

Effects of the anion adsorption and pH on the formic acid oxidation reaction on Pt(111) electrodes.

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Abstract.

The effects of solution pH and anion adsorption for the formic acid oxidation reaction on the Pt(111) electrode have been examined using electrochemical techniques. Regarding the pH effects, it has been found that oxidation currents for this reaction increases as the pH increases, which indicates that solution formate is involved in the reaction mechanism. Unexpectedly, the adsorption of sulfate on the Pt(111) electrode has a positive effect on the oxidation of formic acid, which also suggests that adsorbed anions are also involved in the mechanism. The activation energy calculated from temperature dependent measurements diminishes with the solution pH and also in the presence of adsorbed sulfate. These measurements corroborate the involvement of solution formate and anions in the oxidation mechanism. Using these results, a rate equation for the oxidation of formic acid is proposed. The current values calculated from this equation are in very good agreement with the experimental currents in perchloric acid solutions.

Keywords: Pt(111) electrode, formic acid oxidation, anion adsorption, pH effects.

1. Introduction.

The formic acid oxidation reaction has been widely studied because its possible use in fuel cell technologies. The reaction involves only two electrons in the oxidation to CO_2 , and for that reason, it has a lower energy density (kW/kg) when compared with other organic molecules, such as methanol or ethanol. In spite of that, the practical electrocatalysts (normally composed of platinum or palladium) have higher turnover at comparable potentials. Thus, the cell power per mass of precious metal is higher than that obtained for ethanol or methanol.

The reaction mechanism of the formic acid oxidation reaction has two possible routes, as initially proposed by Capon and Parsons [1-3] and confirmed by DEMS [4]. In one of the routes, the first step is a dehydration step, to yield an adsorbed CO molecule. Adsorbed CO is difficult to oxidize to CO_2 and blocks the surface, hindering the progress of the reaction. The other route goes through the so called active intermediate. In this route, formic acid probably adsorbs on the surface in some form, forms an active intermediate, which is immediately transformed into CO_2 . For this reason, this route is more efficient in the oxidation, since the overpotentials are lower, but its performance is hindered by the presence of CO.

Recently, significant efforts have been devoted to determine the nature of the active intermediate [5-7]. The initial works of Osawa and collaborators proposed that adsorbed formate in a bridge-bonded configuration with its two oxygen atoms bound to two surface platinum atoms (bridge bonded bidentate formate) geometry was the active intermediate, since this species was detected in ATR-SEIRAS experiments and a qualitative correlation between the reactivity and the amount of adsorbed formate was found [8-11]. However, other experiments seemed to contradict this initial assignment, proposing other species as the active intermediate [12, 13]. All these data resulted in a debate regarding the role of adsorbed bridge bonded bidentate formate in the reaction mechanism, which still is not solved. Recently, a

new species has been added to the mechanism, since it has been found that that solution formate plays a very important role in the oxidation mechanism [14].

In all of these manuscripts, polycrystalline electrodes were used. Formic acid oxidation is a reaction very sensitive to the surface structure, as the studies with single crystal electrodes reveal [15]. If a detailed determination of the reaction kinetics is required, the use well-defined surfaces can provide valuable information on the reaction. Very well controlled conditions are normally required in order to untangle the effect of the different parameters and their relationships in the oxidation mechanism. For that reason, the use of low index planes, namely Pt(111), Pt(100) and Pt(110) surfaces, which ideally have only one type of site on the surface, simplifies the problem and allows establishing clear relationships between site and type of reactivity. Among them, the Pt(111) surface is the most stable surface within the potential range of interests [16] and is considered to be the most frequent orientation in practical nanoparticles [17]. Under these conditions, it is possible to determine the activity of the electrode for both routes independently [18]. Consequently, absolute reaction rates and potential regions in which each route is active can be determined as a function of the electrode structure [19, 20].

In this manuscript, the oxidation of formic acid on Pt(111) electrodes is studied in solutions containing perchloric, sulfuric and acetic acid in the pH range between 0 and 2. From the temperature dependence of the activity through the active intermediate, apparent activation energies are calculated. All these data will be used to determine the role of the adsorbed anion, formic acid and formate concentration in the oxidation mechanism. This will allow establishing an explicit rate equation for the oxidation through the active intermediate route that will be compared to the observed behavior. In this equation, the solution formate concentration, and the coverage of adsorbed formate and that of other adsorbed species will be considered.

2. Experimental.

Platinum single crystal electrodes were oriented, cut and polished from small single crystal beads (2.5 mm diameter) following the procedure described by Clavilier and co-workers [21, 22]. The electrodes were cleaned by flame annealing, cooled down in H₂/Ar and protected with water in equilibrium with this gas mixture to prevent contamination before immersion in the electrochemical cell, as described in detail elsewhere [22, 23]. The voltammetric profiles, and therefore the surface structure of the electrodes, are stable upon cycling provided that oxide formation is avoided. It is known that oxidation/reduction cycles create defects on the electrode surface [16, 24]. For that reason, the upper potential limit of the scan is always maintained below 1.1 V for the Pt(111) electrode.

Experiments were carried out in a classical two-compartment electrochemical cell deaerated by using Ar (N50, Air Liquide in all gases used), including a large platinum counter electrode and a reversible hydrogen (N50) electrode (RHE) as reference. For the determination of the activation energy, the electrochemical cell was immersed in a water bath to control the temperature in a range between 278 and 333 K. The reference electrode was kept at room temperature (298 K) and all the measured potentials are referred to a RHE electrode at 298 K. For that reason, the measured potentials were corrected with the thermodiffusion potential using the procedure explained in reference [25]. All the potentials are quoted vs. the RHE at 298 K unless otherwise stated. Solutions were prepared from sulfuric acid, perchloric acid, sodium perchlorate, acetic acid, formic acid (Merck suprapur in all cases) and ultrapure water from Elga. The cleanliness of the solutions was tested by the stability of the characteristic voltammetric features of well-defined single crystal electrodes.

The potential program for the transients was generated with an arbitrary function generator (Rigol, DG3061A) together with a potentiostat (eDAQ EA161) and a digital

recorder (eDAQ, ED401). To avoid any interference of the diffusion of formic acid in the reaction rate, stationary conditions were attained by using a hanging meniscus rotating disk configuration at 900 rpm (controlled by a Radiometer CTV 101).

3. Results.

3.1. Effect of the solution pH.

It has been recently shown that the pH affects significantly the currents for formic acid oxidation on platinum polycrystalline electrodes [14]. These experiments were carried out in different phosphate buffers. In order to verify the effects of pH in the oxidation of formic acid on Pt(111) electrodes, the oxidation currents for this electrode at different pHs have been measured. However, to prevent any possible interference in the oxidation currents as the pH changes, solutions have to be chosen carefully. First, specific adsorption of anions should be avoided, since this process can alter the reaction kinetics, as will be shown later. On the other hand, special care should be taken to maintain the interfacial pH constant during the process, since two protons are generated per formic acid molecule. Thus, solutions with a large buffering power should be used. The absence of specific adsorption precludes the use of the typical buffering solutions, such as phosphate buffers, since the different phosphate anions adsorb specifically on the (111) surface [26, 27]. For that reason, the solutions were prepared with perchloric acid and sodium perchlorate and the higher studied pH was close to 2.

As can be seen in figure 1, an increase in the oxidation currents are observed as the pH shifts from ca. 0 to 2. Also, the overall shape of the voltammetric profile in the negative scan remains almost constant. On the other hand, the difference between the currents measured in the positive and negative scan directions also increases with pH. This hysteresis is associated to the formation of CO in the dehydration reaction of formic acid at low potential values [1-4], which blocks the surface and affects the currents measured in the positive scan direction .

For the Pt(111) electrode, CO formation is restricted to the defects on the surface and takes place at potentials below 0.3 V [20, 28, 29]. There is a clear relationship between the hysteresis and the CO formation rate as shown in the studies with stepped surfaces [20], and thus the larger hysteresis as the pH increases has to be associated to an increase in the CO formation rate at defects at low potentials. Since CO is oxidized above 0.75 V [30], the currents measured in the negative scan direction correspond exclusively to the oxidation of formic acid through the active intermediate route [20]. The constancy of the shape in the negative scan direction suggests that the oxidation mechanism is the same, so that the current increase should be related to the increase in concentration of a relevant species in the oxidation mechanism. Being formic acid a weak acid with a $pK_a=3.75$, the change in pH alters the ratio between formate and formic acid in solution. Thus, the current increase can be related to the increase in the concentration of formate in solution, as has been previously proposed [14]. In the RHE scale (figure 1, top panel), the onset for formic acid oxidation only moves slightly towards more negative values as the pH increases.

To check the reaction order with respect to the concentration of formate, currents at constant absolute potential (vs. SHE) from figure 1 lower panel have been plotted vs. pH. Figure 2 shows the currents measured at 0.35 and 0.50 V vs. SHE in the negative scan direction, which correspond exclusively to the activity of the surface through the active intermediate route in absence of CO [20]. As can be seen, there is a linear relationship between the pH and the logarithm of the current density, in which the slope is between 0.35 and 0.4. Since in this pH range, solution formate concentration is proportional to the proton concentration, the slope of this plot can also be considered the reaction order for solution formate in the rate equation.

3.2. Effect of the specific adsorption of anions.

Adsorbed species on the electrode surface alter the reactivity since they change the interaction between the relevant species in the mechanism and the surface. As solution pH affects the formic acid oxidation currents (and therefore the reaction rate), the study of the effect of the specifically adsorbed anions in the reaction rate should be carried out at constant pH. Figure 3 show the voltammetric profiles for the clean electrolyte and for formic acid oxidation in 0.5 M HClO₄ and 0.5 M H₂SO₄, solutions whose pHs can be considered very similar. As can be seen, maximum currents for both media are almost the same. However, it should be noted that currents for the sulfuric acid solution are slightly higher and the onset is displaced towards more negative potentials. This behavior is rather unexpected. From the pH perspective, solution pH in the sulfuric acid solution can be somehow higher due to the second acid/base equilibrium of the molecule. According to the previous results, the higher pH should correspond to lower currents. Also, the presence of strongly adsorbed sulfate should lead to a significant diminution in the currents, as happens to other organic molecules such as methanol [31]. On the other hand, significant currents for formic acid oxidation are obtained in the region where sulfate anions are adsorbed [32] and the current decay after the maximum takes place at more positive potential values for the sulfuric acid solution. All these results indicate that the adsorption of sulfate on the electrode surface has an unexpected positive effect for the oxidation of formic acid.

To check whether this enhancement is exclusive of sulfate or can be observed with other anions, the effect of acetic acid was also studied. In order to maintain the solution pH below to 2, 1 mM acetic acid was added to a 0.1 M perchloric acid solution (figure 4). For comparison, the effect of the addition of 1 mM H₂SO₄ was also studied. It should be borne in mind that the adsorption of acetate is stronger than that of sulfate, as can be observed in the voltammetry of the Pt(111) electrode (see figure 11). As shown in this figure, the effects of

the addition of sulfate and acetate to the 0.1 M perchloric acid solution are similar. In this case, the change in the onset is negligible, due to the lower concentration of the anions. However, in spite of the specific adsorption of anions, currents are maintained when compared to pure perchloric acid solutions.

3.3. Determination of the activation energy for the direct oxidation path.

Additional information on the mechanism of formic acid oxidation can be obtained if the activation energy is determined. To ensure that the activation energy corresponds to the direct route, pulsed voltammetry has been used [18, 19]. Each transient obtained from the pulsed voltammetry has been fitted to the equation

$$j = j_{\theta=0} \left(\frac{1}{1 + k_{ads} t (p-1)} \right)^{\frac{1}{p-1}} \quad (1)$$

where $j_{\theta=0}$ represents the current through the direct route in absence of poison, the so-called intrinsic activity of the electrode [18], k_{ads} is the CO formation rate from formic acid and p is the number of sites required for the adsorption of formic acid to yield CO. According to this model, the transients should have a decay, which depends on the value of k_{ads} , and the extrapolation of the transients to $t=0$ gives the value of $j_{\theta=0}$. This equation has been proved to fit adequately the observed transients for formic acid oxidation on single crystal electrodes [19, 20] and nanoparticle electrodes [33]. For all the observed transients, the decay was very small and therefore no accurate determination of the parameter p could be made. As the usual value is close to 2 [19, 20], in all the fittings for this electrode the value of p was set to 2.

Transients for the oxidation of 0.1 M formic acid with the pulsed voltammetry technique were recorded between 5 and 45 °C to determine the change of $j_{\theta=0}$ with potential and temperature for the following supporting solutions: 0.1 M HClO₄, 0.5 M H₂SO₄, 0.1 M HClO₄ + 10 mM H₂SO₄ and 0.1 M HClO₄ + 10 mM CH₃COOH, 0.05 M HClO₄ + 0.05 M

KClO₄ (pH=1.48) and 0.01 M HClO₄ + 0.09 M KClO₄ (pH=1.87). With these solutions, the anion and pH effects in the activation energy can be studied. Figure 5 shows the results of $j_{\theta=0}$ obtained for the oxidation of 0.1 M HCOOH in 0.1 M HClO₄ at selected temperatures. It should be noted that the error in the determination of $j_{\theta=0}$ is well below 1% in all cases, due to almost negligible k_{ads} values obtained from the fittings. As expected, currents increase with temperature and the onset for the oxidation shifts towards more negative values.

The activation energy can be obtained from the Arrhenius plots as shown in figure 6. In all cases, the plots were linear, within the experimental error of the measurements. From the slope of the $\log(j_{\theta=0})$ vs. $1/T$, the apparent activation energy was determined for all the solutions. These values are plotted vs. the electrode potential for the different solutions in figure 7. For the effect of the anions present in solution, two different behaviors can be observed. In the solutions containing perchloric acid, the apparent activation energy is almost independent of the anion present in solution. For these curves, there is a small region between 0.3 and 0.4 V where the activation energy diminishes from values around 55-60 to 45 kJ mol⁻¹. From that potential, the activation energy slowly increases up to 0.7 V. At this point, there is a sharp diminution of the activation energy. On the other hand, for the sulfuric acid solution, there is a continuous diminution of the activation energy from values of ca. 70 kJ mol⁻¹ at 0.3 V to 35 kJ mol⁻¹ at 0.6 V. From this potential, values increase and reach a stable value of ca. 60 kJ mol⁻¹ at 0.8 V. These results clearly indicate that the adsorption of the anions have a strong influence in the kinetics of the reaction. Although the details of this dependence will be discussed in the following section, a preliminary explanation can be given here. The initial diminution in the activation energy can be related to the initial stages of the adsorption of formate or any other anion present in solution. In the absence of strong adsorption, as in the case of 0.5 M H₂SO₄ solutions, after the initial triggering event of the reaction, the activation energy remains nearly constant until OH adsorption occurs on the

electrode. For the perchloric acid solutions with acetic acid or sulfuric acid, it is probable that OH replaces the adsorbed anion at the more positive potentials in a process without a significant charge transfer [34]. The adsorption of OH leads to the deactivation of the surface for the direct oxidation and to a significant diminution of the activation energy. For the sulfuric acid solution, there is a clear minimum in the activation energy curve. The region where the minimum activation energy is obtained coincide with the presence of the small bump that can be observed in the voltammetric profile in the supporting electrolyte (figure 3). This bump has been associate to an order transition in the sulfate adlayer that leads to the formation of large ordered domains [35-37].

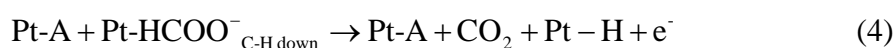
Regarding the pH effect, a clear diminution in the activation energy is observed as the pH increases, which corroborates the results observed by voltammetry (figure 7, lower panel). The lower apparent activation energy implies that the formation of the reaction intermediate is facilitated at higher pHs. Activation energies as low as 25 kJ/mol are obtained at pH=1.87. It should be stressed that the measured value is the apparent activation energy with contains not only information on the true activation energy of the rate determining step, but also on the activation energy for all the previous steps [38]. If solution formate is involved in the rate determining step, this species should be produced from the acid/base equilibrium of formic acid/formate at very low pHs. The free energy of this equilibrium reaction contributes in these cases to the apparent activation energy. Thus, the apparent activation energy diminution as the pH increases can be related to the increase in the concentration of solution formate that diminishes the requirements to produce it from formic acid. It should also be highlighted that for the sulfuric acid solution activation energy values are also close to those obtained at higher pH in perchloric acid solutions, which also suggests that adsorbed sulfate facilitates the oxidation of formic acid.

4. Discussion.

The results presented here clearly points out the role of several species in the whole mechanism through the direct route. From the dependence of the current densities and activation energy with the pH it is seems clear that formate anion is playing a significant role in the mechanism, as has been already suggested [14]. As the pH increases, the effective concentration of formate for a given initial concentration of formic acid increases and thus current increase. On the other hand, pre-adsorbed anions, as sulfate, have a beneficial effect in the oxidation currents. A clear example of that is the figure 3, in which a lower onset for the formic acid oxidation reaction is observed in the presence of sulfuric acid. Thus, it can be proposed that adsorbed anions and formate are involved in the oxidation mechanism through the following scheme:



where A is an adsorbed anion present on the surface (either sulfate, or acetate or bidentate formate). In the rds, the adsorbed anion and the formate coming from solution interacts with the surface through the C-H bond, according to the equation:



The C-H down configuration is that in which the H is close to the surface, but it does not imply necessarily that the C-H bond is perpendicular to the surface. Several configurations can be proposed here, such as monodentate adsorbed formate or that proposed in reference [39]. This type of step, in which the oxidation of formate is requires an additional adsorbed anion in the vicinity, has been already proposed by DFT calculations using a continuous solvation model and discrete water molecules [39]. It has been shown that the adsorbed formate molecule in a bridge-bonded bidentate configuration (with the two oxygen atoms in the carboxylic group pointing towards the surface) is a key element in the process. The

presence of bridge-bonded bidentate adsorbed formate facilitates the adsorption of an additional formic acid molecule with C-H down configuration. In this position, the cleavage of the H-C has a low activation energy, yielding CO₂ [39]. On the other hand, the calculated activation energy for the cleavage of the H-C bond from the bridge bonded bidentate formate is very high and, thus, this event is not likely [39]. With respect to the DFT model, the only significant difference is that formate, not formic acid, is the species that adsorbs with the CH down configuration, in order to justify the dependence of the currents with the pH. Additionally, it will be considered that not only adsorbed formate facilitates the CH down adsorption of the formic acid molecule, but also other adsorbed anions such as sulfate or acetate can play similar roles.

Before formulating a rate equation, it should be also take into account that OH adsorption do not have an active role in the oxidation of formic acid. As can be seen in figure 2, the presence of adsorbed OH causes the opposite effect. At potentials above 0.6 V in perchloric acid solutions, where OH adsorption occurs, currents diminish and reach negligible values at 0.8 V. Thus, the oxidation of formic acid requires a preadsorbed anion and a free site where formate can adsorb the current for the oxidation of formic acid. The corresponding kinetic equation is then:

$$j = Fk^o \exp\left(\frac{F(E - E^o)}{\alpha RT}\right) \theta_A (1 - \theta_A - \theta_{OH}) [\text{HCOO}^-] \quad (5)$$

where k^o is the standard rate constant, E^o the standard potential for the oxidation of formic acid, α is the symmetry factor of the reaction, θ_A and θ_{OH} are the specific anion and OH coverages and the rest of symbols have the usual meaning. This equation is the direct consequence of reaction (4), which is the rds. Since the rds is the first electron transfer, it

should include the potential dependent term $\exp\left(\frac{F(E - E^o)}{\alpha RT}\right)$, with an α value close to 0.5.

Also, the step requires the presence of an adsorbed anion (sulfate or bridge-bonded bidentate formate) with represented by its coverage value, θ_A and an adsorbed formate ion in a C-H down configuration. This is an intermediate species, which has been formed through reaction (2) and requires the presence of a free Pt site and a formate ion from solution. Thus, the terms referring to the Pt free sites $(1-\theta_A-\theta_{OH})$ and formate solution concentration $[HCOO^-]$ should appear also in the equation.

This rate equation is different from that proposed in reference [14] to explain the pH behavior of the oxidation current. In this new equation, an additional term, the anion coverage, has been included to explain the lower onset for formic acid oxidation in the presence of sulfate. In phosphate buffer solutions, it was found that the current increases with pH up to values close to 4 and then diminishes from that point [14]. The equation proposed here is also able to reproduce the behavior, since the increase in the with the pH is linked to the formate concentration and the diminution above pH=4 is associated to the $(1-\theta_A-\theta_{OH})$ term, as has been demonstrated in [14]. The addition of θ_A to the rate equation does not alter the behavior proposed in the previous reference, since it is only playing an important role in defining the currents for low coverages, that is, at the onset of formic acid oxidation.

This equation will be tested for the oxidation of formic acid in perchloric acid solutions. For that, the value of the bridge-bonded formate coverage (θ_A) as a function of the electrode potential has to be known from independent measurements. In a previous paper [40], the value of θ_A during formic acid oxidation in perchloric acid solutions was determined by using fast scan voltammetry. Since formic acid oxidation currents are not dependent on the scan rate [41], it is possible to determine adsorption currents for formate at scan rates around 50 V s^{-1} . At 50 mV s^{-1} , the current due to the adsorption of formic acid is negligible in comparison to those obtained for formic acid oxidation. At 50 V s^{-1} , the current for the adsorption process has increases 1000 times, and is much bigger than the oxidation currents

and therefore, the curve for formate coverage vs. potential can be estimated from the integration of the voltammetric profile in the region where formate adsorption takes place after subtraction of the typical double layer. From the curve θ_A vs. E from [40], the current density for formic acid oxidation can be calculated according to equation (5) and compared to the experimental current. Figure 8 shows the comparison between the measured voltammetric profile in the negative scan direction for formic acid oxidation in the solution used to measure θ_A and the calculated current using equation (5). The negative scan direction is used because the surface is free from adsorbed CO. For the calculation, α was equal to 0.45, E^o was 0 V and $Fk^o[\text{HCOO}^-]$ was 9.6×10^{-4} mA cm⁻². As can be seen, the model is able to reproduce the shape, maximum position and the decay after the maximum for formic acid oxidation. However, the fitting is not perfect probably due to the way the formate coverage was estimated, especially at low potential values. Between 0.3 and 0.45 V, formate adsorption competes with hydrogen adsorption. For the estimation of the coverage, it has been assumed that hydrogen adsorption coverage was equal to that obtained in absence of formic acid in solution and this fact may have led to an underestimated value of the formate coverage. A more accurate method to obtain θ_A would have required the use of the thermodynamic treatment of reference [42]. However, under the present conditions, it is not possible to use such treatment, because the the voltammetric profile at 50 V s⁻¹ is not perfectly symmetrical.

The model presented in equation 4 also explains the activation energies measured in figure 7. The apparent activation energy, which is the measured value, is then defined as:

$$Ea_{app}^{\ddagger} = -R \frac{d \ln(j)}{d \frac{1}{T}} = -R \left(\frac{d \ln(k^o)}{d \frac{1}{T}} + \frac{d \ln(\theta_A)}{d \frac{1}{T}} + \frac{d \ln(1 - \theta_A - \theta_{OH})}{d \frac{1}{T}} \right) \quad (6)$$

In this equation, the real activation energy, which can be related to the value determined by DFT, is:

$$Ea^{\ddagger} = -R \frac{d \ln(k^{\circ})}{d \frac{1}{T}} \quad (7)$$

It is expected that this value is independent of the electrode potential. The terms related to the anion and OH coverage are clearly dependent on the electrode potential, which causes the different values obtained at different electrode potentials. At low potentials, the dominant

term in this potential dependence is $\frac{d \ln(\theta_A)}{d \frac{1}{T}}$. The evolution of the anion coverage with the

temperature can be estimated using the voltammetric profile measured at different temperatures. As can be seen in figure 9 for 0.5 M sulfuric acid solution, the onset of sulfate adsorption is displaced towards more positive values. In the case of acetate, a similar behavior is observed and a similar behavior is also expected for formate adsorption. This implies that at constant electrode potential, the anion coverage diminishes with the temperature, which should lead to a diminution of the activation energy in this potential region, as observed in all solutions, At high potential values, the term that dominates the change with the electrode

potential is $\frac{d \ln(1 - \theta_A - \theta_{OH})}{d \frac{1}{T}}$. Thus, the way the anion or OH coverage reaches the maximum

value and how it evolves with the temperature should determine the changes of the apparent activation energy in this region.

In the case of formate, which will be the adsorbed anion in 0.1 M HClO₄, and acetate (in 0.1 M HClO₄ + 10 mM HAc), the adsorption strength is similar, as shown in reference [40], and therefore, they have similar values. For the solution containing 0.1 M HClO₄ + 10 mM H₂SO₄, the adsorption of sulfate is weaker than that of acetate, as figure 10 demonstrate. In this case, formate adsorption is probably stronger than sulfate adsorption at this concentration. Therefore, the anion adsorbed on the electrode surface in this supporting

electrolyte is formate, which gives apparent activation energies equal to those obtained in pure perchloric acid solution.

The only apparent discrepancy of the proposed model and the obtained results is the order with respect to the formate concentration. According to equation (5), the order should be 1, but the measured order is around 0.4. The real order can only be obtained if the rest of the parameters (coverages and electrode potential) are constant. In figure 2, the electrode potential is maintained constant. However, the anion coverage is clearly dependent on the pH and for that reason, the measured value deviates from the real value to lower values. This implies that a given electrode potential in the SHE scale, the measured coverage of formate diminishes with the pH.

5. Conclusions.

The results presented demonstrate the complexity of the formic acid oxidation reaction, since it involves the presence of at least two adsorbed species: an anion (which could be sulfate, acetate or bridge-bonded bidentate formate) and solution formate. This latter species should interact with the surface with the C-H bond close to the surface, so that the cleavage of the C-H bond could occur. Also, it explains the controversy regarding the role of adsorbed bridge-bonded bidentate formate in the mechanism. It takes part in the mechanism, as ATR-SEIRAS results indicates [9], although it is not the molecule that decomposes to give CO₂. CO₂ is generated from a solution formate which interacts with the surface through the C-H bond.

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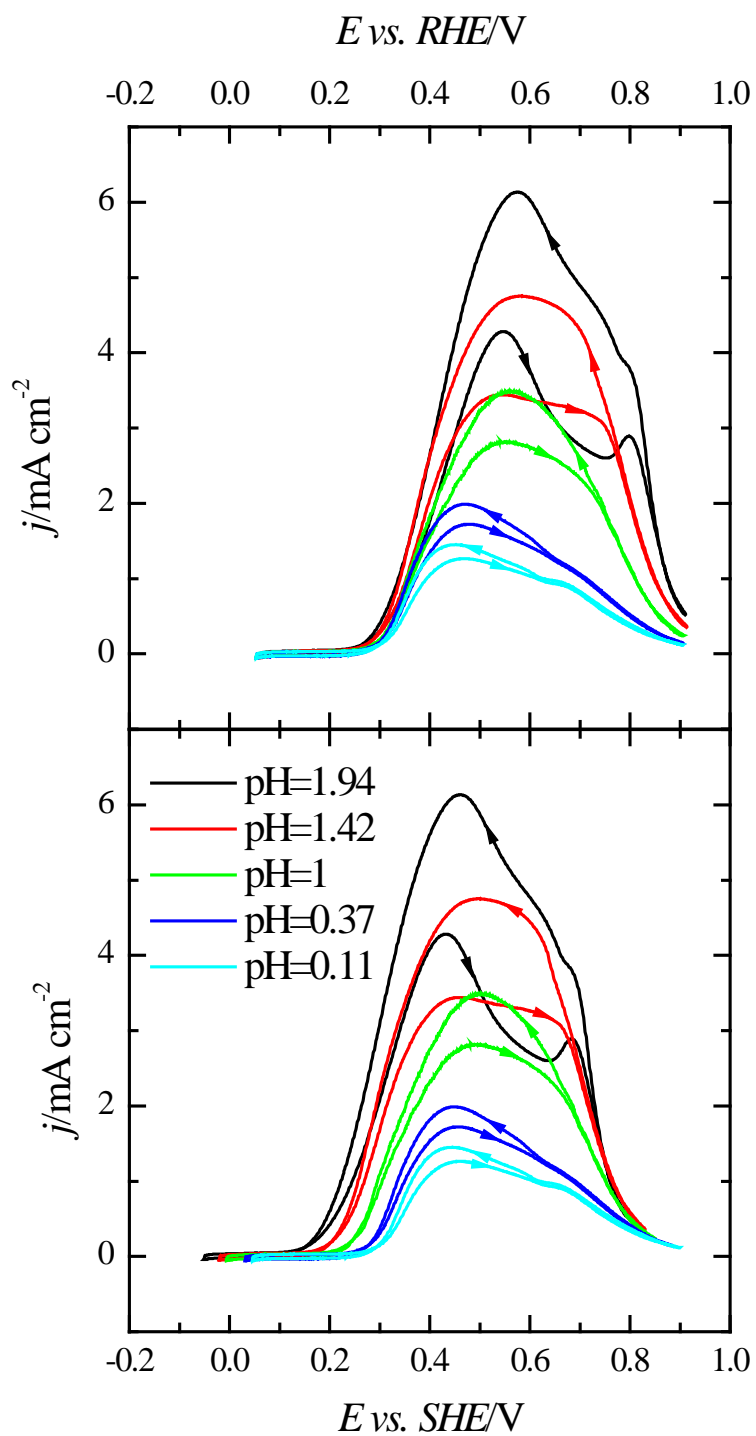


Figure 1. Voltammetric profiles for the oxidation of 0.1 M formic acid in different solutions on the Pt(111) electrode: 1 M HClO₄ (pH=0.11), 0.5 M HClO₄ (pH=0.37), 0.1 M HClO₄ (pH=1.0), 0.05 M HClO₄ + 0.05 NaClO₄ (pH=1.42) and 0.01 M HClO₄ + 0.09 NaClO₄ (pH=1.94).

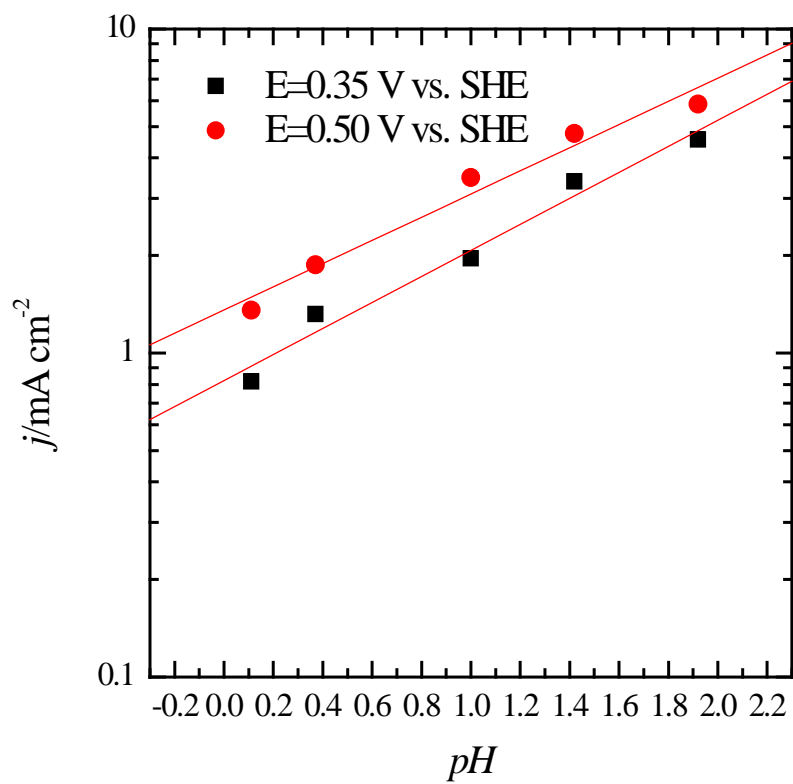


Figure 2. Currents at constant potential for formic acid oxidation vs. solution pH. Data taken from figure 1.

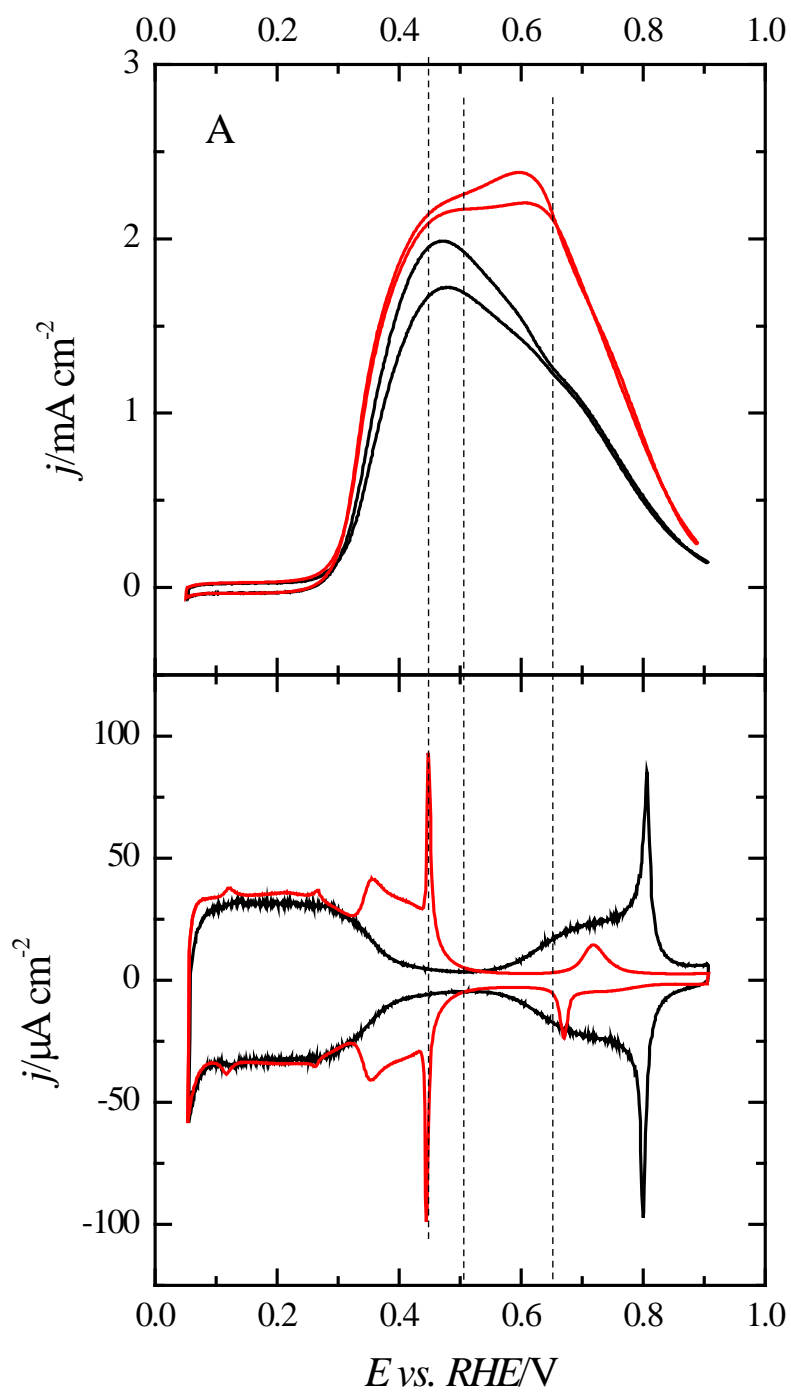


Figure 3. A) Voltammetric profile for the Pt(111) electrode in 0.5 M HClO_4 + 0.1 M HCOOH (black line) and 0.5 M H_2SO_4 + 0.1 M HCOOH (red line) B) Voltammetric profile for the Pt(111) electrode in 0.5 M HClO_4 (black line) and 0.5 M H_2SO_4 (red line)

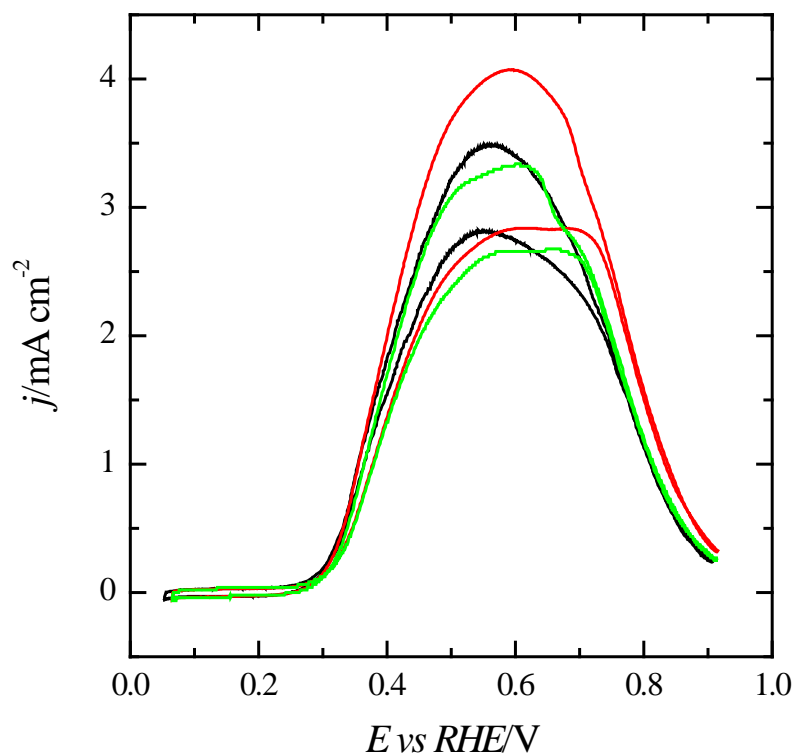


Figure 4. A) Voltammetric profile for the Pt(111) electrode in 0.1 M HClO₄ + 0.1 M HCOOH (black line), 0.1 M HClO₄ + 1 mM H₂SO₄ + 0.1 M HCOOH (red line) and 0.1 M HClO₄ + 1 mM HAc + 0.1 M HCOOH (green line).

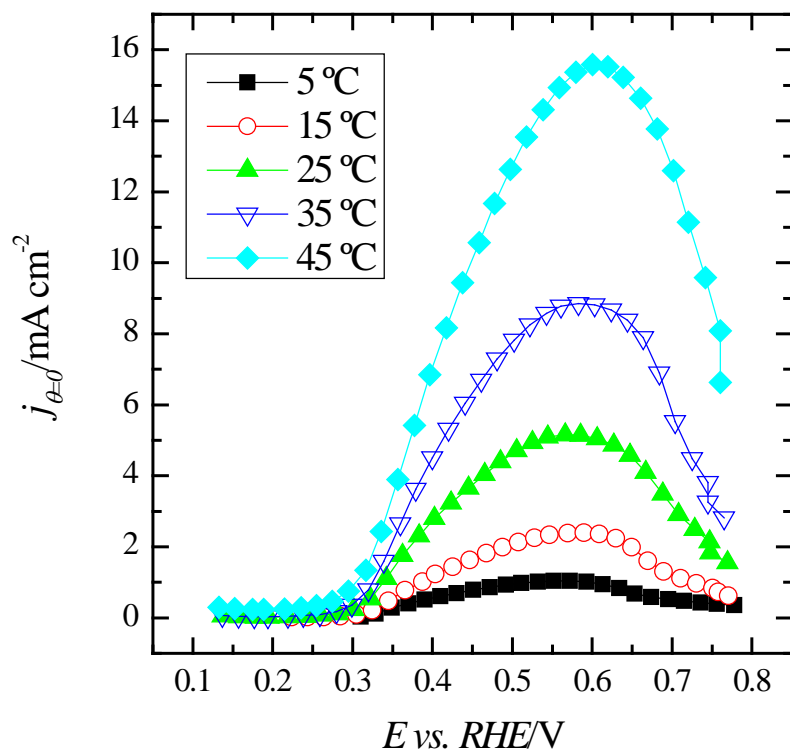


Figure 5. Values of $j_{\theta=0}$ at different temperatures vs. electrode potential measured in 0.1 M HClO_4 + 0.1 M HCOOH solutions for the Pt(111) electrode.

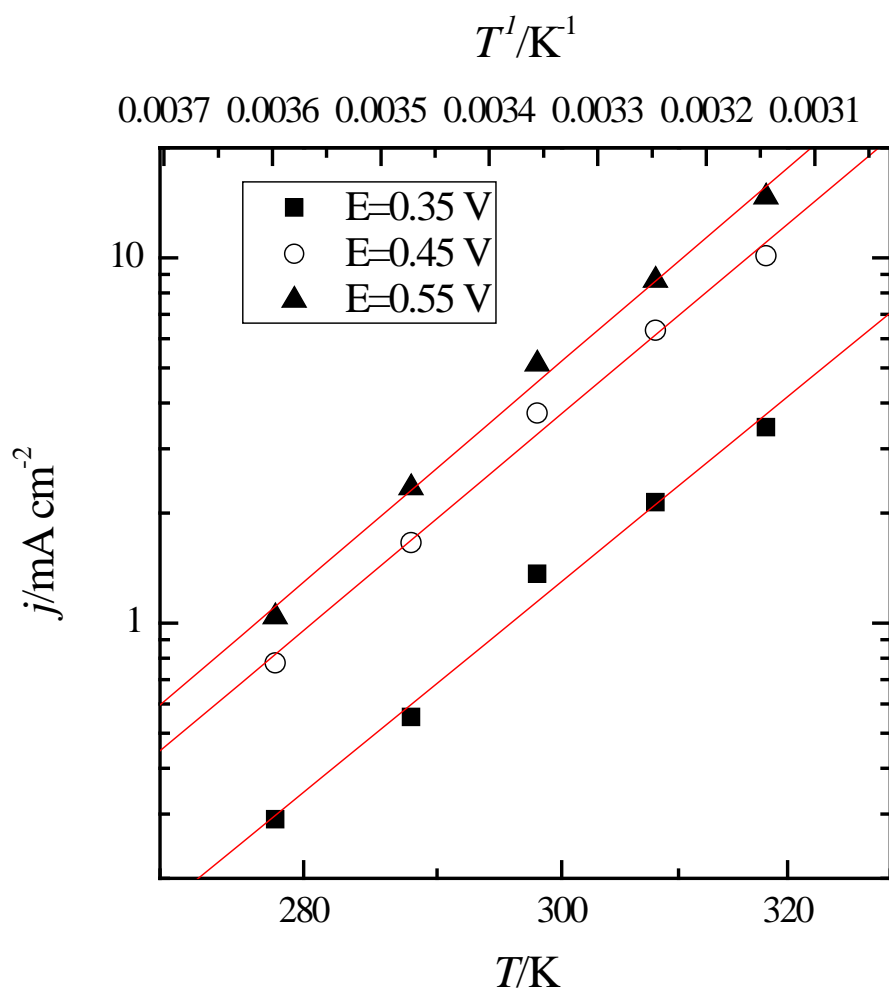


Figure 6. Arrhenius plots for $j_{\theta=0}$.

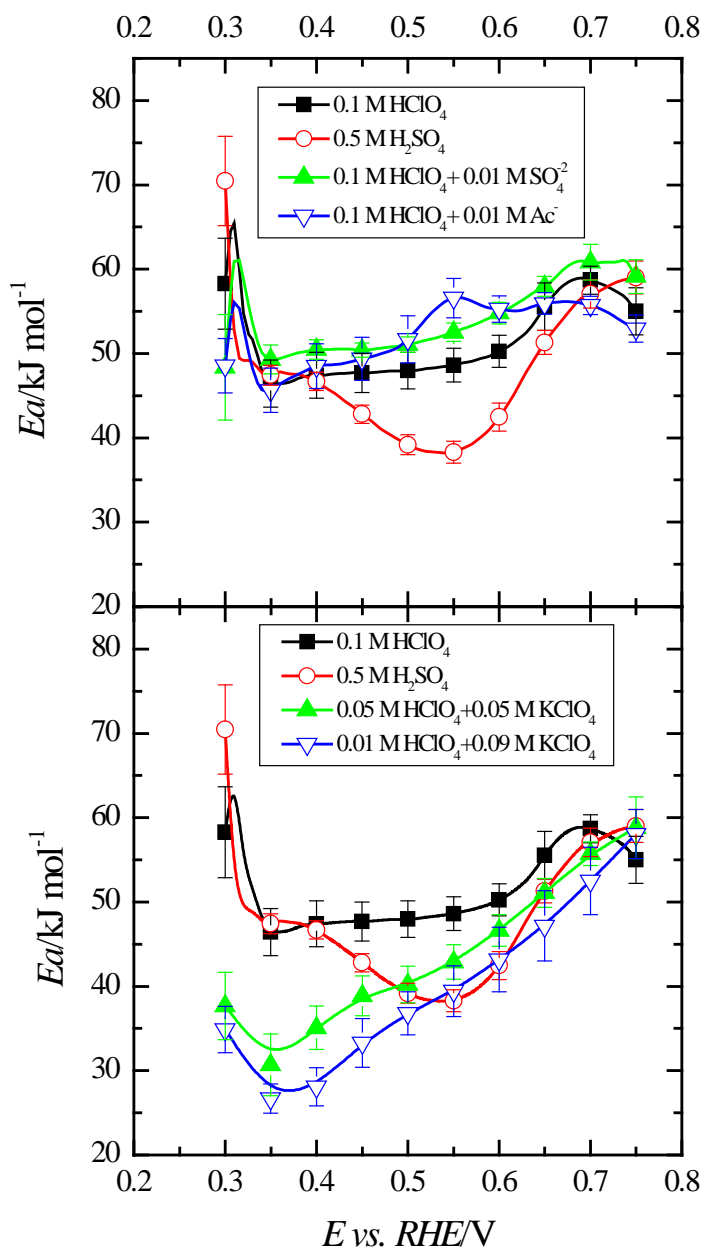


Figure 7. Apparent activation energy vs. electrode potential determined for the oxidation of 0.1 M HCOOH in different solutions on the Pt(111) electrode.

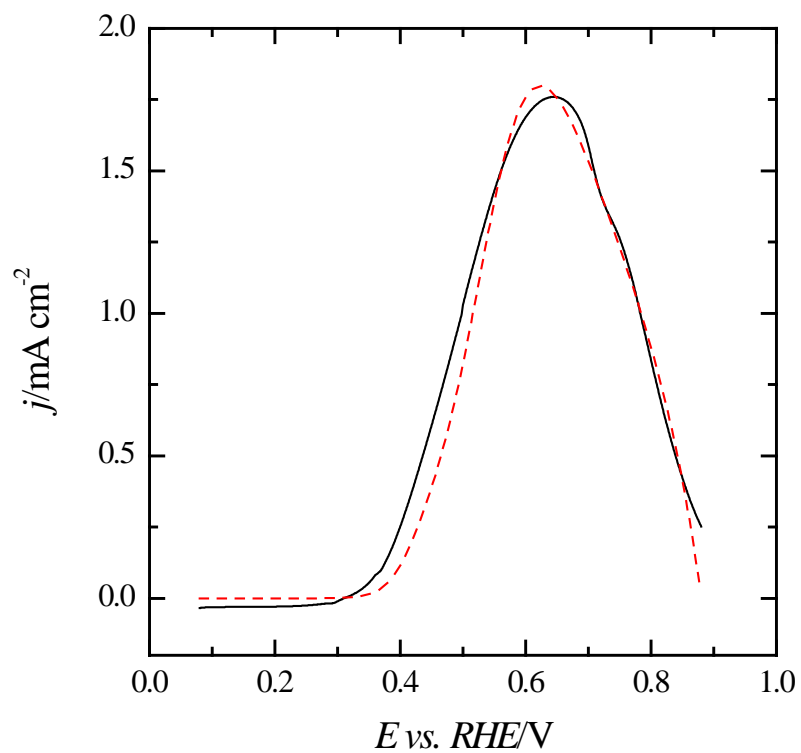


Figure 8. Comparison of the negative scan direction of the voltammogram recorded in 0.1 M HClO_4 + 0.05 M HCOOH for the Pt(111) electrode (full line,) and the calculated current using equation (5). θ_A values for this equation are taken from reference [40].

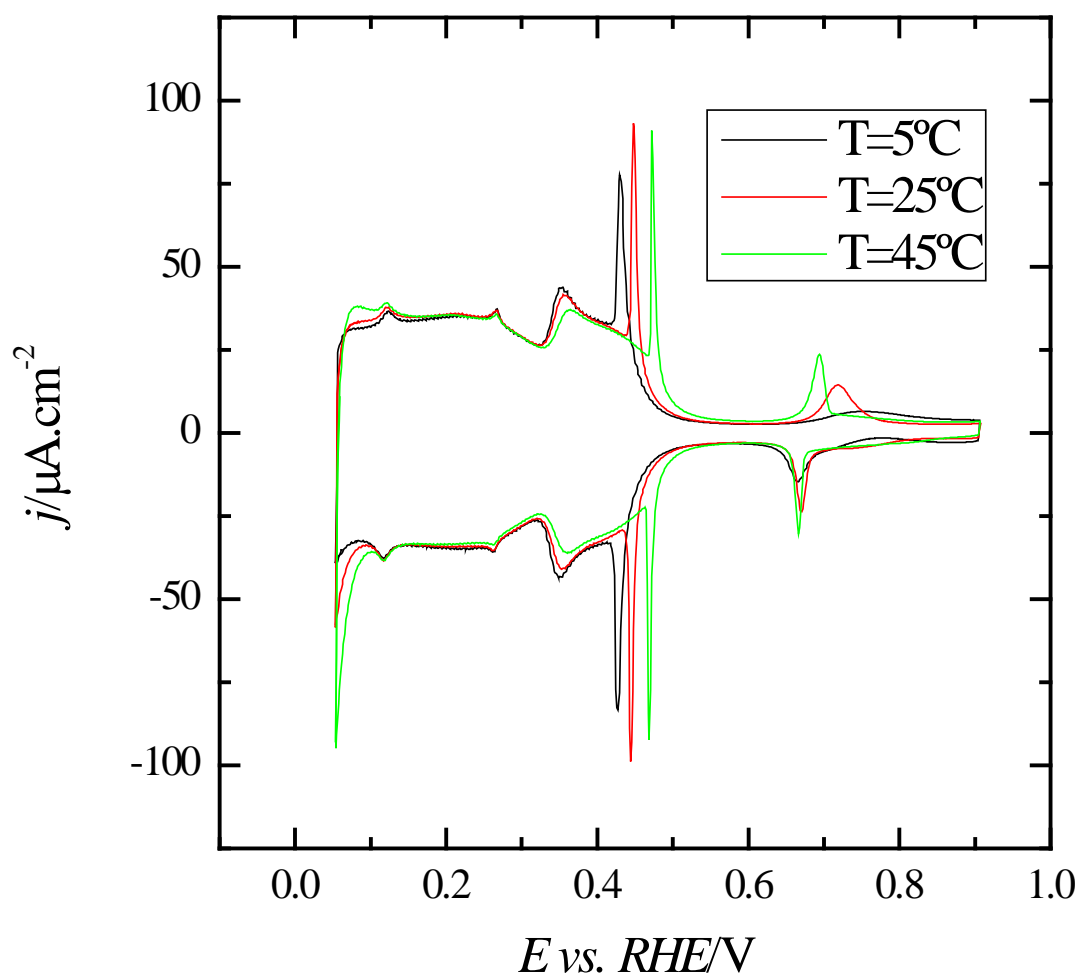


Figure 9. Voltammetric profile of the Pt(111) electrode in 0.5 M H_2SO_4 at different temperatures

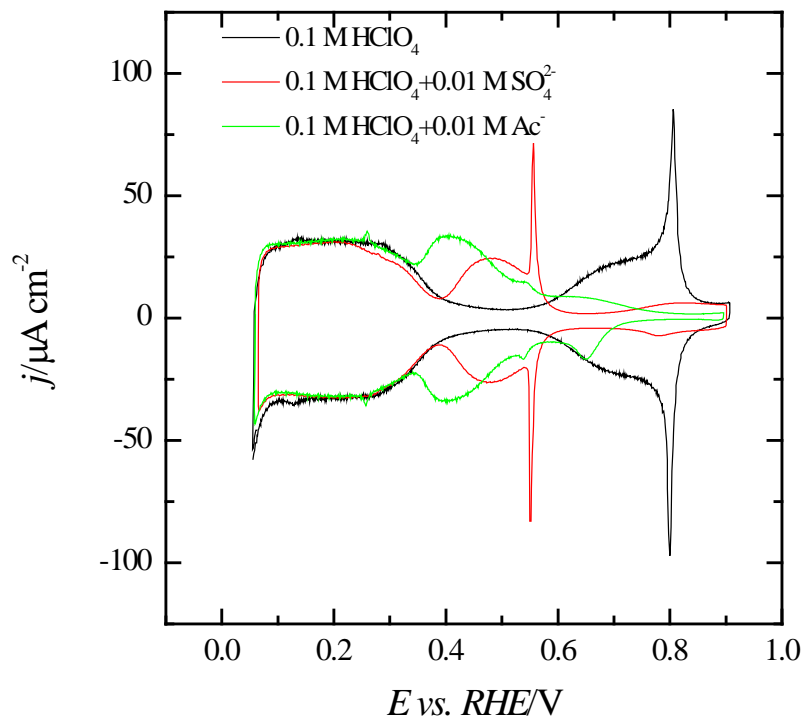


Figure 10. Voltammetric profile of the Pt(111) electrode in different solutions.

