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

Vanessa L. Oliveira [1,2], Yvonne Soldo-Olivier [1,3], Edson A. Ticianelli [2], Marian Chatenet [1], Eric Sibert [1,+]

[1] *Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP (Institute of Engineering, Uni. Grenoble Alpes), LEPMI, 38000 Grenoble, France*

**Institute of Engineering and Management Univ. Grenoble Alpes*

[2] *Instituto de Química de São Carlos, Universidade de São Paulo, Av. Trab. São-carlense 400, CP 780, CEP 13560-970 São Carlos, SP, Brazil*

[3] *CNRS Université Grenoble Alpes, Institut Néel, 38042 Grenoble, France*

[+] Corresponding author: eric.sibert@lepmi.grenoble-inp.fr

ORCID:

Yvonne Soldo-Olivier: 0000-0003-1624-0159

Edson A. Ticianelli: 0000-0003-3432-2799

Marian Chatenet: 0000-0002-9673-4775

Eric Sibert: 0000-0003-4084-1624

Abstract

The influence of Pd nano-layers electro-deposited onto Pt(111) single-crystal has been systematically studied towards the formic acid electrochemical oxidation reaction in H_2SO_4 and $HClO_4$. The studied Pd_{xML}/Pt(111) surfaces (x = 1, 2, 5 and 16 monolayers –ML-) are all more active than Pt(111) towards formic acid oxidation, even if the activity is very sensitive to the Pd film thickness and morphology. In sulfate solution, the competitive adsorption of long range ordered (bi)sulfate on the pseudomorphic Pd terraces effectively hinders the formic acid oxidation only on the thinnest films. We could observe the different role of the (bi)sulfate adsorption on the first and on the following deposited Pd layers. The sulfate adsorption competitive role rapidly fades away beyond about 5 ML of equivalent thickness, due to the surface roughness increasing and terraces width diminishing.

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

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

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

1. Introduction

Small organic molecules, especially liquid C1-species, are attracting attention as potential fuels for low temperature fuel cells, due to their propensity to be easily stored and to the absence of C-C bonds that are difficult to break [1]. In this perspective, methanol (CH_3OH), formaldehyde (HCHO) and formic acid (HCOOH) are among the most investigated candidates. Despite an apparent simplicity, the complete oxidation of these compounds involves several electron transfers that occur in multiple steps, leading to a difficult overall optimization of appropriate electrocatalysts [2].

Typically, methanol electrooxidations on Pt in acidic media proceeds following two main reaction paths. The indirect path starts with carbon atom dehydrogenation and adsorption. It is followed by adsorbed CO formation that blocks active sites and results in overall slow reaction kinetics. On the contrary, the direct path starts with oxygen atom adsorption. Then, formaldehyde and formic acid can be produced as side products and/or reaction intermediates before CO_2 is formed as a final product. So, improving the activity of an electrode for formaldehyde and formic acid oxidation is not only interesting by itself, but also for the methanol oxidation efficiency.

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

The main approach to counteract the CO_{ads} formation and poisoning is to use a bifunctional bimetallic electrocatalyst [6]. In this strategy, one of the two metals, usually platinum, efficiently dehydrogenates/oxidizes the initial molecule, at least until the formation of adsorbed CO_{ads}. In complement, the second one is a more oxophilic metal that dissociates water molecule into OH_{ads}, which can react with CO_{ads} to produce CO_2 in the well-known Langmuir-Hinshelwood reaction, thereby freeing active sites for further activity.

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

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

Several studies have been made on metallic single crystals modified by Pd deposition towards the formic acid oxidation reaction. Kibler *et al.* [11] measured the formic acid oxidation activity of a pseudomorphic atomic Pd surface layer on different substrates (Au, Pt, Pd, Ir, Rh…) with (111) surface orientation in 0.1 mol L^{-1} H_2SO_4 and found that the activity is very sensitive to the nature of the substrate. More in detail, Pd deposited on Pt(111) was found to exhibit a higher activity compared to all the studied mono-metallic substrates or bulk Pd(111) surface. The authors suggest that, for all these systems, the electronic modification of the Pd monolayer is essentially due to the geometric factor, associated to the lateral strain of the Pd layer. This lattice mismatch would induce a d-band shift, directly influencing bonding energies, as calculated by Nørskov's group [13].

Llorca *et al.* [14] investigated this reaction on Pt(111) surface modified by Pd forced deposition with coverages up to one atomic layer in 0.5 mol L^{-1} H_2SO_4. As Pd addition only induced marginal activity improvement, the authors suggested that CO poisoning, although existing on free Pt(111), has limited extend on the overall activity; therefore even if the Pd addition lowers poisoning, it cannot greatly change the activity that is already good. In opposite, Baldauf *et al.* [15], using electrochemical deposition of Pd at 0.27 V *vs.* SCE on Pt(111) in 0.1 mol L^{-1} H_2SO_4, observed changes in the activity for coverage of 0.5 and 1 monolayer (ML). A new oxidation peak, reversible between positive and negative scans of the cyclic voltammetry, appears and grows at lower potential. It is associated to oxidation of formic acid through the direct path on Pd areas. Nevertheless, the irreversible peaks associated to the oxidation through the indirect path on Pt surface are still present at higher potential. Maximum oxidation currents are slightly decreased compared to free Pt. For thicker deposits, from 2 to 5 ML as equivalent thickness on Pt(111) (the equivalent thickness x ML is calculated assuming a layer-by-layer growth mechanism with a two-electron-transfer process and one deposited Pd atom per surface Pt atom), only a large reversible oxidation peak is observed, suggesting that only the direct path remains on Pd. The activity is higher than on free Pt, 0.5 and 1 ML Pd coverages.

Arenz *et al.* [9,16] studied the activity of a fraction up to 1 ML of Pd on Pt(111), as well as a PtPd(111) bulk alloy in 0.1 mol L^{-1} $HClO_4$. Both systems revealed a strong activity enhancement compared to Pt(111), supporting the idea that the direct path is favored on Pd, as shown by infrared measurements.

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

Anion sensitivity was also seen for Pd films up to 2 ML on Pt(111) [1]. Deposits were obtained after rapid immersion of the electrode in about 10^{-5} M $Pd(NO_3)_2$ solution followed by reduction of Pd salts and deposition in hydrogen atmosphere. In aqueous perchloric acid, adsorbed palladium promotes formic acid electrooxidation and a maximum oxidation rate is found when a single Pd layer is deposited. In contrast, voltammetries recorded in aqueous sulphuric acid show a strong inhibition of this reaction, which was attributed to extensive specific adsorption of (bi)sulphate anions, competing with adsorption of formic acid molecules.

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

The Pd_{1ML}/Pt(111) deposit consists of a complete underpotentially deposited (UPD) monolayer, pseudomorphic with the substrate (matching with the lattice of the crystalline substrate) [19]. *In situ* surface X-Ray diffraction (SXRD) and *ex situ* AFM experiments made by some of the authors of the present paper allowed the detailed structural and morphological characterization of multilayered Pd nanofilms deposited in $PdCl_2$ 10^{-4} M + HCl 3 10^{-3}+ H_2SO_4 0.1 M solution [20,21]. For Pd_{2ML}/Pt(111), the first Pd layer is complete (UPD), the coverage of the second layer is about 80% and the coverage of the third one is only 20%; for Pd_{14ML}/Pt(111), the first ten Pd layers are complete and the coverage progressively decreases until the twentieth layer, which is nearly empty. The first ten Pd atomic planes are all pseudomorphic *i.e.* in-plane lattice parameters of Pd layers are equal to that of the Pt(111) substrate, while the next Pd layers are progressively relaxing to Pd bulk lattice parameters. These measurements enable establishing a direct relationship between surface structure and electrochemical characterization of the Pd/Pt(111) layers. Hence, the voltammetry in acidic media allows determining the structure of the first deposited Pd layers onto Pt(111), without resorting to physical characterization. *Ex situ* AFM images [18] show that up to 4 ML the deposits present uniform flat zones, while roughness rapidly increases beyond this thickness inducing the decrease of the terraces width.

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

This detailed surface characterization coupled to the electrochemical study of the Pd_{xML}/Pt(111) system towards formic acid oxidation reaction represents a unique opportunity to correlate the surface structure to the reactivity. The present paper aims at studying the influence of fine-tuned Pd/Pt(111) layers towards the electrooxidation of formic acid. The study is performed in both H_2SO_4 and $HClO_4$ solutions, to specifically address the mechanisms underlying the competitive adsorption between intermediate formate species and (bi)sulfate, compared to perchlorate.

2. Experimental details

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

For each experiment, the single crystal surface was cleaned and regenerated using flame-annealing (butane + air). It was cooled in a reducing atmosphere (N_2/H_2 90:10) and finally put in contact with ultrapure water saturated with the same mixture, as described previously [18,20]. A droplet of pure water was maintained at the electrode surface to avoid contamination during all transfers between cooling glassware and cells dedicated to electrochemical Pd deposition and characterization. Both cells were made of Pyrex and double-walled designed to allow circulation of thermostated water for temperature control at 25 ± 1°C.

A cyclic voltamperogram in 0.1 mol L^{-1} H_2SO_4 prepared from Merck sulfuric acid (Suprapur, 96 %) in ultrapure water (Millipore Elix + Milli-Q gradient, 18.2 MΩ cm, < 3 ppb Total Organic Content) was recorded before each deposition experiment to assess the Pt(111) surface quality and address the absence of contaminants in the system [23–27].

A 0.1 mol L^{-1} H_2SO_4 + 3 10^{-3} mol L^{-1} HCl (Merck, Suprapur 30%) + 10^{-4} mol L^{-1} $PdCl_2$ (Alfa Aesar, 99%) solution was employed for palladium electrochemical deposition. The Pt(111) electrode was first introduced at *E* = 1.05 V *vs*. RHE (at a potential where no Pd deposition occurs) and then the potential was scanned negatively to induce the Pd deposition. The single Pd atomic layer deposition ($x = 1$) was achieved by underpotential deposition (UPD): the potential was simply scanned very slowly (v = 0.1 mV s^{-1}) to separate UPD and bulk deposition and held in-between. For thicker deposits (Pd_{xML}/Pt(111) with x = 2, 5 and 16 ML), the Pd quantity was adjusted by precisely measuring the coulometric charge assuming a layer-by-layer pseudomorphic deposit (*i.e.* one palladium atom per each surface platinum atom and for each layer) and two electrons transferred for each Pd atom [18,20,21]. Practically, the potential of the Pt(111) electrode was scanned down (v = 0.1 mV s^{-1}) to Pd bulk and diffusion-limited deposition (*E* = 0.701 V *vs.* RHE). The potential was then maintained at this value until the required Pd quantity was obtained. After this, Pd_{xML}/Pt(111) electrodes were emerged from the deposition solution, rinsed with ultra-pure water and transferred to the characterization cell with pure acidic electrolyte (H_2SO_4 or and $HClO_4$) for control.

The electrooxidation of formic acid on the different Pt(111) and Pd_{xML}/Pt(111) electrodes was investigated in 0.1 mol L^{-1} H_2SO_4 + 0.1 mol L^{-1} HCOOH and 0.1 mol L^{-1} $HClO_4$ + 0.1 mol L^{-1} HCOOH solutions.

3. Results and discussion

3.1 Palladium deposition and electrochemical characterization in sulfuric acid

As discussed in the introduction paragraph, electrochemical characterization in sulfuric acid allows determining the atomic structure of the first Pd deposited layers. Figure 1 exhibit representative cyclic voltamperograms (CVs) in aqueous sulfuric acid (0.1 mol L^{-1} H_2SO_4) of freshly-prepared Pd nanofilms and of the free Pt(111) surface, also provided as benchmark. The Pt(111) surface (Figure 1, black curves) exhibits the characteristic butterfly envelope, confirming the quality and cleanness of the Pt(111) electrode surface [24–27]. Once Pd has been deposited, the corresponding voltamperograms (Figure 1) are completely different, in accordance with the literature [9,18,20,21,28–30].

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

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

Both pairs of peaks, associated with the first Pd layer and the “second and following” layers, are associated with simultaneous hydrogen adsorption/desorption and sulfate desorption/adsorption [12,30,31]. Adsorbed sulfates are forming an ordered structure $(\sqrt{3}\times\sqrt{7})R19.1°$ on the Pd overlayers on Pt(111) [30], as on Pt(111) [32] and bulk Pd(111) [33]. The sharpness of these adsorption peaks is associated with the presence of a long-range order both on Pt(111) [26] and Pd(111) [33,34]. In opposite, the broadening of the adsorption peaks observed with thicker Pd deposit is related to the narrowing of flat Pd terraces and the reduction in size of long-range ordered sulfate domains [35].

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

3.2 Formic acid electrooxidation on Pd_{xML}/Pt(111)

Figure 2 shows a set of CVs during formic acid electrooxidation on Pd_{xML}/Pt(111) and Pt(111), using 0.1 mol L^{-1} H_2SO_4 (a) and 0.1 mol L^{-1} $HClO_4$ (b) electrolytes. All Pd_{xML}/Pt(111) surfaces exhibit higher activity than Pt(111) for this reaction in both solutions. As already suggested in the literature, the lower activity of Pt versus Pd is attributed to different overall reaction pathways for formic acid electrooxidation on the two metals [1,14,16,36]. More specifically, “poisoning species”, the most important being adsorbed CO, may hinder the electrooxidation of formic acid on Pt, by blocking the active sites required for the adsorption of the HCOOH molecules themselves, or for the H_2O adsorption and dissociation that are also needed for the reaction [16,37]. In both media, CVs on Pt(111) are showing a strong difference between the forward and backward scans, the second presenting larger currents. This is due to the removal of CO at high potential, associated with the peak at $E = 0.75$ V *vs.* RHE, providing a less blocked surface during the backward scan. In opposite, for Pd surfaces, the forward and backward scans are much similar, with slightly less current for the backward scan. This indicates that no consequent surface blocking by CO_{ads} is occurring (if any), in accordance with the direct path mechanism.

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

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

Concerning the formic acid electro-oxidation activity in sulfate electrolyte, voltammetries show a general increase of the formic oxidation current with thickness, although the electrochemical response is characterized by a specific behavior as a function of the number of deposited Pd layers. For Pd_{1ML}/Pt(111), there is a single oxidation peak slightly above 0.2 V *vs.* RHE, at the same potential where the sharp (bi)sulfate adsorption peak is observed in sulfuric acid solution (Figure 1): this maximum is followed by a rapid decrease of the oxidation current. For Pd_{2ML}/Pt(111), at this same potential, the curve presents only a shoulder and the current continues to increase up to around 0.37 V *vs.* RHE: beyond this value the signal rapidly drops. The current decrease is now in the potential region where (bi)sulfate adsorption takes place on the free second and following Pd atomic layers.

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

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

For Pd_{16ML}/Pt(111), the current continuously increases up to about 0.5 V *vs.* RHE (only a bump at about 0.37 V *vs.* RHE is visible). At this highest thickness, it clearly appears that (bi)sulfate adsorption has a lost effectiveness in hindering formic acid oxidation. This thickest deposit is also exhibiting the highest difference between the positive and negative scans. The corresponding current excess during the positive scan should be ascribed to the release of hydrogen absorbed in palladium at low potential.

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

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

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

Figure 3 shows the comparison of formic acid activity in both media for the same Pd layer thicknesses. Two different potential regions are present. Scanning from low potential, the formic acid electro-oxidation activity firstly grows similarly in both media. The reaction onset is not affected by the nature of the anions presents in solution; also, current intensity behavior is very close. Contrarily, beyond about 0.25 V *vs.* RHE, where (bi)sulfate adsorption is observed in the absence of formic acid, oxidation currents behave differently: the activity is always larger with perchlorate than with sulfate. Nevertheless, this deviation diminishes beyond about 5 ML, where, contrarily to perchlorate, formic acid oxidation activity in presence of sulfate significantly increases: finally, current intensities tend to converge at the highest thickness. This observation is in complete agreement with the fact that only adsorbed (bi)sulfate on the pseudomorphic terraces of the thinnest electrodes, where they form a well-ordered structure, act as an effective barrier to formic acid oxidation. As thickness increases, formic acid oxidation is less and less hindered by the(bi)sulfate adsorption. Beyond about 4-5 ML, formic acid oxidation is stopped in both solutions (sulfate and perchlorate) at higher potential, close to about 0.5 V *vs.* RHE, where Pd surfaces deactivate owing to metal-oxides formation.

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

If such remarkable activity for $Pd_{1ML}/Pt(111)$ were due to the larger creation of poisoning species like CO_{ads} at higher thickness, where the abrupt increase of the surface roughness compared to 1 ML induces a large number of under-coordinated atoms at the edges [30], this process should also be observed in the voltamperometries. Indeed, such a contamination is not shown by cyclic voltamperograms, that present similar current intensities during positive and negative scans (contrarily to what is observed for free Pt(111)). The higher activity of Pd_{1ML}/Pt(111) compared to thicker samples must hence be ascribed to specific electrocatalytic properties of the first Pd atomic layers, due to distinguished atomic and/or electronic structural properties. Regarding the lattice parameters of the first and second plane atomic structure, SXRD measurements have shown that they have the same values in both samples. All the Pd atomic layers are pseudomorphic and none of the 1 ML or 2 ML deposits undergo hydride formation (it can only occur between the second and the third atomic Pd layers, but the occupation rate of this last layer can here be neglected) [20]. These arguments clearly indicate that the specific activity of Pd_{1ML}/Pt(111) compared to Pd_{2ML}/Pt(111) cannot be ascribed to geometric effects or to hydride formation. Electronic effect must rather be considered. Indeed, the electronic interactions between the surface Pd atoms and the underlying layers are different between the 1 ML and 2 ML deposits. Pd surface atoms for Pd_{1ML}/Pt(111) are bounded to the underlying Pt atoms and have no Pd top neighbors, while most of Pd surface atoms for Pd_{2ML}/Pt(111) are deposited onto Pd and are not in contact with Pt atoms [20]. The ligand effect induced by the Pt substrate seems thus to be the major responsible of the higher formic acid oxidation activity in perchlorate media of Pd_{1ML}/Pt(111) compared to Pd_{2ML}/Pt(111). Chen *et al.* [41] recently demonstrated that adsorption/desorption peaks observed at low potential on Pd_{1ML}/Pt(111) in perchloric acid solution are not associated with hydrogen adsorption only, but also to hydroxyl adsorption and, moving to higher potential, to perchlorate specific adsorption. Although the presence of hydroxyl at such low potential (starting at 0.246 V *vs.* RHE) may explain the high activity toward formic acid electrooxidation, the lack of similar experiments on thicker Pd deposits does not allow to draw any reliable conclusion on this aspect.

4. Conclusions

The influence of Pd modified Pt(111) surfaces on the electrochemical oxidation reaction of formic acid was investigated. We coupled our previous *in situ* SXRD structural characterization of the Pd nanofilms with the voltammetries recorded on $Pd_{xML}/Pt(111)$ ($x = 1, 2, 5, 16$) in H_2SO_4 and $HClO_4$ solutions supporting electrolyte.

The higher electrocatalytic activity of the $Pd_{xML}/Pt(111)$ samples compared to Pt(111) is confirmed in both acidic media, even if the effect is more pronounced in $HClO_4$ compared to H_2SO_4. Our experiments show that on the thinnest films, up to about 5 ML, the decay of formic acid is governed by the well-ordered structure of the adsorbed (bi)sulfate of the electrode, acting as an effective barrier to formic acid adsorption. We could detail the specific role of the competitive (bi)sulphate adsorption on the first and on the following free pseudomorphic Pd terraces. Such effect diminishes with thickness, as terraces width decreases with the roughening of the surface. Beyond about 5 ML, decaying of formic acid activity is in both solutions close to 0.5 V *vs.* RHE, due to the oxidation of the Pd surface, and activities in the two media tend to converge for the highest thickness.

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

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Conflict of Interest

The authors declared that they have no conflict of interest.

6. References

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

Vanessa L. Oliveira [1,2], Yvonne Soldo-Olivier [1,3], Edson A. Ticianelli [2], Marian Chatenet [1], Eric Sibert [1,+]

[1] *Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP (Institute of Engineering, Uni. Grenoble Alpes), LEPMI, 38000 Grenoble, France*

**Institute of Engineering and Management Univ. Grenoble Alpes*

[2] *Instituto de Química de São Carlos, Universidade de São Paulo, Av. Trab. São-carlense 400, CP 780, CEP 13560-970 São Carlos, SP, Brazil*

[3] *CNRS Université Grenoble Alpes, Institut Néel, 38042 Grenoble, France*

[+] Corresponding author: eric.sibert@lepmi.grenoble-inp.fr

ORCID:

Yvonne Soldo-Olivier: 0000-0003-1624-0159

Edson A. Ticianelli: 0000-0003-3432-2799

Marian Chatenet: 0000-0002-9673-4775

Eric Sibert: 0000-0003-4084-1624

Figure Captions

Fig 1. Cyclic voltammograms for the Pt(111) and Pd_{xML}/Pt(111) electrodes in H_2SO_4 0.1 mol L^{-1}, $v = 50$ mV s^{-1}. Inset: same data, current scale multiplied by 4.

Fig 2. Cyclic voltammograms for the Pd_{xML}/Pt(111), $v = 50$ mV s^{-1} in (a) in H_2SO_4 0.1 mol L^{-1}+ formic acid 0.1 mol L^{-1}, (b) $HClO_4$ 0.1 mol L^{-1}+ formic acid 0.1 mol L^{-1}.

Fig 3. Comparison of formic acid 0.1 mol L^{-1} oxidation in H_2SO_4 0.1 mol L^{-1} (black curve) and $HClO_4$ 0.1 mol L^{-1} (red curve) on Pd_{xML}/Pt(111) for different thicknesses. Same conditions as Figure 2. Inset: current maximum during positive scan from cyclic voltammograms.

Figure 1

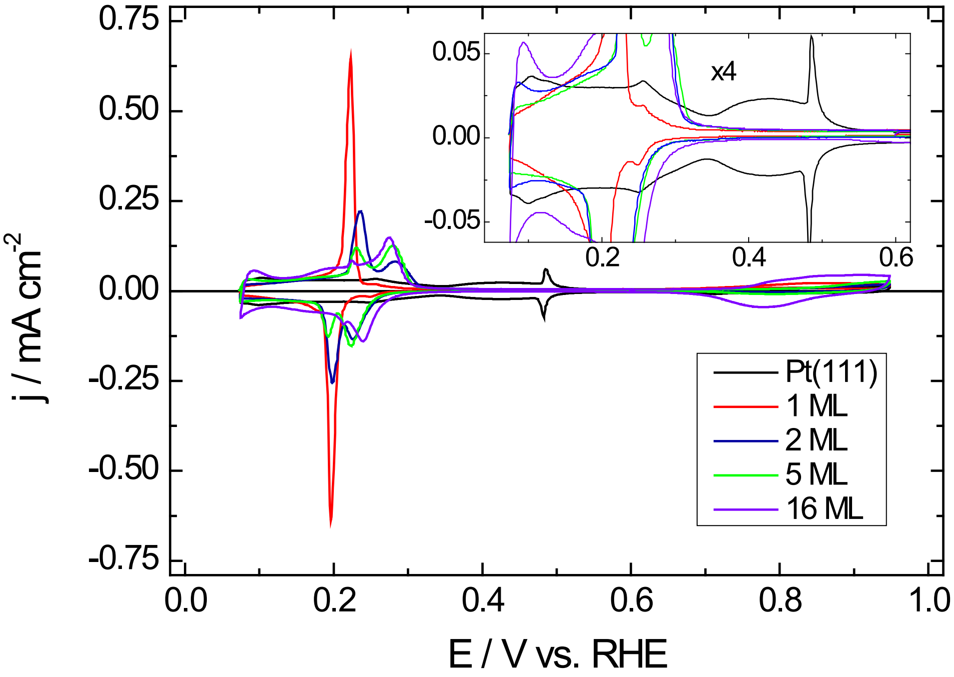
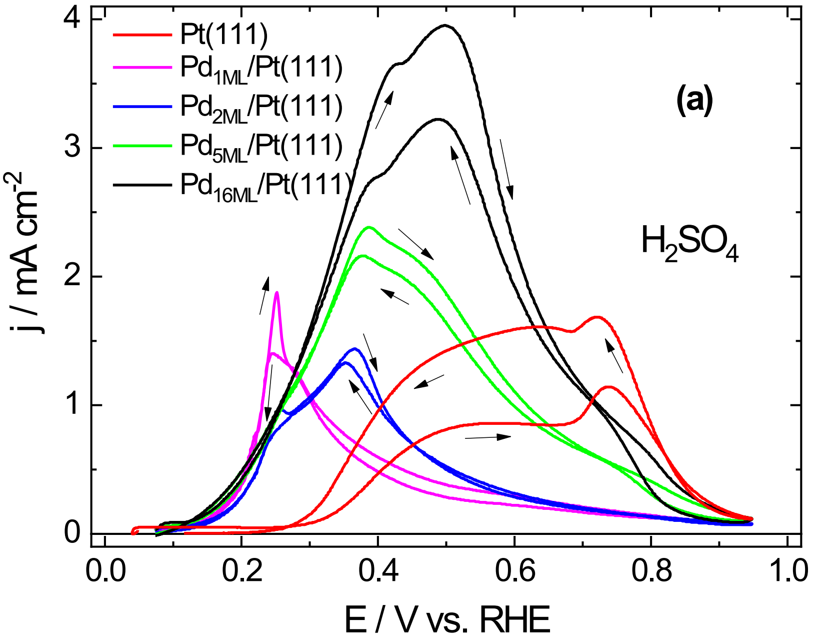

0.75
0.50
0.25
0.00
-0.25
-0.50
-0.75
j / mA cm^{-2}
0.0
0.2
0.4
0.6
0.8
1.0
E / V vs. RHE
0.05
0.00
-0.05
0.2
0.4
0.6
x4
Pt(111)
1 ML
2 ML
5 ML
16 ML

Figure 2


Pt(111)
$Pd_{1ML}/Pt(111)$
$Pd_{2ML}/Pt(111)$
$Pd_{5ML}/Pt(111)$
$Pd_{16ML}/Pt(111)$
(a)
H_2SO_4
j / mA cm^{-2}
E / V vs. RHE
0
1
2
3
4
0.0
0.2
0.4
0.6
0.8
1.0

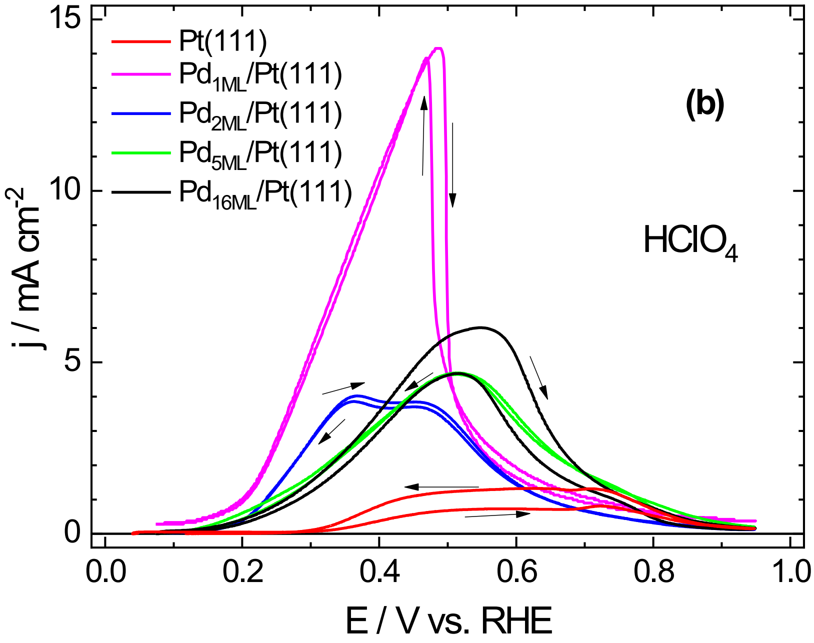
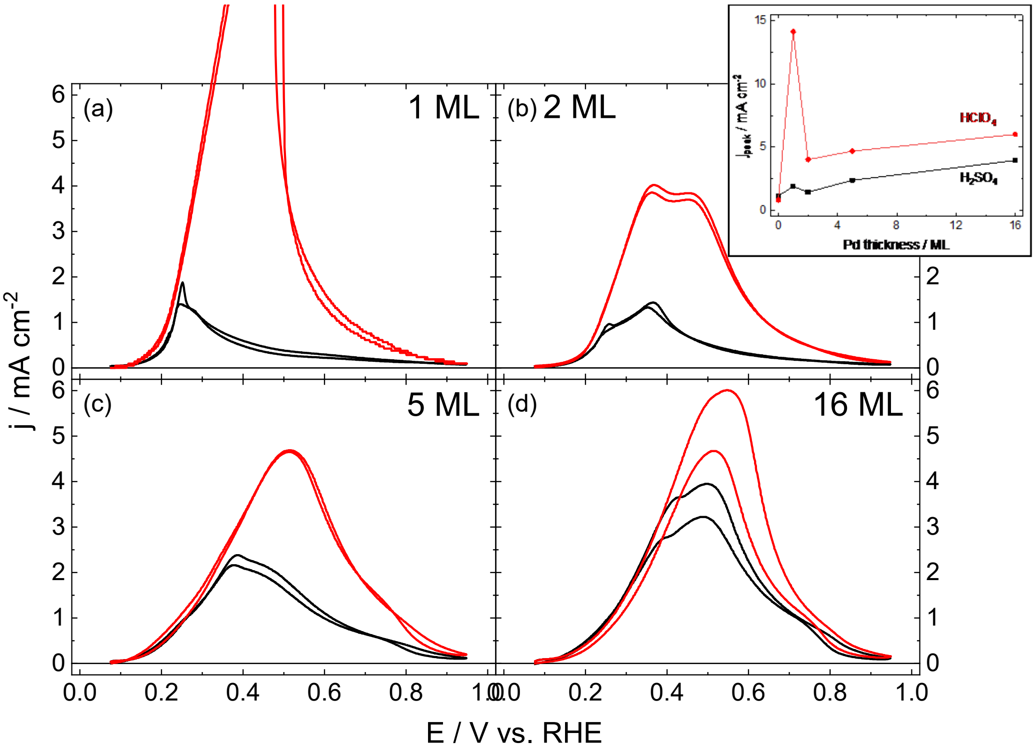

Pt(111)
$Pd_{1ML}/Pt(111)$
$Pd_{2ML}/Pt(111)$
$Pd_{5ML}/Pt(111)$
$Pd_{16ML}/Pt(111)$
(b)
$HClO_4$
j / mA cm^{-2}
E / V vs. RHE
0
5
10
15
0.0
0.2
0.4
0.6
0.8
1.0

Figure 3


(a)
1 ML
(b)
2 ML
(c)
5 ML
(d)
16 ML
j / mA cm^{-2}
0
1
2
3
4
5
6
0.0
0.2
0.4
0.6
0.8
1.0
E / V vs. RHE
j_{peak} / mA cm^{-2}
0
5
10
15
0
4
8
12
16
Pd thickness / ML
HClO$_4$
H$_2$SO$_4$

Supporting Information

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

Vanessa L. Oliveira [1,2], Yvonne Soldo-Olivier [1,3], Edson A. Ticianelli [2], Marian Chatenet [1], Eric Sibert [1,+]

[1] *Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP (Institute of Engineering, Uni. Grenoble Alpes), LEPMI, 38000 Grenoble, France*

**Institute of Engineering and Management Univ. Grenoble Alpes*

[2] *Instituto de Química de São Carlos, Universidade de São Paulo, Av. Trab. São-carlense 400, CP 780, CEP 13560-970 São Carlos, SP, Brazil*

[3] *CNRS Université Grenoble Alpes, Institut Néel, 38042 Grenoble, France*

[+] Corresponding author: eric.sibert@lepmi.grenoble-inp.fr

ORCID:

Yvonne Soldo-Olivier: 0000-0003-1624-0159

Edson A. Ticianelli: 0000-0003-3432-2799

Marian Chatenet: 0000-0002-9673-4775

Eric Sibert: 0000-0003-4084-1624

1. Characterization after formic acid electrooxidation on $Pd_{xML}/Pt(111)$

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 $Pd_{xML}/Pt(111)$ 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.

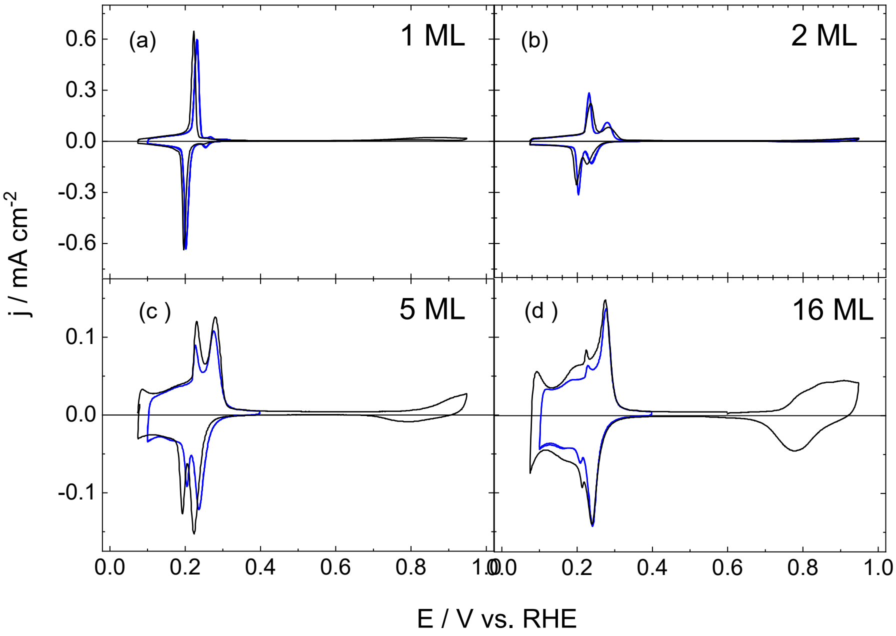


Figure S1. Cyclic voltammograms for $Pd_{xML}/Pt(111)$ with (a) x = 1, (b) x = 2, (c) x = 5, (d) x = 16 in H_2SO_4 0.1 mol L^{-1}, before (black line) and after (blue line) formic acid electrooxidation experiments.