



Short communication

New insights on the electrochemical oxidation of ethanol on carbon-supported Pt electrode by a novel electrochemical mass spectrometry configuration

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ABSTRACT

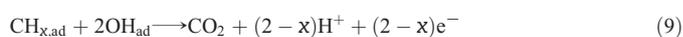
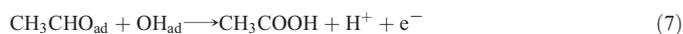
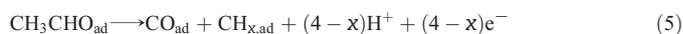
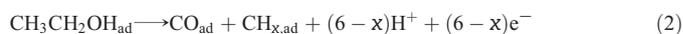
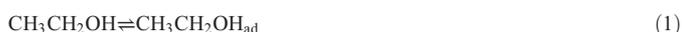
Herein, we demonstrate the versatility and high sensitivity of the meniscus-based approach of a novel on-line electrochemical mass spectrometry (EC-MS) by studying the formation of gaseous/volatile products during ethanol oxidation on carbon-supported Pt electrode. In this way, methane is detected for the first time during ethanol adsorption at this electrode. Accordingly, new insights on the ethanol oxidation reactions are achieved.

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1. Introduction

The electrochemical adsorption and oxidation of ethanol on platinum-based electrodes is one of the most studied reactions in electrocatalysis during the last decades. It is a key model reaction as well as a highly important process considering its potential application in the fuel cells field [1–4]. Ethanol holds high energy density (8.03 kWh kg⁻¹) and high solubility in liquid electrolytes [4,5]. It has other advantages such as its availability at low cost, renewable origin and easy handling, transport and storage [5].

The full oxidation of ethanol to carbon dioxide has a favorable thermodynamic potential of 0.08 V (vs. RHE), although the efficiency of direct ethanol fuel cells is drastically limited by the formation of partial oxidation products (maintaining intact the carbon-carbon bond, such as acetaldehyde and acetic acid) and strongly adsorbed intermediates (e.g. CO_{ad} and CH_x-species) [4,6]. Although the mechanism of the ethanol oxidation reaction at Pt-based electrodes is complicated and still not clear, commonly it was proposed that involves the dissociative adsorption of ethanol to produce adsorbed species (CO and CH_x) at low potentials and the formation of acetaldehyde, acetic acid and as a minor extent carbon dioxide at high potentials [4,6], following the subsequent general reaction scheme:



In this mechanism, the only C₂ species at the surface are ethanol and acetaldehyde, which adsorb reversible (Eqs. 1 and 4, respectively) and then dissociates as the potential is increased positively (Eqs. 2 and 5, respectively). On the other hand, it is well established that ethane is formed during reduction of the adsorbates formed from ethanol [7,8]. In references 4 and 6, the reduction of (CH₃CHO)_{ad} formed in Eq. 3

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produces this ethane. However, studies on the adsorption of acetaldehyde [9] have shown that ethane was detected only in the potential region of hydrogen evolution (otherwise only methane was detected), but is not the case of the adsorption of ethanol, where the production of the C₂-hydrocarbon is observed at higher potentials. So, it seems that other adsorbates (different from (CH₃CHO)_{ad}), are responsible for the production of ethane and consequently, some aspects of ethanol mechanism remain still unclear.

With the purpose of achieving further insights on the mechanism of ethanol adsorption electrooxidation, a novel on-line electrochemical mass spectrometry (EC-MS) configuration was applied. Thus, appropriate mass to charge (*m/z*) ratios were selected to follow the formation of gaseous and volatile products as a function of the potential.

2. Experimental

2.1 All electrochemical measurements were performed in a conventional three-electrode cell controlled by a PC Autolab potentiostat-galvanostat PGSTAT30. A reversible hydrogen electrode was used as reference (RHE) and a carbon row as counter electrode. CO stripping experiments were obtained after bubbling CO (N47) through the cell for 15 min while keeping the working electrode at 0.07 V, followed by argon (N50) purging and electrolyte exchange to remove the excess of CO.

2.2 The EC-MS arrangement used in this paper allows the continuous detection of gaseous and volatile species produced during the electrochemical reaction. No differential pumping is needed during the measurement due to the small amount of gas that enters into the mass spectrometer. Briefly, the analysis system consists of a commercial mass spectrometer (Omnistar™, Pfeiffer) with a PTFE capillary (Supelco) as inlet. Scheme 1 shows the electrochemical mass electrode (EC-ME), in which the PTFE capillary was fixed in a carbon disk with a hole in the middle and a small porous PTFE membrane (Gore-Tex) is located onto the tip. Then, 10 μL of the catalytic ink was dried onto the PTFE membrane of EC-ME, so only very small amounts of catalysts are needed for the studies.

With this EC-MS set-up, mass spectrometry cyclic voltammograms (MSCVs) and mass transients (MST) can be recorded simultaneously with the cyclic voltammograms (CVs) and chronoamperometric curves (CTs), respectively. It is remarkable that ionic currents are on-line with the faradaic ones, as it can be observed in Fig. 1 for CO stripping at Pt/C catalyst in acidic medium at a scan rate of 5 mV s⁻¹. The MSCVs for *m/z* = 22 (CO₂⁺) and 44 (CO₂⁺) are associated with carbon dioxide formation. From these ionic currents, the onset potential for the CO oxidation reaction on Pt/C can be accurately established at 0.6 V. At more positive potentials, complete CO removal with an anodic

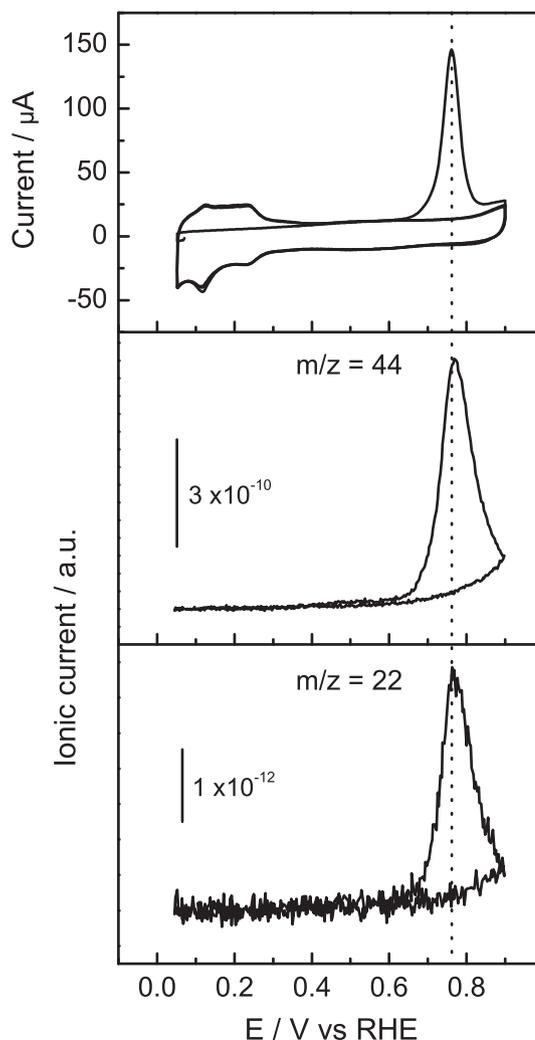
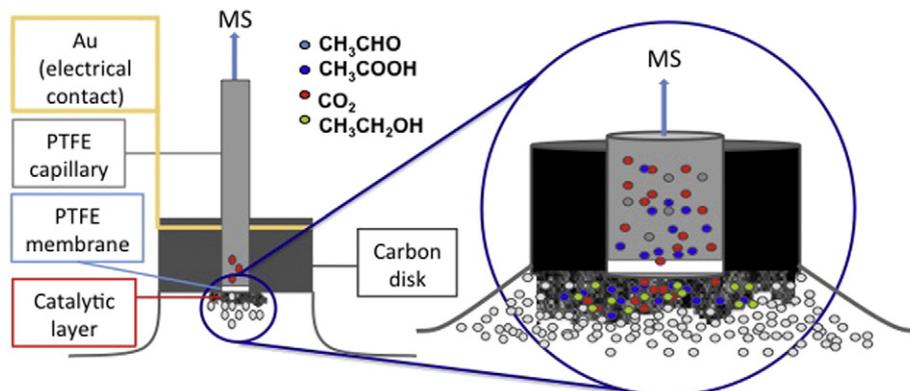


Fig. 1. CV and MSCV for CO stripping. Faradaic current (top panel) and ionic current for *m/z* = 22 and 44 signals (middle and bottom panels) registered during a CO_{ad} monolayer electrooxidation on 20 wt.% Pt/C catalyst in 0.5 M H₂SO₄. *v* = 5 mV s⁻¹; *T* = 25 °C.

peak centered at ca. 0.78 V occurs from both CV and MSCVs.

2.3 EC-MS calibration. CO₂ and CH₃CHO are produced during ethanol electrooxidation and they develop the same *m/z* signal of 44 (CO₂⁺ and CH₃CHO⁺). Therefore, the *m/z* = 22 signal (CO₂⁺) was used to follow, distinguish and quantify the amount of CO₂ produced. The current efficiency for ethanol



Scheme 1. The image shows the principal characteristics of the new EC-MS configuration: PTFE capillary (gray), carbon disk with a hole in the middle (black) and PTFE membrane (white).

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