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Investigation of the interfacial properties of platinum stepped surfaces using peroxodisulfate reduction as a local probe

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Abstract

Peroxodisulfate (PDS) reduction has been investigated by electrochemical and FTIR techniques in a wide pH range, on platinum stepped single crystals electrodes vicinal to the (111) pole. PDS reduction is a structure-sensitive reaction and proceeds on well differentiated potential regions for terrace and step sites. This fact allows gaining local information about the individual behavior of those sites. The reaction proceeds at appreciable rate in a narrow potential range, being inhibited in the low and high potential regions of the voltammogram. The inhibition of the reaction at low potentials is most likely associated with a change in the sign of the charge on the electrode, from positive to negative. Therefore, PDS reduction gives an approximate indication of the position of the potential of zero free charge (pzfc). In this way, two local values of pzfc, associated with terrace and steps sites, can be determined. Such values of local pzfc are compared with the local values of potential of maximum entropy (pme) of double layer formation deduced from laser induced T-jump experiment. Good agreement between both magnitudes is found, especially for terraces. The local pzfc on terraces shifts to more positive potentials as the terrace length diminishes, while the local pzfc for steps remains constant. The inhibition of PDS reduction at high potentials can also be related with a second inversion in the sign of the electrode charge. Therefore, PDS reduction

can be used to determine a second pzfc on the (111) terraces at high potentials, revealing a non-monotonic charge – potential relationship. Spectroscopic experiments allow the identification of the species involved in PDS reduction.

Keywords: Peroxodisulfate reduction; Platinum stepped surfaces; Potential of zero charge; free charge; Water structure

1. Introduction

On platinum electrodes, the peroxodisulfate (PDS) reduction shows a clear sensitivity to the charge on the electrode [1] resulting in the complete inhibition of the reduction current for negative polarization of the electrode potential. The electrostatic interaction between the anion and the negative charge on the electrode appears as the responsible for this inhibition. This is clearly evidenced in the evolution of PDS reduction curves with pH on Pt(111), where the inhibition potential lies on the double layer region and, therefore, cannot be ascribed to competitive hydrogen adsorption [1]. This inhibition potential emerges as a possible indication of the transition from positive to negative charge on the electrode and, therefore, for the approximate location of the pzfc. The comparison with other approaches, based on CO displacement [2, 3], N₂O reduction [4] and laser induced temperature jump experiment [3, 5], validates the identification of the potential of inhibition of the PDS reduction with the potential of zero free charge (pzfc). PDS reduction can proceed either through an outer sphere or through an inner sphere reaction. The latter mechanism involves formation of adsorbed intermediates. The high structure sensitivity of PDS reduction seems to point that an inner sphere pathway operates on platinum electrodes, while the outer sphere reaction does not take place at significant rate in the potential window under study.. In consequence, the application of Frumkin theory used in Hg or Au electrodes to explain the electroreduction of anions is not possible here.

The pzfc for platinum or other metals that adsorb hydrogen is equivalent to the potential of zero charge (pzc) found in mercury or coinage metal electrodes [6]. The pzc is a key parameter in the study of electrode/electrolyte interface. For liquid metal electrodes, the pzc is easily determined by means of electrocapillary curves [7]. For some solid electrodes, the pzc is also easily determined by looking for the minimum in the differential capacity predicted by Gouy-Chapman theory [8]. In the platinum/electrolyte interface, such methods are precluded as a consequence of the charge transfer processes associated to pseudo-capacitive reactions. In addition, according to Frumkin [6], two kinds of pzc should be defined in this case: The potential of zero total charge (pztc) and the potential of zero free charge (pzfc). The former corresponds to a situation where the free charge is balanced by the charge involved in adsorption processes, while in the latter case the free charge is zero [9].

The charge displacement experiment, typically performed using CO as displacing agent, has been used to determine the pztc of the platinum/electrolyte interface [10-12]. From this information, the pzfc can only be estimated for the particular case of Pt(111) in the absence of specific anion adsorption and under the application of some extra thermodynamic approximations [10, 12-16]. Moreover, the CO charge displacement only provides information for the overall surface, and does not discriminate between the different local contributions, mainly terraces and steps, to the overall charge state [16-18]. This individual information can be important to rationalize the behavior of complex surfaces and its reactivity [19-24]. The uneven distribution of charges on heterogeneous electrode surfaces is often accepted to explain the interfacial properties of stepped or defective surfaces. Such concept is normally sustained by the well accepted notion of local work function and the parallelism between this property and the pzc. [4, 25, 26]. Such heterogeneity is probably limited to the inner region of the

double layer while the effect in the diffuse layer has been debated in classical works dealing with pzc of polycrystalline Ag and Au electrodes [27].

Using N_2O reduction as probe reaction and working with stepped platinum single crystals belonging to the series $\text{Pt(S)}[(n-1)(111)\times(110)]$, Attard et al. found that the local pztc on (111) terraces diminishes as the step density increases, while the local pztc on (110) steps remains constant [18]. A good agreement between the overall pztc values from CO charge displacement and weighed local values from N_2O reduction was found.

On the other hand, the notions of pzc and pzfc are also closely linked to the concept of potential of maximum entropy (pme) of double layer formation [28, 29]. The main contribution to the entropy of the interphase comes from the orientation of water molecules and therefore is very sensitive to the electric field and the separation of charges. For gold electrodes, it has been demonstrated that the pme lies very close to the position of the Gouy-Chapman minimum [30-33]. By performing a very fast temperature change, in the submicrosecond time domain, the capacitive contribution can be separated from the contribution of adsorption processes. Then, the laser-induced temperature jump method is suitable for the determination of the pme of electrodes that adsorb hydrogen. Interestingly, the values of pme and pzfc calculated from CO displacement for Pt(111) are very close [9]. Local pme's of platinum stepped surfaces belonging to the series $\text{Pt(S)}[(n-1)(111)\times(110)]$ and $\text{Pt(S)}[n(111)\times(100)]$ have been reported [34, 35]. The local pme on (110) and (100) steps remains constant as step density increases; the same trend is observed with N_2O reduction [17, 18]. However, the local pme of (111) terraces shifts to more positive potential values as the terraces are shorter, in opposite trend to the results coming from N_2O reduction. The laser-induced temperature jump experiments also points out a non-monotonous behavior of charge on

platinum electrodes [5], with a second inversion of the sign of the measured signal (the thermal coefficient of the interfacial potential drop) at high potentials, as a consequence of the oxidation of the surface [36]. Such result was anticipated for polycrystalline platinum by Balashova et al. (reference 66 in [6]) and confirmed using radiotracers techniques by Kolotyrykina et al. (reference 69 in [6]) and Wicowski et al. [37]. The existence of a second pzc/pzfc has been recently theoretically modeled by Eikerleing et al. [38].

In this study, we use PDS reduction as a surface probe to investigate the local properties of stepped surfaces vicinal to the {111} pole of platinum single crystals in a wide pH range. A major difference between the PDS reduction and other local probes is that the PDS ion and its reduction product, sulfate, are not neutral and, therefore, can interact with the charge on the surface or with the electric field at the interphase. Also, comparison between data from PDS and N₂O reduction, CO charge displacement and pme is attempted to try to understand the stepped surface/electrolyte interface.

2. Experimental

The electrodes were oriented, cut, and polished following Clavilier's procedure [39]. Prior to any experiment, the electrodes were annealed in a Bunsen flame (propane+air), cooled down in a H₂+Ar (1:3) mixture and quenched with ultrapure water in equilibrium with these gases. All solutions were prepared with ultrapure water from Elga (18.2 MΩ cm), HClO₄ (70%, Merck, Suprapur), LiClO₄, NaClO₄, KClO₄, CsClO₄ (all Merck, Suprapur) and K₂S₂O₈ (Fluka, p.a.). Before each experiment, solutions were degassed with Argon (N-50, Air Liquide) for at least 10 minutes and a blanket of this gas was kept over the solution during experiments, to prevent the presence of oxygen. Electrochemical experiments were performed at room temperature in a classical two-compartment cell, with a large area platinum counter electrode in the

same compartment as the working electrode and a reference hydrogen electrode (RHE) in a separated compartment containing the same working solution and connected to the main compartment through a Luggin-Haber capillary. The measurements were performed with a EG&G PARC 175 signal generator, an eDAQ EA161 potentiostat and an eDAQ e-corder ED401 recording system.

In situ FTIR experiments were carried out using a Nicolet 8700 (Thermo Scientific) spectrometer equipped with a mercury cadmium telluride (MTC-A) detector using p or s-polarized light, as indicated. The spectroelectrochemical cell was equipped with a CaF_2 window bevelled at 60° . SNIFTIRS is used to study the PDS reduction. 10 sets of 100 interferograms were collected alternatively at the sample and reference potentials and averaged together. The working electrodes used in the spectroelectrochemical study have approximately 4.5 mm in diameter and were prepared and treated before experiments in analogous way as the electrodes used in electrochemical experiments. All spectroelectrochemical experiments were performed at room temperature with a RHE as reference and a large platinum foil as counter electrode.

3. Results

3.1. $\text{Pt(S)}[(n-1)(111)\times(110)]$

The vicinal surfaces having Miller indices $\text{Pt}(n,n,n-2)$ were studied first. The structure of these surfaces can be described using the notation introduced by Lang, Joyner and Somorjai [40] as $\text{Pt(S)}[n(111)\times(111)]$ where n is the length of the terrace. Since the junction of two (111) sites forms a (110) step, these surfaces can be also noted as $\text{Pt(S)}[(n-1)(111)\times(110)]$. The latter description is preferred from the point of view of hydrogen adsorption at the steps, since this takes place at 0.12 V, which is the same potential as on the $\text{Pt}(110)$ basal plane. STM studies have shown that, after flame annealing, these surfaces are composed by terraces having the nominal length separated

by monoatomic steps [41, 42]. **Figure 1A** shows the voltammograms recorded in 0.1 M perchloric acid solutions containing 10^{-3} M PDS. The addition of PDS leaves the hydrogen underpotential deposition (H_{upd}) region (0.06-0.35 V) essentially unaffected, for electrodes with large terraces. The OH adsorption (0.65-0.85 V) region, however, becomes suppressed for all electrodes, without distinction of the terrace length. This indicates the specific adsorption of the PDS/sulfate anion at these potentials. The reduction of PDS on this family of stepped surfaces takes place in two distinct potential regions, which can be assigned to the processes undergone on terraces and steps, after comparison with the reactivity on the corresponding basal planes and the evolution of the voltammetric profile with the change of the step density. Thus, the region between 0.45 and 0.65 V would correspond to PDS reduction on terraces of (111) symmetry. The sharp spike at 0.60 V on Pt(111) likely corresponds to an order/disorder phase transition in the layer of adsorbed sulfate and interestingly coincide with the onset/inhibition of the PDS reduction. As in the latter case, this transition is only observed on wide terraces and if a rigorous cleaning procedure is followed. **Fig. SII** shows that the concentration of sulfate required to observe the spike at the same potential as in the PDS containing solutions is 10^{-3} M. In the same way, the current observed in the region between 0.14 and 0.18 V would correspond to PDS reduction on steps with (110) symmetry, since the reduction process occurs in the same potential region as on the Pt(110) basal plane.

Figure 1B shows the PDS reduction at pH 5 (0.003 M HClO_4 + 0.1 M NaF). The H_{upd} region remains unaltered for potentials lower than 0.18 V (it should be noted that the RHE shifts with the pH). Then, a reduction current is observed around 0.20 V, which corresponds to PDS reduction on (110) monoatomic steps. For electrodes with wide terraces, the current for solutions with and without PDS coincide in the so-called

double layer region. After that, a reduction current is observed in the zone of OH adsorption, which can be assigned to PDS reduction on (111) terraces. As expected, at pH 5, the adsorption strength of PDS or sulfate is correspondingly lower and some OH adsorption is observed in electrodes with $n \geq 20$. The PDS reduction at pH 2, 3 and 4 (in all cases mixtures $\text{HClO}_4 + \text{NaF}$) in a set of representative stepped surfaces is shown in Supplementary Information, **Fig. SI2**. At this intermediate pH values, a similar behavior to that observed at pH 1 and 5 is obtained and PDS reduction takes place in all cases in two potential regions, one related to reduction on step sites and another related to reduction on terraces. An interesting fact to note is that the onset of the reaction and the inhibition potential on the terraces are not related to the relative position of the hydroxyl or hydrogen adsorption region. This result supports the idea that competitive adsorption is not the main factor governing the rate of PDS reduction.

Some characteristic data can be obtained from these voltammograms. First of all, qualitative information can be gained from the peak current density involved in PDS reduction in both potential ranges, at the different pHs. The peaks current density diminishes quite linearly as the length of the terrace diminish, whereas that on the steps increases, for both pH solutions, **figure 2A** and **2B**. The peak potential of the PDS reduction at pH 1 and 5 on the (111) terrace moves to more positive potentials as the terraces become shorter, as can be seen in **figure 2C** and **2D**, respectively. In this way, there is a good linear correlation between peak potential and step density. The dependence of the peak potential on the terrace (in the RHE scale) with the pH is approximately 60mV/pH unit. On the other hand, the onset of the reduction is around 0.70 and 0.80 V vs RHE at pH 1 and 5, respectively, for all electrodes with terraces of (111) symmetry, independent of step density. Unlike the reaction on terraces, the peak

potential of PDS reduction on the (110) steps remains approximately constant at 0.18 and 0.20 V vs RHE at each pH as the step density increases.

3.2 Pt(S)[n(111)x(100)]

A similar response is observed for the stepped surfaces belonging to the Pt(S)[n(111)x(100)] series. The Miller indices for these surfaces are: Pt(n+1,n-1,n-1). As before, previous STM measurements demonstrate the agreement between the surface periodicity and the hard sphere model, when the flame annealing treatment followed by hydrogen cooling is used [42]. PDS reduction is shown in **Fig. 3A** and **3B**. Again, as with the precedent series of surfaces, the H_{upd} on terraces remains unaltered in the presence of PDS, and the voltammetric signals recorded from solutions with and without PDS coincide nicely in the lower potential range ($E \leq 0.25$ V) for both solutions of different pH. Also, as in the previous case, two potential regions can be distinguished for PDS reduction. At pH 1, the region between 0.45 and 0.65 V corresponds to reduction on terraces of (111) symmetry. On the other hand, at pH 5 (mixtures of $\text{HClO}_4 + \text{NaF}$) the reduction on (111) terraces takes place between 0.60 and 0.75 V. This behavior mimics that described for the series Pt(S)[(n-1)(111)x(110)]. In this scenario, the reduction current around 0.30 and 0.38 V at pH 1 and 5, respectively, would correspond to PDS reduction on steps with (100) symmetry, very different to that observed in the previous series in which the reduction process at the (110) steps takes place at 0.16 and 0.22 V for the same pH values. Again, the argument to assign this reduction to the contribution of the step is the increase of this process with the step density. In **figure SI3** in the supporting information, the PDS reduction on Pt(S)[n(111)x(100)] are shown at pH 2, 3 and 4 (in all cases using $\text{HClO}_4 + \text{NaF}$ mixtures).

As before, the peak current densities associated to the reduction on terraces diminish as the terraces become shorter and that on the steps increase (**Fig. 4A and 4B**). Also, the reduction peak potential on the terraces shifts to more positive values as the step density increases. This behavior is similar to that observed for (111) terraces separated by (110) steps, although the shift is less pronounced with (100) steps than with (110) steps. Also as before, while the peak current density increases as the step density increases, the peak potential for PDS reduction at the step sites remains quite constant around 0.30 and 0.38 V at pH 1 and 5, respectively (**Fig. 4C and 4D**).

3.3. Cation effects

Figure 5A and 5B shows the PDS reduction on Pt(443) electrode in 0.001 M HClO_4 and 0.001 M HClO_4 + 0.01 M XClO_4 ($\text{X} = \text{Li}, \text{Na}, \text{K}$ or Cs), respectively. The PDS reduction on the step is completely inhibited in solutions containing only perchloric acid, whereas the reduction on the terrace is unaffected. Thus, the addition of alkali metal perchlorates induces PDS reduction on the step without modifying the process taking place on the terrace. The cation-induced effect is more pronounced in the solution containing Cs^+ , while the presence of Li^+ has the lowest effect. The complete trend is $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. To confirm that the induced reduction effect on the step is caused by the cation and not by the anion, a series of similar experiments were performed in sulfuric acid. **Figure SI4** shows the effect of the addition 0.01 M Na_2SO_4 in 0.0005 M H_2SO_4 (pH 3.2). The presence of Na^+ has the same effect on the step reactivity than that observed with perchlorate solutions. Interestingly, the PDS reduction on the terrace is inhibited as a consequence of the strong adsorption of sulfate that blocks the platinum sites for reaction. The anions affect the reactivity on terraces but not on the steps, while the cations play the opposite role. Also, to remark the predominant effect of the cation over the anion on the behavior of the step, the PDS

reduction was conducted in 0.01 M HClO_4 and 0.01 M $\text{HClO}_4 + 0.01 \text{ KClO}_4$ (**Figure SI5**). Similarly to the result observed in pH 3, PDS reduction is inhibited on the step in the solution containing only perchloric acid whereas the addition of K^+ , induces PDS reduction on the step. Remarkably, characteristic parameters for PDS reduction (peak potential and current) on the terrace remain the same in both solutions.

Figure 6A and **6B** shows PDS reduction on Pt(755) electrode in 0.001 M HClO_4 and 0.001 M $\text{HClO}_4 + 0.01 \text{ M XClO}_4$ ($\text{X} = \text{Li, Na, K or Cs}$). Although in this case PDS reduction is not completely inhibited on the (100) step in solutions containing only perchloric acid, the addition of different alkali cations has a similar promotion effect to that observed for (110) steps. Moreover, the cation-induced reactivity trend is the same. It is interesting to remark that PDS reduction stoichiometry does not involve water, and thus cation-induced water reactivity can be considered less likely than in other cases, such as oxygen reduction [44, 45], in which the cation effect could be reflecting a change in water properties induced by solvation.

3.4. Adsorption of the reaction product on steps

The voltammetric peaks at 0.12 V on vicinal Pt(111) electrodes have been traditionally assigned to hydrogen adsorption on (110) steps, without contribution from anion adsorption. Such conclusion is based on the independence of the charge and shape of the peak in the presence of some specifically adsorbing anions [46, 47]. In recent studies this interpretation is questioned due to the anomalous shift with pH of these peaks [48]. For (100) steps, presence of specifically adsorbing anions changes the shape of the voltammetric peak, signaling the possible competitive adsorption of anions on the steps [49]. In this regards, some contribution of anion specific adsorption has been suggested in perchloric acid solutions with the same pH (the peak at 0.27 V shifts to

higher potentials) [50]. It is generally accepted that PDS reduction takes place on surface sites free of adsorbates and hence, sulfate adsorption could diminish the activity of step sites. If this self-poisoning step, caused by adsorption of the product exists, some modification of the reaction rate should be observed as the reaction proceeds at constant potential. Then, in order to examine the interaction between the sulfate anion and the steps of (110) and (100) symmetry, the behavior of the PDS reduction in presence of sulfate anions was analyzed. For this, some electrodes composed of medium size (111) terraces separated by either (110) or (100) steps were chosen: Pt(775), and Pt(755). As seen in the figure 7 the current density decreases on the surfaces having steps of (100) symmetry as the concentration of sulfate is 0.01 M, whereas the current density at 0.17 V remains approximately constant in the case of steps of (110) symmetry. In both family of surfaces the PDS reduction is inhibited on the (111) terraces. This suggests that the sulfate interacts more strongly with steps of (100) symmetry than with steps of (110) symmetry at the potentials where the reaction takes place.

3.5 Spectroelectrochemical results

SNIFTIR experiments were carried out to gain information about the chemical identity of the species involved in PDS reduction on single crystals electrodes. Although the thin layer configuration is not optimal to study this particular reaction, it is necessary for the use of single crystal surfaces. **Figure 8A** and **8B** shows a set of spectra collected with p-polarized light in a solution containing 0.1 M HClO_4 + 10^{-3} M PDS at representative potential values for Pt(111). A negative-going band around 1250 cm^{-1} appears at potentials above 0.60 V. The center of this band shifts from 1240 cm^{-1} to 1260 cm^{-1} when the potential increases from 0.7 V to 0.8 V. This potential dependence demonstrates that this band corresponds to species adsorbed on the electrode surface. **Figure 8C** shows the dependence of the 1250 cm^{-1} band center with the potential. The

Stark coefficient calculated for this band is $103 \text{ cm}^{-1} \text{ V}^{-1}$, which is similar to that found for the sulfate adsorption on Pt(111) [51, 52]. However, the identity of the species adsorbed at potentials higher than 0.60 V, can correspond to sulfate or PDS. A group of bands in the region around 1100 cm^{-1} is also visible; these bands do not show dependence with the potential. Therefore, these bands would correspond to species in solution (PDS or sulfate coming from PDS reduction or even perchlorate [53]). **Figure SI6** shows transmission spectra for PDS in a 0.1 M HClO_4 solution, evidencing clear bands at 1270 and 1048 cm^{-1} in accordance with literature information [54]. The stretching of the O-O bond is most likely below 1000 cm^{-1} [55] and therefore not visible due to the cut off of the CaF_2 window. Therefore, the spectroscopic result does not allow a conclusive identification of the nature of adsorbed species to either sulfate or PDS.

Figures 9A and **9B** show sets of spectra collected in solutions containing 0.1 M HClO_4 + 10^{-3} M PDS at representative potential values for Pt(443) and Pt(322) electrodes, respectively. A band around 1250 cm^{-1} appears for both surfaces at potentials above 0.60 V. The dependence of this band with the potential is similar to the one found with Pt(111). The bands around 1100 cm^{-1} can also be observed. This region probably contains some contribution from adsorbed species on step sites [56] but it is difficult to unequivocally assign this region of the spectra due to the presence of perchlorate bands [53].

4. Discussion

Figure 10A and **10B** compare the variations of $E@j=0$ for (111) terrace in stepped surfaces vicinal to pole (111) with the local pztc on the terrace estimated from N_2O reduction (only for surfaces with (110) steps) and the values of local pme gained from the temperature jump laser heating experiments, as a function of the step density.

The plot is done in the SHE scale, since it involves data from experiments performed at different pH values. For PDS reduction, only the data from experiments performed at pH 5 is used, since at this pH the separation between terrace and step contributions is larger. In this way, we avoid having to deconvolute the different signals, a procedure that can introduce uncertainty in the analysis. In the same way that in our previous communication [1], we use the $E@j=0$ as indicator of the approximate position of the local pzfc on terraces of different length and steps. The $E@j=0$ in (111) terraces move to more positive potentials as the step density increases, independently of the symmetry of the step. The trend is the same as that found for the pme [5], but opposite to that found with N_2O reduction [18]. The origin of this difference can be the different charge in N_2O and PDS, that might result in a lack of sensitivity of the N_2O reduction to follow the variation of the free charge. The reduction of the PDS anion requires a previous adsorption on the electrode surface. During the approximation of the ion to the electrode surface, the negative charge in PDS anion will interact with other molecules and it will also be influenced by the electric field in the interphase. Those interactions will most likely be different from those encountered by the neutral N_2O molecule. Therefore, it is expected that the electroreduction of N_2O and PDS anion show different dependence on the electrode charge. The values of local pme and $E@j=0$ on the terrace are similar, especially for a lower step density. The positive shift of $E@j=0$ as the step density increases is different for the trend described for the local work function (WF) on terraces on stepped surfaces observed in ultra-high vacuum. In this case, it is well established that the local WF remains constant regardless of the terrace length [26, 57]. This apparently contradictory result can be rationalized taking into account the effect of the interfacial water. In the electrochemical interface, the electrode surface is always in contact with a large quantity of water molecules [58]. These molecules are generally

arranged as a water network that is more or less organized depending on the terrace length. This fact was used in the past to explain why the local pme on terraces move to more positive potentials as the step density increases [5]. PDS adsorption is energetically more favorable on surfaces with less organized water since it will be easier for the anion to compete for adsorption sites on the electrode surface with less organized than with highly organized water network. Therefore, the disruption of the water network on terraces caused by the introduction of steps causes a diminution on the overpotential for the PDS reduction and a positive displacement of $E@j=0$ the step density increases.

In conclusion, the PDS reduction emerges as an inexpensive and effortless charged surface probe to estimate the (local) pzfc on stepped platinum single crystals. At this point, we want to use the PDS reduction to check the Frumkin hypothesis about the presence of two pzfc [6, 59]. Frumkin established that the formation of a layer of oxygen adatoms was responsible for the non-monotonic surface charging behavior observed experimentally on Pt/Pt electrodes. Signs of this non-monotonic behavior of charge were also observed experimentally more recently [5, 6, 37, 60] and theoretically modelled by Eikerling et al. [38, 61] supporting that idea of a second region of negative charge associated to the formation of an oxide layer. **Figures 9A and 9B** show the onset/inhibition potential in the high potential region for PDS reduction on (111) terraces in surfaces with both kinds of steps, as a function of step density. The negative-going scan was used for the preparation of this plot. This second onset/inhibition is almost independent of the step density unlike the $E@j=0$ discussed earlier. This second onset/inhibition potential can be taken as an indication of a second potential of zero free charge on the platinum surface, if we accept that the onset/inhibition for PDS reduction is caused by a change on the sign of the charge on the electrode. This idea is supported

by the inversion of the thermal coefficient of the double layer, as measured with the T-jump experiment, suggesting an inversion of the orientation of water dipoles in this potential region. At pH 1, the onset/inhibition potential for Pt(111) is around 0.68 V vs RHE, a value that is close to the one reported by Eikerling in reference [38]. Meanwhile, at pH 5 the onset/inhibition potential is around 0.90 V vs RHE. Taking into account the onset/inhibition potential for all the solutions with different pH investigated in this study, a slope of 55mV/pH unit is obtained, in the RHE scale. This value implies that the second pzfc is nearly independent of the pH in the SHE scale, as the first pzfc. Coming back to the observed independence of $E@j=0$ on the step density, it is interesting to note that the onset potential for the surface oxidation on stepped surfaces vicinal to the (111) pole is also independent on the step density [62, 63]. This fact supports the idea that inhibition of PDS and surface oxidation are related.

Figure 10A and **10B** depicts $E@j=0$ for (110) and (100) steps. The $E@j=0$ on steps remains approximately constant regardless of the step density. This behavior is similar to that found with N_2O reduction experiments [18] or with laser-induced temperature jump method [34]: in both cases the local contribution of steps remains constant. However, a large discrepancy between the values of the local pzfc, as estimated from PDS reduction and the values coming from N_2O reduction or pme exist at pH 5. Since the reduction of PDS coincides with the hydrogen adsorption on steps, the differences found for both kind of steps on the local values found here, can be originated on the anomalous behavior of this kind of sites with the pH (shift with pH different from 60mV/pH unit). In this sense, when the comparison is performed with values obtained at the same pH, the differences decrease.

On the other hand, the experiments with cations remark the influence of water in the electrochemical reactivity. Inhibition of PDS reduction on the step in solutions

containing only perchloric acid reveals the strong adsorption by water or (less likely) hydroxide on the step that blocks surface sites for the reaction. The addition of cations diminished the strength of water or hydroxide adsorption allowing the adsorption and subsequent reduction of PDS. Even more, we found that the ability to induce the reduction on step depends on the cation nature. Cs^+ has the largest induced effect followed by K^+ and Na^+ . Meanwhile Li^+ shows the smallest induced effect on the PDS reduction on the step. The same trend is found in numerous works where the effects of alkali metal cations are studied in connection with the reactivity [45, 64-66]. Recently, Koper et al. combined experimental and computational methods to show that alkali cations disrupt the hydrogen bonding network between co-adsorbed hydroxide and water, weakening the hydroxide adsorption [48, 67]. Also, they concluded that cations which retain a greater amount of positive charge on adsorption cause the greatest weakening of hydroxide adsorption on the step, which is the cesium cation, in this case. These results are consistent with the findings of the present study. Also, the existence of ion-pair formation to some extent between the cation and the PDS cannot be discarded. Ion pair formation was assumed to explain in part the influence of cations in the rate of PDS reduction on amalgamated copper electrodes [43]. Frumkin et al. show that the rate of PDS reduction increases in the sequence $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$. This is the same order of adsorbability of the cations which goes in parallel with the ability to form ion pairs. The formation of ion pairs will reduce the charge of the approaching PDS anion, therefore decreasing the electrostatic repulsion with the charged surface. The same order is found here for at inner sphere reaction.

The differences in the sulfate interaction with (100), (110) steps or (111) terraces at distinct pHs is indicative of the state of charge of the surface at a given potential value. Even more, this fact remarked that, in stepped surfaces, different charge states are

present, i.e. the different local symmetries (terraces, steps, kinds, adatom, etc.) present on the surface carry a particular charge (in sign and magnitude) that can be different from the charge present in other elements. Also, the preferential adsorption of sulfate on the (100) step can be an indication that two pzc exist for this kind of step: one, without sulfate and other with the electrode with sulfate.

5. Conclusions

PDS reduction has been studied on stepped surfaces vicinal to (111) pole in a wide pH range. PDS reduction takes place on terraces and steps in well-differentiated potential regions (especially at less acid pHs). It makes the PDS reduction a surface probe valid to investigate individually the behavior of terraces and steps in the Pt(hkl)/electrolyte interface, with the changes of the reduction current giving an indication about the position of the local pzfc values. The local pzfc on terraces move to more positive potentials as the terraces are shorter. These results are in good agreement with local pme values reported in the past. The local pzfc on steps (100) and (110) remains constant as the step density increase, a result that is similar to that found with N₂O reduction or local pme measurements. A second pzfc for (111) terraces in both families of surfaces studied here is located at the high potential region. This second potential is independent of terrace length and seems to depend on the onset potential for oxygen/OH layer on the electrode surface. The trend $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ is found for the capacity of alkali cations to induce the reaction on steps. Also, the experiments with alkaline cations point out the importance of water on electrochemical reactivity.

The sensitivity of PDS reduction to the different surface symmetries suggest that it can be used also to characterize more complex platinum structures such as nanoparticles.

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Figures

Figure 1. Cyclic voltammograms of 10^{-3} M PDS reduction on Pt(S)[(n-1)(111)x(110)] electrodes in (A) pH 1 (0.1 M HClO_4) and (B) pH 5 (HClO_4 + NaF mixture) . Scan rate: 50 mV/s.

Figure 2. Experimental terrace (black squares) and steps (red circles) peak current (A and B) and peak potential (C and D) for Pt(S)[(n-1)(111)x(110)] at pH 1 (right side) and pH 5 (left side).

Figure 3. As in Fig. 1 but with the Pt(S)[n(111)x(100)] series.

Figure 4. As in Fig. 2 but with the Pt(S)[n(111)x(100)] series.

Figure 5. Cyclic voltammograms of 10^{-3} M PDS reduction on Pt(443) in (A) 10^{-3} M HClO_4 and (B) 10^{-3} M HClO_4 + 10^{-2} M XClO_4 ($\text{X}=\text{Li}, \text{Na}, \text{K}, \text{Cs}$). Scan rate: 10 mV/s.

Figure 6. Cyclic voltammograms of 10^{-3} M PDS reduction on Pt(755) in (A) 10^{-3} M HClO_4 and (B) 10^{-3} M HClO_4 + 10^{-2} M XClO_4 ($\text{X}=\text{Li}, \text{Na}, \text{K}, \text{Cs}$). Scan rate: 10 mV/s.

Figure 7. Cyclic voltammograms of 10^{-3} M PDS reduction on Pt(775) (A) and Pt(755) (B) in 10^{-1} M HClO_4 (blue line) and 10^{-1} M $\text{HClO}_4 + 10^{-2}$ M H_2SO_4 (red line). Scan rate: 50 mV/s. Blanks in 0.1 M HClO_4 are shown for sake of comparison.

Figure 8. *in situ* SNIPTIRS spectra of the Pt(111) electrode in 0.1 M HClO₄ + 10⁻³ M PDS solution at p-polarized light A) lower potentials B) higher potentials and C) Band center frequency as a function of potential. Reference spectra taken at 0.10 V.

Figure 9. SNIFTIRS spectra of the A) Pt(322) and B) Pt(443) electrodes in 0.1 M $\text{HClO}_4 + 10^{-3}$ M PDS solution at p-polarized light. Reference spectra taken at 0.075 V.

Figure 10. Comparison of $E@j=0$ (squares), local pme (circles), and local pztc (triangles) for (111) terraces on (A) $\text{Pt(S)}[(n-1)(111)x(110)]$ and (B) $\text{Pt(S)}[n(111)x(100)]$

Figure 11. Second $E@j=0$ for (111) terraces on (A) $\text{Pt(S)\{(n-1)(111)x(110)\}}$ and (B) $\text{Pt(S)[n(111)x(100)]}$. Data taken at pH 5.

Figure 12. Comparison of $E^{\text{STEP}}@j=0$ (circles) and local pme (squares) for (A) (110) and (B) (100) steps. Filled circles (pH 5) and hollow circles (pH 3). Mixtures NaF and HClO_4 were used. The data of local pme was taken at pH 3 from reference [34]. The dashed lines point out the peak potential for the hydrogen adsorption/desorption in the blank voltammogram at different pH.

Highlights

- Peroxodisulfate reduction is investigated on platinum stepped single crystal surfaces.
- This reaction is sensitive to the crystallographic structure of the surface
- The rate of the reaction is sensitive to the local nature of the charge on the surface
- This allows detection of local values of the potential of zero free charge
- The dependence of local values of potential of zero charge on terrace length is investigated