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## ► To cite this version:

Vanessa Oliveira, Y. Soldo, Edson Ticianelli, Marian Chatenet, Eric Sibert. Formic Acid Electrooxidation on Palladium Nano-Layers Deposited onto Pt(111): Investigation of the Substrate Effect. *Electrocatalysis*, 2023, 14 (4), pp.561-569. 10.1007/s12678-023-00816-z . hal-04034823

**HAL Id: hal-04034823**

<https://hal.univ-grenoble-alpes.fr/hal-04034823v1>

Submitted on 27 Jul 2023

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1 ***Formic acid electrooxidation on palladium nano-layers deposited***  
2 ***onto Pt(111): investigation of the substrate effect***

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18 **Abstract**

19 The influence of Pd nano-layers electro-deposited onto Pt(111) single-crystal has  
20 been systematically studied towards the formic acid electrochemical oxidation reaction  
21 in H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub>. The studied Pd<sub>x</sub>ML/Pt(111) surfaces ( $x = 1, 2, 5$  and 16  
22 monolayers –ML-) are all more active than Pt(111) towards formic acid oxidation, even  
23 if the activity is very sensitive to the Pd film thickness and morphology. In sulfate  
24 solution, the competitive adsorption of long range ordered (bi)sulfate on the  
25 pseudomorphic Pd terraces effectively hinders the formic acid oxidation only on the  
26 thinnest films. We could observe the different role of the (bi)sulfate adsorption on the  
27 first and on the following deposited Pd layers. The sulfate adsorption competitive role

28 rapidly fades away beyond about 5 ML of equivalent thickness, due to the surface  
29 roughness increasing and terraces width diminishing.

30 In perchlorate media, anions do not adsorb competitively with formic acid  
31 intermediates, allowing a larger activity of the formic acid oxidation up to about 5 ML.  
32 At higher thicknesses, the difference in activity between the two electrolytic media is  
33 reduced and it drops in both electrolytes close to 0.5 V *vs.* RHE, where Pd surface  
34 oxides are formed.

35 Coupling the electrochemical results with the Pd layers structural description  
36 previously obtained from *in situ* SXRD experiments, the outstanding activity of  
37 Pd<sub>1ML</sub>/Pt(111) observed in perchloric solution can be explained by the ligand effect of  
38 the underlying platinum atoms on the first pseudomorphic Pd layer. This advantageous  
39 effect is lost for Pd deposits thicker than 1 ML.

40

41 **Keywords:** Pt(111) single crystal; palladium layers; formic acid  
42 electrooxidation; ligand and geometric effects.

43

44

## 45 **1. Introduction**

46 Small organic molecules, especially liquid C1-species, are attracting attention as  
47 potential fuels for low temperature fuel cells, due to their propensity to be easily stored  
48 and to the absence of C-C bonds that are difficult to break [1]. In this perspective,  
49 methanol (CH<sub>3</sub>OH), formaldehyde (HCHO) and formic acid (HCOOH) are among the  
50 most investigated candidates. Despite an apparent simplicity, the complete oxidation of  
51 these compounds involves several electron transfers that occur in multiple steps, leading  
52 to a difficult overall optimization of appropriate electrocatalysts [2].

53 Typically, methanol electrooxidations on Pt in acidic media proceeds following  
54 two main reaction paths. The indirect path starts with carbon atom dehydrogenation and  
55 adsorption. It is followed by adsorbed CO formation that blocks active sites and results  
56 in overall slow reaction kinetics. On the contrary, the direct path starts with oxygen  
57 atom adsorption. Then, formaldehyde and formic acid can be produced as side products  
58 and/or reaction intermediates before CO<sub>2</sub> is formed as a final product. So, improving the  
59 activity of an electrode for formaldehyde and formic acid oxidation is not only  
60 interesting by itself, but also for the methanol oxidation efficiency.

61 This two-paths mechanism is very common for the electrooxidation of small  
62 organic molecules and also applies to formaldehyde and formic acid oxidation. The  
63 selectivity between the two paths not only depends on the considered reaction, but is  
64 always also governed by the surface structure of the electrode and the competitive anion  
65 adsorption at its surface [3,4]. For the specific case of formic acid oxidation on  
66 platinum, recent works highlight that a third path, with formate adsorption acting  
67 mainly as poisoning specie, is possible [5].

68 The main approach to counteract the CO<sub>ads</sub> formation and poisoning is to use a  
69 bifunctional bimetallic electrocatalyst [6]. In this strategy, one of the two metals,

70 usually platinum, efficiently dehydrogenates/oxidizes the initial molecule, at least until  
71 the formation of adsorbed  $\text{CO}_{\text{ads}}$ . In complement, the second one is a more oxophilic  
72 metal that dissociates water molecule into  $\text{OH}_{\text{ads}}$ , which can react with  $\text{CO}_{\text{ads}}$  to produce  
73  $\text{CO}_2$  in the well-known Langmuir-Hinshelwood reaction, thereby freeing active sites for  
74 further activity.

75 While ruthenium is the most commonly-used second metal [6,7], palladium is  
76 also gaining attention because (i) it is more oxophilic than platinum, (ii) has some  
77 activity for the oxidation reactions at stake and (iii) can absorb hydrogen [8,9], playing a  
78 (positive) role in the several dehydrogenation steps of C1-species oxidation.  
79 Measurements on the three basal planes of Pd showed a high rate for formic acid  
80 oxidation [10].

81 In the context of bimetallic catalysts, the use of well-ordered single crystals  
82 surfaces modified by a foreign metallic atom deposition is not new in electrocatalysis.  
83 Such modified ordered surfaces can provide original activities, typically due to strain or  
84 ligand effects [11]. Moreover, their well-defined surface organization at the atomic level  
85 with equivalent and uniformly-distributed active sites enables to (more) easily  
86 understand complex electrochemical processes [1,8,9,12].

87 Several studies have been made on metallic single crystals modified by Pd  
88 deposition towards the formic acid oxidation reaction. Kibler *et al.* [11] measured the  
89 formic acid oxidation activity of a pseudomorphic atomic Pd surface layer on different  
90 substrates (Au, Pt, Pd, Ir, Rh...) with (111) surface orientation in  $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  and  
91 found that the activity is very sensitive to the nature of the substrate. More in detail, Pd  
92 deposited on Pt(111) was found to exhibit a higher activity compared to all the studied  
93 mono-metallic substrates or bulk Pd(111) surface. The authors suggest that, for all these  
94 systems, the electronic modification of the Pd monolayer is essentially due to the

95 geometric factor, associated to the lateral strain of the Pd layer. This lattice mismatch  
96 would induce a d-band shift, directly influencing bonding energies, as calculated by  
97 Nørskov's group [13].

98 Llorca *et al.* [14] investigated this reaction on Pt(111) surface modified by Pd forced  
99 deposition with coverages up to one atomic layer in 0.5 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>. As Pd addition  
100 only induced marginal activity improvement, the authors suggested that CO poisoning,  
101 although existing on free Pt(111), has limited extend on the overall activity; therefore  
102 even if the Pd addition lowers poisoning, it cannot greatly change the activity that is  
103 already good. In opposite, Baldauf *et al.* [15], using electrochemical deposition of Pd at  
104 0.27 V *vs.* SCE on Pt(111) in 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>, observed changes in the activity for  
105 coverage of 0.5 and 1 monolayer (ML). A new oxidation peak, reversible between  
106 positive and negative scans of the cyclic voltammetry, appears and grows at lower  
107 potential. It is associated to oxidation of formic acid through the direct path on Pd areas.  
108 Nevertheless, the irreversible peaks associated to the oxidation through the indirect path  
109 on Pt surface are still present at higher potential. Maximum oxidation currents are  
110 slightly decreased compared to free Pt. For thicker deposits, from 2 to 5 ML as  
111 equivalent thickness on Pt(111) (the equivalent thickness  $x$  ML is calculated assuming a  
112 layer-by-layer growth mechanism with a two-electron-transfer process and one  
113 deposited Pd atom per surface Pt atom), only a large reversible oxidation peak is  
114 observed, suggesting that only the direct path remains on Pd. The activity is higher than  
115 on free Pt, 0.5 and 1 ML Pd coverages.

116 Arenz *et al.* [9,16] studied the activity of a fraction up to 1 ML of Pd on Pt(111), as well  
117 as a PtPd(111) bulk alloy in 0.1 mol L<sup>-1</sup> HClO<sub>4</sub>. Both systems revealed a strong activity  
118 enhancement compared to Pt(111), supporting the idea that the direct path is favored on  
119 Pd, as shown by infrared measurements.

120 As first shown on polycrystalline Pd film deposited onto silicon with infrared  
121 measurements, the activity of formic acid oxidation is also anion-sensitive: contrarily to  
122 perchlorate, a competitive adsorption was observed between intermediate formate and  
123 (bi-)sulfate [17].

124 Anion sensitivity was also seen for Pd films up to 2 ML on Pt(111) [1]. Deposits  
125 were obtained after rapid immersion of the electrode in about  $10^{-5}$  M  $\text{Pd}(\text{NO}_3)_2$  solution  
126 followed by reduction of Pd salts and deposition in hydrogen atmosphere. In aqueous  
127 perchloric acid, adsorbed palladium promotes formic acid electrooxidation and a  
128 maximum oxidation rate is found when a single Pd layer is deposited. In contrast,  
129 voltammeteries recorded in aqueous sulphuric acid show a strong inhibition of this  
130 reaction, which was attributed to extensive specific adsorption of (bi)sulphate anions,  
131 competing with adsorption of formic acid molecules.

132 From the experimental point of view, Pd electrochemical deposit on Pt(111) in  
133 acidic media can be tailored in a reproducible way at several well-defined thicknesses  
134 when the first Pd layer is underpotentially deposited and following layers are obtained  
135 scanning the potential very slowly ( $v = 0.1 \text{ mV s}^{-1}$ ) down to a potential between UPD  
136 and bulk deposition and holding it in-between [18].

137 The  $\text{Pd}_{1\text{ML}}/\text{Pt}(111)$  deposit consists of a complete underpotentially deposited  
138 (UPD) monolayer, pseudomorphic with the substrate (matching with the lattice of the  
139 crystalline substrate) [19]. *In situ* surface X-Ray diffraction (SXRD) and *ex situ* AFM  
140 experiments made by some of the authors of the present paper allowed the detailed  
141 structural and morphological characterization of multilayered Pd nanofilms deposited in  
142  $\text{PdCl}_2$   $10^{-4}$  M +  $\text{HCl}$   $3 \cdot 10^{-3}$  +  $\text{H}_2\text{SO}_4$  0.1 M solution [20,21]. For  $\text{Pd}_{2\text{ML}}/\text{Pt}(111)$ , the first  
143 Pd layer is complete (UPD), the coverage of the second layer is about 80% and the  
144 coverage of the third one is only 20%; for  $\text{Pd}_{14\text{ML}}/\text{Pt}(111)$ , the first ten Pd layers are

145 complete and the coverage progressively decreases until the twentieth layer, which is  
146 nearly empty. The first ten Pd atomic planes are all pseudomorphic *i.e.* in-plane lattice  
147 parameters of Pd layers are equal to that of the Pt(111) substrate, while the next Pd  
148 layers are progressively relaxing to Pd bulk lattice parameters. These measurements  
149 enable establishing a direct relationship between surface structure and electrochemical  
150 characterization of the Pd/Pt(111) layers. Hence, the voltammetry in acidic media  
151 allows determining the structure of the first deposited Pd layers onto Pt(111), without  
152 resorting to physical characterization. *Ex situ* AFM images [18] show that up to 4 ML  
153 the deposits present uniform flat zones, while roughness rapidly increases beyond this  
154 thickness inducing the decrease of the terraces width.

155         The hydrogen insertion, obtained applying a sufficiently low potential to the  
156 electrode, was also monitored by measuring the changes in the deposit lattice  
157 parameters associated with hydride (Pd-H( $\beta$ ) phase) formation. No structural  
158 modifications are observed for the first two Pd layer, both for thin or thicker deposits,  
159 revealing that no hydride species are formed, not only between last the Pt and first Pd  
160 layers, but also between the first and the second Pd atomic layers. Anisotropic  
161 expansions in parallel and normal directions to the surface were recorded starting from  
162 the third atomic Pd layer, corresponding to hydriding.

163         This detailed surface characterization coupled to the electrochemical study of the  
164 Pd<sub>xML</sub>/Pt(111) system towards formic acid oxidation reaction represents a unique  
165 opportunity to correlate the surface structure to the reactivity. The present paper aims at  
166 studying the influence of fine-tuned Pd/Pt(111) layers towards the electrooxidation of  
167 formic acid. The study is performed in both H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> solutions, to specifically  
168 address the mechanisms underlying the competitive adsorption between intermediate  
169 formate species and (bi)sulfate, compared to perchlorate.



170

## 171 **2. Experimental details**

172 The working electrode (WE) was a Pt(111) single crystal cylinder with a 5 mm  
173 diameter. The reference electrode (RE) was a saturated calomel electrode (SCE). It was  
174 held in a separated compartment with a Luggin capillary connecting to the  
175 electrochemical cell. The counter electrode was a Pt grid; a Pt sphere was used as the  
176 auxiliary electrode to lower the electromagnetic noise. Detailed procedures are  
177 described in Ref. [22]. An EG&G Princeton Applied Research, Model 273A  
178 potentiostat/galvanostat with computer control was used for all the electrochemical  
179 measurements.

180 For each experiment, the single crystal surface was cleaned and regenerated  
181 using flame-annealing (butane + air). It was cooled in a reducing atmosphere (N<sub>2</sub>/H<sub>2</sub>  
182 90:10) and finally put in contact with ultrapure water saturated with the same mixture,  
183 as described previously [18,20]. A droplet of pure water was maintained at the electrode  
184 surface to avoid contamination during all transfers between cooling glassware and cells  
185 dedicated to electrochemical Pd deposition and characterization. Both cells were made  
186 of Pyrex and double-walled designed to allow circulation of thermostated water for  
187 temperature control at  $25 \pm 1^\circ\text{C}$ .

188 A cyclic voltamperogram in  $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  prepared from Merck sulfuric  
189 acid (Suprapur, 96 %) in ultrapure water (Millipore Elix + Milli-Q gradient,  $18.2 \text{ M}\Omega$   
190  $\text{cm}$ ,  $< 3 \text{ ppb}$  Total Organic Content ) was recorded before each deposition experiment to  
191 assess the Pt(111) surface quality and address the absence of contaminants in the system  
192 [23–27].

193 A  $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 3 \cdot 10^{-3} \text{ mol L}^{-1} \text{ HCl}$  (Merck, Suprapur 30%) +  $10^{-4} \text{ mol L}^{-1}$   
194  $\text{PdCl}_2$  (Alfa Aesar, 99%) solution was employed for palladium electrochemical

195 deposition. The Pt(111) electrode was first introduced at  $E = 1.05$  V vs. RHE (at a  
196 potential where no Pd deposition occurs) and then the potential was scanned negatively  
197 to induce the Pd deposition. The single Pd atomic layer deposition ( $x = 1$ ) was achieved  
198 by underpotential deposition (UPD): the potential was simply scanned very slowly ( $v =$   
199  $0.1$  mV s<sup>-1</sup>) to separate UPD and bulk deposition and held in-between. For thicker  
200 deposits (Pd<sub>xML</sub>/Pt(111) with  $x = 2, 5$  and  $16$  ML), the Pd quantity was adjusted by  
201 precisely measuring the coulometric charge assuming a layer-by-layer pseudomorphic  
202 deposit (*i.e.* one palladium atom per each surface platinum atom and for each layer) and  
203 two electrons transferred for each Pd atom [18,20,21]. Practically, the potential of the  
204 Pt(111) electrode was scanned down ( $v = 0.1$  mV s<sup>-1</sup>) to Pd bulk and diffusion-limited  
205 deposition ( $E = 0.701$  V vs. RHE). The potential was then maintained at this value until  
206 the required Pd quantity was obtained. After this, Pd<sub>xML</sub>/Pt(111) electrodes were  
207 emerged from the deposition solution, rinsed with ultra-pure water and transferred to the  
208 characterization cell with pure acidic electrolyte (H<sub>2</sub>SO<sub>4</sub> or and HClO<sub>4</sub>) for control.

209 The electrooxidation of formic acid on the different Pt(111) and Pd<sub>xML</sub>/Pt(111)  
210 electrodes was investigated in  $0.1$  mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> +  $0.1$  mol L<sup>-1</sup> HCOOH and  $0.1$  mol L<sup>-1</sup>  
211 HClO<sub>4</sub> +  $0.1$  mol L<sup>-1</sup> HCOOH solutions.

212

### 213 **3. Results and discussion**

#### 214 **3.1 Palladium deposition and electrochemical characterization in sulfuric acid**

215 As discussed in the introduction paragraph, electrochemical characterization in  
216 sulfuric acid allows determining the atomic structure of the first Pd deposited layers.  
217 Figure 1 exhibit representative cyclic voltamperograms (CVs) in aqueous sulfuric acid  
218 ( $0.1$  mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub>) of freshly-prepared Pd nanofilms and of the free Pt(111) surface,  
219 also provided as benchmark. The Pt(111) surface (Figure 1, black curves) exhibits the

220 characteristic butterfly envelope, confirming the quality and cleanness of the Pt(111)  
221 electrode surface [24–27]. Once Pd has been deposited, the corresponding  
222 voltamperograms (Figure 1) are completely different, in accordance with the literature  
223 [9,18,20,21,28–30].

224 For Pd<sub>1ML</sub>/Pt(111), the platinum signature is no longer visible (Figure 1, red  
225 curve), showing that the Pt(111) surface is fully covered by a complete UPD layer of  
226 Pd. A new pair of sharp peaks appears around 0.21 V vs. RHE, associated to the  
227 adsorption of electrolyte species on the first pseudomorphic Pd monolayer [22,30]. For  
228 multilayered palladium deposits (Figure 1, blue, green and violet curves), a second pair  
229 of broader peaks is present around 0.26 V vs. RHE, attributed to adsorption on second  
230 and following Pd atomic layers [22,24]. For Pd<sub>2ML</sub>/Pt(111), position and peaks  
231 intensities indicate that the Pd film structure is very close to that revealed by *in situ*  
232 SXRD experiments: a large part of the first Pd layer (close to 80%) is covered by the  
233 second and following layers, while less than about 20% of the first Pd layer is still free.

234 Peaks corresponding to the first Pd layer are still partially present up to 5 ML,  
235 showing that free first Pd layer regions, even if smaller and smaller in size, still remain  
236 in contact with the electrolyte. Finally, the electrochemical response of Pd<sub>16ML</sub>/Pt(111)  
237 corresponds to a full covered first Pd layer.

238 Both pairs of peaks, associated with the first Pd layer and the “second and  
239 following” layers, are associated with simultaneous hydrogen adsorption/desorption and  
240 sulfate desorption/adsorption [12,30,31]. Adsorbed sulfates are forming an ordered  
241 structure ( $\sqrt{3}\times\sqrt{7}$ )R19.1° on the Pd overlayers on Pt(111) [30], as on Pt(111) [32] and  
242 bulk Pd(111) [33]. The sharpness of these adsorption peaks is associated with the  
243 presence of a long-range order both on Pt(111) [26] and Pd(111) [33,34]. In opposite,  
244 the broadening of the adsorption peaks observed with thicker Pd deposit is related to the

245 narrowing of flat Pd terraces and the reduction in size of long-range ordered sulfate  
246 domains [35].

247 After experiments in formic acid, the electrodes were checked again in sulfuric  
248 acidic solution, in order to probe possible surface irreversible modifications. The  
249 adsorption/desorption charge is preserved, along with the signature of the palladium  
250 layers (Supporting Information, Figure S1). Hence, this oxidation (formic acid is a mild  
251 reducer) does not lead to irreversible structural modification of the Pd<sub>x</sub>ML/Pt(111)  
252 surfaces, in opposite for instance to what was observed in presence of a strong reducer  
253 like borohydrides [8].

254

### 255 **3.2 Formic acid electrooxidation on Pd<sub>x</sub>ML/Pt(111)**

256 Figure 2 shows a set of CVs during formic acid electrooxidation on  
257 Pd<sub>x</sub>ML/Pt(111) and Pt(111), using 0.1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> (a) and 0.1 mol L<sup>-1</sup> HClO<sub>4</sub> (b)  
258 electrolytes. All Pd<sub>x</sub>ML/Pt(111) surfaces exhibit higher activity than Pt(111) for this  
259 reaction in both solutions. As already suggested in the literature, the lower activity of Pt  
260 versus Pd is attributed to different overall reaction pathways for formic acid  
261 electrooxidation on the two metals [1,14,16,36]. More specifically, “poisoning species”,  
262 the most important being adsorbed CO, may hinder the electrooxidation of formic acid  
263 on Pt, by blocking the active sites required for the adsorption of the HCOOH molecules  
264 themselves, or for the H<sub>2</sub>O adsorption and dissociation that are also needed for the  
265 reaction [16,37]. In both media, CVs on Pt(111) are showing a strong difference  
266 between the forward and backward scans, the second presenting larger currents. This is  
267 due to the removal of CO at high potential, associated with the peak at  $E = 0.75$  V vs.  
268 RHE, providing a less blocked surface during the backward scan. In opposite, for Pd  
269 surfaces, the forward and backward scans are much similar, with slightly less current for

270 the backward scan. This indicates that no consequent surface blocking by  $\text{CO}_{\text{ads}}$  is  
271 occurring (if any), in accordance with the direct path mechanism.

272 Beyond the general benefit for formic acid oxidation adding Pd on Pt(111),  
273 specific behaviors as a function of the equivalent Pd film thickness are observed in the  
274 two electrolytes.

275 In presence of sulfate (Figure 2a), the onset of electrooxidation on Pt(111) is  
276 measured at around  $E = 0.3 \text{ V vs. RHE}$ , corresponding to the potential where a large  
277 part of the surface is no more blocked by adsorption, as last vestiges of adsorbed  
278 hydrogen are desorbing from the Pt(111) surface, and not yet majorly covered by  
279 adsorbed sulfate species. When palladium is deposited on the electrode, the onset of  
280  $\text{HCOOH}$  electrooxidation, very close for all Pd modified samples, advantageously shifts  
281 to more negative potentials (by *ca.*  $0.2 \text{ V}$ ). Ahmed *et al.* [1] already observed this  
282 behavior, and correlated it to the change in potential zero total charge values between  
283 clean Pt(111) and Pd/Pt(111). Higher activity for  $\text{Pd}_{1\text{ML}}/\text{Pt}(111)$  versus Pt(111) was also  
284 predicted using DFT calculations [38].

285 Concerning the formic acid electro-oxidation activity in sulfate electrolyte,  
286 voltammetries show a general increase of the formic oxidation current with thickness,  
287 although the electrochemical response is characterized by a specific behavior as a  
288 function of the number of deposited Pd layers. For  $\text{Pd}_{1\text{ML}}/\text{Pt}(111)$ , there is a single  
289 oxidation peak slightly above  $0.2 \text{ V vs. RHE}$ , at the same potential where the sharp  
290 (bi)sulfate adsorption peak is observed in sulfuric acid solution (Figure 1): this  
291 maximum is followed by a rapid decrease of the oxidation current. For  $\text{Pd}_{2\text{ML}}/\text{Pt}(111)$ , at  
292 this same potential, the curve presents only a shoulder and the current continues to  
293 increase up to around  $0.37 \text{ V vs. RHE}$ : beyond this value the signal rapidly drops. The

294 current decrease is now in the potential region where (bi)sulfate adsorption takes place  
295 on the free second and following Pd atomic layers.

296 Data of these two samples already allow a detailed description of the role of  
297 (bi)sulfate adsorption as a competitive process hindering formic acid oxidation. For the  
298 thinnest films, the responsible for the rapid oxidation current dropping is the long range  
299 ordered competitive (bi)sulfate adsorption on the pseudomorphic terraces of the Pd free  
300 surface On Pd<sub>1ML</sub>/Pt(111), it concerns the adsorption on the first Pd layer, at about 0.2 V  
301 vs. RHE. On the other hand, this adsorption is no longer strong enough to effectively  
302 stop the formic acid oxidation on Pd<sub>2ML</sub>/Pt(111), where the uncovered part of the first  
303 atomic Pd layer represents a minor part of the total electrode area; it only succeeds in  
304 slowing down the reaction. For this thickness, it is the competitive (bi)sulfate long range  
305 ordered adsorption on the terraces of the second and following Pd planes, at about 0.37  
306 V vs. RHE, that effectively stops the oxidation reaction.

307 For Pd<sub>5ML</sub>/Pt(111), only a barely visible shoulder is present at about 0.2 V vs.  
308 RHE. In this sample, no significant influence of the competitive adsorption on the first  
309 Pd layer is present, in agreement with the fact that at this thickness the largest part of  
310 the first Pd layer is covered. The current maximum is still located in the potential region  
311 of (bi)sulfate adsorption on the Pd layers terraces beyond the first Pd plane, close to  
312 0.37 V vs. RHE, indicating that this competitive adsorption still plays a role in the  
313 formic acid oxidation activity decrease. Nevertheless, it is less effective, as shown by  
314 the less abrupt current drop after the maximum compared to the thinner samples. Only  
315 beyond about 0.5 V HER the signal decrease accentuates, corresponding to the potential  
316 region where Pd surface starts to oxidize.

317 For Pd<sub>16ML</sub>/Pt(111), the current continuously increases up to about 0.5 V vs.  
318 RHE (only a bump at about 0.37 V vs. RHE is visible). At this highest thickness, it

319 clearly appears that (bi)sulfate adsorption has a lost effectiveness in hindering formic  
320 acid oxidation. This thickest deposit is also exhibiting the highest difference between  
321 the positive and negative scans. The corresponding current excess during the positive  
322 scan should be ascribed to the release of hydrogen absorbed in palladium at low  
323 potential.

324 The comparison with pure Pd(111) surface in reference [39] is showing a  
325 voltammetric profile similar to the present Pd<sub>5ML</sub>/Pt(111), both in term of current and  
326 potential at the current maximum. The morphological evolution of the Pd surface as a  
327 function of the thickness as reported by Lebouin *et al.* [18] is particularly useful to  
328 understand these observations. AFM images have shown that the Pd terraces width  
329 largely decreases beyond about 4 ML as equivalent thickness, inducing the formation of  
330 surface defaults which represent new adsorption sites. Our electrochemical results are in  
331 complete agreement with this description: only when pseudomorphic Pd terraces width  
332 is sufficiently large to allow long range ordered (bi)sulfate adsorption, anion adsorption  
333 effectively inhibit formic oxidation. As for equivalent thickness increases beyond about  
334 4-5 ML, the surface becomes quite rough and the terraces width shrinks, long range  
335 ordered competitive adsorption is no more possible: as a result, formic acid oxidation  
336 activity is larger and stops only at higher potential, where Pd surface oxidation process  
337 begins. As a confirmation, the activity of pure Pd(111) in reference [39] is also lower  
338 than that of Pd<sub>16ML</sub>/Pt(111), although the lattice parameter of the Pd surface layer in  
339 Pd<sub>16ML</sub>/Pt(111) is relaxed to the one of Pd(111) [21]. The electronic effect of the  
340 substrate should also be negligible for a such thick deposit. So, the only difference  
341 between the two surfaces is their roughness, with wide flat areas for Pd(111) allowing  
342 long range ordered (bi)sulfate, in opposite to narrow terraces for Pd<sub>16ML</sub>/Pt(111) not  
343 allowing it.

344 In presence of perchlorate (Figure 2b), the onsets of electrooxidation are very  
345 similar to sulfuric media. It is around  $E = 0.3$  V vs. RHE for Pt(111), and at  $E = 0.2$  V  
346 vs. RHE for Pd surfaces, *i.e.* at the end of hydrogen desorption on both surfaces. Then,  
347 sweeping to higher potential values, Pd<sub>1ML</sub>/Pt(111) exhibits the steepest current increase  
348 and reaches the highest current maximum of all Pd deposits. Currents during positive  
349 and negative scans are very similar. This is quite different from previous work from  
350 Liang *et al.* [40]. They show a high irreversibility with low current at positive scan and  
351 a peak at the beginning of negative scan, that should correspond to the oxidation of a  
352 blocking/poisoning specie. One hypothesis would be that the higher formic acid  
353 concentration (0.5 M instead of 0.1 M in the present work) is producing more poisoning  
354 species, inducing a fast surface blocking. Uncompensated ohmic drop with high  
355 currents measured in ref. [40] may also explain the observed shape with limited current  
356 during the forward scan and the kind of switch at the beginning of the backward scan.

357 Pd<sub>2ML</sub>/Pt(111) presents an intermediate case, with initial current increase smaller  
358 than the Pd<sub>1ML</sub>/Pt(111) electrode, but larger than thicker Pd deposits. In opposite, the  
359 current maximum is the lowest of all Pd deposits. The 5 and 16 ML deposits are  
360 showing similar behaviors with oxidation currents smaller than for the 1 and 2 ML until  
361  $E = 0.4$  V vs. RHE. Like in sulfate media, the thickest Pd deposit is also showing the  
362 highest current excess during the positive scan, attributed to hydrogen de-insertion. The  
363 activity of Pd(111) in reference [39] is lower than for Pd<sub>1ML</sub>/Pt(111), with a current  
364 maximum around 10 mA.cm<sup>-2</sup> at 0.5 V vs. RHE, versus 10 mA.cm<sup>-2</sup> at 0.5 V vs. RHE  
365 for the latter, this value being larger than for all other Pd deposits.

366 Figure 3 shows the comparison of formic acid activity in both media for the  
367 same Pd layer thicknesses. Two different potential regions are present. Scanning from  
368 low potential, the formic acid electro-oxidation activity firstly grows similarly in both



369 media. The reaction onset is not affected by the nature of the anions presents in  
370 solution; also, current intensity behavior is very close. Contrarily, beyond about 0.25 V  
371 vs. RHE, where (bi)sulfate adsorption is observed in the absence of formic acid,  
372 oxidation currents behave differently: the activity is always larger with perchlorate than  
373 with sulfate. Nevertheless, this deviation diminishes beyond about 5 ML, where,  
374 contrarily to perchlorate, formic acid oxidation activity in presence of sulfate  
375 significantly increases: finally, current intensities tend to converge at the highest  
376 thickness. This observation is in complete agreement with the fact that only adsorbed  
377 (bi)sulfate on the pseudomorphic terraces of the thinnest electrodes, where they form a  
378 well-ordered structure, act as an effective barrier to formic acid oxidation. As thickness  
379 increases, formic acid oxidation is less and less hindered by the (bi)sulfate adsorption.  
380 Beyond about 4-5 ML, formic acid oxidation is stopped in both solutions (sulfate and  
381 perchlorate) at higher potential, close to about 0.5 V vs. RHE, where Pd surfaces  
382 deactivate owing to metal-oxides formation.

383 A very specific behavior is nevertheless observed for Pd<sub>1ML</sub>/Pt(111) in  
384 perchlorate, where the activity is the highest; it dramatically decreases at higher  
385 thickness, already starting from two layers (Pd<sub>2ML</sub>/Pt(111), Figure 3). Such behavior  
386 was already observed by Ahmed *et al.* [1], but they had no structural description of the  
387 electrode, preventing any understanding of the underlying mechanism. The activity is  
388 also higher than the one of pure Pd(111) [39].

389 If such remarkable activity for Pd<sub>1ML</sub>/Pt(111) were due to the larger creation of  
390 poisoning species like CO<sub>ads</sub> at higher thickness, where the abrupt increase of the  
391 surface roughness compared to 1 ML induces a large number of under-coordinated  
392 atoms at the edges [30], this process should also be observed in the voltamperometries.  
393 Indeed, such a contamination is not shown by cyclic voltamperograms, that present

394 similar current intensities during positive and negative scans (contrarily to what is  
395 observed for free Pt(111)). The higher activity of Pd<sub>1ML</sub>/Pt(111) compared to thicker  
396 samples must hence be ascribed to specific electrocatalytic properties of the first Pd  
397 atomic layers, due to distinguished atomic and/or electronic structural properties.  
398 Regarding the lattice parameters of the first and second plane atomic structure, SXRD  
399 measurements have shown that they have the same values in both samples. All the Pd  
400 atomic layers are pseudomorphic and none of the 1 ML or 2 ML deposits undergo  
401 hydride formation (it can only occur between the second and the third atomic Pd layers,  
402 but the occupation rate of this last layer can here be neglected) [20]. These arguments  
403 clearly indicate that the specific activity of Pd<sub>1ML</sub>/Pt(111) compared to Pd<sub>2ML</sub>/Pt(111)  
404 cannot be ascribed to geometric effects or to hydride formation. Electronic effect must  
405 rather be considered. Indeed, the electronic interactions between the surface Pd atoms  
406 and the underlying layers are different between the 1 ML and 2 ML deposits. Pd surface  
407 atoms for Pd<sub>1ML</sub>/Pt(111) are bounded to the underlying Pt atoms and have no Pd top  
408 neighbors, while most of Pd surface atoms for Pd<sub>2ML</sub>/Pt(111) are deposited onto Pd and  
409 are not in contact with Pt atoms [20]. The ligand effect induced by the Pt substrate  
410 seems thus to be the major responsible of the higher formic acid oxidation activity in  
411 perchlorate media of Pd<sub>1ML</sub>/Pt(111) compared to Pd<sub>2ML</sub>/Pt(111). Chen *et al.* [41]  
412 recently demonstrated that adsorption/desorption peaks observed at low potential on  
413 Pd<sub>1ML</sub>/Pt(111) in perchloric acid solution are not associated with hydrogen adsorption  
414 only, but also to hydroxyl adsorption and, moving to higher potential, to perchlorate  
415 specific adsorption. Although the presence of hydroxyl at such low potential (starting at  
416 0.246 V vs. RHE) may explain the high activity toward formic acid electrooxidation, the  
417 lack of similar experiments on thicker Pd deposits does not allow to draw any reliable  
418 conclusion on this aspect.

419

#### 420 **4. Conclusions**

421

422 The influence of Pd modified Pt(111) surfaces on the electrochemical oxidation  
423 reaction of formic acid was investigated. We coupled our previous *in situ* SXRD  
424 structural characterization of the Pd nanofilms with the voltammeteries recorded on  
425 Pd<sub>x</sub>ML/Pt(111) ( $x = 1, 2, 5, 16$ ) in H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub> solutions supporting electrolyte.

426 The higher electrocatalytic activity of the Pd<sub>x</sub>ML/Pt(111) samples compared to  
427 Pt(111) is confirmed in both acidic media, even if the effect is more pronounced in  
428 HClO<sub>4</sub> compared to H<sub>2</sub>SO<sub>4</sub>. Our experiments show that on the thinnest films, up to  
429 about 5 ML, the decay of formic acid is governed by the well-ordered structure of the  
430 adsorbed (bi)sulfate of the electrode, acting as an effective barrier to formic acid  
431 adsorption. We could detail the specific role of the competitive (bi)sulphate adsorption  
432 on the first and on the following free pseudomorphic Pd terraces. Such effect diminishes  
433 with thickness, as terraces width decreases with the roughening of the surface. Beyond  
434 about 5 ML, decaying of formic acid activity is in both solutions close to 0.5 V vs.  
435 RHE, due to the oxidation of the Pd surface, and activities in the two media tend to  
436 converge for the highest thickness.

437 In perchlorate, the Pd<sub>1</sub>ML/Pt(111) shows an outstanding activity. Thanks to the  
438 detailed structural description of the surface Pd layers, we could demonstrate that, in the  
439 absence of competing anion adsorption (which would be the case with (bi)sulfates), a  
440 major role in formic acid oxidation activity is played by the ligand effect and not by  
441 geometrical strains. This advantageous ligand effect is lost for thicker Pd deposits.

442

#### 443 **5. Acknowledgments**

444 This work has been financially supported by the CAPES (project 728714-3).

#### 445 **Conflict of Interest**

446 The authors declared that they have no conflict of interest.

447

448

#### 449 **6. References**

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# ***Formic acid electrooxidation on palladium nano-layers deposited onto Pt(111): investigation of the substrate effect***

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## Figure Captions

Fig 1. Cyclic voltammograms for the Pt(111) and Pd<sub>xML</sub>/Pt(111) electrodes in H<sub>2</sub>SO<sub>4</sub> 0.1 mol L<sup>-1</sup>,  $\nu = 50 \text{ mV s}^{-1}$ . Inset: same data, current scale multiplied by 4.

Fig 2. Cyclic voltammograms for the Pd<sub>xML</sub>/Pt(111),  $\nu = 50 \text{ mV s}^{-1}$  in (a) in H<sub>2</sub>SO<sub>4</sub> 0.1 mol L<sup>-1</sup>+ formic acid 0.1 mol L<sup>-1</sup>, (b) HClO<sub>4</sub> 0.1 mol L<sup>-1</sup>+ formic acid 0.1 mol L<sup>-1</sup>.

Fig 3. Comparison of formic acid 0.1 mol L<sup>-1</sup> oxidation in H<sub>2</sub>SO<sub>4</sub> 0.1 mol L<sup>-1</sup> (black curve) and HClO<sub>4</sub> 0.1 mol L<sup>-1</sup> (red curve) on Pd<sub>xML</sub>/Pt(111) for different thicknesses. Same conditions as Figure 2. Inset: current maximum during positive scan from cyclic voltammograms.

Figure 1

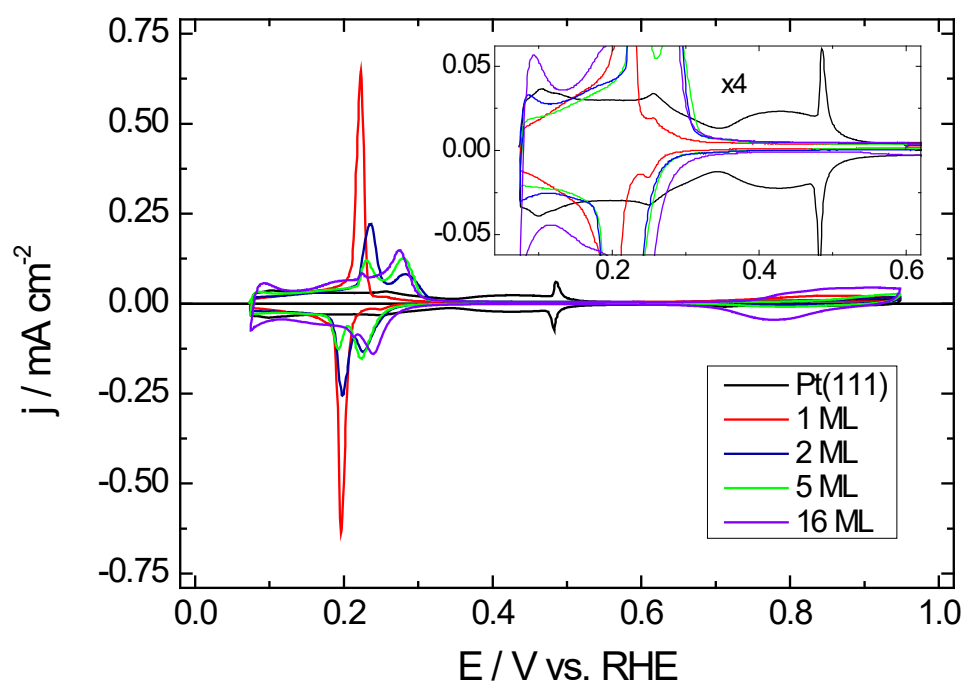


Figure 2

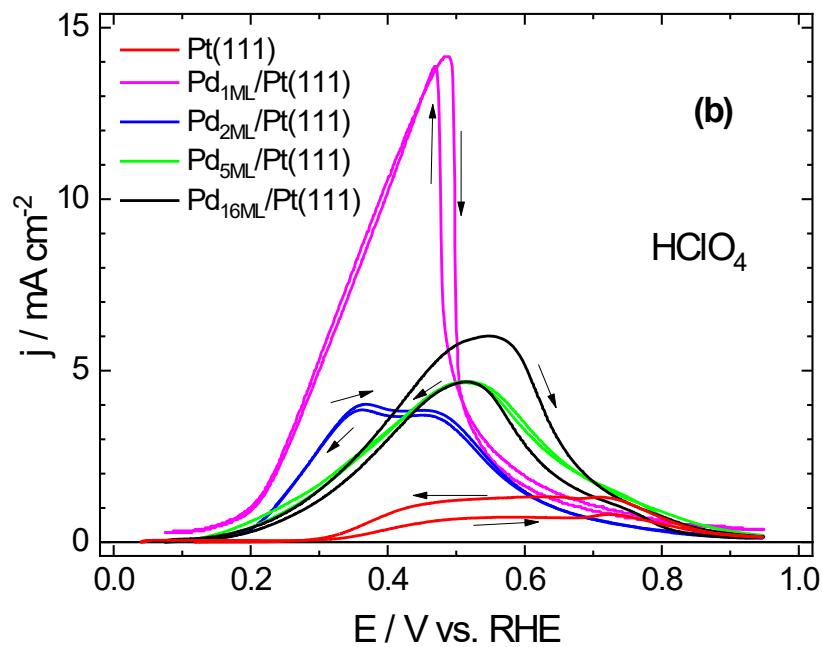
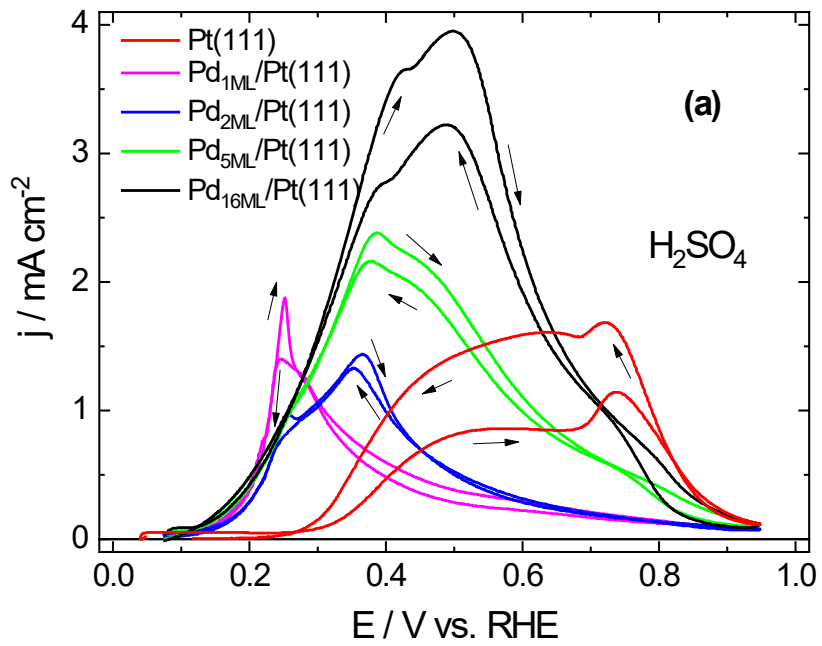
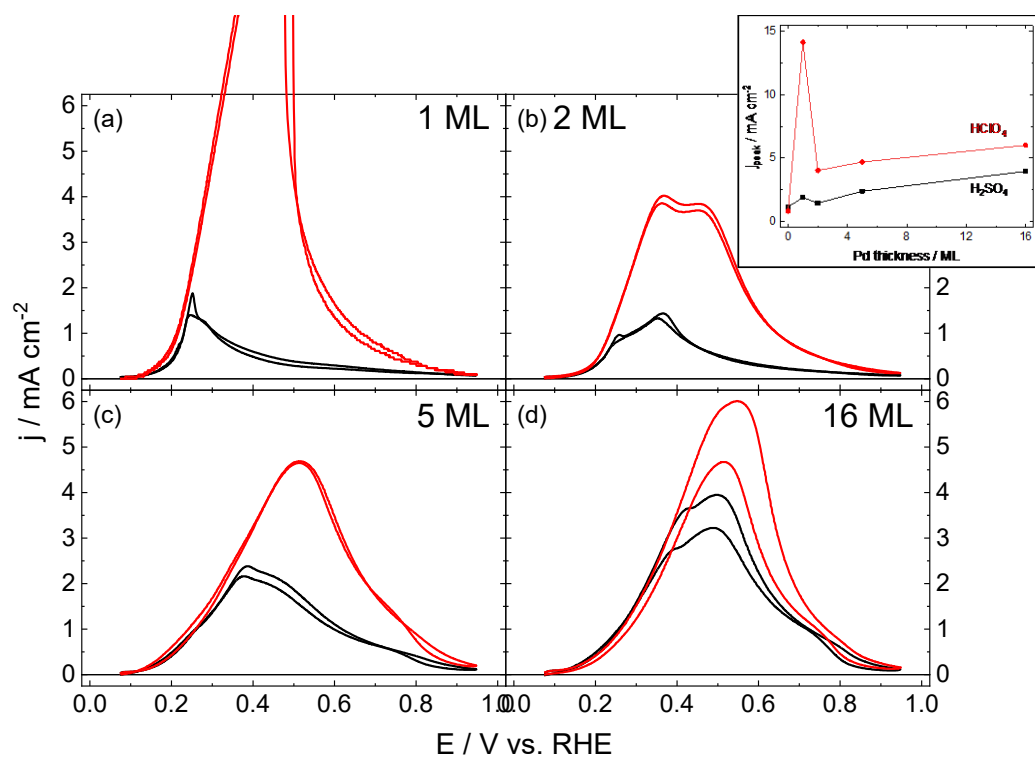


Figure 3



## Supporting Information

### ***Formic acid electrooxidation on palladium nano-layers deposited onto Pt(111): investigation of the substrate effect***

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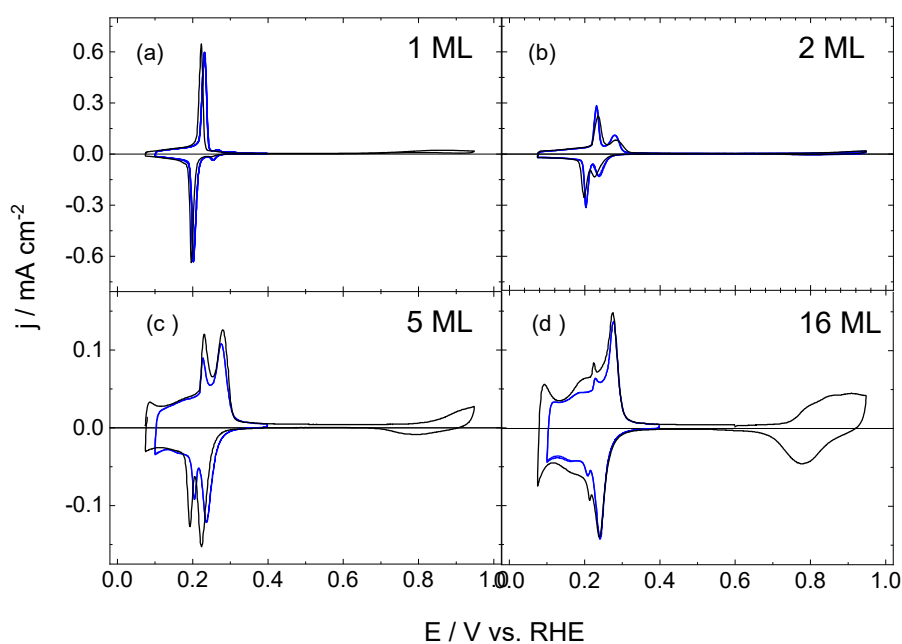
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## 1. Characterization after formic acid electrooxidation on Pd<sub>x</sub>ML/Pt(111)

The electrodes were characterized in supporting acidic medium also after the formic acid electrooxidation experiments, to provide insights about the definition/cleanness of the electrodes surface after the reactivity experiments. The voltammograms recorded after (blue curves) and before (black curves) formic acid electrooxidation (see Figure S1) are very similar: this demonstrates that the Pd<sub>x</sub>ML/Pt(111) surfaces do not undergo consequent irreversible modifications. The lower current densities measured are not surprising, considering that the several transfers undergone by the electrode between the various characterization cells may contaminate its surface.



**Figure S1.** Cyclic voltammograms for Pd<sub>x</sub>ML/Pt(111) with (a) x = 1, (b) x = 2, (c) x = 5, (d) x = 16 in H<sub>2</sub>SO<sub>4</sub> 0.1 mol L<sup>-1</sup>, before (black line) and after (blue line) formic acid electrooxidation experiments.