

The influence of hydrogen peroxide on carbon monoxide electrooxidation at Pt/C and Pt:Ru/C electrodes

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Abstract Polymer electrolyte fuel cells constitute one of the most important efficiency energy converters for non-centralised uses. However, the use of fuels arising from reformat processes significantly lowers the current efficiency because of anodic catalytic poison coming from adsorbed carbon monoxide (CO_{ad}). In this work, the influence of the addition of hydrogen peroxide in the flow current is studied, considering the adsorption and electrochemical oxidation of carbon monoxide on carbon-supported Pt (20% Pt/Vulcan) and Pt:Ru (1:1, 20% Pt:Ru/Vulcan) catalysts in 2 M sulphuric acid. The investigation was conducted applying cyclic voltammetry and *on-line* differential electrochemical mass spectrometry. A series of experiments has been performed to investigate the influence of the temperature as well as the time of contact and the concentration of hydrogen peroxide. Oxidation of CO_{ad} to carbon dioxide occurs at lower potentials in the presence of

hydrogen peroxide. Moreover, it is possible to remove ca. 70% of CO_{ad} on Pt/C electrodes. On the other hand, for PtRu/C electrodes, similar charge values to those of Pt/C electrodes were obtained for the CO stripping, but the process occurs at more negative potentials. In this case, the effect of partial desorption for CO_{ad} by interaction with hydrogen peroxide is added to the bifunctional mechanism usually considered for this alloy.

Keywords Carbon monoxide · Hydrogen peroxide · DEMS · Pt/C · PtRu/C

Introduction

The direct methanol fuel cell (DMFC) represents a promise power source for stationary devices and vehicular transport because of the supply of large energy specific densities. However, the performance of these fuel cells needs to be enhanced, and the main problems are the irreversibility of the oxygen electroreduction reaction, the methanol crossover and the necessity of anodic surface reactivation because of poisoning of the catalyst surface [1, 2].

The electrooxidation of methanol on platinum in acid solution to carbon dioxide and partially oxidised products (HCHO , HCOOH and HCOOCH_3) is accompanied with the formation of strongly adsorbed intermediates. These species poison the catalyst surface and are considered as the main reason for the rather low reaction rate for methanol oxidation. However, the direct electrochemical methanol oxidation is an attractive option for fuel cell application [3]. The numerous studies concerning this electrochemical reaction have been summarised in several review articles [4–6]. A structural effect for methanol oxidation has been observed on low index platinum single crystals [7–11].

This paper is dedicated to Prof. Francisco Nart, in memoriam.

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Spectroscopic methods have been used to elucidate the structure of adsorbed intermediates formed in the mechanism. Adsorbed carbon monoxide (CO_{ad}) [12, 13] as well as COH, HCOH and H_2COH species [11, 14] have been detected on polycrystalline platinum. In situ infrared spectra on Pt(100), Pt(110) and Pt(111) reveal terminally bonded (on-top) CO as the major component of such an adlayer, although bridge-bonded CO is also formed on Pt(111) and Pt(100) [7–11]. For the latter face, inter conversion between CO species occurs in the 0.25–0.50 V potential range vs reversible hydrogen electrode (RHE) [11]. On Pt(111) and Pt(110), beside the detection of CO_{ad} , other hydrogenated adsorbed species such as HCO and COH have been observed [10, 11].

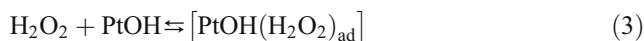
Stonehart [15] has firstly studied the reaction of methanol on unpoisoned polycrystalline platinum by means of cyclic voltammetry using a flow cell technique. During methanol catalytic electrooxidation on platinum, linearly bound carbon monoxide is recognised as the predominant adsorbate at high methanol concentrations and high degrees of surface coverage. On the basis of this knowledge, the elimination of adsorbed carbon monoxide and other possible residues is the main objective in most of the research in the DMFC field. Finally, it has to be considered that also the same problem concerns the development of polymer electrolyte membrane fuel cells (PEMFC), which employs hydrogen obtained from steam-reforming of hydrocarbons or the partial oxidation of alcohols [1, 2].

It was found that the injection of air into the fuel stream oxidises carbon monoxide to carbon dioxide, although the mechanism of this reaction is still unclear [16]. A similar methodology but with hydrogen peroxide also produces the removal of carbon monoxide: The addition of liquid hydrogen peroxide to the humidification water for the fuel gas improves the performance of a PEMFC using reformed methanol or H_2/CO as fuels [17, 18]. It is assumed that the heterogeneous decomposition of H_2O_2 with the formation of active oxygen takes place. In this way, adsorbed CO is oxidised chemically to CO_2 and the blocking of the hydrogen oxidation reaction at the anode avoided. It is demonstrated that a complete recovery of the CO-free performance is achieved for $\text{H}_2/100$ ppm CO [17, 18].

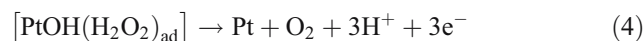
The mechanism of hydrogen peroxide reduction and oxidation on platinum has been extensively studied especially because this species are an undesirable intermediate in the oxygen electroreduction reaction at the fuel cell cathode [19–21]. Both hydrogen peroxide and oxygen are reduced on the platinum surface as follows:



On the other hand, hydrogen peroxide oxidation only occurs on oxidised platinum surfaces [22, 23]. This reaction is the result of a mechanism such as:



where PtOH sites represent the first stage of the surface platinum oxidation on which hydrogen peroxide begins to oxidise. The complex formed in reaction 3 undergoes an internal charge transfer finally leading to the decomposition of hydrogen peroxide:



As a consequence of the applied potential values, platinum is further oxidised to PtO. The same type of interaction between hydrogen peroxide and PtO instead of PtOH in reaction 3 and further oxidation similar to reaction 4 can be proposed.

Simultaneous oxygen electroreduction and methanol oxidation has been studied on carbon-supported platinum by potentiostatic regimes in sulphuric acid at 80 °C [22]. It was found that the two reactions proceed in parallel at the oxide-free platinum surface, i.e. in the 0.20 to 0.70 V potential range. It was also established, applying rotating disc electrode techniques, that methanol residues partially suppress the oxygen reduction current because of poisoning [23]. Besides, the methanol oxidation current is little affected by the presence of oxygen. This indicates that both reactions take place at different sites of the platinum electrode surface [23, 24]. It was concluded that 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 [22].

We have reported the influence of 0.01 M hydrogen peroxide on the adsorption and oxidation of carbon monoxide on sputtered platinum in 2 M H_2SO_4 [25]. It was observed that a 0.01 M hydrogen peroxide solution oxidises CO_{ad} to carbon dioxide at electrode potentials lower than those normally required in 2 M H_2SO_4 solutions, only when the CO_{ad} coverage is less than a monolayer. Besides, it has been proposed that the non-electrochemical hydrogen peroxide decomposition proceeds in the holes of the CO adlayer [25]. Recently, we have shown that at higher concentrations of hydrogen peroxide, it is possible to oxidise larger amounts of CO_{ad} and also methanol and ethanol adsorbed species [26]. It seems that for ethanol species, other adsorbates, such as methyl-containing species, are more difficult to be oxidised by hydrogen peroxide.

In a recent paper [27], the reactions of CO_{ad} on a carbon-supported platinum catalyst (20% Pt/Vulcan) with O_2 in a 2% O_2/Ar saturated electrolyte at 0.06 and 0.26 V were investigated by differential electrochemical mass spectrom-

etry (DEMS) under continuous flow conditions. By simulating the air bleed operation of a PEMFC anode with a CO-saturated Pt/Vulcan catalyst, it is found that the reaction is extremely slow, on the order of 10^{-5} s^{-1} . Only a very small fraction of the consumed O_2 is used for CO oxidation, while the major fraction reacts via the competing oxygen reduction reaction in a two-electron reaction to H_2O_2 . CO-stripping experiments confirm that at 0.06 V, O_2 reduction is possible even on a completely CO-saturated Pt/Vulcan catalyst at a rate limited by O_2 transport. At 0.26 V, the reaction rate is faster, by a factor of about 100 for the CO-saturated surface, but CO oxidation is still a minority reaction compared to O_2 reduction to H_2O or H_2O_2 . O_2 reduction can proceed only after partial CO_{ad} removal, either by reaction with O_2 or by CO stripping. The completely CO-covered catalyst is inert under these conditions [27].

Closely related to the present work is the study on the improvement of the CO tolerance in H_2/CO by adding H_2O_2 to the feed and subsequent decomposition of the H_2O_2 to O_2 in a flow reactor [18].

The aim of the present work is to study the interaction of hydrogen peroxide with the adsorbates obtained from carbon monoxide on carbon-supported Pt and PtRu catalysts in strong sulphuric media with the purpose to test if the behaviour previously observed for sputtered unsupported Pt [25, 26] is also present for the catalysts employed in PEMFCs. Ion currents for carbon dioxide together with faradic currents were followed as a function of the electrode potential to obtain cyclic voltammograms (CVs) and mass spectrometric cyclic voltammograms (MSCVs) applying DEMS.

Experimental

Chemicals and electrochemical set-up

All the solutions were prepared with Millipore-MilliQ* water and analytical grade chemicals. As supporting electrolyte, 2 M H_2SO_4 was used. Saturated CO (with and without 0.08/0.16 M H_2O_2) in the supporting electrolyte was employed as working solution. Ar (99.998%) was used for purging between the experiments through and over the working solutions. The cell was thermostated, and two temperatures were considered (20 and 60 °C).

The experimental set-up involves a flow cell containing ca. 2 ml solution, which enables complete electrolyte exchange under potential control. A micro porous polytetrafluoroethylene membrane interfaces between the electrochemical cell and the ion source of the mass spectrometer. For DEMS experiments, a thin-layer config-

uration is applied, and details of the electrochemical cell are given in [28].

Carbon-supported electrocatalysts (Pt and PtRu 1:1) from ETEK were used (particle size, 2–3 nm). The working electrodes were prepared by a suspension of 3 mg of E-TEK catalyst (20 wt% metal on Vulcan XC-72), 28.5 μl Nafion 5%w solution and 0.75 ml de Milli Q water. An aliquot from the suspension is deposited onto a glassy carbon electrode (0.28 cm^2 geometric area), resulting in a theoretical amount of 6.94 μg in the case of Pt/C and 11.5 μg Pt/Ru (5.7 μg Pt and 5.7 μg Ru) in the case of PtRu/C. However, it has to be taken in mind that the procedure is not completely reproducible (the content of the aliquot could vary depending on the homogeneity of the suspension). Thus, the electroactive area has to be determined for each electrode through the voltammetric charge within the hydrogen ad atom region for Pt/C, after double layer current correction divided by 0.77 [29], and from the charge involved in the CO stripping for PtRu/C electrodes [30]. The values obtained for the electroactive area were 0.6–2.2 cm^2 for Pt/C and 2.9–4.3 cm^2 for PtRu/C.

The experimental set-up allows the simultaneous acquisition of conventional CVs and MSCVs for selected masses. A carbon rod was used as counter electrode, and a RHE was used as reference. All the potentials in the text are referred to this value. The detailed description of the on-line mass spectrometry technique has been previously explained [25, 26].

Procedure

Previous to any measurement, the working electrode was cycled at 0.10 V s^{-1} in the supporting electrolyte between 0.03 and 1.1 V or 0.8 V for Pt/C and PtRu/C, respectively, recording the $m/z=44$ mass signal (carbon dioxide, $[\text{CO}_2]^\cdot+$), being m the mass and z the charge of the fragment, simultaneously to the CV. It was considered that the surface was clean when no potential dependence was observed for this signal.

Single adsorption experiments

After potential cycling in the base electrolyte, the potential was held at $E_{\text{ad}}=0.25$ V until the current reaches a stationary value. Then, the CO-containing solution was introduced into the cell during 600 s of adsorption and replaced by rinsing 300 ml of base electrolyte under potential control at E_{ad} . The CVs were recorded immediately afterwards for CO stripping at 0.005 V s^{-1} , starting from E_{ad} and scanning the potential in the negative direction down to 0.03 V (to check the coverage of the

surface by the adspecies), followed by a positive-going potential scan up to 1.10 V for Pt/C and up to 0.80 V in the case of PtRu/C. For DEMS experiments, after adsorption and electrolyte exchange, the electrode is located near the membrane, and the CVs and MSCVs for $m/z=44$ are acquired.

Combined adsorption experiments

In the case of the study of hydrogen peroxide influence on the adsorption and oxidation of CO on supported catalysts, three different routines were applied. As for the single adsorption, the potential was set to $E_{ad}=0.25$ V. Then, the following experimental procedures were applied:

Routine I: oxidation of CO_{ad} by hydrogen peroxide: At $E_{ad}=0.25$ V, the electrolyte was replaced by the CO-containing solution for $t_{ad}=600$ s. After washing the cell with the supporting electrolyte under potential control, 0.08 or 0.16 M $H_2O_2/2$ M H_2SO_4 was added during 600, 1,200 or 1,800 s (depending on the experiment). Finally, the solution was exchanged with the supporting electrolyte, and the electro-oxidation of the adsorbed species was followed by the CVs (and MSCV for the formation of CO_2 for DEMS studies). The potential is scanned at 0.005 Vs $^{-1}$ from E_{ad} firstly in the negative direction down to 0.03 V followed by a positive-going potential sweep up to 0.80 or 1.10 V for PtRu/C and Pt/C electrodes, respectively. The experience is repeated at different cell temperatures to check for its effect.

Routine II: adsorption of carbon monoxide in the presence of hydrogen peroxide: At $E_{ad}=0.25$ V, the electrolyte was replaced by 0.08 M $H_2O_2/2$ M H_2SO_4 . Then, the CO-containing electrolyte solution was introduced during $t_{ad}=600$ s. The solution was exchanged with supporting electrolyte, and the adsorbed species were oxidised as described in Routine I.

Routine III: simultaneous adsorption of carbon monoxide and hydrogen peroxide: At selected E_{ad} , the electrolyte was replaced by a combined working solution containing CO (saturated solution) in addition to 0.08 M H_2O_2 in 2 M H_2SO_4 during $t_{ad}=600$ s. The cell was washed with pure supporting electrolyte, and the anodic stripping of the residues were recorded as in Routines I and II. The experience is repeated at different cell temperatures to check for its effect.

In all procedures, successive oxidative potential cycles were carried out until the MSCV for a clean platinum surface was obtained. It has been observed that for the second cycle, potential independent CO_2 signals were recorded.

Results and discussion

Interaction of adsorbed carbon monoxide with hydrogen peroxide on Pt/C

In a previous work [25], it was found that 0.01 M hydrogen peroxide oxidises CO_{ad} only when the latter is covering platinum to less than a monolayer. It was concluded that free Pt sites were necessary for the oxygen adsorption produced from hydrogen peroxide, and therefore, a complete CO_{ads} monolayer cannot interact with H_2O_2 . Considering that the reaction of hydrogen peroxide at the platinum surface is diffusion-controlled, and therefore, there is an influence of its solution concentration on the oxygen adsorption process, we decided to check the effect of hydrogen peroxide concentration on a sputtered platinum surface completely covered by carbon monoxide [26]. It was proved that the complete monolayer is desorbed in determined conditions for a 0.1 M concentration of hydrogen peroxide. The maximum surface coverage for CO_{ad} was attained at $E_{ad}=0.25$ V [26], and this potential was selected for further studies, and it is also maintained in the present paper.

The electrochemical response of the adsorbate during the electrooxidation was followed by the CVs and MSCVs for $m/z=44$ ($[CO_2]^+$). As CO_2 is the sole electrooxidation product from the residues, the integration of the mass signal for $m/z=44$ in a whole potential cycle is used as a criterion for the evaluation of the relative coverage by the adspecies. These values are summarised in Table 1 for all experiments.

Direct oxidation of CO_{ad} at Pt/C in a thin-layer configuration is given in Fig. 1 (solid line). The widespread behaviour for the oxidation of CO at these materials is observed with the onset for the oxidation at 0.70 V, attaining a peak at 0.81 V. The same figure shows the results obtained after interaction of the adlayer with

Table 1 Integrated ion currents for $m/z=44$ signal ($[CO_2]^+$) obtained after adsorbate oxidation in 2 M H_2SO_4 at $T=20$ °C

| | Q (μC cm $^{-2}$) | Percent of CO monolayer oxidised by H_2O_2 |
|-------------------|----------------------------|----------------------------------------------|
| Pt/C | | |
| Single adsorption | $1.04 \cdot 10^{-4}$ | 0 |
| Routine I | $5.03 \cdot 10^{-5}$ | 52 |
| Routine II | $5.37 \cdot 10^{-5}$ | 48 |
| Routine III | $3.17 \cdot 10^{-5}$ | 69 |
| Pt:Ru/C | | |
| Single adsorption | $1.01 \cdot 10^{-4}$ | 0 |
| Routine I | $4.00 \cdot 10^{-5}$ | 60 |
| Routine II | $3.70 \cdot 10^{-5}$ | 63 |
| Routine III | $3.69 \cdot 10^{-5}$ | 63 |

The charge (Q) is referred to the real electrochemical area of the porous electrode and corrected by the cell constant in the DEMS study.

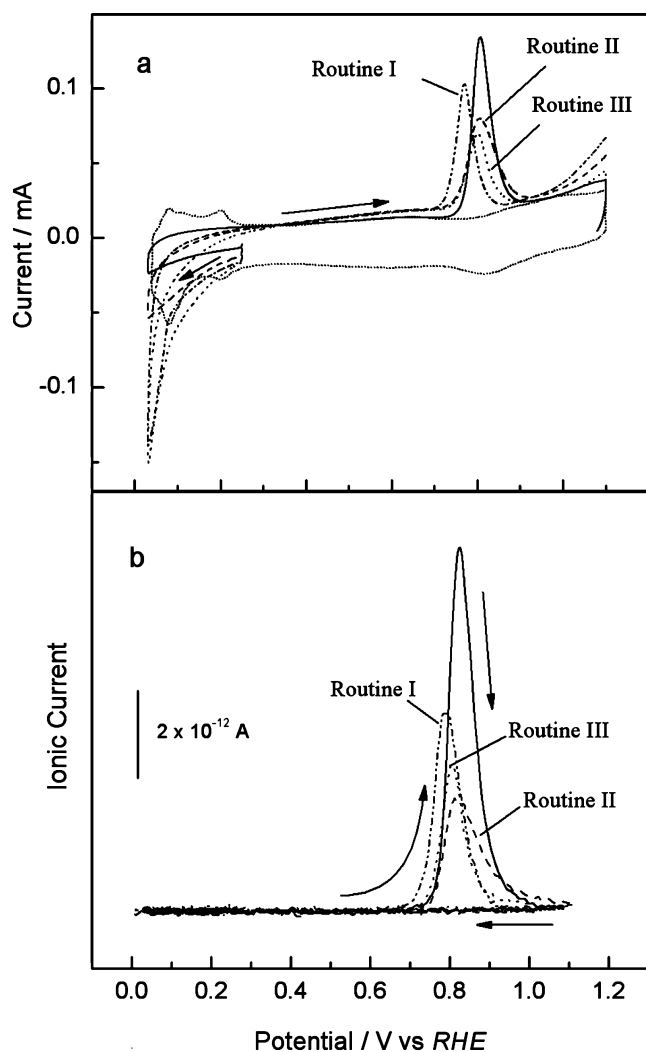


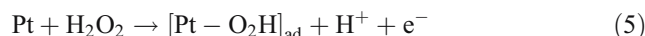
Fig. 1 Oxidation of CO_{ad} formed on Pt/C after adsorption during 600 s at $E_{\text{ad}}=0.25$ V. Thin layer configuration. **a** CVs and **b** MSCVs for $m/z=44$ $[\text{CO}_2]^+$ during the anodic stripping. The following procedures were applied: direct oxidation (solid line); Routine I (dashed-dotted line); Routine II (dashed line) and Routine III (dotted line). CV for Pt/C in the supporting electrolyte (short-dotted black line). Hydrogen peroxide concentration=0.08 M. Supporting electrolyte=2 M H_2SO_4 , $\nu=0.005$ V s^{-1} . $T=20$ $^\circ\text{C}$. Arrows indicate the scan direction. Electroactive area= 0.6 cm^2

hydrogen peroxide. Firstly, it is remarkable that in the corresponding CVs (Fig. 1a), larger double layer currents in the 0.40–0.70 V range and for $E>0.90$ V are observed in all cases probably because of the increase in O-groups at the carbon surface caused by its oxidation with hydrogen peroxide (no potential dependent signal for CO_2 is recorded in the MSCVs in Fig. 1b, indicating that the currents in the CVs are not related with the electrooxidation process of CO adspecies).

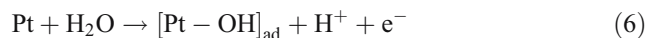
From the MSCV for $m/z=44$ in Fig. 1b (dashed-dotted-dotted line), it is established that a monolayer of CO_{ad} is desorbed to a 52% extent when it interacts with 0.08 M hydrogen peroxide (Routine I). This result allows the

conclusion that a decrease in the amount of adspecies through the interaction with hydrogen peroxide is also possible for supported Pt catalysts. Accordingly, the presence of free sites is not the unique determining factor in the interaction of the CO adlayer with hydrogen peroxide but also the concentration of the latter, as established before for sputtered Pt [26]. However, in the present case, the complete suppression of the adsorbate is not achieved for similar experimental conditions than in [26].

Information about the competition of CO and hydrogen peroxide for Pt sites can be obtained when hydrogen peroxide interacts with the surface before the adsorption of CO (Fig. 1, dashed line, Routine II). In this case, smaller amount of CO_{ad} is produced during adsorption in the presence of 0.08 M H_2O_2 , and the integration of the mass signal for CO_2 (Fig. 1b, dashed line) indicates a diminution of 48% of the residues. The results show that there is practically no difference between the amounts of CO_{ad} from Routines I to II, so the final coverage of the Pt surface is independent of the presence of hydrogen peroxide during CO_{ad} formation or after the monolayer adsorption. Besides, as Routine II involves the first interaction of hydrogen peroxide, the one responsible for the decrease in the CO_{ad} coverage should be different oxygen-containing species than that arising from water discharge. Therefore, the following reaction is proposed in the presence of hydrogen peroxide [31]:



And in the case of water:



The presence of peroxides species is responsible of CO_{ad} oxidation in Routine I and the decrease in CO_{ad} coverage in Routine II.

The competitive reaction is better studied applying a simultaneous adsorption (Routine III), because hydrogen peroxide and CO contact the Pt surface at the same time (Fig. 1, dotted line). The MSCV for $m/z=44$ (Fig. 1b dotted line) reveals that the final coverage by CO adsorbates is the lowest of all (Table 1). This means that there is a continuous synergetic effect between the constantly renovated presence of surface CO and HO_2 . Said in other words, there is always a source of hydrogen peroxide or carbon monoxide, where in Routines I and II, there is lack of one or the other.

The difference between the results from Routines II and III can be explained considering the importance of the concentration of hydrogen peroxide in this process, and assuming that dilution of the initial H_2O_2 concentration cannot be avoided in Routine II (because of the introduction of the CO-saturated solution; for Routine III, the

working solution could be exchanged several times to ensure the complete replacement of the base electrolyte).

The fact that the residues cannot be completely removed from the surface suggests that not only the requirement of free Pt sites for the interaction of hydrogen peroxide, but also sites available for the CO_{ad} oxidation process are needed. To get a deeper insight into this reaction, other adsorption potential can be used to involve lower coverages of CO adsorbates. This has been earlier performed using different electrode potentials for sputtered Pt [25], and even under these circumstances, a small contribution of CO_{ad} species was still apparent. In the present paper, the coverage decreases when the adsorption occurs from a solution containing both CO and hydrogen peroxide (Routine III). Therefore, at 0.25 V, the competition between heterogeneous hydrogen peroxide decomposition and the adsorption of CO results in the hindrance of CO_{ad} formation.

In the previous analysis, onset and peak potentials for CO_{ad} electrooxidation have not been discussed. Both onset and peak potentials depend not only on the CO coverage (a shift to more negative potentials is expected when the coverage is decreased) but also on the dimension of the CO islands formed at the surface [25], which could be different for the different routines even if the same coverage is obtained. On the other hand, it has to be considered that DEMS experiments have been performed in a thin-layer configuration, where the hindrance of diffusion can influence these potential values (but not the total amount of CO completely oxidised to CO_2 in one potential cycle).

To avoid the problems of the thin-layer configuration, conventional electrochemical measurements have been performed at 20 °C for Routines I and III, and the results are given in Fig. 2 (black lines). The onset potential is established at 0.73, 0.65 and 0.53 V for the direct electrooxidation, Routines I and III, respectively, and the peak potentials are shifted 0.04 and 0.10 V for the latter routines with respect to the direct electrooxidation. Therefore, two important effects are displayed: The presence of hydrogen peroxides partially inhibits the adsorption of CO on Pt/C and shifts negatively the potential for the oxidation of this adsorbate.

The influence of the cell temperature in the experiments is also reported here (Fig. 2, grey lines). The effect of increasing the temperature (from 20 to 60 °C) produces, as expected, the negative potential shift of the electrooxidation curves. The onset potential for direct CO_{ads} oxidation is shifted 0.15 V towards lower potentials. The charge involved in this stripping peak is higher than at 20 °C; however, from the CV in the hydrogen region, where an enhancement of the current related to the adsorption/desorption of hydrogen is apparent, it can be

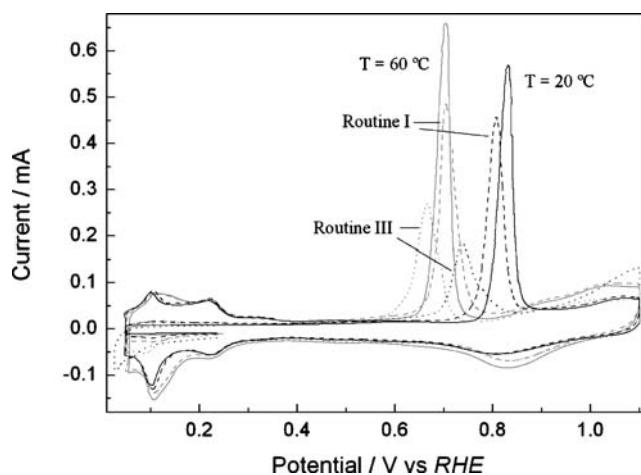


Fig. 2 Oxidation of carbon monoxide adsorbates formed on Pt/C at $E_{\text{ad}}=0.25$ V during 600 s, applying Routine I and III at different temperatures. Conventional configuration. Supporting electrolyte= 2 M H_2SO_4 , $v=0.005$ V s^{-1} . CVs (first and second cycle) for CO_{ad} direct electrooxidation on Pt/C (solid line) at $T=20$ °C (black) and 60 °C (grey); applying Routine I (dashed line) at $T=20$ °C (black) and 60 °C (grey) and applying Routine III (dotted line) at $T=20$ °C (black) and 60 °C (grey). Hydrogen peroxide concentration=0.08 M. Electroactive area=2.2 cm^2

concluded that an increase in the electroactive area of the electrode occurs, which justifies this charge. The effect of the interaction of CO residues with hydrogen peroxide at 60 °C is similar to that at 20 °C. As described before, the effect of hydrogen peroxide at room temperature produces also a potential shift to lower values, denoting a decrease in the adsorption strength of CO_{ads} to platinum. The potential shift of the peak value in the presence of hydrogen peroxide at 60 °C is lower, that is, a maximum shift of 0.04 V is recorded in comparison with the 0.10 V shift obtained at room temperature. In the case of Routine III, this effect is the lowest of all experiments (Fig. 2). The reason for this behaviour could be, firstly, that the shift of the onset and peak potentials with the coverage is less pronounced at 60 °C, and secondly, that the coverage at 60 °C is in all cases higher than at 20 °C, and accordingly, different values for the shift are expected at this temperature.

The next step in these studies was to elucidate if the residential time for hydrogen peroxide interaction plays a role on the amount of CO adsorbed on Pt/C (Fig. 3 for Routine III). No strong influence was observed. Thus, increasing the time of contact of the CO_{ad} layer with hydrogen peroxide 0.08 M from 600 to 1,800 s, the diminution in the amount of CO_{ad} is less than 10% (similar oxidation charges are obtained at 1,200 and 1,800 s), implying a saturation effect by hydrogen peroxide surface decomposition. Almost no shift in the onset as well as the peak potentials for CO_{ads} oxidation is observed in these experiments (Fig. 3).

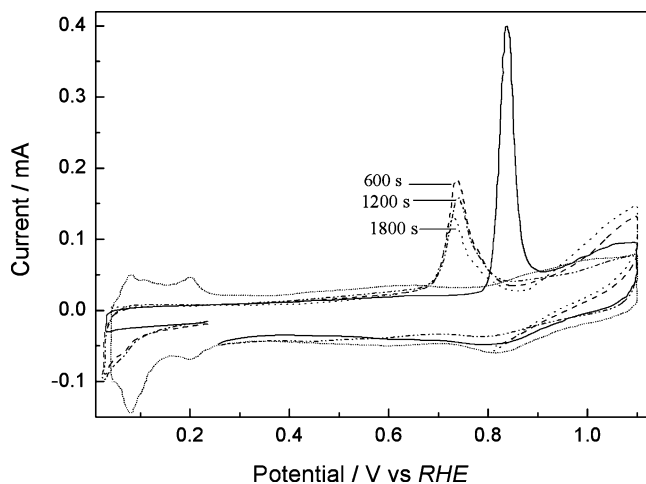


Fig. 3 Oxidation of carbon monoxide adsorbates formed on Pt/C at $E_{\text{ad}}=0.25$ V, applying Routine III at different adsorption times. Conventional configuration. Supporting electrolyte=2 M H_2SO_4 , $\nu=0.005$ V s^{-1} , $T=20$ °C. CV of Pt/C in the supporting electrolyte (short-dotted line). CVs for CO_{ad} electrooxidation on Pt/C in the supporting electrolyte (direct oxidation, solid line) and applying Routine III during 600 s (dashed line), 1,200 s (dashed-dotted line) and 1,800 s (dotted line). Hydrogen peroxide concentration=0.08 M. Electroactive area=1.0 cm^2

Interaction of adsorbed carbon monoxide with hydrogen peroxide on PtRu/C

The electrochemical response of the adsorbate during the electrooxidation in 2 M H_2SO_4 at room temperature was followed by the CVs and MSCVs for CO_2 (Fig. 4). Again, CO_2 is the sole electrooxidation product from the residues, and the integration of the mass signal for $m/z=44$ in a whole potential cycle can be used as a criterion for the evaluation of the relative coverage by the adspecies.

Direct electrooxidation of CO_{ad} at PtRu/C in the thin-layer configuration develops a peak centred at 0.50 V with an onset potential for the process at 0.37 V. The MSCVs in Fig. 4b clearly show that the same amount of adsorbed species are present on the surface independently of the routine applied for the interaction with hydrogen peroxide, attaining a decrease of approximately 63% with respect to the direct oxidation charge (this value is similar to the maximum one achieved for Pt/C only with Routine III).

CVs in a conventional cell were recorded to investigate the effect of the different procedures on the onset and peak potentials for CO stripping, avoiding the diffusion restrictions in a thin-layer cell. Results for Routines I and III can be seen in Fig. 5 for 0.08 M hydrogen peroxide. From the potentiodynamic responses arising from Routine I (dashed black line in Fig. 5) and Routine II (not shown), there is a significance broadening in the CO_{ads} oxidation peak for the adlayer obtained after interaction with hydrogen peroxide (Routine I) or during the adsorption in the presence of this compound

(Routine II) not observed for the simultaneous adsorption in Routine III (dashed gray line in Fig. 5)

In general, the effect of the interaction with hydrogen peroxide on the negative potential shift of the oxidation peaks is significantly lower for PtRu/C (ca. 0.03 V) than for Pt/C electrodes. However, it has to be said that a large shift (ca. 0.10 V) in the onset potential for CO_{ads} oxidation is established in the case of Routines I and II. This is very important for the application in a fuel cell because it means the removal of CO from the surface starts at very low potentials.

The importance of hydrogen peroxide concentration was demonstrated increasing the value to 0.16 M and repeating

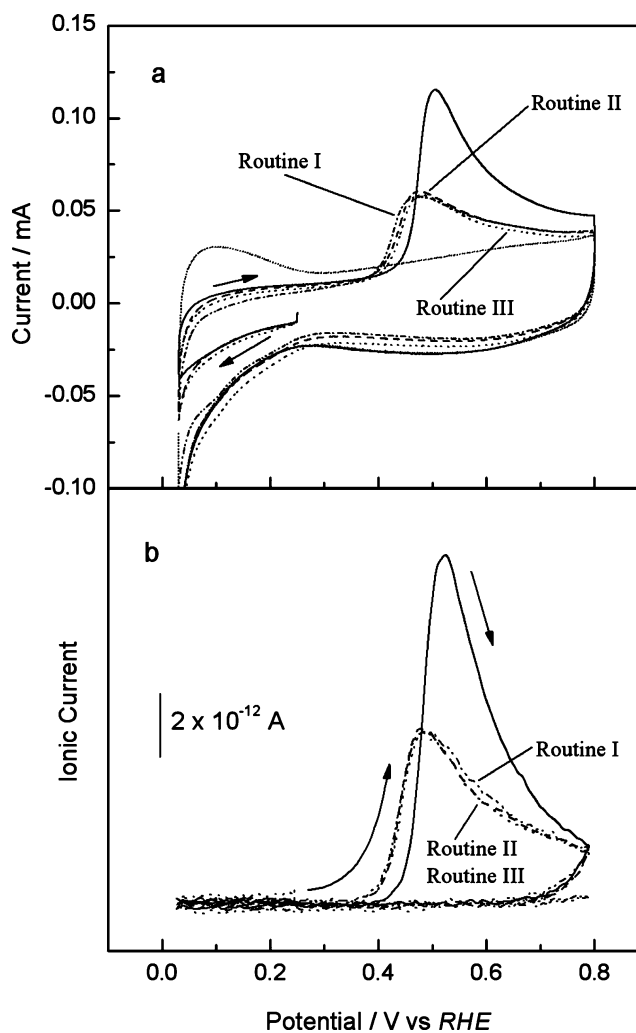


Fig. 4 Oxidation of CO_{ad} formed on PtRu/C after adsorption during 600 s at $E_{\text{ad}}=0.25$ V. This layer configuration. **a** CVs and **b** MSCVs for $m/z=44$ [CO_2] $^+$ during the anodic stripping. The following procedures were applied: direct oxidation (solid line); Routine I (dashed-dotted line); Routine II (dashed line) and Routine III (dotted line). CV for PtRu/C in the supporting electrolyte (short-dotted black line). Hydrogen peroxide concentration=0.08 M. Supporting electrolyte=2 M H_2SO_4 , $\nu=0.005$ V s^{-1} , $T=20$ °C. Arrows indicate the scan direction. Electroactive area=2.9 cm^2

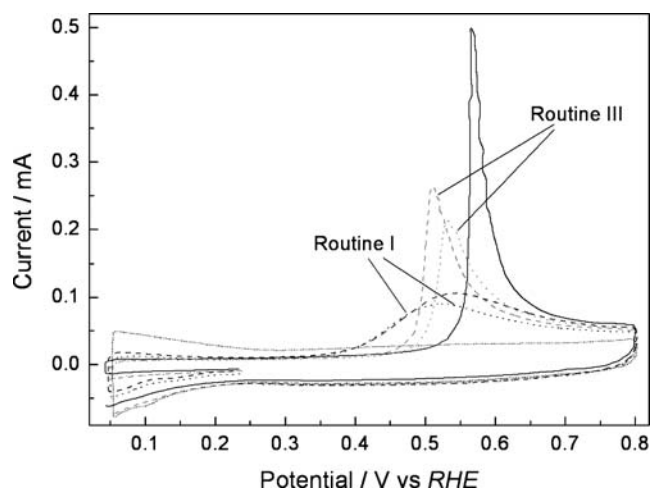
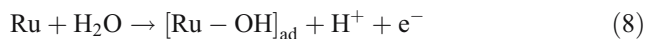
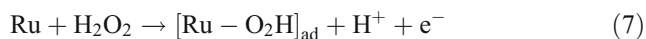


Fig. 5 Oxidation of carbon monoxide adsorbates formed on PtRu/C at $E_{\text{ad}}=0.25$ V during 600 s, applying Routine I and III. Conventional configuration. Supporting electrolyte=2 M H_2SO_4 , $\nu=0.005$ V s^{-1} . $T=20$ °C. CV for PtRu/C in the supporting electrolyte (short-dotted black line). CVs for CO_{ad} direct electrooxidation on PtRu/C (black solid line) and after applying Routine I (black) and III (grey) with 0.08 M (dashed line) and 0.16 M hydrogen peroxide (dotted line). Electroactive area= 4.3 cm^2

the experiments for $E_{\text{ad}}=0.25$ V (Fig. 5, dotted lines). A decrease of about 20% is observed in the amount of residues by increasing the concentration from 0.08 to 0.16 M H_2O_2 in Routine I, although the oxidation takes place in the same potential region. On the other hand, for the experiments involving the competition of CO and H_2O_2 for Pt/Ru sites (Routine III), the electrooxidation occurs at more positive potentials using the 0.16 M concentration than in the case of the 0.08 M, suggesting a more compact layer in the former case.

It has to be taken into account that the adsorption of CO occurs at room temperature at both Pt and Ru active sites. Therefore, both Ru and Pt appear as active sites, and the following reactions for Ru have to be considered in addition to Eqs. 5 and 6:



In this case, it can be also observed:



Together with the adsorption of CO on platinum:



In the case of PtRu/C catalysts, the bifunctional mechanism for CO oxidation has been earlier proposed by Watanabe and Motoo [32] and later demonstrated by many authors [33–37]. The interaction with hydrogen peroxide also produces, as in the case of Pt/C, a decrease in the

amount of adspecies and a negative shift for CO oxidation. Therefore, in addition to the bifunctional mechanism, the presence of O_2H species formed in Eqs. 5 and 7 also influences the CO oxidation reaction. The fact that these effects are less pronounced for PtRu/C than in the case of Pt/C catalysts could be explained assuming that reaction 5 but not Eq. 7 prevails in the alloy (and therefore, all metal atoms are not involved).

The electrochemical responses for similar experiments changing the solution temperature were also performed, which are depicted in Fig. 6 for room temperature (20 °C) and 60 °C. The comments here are similar to Pt/C electrodes: In this case, a ca. 0.06 V shift to lower onset potentials is observed at 60 °C and also a decrease in the amount of CO_{ads} oxidation charge after interaction with hydrogen peroxide.

In the absence of peroxide species, the width at half maximum ($w_{1/2}$) is significantly larger at 60 °C, i.e. 0.048 V at 60 °C compared to 0.025 V at 20 °C. The effect of the addition of peroxide species produces even higher values of $w_{1/2}$; for example, for Routine I, it increases from 0.054 V at 20 °C to 0.150 V at 60 °C. Finally, for Routine III, it increases from 0.042 V at 20 °C to 0.190 V at 60 °C. Said in other words, the increase in the values of $w_{1/2}$ after the contact with hydrogen peroxide can be explained by a constant interaction between the adsorbed species, that is, of the species arising from reactions 7 and 8 with Eq. 9. This means that there is a dynamic surface process coming from the surface mobility of $\text{Ru}-\text{O}_2\text{H}_{\text{ads}}$ and $\text{Ru}-\text{OH}_{\text{ads}}$ with $\text{Ru}-\text{CO}_{\text{ads}}$.

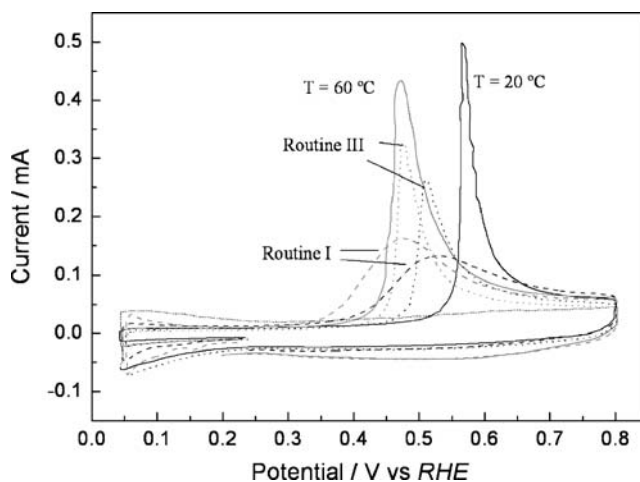


Fig. 6 Oxidation of carbon monoxide adsorbates formed on PtRu/C at $E_{\text{ad}}=0.25$ V during 600 s, applying Routine I and III at different temperatures. Conventional configuration. Supporting electrolyte=2 M H_2SO_4 , $\nu=0.005$ V s^{-1} . CV for PtRu/C in the supporting electrolyte (short-dotted black line). CVs for CO_{ad} direct electrooxidation on PtRu/C (solid line) at $T=20$ °C (black) and 60 °C (grey); applying Routine I (dashed line) at $T=20$ °C (black) and 60 °C (grey) and applying Routine III (dotted line) at $T=20$ °C (black) and 60 °C (grey). Electroactive area= 4.3 cm^2

The effect produced by the increment in the solution concentration of hydrogen peroxide is similar to increasing the time at which the hydrogen peroxide concentration is in contact with the electrode surface. Thus, the values of $w_{1/2}$ for Routine I increase from 0.074 V in 0.08 M to 0.138 V in 0.16 M concentration, whereas for Routine III change from 0.054 V to 0.198 V in 0.08 M and 0.16 M hydrogen peroxide solution concentration, respectively.

The results obtained on PtRu/C about the residual charge density of CO_{ads} oxidation are equivalent to those observed on Pt/C, but the onset potentials for CO_{ads} oxidation are nearly 0.30 V lower on PtRu/C than on Pt/C, coinciding with the early appearance of the OH_{ads} nucleating sites at Ru surfaces (ca 0.3 V lower than Pt) [32].

Conclusions

1. CO adsorbates can be oxidised by hydrogen peroxide to carbon dioxide on Pt/C electrodes in 2 M sulphuric acid solutions. This process occurs at potentials lower than those normally found at Pt/C in acid solutions free from hydrogen peroxide.
2. The effect of hydrogen peroxide is dependent on hydrogen peroxide solution concentration and contact time with CO adsorbates. These parameters need to be optimised to obtain the maximum efficiency when applied to a fuel cell.
3. Hydrogen peroxide addition in the fuel flow does not lead to a total inhibition of the carbon monoxide desorption peak, however, it allows the use of anodes more tolerant towards the catalytic poison. It was possible to remove ca. 70% of adsorbed carbon monoxide on Pt/C and PtRu/C electrodes.
4. In the case of PtRu/C electrodes, similar charge values for the CO stripping to those for Pt/C electrodes are obtained. However, the onset potential is 0.1 V more negative than the direct oxidation at PtRu/C (and therefore 0.40 V with respect to the direct oxidation at Pt/C), thus combining the bifunctional mechanism and the chemical effect of hydrogen peroxide. This is very important for the application in a fuel cell because it allows the removal of CO from the surface at lower potentials than the operational value in this device.

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