



# The role of formic acid/formate equilibria in the oxidation of formic acid on Pt (111)

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## ARTICLE INFO

### Keywords:

Formic acid  
Platinum  
Single crystal  
Formate adsorption  
Perchlorate  
DFT

## ABSTRACT

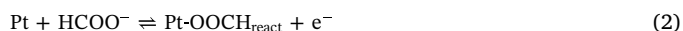
The formic acid oxidation reaction has been studied in concentrated perchloric acid solutions (up to 9.14 M (60%)) on the Pt (111) surface to explore the relationships between interfacial properties and kinetics. It is found that, as the concentration of perchloric acid in the supporting electrolyte increases, the current markedly decreases, making it possible to detect adsorbed formate on the surface by voltammetric methods. With the aid of DFT calculations, it is shown that the diminution in current is the result of two opposing factors: the reduction in the concentration of free formate in solution and electrode charge effects which encourage the adsorption of formate in a particular configuration. Additionally, the electrochemical behavior under highly acidic conditions suggests the formation of clathrate structures and emphasizes the relevance of the water structure effect in electrode adsorption processes.

## 1. Introduction

The electrocatalysis of the formic acid oxidation reaction (FAOR) is attracting much attention due to its possible use in fuel cells since it has some advantages compared to other fuels: low operating temperature, fast kinetics and relative low crossover across the membrane [1]. As a catalyst, platinum is one of the most studied metals because of its good electrocatalytic properties [2,3]. The FAOR mechanism on platinum is structure sensitive and has a dual path [4,5]: the direct pathway, via an active intermediate, and the slower poisoning route, in which CO forms before complete oxidation to CO<sub>2</sub>. Although the Pt(100) surface presents the highest activity toward CO<sub>2</sub> through the direct route (up to 107 molecules of CO<sub>2</sub> s<sup>-1</sup> Pt site<sup>-1</sup>), it is inhibited by the slower path which involves formation of CO, which blocks the surface until it is oxidized at higher overpotentials [6]. On the other hand, the Pt (111) surface is the best option for avoiding the poison blockage. Although the measured turnover frequency on Pt(111) is much lower (5.2 molecules s<sup>-1</sup> Pt site<sup>-1</sup>), CO formation is not detected during the timescale of the experiment, and thus formic acid is oxidized only through the active intermediate path. For this reason, the Pt(111) electrode was chosen for this research.

Moreover, the FAOR activity is also very dependent on the pH, as revealed by studies in solutions with different pH values. The activity increases with pH up to pH = 4, which coincides with the pK<sub>a</sub> of formic

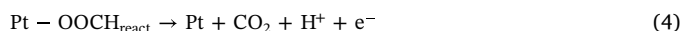
acid (3.75), in parallel with the increase in the concentration of formate in the solution [7,8], implying that formate species play a key role in the reaction. This behavior indicates that before the rate-determining step (rds) one proton has been transferred, i.e., either solution formate is the reactive species that adsorbs on the surface according to:



(where the subscript 'react' indicates the reactive species), or formic acid interacts with the surface giving rise to an adsorbed formate species while releasing one proton:



In this case the rds should be the second electron transfer, which will form CO<sub>2</sub> and free up the platinum sites again:



Assuming that reactions (1), (2) and (3) are very fast, the reaction rate will depend on the ratio [HCOOH]/[H<sup>+</sup>], that is, on the effective formate concentration.

Regarding the nature of the adsorbed formate species that react and yield CO<sub>2</sub>, it was initially proposed that adsorbed bridge-bonded formate, a species detected by IR methods [9–13], was the active

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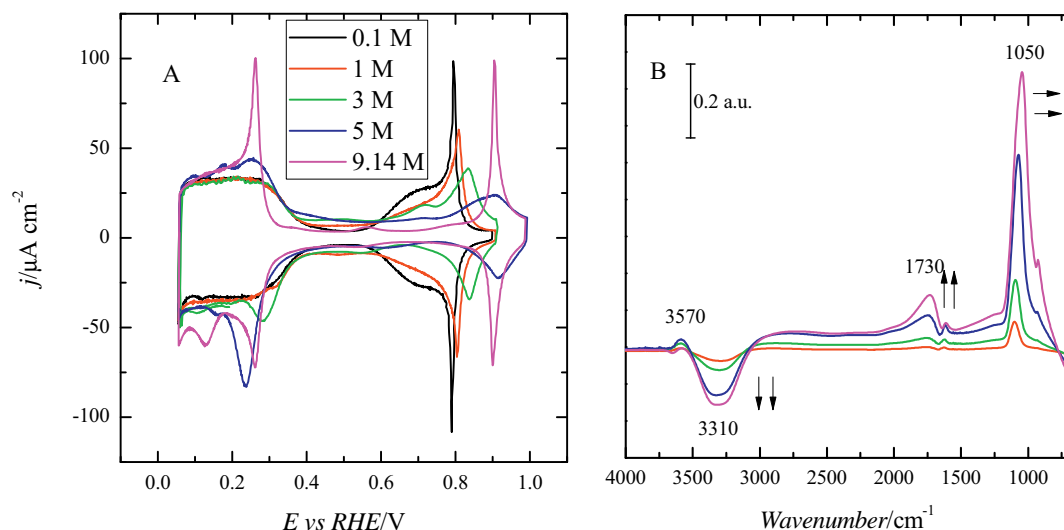
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<https://doi.org/10.1016/j.elecom.2018.11.011>

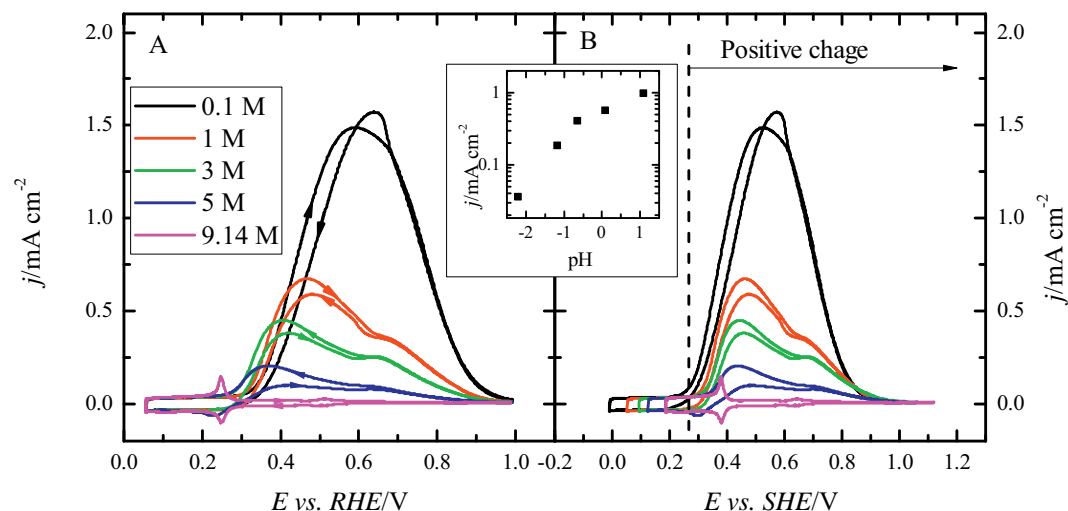
Received 22 October 2018; Received in revised form 15 November 2018; Accepted 16 November 2018

Available online 17 November 2018

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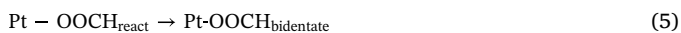


**Fig. 1.** (A) Voltammetric profiles for the Pt(111) electrode in different perchloric acid solutions (scan rate  $50 \text{ mV s}^{-1}$ ). (B) FTIR transmission spectra for the solutions taking the spectrum for water as reference.



**Fig. 2.** Voltammetric profiles for the Pt(111) electrode in different perchloric acid solutions +  $0.01 \text{ M HCOOH}$  (scan rate  $50 \text{ mV s}^{-1}$ ) on (A) the RHE scale and (B) the SHE scale. The dashed line indicates the position of the pzc. Inset: plot of the current density at  $0.4 \text{ V (SHE)}$  vs. pH.

intermediate. However, the cleavage of the C–H bond in this configuration has a very large activation energy, and for this reason it is unlikely to be the active intermediate [14]. Moreover, active intermediates are short-lived, which makes them difficult to detect using spectroscopic techniques. On the other hand, DFT calculations also suggest that this active intermediate is formate but adsorbed in a monodentate form [6,14], because in this configuration the activation barrier is very low. Since the bidentate form is much more stable than the monodentate form [6], the reaction (5) is very favorable:



Effective catalysis requires stabilization of the monodentate form or the hindrance of its transformation into the bidentate stable configuration. In this respect, the presence of adatoms stabilizes the monodentate configuration [15,16], whereas the presence of adsorbed species such as formate [6] or sulfate [17] hinders the transformation.

To explore the kinetics of the reaction through its active intermediate, the FAOR has been investigated under extremely acidic solutions, up to concentrated perchloric acid. The idea is to shift the solution formic acid/formate equilibria to values in which the number of formate anions is very low. Additionally, because pH changes in the

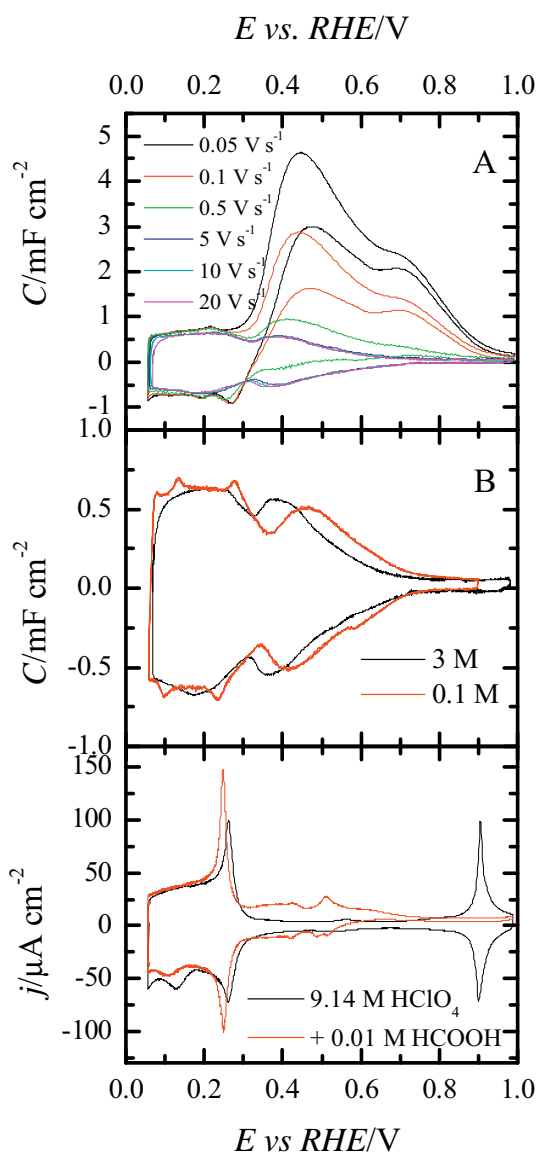
electrolyte imply charge changes in the electrode, along with the active potential region, the approach also makes it possible to explore the effect of electrode charge on reactivity. In doing so, adsorbate-related perchlorate features have been observed, likely involving changes in the water network under highly acidic conditions.

## 2. Experimental and theoretical methods

The experimental protocols have been described elsewhere [18–20], as well as the ATR experiments [21]. In this case, a ZnSe prism was used. Details of the DFT calculations have been given in [6]. Solutions were prepared with perchloric acid (60% Merck p.a. EMSURE® ACS), formic acid (Merck KGaG, 98%) and ultrapure water (Elga PureLab Ultra 18.2 MΩ cm). Argon (N50) and hydrogen (N50) from Air Liquide were used.

## 3. Results and discussion

Before studying the FAOR under different pH conditions, the behavior of the electrode in the supporting electrolyte should be considered. Fig. 1A shows the different voltammetric profiles obtained as



**Fig. 3.** (A) Voltammetric profiles in capacitance for the Pt(111) electrode in 3 M HClO<sub>4</sub> + 0.01 M HCOOH at different scan rates. (B) Comparison between the voltammetric profiles of Pt(111) in 3 M HClO<sub>4</sub> + 0.01 M HCOOH at 20 V s<sup>-1</sup> and in 0.1 M HClO<sub>4</sub> + 0.01 M HCOOH at 50 V s<sup>-1</sup>. (C) Comparison between the voltammetric profiles of Pt(111) in 9.14 M HClO<sub>4</sub> in the presence and absence of 0.01 M HCOOH at 50 mV s<sup>-1</sup>.

the perchloric acid concentration increases. As can be seen, significant changes can be observed in the hydrogen and OH adsorption region as the pH diminishes. In the hydrogen adsorption region, new peaks appear at ca. 0.26 V for concentrations higher than 3 M. Moreover, OH adsorption peaks are displaced to positive potentials and, in some cases, almost disappear. It could be argued that these changes are related to the traces of chloride that perchloric acid may contain. However, the observed modifications are not compatible with this hypothesis. First, the voltammetric profiles have different features to those obtained in the presence of chloride [22]. Second, the observed changes from 3 to 9.14 M concentration are not compatible with a three-fold increase in the concentration of the species responsible for the change. Thus, these changes must be related to some other species whose concentration increases significantly. According to previous reports on highly concentrated perchloric acid solutions [23–25], perchlorate and water species promote the formation of clathrate compounds. These clathrate conformations may be responsible for the modifications in the

voltammetric profile in highly acidic solutions. To detect changes in the solution, the IR transmission spectra obtained for increasing concentrations of HClO<sub>4</sub> (using as a reference the spectrum taken in water) are shown in Fig. 1B. They present similar features to those reported in the literature [25]. Three different bands are observed: the adsorbate perchlorate anion band (from 1050 to 1100 cm<sup>-1</sup>), the bipolar O–H bending band of water around 1600–1750 cm<sup>-1</sup> and the O–H stretching water bands between 3100 and 3600 cm<sup>-1</sup>. The O–H bending bands appear at higher wavenumber values than those reported in the literature [24,25]. According to a work by Osawa on perchlorate adsorption on Au(111) [26], the bands at wavenumbers around 1700–1740 cm<sup>-1</sup> are associated with the asymmetric H-O-H bending mode of the hydronium ion. Displacement of the adsorbate perchlorate anion band to a lower wavenumber suggests a change in the internal structure of water around perchlorate [25]. Moreover, the IR water bands are indicative of a structure-breaking effect on the hydrogen bond network of water by the perchlorate anions as this is detected in the O–H stretching bands, with an increase in the absorbance of the band at 3590 cm<sup>-1</sup>, a decrease in the band at around 3300 cm<sup>-1</sup> and a slight wavenumber displacement from 1740 cm<sup>-1</sup> to 1720 cm<sup>-1</sup> in the O–H bending band [25]. These conformational changes in the water network are confirmed by studies in supersaturated perchlorate solutions using Raman spectroscopy [24]. It has been proposed that the hydrogen bonds in the exterior water layer are broken by perchlorate anions at the highest concentrations employed here. The appearance of new peaks in the region between 0.1 and 0.4 V and the decrease in the OH adsorption peak current at around 0.9 V could be a consequence of the effects on the OH and H adsorption. Ambient pressure XPS shows that OH can be adsorbed on Pt electrodes in several configurations under different hydration conditions [27]. Thus, the interaction of water with the adsorbed species is crucial for the adsorption mode and energetics, so that the formation of clathrates modifies these interactions with water and new peaks appear. Moreover, the reversibility of the peaks implies that these processes are not controlled by diffusion, indicating that the concentration of these clathrate species is higher than 1 mM.

When formic acid is added to the solution, the currents for the FAOR decrease as the perchloric acid concentration increases (Fig. 2A). Additionally, the onset potential shifts to lower values. Note that poison formation does not take place because the currents in the positive and negative scan directions are equal [28]. The diminution of the currents as the pH increases clearly indicates that protons are released before the rds, as proposed in Eqs. (1)–(4). It should be stressed that the formation of clathrates is not the cause of this diminution, because it is observed even in the perchloric acid concentration range where the formation of these species is negligible [17]. To perform a quantitative analysis of the effect of pH on the reaction kinetics, the reaction order must be calculated. Reaction orders are obtained by plotting the currents at a constant potential (in the SHE). In order to do this, the voltammograms were plotted on the SHE scale (Fig. 2B), using the activity coefficients for protons obtained from reference [29]. As can be seen from the inset of Fig. 2, the double logarithmic plot is not linear, revealing a complex dependence of currents on pH. In fact, the slope is lower than 1, the expected value for the mechanism proposed in Eqs. (1)–(4), implying that other parameters are affecting the reactivity.

As noted previously, the presence of anions (bidentate adsorbed formate) on the electrode surface affects the reactivity. To study this, fast voltammetric experiments can be used [30]. The underlying idea is that formate adsorption (a pseudo-capacitive process) is significantly faster than the faradaic currents. As shown in Fig. 3A, the faradaic currents corresponding to the FAOR are visible at low sweep rates but disappear at 5–10 V s<sup>-1</sup> with the voltammograms, plotted as capacitance vs. E, overlapping. Also, the onset of the FAOR coincides with the onset of the bidentate formate adsorption process and the currents diminish upon completion of the adlayer, in qualitative agreement with the previously proposed mechanism [17]. The formate adsorption

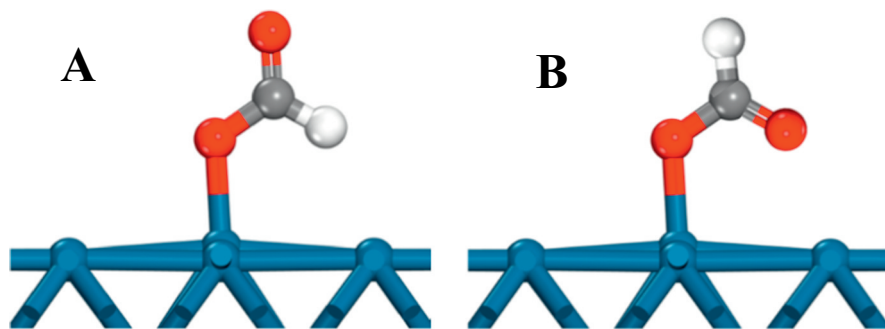
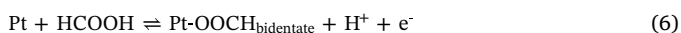


Fig. 4. Two possible configurations of monodentate adsorbed formate.

process can even be observed at the usual scan rate for the highest concentration (Fig. 3C), due to the almost negligible currents for FAOR. The OH adsorption process at high potentials is inhibited and new reversible features appear between 0.3 and 0.6 V, which are related to the adsorption of bidentate adsorbed formate. Additionally, the sharpening and displacement to more negative values of the peaks at ca. 0.26 V clearly indicate that those features are related to the adsorption energetics of the OH species induced by the presence of clathrates, whose concentration increases as the total concentration of the solution species increases. The bidentate adsorption process occurs in acidic solutions according to the global reaction:



The observation of this process even in very acidic conditions implies that this process is fast and that the  $K_a$  of the adsorbed species is very high. In principle, it is expected that a process governed by Eq. (6) would take place at constant RHE potentials. However, as can be seen from the comparison with 0.1 M  $\text{HClO}_4$  solutions (Fig. 3B), as the pH decreases the whole wave is displaced to more negative potentials on the RHE scale. Owing to the intrinsic relationship between the adsorption of bidentate and monodentate formate, this fact explains the lower onset potential as the pH decreases. It should be stressed that the adsorption of bidentate formate is a dynamic process, with the individual species forming the adlayer continuously changing with time, thus leaving open the possibility for formate to adsorb in a monodentate configuration to some extent.

Adsorption processes also depend strongly on the electronic properties of the surface, which, in turn, are altered by the surface charge of the electrode [31]. The potential of zero free charge (pzfc) of Pt(111) in the absence of specific adsorption is ca. 0.28 V vs. SHE [32], which implies that as the pH diminishes, the whole reaction is taking place on a surface with a progressively lower negative charge or higher positive charge, as shown in Fig. 2B. To explore the effects of surface charge on the adsorption of formate on the Pt(111) electrode, DFT calculations on neutral and positively charged surfaces were performed. Monodentate formate can be stably adsorbed on the Pt(111) surface in two possible configurations (Fig. 4): one with the C–H bond pointing toward the surface (A), which eventually leads to cleavage of the C–H bond; and one with the C–H bond in the upright position (B), which can easily evolve to bidentate adsorbed formate. It is found that, for both formate configurations, the adsorption energy for the overall reaction according to Eq. (6) is higher (more favorable) on positively charged surfaces, which explains the differences observed in Fig. 3A regarding the pH. Moreover, the positive charge favors the adsorption of monodentate formate in a favorable configuration to yield complete oxidation to  $\text{CO}_2$ . Under neutral charge conditions, the solvated configuration B is ca. 0.17 eV more stable than A, whereas the opposite is observed when the surface charge is ca.  $13 \mu\text{C cm}^{-2}$ . In this case, the energy for solvated configuration A is ca. 0.19 eV lower than that of B. This implies that the positive charge favors adsorption in the correct configuration to yield  $\text{CO}_2$ . The more energetically favorable adsorption of formate species

and the preference for configuration A partially compensate for the diminution of the solution formate and explain why the reaction order is lower than 1 (inset of Fig. 2). Since bidentate adsorbed formate is present on the surface and facilitates the oxidation, the overall current is heavily dependent on this coverage. Thus, the bidentate adsorbed formate coverage is different for each point, and the deviation from linearity reflects mainly these changes in coverage.

#### 4. Conclusions

The acid–base equilibrium between formic acid and the formate anion is a key factor in the FAOR. Highly acidic solutions of perchloric acid allow the observation of the formate adsorption process even at normal scan rates such as  $0.05 \text{ V s}^{-1}$ , due to the negligible currents caused by the decrease of the formate anion in solution. They also favor the study of kinetic parameters in the FAOR. The observed diminution of the currents as the pH becomes more acidic, which is smaller than that predicted by a simple rate equation, is the result of two opposing factors: the diminution of the free formate concentration in solution and the more favorable adsorption of formate in the correct configuration due to an increase in the positive electrode charge. In addition, the electrochemical behavior of highly acidic solutions reveals changes in the structure due to the formation of a clathrate structure between  $\text{ClO}_4^-$  and  $\text{H}_2\text{O}$  in highly concentrated solution. Forthcoming publications will provide new data on the behavior of these highly acidic solutions by using different platinum single crystal electrodes and different anions (sulfate and phosphate) with concentrated formic acid solution.

#### Acknowledgments

This work has been financially supported by the Ministerio de Economía, Industria y Competitividad through the project CTQ2016-76221-P. CBR also thanks his Postdoctoral fellowship to Generalitat Valenciana (APOSTD/2017/010).

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