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On the open-circuit interaction between methanol and oxidized platinum electrodes

Elton Sitta · Hamilton Varela

Abstract In the present work, results of the interaction between methanol and oxidized platinum surfaces as studied via transients of open-circuit potentials are presented. The surface oxidation before the exposure to interaction with 0.5 M methanol was performed at different polarization times at 1.4 V vs reversible hydrogen electrode (RHE). In spite of the small changes in the initial oxide content, the increase of the pre-polarization time induces a considerable increase of the time needed for the oxide consumption during its interaction with methanol. The influence of the identity of the chemisorbing anion on the transients was also investigated in the following media: 0.1 M $HClO_4$, 0.5 M H_2SO_4, and 0.5 M H_2SO_4+0.1 mM Cl^-. It was observed that the transient time increases with the energy of anion chemisorption and, more importantly, without a change in the shape of the transient, meaning that free platinum sites are available at the topmost layer all over the transient and not only in the potential region of small oxide 'coverage'. The impact of the pre-polarization time and the effect of anion chemisorption on the transients are rationalized in terms of the presence of *surface* and *subsurface* oxygen driven by place exchange.

Keywords Methanol oxidation · Platinum oxide · Open-circuit potential transients

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Introduction

Methanol is certainly one of the most promising organic molecules to be used in large-scale fuel cell systems. Given its importance in energy conversion devices such as the direct methanol fuel cell (DMFC) [1–3], the methanol electrooxidation reaction has been extensively studied in the last decades. Problems concerning the high overpotential and the existence of parallel reaction pathways present in this reaction makes its understanding a very challenging task. From the fundamental side, studies have been carried out on both polycrystalline and single crystals surfaces by means of different electrochemical approaches sometimes coupled to auxiliary in situ and on line techniques [4–16]. Such studies have been mainly devoted to the understanding of: (1) the relationship between reaction rate and applied potential; (2) the impact of the interfacial structure on reaction rate and selectivity; (3) the nature and geometry of adsorbates; (4) the effect of composition and concentration of methanol and supporting electrolyte; (5) the role played by anion chemisorption; (6) the nature of strongly and weakly bonded reaction intermediates, etc. However, in spite of the considerable amount of mechanistic information available, many aspects associated to methanol electrooxidation including kinetic instabilities [17–20] (Martins AL, Varela H, 2007, manuscript in preparation) are still to be explained.

More applied studies have also been taken to establish the interactions between the anode, membrane, and cathode in a DMFC. The membranes usually employed in DMFCs are optimized for proton conduction and are not efficient regarding methanol blocking. As a consequence, methanol molecules are transported from the anodic to the cathodic compartment by diffusion, due to a concentration gradient, and to a lesser extent [21], by electro-osmosis, owing to

proton migration through the membrane. This problem has been referred to as methanol crossover and represents a severe limitation to the effective use of DMFC, once the presence of methanol at the cathode results in a mixed potential and an overall performance decrease [2, 22, 23].

A simple but useful method to investigate the effect of methanol crossover consists of studying the interactions of methanol with oxidized surfaces under open-circuit conditions [21, 24, 25]. Oxley et al. [26] in the 1960s studied the effect of methanol in oxidized platinum black surfaces in 5 N sulfuric acid and observed that at high temperature (in the range of 60 °C), methanol is spontaneously decomposed with gas evolution. The authors infer that these gases would be CO_2 and H_2. In a series of papers, Podlovchenko et al. [27–32] studied the transients of the open-circuit potential resulting to the interaction of some HCO compounds with oxide-covered platinum surfaces. The method consists of performing a fast cathodic sweep (1 to 3 Vs^{-1}) starting at different potentials along the transients and allows at calculating the oxygen coverage as a function of potential [27, 28]. In most cases, the authors studied the effect of the identity and concentration of the organic concentration and of the electrode roughness on the transients. Specifically in the case of methanol [32] interaction with one "monolayer" (ML) of oxide-covered smooth platinum surface, the authors identified an initial region between 1.1 and 0.86 V vs RHE (from hereon all potentials are quoted with respect to the reversible hydrogen electrode, RHE) in which the oxygen coverage would decrease from 1 to 0.8 ML and corresponds to the major part of the transient. Along this region, the oxygen consumption would be achieved by direct interaction with methanol present at the reaction plane. After that, a second region in which the potential drops very fast from 0.86 to 0.68 V corresponding to a decrease in the oxygen coverage from 0.8 to 0.2 ML is observed. In this region, oxide consumption is mainly attained by the mechanism of "conjugated reactions" in which the electrochemical oxidation of methanol is coupled to the reduction of oxygen [32].

The present contribution aims at studying some aspects of the platinum oxide consumption during its interaction with methanol under open-circuit conditions. The study is conducted in terms of the transients of the open-circuit potential and two, previously unreported aspects are investigated: the impact on the transients of (a) the pre-polarization time in which the electrode was kept at 1.4 V to form the oxide layer and (b) of the anion chemisorption.

Experimental

Solutions were prepared using Millipore® water (18.2 MΩ. cm), methanol (chromatography grade, J. T. Backer®),

perchloric acid (Suprapur 70–72% Merck®), sulfuric acid (PA 98%, Mallinckrodt®), and chloride acid (36–38 % Mallinckrodt®). The working electrode was a platinum flag of 0.52 cm^2 in geometric area and roughness factor of 2.8. The counter electrode was a platinum sheet with high active area. A RHE prepared either with sulfuric or perchloric acid with identical concentration than that used in the supporting electrolyte served as reference electrode. An Autolab® potentiostat model PGSTAT3002 equipped with the Scan-Gen module (analog scan generator) was used. Before each experiment, the solution was purged with nitrogen (99.996%, White Martins®), and during all experiments, a nitrogen atmosphere was kept. All experiments were carried out at room temperature (25±1 °C).

Before each experiment, the working electrode was cycled between 0.05 and 1.3 V at 100 mVs^{-1} for about 100 cycles. After this voltammetric treatment, the platinum oxide layer was formed according to the following procedure: the electrode was initially polarized at 0.05 V for about 20 s, jumped to 1.4 V, and kept at this potential during a certain time t_P. At this point, the circuit was opened and a sufficient quantity of methanol to yield a final concentration of 0.5 M was injected in the cell. In all transients presented, the injection corresponds to $t=0$. The mass transport of the injected methanol was facilitated by means of a rotating Teflon-coated bar placed at the bottom of the cell. A magnetic stirrer (Marconi MA-089) was employed and a rotation speed of 720 rpm kept in all experiments in which methanol was injected.

Results and discussion

Oxide formation

The procedure adopted to quantify the amount of oxide formed during the pre-polarization at 1.4 V is illustrated in Fig. 1a. The resulting cathodic profiles (and also an anodic one for comparison) are displayed in Fig. 1b. The general features of the cyclic voltammograms are in agreement with that expected for a clean platinum surface and a well-controlled electrochemical environment. The main effects of increasing the pre-polarization time, t_P, at which the electrode potential was kept at 1.4 V are the increase in the reduction charge during the negative going sweep and the shift of the reduction peak potential toward less positive values. Moreover, in the range of t_P employed in this study, the reduction peak (named OC1 by Conway et al. [33]) is likely to be a signature of a single event, in contrast to that observed during the positive going scan where a very broad region is seen. The existence of a single reduction peak is observed up to the limit of an oxygen content of 2 ML and reflects the presence of a quasi-2D structure. All these
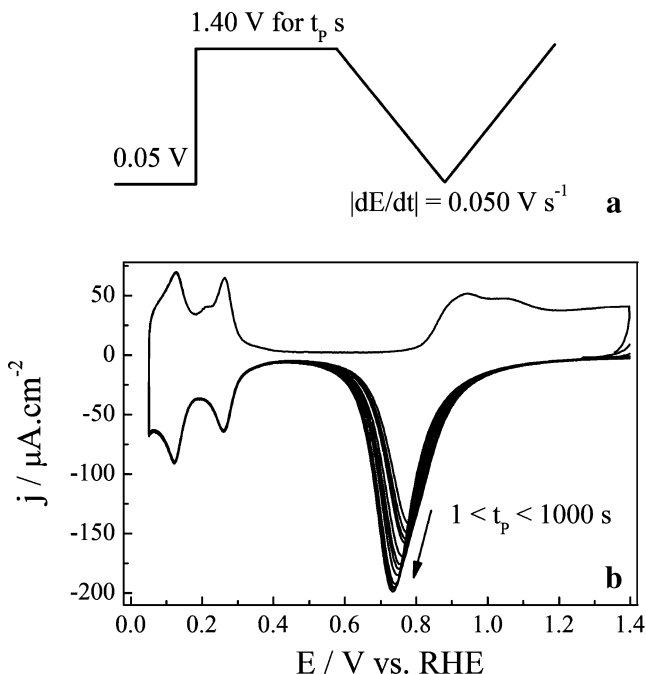
Fig. 1 a Potential program to grow the oxide layer and measure its content, and **b** the resulting cathodic profiles during oxide reduction. Electrolyte: 0.5 M H_2SO_4

observations are known for a long time [34–36] and are presented in this paper for the sake of completeness, as they will be important in the discussion that follows.

The amount of oxide formed at 1.4 V was calculated by considering the oxidation charge of two electrons per platinum atom to form PtO (vide infra) and the following relation:

$$\theta_O = \frac{q_O}{2q_H}$$

where θ_0 is the initial amount of oxide in monolayers (ML), q_O is the oxide reduction charge, and q_H is the charge obtained in the region of overpotential deposited hydrogen, as obtained under voltammetric conditions. The resulting initial oxide content as calculated by the reduction charge obtained under voltammetric conditions varied from 1.15 to 1.44 (±7%) ML. In both cases, the double layer contribution was subtracted from the q_o and q_H calculated values. Polarization times up to 3,600 s were used when $HClO_4$ was used as supporting electrolyte, similar profiles to that presented in Fig. 1b were obtained, and θ_0 ranged from 1.14 to 1.46 (±7%) ML. As will become clear in the discussion below, the term oxide content instead of oxide coverage will be used when referring to the total amount of oxide formed, which in turn, is divided into *surface* and *subsurface* oxygen states.

The influence of the pre-polarization time

Figure 2 shows the transients of the open-circuit potential during oxide consumption after methanol injection in a 0.5 M H_2SO_4 aqueous solution. Using the procedure just

described, oxide covered surfaces were obtained at 1.4 V and at different pre-polarization times. After that, the electrode was subjected to interaction with added methanol. As a blank, the dotted line (curve 7′) shows the transient in the open-circuit potential for the surface prepared with a $t_P = 1,000$ s but, in contrast with curve 7, in the absence of methanol. As expected, the comparison of this blank with curves 1 to 7 confirms the fact that changes in the open-circuit potential are solely due to the interaction with methanol. Immediately after the methanol injection the potential drops to values of ca. 1.1 V and remains in an intermediate potential region between 1.0 and 0.85 V. After that, the open-circuit potential suddenly drops to values of about 0.2–0.3 V, which, under these conditions, corresponds to a signature of an oxygen-free platinum surface. Afterwards, a further slow potential increase up to an equilibrium value of ca. 0.45 V is attained at about 100 s. This final state does not depend on the pre-polarization time and is still far below the value corresponding to the mixed potential observed in presence of oxygen [21]. For comparison, in a DMFC, the open-circuit potential is known to be reduced by ca. 200 mV due to the formation of a mixed potential at the cathode after interaction with methanol.

As clearly seen in Fig. 2, the time required for the initial potential decrease, i.e., the abrupt drop after methanol injection, has a weak dependence on the pre-polarization time, and in any case, most of the time is spent in the intermediate potential range (from ca. 1.1 to 0.85 V). The time between the methanol injection and the sudden drop after this *intermediate region* is referred to as τ and is found to increase with the pre-polarization time. Values for τ of about 5 and 60 s for methanol concentrations of 0.4 and 2 M and were reported by one of us (E. Sitta) in a rather
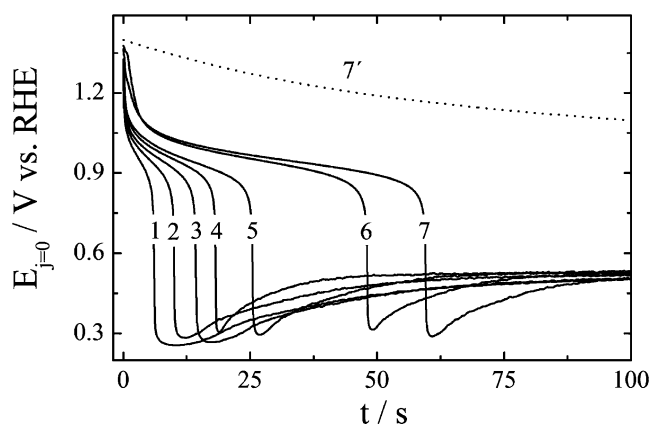

Fig. 2 Transients of the open-circuit potential during methanol interaction with oxide-covered platinum surface. The supporting electrolyte was 0.5 M H_2SO_4, and at $t=0$, methanol was injected, yielding a concentration of 0.5 M. The platinum surface was oxidized during pre-polarization at 1.4 V for $t_P = 1$ *1* s, *2* 5 s, *3* 15 s, *4* 50 s, *5* 100 s, *6* 500 s, and *7* 1,000 s. The *dotted line*, curve 7, shows the transient for $t_P = 1,000$ s but without methanol injection
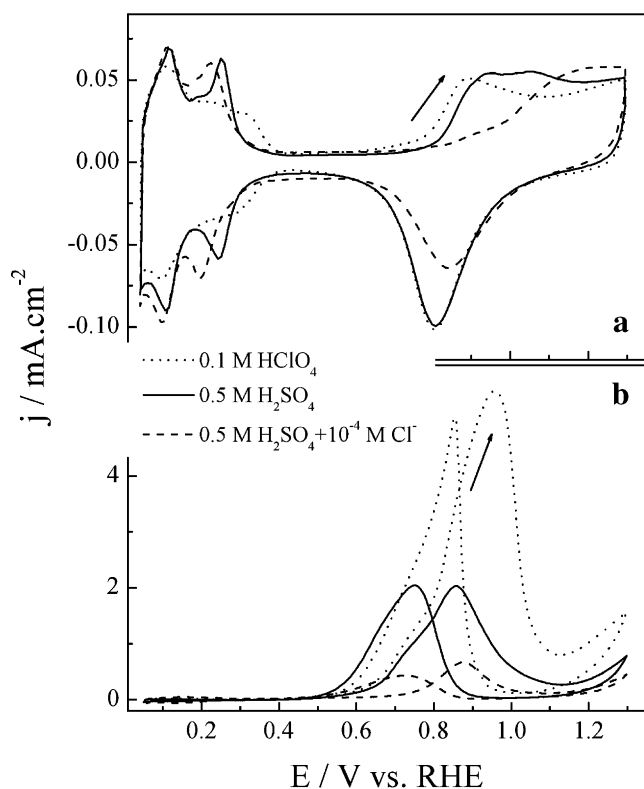
Fig. 3 Cyclic voltammograns for polycrystalline Pt in **a** 0.1 M HClO$_4$ (*dotted line*), 0.5 M H$_2$SO$_4$ (*full line*), and 0.5 M H$_2$SO$_4$+10^{-4} M Cl$^-$ (*dashed line*); and **b** with 0.5 M MeOH. Sweep rate=0.05 V s^{-1}

comparable situation [21]. Studies of the interaction between methanol and oxide-covered platinum surface under relatively similar conditions were carried out by Podlovchenko et al. [32]. Their experiments were performed with a polycristaline platinum electrode and in 0.5 M H$_2$SO$_4$ supporting electrolyte as in the present case. The authors varied the methanol concentration and kept the oxygen 'coverage' at 1 ML. Under those conditions, values for τ were found to lie in the range between about 1,000 and 5,000 s for methanol concentrations between 0.1 and 0.01 M. As in the present case, most of the time in the interval $0<t<\tau$ was spent in the intermediate potential region (from 1.1 to 0.85 V), and nearly no appreciable change in the time for the initial potential decay was detected for different methanol concentrations. Previous results also indicate that the *initial potential drop* is nearly independent on the nature of the organic species [27–32]. In fact, the dissimilarities between the transients of the open-circuit potentials when an oxide-covered surface interacts with an organic C1 molecule, be it formaldehyde, methanol, or formic acid, occur in terms of the time during the slow potential drop in the intermediate region. Likewise, τ increased in the following sequence: CH$_2$O<HCOOH< CH$_3$OH, under otherwise identical conditions [27–32]. Specifically in the case of the interaction of 0.02 M of methanol with a nominal oxide 'coverage' of 1 ML,

Podlovchenko et al. [32] described the initial region between 1.1 and 0.86 V as equivalent to a change in the oxygen coverage from 1 to 0.8 ML. Along this region, the oxygen consumption would be achieved by direct interaction with methanol at the reaction plane in the so-called Eley–Rideal (ER) mechanism [37–39].[1] After that, a second region in which the potential drops very fast from 0.86 to 0.68 V corresponding to a decrease in the oxygen coverage from 0.8 to 0.2 ML is observed. In this case, the oxide consumption is mainly attained by the mechanism of "conjugated reactions" in which the electrochemical oxidation of methanol is coupled to the reduction of oxygen [32].

As already mentioned, the variation of the oxide content formed before the interaction with methanol is rather small, cf. 1.15 to 1.44 (±7%) ML. Therefore, it is believed that the considerable effect evidenced in the transient times shown in Fig. 2 reflects not only the difference in the oxygen content but also in the pre-polarization itself. In other words, the increase of t_P not only increases the oxide content but also makes the reduction owing to its interaction with methanol more difficult. This argument is based on the phenomena of place exchange observed during the pre-polarization time and will be further discussed below.

The influence of anion chemisorption

Taking the advantage of the competition for free platinum sites between methanol, or its residues, and anions present in the supporting electrolyte, further insight into the mechanism underlying the interaction between methanol and the oxide covered platinum surface can be provided by recording the open-circuit transients in the presence of anions with different energy of chemisorption. To do so, the following species in the order of its chemisorption strength on platinum surface were investigated: Cl$^-$ > SO$_4^{2-}$ > ClO$_4^-$. The impact of the different anions on the system's behavior can be initially approached in terms of the voltammetric profiles in the supporting electrolyte, as shown in Fig. 3a. In these cyclic voltammograms, it is clearly seen that the onset of oxide formation is considerably retarded to more positive potentials as the energy of chemisorption increases. This can be interpreted as the anion chemisorption becomes more favored than the surface oxidation, or O^{2-} chemisorption, vide infra, as the chemisorption strengths. As a consequence, the surface oxidation is postponed to more positive potentials in the sequence of Cl$^-$ > SO$_4^{2-}$ > ClO$_4^-$. As a result, the

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[1] This mechanism is often referred to as Eley–Rideal [10] by the electrochemistry community, but the terms Rideal–Eley [38, 39] and even Langmuir–Rideal [37] are also found in some classical texts.
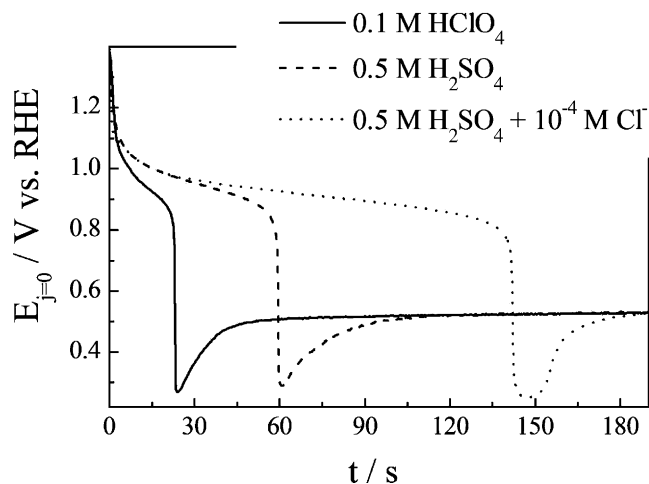
Fig. 4 Transients of the open-circuit potential during interaction between an oxidized platinum surface (t_P at 1.4 V for 1,000 s) and 0.5 M methanol in 0.1 M HClO$_4$ (*full line*), 0.5 M H$_2$SO$_4$ (*dashed line*); 0.5 M H$_2$SO$_4$+10^{-4} M Cl$^-$ (*dotted line*). The chloride ions was injected with together with methanol at $t=0$

amount of oxide formed, under otherwise the same conditions, decreases in the presence of strongly chemisorbing anions. This is more transparent in the case of chloride ions, as evidenced in the reduction charge in the negative going scan. The effects of competitive chemisorption of chloride ions on the initial stages of platinum oxide formation under voltammetric conditions have recently discussed by Jerkiewicz et al. [40] and Conway et al. [41]. Finally, it can be seen that anion chemisorption occurs already at rather low potentials as observed in the squeezing of the hydrogen OPD/UPD regions.

The presence of different anions in the electrolyte strongly affects the methanol eletrooxidation, as given in Fig. 3b. Overall, the competition for free platinum sites between methanol and chemisorbing anions primarily results in a current decrease when sulfate and chloride species are added. The maximum current density reached in the presence of chloride ions is smaller than 1 mAcm^{-2}, whereas when perchloric acid is used as supporting electrolyte, this maximum is almost 5 mAcm^{-2} for the same alcohol concentration. When only sulfuric acid is used as supporting electrolyte an intermediate current density of about 2 mAcm^{-2} value is observed. The impact of anion chemisorption on methanol electrooxidation has been extensively reported in the literature [14, 42–44]. In most cases, the activity decrease accompanies the trend in the increase of the energy of chemisorption of anions. The anion chemisorption can even completely inhibit methanol adsorption and further oxidation in a certain range of applied potential. Sobkowski and Wieckowski [42] reported that in a 0.5 M H$_2$SO$_4$ solution, addition of 2 mM of chloride ions is enough to completely suppress methanol adsorption.

The interaction between the oxide covered platinum surface and methanol was studied in perchloric acid and in sulfuric acid with a small amount of chloride ions. As already mentioned, the presence of chloride ions is known to influence the oxide formation [40, 41] due to its strong chemisorption on platinum sites and consequent site blockage. To circumvent this difficulty when studying the influence of chloride ions, the pre-oxidation step was carried out under identical conditions as those employed in the experiments using only sulfuric acid (see Fig. 2), and after that, a solution containing methanol and chloride ions was injected and the transients registered. To give an example of the anion influence on the platinum oxide consumption, Fig. 4 depicts the transients for a surface initially subjected to a pre-oxidation at 1.4 V for (t_P=) 1,000 s. Overall, the shape of the potential decay is very similar in the three cases and the increase in the time τ follows the energy of chemisorption of the anions present in the electrolyte. As observed for sulfuric acid and different t_P depicted in Fig. 2, the time spent in the initial potential drop is very similar in the three cases, i.e., irrespective of the anion present in the electrolyte, and the main contribution to τ is the time spent during the slow drop in the intermediate potential region.

The results of τ as a function of t_P for the transients of the open-circuit potential in the presence of different anions are summarized in Fig. 5 in a bi-log plot. As exemplified in Fig. 4, for all pre-polarization times used, τ increases accompanying the increasing in the anion chemisorption strength. In this representation, a nearly linear relationship is observed in case of perchloric and sulfuric acid. The considerable scattering observed when chloride ions are added might be due to its high energy of chemisorption and probably also to the fact that, in this case, chloride ions are
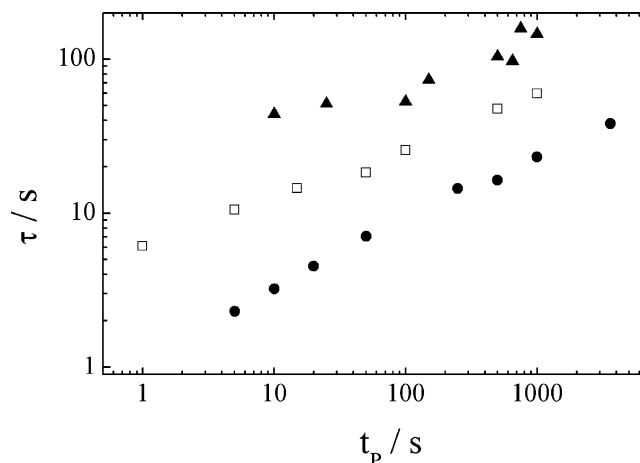

Fig. 5 log–log dependence of τ with the pre-polarization time t_P, in the following electrolytes: 0.1 M HClO$_4$ (*filled circles*), 0.5 M H$_2$SO$_4$ (*open squares*), and 0.5 M H$_2$SO$_4$+10^{-4} M Cl$^-$ (*filled triangles*)

not initially present but are added together with methanol and, at this concentration, might be influenced by transport limitations. The results are reproducible and variations in τ under identical conditions were within 5% range.

The fact that the time for the oxide consumption becomes longer with the increasing of energy of chemisorption of anions implies that free platinum sites are available for anion chemisorption along the transients of the open-circuit potential. In fact, an important point to be stressed here concerns the similarities observed in the shape of the transients of open-circuit potential, nearly irrespective of the identity of the chemisorbing anions. In other words, the general features of the potential decay profiles are preserved and basically only a change in the duration of the transient is observed. This observation can be interpreted as an evidence that the site blocking owing to anion chemisorption occurs all over the transient and not only in restricted potential region. According to the scenario described by Podlovchenko et al. [32], the slowest part of the potential decay (from 1.1 to 0.86 V) is connected to the decrease in the oxygen 'coverage' from 1 to 0.8 ML. As anion chemisorption is negligible on PtO sites, the increase of the transient time τ when anions with higher energy of chemisorption are added implies that anion chemisorption competes for available free platinum sites with methanol and its residues during the transient of the open-circuit potential. Moreover, it is very likely that this competition occurs all over the transients and not only in regions of smaller oxygen coverage (for instance, in the range between 0.8 and 0.2 ML) which, according to reference [32], would correspond to the fast transition from ca. 0.86 and 0.68 V. As further discussed below, due to the *process of place exchange*, part of the oxide is composed by *subsurface* oxygen ,and free platinum sites are always available for anion and methanol chemisorption. Place exchange assures that a full carpet of chemisorbed oxygen is never present and, up to at least, an oxidation level of about 2 MLs of PtO (i.e., a charge of 840 mC cm^{-2}), only a fraction of a ML is actually exposed at the topmost layer. The additional oxygen stays as subsurface species and is slowly expelled from the platinum metallic lattice as reduction proceeds. Therefore, the oxide coverage as a function of potential, as estimated by Podlovchenko et al. [32] must be interpreted as the whole amount of oxide which in turn is composed by subsurface and surface oxygen. Aiming at making this argument more transparent, the mechanism of platinum oxide formation is briefly reviewed in the next subsection.

Place exchange and mechanistic considerations

In contrast to earlier beliefs, it has been recently stated that the oxidation of a platinum surface proceeds directly to PtO without the intermediate PtOH [45–48]. In this way, the platinum oxide formation proceeds through the direct discharge of water molecules forming PtO,

$$Pt + H_2O \rightarrow Pt - O + 2H^+ + 2e^-. \tag{1}$$
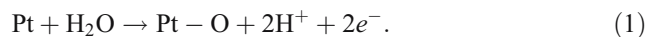
Further surface oxidation occurs via a 'post electrochemical' process called place exchange, in which platinum atoms move out of their lattice positions driven by the electrochemical potential gradient across the metal/electrolyte interface [34, 36, 49], schematically,
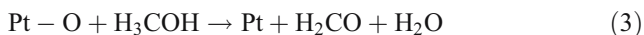
$$Pt - O \rightarrow O - Pt. \tag{2}$$

Step 2 has been assigned by Bockris et al. [50] as being the rate determining one during the oxide formation. The place exchange process occurs as a prerequisite to the further surface oxidation and is known to happen as early as when just a small fraction of monolayer is complete. Under voltammetric conditions, this fraction can be quantified in terms of the size of the potential window in which the anodic and cathodic profiles remain symmetrical, i.e., the extent in which no hysteresis between positive and negative going sweeps is observed. Thus, as hysteresis in the voltammetric sweep is already observed for an oxidation charge equivalent to an oxygen content of about 10% of a ML [49], it can be inferred that this content would correspond to the amount of surface oxygen, and up to moderate oxidation level of, say 2 ML, this amount remains more or less constant, immaterial to the total oxygen content.

Along with the hysteresis, the effect of the irreversibility involved in the steps of oxide formation and reduction is also associated with the trend observed in some noble metals in which the longer the time for which the oxide has been formed, the lower is the potential required for its electrochemical reduction [33], as already seen in Fig. 1b. Accordingly, increasing the pre-polarization stage implies an increase in the stability of the oxide layer formed, which is reflected in the transient duration. Although this argument already suffice to indicate the impact that t_P has on τ, one has to be aware that the two situations in which the oxide is reduced, i.e., electrochemically and due to its interaction with methanol, are not completely equivalent from the kinetic and thermodynamic points of view, so that the comparison between the shift in the reduction potential towards less positive values during the negative going sweep, cf. Fig. 1b, and the increase of the transient time, Fig. 2, with the pre-polarization time are more qualitative.

Despite the many studies carried out in the recent years [4–16], the detailed reaction mechanism of the electrooxidation of methanol is still a major issue of debate. The situation seems ever more complicated for the adsorption and electrooxidation of methanol in the region of high potentials, as reported inn this paper. Next, the possible

reactions that might occur during the transients of the open-circuit potential are summarized.

The initial drop just after the methanol injection would exclusively correspond to the consumption of the topmost oxygen layer by methanol via an ER mechanism. According to this mechanism, the activated complex is formed between an adsorbed specie, oxygen in the present case, and a non-adsorbed one, i.e., a methanol molecule at the reaction plane. The following reactions account for the possible pathways:

$$Pt - O + H_3COH \rightarrow Pt + H_2CO + H_2O \qquad (3)$$

$$2Pt - O + H_3COH \rightarrow 2Pt + HCOOH + H_2O \qquad (4)$$

$$3Pt - O + H_3COH \rightarrow 3Pt + CO_2 + 2H_2O \qquad (5)$$

The occurrence of steps 3, 4, and 5 is believed to be more prominent in situations of high surface occupancy by oxygen and chemisorbed anions. Besides carbon dioxide resulting from the complete oxidation, dissolved formaldehyde (H_2CO) and formic acid (HCOOH) are commonly identified as by-products of the methanol electrooxidation on platinum (see for instance [13, 15], and references therein). As far as DMFCs are concerned, CO_2 produced at the cathode has been experimentally verified [2, 21, 51]. Manzhos et al. [29] suggested that at high oxide coverage, the reaction occur via an ER mechanism.

Steps 3, 4, and 5 account not only for the methanol interaction with platinum oxide producing partial oxidized products (H_2CO and HCOOH) and CO_2 but also freeing platinum sites. Methanol molecules can adsorb on free platinum sites already at very low potentials giving partially dehydrated methanol residues as firstly suggested by Bagotsky [52] in his seminal paper:

$$Pt + H_3COH \rightarrow Pt - CH_2OH + H^+ + e^- \qquad (6)$$

$$Pt + Pt - CH_2OH \rightarrow Pt_2 - CHOH + H^+ + e^- \qquad (7)$$

$$Pt + Pt_2 - CHOH \rightarrow Pt_3 - COH + H^+ + e^- \qquad (8)$$

Reactions 6 and 7 are usually referred to as the rate determine steps, depending on the platinum surface under investigation. The presence of intermediates such as –CH_xOH and –COH has been confirmed by in situ infrared spectroscopy [4, 11, 13, 53]. Indeed, the sequence of methanol chemisorption via dehydrogenation, steps 6, 7, and 8, is possible in the presence of neighboring platinum sites [52] positioned in a certain configuration [54]. In presence of few available site due to the presence strongly

chemisorbed species, the O–H bond scission becomes more probable, and the adsorption via methoxide formation might be favored [14, 15].

Given the need for contiguous free platinum sites, the occurrence of methanol dehydrogenation, cf. steps 6, 7, and 8, is very sensitive to competition with chemisorbed anions. Therefore, their occurrence becomes more probable as the oxygen coverage decreases, which in turn might be due to steps 3, 4, and 5. This is especially true if one realizes that anion chemisorption is stronger at high overpotential values where the slowest portion of the transient takes place.

Additionally to steps 6, 7, and 8, the partially dehydrated methanol residues can also react with platinum oxide at neighboring sites, as in the case of –CH_2OH for instance,

$$2Pt - CH_2OH + Pt - O \rightarrow 3Pt + 2H_2CO + H_2O.$$
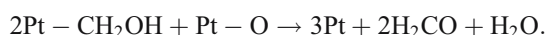
In this way, the same soluble products given in steps 3, 4, and 5, but at this time via the Langmuir–Hinshelwood mechanism, in which the activated complex is formed between two chemisorbed species can evolve. If they occur at all, such steps would play a role at high and moderate oxygen coverage.

Adsorbed carbon monoxide is formed via additional dehydrogenation of –COH intermediate. CO_{ad} can occupy one or two free platinum sites in the so-called linear and bridge bonded configurations, respectively,

$$Pt_3 - COH \rightarrow Pt - CO + H^+ + e^- + 2Pt \qquad (9)$$

$$Pt_3 - COH \rightarrow Pt_2 - CO + H^+ + e^- + Pt \qquad (10)$$
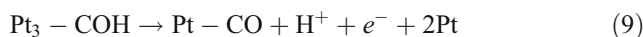
The nature of CO coordination is a function of factors such as potential and coverage, but in general, the linearly bonded CO, step 9, is known to prevail over the bridge coordinated configuration [13, 55]. In any case, the adsorbed CO can be further oxidized to CO_2:

$$Pt_x - CO + Pt - O \rightarrow (x + 1)Pt + CO_2 \qquad (11)$$
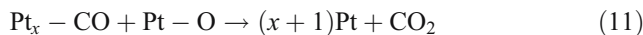
Reactions 6, 7, 8, 9, and 10 involve electron transfer, and as the system is kept under open-circuit conditions to occur, they have to be coupled to the oxygen electroreduction:

$$Pt - O + 2H^+ + 2e^- \rightarrow Pt + H_2O. \qquad (12)$$
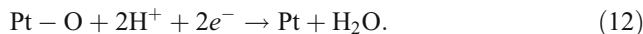
The combination between electrochemical steps of oxidation and reduction taking place at the same electrode have been usually referred to as "chemical short" [56], internal short-circuit [23], or conjugated reactions [28–32]. This mechanism is the cause of the parasitic anodic current at the cathode as a result of methanol leakage from the anodic compartment in a DMFC.

Out of the steps compiled in this paper, surface oxygen is present in steps 3, 4, 5, 11, and 12. As already stated, due to the place exchange mechanism, part of the oxygen of the

oxide layer remains as subsurface species and emerge to the topmost layer as when the surface coverage becomes smaller than a certain fraction of a ML. Thus, the rates of steps 3, 4, 5, 6, 7, 8, 11 and, more importantly, the oxygen electroreduction, step 12 which controls, or is coupled to, steps that involve electrooxidation of methanol residues are in principle dictated by the emergence of subsurface oxygen, or the reverse of step 2,

$$O - Pt \rightarrow Pt - O. \tag{13}$$

Summary and conclusions

The interaction of methanol with oxidized platinum surfaces was studied via transients of open-circuit potentials. Differently from previous reports, the studies were carried out by varying the pre-oxidation conditions in which the platinum oxide was formed. The surface oxidation before the exposure to interaction with methanol was performed at different polarization times, t_P, during an oxidative stage at 1.4 V vs RHE. In spite of the small change in the initial oxide content, the pre-polarization was found to significantly considerable increase the time in which the oxide is consumed during its interaction with methanol. This effect was explained in terms of the higher stability of the platinum oxide formed at longer pre-polarization times, which is also observed during conventional electrochemical reduction. In addition, results indicated a linear dependence in the $\log \tau$ vs $\log t_P$ representation, where τ is the duration of the open-circuit transient.

The influence of the identity of the chemisorbing anion on the transients was investigated in the following media: 0.5 M H_2SO_4, 0.1 M $HClO_4$, and 0.5 M H_2SO_4+0.1 mM Cl^-. It was observed that the higher the energy of anion chemisorption, i.e., $ClO_4^- < SO_4^{2-} < Cl^-$, the longer was the transient of the open-circuit potential. Moreover, the shapes of the transients were nearly identical irrespective of the anion present. These results were interpreted in terms of the availability of free platinum sites all over the transients and not only along the potential region in which the oxygen content is small. The presence of free platinum sites at potentials as high as 1.1 V vs RHE and for high oxide content is in agreement with the occurrence of place exchange. Place exchange implies the coexistence of the surface and subsurface oxygen states, and nearly irrespective of the total oxide content, free platinum sites are always available at the topmost layer. As far as methanol (electro)oxidation is concerned, the steps related to methanol dehydrogenation are likely the ones to be influenced by competition with anion chemisorption.

Nanogravimetric analysis [57] and the method of fast cathodic potentiodynamic pulses [27, 28], or more interest-ing, the combination of both could certainly be of help in quantifying the anion coverage along the transients and eventually the nature of some of the intermediate species. Such experiments are currently in progress in our laboratory.

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