



Short communication

Preliminary study of ethanol electrooxidation in the presence of sulfate on polycrystalline platinum

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ABSTRACT

The electrooxidation of ethanol and its inhibition by the presence of adsorbed sulfate have been investigated by cyclic voltammetry and chronoamperometry using several concentrations of sulfuric acid on smooth polycrystalline platinum. The results show that the concentration of sulfuric acid influences the current in both potentiostatic and potentiodynamic experiments. The results are interpreted in terms of the competitive adsorption of sulfate and ethanol on the same Pt sites and suggest that, when the sulfuric acid concentration is increased, there is a reduction of Pt free sites able to adsorb and oxidize ethanol. The voltammetric data reveal that the peak currents observed during ethanol oxidation are not affected in the same way by the presence of H_2SO_4 , which, based on previously obtained FTIR results, suggests that the sulfate adsorption is able to inhibit the oxidation of ethanol in a selective way.

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1. Introduction

The inhibitory nature of sulfate in the oxidation of organic molecules is well known in the literature [1–4]. Studies on sulfate ions are important because sulfate ions are widely used in supporting electrolytes for electrochemical studies. In the early 1980s Snel and Keenan showed that the current peak values for the three anodic waves of ethanol oxidation in polycrystalline Pt are lower in the presence of H_2SO_4 than HClO_4 [1]. Due to strong specific adsorption on Pt, sulfate and bisulfate has been widely investigated in the last 20 years on lower-index surfaces of this metal [5–10].

Iwasita et al. investigated the adsorption of sulfate on Pt (100), (110) and (111) [11]. Using FTIR in situ, the authors conclude that sulfate has a tendency to attain the maximum possible coordination. As a consequence, sulfate exhibits triple coordination on Pt (111) and double coordination on Pt (100) and Pt (110).

Results obtained from radiochemical measurements show that the maximum coverage of Pt (111) in 10^{-3} M H_2SO_4 is 2.4×10^{14} ions cm^{-2} [12]. A fast calculation shows that about half of the surface is covered by SO_4^{2-} ions. This relatively high coverage implies that the presence of sulfate can influence the adsorption and oxidation of organic molecules.

Similarly, Iwasita et al. have investigated the electrooxidation of methanol in the presence of 0.5 M H_2SO_4 on smooth polycrystalline Pt and Pt (111) [3,4]. Using HPLC and FTIR in situ, the authors show that methanol electrooxidation at Pt (111) occurs via parallel pathways that produce HCHO, HCOOH and CO_2 . Moreover, the authors conclude that the CO_2 pathway is inhibited in the presence of sulfate, while those involving the production of formaldehyde and formic acid are not affected.

Despite the interesting findings of Iwasita and co-workers concerning methanol oxidation in the presence of H_2SO_4 [3,4] and the several papers devoted to the study of sulfate adsorption on Pt [13–15], Au [16–20], Pd [21–23], Rh [24] and other metals [25–27], there have, until now, been no further papers on sulfate adsorption in the presence of ethanol after the introductory investigation made by Snel and Keenan, at least to our knowledge.

The electrooxidation of ethanol has been a matter of growing interest in the last few years [28–35], because ethanol can be used in fuel cells, mainly due to its renewable nature and high energetic content [36]. Another important aspect concerning ethanol is the fact that it has the simplest carbon chain of all alcohols (2 atoms). Thus, studies involving ethanol are relevant for the development of catalysts able to break C–C bonds. These characteristics have made ethanol oxidation a central point of interest from both fundamental and applied points of view.

This paper presents a preliminary study of the catalytic activity of smooth polycrystalline Pt on the electrochemical oxidation of ethanol as a function of the concentration of sulfuric acid. The

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study was performed with potentiodynamic (cyclic voltammetry) and potentiostatic (chronoamperometry) techniques.

2. Experimental

For the electrochemical experiments the working electrode was a double-sided Pt sheet with an area of 0.5 cm^2 ($0.5 \text{ cm} \times 0.5 \text{ cm}$). The real Pt surface area was determined as 1.16 cm^2 by integration of the charge corresponding to the desorption of a monolayer of hydrogen in the cyclic voltammogram in the presence of $0.5 \text{ M H}_2\text{SO}_4$ (Merck) which corresponds to a roughness factor of roughly 2.3. This area was used to estimate the current densities in the present work. The counter electrode was a platinum sheet with an area of 1.5 cm^2 . All potentials were measured against a reversible hydrogen electrode and are presented on the same scale.

Before each experiment the working electrode was immersed in hot concentrated sulfuric acid for few minutes, thoroughly washed with Milli-Q® water and transferred to the electrochemical cell containing the supporting electrolyte. Next, the electrode was cycled between 0.05 and 1.45 V at 100 mV s^{-1} until the voltammetric profile was reproducible. Thus, the working electrode was kept at 0.05 V and ethanol (J.T. Baker) was added to the cell to reach 0.1 M. This concentration was chosen because a previous work showed that it is the one that generates the best selectivity towards CO_2 formation [33].

The solutions were prepared with Milli-Q® water ($18.2 \text{ M}\Omega \text{ cm}$) and deaerated with N_2 (analytical grade). All experiments were performed at room temperature ($25.0 \pm 1.0^\circ \text{C}$). Further details about the experimental settings will be presented in the next section.

3. Results and discussion

3.1. Current–time behavior

To estimate the influence of the supporting electrolyte on the ethanol electrooxidation, a series of chronoamperometric experiments was performed. For this, the working electrode remained polarized at 0.05 V for 15 min in a solution containing 0.1 M ethanol and H_2SO_4 in concentrations of 0.05, 0.1, 0.3 and 0.5 M. Subsequently, the potential was stepped to 0.5 V and the electrode remained at this potential for additional 20 min. For each H_2SO_4 concentration, three experiments were performed. The cor-

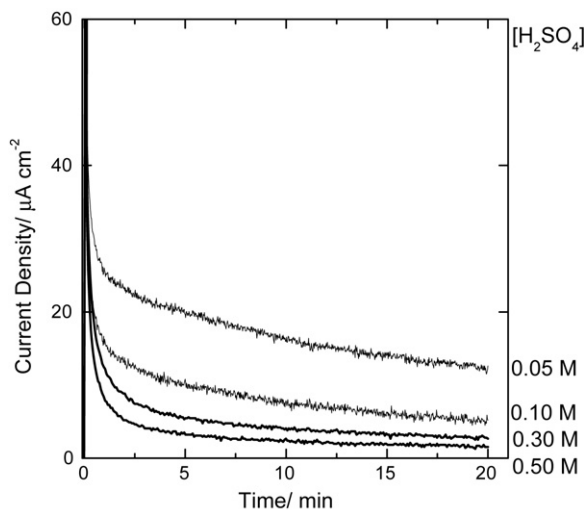


Fig. 1. Chronoamperograms at 0.5 V for 0.1 M $\text{C}_2\text{H}_5\text{OH}$ and H_2SO_4 in different concentrations (indicated in the figure). $T = 25^\circ \text{C}$. The initial potential is 0.05 V.

responding $i-t$ curves for each H_2SO_4 concentration are presented in Fig. 1.

All the results are presented on the same scale. It should be noted that the quasi-stationary currents depend on the sulfuric acid concentration. From repetitive experiments, such as those shown in Fig. 1, we calculate the average current density after 20 min of polarization at 0.5 V and plot this value against the sulfuric acid concentration. The results are shown in Fig. 2.

The reduction in the activity of Pt towards ethanol oxidation with the increase of sulfate and/or bisulfate (the exact nature of the ions is beyond the scope of the present paper) concentration presented in Fig. 2 can be explained based on the specific adsorption of these ions at the Pt surface. Above the potential of zero charge, which is estimated for Pt (1 1 1) as around 0.35 V [37], the surface of the electrode presents a lack of electrons. This partial positive charge facilitates the adsorption of anions. Thus, sulfate ions must compete with organic molecules and then fragments of their oxidation for the same Pt sites, provoking a diminution of the sites able to oxidize ethanol. The result is a steep lowering of the activity when the sulfate concentration rises.

3.2. Potentiodynamic results—the effect of H_2SO_4 concentration

Fig. 3a–e show the cyclic voltammograms recorded at 50 mV s^{-1} on polycrystalline Pt in solutions containing 0.1 M ethanol in 0.1 M HClO_4 (Fig. 3a) or in H_2SO_4 at the concentrations of 0.05 M (Fig. 3b), 0.1 M (Fig. 3c), 0.3 M (Fig. 3d) and 0.5 M (Fig. 3e). HClO_4 was chosen because ClO_4^- presents negligible adsorption on Pt surfaces. Fig. 3a–e present the voltammograms obtained immediately after polarization of the working electrode at 0.05 V.

A comparison of the peak current values for the concentrations of H_2SO_4 and HClO_4 investigated shows that the oxidation currents are clearly affected by the growing adsorption of sulfate ions. More interesting is the fact that peak 1 is more affected than peak 2 by the increase in concentration. For all the conditions studied, a new oxidation current arises around 0.84 V, peaking

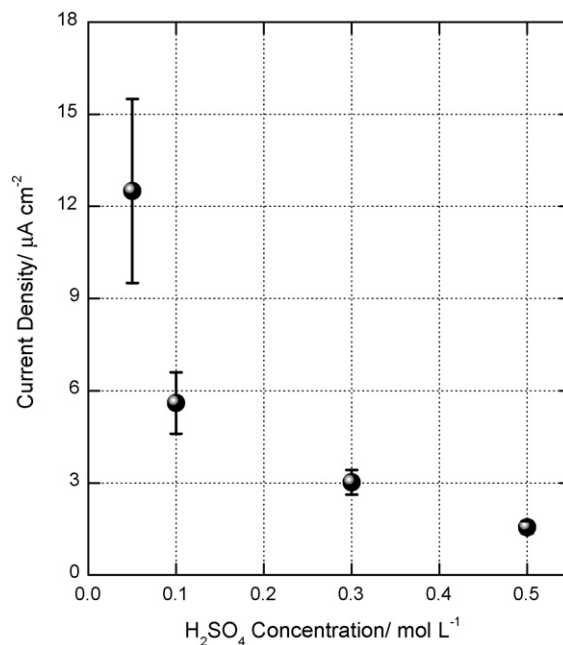


Fig. 2. Activity towards 0.1 M ethanol electrooxidation as a function of H_2SO_4 concentration. The data were obtained after 20 min of electrode polarization at 0.5 V. Each point represents an averaged current obtained from at least three experiments. $T = 25^\circ \text{C}$.

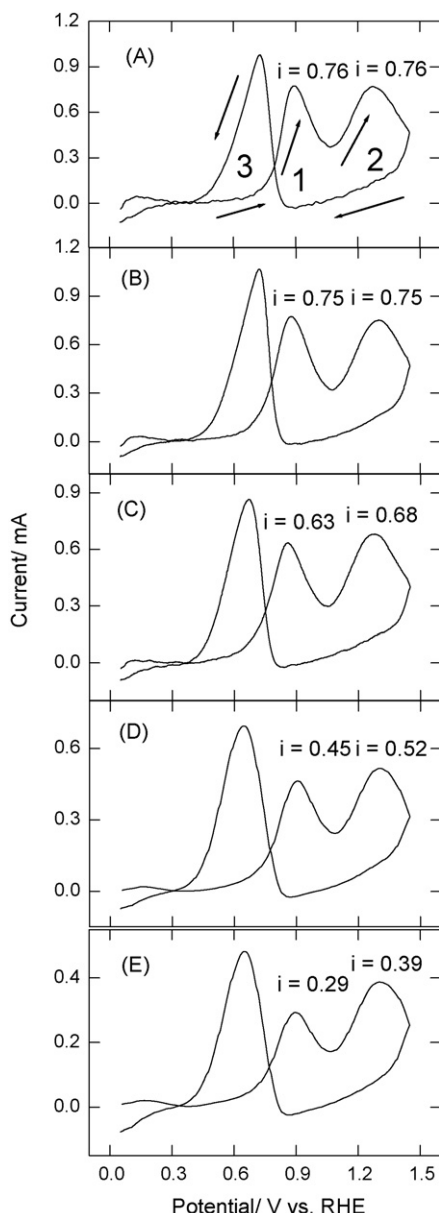


Fig. 3. Cyclic voltammograms of Pt in the presence of 0.1 M C_2H_5OH and 0.1 M $HClO_4$ (A) or H_2SO_4 concentrations of (B) 0.05 M, (C) 0.10 M, (D) 0.30 M and (E) 0.50 M. $\nu = 50 \text{ mV s}^{-1}$. Numbers in the upper part of the figures refer to the current values (i) for peaks 1–3. $T = 25^\circ\text{C}$.

at 0.65 V (peak 3) during the voltage-decreasing scan. The presence of anodic (oxidation) currents during the voltage-decreasing scans has been observed in voltammetric studies involving the oxidation of several organic molecules, such as methanol, ethanol, formic acid and acetaldehyde [1,3,4,33,38,39]. The results can be interpreted in terms of the competitive adsorption of water and organic molecules at platinum surfaces and can be rationalized as follows. According to Iwasita and Pastor, increasing the potential results in two opposing effects [40]: on one hand, the steps of oxidation are favored at higher potentials due to the increase in the charge transference rate. On the other hand, higher potentials tend to increase the strength of the interactions between water molecules (or their fragments) and Pt, which inhibits the adsorption of ethanol.

The combination of both these effects results in a compromise that generates a current peak. Moreover, both of the effects

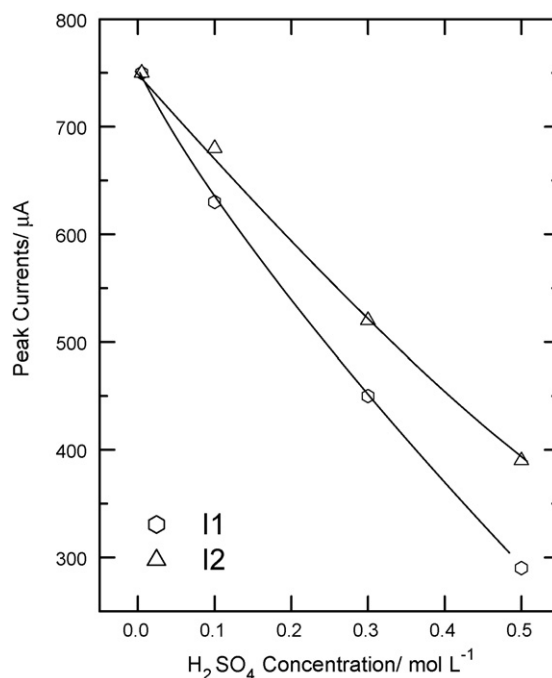


Fig. 4. Values of the current for peaks 1 (I1) and 2 (I2) as a function of the H_2SO_4 concentration. Data extracted from Fig. 3.

are potential-dependent, which explains the occurrence of current peaks in both scan directions [40].

In an attempt to estimate the effect of sulfate adsorption, we decided to compare the oxidation currents at peaks 1 and 2. We are aware that the choice of a baseline current for a reaction as complex as the ethanol electrooxidation is somewhat speculative. Because of this difficulty, we decided to analyze the peak currents instead of the charges involved in the respective oxidations. We believe that this procedure helps to clarify some important aspects related to ethanol oxidation in the presence of H_2SO_4 without damage to the analysis. The respective values for the current at peaks 1 and 2 are plotted in Fig. 4 as function of the sulfuric acid concentration.

Results show a progressive reduction in the oxidation currents, which suggests the replacement of organic fragments by sulfate ions on the surface of Pt. Moreover, these results show that the current at peak 1 (I1) diminishes more rapidly than the one at peak 2 (I2). Fig. 5 confirms this tendency. Data are presented as the ratio I1/I2 for each sulfuric acid concentration.

Fig. 5 shows that for 0.05 M H_2SO_4 , the I1/I2 ratio is close to 1.0. When the sulfuric acid concentration is increased the current at peak 1 is responsible for progressively lower contributions to the global current (i.e., the current associated with peaks 1 and 2 in the forward potential scan), reaching 0.74 for 0.5 M H_2SO_4 . This result has important implications for the electrooxidation of ethanol, even though, at this stage, we cannot associate individual pathways with the oxidation currents. Despite this limitation, the results show that the oxidation peak located at around 0.8 V is more strongly inhibited by the presence of sulfate than that at 1.3 V. In other words, sulfate adsorption is able to inhibit the oxidation of ethanol and its intermediates in a selective way. We believe that this behavior can be interpreted as follows.

Based on the well-accepted statement that the CO_2 formation pathway follows a Langmuir–Hinshelwood mechanism [33], it can be assumed that the strong adsorption of sulfate at low potentials inhibits the adsorption of ethanol and/or fragments, preventing the production of CO_2 . The range of potentials where peak 2 arises is characterized by the large production of acetic acid when ethanol is

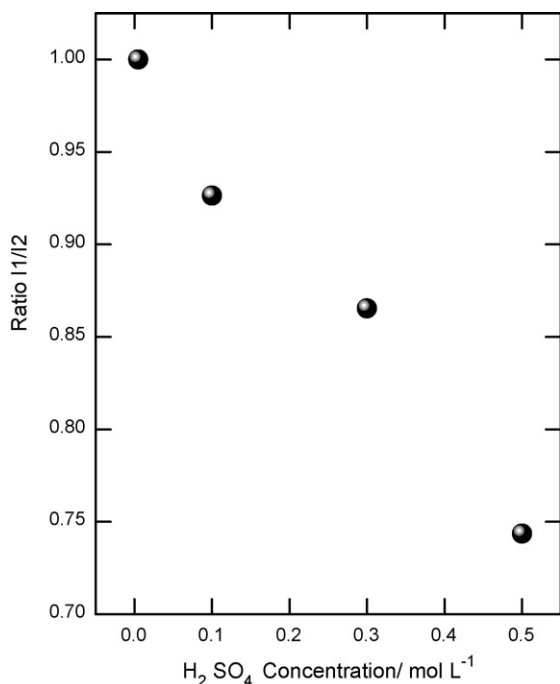


Fig. 5. Ratio I1/I2 obtained from Figs. 3 and 4 as a function of the H₂SO₄ concentration.

oxidized in the presence of perchloric acid [34]. As discussed previously [33], pathways involving the production of acetaldehyde and acetic acid are less site demanding than the one involving the formation of CO₂. We believe that acetic acid production might be governed by an Eley–Rideal mechanism, where water (or an oxygen-containing species) plays the role of the unique adsorbed partner.

In this sense, taking into account that the interaction between water and metal is greatly favored at high potentials on Pt [38], it seems that, at potentials in the range of the occurrence of peak 2, this interaction is strong enough to allow water to displace sulfate and/or bisulfate from the surface. The adsorbed oxygen species could act as oxygen donors, allowing the acetic acid production to proceed, which could explain the large peak currents observed around 1.0 V.

In order to confirm this effect in terms of the oxidation pathways of ethanol we decided to follow the oxidation reaction by using FTIRS in situ. The results are being analyzed and will be published in the future.

4. Concluding remarks

- On polycrystalline Pt, in the presence of ethanol, the current for ethanol oxidation is strongly dependent on the concentration of H₂SO₄. Potentiostatic data show that the maximum current density (around 13 μA cm⁻²) is obtained with a H₂SO₄ concentration of 0.05 M. When the H₂SO₄ concentration is increased, the current densities decrease to negligible values after 20 min of polarization. The results are interpreted based on the specific adsorption of sulfate and/or bisulfate on Pt, which inhibits the adsorption of ethanol.
- Cyclic voltammograms show that the growing concentration of sulfate (or bisulfate) inhibits both the oxidation peaks located at about 0.8 and 1.3 V.

- Additionally, the oxidation peak located at lower potentials is more strongly inhibited than the one at 1.3 V when the H₂SO₄ concentration is increased. Results are interpreted in terms of the dominance of different pathways of ethanol oxidation for each peak.
- The preliminary results presented in this paper suggest that the CO₂ formation pathway (which follows a L–H mechanism) is more strongly affected by the co-adsorption of sulfate than the pathways involving the formation of acetaldehyde and acetic acid.

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