

Parallel pathways of ethanol oxidation: The effect of ethanol concentration

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Abstract

In this work, we investigate the effects of ethanol concentration on the yields of CO₂, acetic acid and acetaldehyde as electrooxidation products. FTIR spectra show that the main oxidation product at low ethanol concentrations is acetic acid, CO₂ being produced to a minor extent. For concentrated ethanol solutions, the pathway producing acetaldehyde becomes dominant. The CO₂ production passes through a maximum at 0.025 M C₂H₅OH and then decreases. The intensity of the IR absorption band for CO_{ad}, which is one of the adsorbed intermediates, is practically independent of ethanol concentration.

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1. Introduction

The electrochemical oxidation of ethanol on platinum electrodes has been a subject of permanent interest in the last twenty years [1–7]. Ethanol, being a renewable fuel, would be a candidate for fuel cell applications. Such interest is justified by the energy content of ethanol, which corresponds to 12 e⁻ per molecule for total ethanol oxidation. However, the total conversion of ethanol to CO₂ is the central challenge in the electrocatalysis of this alcohol [1,3,5].

Several spectroscopic and electrochemical techniques have been applied to elucidate the mechanism of ethanol electrooxidation on Pt-based materials [2,3,8–10]. Ethanol undergoes parallel reactions, producing acetaldehyde, acetic acid and CO₂ as shown in Fig. 1, where the respective number of electrons for the different path-

ways are indicated. It was shown in recent studies using Pt, Pt–Sn and Pt–Re as catalysts [11–13] that ethanol oxidation pathways are sensitive to the catalysts nature and bifunctional mechanism and ligand effect have been suggested as responsible for the gain in the catalytic activity. On the basis of FTIR spectra, the yield of products in 0.1 M ethanol solution has been reported in early papers by Weaver and co-workers [2,3]. The polluting nature of acetaldehyde and the “end-product” character of acetic acid are disgusting factors in this system and, therefore, the search for catalysts to produce selectively oxidation to CO₂ is a major goal of research activities on ethanol today. However, to our knowledge, no quantitative and systematic investigation of the effect of ethanol concentration on the parallel reactions was reported until now, although it was early recognized that the relative amount of products depends on ethanol concentration [9,14]. This issue is the main concern of the present work.

We present here a systematic study on the concentration-dependence of the yield of products on polycrystalline Pt, as measured from in situ FTIR spectra. The

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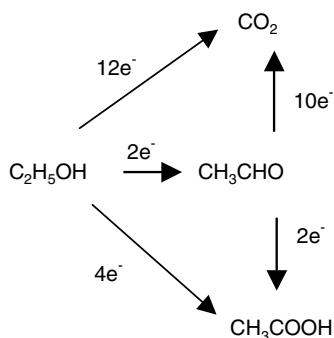


Fig. 1. Schematic representation of the parallel pathways for ethanol oxidation.

study is complemented with corresponding data on the total current for ethanol oxidation at a constant potential of 0.5 V.

2. Experimental

The working electrode was a smooth polycrystalline Pt disk with a geometric surface area of 0.78 cm². The real surface area of this electrode was determined by integration of the charge in the hydrogen region of the cyclic voltammogram. This area was used in the calculation of the current densities and the amounts of products measured along this work. The counter electrode was a platinum sheet with 1.2 cm². All potentials were measured against a reversible hydrogen electrode in the same electrolyte.

Before each experiment, the Pt disk was flame annealed for 1 min and cooled in an argon atmosphere. The electrode was immediately transferred to the electrochemical cell containing 0.1 M HClO₄. The state of the electrode surface was checked by cyclic voltammetry in a meniscus configuration, between 0.05 and 1.4 V with a scan rate of 50 mV s⁻¹. Then, the potential was kept at 0.05 V and ethanol (J. T. Baker) was admitted in the cell to reach the given concentration.

All the experiments were performed at room temperature (25 ± 1.0 °C). The solutions were prepared with Milli-Q water (18.2 MΩ cm) and deaerated with N₂ (4.6) or Argon (4.8).

FTIR spectra were measured using ethanol at different concentrations in the range between 10⁻² and 1.0 M using 0.1 M HClO₄ as supporting electrolyte (Alfa Aesar) p.a. The cell used for these experiments is described in detail elsewhere [15]. Reflectance spectra were calculated as the ratio (R/R_0) where R represents a spectrum at the sample potential and R_0 the spectrum collected at 0.05 V. Positive and negative bands represent, respectively, the consumption and production of substances at the sample potential. The electrochemical IR cell was fitted with a planar ZnSe window. This win-

dow material has the advantage of being transparent to IR radiation down to ca. 800 cm⁻¹. Spectra were computed from the average of 30 interferograms. The spectral resolution was set to 8 cm⁻¹.

3. Results and discussion

3.1. Potentiodynamic data

Fig. 2 shows cyclic voltammograms recorded at 50 mV s⁻¹ for two ethanol concentrations. Two oxidation peaks, centered at ca. 0.8 and 1.3 V, are observed during the positive-going scan and a reactivation peak, which becomes more prominent in the 1.0 M solution, is observed on the negative-going scan.

For all concentrations studied in this work, in situ FTIR spectra were measured at different potentials. As an example, the series of spectra for the 1.0 M solution is shown in Fig. 3. First, a reference spectrum R_0 was measured at 0.05 V and then sample spectra were collected after applying successive potential steps of 50 mV up to a potential of 1.0 V. The most important features related to ethanol oxidation products are listed in Table 1.

It is worth noting that the band for CO₂ (2343 cm⁻¹) is a relatively weak feature in the spectra, even at the highest potentials. Taking into account that CO₂ has the highest absorptivity from all soluble products (see below), the weak band intensity indicates a low level of CO₂ formation. This was observed along the series of concentrations studied in the present work.

The band observed at 933 cm⁻¹ is the only acetaldehyde feature not superimposed on other bands and will, therefore, be used for quantitative purposes [2,3]. The

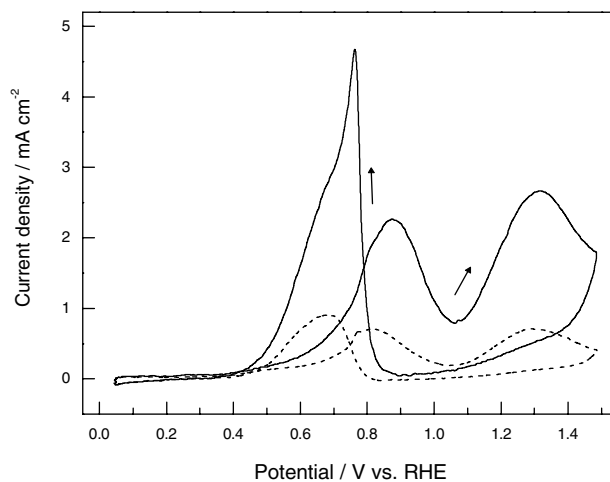


Fig. 2. Cyclic voltammograms at 50 mV s⁻¹ for the electrooxidation of: 0.1 M (dashed line) and 1 M of ethanol (full line) on smooth polycrystalline Pt. Sweeps are from 0.05 to 1.45 V vs. RHE. $T = 25\text{ }^\circ\text{C}$.

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