Carbon supported PdM (M = Fe, Co) electrocatalysts for formic acid oxidation. Influence of the Fe and Co precursors

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Abstract

Pd and PdM (M = Fe and Co) nanostructured electrocatalysts were synthesized by the impregnation method and supported on carbon black Vulcan XC-72R for the formic acid oxidation reaction, FAOR, in acid medium. Nitrates or chlorides were used as Fe and Co precursors to study the counter ion role on the physicochemical features and electrochemical performance of the electrocatalysts. TEM analysis showed that PdM was deposited on the carbon material with a particle size around 2-3 nm. From XRD, peaks associated with the fcc palladium planes were observed along with evidence of PdM alloy formation, particularly when the nitrate salts were used as metal precursors. Furthermore, XPS analyses indicated that nitrates promote the metal oxide formation to a greater extent than chlorides, mainly for Pd. PdCo electrocatalyst obtained from nitrates exhibited the highest performance for FAOR with a steady state current density of 451 and 313 $\mu\text{A cm}^{-2}$ at 200 and 400 mV respectively, which is in both cases, 3 times larger than that developed for a commercial Pd/C catalyst.

Key words: Palladium; palladium-iron; palladium-cobalt; formic acid oxidation; CO oxidation

1. Introduction

Direct formic acid fuel cells (DFAFCs) have attracted considerable interest as a promising alternative for clean energy generation due to their overall efficiency and low pollutant emissions [1]. The use of formic acid as fuel presents potential advantages such as its non-toxicity, stability at ambient temperature and low permeation through the Nafion® membrane (crossover effect) [2-5]. In addition, formic acid can be used in high concentrations, up to 20 M as compared with methanol [4, 6, 7].

Further, it has been stated that the formic acid oxidation reaction (FAOR) mechanism possibly evolves through either a direct or an indirect route. The former involves its direct oxidation into carbon dioxide, whereas dehydration of formic acid to adsorbed carbon monoxide and its subsequent oxidation into carbon dioxide constitutes the latter [8-11].

The rate of FAOR can increase when using an electrocatalyst that usually consists of metal nanoparticles dispersed on convenient carbon materials with different structures, morphologies and sizes [12]. These carbonaceous supports increase the active surface area and hence, enhance the electrochemical activity. In addition, carbon supported materials display adequate physicochemical and chemical properties, such a large specific surface area, high conductivity and stability, which play a fundamental role on the overall electrocatalysts efficiency [13].

Electrocatalysts based on Pt and its alloys have been widely studied for FAOR. Although generally speaking Pt-based electrodes exhibit a good performance toward FAOR, different disadvantages must be addressed, such as its high cost and the surface poisoning arising from significant CO adsorption as reaction intermediary, which blocks the direct formic acid oxidation [14]. In order to improve the FAOR efficiency, notable efforts have been made into designing more active electrocatalysts. Pd has attracted special attention due to its higher activity for FAOR

as compared with pure Pt [14-18]. It is well known that Pd-based catalysts favor oxidation reactions of various organic molecules such as: methanol, ethanol and formic acid. This is because the use of Pd-based as a catalyst has some advantages as tolerance to CO as well as, good catalytic activity [19, 20].

However, the stability of monometallic Pd is not satisfactory and its performance needs to be improved in terms of CO tolerance. In order to address these issues, the use of bimetallic nanocatalytic systems adding a second transition metal, such as Fe, Co, Ir, Au, Cu, Sn, Ni, Ag to the Pd structure have been proposed [21-33].

Several electrocatalysts synthesis methods have been reported in the literature, which usually involve the reduction of a metal salt with a chemical agent (e.g. H₂, sodium borohydride, ethylene glycol, hydrazine) [34-36]. Different metal precursor salts have been used such as chlorides, nitrates and sulfates. However, up to now the role of the counter ion of the metal precursor salt on the catalytic performance has not been thoroughly studied. The use of different counter ions could result in electrocatalysts with different physicochemical properties and thus, the activity for FAOR could be modified.

This work deals with the effect of Fe and Co precursor (P) salts namely: chlorides (Cl) or nitrates (N) on the electrochemical performance toward FAOR of PdM-P/C (M = Fe or Co) electrocatalysts. Carbon-supported electrocatalysts were synthesized by the impregnation method using sodium borohydride as reducing agent. Iron/Cobalt chloride/nitrates were used as metal precursors. Pd/C catalyst was also synthesized as comparison. The resulting catalysts were characterized by different analytical techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) analysis. The electrochemical performance was studied by cyclic voltammetry and chronoamperometry in 0.5 M H₂SO₄. Under laboratory temperature conditions, namely 25 °C.

2. Experimental Setup

2.1 Electrocatalysts synthesis

The carbon-supported Pd electrocatalyst was synthesized using sodium borohydride, NaBH_4 (Sigma-Aldrich, 99.9%) as reducing agent and the commercial carbon black Vulcan XC-72R (Cabot) as support. Briefly, the carbon Vulcan was dispersed in deionized water followed by ultrasonication for 1 hour. Subsequently, a 5 mM Na_2PdCl_4 (Sigma Aldrich, 98%) solution was added to that containing the support and the pH was set to 5 with 0.5 M NaOH (Sigma-Aldrich, 99.99%); then, a 26 mM NaBH_4 solution was added slowly. The resulting electrocatalyst (named as Pd/C) was filtered followed by repeated washing and drying at 70 °C overnight.

For PdFe and PdCo catalysts, the Pd precursor was 5 mM of H_2PdCl_4 synthesized as follows: PdCl_2 (Sigma-Aldrich, 99%) was diluted and brought to boiling with hydrochloric acid, 0.25 M HCl (Sigma-Aldrich, 36.5%) under reflux. Then 5 mM Fe or Co precursor chlorides or nitrates-base salts were dissolved in water. Nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma-Aldrich, 98%; $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, 98%) or chloride (FeCl_3 , Sigma-Aldrich, 97%; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, 98%) salts were used as metal precursors to obtain the corresponding PdM-P/C (M = Fe or Co) electrocatalysts. Finally, the mixture of both metallic precursors was added to the support dispersion following the same synthesis method used for the Pd/C catalyst. Catalysts obtained from nitrates were denoted as PdM-N/C, while those obtained from chlorides were labeled as PdM-Cl/C. The metal molar ratio in the PdFe and PdCo electrocatalysts was 1:1. Appropriate amounts of metal precursors were used to obtain a theoretical metal loading of 20 wt% onto Vulcan XC-72R.

2.2 Physicochemical characterization

The Pd-based electrocatalysts were characterized by EDX, XRD, XPS and TEM to study the composition, structure and particle size of the resulting nanoparticles, as well as their dispersion onto the carbon support.

To establish the powder electrocatalyst composition a Hitachi S-3400N SEM equipment was used coupled with a Röntec XFlash Si(Li) detector for EDX analysis.

XRD patterns were recorded using a Bruker AXS D8 Advance diffractometer with a θ – θ configuration and Cu K α radiation ($\lambda = 0.15406$ nm). Scans were carried out at $1.0^\circ \text{ min}^{-1}$ for 2θ values from 10 to 80° .

TEM micrographs were obtained in a JEOL-2000 FXII microscope equipped with a LaB₆ gun operated at 200 keV. The samples were dispersed in ethanol, and a drop of the resulting dispersion was carefully deposited on a copper grid. Particle size distribution of the synthesized electrocatalysts was obtained using the Digital Micrograph software counting over 200 particles from different areas.

XPS measurements were performed in an Escalab 250 Thermo Scientific (base pressure $\sim 2 \times 10^{-9}$ mbar) equipment with an Al filament emitting X rays at 1486.6 eV. The Advantage 5 software was used for fitting the XPS profiles with Gaussian-Lorentzian (GL) line shape functions, calibrated by assigning a binding energy (BE) value of 285 eV to the C1s.

2.3 Electrochemical characterization

The electrochemical performance of the synthesized electrocatalysts was studied by means of cyclic voltammetry (CV) and chronoamperometry (CA) in a conventional three-electrode electrochemical cell coupled with a μ -Autolab Metrohm type III series μ 3Aut70922 potentiostat-galvanostat. A glassy carbon bar (5.0 mm of diameter) was used as working electrode substrate, together with a graphite bar as counter electrode and a Ag/AgCl/3.0 M KCl inserted in a Luggin capillary as reference electrode, to which all potentials herein are referred to. The working electrodes were prepared as follows: first, the glassy carbon surface was polished with 0.3 μm alumina slurry, followed by water washing and sonication. Then, a 20 μL aliquot of each electrocatalyst ink was deposited over the glassy carbon electrode and subsequently dried under a N₂ (INFRA air products, High purity) stream. Catalyst inks were prepared mixing 2 mg of the corresponding electrocatalyst with 15 μL of Nafion (5% wt. % alcohol base, Sigma-Aldrich) and 500 μL of ultrapure water (Milli-Q[®] 18.2 M Ω •cm). The mixture was sonicated for 40 minutes to obtain a homogeneous suspension.

Electrochemical experiments were carried out at room temperature and atmospheric pressure. The working electrode was immersed in the supporting electrolyte 0.5 M H₂SO₄ (Sigma Aldrich, 99.999 %) deaerated with N₂. The electrocatalysts were cycled from -200 to 1000 mV at 500 mV s⁻¹ for 20 complete cycles to clean the surface. Then, 3 cyclic voltammograms (CVs) were recorded at 20 mV s⁻¹ in the same potential range to activate the surface. The last voltammogram was termed as blank.

CO-stripping voltammograms were monitored to study the performance of the catalysts toward CO electrooxidation. For such a purpose, CO (INFRA air products, High purity) was adsorbed on the electrocatalyst by bubbling it through the working electrolyte during 15 min at -170 mV. Then, the solution was saturated with N₂ for 20 min to remove the CO excess and a cyclic voltammetry was carried out from -200 to 1000 mV at 20 mV s⁻¹ for 3 cycles. Electrochemically active surface areas, EASA, were obtained by the ratio between the experimental charge (obtained by CO stripping peak integration) and the charge density corresponding to a CO adsorbed monolayer oxidation on Pd polycrystalline surface (315 $\mu\text{C cm}^{-2}$) [23]. The faradaic currents were normalized by the respective EASA to obtain the current densities ($\mu\text{A cm}^{-2}$) given in the text.

The FAOR voltammograms were assessed in 0.5 M H₂SO₄ + 2.0 M HCOOH (Sigma Aldrich, 95%) by cycling the potential between -200 and 1000 mV at 20 mV s⁻¹. Chronoamperometry evaluation of the current density response at steady state conditions (j_{ss}) was carried out stepping the potential to 200 and 400 mV, both for 900 seconds.

The electrochemical performance of the synthesized catalysts was compared with that obtained using a commercial Pd/C catalyst (Sigma-Aldrich, 30 wt. %). This electrocatalyst has been labeled as Pd_{SA}/C in the text.

3. Results and discussion

3.1 Physicochemical characterization

The metal content of the Pd-based catalysts was studied by EDX (Table 1). All the laboratory-made electrocatalysts presented a metal loading similar to the nominal value (20 wt.%). Additionally, the EDX atomic ratio was around 50:50 for the bimetallic catalysts in agreement with the theoretical values.

Figure 1a shows the XRD patterns of Pd_{SA}/C and synthesized electrocatalysts. A characteristic peak at around $2\theta = 25^\circ$, associated with the graphite (002) diffraction plane of the support was shown by all synthesized electrocatalysts. Also, their diffraction patterns exhibit three characteristic peaks at around $2\theta = 40.09^\circ$, 46.63° and 68.08° , which are assigned to (111), (200) and (220) planes of Pd fcc. Comparing the position of Pd-related peaks of the synthesized Pd/C catalyst and bimetallic catalysts, a shift to higher 2θ values was observed for the bimetallic catalysts obtained from nitrate salts (see Table 1 and Figure 1b), which may be explained by the contraction of the Pd lattice structure by the introduction of the second metal Fe or Co. However, this shift is not as evident for catalysts obtained from chlorides due to a lower alloying degree. Other authors have obtained poor alloying after using synthesis methods of electrocatalysts involving low temperatures [20, 37-40]. Reduction treatments at higher temperatures or the control of other experimental conditions (such as pH, concentration, reducing agent, stabilizing agent, synthesis method) resulted in nanoparticles with an improved alloying degree, as well as cluster-type and core-shell morphologies [18, 41-43]. Finally, monometallic Pd catalysts (Pd/C and Pd_{SA}/C) showed a diffraction peak around 34° associated to PdO formation. PdM-Cl catalyst displays some relatively low intensity peaks on the XRD patterns at $2\theta = 35.76^\circ$ and 65.63° that can be associated with Fe₃O₄ and Co₃O₄ respectively.

In order to further characterize the catalysts, the XPS technique was used. Figure 2 presents XPS spectra recorded from PdM catalysts synthesized in this work. From these images it is possible to note that regardless of the precursor salt, Co (see Figure 2a) and Fe (see Figure 2b) were fully oxidized at the surface. In the case of Co the main component was Co₃O₄ [44, 45] while for Fe it was present as a mixture of FeO, Fe(OH)₂ (Fe(II)) and Fe₃O₄ (Fe(II) and Fe(III)) species [46]. As can be noted

from Figures 2c (chloride precursor) and 2d (nitrate precursor), Pd was formed by Pd(0), PdO (Pd(II)) and PdO₂ (Pd(IV)). However, the metal to oxide ratio was greater when the chloride precursor was used, this result was the same regardless of the second metal.

Figure 3 shows the TEM images and particle size distributions of the synthesized electrocatalysts. In general, a good dispersion of the metal nanoparticles on the carbon support was obtained for all the samples. In addition, narrow particle size distributions were obtained for all Pd-based electrocatalysts with a mean particle size ranging from 2 to 3 nm. These results show that the chloride and nitrate salts did not have a significant effect on the sizes of the nanoparticles obtained. According to the bibliography nanoparticles with an average size around of 2.2 to 9.0 nm have a good electrocatalytic activity towards the FAOR [3, 27]. Thus, the synthesized electrocatalysts seem to be promising candidates for FAOR. Finally, the commercial catalyst presented larger average particle size (7 nm).

3.2 Electrochemical characterization

3.2.1 Electrochemical features in the base electrolyte

The electrochemical features of the Pd-based synthesized catalysts was evaluated in 0.5 M H₂SO₄ by cyclic voltammetry, cycling the potential from -200 to 1000 V at 20 mV s⁻¹ and starting from the open circuit potential (OCP) in the anodic direction. The blank voltammograms obtained for all synthesized catalysts are shown in Figure 4.

All the electrocatalysts evidenced the characteristic Pd features reported in the literature [27, 47]. The potential scan in the negative direction shows hydrogen adsorption/absorption, followed by the hydrogen evolution reaction at potentials below -150 mV. During the anodic sweep, hydrogen desorption takes place and palladium oxide is formed at potentials greater than 600 mV, which are reduced in the negative scan at around 500 mV. In the potential interval from 100 to 200 mV

the current density remains constant and is associated to interfacial electrical control (double layer). Interestingly, the PdFe electrocatalyst synthesized using nitrates as a metal precursor (PdFe-N/C) presented another oxidation peak from 300 to 500 mV which could be associated with the oxidation of exposed Fe. Han and Xu [48] synthesized PdFe alloy nanoparticles, where the voltammogram, see Figure 4a in 48, also showed an oxidation peak prior to that of Pd oxide formation, that corresponded to the electrochemical oxidation of exposed Fe atoms from the surface layer.

3.2.2. CO stripping

CO stripping voltammetry was used to obtain the electroactive surface area (EASA) of Pd-based electrocatalysts and to evaluate the catalyst surface tolerance for CO poisoning. Figure 5 shows the results obtained for all the electrocatalysts.

During the anodic sweep of the first scan (solid curves) the hydrogen adsorption/absorption/desorption region is totally blocked confirming that CO was adsorbed at the catalyst surfaces. Two peaks attributed to CO electrooxidation are discerned for all the electrocatalysts, with the exception of the commercial catalyst which presented a main peak at 723 mV. The location of the peaks depends on the electrocatalyst: the first contribution (peak I) is centered within the 558 to 673 mV, while the second one (peak II) occurs at potentials from 707 to 723 mV. Bimodal CO oxidation profiles have been already reported by other authors on Pd electrocatalysts supported on carbon materials [47, 49, 50]. The maximum oxidation potentials of both peaks and the onset potential for the CO oxidation reaction are summarized in Table 2.

A different catalytic activity toward CO electrooxidation is evident, which is ascribed to differences in the size and structure of metal nanoparticles [51]. In this context, the commercial catalyst requires a more positive potential to oxidize CO compared with the synthesized Pd/C. In fact, the main oxidation occurs at 716 mV in the catalyst obtained by reduction with NaBH_4 , while 723 mV are required in the commercial one. Further, the first oxidation contribution does not appear at $\text{Pd}_{\text{SA}}/\text{C}$ surface. These results clearly indicate that the synthesized catalyst with a particle

size around 2 to 3 nm display an improved activity toward CO oxidation than the commercial catalyst with a larger particle size. Thus, larger particle sizes led to a less activity for CO removal.

The second metal addition (Fe or Co), favored CO oxidation since the onset potential shifted to more negative potentials from 538 mV at Pd/C to 423 - 507 mV for the bimetallic electrocatalysts. Thus, bimetallic surfaces seem to favor CO oxidation. In addition, an improved condition for CO removal was obtained on the bimetallic catalyst PdCo-N/C compared to PdCo-Cl/C. Similar particle sizes (2 to 3 nm) were obtained for all the samples and hence, these differences are associated with the different composition/structure of the catalysts. Nitrate precursors resulted in a higher alloying degree (in agreement with the XRD results), which seems to favor the activity towards CO electrooxidation in the case of the PdCo catalyst. Interestingly, the PdCo-N/C catalyst exhibited the lowest potential for the main oxidation peak (peak II) with a current density ($85.25 \mu\text{Acm}^{-2}$) maximum at 707 mV. Peak I appeared also at low potentials (620 mV).

Finally, it is important to note that after CO oxidation the electrochemical behavior is similar to the blanks reported before (compare red lines in Figure 5 with lines of Figure 4), which evidences that CO was removed completely from the base electrocatalyst.

3.2.3 Formic acid oxidation reaction

The performance of the electrocatalysts toward FAOR was studied in 0.5 M H_2SO_4 + 2.0 M HCOOH cycling the potential from -200 to 1000 mV Figure 6 shows the results of all the catalysts.

All the Pd-based electrocatalysts display similar features: during the positive-going potential scan, a rise in the faradaic current density is evident, exhibiting an anodic peak with its maxima dependent on the catalyst (in the 270 to 638 mV potential range). A close inspection of FAOR voltammograms evidences that bimetallic catalysts present the maxima at potentials around 200 - 300 mV during the positive-going potential scan, with the exception of PdFe-Cl/C with the main oxidation (488 mV) at potentials similar to monometallic Pd catalysts (448 at Pd/C and 638 mV at

the commercial electrode). In the cathodic sweep, once Pd oxide reduction takes place, formic acid is again re-oxidized displaying even higher current densities than those developed during the anodic excursion, which is explained by a high tolerance to catalyst poisoning [50, 52]. Table 3 displays the main oxidation potential (E_p) and the peak current density (j_p) developed during the anodic excursion.

Pd_{SA}/C displayed the largest current density but the main peak for formic acid oxidation during the anodic excursion appeared at more positive potentials. Indeed, the anodic peak position developed during the forward scan of Pd-based electrocatalysts follows this sequence: Pd_{SA}/C (638 mV) > PdFe-Cl/C (488 mV) > Pd/C (448 mV) > PdCo-Cl/C (287 mV) > PdFe-N/C (273 mV) > PdCo-N/C (270 mV). Thus, the second metal addition in general resulted in an improved condition toward FAOR for all the electrocatalysts, with the exception of PdFe-Cl/C. This catalyst presented a behavior similar to the synthesized monometallic catalyst (Pd/C). In other words, bimetallic electrodes showed the highest current density toward FAOR in the potential range from 200 to 300 mV, while pure Pd catalysts and PdFe-Cl/C presented a higher efficiency at potentials around 400 – 600 mV.

As is well known, for the electrocatalytic oxidation of HCOOH, there are usually involved the so-called dual pathways, which are dehydrogenation and dehydration, as represented by reactions (1) and (2), respectively [53, 54] :

Although the dehydrogenation is the main pathway on Pd catalyst, recent studies reveal that CO_{ads} can still accumulate on the surface of Pd, leading to the degradation of the catalytic performance over time under DFAFC conditions [55]. Therefore, according to the fact that PdCo-N/C catalyst showed high catalytic activity towards CO electrooxidation, it was expected good performance also during the formic acid electrooxidation.

The steady state anodic current density (j_{ss}) was evaluated through chronoamperometry at 200 and 400 mV during 900 seconds. The j_{ss} - t plots for all the electrocatalysts are shown in Figure 7, while Table 4 reports the current densities

of the catalysts evaluated at 900 seconds at both potentials. The j_{ss} at 200 mV followed this sequence: PdCo-N/C > PdFe-N/C > Pd_{SA}/C > Pd/C > PdFe-Cl/C > PdCo-Cl/C, while the j_{ss} at 400 mV followed this sequence: PdCo-N/C > PdFe-N/C > PdFe-Cl/C > Pd_{SA}/C > Pd/C > PdCo-Cl/C.

Interestingly, the PdCo-N/C exhibited the largest current density at both potentials, with an anodic current density around two and three times larger than the monometallic catalysts (Pd/C and Pd_{SA}/C).

Regarding the effect of the Fe/Co metal precursor, the bimetallic catalysts obtained from nitrates (PdCo-N/C and PdFe-N/C) showed higher activity towards FAOR compared to their analogues (PdCo-Cl/C and PdFe-Cl/C, respectively). Moreover, PdCo-N/C depicted better catalytic activity than PdFe-N/C probably due to a greater alloying degree between Pd and Co.

Conclusions

In this work, the effect of the Fe/Co metal precursor salt (nitrates or chlorides) on the physicochemical properties and catalytic activity for CO oxidation and FAOR of Pd-M/C (M = Fe or Co) electrocatalysts was studied. Catalysts were obtained by impregnation and reduction with sodium borohydride using iron/cobalt chloride/nitrates as metal precursors. Results were compared with a monometallic Pd/C synthesized catalyst obtained by the same methodology.

XRD patterns evidenced that Pd was deposited on the carbon material with a fcc structure. In the case of bimetallic catalysts, the use of nitrates and chlorides allowed obtaining PdM alloys. However Fe/Co precursors from nitrates showed higher alloying degree with Pd, as compared with the PdM-Cl/C catalysts. XPS results demonstrated that nitrates favored the metal oxide formation. Furthermore, high dispersion of metal nanoparticles with an average size of 2-3 nm was observed by TEM for all the catalysts.

CO-stripping voltammograms showed that the addition of the second metal (Fe or Co) resulted in an improved condition for CO removal.

Regarding the activity of catalysts toward FAOR, PdCo-N/C and PdFe-N/C exhibited the highest steady state anodic current densities.

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Table 1. Physical characteristics of the Pd-based electrocatalysts: total metal content and ratio obtained from EDX , 2θ of Pd(111) from XRD and particle size from TEM of the electrocatalysts.

Electrocatalyst	XRD	TEM	SEM-EDX	
	Pd (111)	Particle size	Elemental composition	
	2 Theta / degree	(nm)	Metal content wt. %	Pd:M at. %
Pd/C	40.10	2.98 ± 0.69	21.00	100
Pd _{SA} /C	40.09	7.00 ± 1.19	29.94	100
PdFe-Cl/C	40.14	2.88 ± 0.66	18.94	45:55
PdCo-Cl/C	40.12	2.89 ± 0.65	20.26	43:57
PdFe-N/C	40.23	2.20 ± 0.42	17.91	45:55
PdCo-N/C	40.33	2.60 ± 0.47	19.46	54:46

Table 2. CO oxidation potentials from cyclic voltammograms shown in Fig. 5 and EASA from CO stripping for the different catalyst.

Electrocatalyst	CO onset potential (mV)	CO oxidation potential peak - I (mV)	CO oxidation potential peak - II (mV)	EASA (cm²)
Pd/C	538	673	716	43.39
Pd_sA/C	551	--	723	13.16
PdFe-Cl/C	423	558	711	9.43
PdCo-Cl/C	507	664	717	17.06
PdFe-N/C	437	610	722	9.94
PdCo-N/C	488	620	707	18.41

Table 3. Potential and current density of the voltammetric peaks of the CVs shown in Fig. 6.

Electrocatalyst	E_p (mV)	j_p ($\mu\text{A cm}^{-2}$)
Pd/C	448	819
Pd_{SA}/C	638	1573
PdFe-C/C	488	550
PdCo-C/C	287	915
PdFe-N/C	273	738
PdCo-N/C	270	908

Table 4. Current density at steady state, at 200 and 400 mV for 900 s in 2.0 M HCOOH + 0.5 M H₂SO₄.

Electrocatalyst	j_{ss} at 200 mV ($\mu\text{A cm}^{-2}$)	j_{ss} at 400 mV ($\mu\text{A cm}^{-2}$)
Pd/C	157.3	96.9
Pd _{SA} /C	214.3	110.2
PdFe-Cl/C	110.9	178.9
PdCo-Cl/C	107.72	70.36
PdFe-N/C	229.3	211.7
PdCo-N/C	451.1	313.1

Figure Captions

Figure 1. a) XRD patterns of the Pd-based electrocatalysts and b) Zoom around the 2 Theta Pd(111) region.

Figure 2. XPS spectra recorded from PdM synthesized catalyst a) Co2p, b) Fe2p, c) Pd3d (for nitrate precursors) and d) Pd3d (for chloride precursors).

Figure 3. TEM images and particle size distribution of the Pd-based electrocatalysts.

Figure 4. Cyclic voltammograms of the Pd-based electrocatalysts recorded in 0.5 M H₂SO₄ at 20 mV s⁻¹.

Figure 5. CO stripping voltammograms recorded with the Pd-based electrocatalysts in 0.5 M H₂SO₄. At 20 mV s⁻¹ scan rate.

Figure 6. Cyclic voltammograms recording during FAOR with the Pd-based electrocatalysts in 2.0 M HCOOH + 0.5 M H₂SO₄, at 20 mV s⁻¹ scan rate. In all cases the potential started at -200 mV in the positive direction.

Figure 7. Potentiostatic current density transients recorded during FAOR, in 2.0 M HCOOH and 0.5 M H₂SO₄, using the synthesized electrocatalysts for two different applied potentials indicated in the figures. The insets show a closed region of the current density at the longest times.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7