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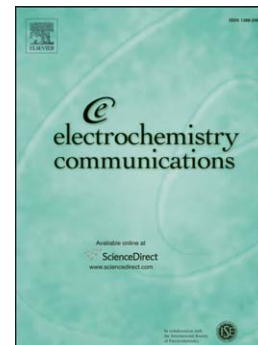
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The breaking of the C-C bond in ethylene glycol oxidation at the Pt(111) electrode and its vicinal surfaces

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Abstract

Ethylene glycol (EG) oxidation has been studied on Pt(111) and its vicinal surfaces in acidic media by cyclic voltammetry and infrared spectroscopy. Even at Pt(111) the C-C bond is readily broken and CO is formed at low potentials. Both types of steps catalyze the EG oxidation to CO₂, being the {110} steps the most catalytic for the splitting of the C-C bond. Spectroscopic results show that glycolic acid and oxalic acid are produced mainly at the close-packed terraces.

Keywords: Ethylene glycol; Platinum single crystal electrodes; Stepped surfaces; In situ FTIR

1. Introduction

Among possible fuels, ethanol CH₃CH₂OH is very promising for a series of reasons [1]. The main problem is the formation of acetate as final product, especially at model Pt(111) electrode. This single crystal contains the most compact arrangement of surface atoms and is expected to be an important fraction of surface sites in platinum nanoparticles. The inclusion of steps in the structure leads to a better performance, because C-C breaking takes place at steps [2, 3]. In contrast, EG seems to effectively dissociate at platinum, in such a way that CO was considered to be the only relevant residue from spontaneous interaction of the fuel with the different basal planes [4]. It appears that the inclusion of an alcohol group in the methyl part of the molecule confers a greater reactivity towards breaking of the C-C bond [5].

This aims to examine in detail the oxidation of EG on Pt(111) and its vicinal surfaces in order to study the reactivity associated to each type of catalytic site.

2. Experimental

Platinum single crystal working electrodes preparation, reagents and experimental procedures, including FTIR set-up, is the same as described in previous papers [1-6]. Pt(111) and its vicinal surfaces Pt(S)[n(111)x(100)], with Miller indices Pt(n+1, n-1, n-1) and Pt(S)[n(111)x(111)] or Pt(S)[(n-1)(111)x(110)], with Miller indices Pt(n, n, n-2), where n is the number of terrace rows, were used.

3. Results and discussion

3.1. Cyclic voltammetry.

Figure 1 shows the activity of a selected set of electrodes in 0.1 M HClO₄ + 0.1 M EG. In the positive-going sweep, the oxidation of EG at Pt(111) presents three characteristic features: (i) a pre-wave at 0.52 V, (ii) an oxidation peak at 0.65 V, and (iii) a shoulder at 0.75 V. After that, the current density drops to zero at higher potentials, after completion of the OH_{ads} layer [7]. In the negative-going sweep, a more intense peak is observed at 0.6 V.

The pre-wave currents increase and shift to lower potentials after the insertion of {100} steps ($n > 16$), Figure 1A. The highest current densities are attained with relatively large terraces. The shoulder at 0.75 V becomes a well defined peak whose intensity progressively increases with step density. Also, the net oxidation current above 0.85 V is higher as the terrace length is decreased, likely due to the formation of O_{ads} at step sites [7]. Conversely, the peak at 0.65 V decreases and shifts to less positive potentials as the step density increases.

EG oxidation on the stepped surfaces belonging to the [1 $\bar{1}$ 0] zone is given in Figure 1B. The higher oxidation currents demonstrate that {110} or {111} steps are more catalytic than {100} steps. Unlike the previous case, the intensity of both peaks at 0.65 V and 0.75V grow as the step density increases, although displace towards more positive potentials. The onset of EG oxidation, however, clearly shifts to lower potentials, even at high step density ($n < 7$). In this series, the oxidation currents above 0.85 V also increase as n decreases, but are lower than those observed for the previous series, pointing out a different reactivity of O_{ads} adsorbed at different steps [7].

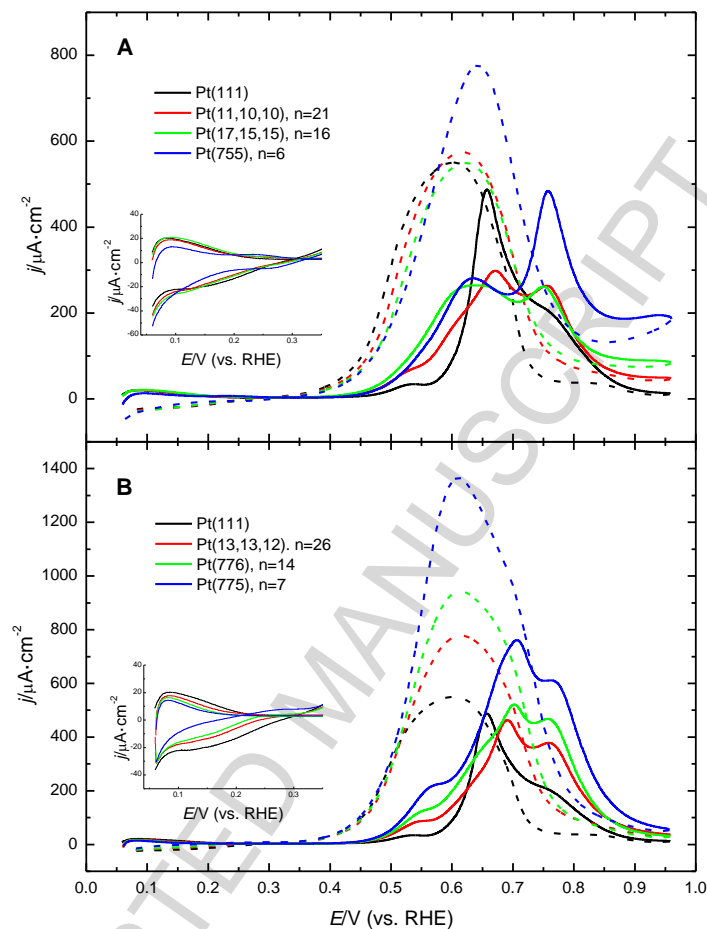


Fig.1. EG oxidation on stepped surfaces vicinal to Pt(111): (A) Pt[n(111)x(100)], (B) Pt[(n-1)(111)x(110)]. Test solution: 0.1 M EG in 0.1 M HClO₄, 50 mV·s⁻¹. Positive (solid line) and negative scan (dashed line) are shown.

3.2. Spectroelectrochemical results.

The inset graphs of Fig. 1A-B show that the platinum surfaces are significantly blocked for hydrogen adsorption. The poisoning is mainly due to adsorbed CO [4] and is higher as the step density increases, especially for the surfaces with {110} steps, revealing faster CO formation at steps. FTIR experiments were carried out to find out details of the different species formed on the electrode surfaces. In the following spectra, positive bands correspond to the products formed at the sampling potential, while negative bands are due to the consumption of species present at the reference potential. The FTIR spectra for the oxidation of EG on Pt(111) electrode are shown in Fig. 2A. The bands at 2032-2063 cm⁻¹ and 1800-1816 cm⁻¹ are assigned to CO stretching in on-top and bridge configurations, respectively. The appearance of these bands indicates that the C-C bond of the EG molecule has been broken at low potentials, resulting in the formation and accumulation of adsorbed CO and demonstrating that CO is the poison present on the electrode surface. This behavior is somewhat different to that shown by ethanol, where the amount of CO formed and accumulated on the Pt(111) surface is very small [1]. The band at 2343 cm⁻¹, corresponding to the asymmetrical stretching mode of CO₂ in solution, is already visible at 0.6 V RHE. For ethanol oxidation, the CO₂ onset potential was 0.7 V and the

IR bands were comparatively smaller. The observation of the CO_2 band at lower potentials in the negative scan reflects that still remains in the thin layer. Nevertheless, the intensity of this band diminishes at potentials lower than 0.6 V, which indicates that some CO_2 is diffusing away from the thin layer and no additional CO_2 is being formed below this potential. Since the quality of the Pt(111) single crystal electrode is better than that previously used, the presence of adsorbed CO must be linked to the nature of the molecule and not to the defects present on the electrode surface [8]. That means that the introduction of an OH group in the molecule, in comparison with ethanol, induces more reactivity towards complete oxidation. The bands at $1735\text{-}1745\text{ cm}^{-1}$ and 1235 cm^{-1} correspond, respectively, to the C=O stretching of a carbonyl group and the C-OH stretching of a carboxylic acid group, and can be tentatively assigned to oxalic and/or glycolic acid. The formation of this latter molecule is corroborated by the presence of the band at 1398 cm^{-1} , assigned to adsorbed glycolate [9, 10]. The band at 1640 cm^{-1} , corresponding to the bending mode of water, is present in all the spectra, and can hide the band associated to $\nu_{\text{as}}(\text{OCO})$ mode of bioxalate, which appears at 1635 cm^{-1} [11] as well as that of 2-hydroxyacetyl [12, 13]. It was proposed that oxalate comes from further adsorption and oxidation of glycolate to oxalate [14] and that 2-hydroxyacetyl is the precursor of CO.

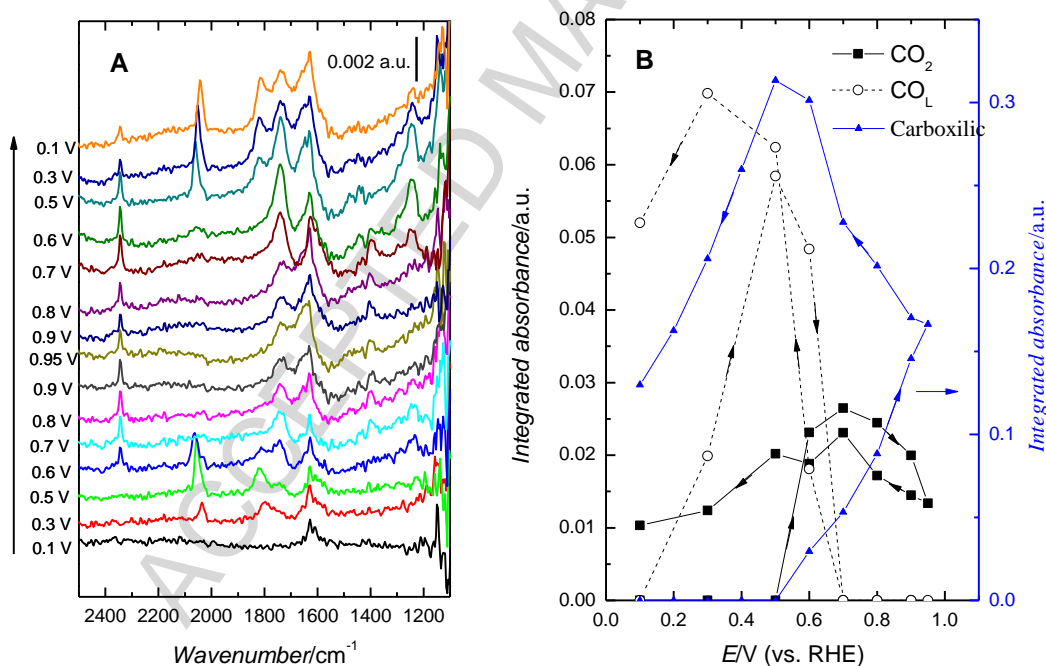


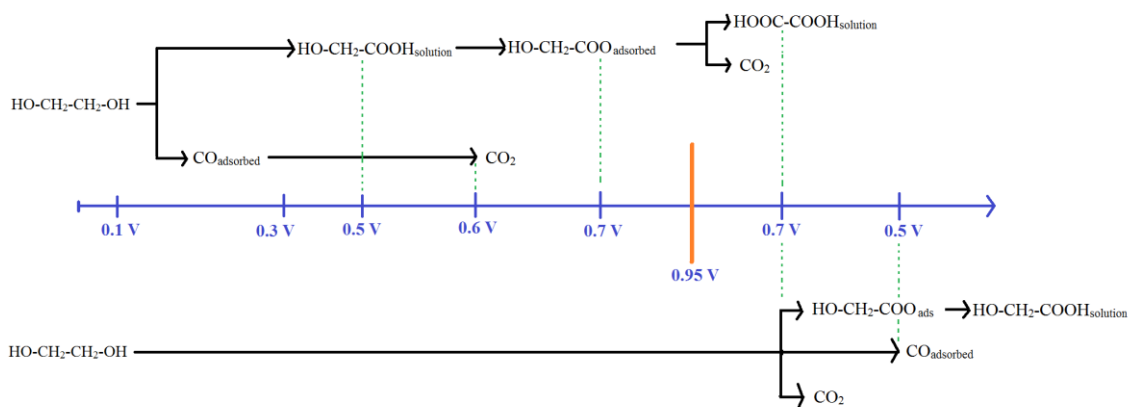
Fig.2. (A) Spectra obtained at different potentials, as labeled, for the oxidation of 0.1 M EG + 0.1 M HClO_4 in H_2O the Pt(111) electrode (reference spectra taken at 0.06V). (B) Plot corresponding to the integration of the bands of CO_2 , CO_L measured in H_2O and carboxylic group measured in D_2O as a function of the applied potential.

Fig. 2A shows that in the positive going sweep of the first cycle is possible to detect the bands associated to the carboxylic group at 0.5 V, but not the one assigned to glycolate adsorption because the amount of acid formed is too small. At 0.6 V, when CO starts to oxidize and the CO_2 band first appears, these two bands become more defined. Only at 0.7 V, when the CO is completely removed from the surface, the band of adsorbed glycolate appears, remaining in the following spectra until the adsorption of CO takes place again in the negative sweep. It is worth to mention that, coinciding with the start of the oxidation wave in the negative scan, the bands

of the C=O and C-OH stretching of the carboxylic acid become more intense, and that glycolate desorbs from the surface. From these spectra, the formation of oxalic acid cannot be asserted. For that reason, FTIR experiments were carried out in D₂O (not shown). The use of D₂O eliminates the interferences of the carbonyl group with the $\delta(\text{OH})$ mode of water, since this band moves from 1640 to 1200 cm⁻¹. In this solvent, a weak band at 1639 cm⁻¹ was observed at 0.6 V in the negative-going sweep, pointing out the formation of bioxalate. This product was not found on polycrystalline Pt [12]. Since the oxidation of oxalic acid to CO₂ only occurs at potentials above 1.1 V [15], the oxidation currents in the negative-going sweep have to be related to the oxidation of EG to CO₂ and glycolic acid, which would generate adsorbed glycolate, and its further oxidation to CO₂ and oxalic acid/bioxalate.

Fig. 2B represents the integration of the bands associated to linear CO, CO₂ from the spectra in H₂O and that associated to the C=O stretching of a carbonyl groups from the spectra in D₂O, as a function of the applied potential. Some conclusions can be drawn from this plot: (i) CO is formed on the Pt(111) electrode at 0.2 V and oxidizes at 0.6 V; (ii) both CO_L and CO_B (not shown in the figure to simplify) are produced in the same potential region in the negative-going sweep; (iii) in the positive-going sweep, CO₂ is formed at 0.6 V from the oxidation of the adsorbed CO; in the negative scan, some CO₂ is also formed between 0.9 V and 0.6 V. This can be deduced from the increase in the signal, which is proportionally lower than the signal associated to the C=O stretching. (iv) Carboxylic groups are formed between 0.6 V and 0.9 V, both in the positive and negative-going sweeps. Once the CO adsorption appears in the spectra, the formation of the carboxylic group stops.

The following scheme summarizes the spectroelectrochemical information for EG oxidation at Pt(111):



Scheme 1. General scheme for the oxidation of EG on Pt(111) electrode.

FTIR spectra were also recorded for Pt stepped surfaces to understand the role of the steps in the formation of the different species. Comparison with the Pt(111) electrode at selected potentials is given in Fig. 3. At 0.4 V, bands associated to CO adsorption are predominant. Moreover, the electrodes with {110} steps show an asymmetrical bipolar band corresponding to linear CO. That indicates that some CO was already adsorbed at the reference potential, which gives the

negative contribution to the band, and its surface concentration has increased during the voltammetric sweep, resulting in a more intense positive band. The almost complete absence of the bridge CO band in this series agrees with the {110} symmetry assignment [16]. As the step density increases this bipolar band becomes more intense, indicating that the presence of {110} defects catalyze the C-C cleavage of the EG molecule, as in ethanol oxidation [2]. Interestingly, the band at 1740 cm^{-1} is not observed at 0.4 V but is clearly observed at 0.6 and 0.8 V.

The electrodes with {100} steps show both linear and bridge CO, as expected [16]. The intensity of both bands is higher as the step density increases, but in a more moderate way than in the previous series. The spectra taken at 0.6 V and 0.8 V show that both types of steps increase the catalytic activity of the electrode in the pathway that leads to CO_2 formation, but also in that in which glycolic acid is formed. As reported for ethanol oxidation [2], the electrodes with {110} steps give a more intense CO_2 band than those with {100} steps and the same terrace width.

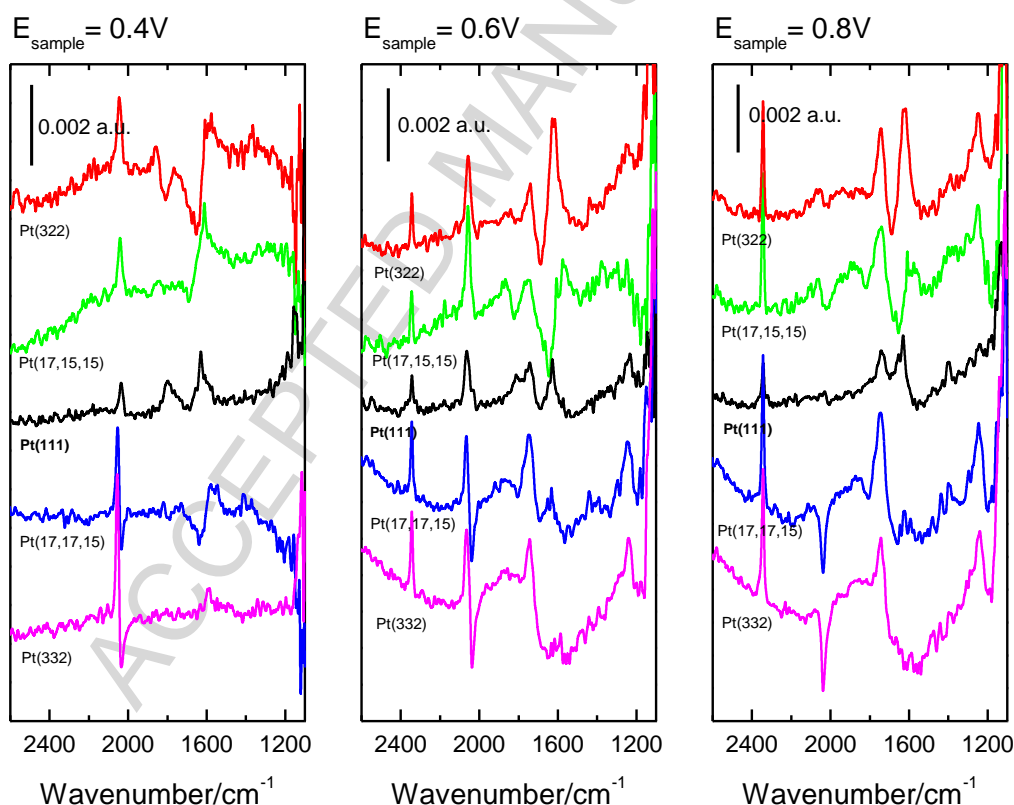


Fig.3. Spectra for the oxidation of 0.1 M EG in 0.1 M HClO_4 on the different stepped surfaces at 0.4 V, 0.6 V and 0.8 V (only positive-going sweep). Reference spectra: 0.06 V.

Further FTIR experiments in D_2O with these stepped surfaces were performed, where no band at 1639 cm^{-1} was found. These results point out that the presence of steps catalyze the EG oxidation to glycolic acid and CO_2 rather than the formation of oxalic acid/bioxalate, which seems to take place on the long terraces of the Pt(111) electrode. This can explain the conclusions reported on polycrystalline Pt-film electrodes[12].

4. Conclusions

Results suggest that CO is readily formed from EG at low potentials, which implies the rupture of the C-C bond. The insertion of an OH group in the molecule, in comparison with ethanol, makes this bond more labile in contact with platinum surfaces. The presence of steps catalyzes the cleavage of the C-C bond, the higher yields of CO₂ observed for electrodes of the series Pt(S)[(n-1)(111)x(110)]. FTIR experiments point out a parallel pathway where glycolic acid is formed, further oxidized to oxalic acid/bioxalate (in long {111} domains) and CO₂ (preferentially in the presence of steps). In spite of greater poisoning at stepped surfaces, the oxidation current is higher at 0.55 V, thus suggesting that both routes are faster at stepped surfaces. It appears that {110} steps catalyze the formation of CO while {100} steps favor the carboxylic acid route. Oxalate/bioxalate was only found at Pt(111).

Acknowledgements

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RESEARCH HIGHLIGHTS

- Pt(111) electrode is very active for the oxidation of ethylene glycol
- The breaking of the C-C bond takes place on the (111) terraces
- Steps are very active for this oxidation

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