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Generation of carbon dioxide from glycerol: Evidences of massive production on polycrystalline platinum

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ABSTRACT

In this work we investigate the glycerol electrooxidation reaction on polycrystalline platinum in acid media. Cyclic voltammetry shows the existence of multiple oxidation peaks, which are related with a complex electrooxidation mechanism. We follow the voltammetric response of Pt in the presence of glycerol by using FTIR in situ. Results show that during glycerol electrooxidation massive amounts of CO_2 are produced. The production of CO_2 begins at low potentials and depends on the previous formation of adsorbed CO. This pathway is accelerated at high potentials and seems to be the main responsible for the rising of the currents observed in the cyclic voltammogram for potentials up to 1.0 V. Moreover, there is a parallel pathway involving the production of a carboxylic acid (probably glyceric acid), but the relative magnitudes of CO_2 bands and acid bands makes clear that the production of CO_2 is the dominant feature of the spectra, suggesting that glycerol can be a suitable candidate for use in direct alcohol fuel cells.

1. Introduction

Glycerol has been considered as a possible fuel in direct alcohol fuel cells, which justifies the advent of fundamental studies about its electrooxidation process in model surfaces, as gold and platinum [1–7] and in applied research [8–10].

Theoretically, the oxidation of 1 mol of glycerol yields 14 F, considering its total conversion to CO_2 [10]. However, the cleavage of C–C bond is a major challenge involving alcohols of small molecular structure [1,11], mainly at smooth surfaces. The limited ability of the catalysts to break these bonds provokes parallel reactions, which produce other oxidation products and cause loss of efficiency. Thus, instead of the formation of CO_2 as a sole oxidation product (ideal energetic situation) we have the establishment of parallel pathways that result in several products with less energetic yield [1,11].

Although the literature concerning glycerol electrooxidation is still scarce, some authors have identified products of incomplete oxidation at both acidic [1] and alkaline media [1,10].

Recently, Simões and co-workers investigated glycerol electrooxidation on platinum, palladium and gold nanoparticles supported onto carbon [10]. By using FTIR in situ analysis the authors propose the formation of glyceraldehyde, glycerate, tartronate 1,3-dihydroxy-2-propanone, mesoxalate and hydroxypyruvate, being the latter one present only on gold [10].

On the other hand, Roquet and co-workers investigated the electrooxidation of glycerol in acidic media on polycrystalline Pt by high-performance liquid chromatography (HPLC) [1]. In order to achieve the minimum concentrations required to identify eventual products and/or reaction intermediates the authors promote long term electrolysis at 0.75 and 1.3 V vs. RHE. The authors identify glyceraldehyde, formic acid, glycolic acid, glyceric acid and tartronic acid as products of electrooxidation, being the relative amounts dependent on the applied potential [1]. However, the need of polarization for long times and at high potentials does not reproduce the usual conditions adopted for electrochemical experiments. Additionally, the intrinsic characteristics of technique used do not allow the formation of CO_2 to be followed.

In a previous paper, Sun and co-workers have investigated the electrooxidation of glycerol on Pt electrodes by voltammetry and FTIR spectroscopy in situ [12]. According to the authors, the oxidation of glycerol on Pt electrodes is a complex process of surface, including dehydrogenation, adsorption and dissociation stages [12]. Based on the data acquired from cyclic voltammetry and FTIR experiments, the authors suggest that glycerol undergoes several processes during its electrooxidation, which include the dissociation and adsorption of intermediates on the Pt surface, the oxidation of theses species and a superficial reactivation of the electrode as the reaction proceeds [12]. The paper of Sun and co-workers represent an important attempt to correlate the electrochemical behavior of glycerol with the spectroscopic data, but at that stage the authors were not able to identify other intermediate species than adsorbed CO (here after designed CO_{ads}) [12].

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More recently, Kwon and Koper combined on-line HPLC and cyclic voltammetry to follow the products of glycerol electrooxidation on Au and Pt electrodes in alkaline media [13]. The authors were able to identify glyceric acid as the first oxidation product of glycerol (observed at low potentials). The authors also report the presence of glycolic acid, formic acid, tartronic acid and oxalic acid as being produced by a further oxidation of glyceric acid, although CO_2 cannot be detected by the characteristics of the technique [13]. This article represents an important advance on the knowledge of the electrooxidation mechanism of glycerol, particularly in alkaline media.

Based on the findings presented here, it is clear that despite the importance of glycerol as a candidate for direct alcohol fuel cells, the mechanism of electrooxidation of this alcohol has to be better understood before practical systems with appropriate catalysts can be designed. In order to bring some additional information about this issue, here we perform an analysis of the FTIR data obtained during the electrooxidation of glycerol on polycrystalline Pt.

2. Experimental

2.1. Chemicals, solutions and electrochemical experiments

Solutions were prepared with Milli-Q® (18.2 MΩ cm) water, glycerol (Labsynth p.a.) and $HClO_4$ (Suprapur, Merck).

The working electrode was a smooth polycrystalline Pt disk (10 mm diameter) with 0.8 cm^2 of real area. N_2 (4.6) was used to purge the solutions before and during the experiments. The counter electrode was a Pt sheet. All potentials were measured against a reversible hydrogen electrode in the corresponding support electrolyte and are presented in the same scale.

Before each experiment, the electrode was annealed in butane flame and cooled in air. Afterwards, the electrode was transferred to the electrochemical cell containing 0.1 mol dm^{-3} $HClO_4$. The state of the surface was checked by cyclic voltammetry between the potentials of 0.05 and 1.45 V. Next, 0.1 mol dm^{-3} of glycerol was admitted in the electrochemical cell and a voltammetric scan was collected at 20 mV s^{-1}.

2.2. FTIR in situ experiments

FTIR in situ experiments were carried out by using a MB-100 spectrometer (Bomem) with a MCT detector. The experiments were made in a room with controlled temperature (25.0 ± 1.0 °C) in the presence of 0.1 mol dm^{-3} glycerol + 0.1 mol dm^{-3} $HClO_4$ p.a. solutions. The spectroelectrochemical cell was described in details previously [14].

Reflectance spectra were collected as the ratio (R/R_0) where R represents a spectrum at a given potential and R_0 is the spectrum collected at 0.05 V. Spectra were computed from 50 interferograms averaged. The spectral resolution was set to 8 cm^{-1}. Spectra were obtained during a slow cyclic voltammogram ($\upsilon = 1$ mV s^{-1}). Such conditions were chosen to allow that spectra were collected at intervals of c.a. 0.05 V among 0.05 and 1.45 V. The electrochemical IR cell was fitted with a CaF_2 planar window for the collection of bands in the range of 3000–1000 cm^{-1}.

3. Results and discussion

3.1. The electrochemical behavior of polycrystalline Pt in the presence of glycerol

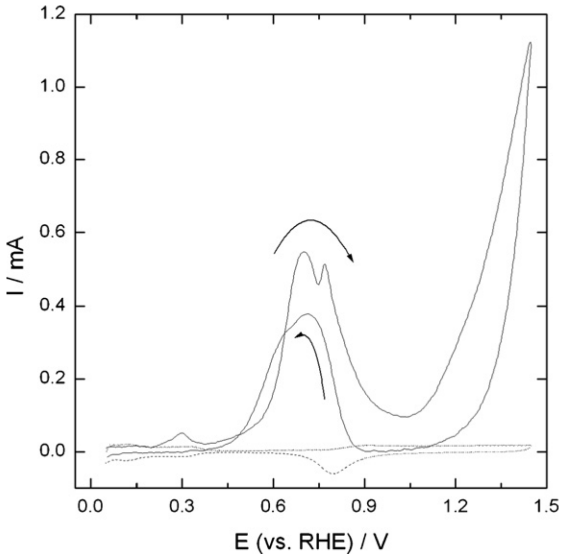

Fig. 1. Cyclic voltammograms of platinum in 0.1 mol dm^{-3} $HClO_4$ (dashed line) and in 0.1 mol dm^{-3} $HClO_4$ + 0.1 mol dm^{-3} glycerol (solid line) $\upsilon = 20$ mV s^{-1}.

Fig. 1 shows cyclic voltammograms recorded at 20 mV s^{-1} in the presence of 0.1 mol dm^{-3} glycerol (solid line) and 0.1 mol dm^{-3} $HClO_4$ (dashed line). Four oxidation regions can be discerned in the presence of the alcohol. The first oxidation currents are discernable at potentials up to 0.2 V, peaking at 0.3 V. This pre-peak is followed by a subtle increase in the anodic currents which suggests that the electrooxidation of glycerol starts at ~0.45 V. After the beginning of glycerol oxidation, the current increases and reaches a double peak with maxima around 0.7 and 0.77 V. Afterwards, the current diminishes and then grows again, reaching its maximum values at the vertex potential (1.45 V). The wide potential range and the shape of the peaks suggest the existence of complex electrooxidation kinetics. During the reversing sweep, the electrooxidation currents experience a steep decrease, reaching negligible values at 1.1 V. Next, there is a region (1.1–0.9 V) where no oxidation currents are observed, followed by a sudden reactivation of the surface.

With the aim of monitoring the potential-dependence of the glycerol oxidation and to interpret the behavior observed in Fig. 1 in terms of the oxidation products, FTIR in situ was used. Results are presented in the next section.

3.2. Following the products of oxidation by FTIR in situ

Fig. 2(a) shows a collection of spectra recorded during a voltammogram taken at 1 mV s^{-1} in the presence of glycerol and $HClO_4$ (0.05 V < E < 1.45 V), whilst Fig. 2(b) shows the details of the development of CO_{ads} band. Because the band corresponding to the formation of CO is too less intense than the others we present the spectra in two different scales. The CO_{ads} band appears at 0.2 V due to the presence of linearly CO_{ads} and its development coincides with the rising of anodic currents in Fig. 1, suggesting that the pre-peak of the voltammogram is due to the beginning of a dissociative adsorption of glycerol, which produces CO_{ads}.

Additional bands appear around 0.5 V and are centered at 2343, 1736, 1297, 1227 and 1100 cm^{-1} (Fig. 2(a)). Their nature will be discussed later.

For purposes of following the end-oxidation products, we will firstly focus our attention on the bands centered at ~2050 and 2343 cm^{-1}, which are associated to the presence of CO and CO_2, respectively. Fig. 3 shows the integrated absorbance signals as a function of the potential for both these species. CO_{ads} starts to being formed at 0.2 V and the signal grows until 0.45 V, which is the potential where CO_2 begins to be produced. This behavior indicates that CO is the intermediate of CO_2, as already observed for other reactions involving organic molecules [15,16]. However,