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Heterogeneously assisted oxidation of adsorbates from carbonmonoxide, methanol and ethanol by hydrogen peroxide solutions on platinum electrodes in sulphuric acid

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Abstract

The influence of hydrogen peroxide on the adsorption and oxidation of carbon monoxide, methanol and ethanol adlayers on porous Pt electrodes were studied in 2 M sulphuric acid solution by means of cyclic voltammetry and differential electrochemical mass spectrometry (DEMS). The oxidation of adsorbed species is observed at electrode potentials far less negative than those required for electrochemical adsorbate oxidation. The oxidation by H_2O_2 is dependent on its concentration in solution, as well as on the adsorbates and their coverages. In all cases the isolated adlayers are oxidised by dissolved H_2O_2. However, the presence of H_2O_2 during adsorption partially inhibits adlayer formation from CH_3OH and C_2H_5OH, but avoids almost completely the adsorption of carbon monoxide. The removal of the residues from the surface by dissolved hydrogen peroxide probably occurs through O_{ad} species formed during the heterogeneous decomposition reaction of H_2O_2 on Pt.

1. Introduction

The direct methanol fuel cell (DMFC) is an attractive electrochemical energy conversion system for portable devices and vehicle applications due to the theoretical large energy density of methanol as direct fuel. However, the performance of these devices is lower than compared with pure hydrogen fuel. This fact is due to catalyst poisoning at the fuel cell anode by adsorbed intermediates, the low electrochemical kinetics of the oxygen electroreduction reaction at the cathode and methanol crossover through the polymer electrolyte leading to a mixed potential at the cathode [1, 2].

During the electrochemical oxidation of methanol on platinum, linearly bound CO is the predominant adsorbate at high methanol concentrations and high surface coverages. The identity and reactivity of other adsorbed species have been a topic of controversy [3–5]. The elimination of adsorbed CO and other possible residues are an important issue in DMFC research. The same problem, i.e. poisoning of the anode surface by adsorbed CO, appears in polymer electrolyte fuel cells (PEFCs) running with CO containing hydrogen as fuel which is produced by reforming of natural gas or methanol [6, 7].

The injection of air into the fuel gas stream of a PEFC oxidises CO to CO_2 under relative mild conditions (20–80 °C and 0.1–0.5 MPa) [8]. A similar approach for CO mitigation is the use of hydrogen peroxide. In both cases heterogeneous CO oxidation should take place by adsorbed oxygen species [9, 10] according to the following reaction:

$$Pt(O)_{ad} + Pt(CO)_{ad} \rightarrow CO_2 + 2Pt \qquad (1)$$

In the case of the H_2O_2 method [9], $(O)_{ad}$ species are formed through the heterogeneous decomposition of H_2O_2 on Pt followed by the adsorption of oxygen:

$$H_2O_2 \rightarrow H_2O + 1/2O_2 \qquad (2)$$

$$O_2 + 2Pt \rightarrow 2Pt(O)_{ad} \qquad (3)$$

or by the direct adsorption of H_2O_2 producing $Pt(O)_{ad}$:

$$H_2O_2 + Pt \rightarrow Pt(O)_{ad} + H_2O \qquad (4)$$

The CO adsorption is the poisoning reaction at the fuel cell anode when CO containing fuel gases (for example H_2 /CO gas mixtures) are used according to the following reaction:

$$H_2/CO + Pt \rightarrow Pt(CO)_{ad} + H_2 \qquad (5)$$

Thus, hydrogen molecules cannot react at Pt leading to a significant performance loss of the fuel cell. $(CO)_{ad}$ is also formed during methanol and ethanol adsorption.

Reactions (1)–(5) are heterogenous processes, meaning that they are non-electrochemical pathways. Consequently, no dependence on the electrode potential should be expected.

In parallel, the electrochemical CO oxidation takes place in a potential range which enables the chemisorption of H_2O molecules according to the following reaction sequence:

$$Pt + H_2O \rightarrow PtOH + H^+ + e^- \tag{6}$$

$$PtOH + Pt(CO)_{ad} \rightarrow 2Pt + CO_2 + H^+ + e^- \tag{7}$$

The electrochemistry of hydrogen peroxide at Pt has been extensively studied. H_2O_2 formation is an undesirable intermediate during oxygen electroreduction at the cathode [11–13]. Both hydrogen peroxide and oxygen are reduced on Pt as follows:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{8}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{9}$$

On the other hand, H_2O_2 oxidation only takes place on the oxidised Pt surface [14, 15]:

$$H_2O_2 + PtOH \rightleftharpoons PtOH(H_2O_2)_{ad} \tag{10}$$

and the complex undergoes an internal charge transfer, finally leading to the electrochemically decomposition of hydrogen peroxide:

$$PtOH(H_2O_2)_{ad} \rightarrow PtOH + O_2 + 2H^+ + 2e^- \tag{11}$$

Simultaneous oxygen electroreduction and methanol oxidation has been studied on carbon supported Pt in sulphuric acid at 80 °C [16]. It was found that the two reactions proceed in parallel on the oxide free Pt surface (0.20–0.70 V_{RHE} potential range). By applying the rotating disc electrode technique it was shown that methanol residues partially suppress the oxygen reduction because of poisoning the cathode [17]. Besides, the methanol oxidation current is little affected by the presence of oxygen. This indicates that both processes take place at different sites of the Pt surface [17, 18]: methanol oxidation probably occurs close to surface defects and edges needed for the electrochemical adsorption of hydroxyl radicals, whereas oxygen reduction takes part on flat regions of the surface [14].

In previous work the influence of 0.01 M H_2O_2 on the adsorption and oxidation of CO on Pt in 2 M H_2SO_4 has been studied [19]. It was observed that H_2O_2 dissolved in water can oxidise adsorbed CO to CO_2 at electrode potentials lower than those normally required for electrochemical oxidation. The CO removal by 0.01 M H_2O_2 has only been observed when the CO_{ad} coverage is less than a monolayer. It has been proposed that non-electrochemical H_2O_2 decomposition took place in the holes of the CO adlayer on Pt [19].

The aim of the present work is to study small organic molecules such as methanol in H_2O_2/H_2SO_4 on Pt, which is relevant for DMFC development with liquid methanol feed. In the case of ethanol, it was proved that significant amounts of C_2 species are adsorbed on the platinum surface [20–22]. Therefore, ethanol could be a valuable model for the oxidation of higher organic molecules and the removal of adsorbed intermediates by means of H_2O_2. Furthermore, the dependence of the H_2O_2 concentration on these oxidation reactions is of great practical interest for fuel cell applications.

In order to study the heterogenous (1)–(5) and electrochemical (6)–(9), (11) reactions, cyclic voltammetry was combined with differential electrochemical mass spectrometry (DEMS). This is a powerful on-line technique for product identification of electrochemical reactions developed by Wolter and Heitbaum in 1984 [23].

2. Experimental

2.1. *General*

The experimental set-up involved a flow cell containing ca. 2 ml solution, which enabled a complete electrolyte exchange under potential control. The working electrode was porous Pt (0.78 cm^2 geometric area) sputtered onto a microporous *PTFE* membrane that served as interface between the electrochemical cell and the ion source of the mass spectrometer. The experimental set-up allowed the simultaneous acquisition of mass spectrometric cyclic voltammograms (*MSCVs*) for selected m/z ratios, m being the mass and z the charge of the fragment, and conventional cyclic voltammograms (*CVs*). A Pt wire was the counter electrode and a reversible hydrogen electrode (*RHE*) was used as reference. All potentials are referred to this electrode. The detailed description of the on-line mass spectrometry technique can be found elsewhere [23, 24].

Solutions were prepared with Millipore-MilliQ* water and analytical grade chemicals. 2 M H_2SO_4 was used as supporting electrolyte to simulate the experimental conditions for Nafion^R membranes [19]. 0.1 M CH_3OH, 0.1 M CH_3CH_2OH and saturated CO (with and without 0.01 or 0.1 M H_2O_2) in the supporting electrolyte were employed as working solutions. Ar (99.998 %) was used for purging between the experiments through and over the working solutions. All experiments were conducted at room temperature.

2.2. *Procedure*

Previous to any measurement, the working electrode was activated by potential cycling at 0.10 V s^{-1} in 2 M H_2SO_4 between hydrogen and oxygen evolution. The Pt electrode was considered to be clean when no potential dependence was observed for m/z = 44 (carbon dioxide, $[CO_2]^{\cdot +}$) which confirms the absence of organic impurities. The real surface area, obtained from the voltammetric charge within the hydrogen adatom region [25], was 22 cm^2.

2.2.1. *Single adsorption experiments*

These studies consisted of the following steps:

(i) After the platinum electrode was activated in the base electrolyte, the potential was held at E_{ad} until the current reached a steady value. Then, the electrolyte saturated with CO, dissolved CH_3OH or dissolved C_2H_5OH was introduced into the cell.

(ii) After 300 s, the CO or alcohol-containing solution was replaced by rinsing 200 ml of the supporting electrolyte under potential control at E_{ad}. The *CVs* and *MSCVs* for $m/z = 44$ were recorded immediately afterwards, starting from E_{ad} in the positive-going potential scan for ethanol adsorbates, and negatively down to 0.03 V followed by a positive-going scan in the case of methanol and CO adsorbates up to 1.50 V.

2.2.2. *Combined adsorption experiments*

To study the influence of H_2O_2 on the adsorption and oxidation of CO, CH_3OH and C_2H_5OH on Pt, three different routines were applied. The background of these different experimental procedures is to simulate the poisoning of a fuel cell anode by CO, CH_3OH or C_2H_5OH adsorbates and to study the behaviour of a fuel cell anode after introducing H_2O_2. Thus, the potential was set to E_{ad} and the following experimental procedures were applied below.

Routine I: Oxidation of carbonaceous adsorbates by H_2O_2

(i) At selected E_{ad}, the electrolyte was exchanged against the alcohol or CO-containing solution for $t_{ad} = 300$ s.

(ii) After rinsing the cell with supporting electrolyte under potential control, 0.01 M or 0.1 M H_2O_2 in 2 M H_2SO_4 was added.

(iii) Finally, after 300 s the solution was completely replaced by the supporting electrolyte and the electrooxidation of the adsorbed species followed by both *CV* and *MSCV* for the formation of CO_2 ($m/z = 44$). The potential scanning started from E_{ad} up to 1.50 V for ethanol residues, and first negatively down to 0.03 V followed by a positive-going potential scan for methanol and CO adspecies.

Routine II: Adsorption of CO, CH_3OH or C_2H_5OH in the presence of H_2O_2

(i) At the selected E_{ad}, the electrolyte was exchanged against 0.01 or 0.1 M H_2O_2 in 2 M H_2SO_4. Then the alcohol or CO-containing electrolyte solution was introduced for $t_{ad} = 300$ s.

(ii) The solution was completely replaced with the supporting electrolyte and the adsorbed species were oxidised as described in *Routine I.*

Routine III: Simultaneous adsorption of CO, CH_3OH or C_2H_5OH and H_2O_2

(i) At the selected E_{ad}, the electrolyte was exchanged against a combined working solution containing the alcohol or CO in addition to 0.01 or 0.1 M H_2O_2 in 2 M H_2SO_4.

(ii) After 300 s, the cell was washed with pure supporting electrolyte and the anodic stripping of the residues recorded as in *Routine I* and *II.*

In all procedures successive oxidative potential cycles were carried out up to the complete adsorbate removal from the surface.

3. Results

3.1. *Reactivity of H_2O_2 on Pt in 2 M H_2SO_4*

To understand the effect of H_2O_2 on adsorbates coming from carbon monoxide, methanol and ethanol, the electrochemical behaviour of hydrogen peroxide was firstly studied using DEMS. The potentiodynamic curve for 0.01 M H_2O_2 in 2 M H_2SO_4 was followed by the *CV* and the *MSCV* for $m/z = 32$ ($[O_2]^{\cdot+}$) between 0.03 and 1.50 V (Figure 1, dashed line). Below 0.90 V, a cathodic current is observed in the *CV* (Figure 1(A), dashed line) due to reactions (8) and (9) in combination with reaction (2). This faradaic current increases with higher H_2O_2 concentration (not shown in Figure 1) indicating that the rate-determining step is diffusion controlled. On the other hand, above 0.90 V the faradaic current due to H_2O_2 electrooxidation (according to reactions (10) and (11)) is also diffusion controlled. This was verified by stirring through Argon bubbling which leads to a higher limiting current at $E > 0.9$ V and an increase in the signal for $m/z = 32$ (Figure 1(B), dashed line). The hysteresis observed in the faradaic and ion currents in Figure 1(A,B) can be explained by the mechanism for H_2O_2 oxidation (reactions (10) and (11)): the requirement of an oxidised Pt surface implies a different potential range for the oxygen formation from H_2O_2 during the positive- and negative-going potential scan.

3.2. *Interaction of adsorbed CO with H_2O_2*

In previous work [19] it was found that adsorbed CO is only oxidised by 0.01 M H_2O_2 at Pt when its coverage is lower than a monolayer. It was concluded that free platinum sites are necessary for the oxygen adsorption produced from H_2O_2 through reaction (4). Thus, a complete monoloyer of CO_{ad} on Pt cannot interact with H_2O_2 and should be chemically stable towards oxidation. In the present paper, two different H_2O_2 concentrations were used (0.01 and 0.1 M) in order to study its concentration influence on $(CO)_{ad}$ oxidation. The electrochemical response of the adsorbate during the electrooxidation was followed by the *CVs* and *MSCVs* for $m/z = 44$ ($[O_2]^{\cdot+}$). Assuming CO_2 as the sole electrooxidation product from $(CO)_{ad}$ as well as CH_3OH and C_2H_5OH adsorbates, the integration of this signal in a whole potential cycle should be proportional to the adsorbate coverage. In this way, relative coverages of adsorbed species can be compared. These values are

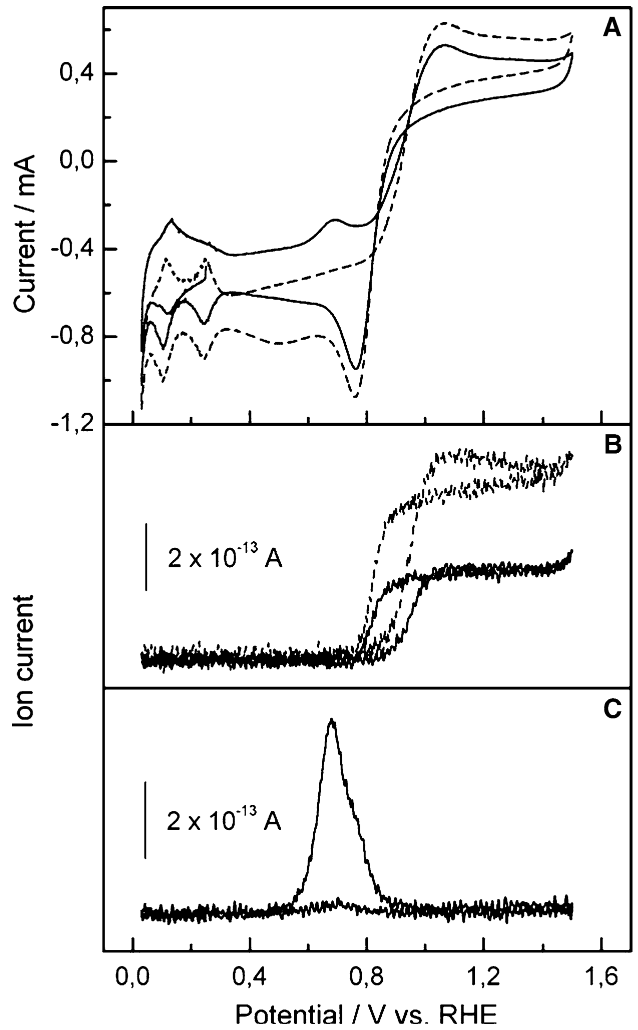

Fig. 1. Electrochemical behaviour of 0.01 M H_2O_2/2 M H_2SO_4 on an adsorbate free Pt electrode and on Pt covered with methanol adsorbate; supporting electrolyte: 2 M H_2SO_4; v = 0.01 V s^{-1}; T = 25 °C; arrows indicate the potential scan direction. (A) *CV* of 0.01 M H_2O_2 on bare Pt (dashed line) and on Pt covered by methanol adsorbates formed at E_{ad} = 0.25 V during 5 min (solid line); (B) *MSCV* for m/z = 32 $[O_2]^+$; and (C) *MSCV* for m/z = 44 $[CO_2]^+$ in the same conditions.

summarised in Table 1 for all experiments reported in the present work.

Figure 2(A) solid line shows the CV for $(CO)_{ad}$ oxidation after the adsorption experiment described in Section 2.2.1. The corresponding *MSCV* for m/z = 44 is given in Figure 2B solid line and the integration of the ion current yields 12.68×10^{-13} C cm^{-2} (Table 1). When *Routine I* is applied (Figure 2(A, B), dashed line), the integrated ion current is 3.14×10^{-13} C cm^{-2} (Table 1), i.e. 75% of the CO_{ad} layer is desorbed during introduction of H_2O_2. According to this result, the presence of free sites is not the unique determining factor in the interaction of the CO adlayer with H_2O_2, but also the concentration of the latter.

On the other hand, a small amount of CO_{ad} is produced in the presence of 0.1 M H_2O_2 (Figure 2(C,D) solid line, *Routine II*). Finally, no CO adlayer formation is observed when the adsorption experiment is conducted in a 0.1 M H_2O_2/2 M H_2SO_4 solution saturated with CO. This results clearly shows that 0.1 M H_2O_2 inhibits the formation of the CO adlayer.

Table 1. Integrated ion currents (Q_{ad}) for the mass signal m/z = 44 (due to CO_2 formation) obtained after adsorbate oxidation in 2 M H_2SO_4; the charge density Q_{ad} is referred to the real electrochemical area of the porous Pt electrode

	$Q_{ad}/ \times 10^{13}$ C cm^{-2}				
	Ead/V	Single adsorption	Routine I	Routine II	Routine III
CO	0.25	12.68			
CO/0.1 M H_2O_2	0.25		3.14	2.46	No residue
Methanol	0.15	2.37			
	0.20	5.91			
	0.25	7.31			
Methanol/0.01 M H_2O_2	0.15		1.17	2.46	5.92
	0.25		3.10	4.37	4.44
Methanol/0.1 M H_2O_2	0.25		0.65	4.40	3.75
Ethanol	0.20	10.1			
	0.25	10.7			
	0.30	10.5			
Ethanol/0.1 M H_2O_2	0.25		1.89	6.52	7.67

3.3. *Interaction of methanol adsorbates and H_2O_2*

Experiments reported in [19] have demonstrated that $(CO)_{ad}$ is oxidised in a 0.01 M H_2O_2 solution at a partially covered Pt surface. It is known from infrared studies that methanol adsorption yields carbon monoxide [3–5, 26–29]. Therefore, the oxidation of adsorbed intermediates formed during methanol oxidation is also expected in the same medium, as a full coverage on Pt is not achieved.

The first step in studying methanol adsorption was to evaluate the appropriate adsorption potential (E_{ad}), i.e. that corresponding to the maximum coverage on Pt. These experiments were conducted in 2 M H_2SO_4 at different E_{ad} (E_{ad} = 0.15, 0.20, 0.25 and 0.30 V), using the procedure described in Section 2.1. It was found that after 300 s of adsorption from a 0.1 M CH_3OH solution, a stationary surface coverage was obtained at each potential. Only one potential cycle is necessary for the complete stripping of the adlayer. The maximum surface coverage was attained at E_{ad} = 0.25 V. Therefore, this potential was selected for further studies. It has to be taken in mind that even at this potential the Pt surface is not completely blocked by methanol adsorbates.

The oxidation of methanol residues formed at this potential in the presence of 0.01 M H_2O_2 in the bulk of the solution can be seen in the CV of Figure 1 solid line. After adsorption of methanol and electrolyte replacement, the H_2O_2 containing solution was introduced in the cell at 0.25 V and anodic stripping of the residues was performed. It is observed that the cathodic current in the cyclic voltammogram due to the reduction of H_2O_2 is still

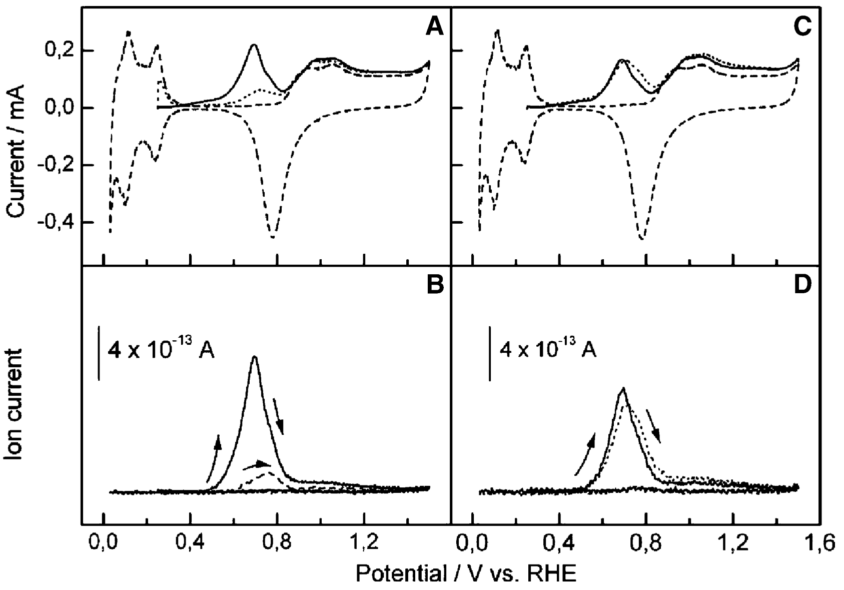

Fig. 2. Adsorption and oxidation of carbon monoxide adsorbates formed on Pt at E_{ad} = 0.25 V during 5 min in a CO saturated electrolyte solution; 0.1 M H_2O_2; v = 0.01 V s^{-1}; T = 25 °C; arrows indicate the potential scan direction. (A) *CVs* for the oxidation of the CO adlayer and (B) corresponding *MSCVs* for m/z = 44 $[CO_2]^{\cdot+}$ for the single carbon monoxide adsorption (solid line) and applying *Routine I* (dotted line). (C) *CVs* for the oxidation of the CO adlayer and (D) corresponding *MSCV* for m/z = 44 $[CO_2]^{\cdot+}$ applying *Routine II* (solid line). *CV* of bare Pt in 2 M H_2SO_4 (dashed line).

apparent, although the hydrogen adsorption/desorption features between 0.03 and 0.3 V are partially supressed by methanol residues (see Figure 1(A) solid line). The oxidation of these adsorbates to CO_2 (Figure 1(C)) occurs in the potential range 0.50–0.90 V and a significant decrease of the integrated signal (about 53%) is observed when compared with the result for the single adsorption experiment at E_{ad} = 0.25 V (Figure 3(B) solid line, see below). This fact confirms that the adlayer formed from methanol at 0.25 V is oxidised by H_2O_2. Then, further experiments at this E_{ad} were performed following the experimental procedures described in Section 2.2.

Figure 3(A, B) dashed line show the results when *Routine I* is applied. After interaction with 0.01 M H_2O_2, the electrooxidation of the remaining residues in pure supporting electrolyte depicts a *MSCV* for m/z = 44 involving an ion charge of 3.10×10^{-13} C cm^{-2}. This value represents a decrease of ca. 58% compared to the amount during the single adsorption experiment (Fig-

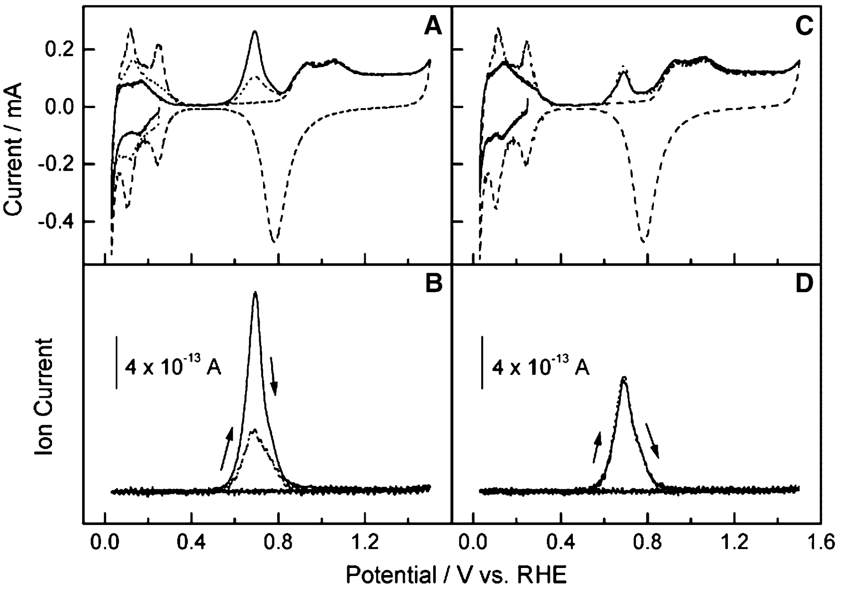

Fig. 3. Adsorption and oxidation of methanol adsorbates formed on Pt at E_{ad} = 0.25 V during 5 min from 0.1 M methanol; 0.01 M H_2O_2; v = 0.01 V s^{-1}; T = 25 °C; arrows indicate the potential scan direction. (A) *CVs* for the oxidation of the organic residues and (B) corresponding *MSCVs* for m/z = 44 $[CO_2]^{\cdot+}$ for the single adsorption of methanol (solid line) and applying *Routine I* (dashed line). (C) *CVs* for the oxidation of the organic residues and (D) corresponding *MSCV* for m/z = 44 $[CO_2]^{\cdot+}$ applying *Routine II* (solid line) and *Routine III* (dotted line). *CV* of bare Pt in 2 M H_2SO_4 (dashed line).

ure 3A and B solid line). Approximately the same value is obtained when H_2O_2 is maintained in the bulk (Figure 1 solid line).

Different information is acquired when H_2O_2 interacts with the surface prior to the adsorption of methanol. Thus, *Routine II* was conducted and the results are given in Figure 3(C, D) solid line. In this case, the integration of the ion current for the CO_2 mass signal yields 4.37×10^{-13} C cm^{-2}, i.e. only 40% of the residues are removed from the surface. Therefore, the presence of methanol in the solution allows this molecule to compete with H_2O_2 for the Pt sites. The competition for the reactive places is better studied applying the simultaneous adsorption (*Routine III*), since H_2O_2 and CH_3OH interact with the surface simultaneously (Figure 3C and D dashed line). The *MSCV* for $m/z = 44$ reveals that the final coverage by methanol adsorbates is similar to that obtained with *Routine II*.

The fact that the residues cannot be completely removed from the surface suggests that not only the requirement of free platinum sites for the adsorption of H_2O_2 determine the oxidation process. To get a deeper insight into this reaction, another adsorption potential involving a lower coverage of methanol adsorbates was chosen, namely $E_{ad} = 0.15$ V (not shown). At this potential the amount of methanol adsorbates (2.37×10^{-13} C cm^{-2}) is approx. 1/3 of that obtained at $E_{ad} = 0.25$ V due to the presence of larger amounts of $(H)_{ad}$. Even under these circumstances, a small contribution of adspecies (1.17×10^{-13} C cm^{-2}) is still apparent when the 0.01 M H_2O_2 solution contacts methanol adsorbates formed at 0.15 V (*Routine I*). No change in the amount of methanol adsorbates is observed in the presence of H_2O_2 (*Routine II*). Surprisingly, the coverage increases when the adsorption occurs from a solution containing both methanol and hydrogen peroxide (*Routine III*). For the explanation of this result it has to be considered that dissociation of methanol occurs producing mainly COH_{ad} or CO_{ad} [3–5] according to:

$$\mathrm{Pt} + \mathrm{CH_3OH} \rightarrow [\mathrm{Pt(COH)_{ad}}] + 3\mathrm{H}^+ + 3\mathrm{e}^- \quad (12)$$

$$\mathrm{Pt} + \mathrm{CH_3OH} \rightarrow [\mathrm{Pt(CO)_{ad}}] + 4\mathrm{H}^+ + 4\mathrm{e}^- \quad (13)$$

On the other hand, at 0.15 V part of the Pt centres is occupied by H_{ad} impeding the adsorption of methanol and a lower coverage is achieved. However, in the presence of H_2O_2, the formation of O_{ad} species induces the desorption H_{ad}:

$$[\mathrm{Pt(O)_{ad}}] + 2[\mathrm{Pt(H)_{ad}}] \rightarrow 3\mathrm{Pt} + \mathrm{H_2O} \quad (14)$$

favouring reaction (12) and (13) to take place at free Pt sites. The difference between the results from *Routine II* and *III* can be explained by the concentration dependence of H_2O_2 assuming that dilution (about 30–40%) of the initial H_2O_2 concentration cannot be avoided when methanol is introduced in the cell in *Routine II*.

In order to study the effect of H_2O_2 concentration, the experiments for $E_{ad} = 0.25$ V were repeated with a 0.1 M solution (not shown). Following *Routine I* the ion charge for adsorbate oxidation is 0.65×10^{-13} C cm^{-2}, i.e. more than 90% of the adsorbate formed at this potential is oxidised by H_2O_2. However, experiments involving the competition of methanol and H_2O_2 for the Pt sites show similar results for 0.1 and 0.01 M H_2O_2 (compare ion charges in Table 1).

3.4. *Interaction of adsorbates from C_2H_5OH with H_2O_2*

As for methanol, adsorption of ethanol on Pt was studied at different E_{ad} (E_{ad} = 0.20, 0.25 and 0.30 V). Two potential cycles up to 1.50 V are required for the complete oxidation of the residues.The electrochemical response of the adsorbate was followed by the signals for $m/z = 44$ and the ion charges for the single adsorption experiment are given in Table 1. Almost the same values for the integral of the CO_2 signals were obtained at the selected potentials. Therefore, in order to compare with methanol, $E_{ad} = 0.25$ V was chosen to study the influence of H_2O_2 on ethanol adsorbate oxidation.

Routine I was performed following the same procedure as that applied to carbon monoxide and methanol. In contrast to previous experiments, the potential was directly scanned in the positive direction after the final electrolyte exchange (see description of *Routines I* and *II* in Section 2.2.2), in order to avoid the partial reduction of the adsorbates [30]. The interaction of ethanol residues formed at $E_{ad} = 0.25$ V with H_2O_2 (Figure 4A and B dashed line), leads to a decrease of the ion charge for the mass signal $m/z = 44$ mass signal of 82% (Table 1).

Ethanol adsorption in the presence of 0.1 M H_2O_2 (Figure 4(C, D) solid line) results in a decreases of 39% of the ionic charge related to CO_2 production, whereas the competition between both C_2H_5OH and H_2O_2 produces only a diminution of 28% (see Table 1).

4. Discussion

From the results in the present work, it is concluded that dissolved H_2O_2 partially oxidises adsorbed CO, originally formed from dissolved CO or from CH_3OH and C_2H_5OH, at lower potentials than those required to enable reactions (6) and (7). In this potential range ($E < 0.40$ V), the electroreduction of H_2O_2 is the most favoured electrochemical reaction occurring and oxidation reactions (either chemical or electrochemical) would not be expected. Moreover, when these adsorbates are covering the Pt surface, a large cathodic current is observed in the *CV* in the presence of a solution H_2O_2 (Figure 1(A)), indicating that the electroreduction of hydrogen peroxide is still possible. This experimental fact has been previously observed for the O_2 electroreduction reaction [16, 17]. It is clear that H_2O_2 also requires free surface sites for the chemical oxidation of the carbonaceous adsorbates through reaction (1). The competition between CO, CH_3OH or C_2H_5OH and H_2O_2 for these centres is based on the difference between the adsorption free energies, the adsorption kinetics and the lateral interactions in the island formation of adsorbates.

In spite of previous results on $(CO)_{ad}$ oxidation [19] with 0.01 M H_2O_2, changes are observed when working with 0.10 M H_2O_2 in solution (Figure 2). In the dilute solution, the competitive adsorption of CO and H_2O_2 leads to the formation of a complete CO adlayer, which is chemical stable towards oxidation. In more concentrated H_2O_2 solution, reaction (1) takes place through a diffusion controlled access of H_2O_2 to Pt surface sites via the formation of $Pt(O)_{ad}$ species (through reactions (3) and/or (4)), even at high CO_{ad} coverages. This was enabled by the sufficient H_2O_2 intake to the electrode/electrolyte interface resulting from the high H_2O_2 bulk concentration. According to Henry's law and a Henry-constant for CO of $K_{CO} = 58.8 \times 10^8$ Pa [31] a maximum CO concentration at 25 °C and $p_{CO} = 0.1$ MPa of approx. 0.6×10^{-3} M can be estimated. Obviously, at high H_2O_2 concentrations, the competing adsorption equilibria between CO/Pt and H_2O_2/Pt is shifted towards a higher coverage of adsorbed oxygen species.

To understand this point, we have to make some comments about the adsorption and oxidation of CO at the electrochemical interface. The presence of water molecules and electrolyte ions were suggested to be in the CO adlayers [32]. Water species have also been detected at potentials as low as 0.05 V, which increases the effective surface coverage by $(CO)_{ad}$ compared with those obtained in UHV conditions [33–35]. Other experiments performed with Pt single crystals in 1 M sulphuric acid have shown that the O–H bond is weakened as a consequence of the strengthening of the Pt–O bond at potentials ca. 0.4 V [36]. Thus, it can be concluded that the progressive formation of Pt–O and Pt–OH adsorbates inside the CO adlayer promotes the chemical oxidation of the film at lower potentials. Accordingly, in the present study, the presence of H_2O_2, and consequently the formation of $(O)_{ad}$ species, produces this "pre-oxidation", which leads to the relaxation of the islands to less compressed states. Then, new H_2O_2 molecules are able to interact with the surface and the process is repeated.

Methanol and ethanol adsorbates interacting with dissolved H_2O_2 also showed a partial oxidation. In the case of methanol, after interaction with 0.1 M H_2O_2, almost all of the species are removed from the Pt surface applying *Routine I*, even at the maximum surface coverage formed at $E_{ad} = 0.25$ V, but only about 53% in 0.01 M H_2O_2 solution. It has been suggested that $(CO)_{ad}$ produced in reaction (13) also originates islands that partially blocked the surface for further methanol adsorption and oxidation [27]. These islands can be broken by surface defects, which allow atomic oxygen adsorption (reaction (4)). The increase of H_2O_2 concentration enhances the efficiency of the chemical oxidation reaction, as expected for a diffusion-controlled process according to reaction (2). However, it has to be mentioned that a small amount of residue is always present on the surface even for H_2O_2 exposure times larger than 10 min, which suggests the presence of traces of other adsorbates different from CO.

The electrochemical response for ethanol adspecies has been reported in the past three decades by many authors [20–22, 37–42]. However, the identification of other adsorbates than $(CO)_{ad}$ was first conducted with

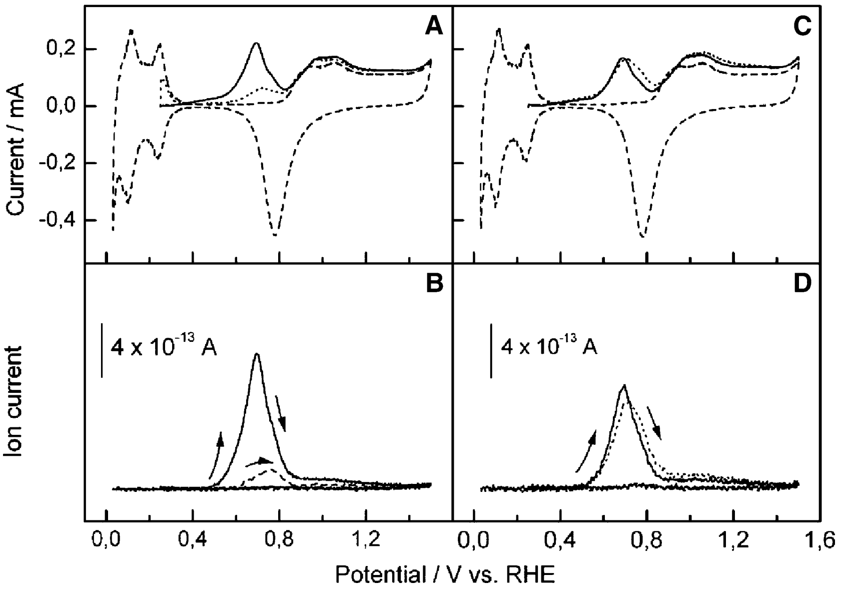

Fig. 4. Adsorption and oxidation of ethanol adsorbates formed on Pt at $E_{ad} = 0.25$ V during 5 min from 0.1 M ethanol; 0.1 M H_2O_2; $v = 0.01$ V s^{-1}; $T = 25$ °C; arrows indicate the potential scan direction. (A) *CVs* for the oxidation of the organic residues and (B) corresponding *MSCVs* for $m/z = 44$ $[CO_2]^{+}$ for the single adsorption of ethanol (solid line) and applying *Routine I* (dashed line). (C) *CVs* for the oxidation of the organic residues and (D) corresponding *MSCV* for $m/z = 44$ $[CO_2]^{+}$ applying *Routine II* (solid line) and *Routine III* (dotted line). *CV* of bare Pt in 2 M H_2SO_4 (dashed line).

the help of DEMS by Willsau and Heitbaum [37], finding a dissociative adsorption process. Moreover, a complete study was conducted through DEMS and FTIRS methodologies [20] to elucidate the nature of adsorbed intermediates and products in ethanol electroadsorption. Besides carbon monoxide adsorbates, ethoxy, ethylate and acetyl species have been detected on platinum in acid media, being oxidised within a different potential range [20, 22]. It was found that a single potential cycle is insufficient to desorb adsorbates from the platinum surface.

The presence of H_2O_2 also produces chemical oxidation of the carbonaceous adsorbates formed from ethanol. It is important to point out that two potential regions are distinguished during the oxidation of ethanol residues. In the presence of H_2O_2 the amount of ethanol adsorbates oxidised before the onset of platinum oxide diminishes, whereas the second contribution that is oxidised in the platinum oxide region increases. From infrared studies, it is known that the first feature is mainly related to linearly bound CO and the second to ethoxy ($-OCH_2CH_3$) and ethylate ($=C(OH)CH_3$) species [20]. The latter intermediates can be decomposed to CO and acetyl groups, and also partially lost in the form of methane, when a voltammetric incursion below 0.20 V is conducted. Thus, the cathodic scan starting from $E_{ad} = 0.25$ V was always avoided in any ethanol adsorption experience.

Similarly to methanol adsorbates, a species which cannot be oxidised by H_2O_2 is still present on the surface even when performing *Routine I* with large exposure times (larger than 10 min) in 0.1 M H_2O_2. This chemically non-oxidisable species is only removed by a second anodic potential cycling in the supporting electrolyte. Since it has been demonstrated from IR spectroscopy that CO is one of the adsorbates involved in methanol and ethanol adsorptions acting as poison, this is the adspecies from these compounds that can be oxidised by H_2O_2. It is remarkable that for ethanol residues the amount of adspecies still present on the electrode after interaction with H_2O_2 is rather higher, especially for *Routines II* and *III* (60–70%). Thus, it is concluded that the chemical nature of this "non-oxidisable" species is different from a simple CO-type adsorbate. It is likely these residues would be the C_2 oxygen-containing adsorbates or the partially oxidised species formed by the interaction of those residues with H_2O_2.

5. Conclusions

As already shown in a previous publication [19], on-line mass spectrometry is a powerful tool to distinguish electrochemical and non-electrochemical reactions taking place on an adsorbate covered Pt electrode in the presence of aqueous H_2O_2 solution. Furthermore, H_2O_2 may be used as a model substance for the investigation of CO mitigation and also for the air bleeding method, since in both cases adsorbed species like $(O)_{ad}$ are being formed.

The experimental findings are summarised as follows:

1. Adsorbed CO is completely oxidised from a Pt surface after interaction with H_2O_2 in 2 M sulphuric acid solutions when an appropriate concentration of H_2O_2 is used. Methanol and ethanol adsorbates are also chemically oxidised by H_2O_2 to CO_2.
2. The oxidation by H_2O_2 occurs at electrode potentials lower than those normally required for the electrochemically adsorbate oxidation on Pt.
3. The effect of H_2O_2 on CH_3OH and C_2H_5OH adspecies oxidation is dependent on H_2O_2 concentration and the adsorption potential. The experimental results indicate that, for ethanol species, other adsorbates (probably C_2-species), cannot be oxidised by H_2O_2.

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