
PdAu/C 50:50	0.85	12.3
PdAu/C 70:30	0.87	12.7
PdAu/C 80:20	0.94	13.8
PdAu/C 90:10	0.92	14.0

80:20, Au shows to be a good option as second metal in Pd binary compositions. Li et al. [22] working with PdAu/Ni electrocatalysts toward formate oxidation observed good results with Pd/Au in 1.5:1 molar ratio; in other words, good results were achieved with higher content of Pd instead of Au in PdAu binary compositions.

According to Qin et al. [26], Pd shows higher electrocatalytic activity for formic acid oxidation than Pt. However, the catalytic activity could be improved by the addition of metal or metal oxide promoters and among them, PdAu binary catalysts have attracted the most attention since the addition of Au could aid the formic acid oxidation in some manner such as electronic modification [25, 26].

Yepez et al. [27] affirm that high coverage of adsorbed hydrogen inhibits the formate adsorption onto Pd surfaces, leading to the slow formate oxidation. Moreover, Hsu et al. [28] affirm that the catalytic efficiency depends on the rate of removing reaction intermediates from the catalyst surface (regenerating more active-sites) and in a simulated result, they observed lower formate and hydroxyl coverages at the same applied potential for Au/Pd nanoparticles than Pd in all formate-based solutions. In other words, they suggested that Pd oxidation has been retarded and formatted consuming rate could have been boosted on the Au/Pd nanoparticles. Thus, as observed in this paper, the Au contributes for the formate oxidation by regenerating active-sites.

Furthermore, Zhou et al. [29] working with PtAu electrocatalysts toward ethanol affirmed that Au works indirectly by increasing the capability of free Pt sites to supply  $-\text{OH}_{\text{ads}}$  species. Probably, this also occurred on the PdAu electrocatalysts.

## Conclusions

PdAu electrocatalysts with Au in small quantities (90:10 and 80:20) prepared by the borohydride process showed to be promiser materials as anode of a formate fuel cell. This

method yields electrocatalysts with mean particle size between 4 and 10 nm for all electrocatalysts. PdAu 90:10 and PdAu 80:20 showed a power density about 15 % higher than the reference material (Pd/C) with the smallest additions of Au, what could be explained by the presence of Au in small quantities that works by regenerating more active-sites of Pd, increasing the kinetic of formate oxidation evidenced by the increased in the power density.

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