# Kinetic Study of the Formic Acid Oxidation on Steady State Using a Flow Cell

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The formic acid oxidation (FAO) reaction is studied on platinum in acid solutions using a specially designed flow cell and different experimental techniques, such as open circuit potential decay, chronoamperometry, voltammetric stripping, HCOOH concentration pulses and rotating disc electrode. It allows for the first time the evaluation of the surface coverage of irreversibly adsorbed reaction intermediates on steady state conditions. It is found that the unique species adsorbed irreversibly is CO (E < 0.5 V). It is demonstrated that a higher potentials the adsorption of the intermediate species involved in the FAO is highly reversible and their decomposition is the rate determining step. From the analysis of the results and taken into account available spectroscopic measurements, a new reaction mechanism is proposed, which is compatible with all the known experimental evidences and allows the interpretations of previous unexplained results.

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The formic acid oxidation (FAO) on metallic electrodes has been intensely studied, particularly because among several candidate fuels for low temperature fuel cells, HCOOH is considered one of the most promising.<sup>1,2</sup> However, in spite of the attention paid to this reaction on platinum, its kinetic mechanism remains uncertain. The different authors only agree in that the reaction mechanism involves basically two parallel pathways, direct and indirect respectively.<sup>2-12</sup> The direct path starts from the HCOOH electroadsorption step giving an active intermediate, which is then oxidized to CO<sub>2</sub>. Meanwhile, the adsorbed carbon monoxide intermediate is formed in the indirect pathway. In this context, it should be taken into account that at room temperature formic acid is thermodynamically unstable, as its decomposition through both dehydrogenation and dehydration processes has negative values of the reaction Gibbs free energies, although the corresponding reaction rates are negligible.<sup>13–15</sup> However, in contact with metals such as those usually employed as electrocatalysts, the spontaneous decomposition is strongly catalyzed, involving adsorbed species.<sup>13–15</sup> In electrochemistry this situation corresponds to the open circuit potential (OCP). Consequently, the kinetic studies of the formic acid electrooxidation should consider the simultaneous occurrence of both processes, catalytic (dehydrogenation and/or dehydration) and electrocatalytic (direct and/or indirect), which are coupled by reaction intermediates that are common to both.

On the other hand, the revision of the literature indicates that the kinetic study of the FAO was preferably carried out on the basis of the voltammetric response in a solution of HCOOH with H<sub>2</sub>SO<sub>4</sub> or HClO<sub>4</sub> as supporting electrolyte.<sup>2–12</sup> There are some studies that have also used chronoamperometric measurements,<sup>7–11,16</sup> dynamic electro-chemical impedance spectroscopy<sup>17,18</sup> and hydrodynamic impedance spectroscopy.<sup>19</sup> In the latter case, a no significant mass transfer effect was reported in the voltammetric anodic peak.

An important advance was achieved by coupling spectroscopic techniques (ATR-FTIRS, SEIRAS, etc.) to voltammetric scans, which enabled the identification of the adsorbed species, as well as their localization in a given potential region of the potentiodynamic sweep.<sup>7–11,20–22</sup> The species detected through these techniques were  $CO_{ad}$  and  $HCOO_{ad}$ . There is also a general consensus in that the contribution of the indirect path involving  $CO_{ad}$  is almost negligible.<sup>7–11,21</sup> In relation to the direct path,  $HCOO_{ad}$  was historically considered as the active intermediate, leading to the formation of  $CO_2$  through the following rate determining step,<sup>6–8</sup>

$$HCOO_{ad} \to CO_2 + H^+ + e^-$$
[1]

1 is not taking place and that HCOO<sub>ad</sub> is just a spectator.<sup>8,9,12,20</sup> This conclusion was based on the absence of a linear relationship between the  $HCOO_{ad}$  band intensity ( $I_{HCOO}$ ), a measure of surface coverage  $(\theta_{HCOO})$ , and the oxidation current (I). It was found that  $I_{HCOO}$  remains invariant during the application of a potential step from 1.2 V to 0.75 V,8 or a stop of 300 s at 0.7 V during a potential sweep,20 while current decreases. Another extremely interesting result obtained in this last work was the different sign of the corresponding slopes of the derivatives (dI/dE and d $I_{HCOO}$ /dE), measured at the restart of the anodic sweep after holding potential at 0.7 V (Figures 6a<sub>1</sub> and 6d<sub>1</sub> in Ref. 20). This behavior was repeated for the potential sweep in the cathodic direction (Figures  $7a_1$  and  $7d_1$  in Ref. 20). These results, together with those corresponding to the potential holding, were used to justify the site-blocking spectator character of HCOO<sub>ad</sub>. Nevertheless, the results only prove that reaction 1 is not verified, but does not inhibit the participation of HCOO<sub>ad</sub> as an intermediate of the FAO.

However, it was recently proposed by different authors that reaction

On the other hand, it should be taken into account that the interpretation of the current-potential dependence obtained by voltammetric sweeps is extremely complex. The current response is determined basically by the sum of the pseudocapacitive contributions due to the different reaction intermediates involved, but there are also contributions due to anions adsorption/desorption processes and the formic acid readsorption. In this context the dynamics of all these processes, coupled to each other, configures a complex system difficult to interpret without a model that establishes cause-effect relationships. The problem is that such kinetic model should include differential mass balances of all the species participating in those dynamic processes, constituting a system too complex to be solved in order to obtain reliable conclusions. As the reaction mechanism is invariant regardless the experimental method used, measurements should be designed in order to enable a simpler interpretation of the results obtained.

In this context, the aim of the present work is the study of the formic acid oxidation reaction, particularly the role played by the adsorbed intermediates  $CO_{ad}$  and  $HCOO_{ad}$ , by steady state chronoamperometry coupled with voltammetric stripping, carried out in a specially designed flow cell. These experiments enable the evaluation at each applied potential of the electrooxidation charges of the reaction intermediates irreversibly adsorbed on platinum. Then, a kinetic mechanism will be proposed and discussed in the context of the present results and the spectroscopic evidences obtained by other authors.

## Experimental

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*Flow cell.*—It was designed and built a device that enables, operating at closed electric circuit and quasi-piston flow, the change of the



Figure 1. Scheme of the experimental set up for the HCOOH electrooxidation measurements.

electrolytic solution in a few seconds, avoiding the mixing of the previous solution with the new one. A scheme of this device is illustrated on Figure 1. It consists in two storage vessels located in the upper part, equipped with a gas bubbling system, which drain the solution by gravity to the flow cell through tubes of approximately one meter height with valves for the flow regulation. A three-way valve at the entrance of the cell enables the selection of the electrolytic solution. The outer flow is carried out through a hydraulic seal, which ensures the isolation of the solution from the environment.

A more detailed scheme of the flow cell is depicted in Figure 2. It consists of three concentric Pyrex glass tubes, being the outer fitted to a teflon body. The two inner tubes are hold by the top part of the outer tube, being the most internal the Luggin capillary tube, which end is located at 0.5 mm from the electrode surface, and it is connected to the vessel containing the reference electrode (Figure 1). The electrolyte



Figure 2. Detailed scheme of the electrochemical cell and flow direction.

solution flows through the space comprised between the central tube and the Luggin capillary tube towards the working electrode. It is evacuated through the space comprised between the central and the outer tubes.

The working electrode consists of a platinum disc of 10 mm in diameter, with an electric contact at the bottom and a perfluoropolymer o'ring at the top, which defines a geometric area of  $0.28 \text{ cm}^2$ . It is supported by a teflon lid, which is bolted to the upper teflon body (Figure 2). A Pt wire is used as counter electrode, surrounding the central tube of the cell. Finally, as a reference electrode it was used a reversible hydrogen electrode in  $0.5 \text{ M H}_2\text{SO}_4$  solution.

Electrochemical measurements.—The electrochemical measurements were carried out almost entirely in the flow cell. Some other complementary experiments were done on a rotating disc electrode in order to evaluate mass transfer effects on the formic acid oxidation reaction. These experiments were carried out in a cell specially built for the use of a rotating electrode. Two electrolyte solutions were used, x M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>, being x = 0.1, 0.5, 1.0 M, for the study of the formic acid oxidation and 0.5 M H<sub>2</sub>SO<sub>4</sub>, employed for the electrode characterization by cyclic voltammetry and for the evaluation of the FAO irreversibly adsorbed intermediates by voltammetric stripping after the removal of formic acid at closed electric circuit. They were prepared with ultrapure water (PureLab, Elga LabWater) and analytical grade reagents. Sulfuric acid solution was deaerated with high purity nitrogen gas (Air Products), while the solutions containing formic acid were saturated with high purity carbon dioxide (Air Products) for the electrocatalytic measurements, which enables the theoretical evaluation of the equilibrium potential of the FAO reaction. Experiments were carried out at room temperature (25°C).

**Open circuit potential (OCP) measurements.**—In order to establish the presence of adsorbed intermediates originated in the HCOOH spontaneous decomposition catalyzed by platinum, OCP measurements were carried out in 0.5 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution in the flow cell. Working electrode was first polarized at 1.2 V during 1 min to oxidize any adsorbed species and then the circuit was opened, allowing the processes that are verified in the electrode/solution interface to evolve spontaneously. The variation of OCP on time was recorded during 10 min and then the electric circuit was closed at the potential reached at this time. Holding this potential the solution was changed to 0.5 M H<sub>2</sub>SO<sub>4</sub> and then a voltammetric stripping at 0.05 V s<sup>-1</sup> was applied up to 1.4 V in the anodic direction followed by the cathodic scan up to 0.05 V.

*Current-potential measurements.*—The study of the formic acid oxidation reaction was carried out by the application of a potential program in the *x* M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub> (x = 0.1, 0.5, 1.0 M) solution, which began with holding the potential at 1.2 V during 1 min in order to oxidize any species that could be adsorbed on the electrode surface. Then, a potential pulse was applied to a given value (0.3 V  $\leq E \leq 0.9$  V) and the resulting current was recorded as a function of time during 10 min. The current value measured at this time was assigned to the applied potential. After this period and holding this potential, electrolyte solution was changed to 0.5 M H<sub>2</sub>SO<sub>4</sub>. Then a voltammetric stripping at 0.05 Vs<sup>-1</sup> was applied from such potential up to 1.4 V in the anodic direction followed by the cathodic scan up to 0.05 V.

The chronoamperometric measurements were complemented by cyclic voltammetry, carried out in the three different HCOOH concentrations (0.1, 0.5 and 1.0 M) at a sweep rate of 0.01 V s<sup>-1</sup> between 0.2 and 1.2 V

# Results

*Electrode area characterization.*—The real area of the working electrode used in the flow cell electrode was evaluated from the underpotentially deposited hydrogen (H<sub>UPD</sub>) charge, measured from the potentiodynamic profile recorded at 0.05 V s<sup>-1</sup> in the N<sub>2</sub> saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution, with the lower limit of the potential sweep at 0.07 V.<sup>23</sup> The resulting charge, after discounting the double layer capacity contribution, represents the 77% of one H<sub>UPD</sub> monolayer. The value obtained was 97.3  $\mu$ C and thus, taking into account that the monolayer charge is 218  $\mu$ C cm<sup>-2</sup>, the resulting electrodic area is 0.58 cm<sup>2</sup>. As the geometric area is 0.28 cm<sup>2</sup>, the corresponding roughness factor is 2.05.

**Open circuit potential.**—Figure 3a shows the transient dependence of the OCP recorded in the 0.5 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. It is observed at first a slow decrease of potential during approximately 80 s, corresponding to the reduction of Pt oxide by HCOOH.<sup>24–26</sup> This is a slow chemical process, even more if it is taken into account that the oxide thickness should be less than one monolayer. After a fast potential decay a plateau is reached, being the potential value after 10 min equal to 0.25 V.

The response to the voltammetric stripping applied after the OCP measurement in the  $0.5 \text{ M H}_2\text{SO}_4$  solution is shown in Figure 3b. This profile exhibits an anodic peak at approximately 0.76 V, which is the same as that observed for the CO<sub>ad</sub> oxidation.

Study of the formic acid oxidation.—The chronoamperometric measurements of the formic acid oxidation were carried out in the x M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub> (x = 0.1, 0.5, 1.0 M) solutions in the potential range 0.3 V  $\leq E \leq 0.9$  V. The resulting current - potential dependence is shown in Figure 4a for the three values of HCOOH concentration solution. Marked increase of current can be observed between 0.4 and 0.5 V and a pronounced decrease starting from 0.8 V, independently of the formic acid concentration. Moreover, Figure 5 illustrates the results of the voltammetric strippings in 0.5 M H<sub>2</sub>SO<sub>4</sub> applied after chronoamperometry. It shows the potentiodynamic pro-



Figure 3. (a) OCP transient after polarization at 1.2 V on Pt in 0.5 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>; (b) voltammetric stripping after OCP at 0.05 V s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

files corresponding to the case of 0.5 M HCOOH + 0.5 M  $H_2SO_4$ solution and different values of the pulse potential. The oxidation peak at 0.76 V, already observed after OCP measurements, is also obtained for potential pulses lower than 0.6 V, indicating the same nature of the adsorbed species in both cases. Meanwhile for potential values higher than 0.6 V, the profile is the same as that of the blank voltammogram. The charge of the stripping peak (calculated as the difference between the voltammetric area under the peak and that of the blank response) was evaluated for each pulse potential. This charge is a measure of the amount of reaction intermediate irreversibly



**Figure 4.** (a) Steady state current obtained after 10 min polarization at different potentials on Pt in *x* M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>. *x*: ( $\bullet$ ) 1 M; ( $\blacksquare$ ) 0.5 M; ( $\bigstar$ ) 0.1 M. (b) Potentiodynamic sweeps at 0.01 V s<sup>-1</sup>. *x*: (continuous line) 1 M; (dash line) 0.5 M; (dash dot line) 0.1 M.



Figure 5. Voltammetric strippings at 0.05 V s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub>, after 10 min polarizations in 0.5 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>. E: (a) 0.325 V; (b) 0.350 V; (c) 0.425 V; (d) 0.450 V; (e) 0.465 V; (f) 0.500 V.

adsorbed on the electrode surface when reaction was interrupted by the solution replacement at closed electric circuit. The dependence of this charge on the pulse potential is shown in Figure 6. It should be noticed that the comparison of these results with those shown in Figure 4a clearly indicates that when the concentration of adsorbed intermediate is maximum, the current of the formic acid oxidation is almost negligible. On the contrary, in the range of potentials where the reaction takes place, the amount of irreversibly adsorbed species is null.

Moreover, Figure 4b shows the current-potential profiles obtained by the application of a potentiodynamic sweep run at 0.01 V s<sup>-1</sup> in the *x* M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub> (x = 0.1, 0.5, 1.0 M) solutions. It can be appreciated in each case the well known hysteresis between the anodic and cathodic cycle, being the profile of this last one more similar to the response corresponding to the steady state (Figure 4a). However, current values are almost one order of magnitude greater in the case of the voltammetric profile with respect to the steady state.

**FAO response to HCOOH concentration step.**—The flow cell designed enables the complete replacement of the electrolyte solution in a few seconds, holding the electrode polarized at a given potential. Thus, it was possible to analyze the kinetic behavior of the formic acid



**Figure 6.** Stripping peak charges for the different polarization potentials in  $x \text{ M HCOOH} + 0.5 \text{ M H}_2\text{SO}_4$ .  $x: (\bullet) 1 \text{ M}; (\blacksquare) 0.5 \text{ M}; (\bigstar) 0.1 \text{ M}.$ 



Figure 7. Effect on the chronoamperometric response at E = 0.6 V of HCOOH concentration pulses in 0.1 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>.

oxidation under successive concentration steps, where solution was changed maintaining the applied potential during the whole process. The experiment was initiated by the application of a given potential pulse in the solution containing the reactant (x M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>) for a certain period of time. Holding this potential, the solution was replaced by that of the supporting electrolyte (0.5 M H<sub>2</sub>SO<sub>4</sub>) and maintained for another period of time. Then the solution was changed again to that containing HCOOH and this sequence was repeated several times. Figure 7 shows the response obtained when the electrode was subjected to a potential pulse at 0.6 V and the concentration of the solution containing HCOOH was x = 0.1 M. In this case the sequence was repeated three times. It is important to note the remarkable speed at which the reaction is annulated in the blank solution, as well as its immediate recovery when the solution is returned to that containing HCOOH.

Effect of CO adsorption on FAO .- It is well known that the adsorbed carbon monoxide CO<sub>ad</sub> is present in the electrode surface during the formic acid oxidation, as there are many spectroscopic evidences.<sup>8,9,20-22</sup> However, unlike the process of CO electrooxidation reaction (E > 0.9 V),<sup>27</sup> the FAO is verified at potentials significantly lower (0.5 V  $\leq$  E  $\leq$  0.9 V). Thus, the addition of CO in the solution where the FAO is taking place could give information about the role of CO<sub>ad</sub> on it. Therefore, the following experiment, carried out in a conventional cell due to the precautions that must be taken for the use of CO, was performed. A potential pulse of 0.6 V was applied in the solution 0.5 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub> under nitrogen gas during 400 s. At this time N2 was replaced by CO for a period of other 400 s. Finally, CO was displaced by N<sub>2</sub> maintaining the applied potential during another 1200 s. Figure 8 shows the current response, where it can be observed that immediately after the substitution of nitrogen by CO the current dropped to zero. After that, when CO was substituted by N<sub>2</sub>, current continues being zero in spite of that formic acid was always in the electrolyte solution.

*Effect of electrode rotation on FAO.*—It should be also important to determine if there is any mass transfer effect on the reaction rate of the formic acid oxidation. The experiment was carried out in a cell specially built for the use of a rotating electrode. A potential pulse of 0.6 V was applied in the solution 0.1 M HCOOH + 0.5 M  $H_2SO_4$  and during its application the rotation rate was varied in the range comprised between 200 and 3000 rpm, increasing as well as decreasing the applied value. Figure 9 shows the resulting current vs.



Figure 8. Effect on the chronoamperometric response at E = 0.6 V of CO bubbling in 0.5 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>.

time plot, where it can be observed that rotation rate does not have any influence on the transient dependence.

### Discussion

The formic acid oxidation reaction,

$$HCOOH \rightleftharpoons CO_2 + 2 H^+ + 2 e^-$$
[2]

in *x* M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution containing CO<sub>2</sub>, being x = 0.1, 0.5 and 1 M, was studied in a flow cell by chronoamperometric measurements. The special design of the cell allowed a fast replacement of the electrolyte solution, in a few seconds, enabling for the first time the evaluation of the irreversibly adsorbed reaction intermediates in the supporting electrolyte solution (0.5 M H<sub>2</sub>SO<sub>4</sub>) by voltammetric stripping runs. These experiments were also complemented by other determinations (open circuit, CO saturated solutions, rotating disc electrodes) in order to elucidate which reaction intermediates participate in the reaction mechanism.

The first result analyzed here corresponds to the behavior of platinum electrode when it is immersed in the solution containing HCOOH at open circuit. As it was already stated, it is well known that Pt is a good catalyst for the spontaneous decomposition of formic acid.<sup>15</sup> It was found that the OCP value in the 0.5 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>



Figure 9. Effect on the chronoamperometric response at E = 0.6 V of electrode rotation rate in 0.1 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>.

solution is 0.25 V (Figure 3a). The voltammetric stripping carried out from this potential in the solution free of HCOOH (Figure 3b) shows an electrooxidation peak at 0.76 V. Both, electrochemical,<sup>28,29</sup> and spectroscopic,<sup>8,9,20-22</sup> evidences indicate that this peak corresponds to the  $CO_{ad}$  species. Thus, it is likely that in these conditions the following spontaneous dissociative adsorption is produced,

$$HCOOH + S \rightarrow CO_{ad} + H_2O$$
 [3]

Reaction 3 is the first step of the spontaneous, potential independent, process of formic acid dehydration catalyzed by platinum. Then, CO<sub>ad</sub> will be oxidized if the electrode potential is increased with respect to the OCP value. Taking into account this result and in order to elucidate the behavior of the Pt electrode in front of the formic acid electrooxidation, it should be useful to compare the current - potential responses on steady state (Figure 4a) with those corresponding to the voltammetric profiles shown in Figure 4b. As it was already mentioned, the current values corresponding to the cathodic sweep are almost one order of magnitude greater than those of the steady state. This difference clearly indicates the significant pseudocapacitive contribution originated in the continuous variation of the surface coverage of the adsorbed species, making more difficult the interpretation. Therefore, the emphasis is put in the analysis of the dependence I-E on steady state (Figure 4a). It can be observed that in all cases the FAO takes place in the potential range comprised between 0.40 and 0.90 V. Then the voltammetric strippings, recorded after each potential pulse, reveal the amount of reaction intermediates irreversibly adsorbed in each case (Figure 5). These profiles show a unique electrooxidation peak assigned to COad, as in the response obtained after the OCP measurement (Figure 3b). The corresponding variation of the peak charges on the polarization potentials are shown in Figure 6. It should be important to note that they are in agreement with the dependence on potential of the integrated bond intensity for CO<sub>ad</sub>, which is proportional to the corresponding surface coverage, measured by Okamoto et al.<sup>17</sup> They obtained this plot by applying an anodic sweep at 0.1 mV s<sup>-1</sup> simultaneously with surface-enhanced infrared absorption spectroscopy (SEIRAS) for linear CO<sub>ad</sub>. Taking into account that these voltammetric profiles show hysteresis between the positive and negative scan and that the chronoamperometric steady state pulses applied in the present work started at 1.2 V, where the Pt surface is partially oxidized, to the selected potential, it should be more appropriate to compare the steady state response with those of the negative going scan. Moreover, the corresponding CO<sub>ad</sub> surface coverage ( $\theta_{CO}$ ) can be evaluated from the peak charges obtained from the voltammetric stripping (Figure 6) on the basis that the monolayer of CO<sub>ad</sub> on polycrystalline platinum is reached with a charge of 287  $\mu$ C cm<sup>-2</sup>.<sup>30</sup> The maximum coverage values, obtained in the potential range 0.30-0.35 V, for the different concentrations of HCOOH are 0.42 (0.1 M), 0.45 (0.5 M) y 0.59 (1.0 M). These values are lower than that corresponding to saturation ( $\theta_{CO}^{sat} = 0.66$ ), which was reached in the case of CO electroadsorption<sup>30</sup> or electrooxidation.<sup>27</sup> These lower values of  $\theta_{CO}$  explains the reason why its electrooxidation during the FAO takes place 0.50 V more cathodic than in the case of the CO oxidation reaction (COOR), where  $E \ge 0.90 \text{ V}^{.27}$  In the present case the source of CO<sub>ad</sub> is the spontaneous dissociative adsorption of HCOOH (reaction 3), which defines a surface coverage less than saturation and thus enables the electroadsorption of water on the free sites,

$$H_2O + S \rightleftharpoons OH_{ad} + H^+ + e^-$$
[4]

Reaction 4 is very fast and therefore it is considered at equilibrium at any potential value.<sup>27,31</sup> It begins to be observed at  $E \ge 0.50$  V on Pt low index planes<sup>32</sup> and even at lower potentials on polycrystalline Pt.<sup>33</sup> Thus, the presence of OH<sub>ad</sub> together with CO<sub>ad</sub> explains the drastic decrease of CO<sub>ad</sub> (Figure 6), due to the following well known reaction,

$$CO_{ad} + OH_{ad} \rightarrow CO_2 + H^+ + e^-$$
 [5]

If the  $CO_{ad}$  surface coverage would be that corresponding to saturation and taking into account that at these potentials it cannot be displaced by the  $OH_{ad}$ , then there would be no free sites and reaction 4 would not

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be feasible in this potential region, and therefore neither reaction 5, as in the case of the COOR.<sup>27</sup> The current vs. time dependence obtained when CO is added in the solution where the FAO is taking place (Figure 8) confirms this result. It can be observed the immediate total inhibition of the current, which remains annulated after the removal of CO in solution by N<sub>2</sub> bubbling during more than 40 min. Thus, the spontaneous reaction 3 followed by the electrochemical reactions 4 and 5 define a pathway in the potential region comprised between 0.4 V and 0.5 V, although its contribution to the formic acid oxidation is not significant. Therefore, another reaction pathway must be considered, involving other reaction intermediates, to describe the FAO in the potential range 0.5–0.9 V. In this sense, it should be taken into account that the presence of HCOO<sub>ad</sub> was observed spectroscopically,<sup>8,11,20</sup> originated in the following electroadsorption reaction,

$$HCOOH + 2 S \rightleftharpoons HCOO_{ad} + H^+ + e^-$$
 [6]

However, the voltammetric stripping (Figure 5) does not show any adsorbed species, demonstrating that this adsorption process is highly reversible. This conclusion is confirmed by the results shown in Figure 7, obtained holding the electrode potential at 0.6 V in the solution containing the reactant (0.1 M HCOOH + 0.5 M H<sub>2</sub>SO<sub>4</sub>) for a certain period of time and then, at constant potential, the solution was replaced by that of the supporting electrolyte  $(0.5 \text{ M H}_2\text{SO}_4)$ , where current fell immediately to zero. Then, when solution was changed again to that containing HCOOH, current was instantaneously restored. As it can be observed in the figure, this sequence was repeated several times with the same result, indicating a highly reversible behavior of the reaction intermediate. These results are also supported by spectroscopic evidences,  $^{7-9,20}$  which show that the unique adsorbed species for E > 0.5 V is HCOO<sub>ad</sub>. The problem that remains unsolved is the absence of a linear relationship between FAO current and  $\theta_{HCOO}$ , which invalidates reaction  $1.^{8,20}$  In this sense, the consideration of HCOO<sub>ad</sub> as a site-blocking spectator is not in agreement with the profiles I(E) and  $\theta_{HCOO}(E)$ . The maximum value of  $\theta_{HCOO}$  (near 0.65 V, Figure 2a<sub>4</sub> in Ref. 20), which should produce a maximum reaction inhibition, does not go along with a decrease in current.<sup>8,20</sup> Moreover, none of the alternative proposals (weak adsorption of HCOO<sup>-</sup>, etc.) can explain the results obtained by H. Okamoto et al.,<sup>20</sup> already described in the Introduction. In this context, and taking into account that the concentration of formate anion in solution is practically null in these experimental conditions, it should be reasonable to consider that HCOO<sub>ad</sub> reacts with OH<sub>ad</sub> originated in the water electroadsorption 4 as follows,

$$HCOO_{ad} + OH_{ad} \to CO_2 + H_2O + 3 S$$
<sup>[7]</sup>

Thus, reaction 7 is proposed as the rate determining step of the FAO and, together with reactions 4 and 6, defines the main reaction pathway. This kinetic mechanism is in agreement with all the experimental results obtained for the FAO. For instance, the invariance over time of  $\theta_{HCOO}$  observed by H. Okamoto et al.,<sup>20</sup> when potential sweep is stopped at 0.7 V in both, anodic (Figs. 6a2 and 6d2) and cathodic (Figs. 7a2 and 7d2) directions. A similar behavior was observed by Y. X. Chen et al.<sup>8</sup> during a potential step from 1.2 V to 0.75 V (Figure 6c in Ref. 8). This invariance is accompanied by a decrease in current, which cannot be assigned to a HCOOH diffusion contribution, as the transient of Figure 9 clearly demonstrates that the FAO current is not affected by changes in the rotation rate. Such decrease should be originated in a slow decrease of the OH<sub>ad</sub> surface coverage due to the slow adsorption of HSO<sub>4</sub><sup>-</sup>, to reach the steady state coverage. Another very important result can be observed in the figures mentioned above, which is related to the different sign of the slopes of current (dI/dE) and HCOO<sub>ad</sub> band intensity  $(dI_{HCOO}/dE)$  when the potential sweep is restarted after the potential hold at 0.7 V (Figures 6 and 7 in Ref. 20), as it was already mentioned in the Introduction. This result, which did not receive much attention, contains substantial information about the FAO kinetic mechanism. The increase in  $\theta_{HCOO}$  observed when the anodic sweep is restarted (Figure  $6d_1$  in Ref. 20) implies that the active sites released by reaction 7 are preferably occupied by HCOO<sub>ad</sub>, producing a decrease in  $\theta_{OH}$ . This process modifies the

rate of reaction 7, as it is proportional to the product  $\theta_{HCOO}$   $\theta_{OH}$ . Thus, in order to determine the influence on reaction rate of such preferential occupancy, a balance of the active sites was carried out at the beginning of the potential sweep, or ending of the potential holding (see Appendix). It could be demonstrated from this balance that the slope of the current-potential dependence at this point (°) verifies the following expression,

$$\left(\frac{dI}{dE}\right)^{o} \propto \theta^{o}_{OH} - \theta^{o}_{HCOO}$$
[8]

Eq. 8 shows that when  $\theta_{HCOO}^o > \theta_{OH}^o$ , as it is expected in this experimental conditions, it is simultaneously verified that,

$$\left.\frac{dI}{dE}\right)^o < 0 \tag{9}$$

$$\frac{d\theta_{HCOO}}{dE}\right)^o > 0$$
 [10]

which is in agreement with the experimental results. It should be noticed that the authors carried out also the potentiodynamic sweep in the cathodic direction with the potential holding at 0.7 V during 300 s (Figs. 7a<sub>1</sub> and 7d<sub>1</sub> in Ref. 20). As it should be expected, current and the HCOO band intensity take the same values as in the previous case, as well as the corresponding slopes, and therefore  $\theta^o_{HCOO}$ and  $\theta^o_{OH}$  will have also the same values. These results validate the hypothesis that the FAO in acid solution proceeds basically through the pathway that involves the highly reversible electroadsorption of the formic acid (reaction 6) followed by the surface reaction 7, rate determining step, which involves the OH<sub>ad</sub> generated by the water electroadsorption reaction 4.

#### Conclusions

Through the use of a flow cell with a new design together with the application of different techniques (open circuit potential decay, chronoamperometry, voltammetric stripping, concentration pulses and rotating disc electrode) and taken into account spectroscopic evidences from the literature, it was possible to propose a kinetic mechanism for the formic acid electrooxidation in acid solution. It was quantified for the first time the surface coverage of CO<sub>ad</sub> at steady state in the range  $0.3 \le E / V \le 0.9$ . It was found that it is observed only in the potential range E < 0.5 V, being always less than the value corresponding to saturation. This enables the adsorption of OH<sub>ad</sub> and thus the oxidative desorption of  $CO_{ad}$  to produce  $CO_2$ . At E > 0.5V, the active intermediate HCOO<sub>ad</sub> is formed, being its reaction with OH<sub>ad</sub> the rate determining step of the main kinetic pathway. The proposed mechanism is in agreement with all the experimental results presented here and allows the interpretation of previous unexplained results.

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# **Appendix: Derivation of Equation 8**

H. Okamoto et al.<sup>20</sup> carried out experiments consisting in the application of a voltammetric sweep with a potential hold at 0.7 V, with the simultaneous measurement of the band intensities of  $CO_{ad}$  ( $CO_L$  and  $CO_B$ ) and  $HCOO_{ad}$ . When the anodic potentiodynamic sweep is reinitiated after holding potential during 300 s, the initial slope of current (Figure 6a<sub>1</sub>) is,

$$\left(\frac{dI}{dE}\right)^o < 0$$
 [A1]

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and that of  $HCOO_{ad}$  band intensity, equivalent to surface coverage (Figure  $6d_1$ ),

$$\left(\frac{d\theta_{HCOO}}{dE}\right)^{b} > 0$$
 [A2]

The evidence given by (A2) implies that the steady coverage reached ( $\theta_{HCOO}^{o}$ ) is increased with the restart of the potential sweep. As reaction 7 is rate determining, current will be proportional to the surface coverages of HCOO<sub>ad</sub> and OH<sub>ad</sub>,

$$I(E) \propto \theta_{HCOO}(E) \theta_{OH}(E)$$
 [A3]

Considering a degree of advancement  $\xi$  for the reaction 7, as potential *E* increases after the potential holding  $\xi$  sites will be released by OH<sub>ad</sub> and 2 $\xi$  sites by HCOO<sub>ad</sub>. Taking into account that such sites will be quickly occupied by HCOO<sub>ad</sub>, as it was observed experimentally (Figure 6d<sub>1</sub>), the following balance can be written,

$$\theta_{OH}(E) = \frac{n_{OH}(E)}{n_{OH}^{max}} = \frac{n_{OH}^o - \xi}{n_{OH}^{max}} = \theta_{OH}^o - \frac{\xi}{n_{OH}^{max}}$$
[A4]

In the case of HCOO<sub>ad</sub> balance, it implies the loss of  $\xi$  moles due to reaction and the readsorption of 1.5  $\xi$  moles on the 3 sites liberated, resulting in a gain of 0.5  $\xi$  moles,

$$\theta_{HCOO}(E) = \frac{n_{HCOO}(E)}{n_{HCOO}^{max}} = \frac{n_{HCOO}^o + 0.5\,\xi}{n_{HCOO}^{max}} = \theta_{HCOO}^o + \frac{0.5\,\xi}{n_{HCOO}^{max}}$$
[A5]

where  $n_i^{max}$  (i = HCOO, OH) are de number of adsorbed moles corresponding to one monolayer. Being  $n^s$  the number of total sites, the relationship between them is,

$$n_{OH}^{max} = 2 n_{HCOO}^{max} = n^s$$
 [A6]

Substituting n<sup>s</sup> in (A4) and (A5),

$$\theta_{OH}(E) = \theta_{OH}^o - \frac{\xi}{n^s}$$
 [A7]

$$\theta_{HCOO}(E) = \theta^o_{HCOO} + \frac{\xi}{n^s}$$
[A8]

Replacing (A7) and (A8) in (A3),

$$I(E) \propto \theta^{o}_{HCOO} \theta^{o}_{OH} + \frac{\xi}{n^{s}} \left( \theta^{o}_{OH} - \theta^{o}_{HCOO} \right) - \left( \frac{\xi}{n^{s}} \right)^{2}$$
 [A9]

The corresponding derivative is,

$$\frac{dI(E)}{dE} \propto \frac{dI(E)}{d\xi} \propto \frac{\left(\theta_{OH}^{o} - \theta_{HCOO}^{o}\right)}{n^{s}} - \frac{2\xi}{n^{s^{2}}}$$
[A10]

Thus, the slope at the restart of the potential sweep turns to be,

$$\frac{dI(E)}{dE}\Big)^{o} \propto \lim_{\xi \to 0} \frac{dI(E)}{d\xi} \propto \frac{\left(\theta^{o}_{OH} - \theta^{o}_{HCOO}\right)}{n^{s}}$$
[8]

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