Journal of Electroanalytical Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Weakening the C—C bond: On the behavior of glyoxylic acid on Pt(111) and its vicinal surfaces

Ricardo Martínez-Hincapié, Rosa M. Arán-Ais *, Juan M. Feliu

Instituto de Electroquímica, Universidad de Alicante, Apdo. 99, E-03080 Alicante, Spain

A R T I C L E I N F O

Article history:
Received 23 February 2016
Received in revised form 21 April 2016
Accepted 26 April 2016
Available online xxxx

Keywords:
Glyoxylic acid
Platinum single crystal electrodes
Stepped surfaces
In situ FTIR

A B S T R A C T

Adsorption and oxidation of glyoxylic acid (GA) on platinum single crystals were investigated by spectroelectrochemical techniques. Among basal planes, Pt(111) is taken as a model surface for reactivity studies in order to point out the C—C bond breaking. For a standard GA concentration (0.1 M), self-poisoning by adsorbed CO (CO_{ads}) is the main process dominating the positive-going sweep. The presence of (110) steps on (111) terraces contribute in the C—C bond cleavage, leading to CO formation, while (100) steps do not show a significant effect. Poison stripping allows GA oxidation in a lower potential range in the negative-going sweep. By working with different GA concentrations (10^{-5}–0.1 M), surface blockage is hindered, pointing out an alternative reaction pathway, where GA is oxidized in a poison-free surface. Fourier transform infrared spectroscopy (FTIR) experiments allowed the identification of CO_2, formic (FA) and oxalic acid (OA) as main products of GA oxidation. We highlight an activity peak at 0.01 M GA, concomitant to the presence of CO_2 absorption bands at lower potentials (0.2 V). The formation of CO_2 at potentials where CO cannot be oxidized suggests a change in the preferential reaction pathway, where GA is completely oxidized through an active intermediate distinct to CO_{ads}.

1. Introduction

Over the past decades, the electro-oxidation of alcohols has attracted much attention in electrocatalysis since these compounds feed the anodes of direct alcohol fuel cells (DAFC) and can be used in the electrochemical synthesis of different substances [1–3]. In the case of ethanol (EtOH) oxidation reaction (EOR), acetic acid formation through the 4e path predominates against the most desirable 12e path leading to CO_2 as final product. The later route can be favored by weakening the C—C bond by placing electron abstractor groups in the molecule, as has been previously demonstrated for ethylene glycol [4]. In the same way, glycolic acid can be oxidized at platinum (Pt) electrodes at low temperature and concentrations [5], in contrast to the aforementioned acetic acid.

Several studies have been carried out on the electrochemistry of glyoxylic acid (GA) on polycrystalline surfaces of different electrode materials such as vitreous carbon [6], gold [7], palladium [8] and platinum [9–11]. The effect of the crystallographic orientation is fundamental from an electrocatalytic point of view, and although GA oxidation was found to be structure sensitive on Pt [11], in situ studies about GA adsorption and reactivity at well-defined metal | solution interfaces are rather scarce [7,11]. In this sense, and owing the complexity of the GA oxidation reaction, the use of single crystal electrodes is expected to overcome some of the difficulties related to the heterogeneity of polycrystalline electrodes, being a powerful tool to understand the catalytic process from a simplified point of view. Moreover, adsorption and oxidation processes can be evaluated by combining cyclic voltammetry with in situ infrared measurements.

The complete oxidation of GA leading to CO_2 as final product is a 4e process:

$$\text{CHO-COOH} + H_2O \rightarrow 2CO_2 + 4e^- + 4H^+. \qquad (1)$$

Literature reports a double-path mechanism for GA oxidation on Pt surfaces, in which the direct oxidation through an active intermediate competes with the formation of poisoning intermediates (PI) that strongly adsorb on the surface. These adsorbed species were suggested to be $(\text{CO-COOH})_{ad}$ [12] from the incomplete oxidation of the GA molecule, and CO_{ad} coming from the dissociative adsorption of GA, this later reaction pointing out the breaking of the C—C bond when the GA molecule contacts the Pt surface. All these studies were performed on concentrated solutions of GA and even in the presence of anions (namely, sulfates) that compete with the adsorption sites on the surface. However, nothing has been reported about the behavior of this molecule at low concentrations using perchloric acid as supporting electrolyte, where competitive anion adsorption is absent. In addition, working with diluted solutions can be useful to favor a particular path among other parallel routes with complex reaction schemes.

---

* Corresponding author.
E-mail address: rosa.aran@ua.es (R.M. Arán-Ais).

http://dx.doi.org/10.1016/j.jelechem.2016.04.047
1572-6657/

Please cite this article as: R. Martínez-Hincapié, et al., Weakening the CC bond: On the behavior of glyoxylic acid on Pt(111) and its vicinal surfaces, Journal of Electroanalytical Chemistry (2016), http://dx.doi.org/10.1016/j.jelechem.2016.04.047

In the present work we aim to study the surface reactivity, namely the adsorption and oxidation of GA on Pt single crystal electrodes, with basal orientations and stepped surfaces vicinal to Pt(111). For this basal plane electrode, Fourier transform infrared spectroscopy (FTIR) in its external reflection configuration has been used to identify the intermediates and products of this reaction at different concentrations. The results here reported show the structure sensitivity of the reaction and the key role that the analyte concentration plays in order to achieve its complete oxidation to CO_2.

2. Experimental

Pt single crystal surfaces were used as working electrodes and were prepared following standard procedures described elsewhere [13]. Before each experiment, the single crystal electrodes were flame-annealed, cooled down in a reductive atmosphere (H_2 + Ar in a 1:3 ratio) and quenched in ultrapure water in equilibrium with this atmosphere before transferring to the electrochemical cell. Preliminary experiments were carried out at room temperature (RT) in a classical two-compartment electrochemical cell, using a Pt wire (99.99%) as counter electrode and a reversible hydrogen (Air Liquid, N50) electrode (RHE) connected to the cell through a Luggin capillary. Solutions were de-aerated by bubbling Ar (Air Liquid, N50), and were prepared from perchloric acid (Merck Suprapur) and GA (Sigma Aldrich, 99%) in ultrapure water from Elga, 18.2 MΩ cm. The electrode potential was controlled using an EG&G PARC 175 signal generator in combination with an eDAQ EA 161 potentiostat and currents were recorded using an eDAQ e-corder ED401 recording system.

Electrochemical characterization of the intermediates on GA oxidation was carried out using a flow cell, which in addition to the components of classical electrochemical cell, has an inlet and outlet through which the solution can be changed while controlling the electrode potential. The key point of this experiment is to control the cleanliness of the cell during the whole procedure.

Further information was gained from spectroelectrochemical experiments, performed with a Nicolet Magna 850 spectrometer equipped with a MCT detector. The spectroelectrochemical cell was provided with a prismatic CaF_2 window beveled at 60°. Unless otherwise stated, spectra shown are composed of 100 interferograms collected with a resolution of 8 cm^{-1} and p polarized light. They are presented as absorbance, according to $A = -\log(R / R_0)$ where R and R_0 are the reflectance corresponding to the single beam spectra obtained at the sample and reference potentials, respectively. All spectroelectrochemical experiments were carried out at RT, with a RHE and a Pt wire used as reference and counter electrodes, respectively.

3. Results and discussion

3.1. Standard cyclic voltammetry on basal orientations

Fig. 1A shows the first cycle of the oxidation of GA on Pt(111), Pt(100) and Pt(110) electrodes in a 0.1 M GA + 0.1 M $HClO_4$ solution. This concentration may be considered as a standard in electrocatalysis for the oxidation of organic molecules. In order to preserve the surface structure of the electrodes, the potential range was restricted between 0.05 and 0.95 V. In the positive-going sweep (solid line), extensive blocking of all surfaces due to strongly adsorbed species is observed. It was found that GA spontaneously dissociates on Pt electrodes yielding CO and other species that block the Pt surface sites suppressing other reactions at potentials lower than the potential at which the adsorbed CO (CO_{ad}) oxidizes to CO_2 [11]. This phenomenon is known as "self-poisoning" and also occurs in the oxidation of most small organic molecules aimed for fuel cell applications [14–18]. A significant difference in electrocatalytic activity can be observed when comparing the three basal orientations: following the onset for the PI oxidation, the trend is Pt(110)< Pt(111) < Pt(100). Their peak current densities are 187, 222 and 544 μA cm^{-2}, while the peak potentials are 0.79, 0.72 and 0.86 V for Pt(111), Pt(110), and Pt(100), respectively. In the negative-going sweep, the so-called intrinsic activity of each electrode is evaluated, being the peak current densities 85, 47 and 17 μA cm^{-2}, and the peak potentials 0.49, 0.45 and 0.38 V for the Pt(111), Pt(110), and Pt(100), respectively, and the onset for the oxidation changes to Pt(100) < Pt(110) < Pt(111). Interestingly, hydrogen adsorption in the low potential region can take place at Pt(100) in a greater extent than on the other basal planes, since a non-negligible charge density is measured in the potential region in which Pt(100) is able to adsorb hydrogen. This adsorption charge, however, may not only be attributed to hydrogen adsorption/desorption, but also to sub-products coming from GA decomposition. The nature of the PI will be clearly identified in the following FTIR experiments, but the charge integrated under the PI oxidation peaks (Q_{PI}) gets some information (Table 1). Comparing these

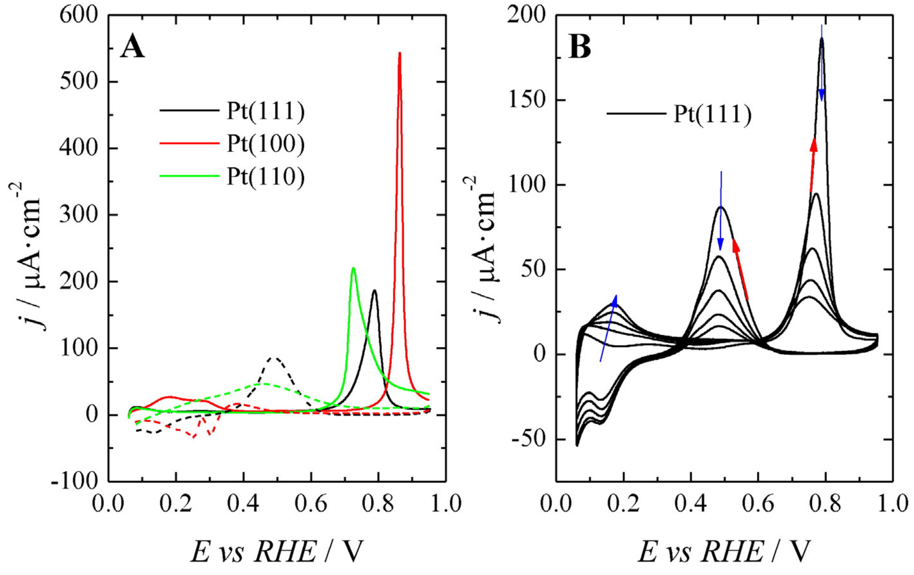

Fig. 1. (A) Cyclic voltammograms for Pt(111), Pt(100) and Pt(110) electrodes in 0.1 M GA + 0.1 M $HClO_4$. Solid-lines and dashed-lines correspond to the positive and negative-going sweeps, respectively. (B) Evolution of the Pt(111) voltammetric profile with successive potential cycles. Red arrows point out the sweep direction; blue arrows indicate the evolution of the different features. Sweep rate, 50 mV s^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Please cite this article as: R. Martínez-Hincapié, et al., Weakening the CC bond: On the behavior of glyoxylic acid on Pt(111) and its vicinal surfaces, Journal of Electroanalytical Chemistry (2016), http://dx.doi.org/10.1016/j.jelechem.2016.04.047