



On the activation energy of the formic acid oxidation reaction on platinum electrodes



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ABSTRACT

A temperature dependent study on the formic acid oxidation reaction has been carried out in order to determine the activation energy of this reaction on different platinum single crystal electrodes, namely Pt(100), Pt(111), Pt(554) and Pt(544) surfaces. The chronoamperometric transients obtained with pulsed voltammetry have been analyzed to determine the current densities through the active intermediate and the CO formation rate. From the temperature dependency of those parameters, the activation energy for the direct reaction and the CO formation step have been calculated. For the active intermediate path, the activation energy are in the range of 50–60 kJ/mol. On the other hand, a large dependence on the electrode potential is found for the activation energy of the CO formation reaction on the Pt(100) electrode, and the activation energy values for this process range between 20 and 100 kJ/mol. These results have been explained using a reaction mechanism in which the oxidation of formic acid requires the presence of a pre-adsorbed anion on the electrode surface.

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1. Introduction

The formic acid oxidation reaction has been extensively studied because its potential use as anode reaction in the fuel cell technology. Additionally, from all the possible carbon containing species studied as tentative fuels, it has the simplest oxidation mechanism [1–3]. In fact, its oxidation to CO₂ only requires the cleavage of two bonds: O–H and C–H. The break of the O–H bond is relatively simple, since the OH group is involved in the acid/base equilibria of the molecule. For the second one, a surface with affinity for hydrogen and dehydration reactions is required. For that reason, the platinum and palladium electrodes show the highest activity.

In spite of the apparent simplicity of the reaction, additional complications in the oxidation mechanism appear on platinum surfaces. On these electrodes, CO formation at low potentials is observed [1]. To produce adsorbed CO, the cleavage of two different bonds should take place: the C–H and the C–OH bonds. The formation of CO creates additional problems in the oxidation of the formic acid molecule. CO is strongly adsorbed on the Pt surface and its final oxidation to CO₂ requires the transfer of an OH group. This latter step has a large overpotential. For this reason, CO is also called the poisoning intermediate, since it blocks the surface for the reaction to continue. On the other hand, the reaction route

which gives directly CO₂ is called the direct oxidation route. For this route, the nature of the intermediate is still subject of discussion [4–11].

In order to get insight into the oxidation mechanism, extensive DFT calculations have been carried out using well defined surfaces [12–15]. In these studies, different intermediates and reaction schemes have been proposed. However, in order to validate those reaction mechanism, the theoretical data for the calculated activation energies should be compared with those obtained experimentally. In this manuscript the activation energies for the formic acid oxidation reaction are measured on single crystal electrodes using different electrolytes. The activation energies will be analyzed in view of the proposed mechanism, and compared with previous results, in order to obtain additional details on the oxidation mechanism. In this way, the measured values will be compared with those obtained from DFT calculations to validate the proposed mechanism.

2. Experimental procedure and numerical treatment of data

2.1. Experimental procedure

Platinum single crystal electrodes were oriented, cut and polished from small single crystal beads (ca. 2.5 mm diameter) following the procedure described by Clavilier [16,17]. The electrodes used in this study were the Pt(111) and Pt(100) low index planes

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and two stepped surfaces: Pt(544) and Pt(554). These surfaces have 9 atom-wide (111) terraces separated by monoatomic (100) and (110) steps, respectively. Before every use, the electrodes were cleaned by flame annealing, cooled down in H₂/Ar and protected with water in equilibrium with this atmosphere. It is known that this procedure gives rise to surfaces whose atomic arrangement corresponds to the nominal one [18]. The voltammetric profile of the electrode in 0.5 M H₂SO₄ is always recorded to assure that the surface is well prepared and clean. The upper potential limit is always chosen so that oxide formation is avoided, to prevent surface disordering [19,20].

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 temperature controlled experiments, the electrochemical cell was immersed in a water bath to control the temperature. Temperature dependent measurements were conducted in a range between 278 and 333 K, using 5 K intervals. For the different experiments, the reference electrode was kept at room temperature (298 K). To transform the direct potential reading to the RHE scale at 298 K values, the direct potential reading should be corrected for the thermodiffusion potential using the procedure explained in reference [21]. Solutions were prepared from sulfuric acid, perchloric acid, formic acid (Merck suprapur in all cases) and ultrapure water from Elga.

The potential program for the pulse voltammetry, which allowed obtaining the current 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 1600 rpm (controlled by a Radiometer CTV 101). Full experimental details on the pulsed voltammetry can be found in reference [22]. In summary, the potential program consists in a series of steps between an upper potential (0.9 V for $T < 298$ K and 0.85 V for $T \geq 298$ K) to oxidized the accumulated CO on the surface and the sampling potential. The duration of the steps was always 1 s.

2.2. Numerical treatment of the transients

In a previous work, transients obtained in the pulsed voltammetry as those shown in Fig. 1 were simulated with a model which took into account direct formic acid oxidation and CO formation through the dehydration reaction [22]. For the oxidation through the active intermediate, it was supposed that the current density depended on the fraction of the surface not covered by CO, $(1 - \theta_{CO})$, and the current that would have been obtained in absence of CO, $j_{\theta=0}$.

$$j = j_{\theta=0}(1 - \theta_{CO}) \quad (1)$$

In turn, the CO coverage will depend on the on the dehydration step, for which the reaction rate was written as:

$$\frac{d\theta_{CO}}{dt} = k_{ads}(1 - \theta_{CO})^p \quad (2)$$

where k_{ads} is the poison formation reaction rate and p is the number of Pt sites required for the dehydration step to occur. The integration of Eq. (2), and substitution in Eq. (1) yielded:

$$j = j_{\theta=0} \left(\frac{1}{1 + k_{ads}t(p-1)} \right)^{\frac{1}{p-1}} \quad (3)$$

This model was used to obtain the values of $j_{\theta=0}$, k_{ads} and p from the fits of this equation to the experimental transients. The fits were very

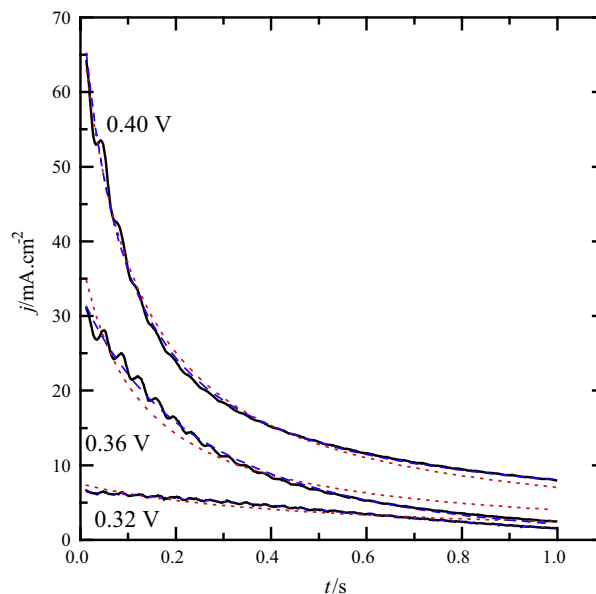
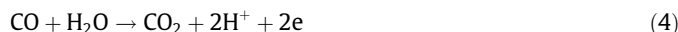


Fig. 1. Transient currents measured during the pulsed voltammetry at different potentials on the Pt(100) electrode at 40 °C in 0.5 H₂SO₄ + 0.1 M HCOOH and fittings according to Eq. (3) (dotted line) and Eq. (8) (dashed line).

good at room temperature, which supported the validity of the model [22,23]. In all cases, p was close to two, which implies that the dehydrogenation reaction requires two contiguous free platinum sites to proceed. However, when this equation is used for $T > 298$ K for the transients obtained in this work, the model deviates from experimental transients (Fig. 1, dotted line). In the model represented by Eq. (3), possible contributions to the total current from the adsorbed CO oxidation process according to the reaction



were not taken into account, because it was experimentally verified that, the CO oxidation rate was negligible at the potentials where CO was formed [22,23]. In the worst case scenario, the Pt(100) electrode, CO formation takes place at $E < 0.50$ V and for those potentials CO oxidation is negligible at room temperature. However, the temperature increase has two major effects: to accelerate CO oxidation process and also to increase the potential window where CO formation occurs. For this reason, the deviations from previous model are due to the contribution of the CO oxidation process to the measured current and, thus, such contribution should be taken into account for the transients at $T > 298$ K. Eq. (2) should be then modified incorporating the possibility of change of CO coverage due to its oxidation according to the proposed mean field Langmuir-Hinshelwood mechanism [3,24,25] as:

$$\frac{d\theta_{CO}}{dt} = k_{ads}(1 - \theta_{CO})^p - k_{ox}\theta_{CO}(1 - \theta_{CO}) \quad (5)$$

where k_{ox} is the rate constant for the CO oxidation process. In the same way, the equation for the current density should incorporate the contributions to the measured current of the CO oxidation reaction as:

$$j = j_{\theta=0}(1 - \theta_{CO}) + qk_{ox}\theta_{CO}(1 - \theta_{CO}) \quad (6)$$

where q is the charge involved to the oxidation of a monolayer of CO (320 $\mu\text{C cm}^{-2}$ for the Pt(100) electrode). In order to solve Eq. (5) for θ_{CO} , p was fixed to 2, because this was the value obtained experimentally [22]. Assuming that $k_{ads} \gg k_{ox}$, θ_{CO} is then:

$$\theta_{CO} = k_{ads} \frac{\exp(k_{ox}t) - 1}{k_{ox} \exp(k_{ox}t) + k_{ads} \exp(k_{ox}t) - k_{ads}} \quad (7)$$

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