



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.

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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 [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 CO₂ 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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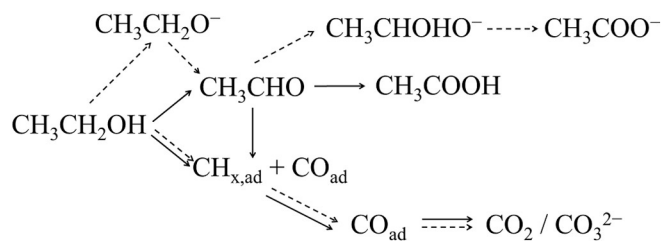


Fig. 1. Simplified reaction pathway of ethanol electro-oxidation. The black lines indicate the reaction path at low pH values and the dotted lines indicate the reaction path at high pH values.

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 $\text{H}_2 + \text{Ar}$ 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 $\text{CH}_3\text{CH}_2\text{OH}$ (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 200Ω (meniscus configuration) while the corresponding value for Pt(poly) was 35Ω .

3. Results

Fig. 2 shows the current sweep of 0.5 M $\text{CH}_3\text{CH}_2\text{OH}$ oxidation in 0.1 M NaOH on Pt(poly) and Pt(111) at $1.0 \mu\text{A s}^{-1}$, Pt(100) and Pt(110) at $0.15 \mu\text{A s}^{-1}$. 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]:

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

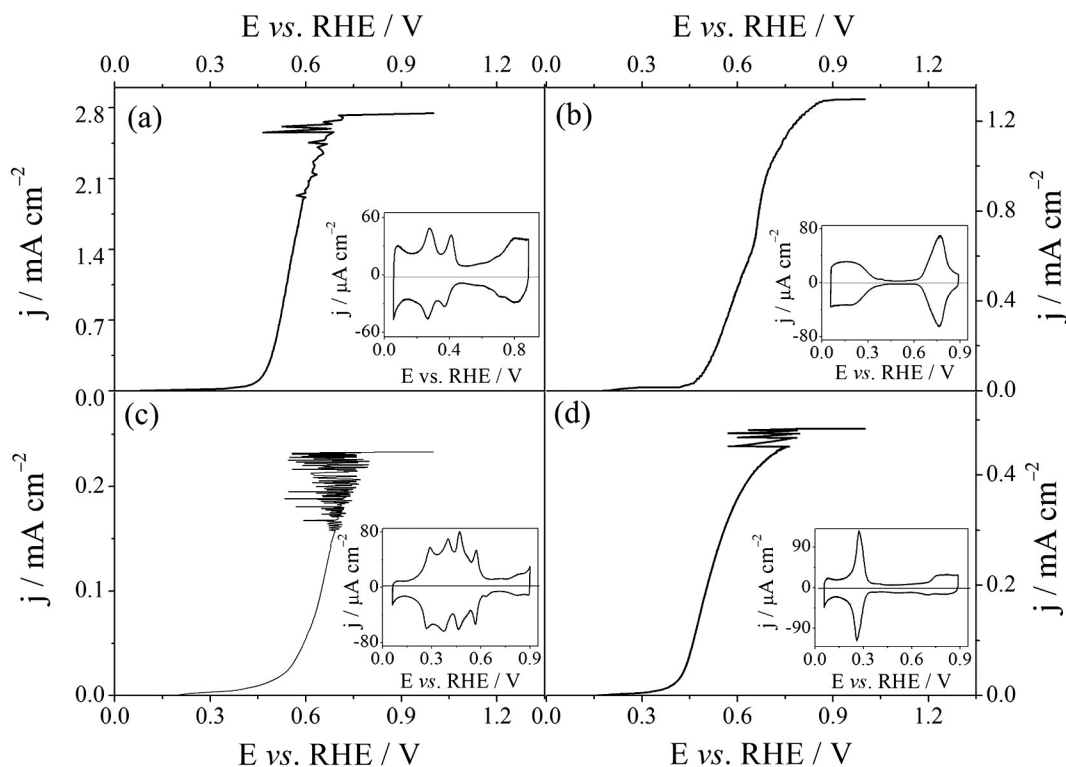


Fig. 2. Galvanodynamic sweep of 0.5 M $\text{CH}_3\text{CH}_2\text{OH}$ oxidation in 0.1 M NaOH on (a) Pt(poly) and (b) Pt(111) at $1.0 \mu\text{A s}^{-1}$, (c) Pt(100) and (d) Pt(110) at $0.15 \mu\text{A s}^{-1}$ and the corresponding blanks of each electrode in the insets, all at 50 mV s^{-1} .

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