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Potential oscillations during electro-oxidation of ethanol on platinum in alkaline media: The role of surface sites

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ABSTRACT

The electro-oxidation of small organic molecules is one of the major areas of interest in electrocatalysis due to its potential use in energy conversion. Instabilities in alkaline solution, particularly in comparison with kinetic properties in a conventional regime, are rarely reported in the literature, despite the fact that the catalytic activity is higher in this medium and the onset potential is shifted to lower values compared to acidic media. Ethanol oxidation on polycrystalline platinum exhibits oscillations under galvanostatic control. As the reaction is structure-sensitive, it is possible to study the contribution of the three platinum basal planes to the complex kinetics. We found that Pt(100) has the major influence in the overall non-linear kinetics of ethanol electro-oxidation on Pt(poly), possibly because it has the highest formation and accumulation rate of CO_{ads}. Based on the differences observed in the galvanostatic transients on Pt(poly), Pt(110) and\ Pt(100), and the absence of this behavior on Pt(111), it is possible to infer that surface sites strongly influence the kinetic scenario during the ethanol oxidation reaction.

1. Introduction

Small organic molecules represent an alternative to hydrogen for use in fuel cell anodes. An understanding of the reaction mechanism is therefore of fundamental interest. Among the organic molecules studied, ethanol is preferred due to its high theoretical energy density ($8.0\ kW\ h^{-1}\ kg$) [1], because it is a renewable fuel that can be produced in large quantities through the fermentation of biomass [2], and because of the low toxicity of both ethanol and its oxidation products [3]. Most of the studies reported in the literature consider the reaction mechanism, identification and quantification of intermediates and products of the ethanol oxidation reaction (EtOR) in acidic media [1,4–6] because proton-exchange membranes are generally used in low-temperature fuel cells. However, the development of alkaline membranes [7] has reinforced interest in this reaction as it is known that the onset oxidation potential of ethanol in alkaline media occurs at lower values, reaches a higher current density than in acid media [3,8], and cheaper catalysts can be used [9].

It is accepted that EtOR on Pt follows two main reaction pathways, irrespective of pH [3,6,8], as shown in Fig. 1. In the C2 pathway, the C—C bond remains intact and ethanol can be oxidized to acetaldehyde and acetic acid. In an alkaline medium, acetate is stable and acetaldehyde undergoes polymerization [10,11]. This can be compared with the C1 pathway, in which C—C bond cleavage takes place, producing adsorbed CO and adsorbed CH_x, which subsequently oxidize to CO_2 which remains in solution as carbonate in alkaline media.

Electrochemical systems far from thermodynamic equilibrium may present complex nonlinear dynamic behavior such as periodic oscillations, quasi-periodicity and chaos [12,13]. A number of electrochemical systems exhibit complex dynamics which promote a higher energy conversion when compared with the same system operating in stationary conditions [14–16]. One of the requirements for the emergence of oscillations is the existence of a negative differential resistance in the voltammogram, i.e., a decrease in the current density as the potential increases [17]. In electrocatalytic oxidation, spontaneous current and potential oscillations can be observed under potentiostatic and galvanostatic conditions, respectively [12,18–20].

It is known that the CV profile obtained during electro-oxidation of organic molecules depends on the crystallographic orientation of the surface of the catalyst [6,21,22], but only a few works consider the use of single crystals to study oscillatory dynamics [23–25]. In these works, formic acid was the organic fuel and the oscillatory behavior was shown to be structure sensitive.

In this communication, we report the oscillatory behavior of EtOR under galvanostatic control in alkaline media, at Pt single-crystal electrodes with basal orientations. Our aim is to analyze the response of the complex kinetics observed at polycrystalline platinum, and to unravel the contributions of the different crystallographic planes to the oscillatory pattern.

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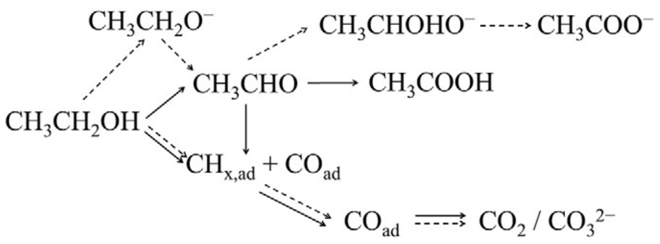

Fig. 1. Simplified reaction pathway of ethanol electro-oxidation. The black lines indicate the reaction path at low pH values and the dotted lines indicate the reaction path at high pH values.
Adapted from reference [3].

2. Experimental

The spherical poly-oriented Pt electrode and bead-type single-crystal Pt electrodes were flame-annealed for 30 s in a gas-oxygen flame, cooled in a $H_2 + Ar$ atmosphere and quenched in ultrapure water before transfer to the electrochemical cell [26]. Electrochemical measurements were carried out in a three-compartment cell at room temperature with a spiral Pt wire as counter electrode and a reversible hydrogen electrode (RHE) as reference.

The geometric area of each electrode was measured using a microscope and ImageJ Software. Cyclic voltammograms of each platinum surface were recorded in Ar-saturated, 0.1 M NaOH (99,99%, Trace Metal Grade, Merck®) at 50 mV s^{-1}. 0.5 M CH_3CH_2OH (Absolute, Emsure®) was oxidized on different Pt surfaces, varying the electrode potential from 0.06 V to 0.9 V at 50 mV s^{-1}. The ohmic drop was corrected for during the experiment by inserting the additional resistance value of the system in the potentiostat software. For the three basal planes, the ohmic drop values were typically around 200 Ω (meniscus configuration) while the corresponding value for Pt(poly) was 35 Ω.

3. Results

Fig. 2 shows the current sweep of 0.5 M CH_3CH_2OH oxidation in 0.1 M NaOH on Pt(poly) and Pt(111) at 1.0 μA s^{-1}, Pt(100) and Pt(110) at 0.15 μA s^{-1}. The current sweep was used to identify the parametric regions of oscillation. The galvanodynamic curves follow the curves of the potentiodynamic sweep at low sweep rates (not shown). The corresponding blanks for each electrode are given in the insets and are similar to those in the literature [11]. Special care was taken to preserve the surface order and the upper potential limit was carefully kept below 1.0 V because it is known that electrochemical oxygen adsorption disturbs the surface structure [27,28]. It can be observed that the activity on Pt(poly) and Pt(111) is higher than that on the other basal planes, with a maximum current density peak of oscillation of 2.7 mA cm^{-2} and 1.3 mA cm^{-2} respectively, followed by 0.48 mA cm^{-2} on Pt(110) and 0.23 mA cm^{-2} on Pt(100). Thus the oscillatory window varies, depending on the electrode used. A very narrow window was observed for all electrodes, with the broadest region obtained on Pt (100) while no oscillatory behavior occurred on Pt (111).

The oscillatory kinetics during EtOR were measured under galvanostatic control, and current sweep experiments used to identify the parametric regions where oscillation occurred. Potential oscillations begin when the systems reach a supercritical Hopf bifurcation around 0.7 V, and vanish as they reach a saddle-node bifurcation around 0.8 V. In addition, the amplitude of the oscillations increases very rapidly with increase in the current value. Thus, the oscillatory window varies depending on the electrode used, the broadest region being observed for Pt(100).

To compare the oscillatory pattern of each electrode under stationary current condition, the size of the galvanodynamic oscillatory region was taken into account. To do this, the applied current was normalized according to the following equation, proposed by Nagao et al. [29]:

$$J_N = (j - j_i)/(j_f - j_i)$$

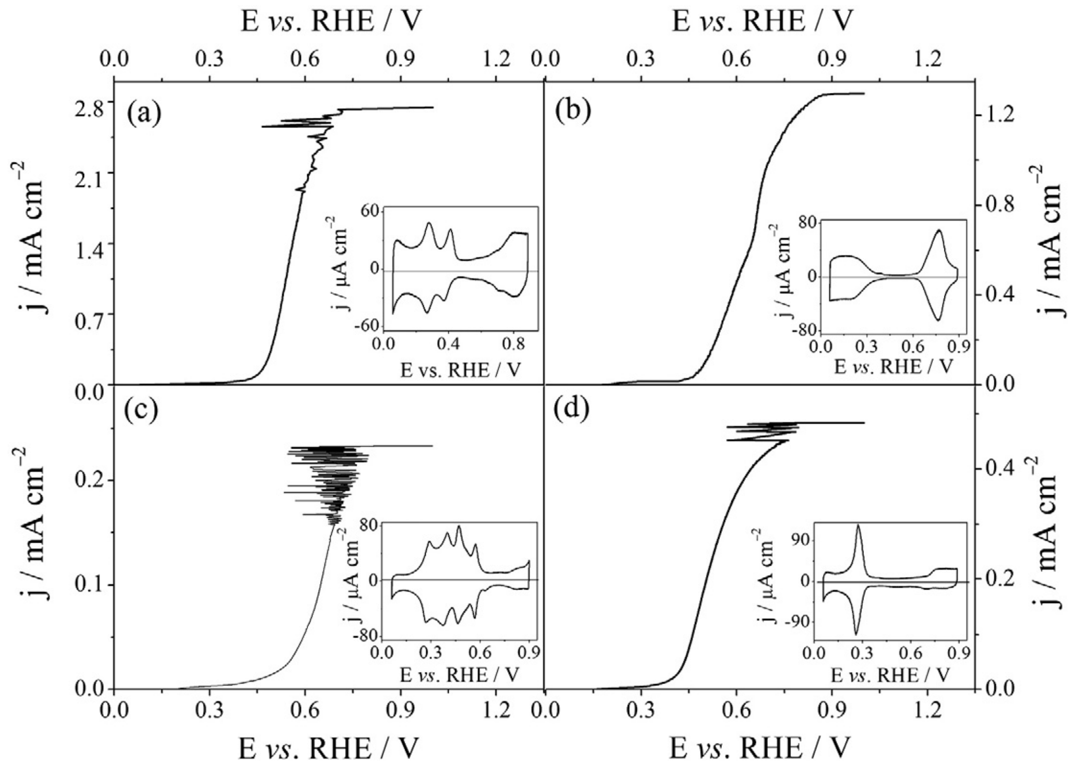

Fig. 2. Galvanodynamic sweep of 0.5 M CH3CH2OH oxidation in 0.1 M NaOH on (a) Pt(poly) and (b) Pt(111) at 1.0 μA s^{-1}, (c) Pt(100) and (d) Pt(110) at 0.15 μA s^{-1} and the corresponding blanks of each electrode in the insets, all at 50 mV s^{-1}.

where j is the applied current density, j_i and j_f are the initial and final currents of the oscillatory potential region, respectively, estimated from the galvanodynamic sweep. In this way, the potential time series obtained from each electrode can be compared for a given applied current. In the case of Pt(111), which did not produce oscillations during the galvanodynamic sweep, a current of 0.98 mA cm^{-2} was applied. This particular orientation might be affected by acetaldehyde polymerization [11]. For the other electrodes the current densities were: 2.31 mA cm^{-2} for Pt(poly), 0.195 mA cm^{-2} for Pt(100) and 0.465 mA cm^{-2} for Pt(110). These are the values related to the normalized current density, J_N, of 0.5 and the associated oscillation patterns are illustrated in Fig. 3.

Transient potential oscillations appear on Pt(poly), Pt(100) and Pt(110) while no oscillatory behavior is seen on Pt(111). The potential range observed during oscillatory EtOR was between 0.45–0.5 and 0.8 V, similar to the results obtained by Samjeské et al. [13] during electro-oxidation of formic acid in acidic solution. The morphologies of the potential time series obtained on Pt(poly) and Pt(100) are quite similar, though the frequency is higher for the former. Further investigations will probably show that some stepped surfaces, vicinal to the Pt(100) pole, contain an ensemble of sites in which the frequency of the oscillations increases. The oscillations presented are a combination of small oscillations between the two peaks of the principal oscillation. They can be represented by the number of cycles of the principal oscillation with number of peaks of the secondary oscillation denoted by a superscript. Different patterns appear during the potential time series at Pt(poly), beginning with period 1^7 , and then going through 1^6 to 1^3 progressively and rapidly, passing to 1^2 and finally ending in a period 1^0 oscillation. The same pattern occurs with Pt (100).

Pt (110) presents mostly 1^3, 1^2 and period 1^0 oscillations over a very short range of time and with a low oscillation frequency. A rapid variation in morphology is noticed, which could be an indication that some uncontrolled parameter is changing very fast during the experiment. It may be assumed that certain chemical species are involved in another feedback loop that gives rise to two chemical oscillators [25] and to the diverse patterns in the time series. Furthermore, for all surfaces studied, an increase in the potential amplitude can be seen over time until the oscillations disappear when the potential reaches a value around 0.8 V.

4. Discussion

The core oscillating mechanism for electro-oxidation of small hydrocarbon molecules includes the co-existence of two poisoning species (CO and OH) that cover the electrode surface and the occurrence of a parallel process with a high turnover rate. The dual path mechanism for ethanol electro-oxidation is consistent with these requirements. The *C*1 pathway of EtOR suggests CO accumulation on the surface until the potential reaches a certain value at which oxides are formed and allows the co-existence of CO and oxygenated species that react via a Langmuir-Hinshelwood (LH) mechanism. On the other hand, the C2 pathway involves ethanol conversion to side products such as acetate and acetaldehyde. This reaction represents a parallel process with respect to the CO electro-oxidation reaction and has a high turnover rate, associated with the main current flow. This is the kinetic scenario against which the temporal behavior seen in Fig. 3 should be understood.

As concluded by Lai et al. [3], the reaction products and byproducts of ethanol electro-oxidation at low and high pH values are not very different. Thus, earlier investigations of product formation during ethanol electro-oxidation in both acidic and alkaline media could be used to analyze the differences in nonlinear behavior. It has been previously shown [5,11,21,30] that surface structure has a significant role on the activity rate of ethanol oxidation and product distribution. The main EtOR products detected on Pt(111) in acidic media were acetic acid and acetaldehyde. Formation of CO and CO_2 was negligible compared to the other products and in alkaline media a large amount of acetate was produced. Lopes et al. [31] also observed acetate as a product and clear identification of carbonate or acetaldehyde was not possible.

The opposite situation was observed in the case of Pt(100), when a substantial amount of CO is formed at low potential values, blocking the surface for further reaction. At higher potential values, acetaldehyde and acetic acid are also detected. The scission of the C—C bond was observed on Pt(110) but the oxidation of acetaldehyde to acetic acid had a lower reaction rate than on the other surfaces.

During the oscillations, CO is progressively accumulated on the surface until the potential rises. At this point, OH_{ads} and CO_{ads} react via the LH mechanism, removing CO from the surface and liberating Pt sites. The potential value goes back to a minimum and another cycle begins. It can therefore be concluded that, in addition to the claim that the main product in EtOR in alkaline media is acetate [11,32], the formation of CO_{ads} and OH_{ads} is key to the emergence of instabilities at Pt(100) and Pt(110). However the other products and/or intermediates are formed, the selectivity and diffusion of these species at different sites and with different rate constants on each surface influence the nonlinear behavior and thus the presence or absence of oscillations. Further studies are ongoing to fully understand the nonlinear kinetic scenario and the absence of oscillatory behavior on Pt(111).

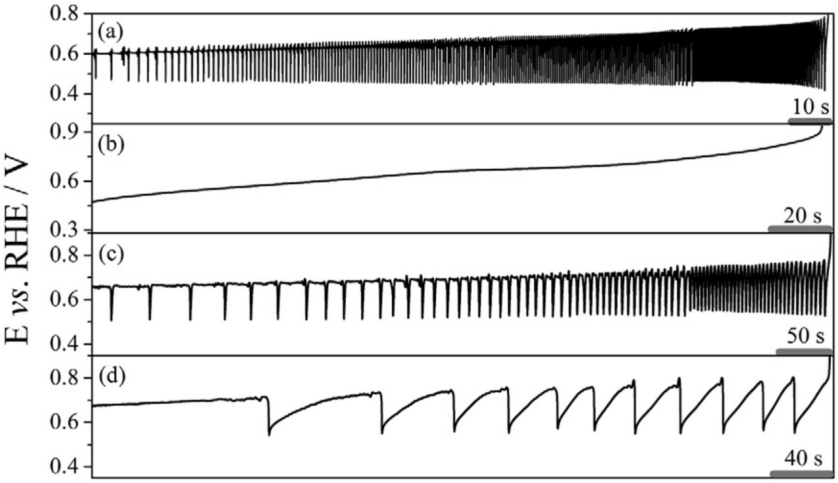

Fig. 3. Potential oscillation during 0.5 M CH_3CH_2OH oxidation on (a) Pt(poly), (b) Pt(111), (c) Pt(100) and (d) Pt(110) in 0.1 M NaOH. Potential-time series performed at a current density of 2.31 mA cm^{-2} for Pt(poly), 0.195 mA cm^{-2} for Pt(100), 0.465 mA cm^{-2} for Pt(110) and 0.98 mA cm^{-2} for Pt(111).

5. Conclusions

The oscillatory behavior of EtOR in alkaline media is studied using polycrystalline platinum and its basal planes. The different crystallographic planes have a strong influence on the reaction path, and thus on the distribution of products and byproducts and also on non-linear dynamic patterns. The similarity of the potential time series obtained on Pt(100) to the Pt(poly) results clearly indicates the major contribution of this surface and its kinetic processes to the overall polycrystalline response. Although CO_{ads} is key in the emergence of instabilities, its selectivity on the different platinum sites, as well as the selectivities of the other species formed during EtOR, influence the nonlinear behavior, and the existence or absence of oscillations. Differences in kinetic parameters and the diffusion of species at each site also affect the oscillatory process. More work is in progress to clarify the role of surface steps, especially those vicinal to Pt(100) and Pt(111), and also to study the oscillatory behavior under potentiostatic control.

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