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# Peroxodisulfate Reduction on Platinum Stepped Surfaces Vicinal to the (110) and (100) Poles

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## Abstract

The reduction of peroxodisulfate anion at stepped platinum single crystal electrodes vicinal to the (110) and (100) poles has been investigated using cyclic voltammetry. Particular emphasis is made in understanding the effect of the cooling atmosphere used after the flame annealing. Two cooling atmospheres have been used: H<sub>2</sub>/Ar and CO. The cooling procedure has a significant influence on the reactivity obtained with the stepped surfaces belonging to both crystallographic zones. For the surfaces composed of (110) terraces and (111) or (100) steps cooled in H<sub>2</sub>/Ar, only one peroxodisulfate reduction peak is observed. On the contrary, for the same surfaces cooled in CO, more than one peak is observed for wide terraces. For surfaces vicinal to the pole (100), the cooling in CO atmosphere seems to produce a surface with higher order than those cooled in H<sub>2</sub>/Ar. The implications of the results on the understanding of the local distribution of charges at heterogeneous surfaces is discussed, identifying local values of the potential of zero charge. Those results are compared, when possible, with results obtained with other techniques.

## 1. Introduction

The widespread implementation of electrochemical technologies requires a deep understanding of the electrode processes at a molecular scale. Studies with platinum single crystals are fundamental to understand the relationship between surface structure and reactivity. Unfortunately, systematic studies using single crystals vicinal to the Pt(100) or Pt(110) poles are scarce although the electrochemical behavior of

polycrystalline platinum and dispersed platinum catalyst resembles more closely that of these surfaces. To the best of our knowledge, there exist only few studies dealing with surfaces belonging to these crystallographic zones [1-9]. The reason for this scarcity lies in the difficulty to prepare surfaces with real structures corresponding to the nominal ones, because surfaces containing (110) or (100) sites tend to suffer processes of surface reconstruction [10-12]. In the case of the (110) surface, the so-called *missing-row* or (1x2) reconstruction takes place after the flame annealing [13, 14]. At the high temperature of the flame, the surface is on the (1x1) state, but the (1x2) structure is formed during the cooling process, when the temperature is below a critical value [14]. In this case, the rate of cooling is important to determine the final structure of the surface and it has been reported that allowing a slow cooling rate before placing the hot crystal in the Ar stream (or Ar+H<sub>2</sub> mixture) results in the (1x2) structure [14]. According to X-Ray diffraction data, this reconstruction is stable in the potential range between 0-0.8 V (vs RHE) [13, 14]. This reconstruction only disappears after the electrode is polarized at higher potentials [13, 14]. On the other hand, in the case of the (100) surface, the (5x20) hexagonal reconstruction is formed on the clean surface after the flame annealing [10, 15]. However, the reconstruction is lifted and the surface reverts to the (1x1) structure when the electrode is brought to contact with water or with an electrolytic solution [16, 17].

It has been shown before that the composition of the cooling atmosphere employed after the flame annealing has a great influence on the final structure of the metallic surface [18-21]. In general, presence of oxygen in the cooling atmosphere tends to disorder the surface while a free-oxygen atmosphere is effective to produce surfaces that correspond better to the nominal hard sphere structure [22]. This is because the oxygen adsorbs strongly on the electrode surface forming surface oxides that favor the place exchange and disorder the surface upon reduction [12]. Other cooling

atmospheres that have been employed include the presence of strongly adsorbed species such as CO [9, 11, 20, 21] or iodide [22, 23].

For Pt(110), air-cooling produces a disordered surface whereas hydrogen-cooling produces a surface with a combination of (1x1) and (1x2) sites, depending on the cooling rate and the ratio of hydrogen and argon [14, 20]. CO-cooling allows obtaining a surface with a higher degree of order most likely because strongly adsorbed CO increases the mobility of surface atoms during the cooling step and forces the lifting of the reconstruction. In the case of Pt(100), the surface structure resulting by cooling in air corresponds to a two-dimensionally disordered surface [24, 25]. The use of a reductive atmosphere for cooling produces an unreconstructed surface that displays large ordered terraces [20, 21]. The formation of a three-dimensional "mesa-like" structure has been also reported [16, 20, 21]. This "mesa-like" structure most likely result as a consequence of the lifting of the reconstruction when the electrode is contacted with the solution to accommodate the excess of atomic density present on the reconstructed adlayer. These structures cause the presence of multiple steps and kinks on a surface that should be theoretically flat and with only one type of surface atoms. Despite the efforts to rationalize the surface of electrodes vicinal to the (100) and (110) poles, the exact structure of these surfaces is still elusive.

In a recent series of papers, we demonstrated the effectiveness of the PDS reduction as a novel probe to study the electrochemical interface between platinum stepped single crystal surfaces vicinal to Pt(111) and aqueous solutions of different pH [26-29]. All stepped electrodes used in our previous reports were composed of terraces of (111) symmetry and steps of either (110) or (100) symmetry [29]. PDS reduction on stepped surfaces vicinal to the (111) pole takes place in two potential regions, that can be attributed to the separate contribution of terrace and step sites, therefore allowing obtaining local information about the distribution of sites of different symmetry on the surface. Moreover, we have postulated before that the reactivity of PDS on platinum



surfaces is dominated by the electrostatic interaction with local excess charge on the surface, therefore, allowing an estimation of local values of the potential of zero charge (pzc). The local's pzc on terrace sites move to more positive potentials as the terraces become shorter. On the other hand, the local's pzc on steps (110 or 100) remains approximately constant regardless of the step density [29]. These trends are in agreement with results coming from the laser induced temperature jump methodology [30, 31]. It is worth recalling at this point that, in the case of platinum electrodes (in general, in the presence of charge transfer processes), two different kinds of pzc need to be considered: the potential of zero free charge (pzfc), which only takes into account the true electronic charge on the metal (balanced by ionic charge in the solution) and the potential of zero total charge (pztc), which considers also the charge involved in adsorption processes [32]. The laser induced temperature jump method allows to locate the position of the potential of maximum entropy (pme) which is closely related with the pzfc [33].

Herein, we use the PDS reduction to investigate the electrochemical behavior of platinum stepped surfaces vicinal to the poles (110) and (100). Similarly to the other crystallographic zones investigated before, observation of several reduction peaks can be used to obtain indirect evidence about the position of local values of the pzc. Also, the use of solutions of different pH allows getting local information about the surface structure in different electrodes.

## 2. Experimental

Two families of surfaces are used. **Figure 1A** and **1B** shows that the first families of surfaces studied are composed by terraces of symmetry (110) with steps (111) or (100). The Miller indices for these surfaces are  $Pt(2n-1 \ 2n-1 \ 1)$  and  $Pt(n \ n-1 \ 0)$ , respectively [34]. **Figure 1C** and **1D** shows that the second set of surfaces are composed by terraces of symmetry (100) with steps (111) or (110). The Miller indices

for these surfaces are Pt(2n-1 1 1) and Pt(n 1 0), respectively [34]. These electrode surfaces were prepared following the Clavilier method [35, 36]. After the flame annealing, two different cooling atmospheres were used. In the first one, the electrodes were cooled in a controlled H<sub>2</sub>/Ar (in a ratio 1:3) atmosphere, while in the second procedure the electrodes were cooled in a CO atmosphere. In both procedures, after the electrodes were cooled, they were protected by a droplet of deoxygenated water saturated in the same gas employed for the cooling (H<sub>2</sub>/Ar or CO) and transferred to the electrochemical cell. These surfaces will be named Pt(hkl)/H<sub>2</sub> or Pt(hkl)/CO, respectively.

Voltammetric measurements were carried out in a conventional two-compartment glass cell using a three-electrode configuration with a large platinum counter-electrode in the same compartment as the working electrode and the reference electrode (a reversible hydrogen electrode, RHE) situated in a separate compartment connected through a Luggin capillary. A EG&G PARC 175 waveform generator together with an eDAQ EA161 potentiostat, and eDAQ e-corder ED401 recording system were used for the voltammetric experiments. The solutions were prepared using HClO<sub>4</sub> (70% Suprapur, Merck), NaF (Suprapur, Merck) and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (99.0%, Fluka) and ultra-pure water (18.2 MΩ cm) from ELGA.

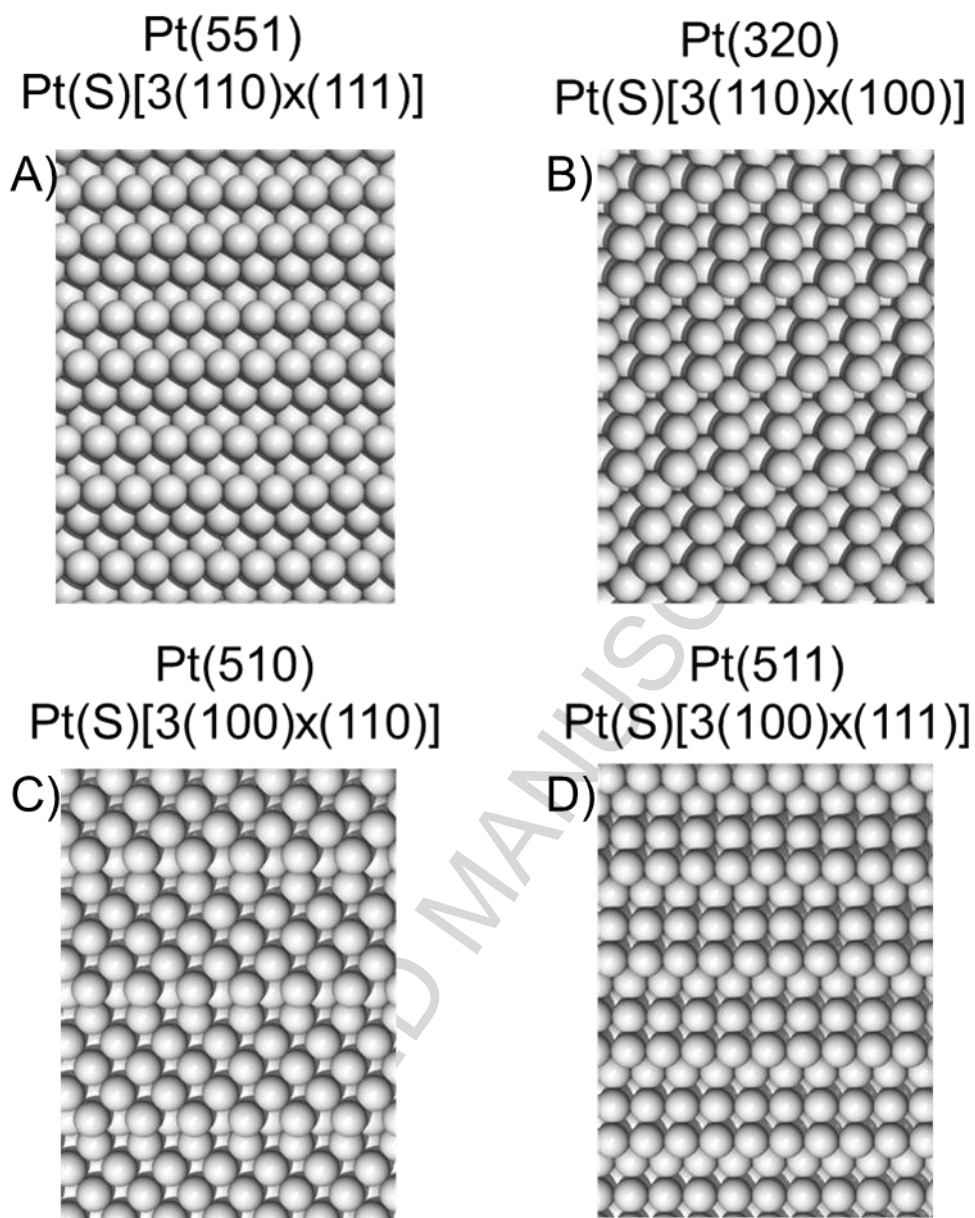


Figure 1. Surface structures of representative electrodes used in this work.

### 3. Results and discussion

#### 3.1 Pt(110) pole

##### 3.1.1 Pt(110). The basal plane.

**Figure 2A** and **2B** shows the PDS reduction in 0.1 M HClO<sub>4</sub> for the Pt(110) electrode cooled in two different atmospheres: hydrogen or carbon monoxide, respectively. Cyclic voltammograms of the PDS reduction on a Pt(110) electrode clearly depend on the cooling atmosphere. The PDS reduction on Pt(110)/H<sub>2</sub> shows only one reduction peak around 0.19 V and an ill-defined shoulder at higher potentials. On the other hand, the reduction peak for PDS on Pt(110)/CO splits into two peaks around 0.17 and 0.186 V. At potentials higher than 0.55 V, the reduction is completely inhibited in both electrodes while the onset of reduction is different on both surfaces: the PDS reduction starts around 0.55 V for Pt(110)/H<sub>2</sub> and at 0.45 V for the Pt(110)/CO. For both electrodes, the voltammetric response at potentials lower than 0.15 V coincides with the blank recorded without PDS. It has been previously suggested that the cooling atmosphere changes the surface state due to the presence or absence of the (1x2) surface reconstruction. Under this framework, the electrode cooled in H<sub>2</sub>/Ar would have the (1x2) structure [14], while the presence of CO in the cooling atmosphere would force the lifting of the reconstruction, resulting in an ordered (1x1) surface [11]. The blank voltammogram for Pt(110)/CO electrode, in 0.1 M HClO<sub>4</sub> shows a multiplicity of peaks that have been associated with differentially charged states. These states in the positive-going sweep correspond to desorption of hydrogen and the simultaneous adsorption of anionic species (OH) [9]. To compare the correlation between the PDS reduction current and the position of the pztc, the integrated charge curve, obtained as previously described [37] in combination with the CO charge displacement, has also been included in the figure and the location of the pztc marked with a circle. The pztc are 0.233 V and 0.245 V for Pt(110)/H<sub>2</sub> and Pt(110)/CO, respectively. It is clear that the main reduction peak is shifted to negative values in comparison with the pztc for both cooling atmospheres. Because it is well known that anion adsorption shifts the pztc in the negative direction and that sulfate is produced during PDS reduction, this shift could be a consequence of the presence of sulfates near the surface of the electrode. In fact, previous studies with Pt(111) have

shown that the amount of sulfate on the surface under these conditions might be around  $10^{-3}$  M [29]. To clarify this point, we recorded the blank voltammogram with this sulfate concentration. The results are shown in the insets to figure 2 (C and D, for  $H_2$  and CO cooled electrode, respectively). The presence of a small amount of sulfate in solution shifts the adsorption states towards negative values, resulting also in a shift of the pztc in the same direction (with sulfate, the pztc values shift to 0.205 and 0.199 V for Pt(110)/ $H_2$  and Pt(110)/CO, respectively). Besides, this experiment shows that the splitting of the PDS reduction peak for the electrode cooled in CO is due to the overlap with the pseudocapacitive response of the surface present in the blank voltammogram, as deduced from the coincidence of the voltammetric peaks.

PDS reduction was also carried out on an Pt(110) electrode cooled in air (not shown). The result is quite similar to that obtained when the surface is cooled in hydrogen: only one reduction peak is observed at nearly the same potential as the electrode cooled in hydrogen.

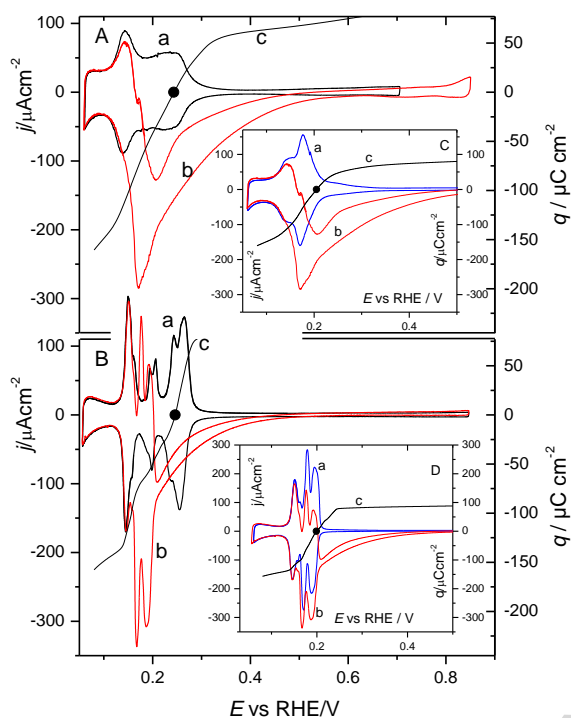


Figure 2. PDS reduction on Pt(110) A) cooled in  $\text{H}_2+\text{Ar}$  mixture; B) cooled in carbon monoxide in 0.1 M  $\text{HClO}_4$  (a) or 0.1 M  $\text{HClO}_4 + 10^{-3}$  M PDS (b). Inset figures (C and D) correspond to voltammograms recorded in solutions with sodium sulfate ( $10^{-3}$  M) for both cooling procedures. Scan rate: 50 mV/s.

### 3.1.2 Pt(S)[n(110)x(111)]

Figure 3A and B shows the PDS reduction on Pt(S)[n(110)x(111)] electrodes cooled in hydrogen and carbon monoxide, respectively. By comparing the CV's of the different electrodes in Fig. 3A it can be noted that the introduction of steps increases the reduction current that reaches a maximum for Pt(991), a surface with a terrace length of 5 atoms. Then, the current density decreases again. Another point that deserves attention is that the step density increases the onset potential for PDS reduction, moving it to more positive potentials in all cases. For Pt(331), a reduction peak is observed around 0.65 V associated to the high density of (111) sites on this surface. Figure 3B shows that PDS reduction on stepped electrodes cooled in CO is quite

different from that on the electrodes cooled in hydrogen. Several reduction peaks are visible similar to the result for Pt(110). As before, the peak splitting is most likely due to the overlap of the reduction current with the pseudocapacitive currents due to adsorption/desorption processes. As steps are introduced, the peak splitting progressively disappears. On Pt(771)/CO only two reduction peaks are observed in the positive-going sweep whereas on the negative-going sweep only one peak remains located at the same potential than on the electrode cooled on hydrogen. For the Pt(331) orientation (see inset in figure 3) significant differences are obtained when both cooling atmospheres are compared. While the electrode cooled in H<sub>2</sub>/Ar shows the peak at 0.6 V attributed to (111) terraces, the electrode cooled in CO does not show any contribution in this potential region. The presence of this peak in the electrode cooled in H<sub>2</sub>/Ar might indicate some degree of faceting that is avoided by cooling in CO. The second voltammogram shows sharper peaks and lower currents suggesting some possible surface annealing.

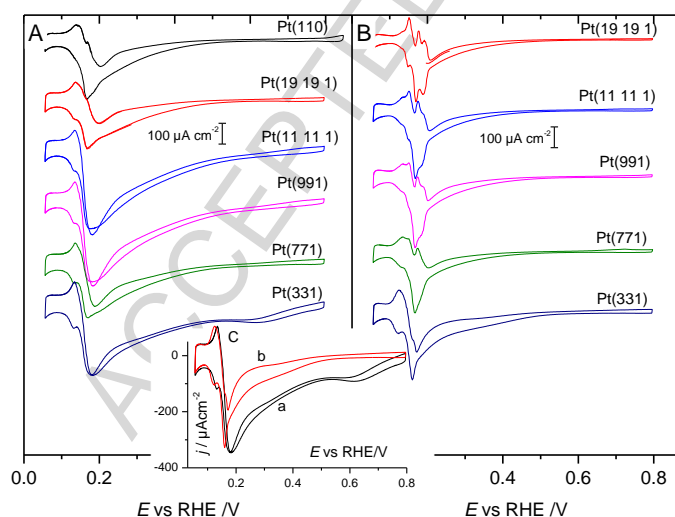


Figure 3. PDS reduction on Pt(S)[n(110)x(111)] cooled in A) H<sub>2</sub>/Ar mixture and B) CO. Inset (C) shows the comparison of the voltammogram obtained for Pt(331) in both cooling atmospheres: a) H<sub>2</sub>/Ar and b) CO. 0.1 M HClO<sub>4</sub> + 10<sup>-3</sup> M PDS. Scan rate: 50 mV/s

### 3.1.3 Pt(S)[n(110)x(100)]

**Figure 4** shows the voltammetric features for PDS reduction on stepped surfaces with (110) terraces and (100) steps cooled in H<sub>2</sub>/Ar and CO. Only one reduction peak is observed for most of the surfaces cooled in hydrogen (**Fig. 4A**). The peak potential is located around 0.17 V (negative-going sweep) / 0.19 V (positive going sweep) and this value remains constant regardless of the step density. For Pt(210), the turning point, two reduction peaks are visible: one peak around 0.20 V and a second, smaller one, around 0.32 V (positive-going sweep, **Fig. 4A**). It can be concluded that the former corresponds to the reduction on (110) sites whereas the latter is most likely due to the reduction on (100) sites. The PDS reduction on (100) monoatomic steps on Pt(S)[n(111)x(100)] electrodes takes place around 0.31 V [29]. Therefore, the process observed here at 0.32 V most likely corresponds to (100) sites. The absence of PDS reduction around 0.32 V ((100) sites) on other stepped surfaces reveals that surface disorder associated to the existence of faceting or reconstruction processes is important on these surfaces, masking the response from (100) sites. On the electrodes cooled in carbon monoxide with wide terraces ( $n \geq 20$ ) it is possible to see three reductions peaks at potentials lower than 0.22 V. As previously mentioned, the splitting of the peak is most likely due to the overlap of pseudocapacitive processes. For intermediate terraces ( $n \approx 10$ ), two reduction peaks are observed at 0.16 and 0.20 V. For Pt(430), a surface with 4-atom terrace length, only one peak appears at 0.18 V. However, significantly larger currents are obtained with the electrode cooled in H<sub>2</sub>/Ar than in CO. For Pt(210) the behavior is similar to the one obtained by cooling in H<sub>2</sub>/Ar, i. e., two reduction peaks at 0.20 and 0.32 V.



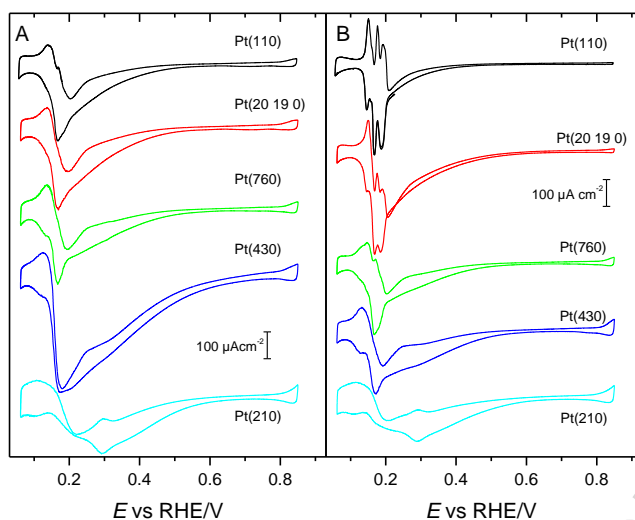


Figure 4. PDS reduction on Pt(S)[n(110)x(100)] electrodes cooled in A) H<sub>2</sub>/Ar and B) CO. 0.1 M HClO<sub>4</sub> + 10<sup>-3</sup> M PDS. Scan rate: 50 mV/s.

### 3.2 Pt(100) pole

#### 3.2.1 Pt(100). Basal plane

Typical voltammograms for PDS reduction on Pt(100) cooled in the two different atmospheres are shown in **Fig. 5**. Both cooling procedures produce very similar blank profiles in the absence of PDS and only subtle changes are observed. In the electrode cooled in CO, the current density at  $E < 0.3$  V is slightly lower than for the electrode cooled in H<sub>2</sub>/Ar. Also, the sharp peak around 0.30 V is more notorious for the electrode cooled in CO. At  $E > 0.5$  V, the current density for both electrodes is similar. The PDS reduction currents recorded on Pt(100) cooled in H<sub>2</sub>/Ar are in agreement with previously reported data [38]. Moreover, the PDS reduction on the electrode cooled in CO is also similar to the electrode cooled in H<sub>2</sub>/Ar. The comparison with an electrode cooled in air (not shown) brings clues to understand the different contributions in the PDS reduction profile. Pt(100) cooled in air produces a surface with a high density of defects [20, 21]. The reduction of PDS on the electrode cooled in air shows a reduction current between 0.3-0.37 V and the shoulder at 0.6 V is less visible. Therefore, we

attribute the shoulder at 0.6 V to the presence of long range ordered (100) terraces. The slightly bigger peak observed with the electrode cooled in CO might suggest that this treatment produces a better ordered surface in agreement with STM results [20, 21].

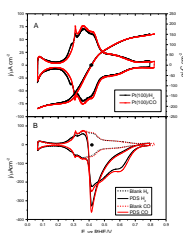


Figure 5: A) Blanks for Pt(100) cooled in different atmospheres (left-axis). The  $q$  vs  $E$  curves are also shown (right-axis) and the position of the pztc pointed out with a black circle. B) PDS reduction on Pt(100) cooled in  $H_2/Ar$  (black curve) and carbon monoxide (red curve)

### 3.2.2 Pt(S)[n(100)x(111)]

The PDS reduction on stepped surfaces with (100) terraces separated by monoatomic steps with (111) symmetry, cooled in  $H_2$  are shown in **Fig. 6A**. As the step density is increased from Pt(100) to Pt(311), two reduction peaks are observed. The peak current at 0.42 V decreases as the terrace length becomes shorter. On the other hand, a peak develops around 0.3 V, increasing as the step density becomes higher. After the comparison with the blank voltammograms for the basal plane and the stepped surfaces, it is possible to conclude that the peak at higher potentials corresponds to the reduction on the (100) terraces whereas the one at lower potentials corresponds to the reduction of PDS on (111) steps or terrace edges. The shoulder located at 0.6 V for the basal plane becomes less visible as the step density increases, reinforcing the idea that this shoulder is indicative of long range order. For Pt(711) (an electrode with a terrace length equal to 4-atoms) the shoulder is completely absent

regardless of the cooling procedure. **Figure 6B** shows cyclic voltammograms for PDS reduction on the Pt(S)[n(100)x(111)] surfaces cooled in CO. The behavior is similar to that found for the same surfaces cooled in H<sub>2</sub>/Ar. There are, however, some differences in the current density associated to the step site that must be pointed out. On the surfaces cooled in CO, the reduction at 0.3 V is less visible than for electrodes cooled in H<sub>2</sub>/Ar (**Fig. 6A and 6B**). This comparison becomes clearer in the inset of figure 6, where the results for Pt(711) on both cooling atmospheres are compared. The peak at 0.30 V is larger on the surface cooled in H<sub>2</sub> while the contribution from (100) terraces is larger on the surface cooled in CO. Therefore, we can conclude that the CO cooling procedure generates a more ordered surface with larger (100) terraces, most likely as a result of a faceting process.

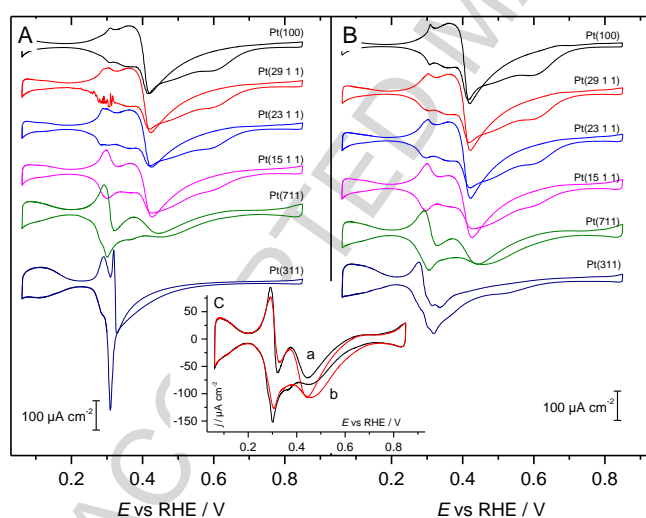


Figure 6: PDS reduction on Pt(S)[n(100)x(111)] electrodes cooled in A) H<sub>2</sub>/Ar ; B) in carbon monoxide. C) comparison of the voltammograms obtained for Pt(711) cooled in a) H<sub>2</sub>/Ar and b) CO. 0.1 M HClO<sub>4</sub> + 10<sup>-3</sup> M PDS. Scan rate: 50 mV/s.

### 3.2.3 Pt(S)[n(100)x(110)]

**Figure 7** shows the PDS reduction on electrodes with Miller indices (n, 1, 0) cooled in H<sub>2</sub> and CO. For electrodes having wide terraces cooled in H<sub>2</sub>/Ar, a reduction peak at 0.41 V is observed whereas the peak at 0.3 V is barely visible. However, a clear increase in the reduction current at 0.3 V was observed with the increase of (110) steps (**Fig. 7A**). On electrodes cooled in CO (**Fig. 7B**) the PDS reduction shows two reduction peaks at 0.41 and 0.30 V, similar to the result for electrodes cooled in H<sub>2</sub>/Ar. In both cases, the potential of the peaks at 0.3 and 0.41 remains at an almost constant value, regardless of the step density. In addition to the similarities just described, some differences are also found between both cooling procedures. The shoulder at 0.6 V for electrodes with wide terraces is more visible in electrodes cooled in CO than for those cooled in H<sub>2</sub>/Ar. Besides, similarly to the result observed on Pt(S)[n(100)x(111)] surfaces, the current density at 0.3 V is lower in surfaces cooled in CO than in hydrogen. (**Fig. 7C**).

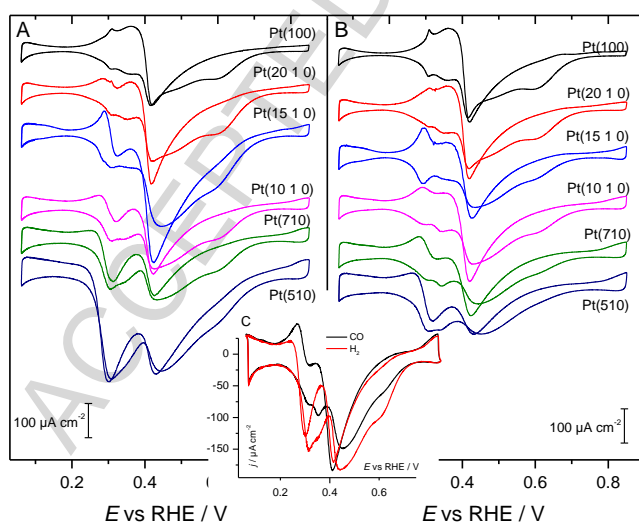
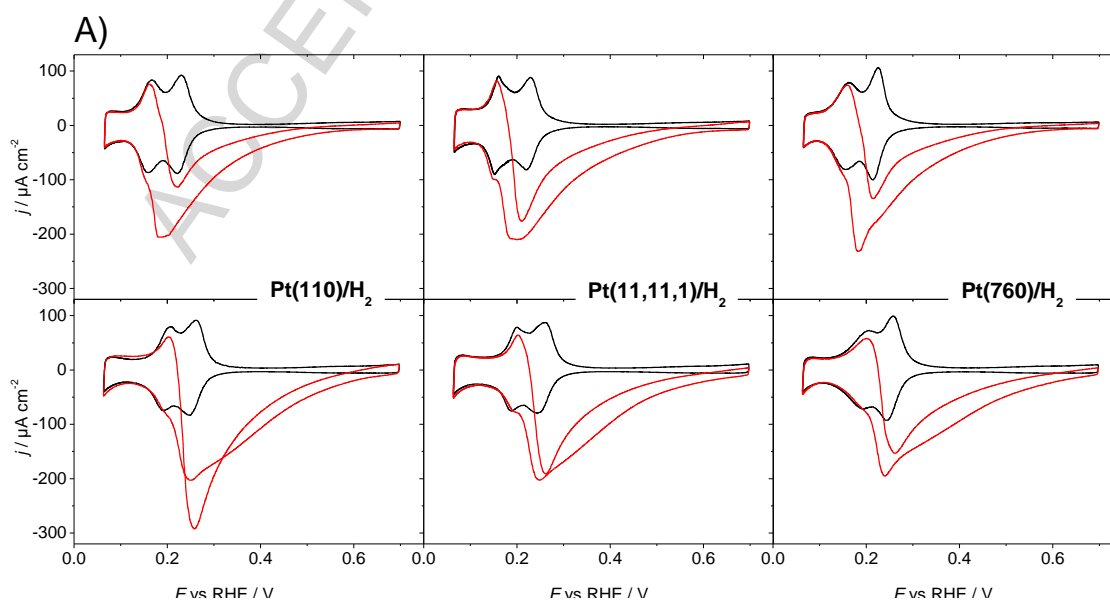


Figure 7. PDS reduction on Pt(S)[n(100)x(110)] cooled in A) H<sub>2</sub>/Ar mixture; B) CO. C) comparison of both cooling treatments for Pt(710). 0.1 M HClO<sub>4</sub> + 1 mM PDS. Scan rate: 50 mV/s

### 3.3 pH effects

#### 3.3.1 (110) pole

**Figure 8A and B** shows the PDS reduction on stepped surfaces vicinal to the (110) pole cooled in H<sub>2</sub>/Ar and CO at pH 3 and 5, respectively. Only one reduction peak is observed on surfaces cooled in H<sub>2</sub>/Ar, similar to the results found at pH 1. Meanwhile, multiple peaks are observed for surfaces cooled in CO. On both pHs, the voltammetric current recorded in solutions with or without PDS coincides at lower potentials values. As the pH becomes more alkaline, the reduction peak moves to more positive potentials in the RHE scale. At pH 3 and 5 the reduction peak on Pt(110)/H<sub>2</sub> is located at 0.215 V and 0.238 V. The situation is similar for surfaces cooled in CO. This potential shift is equal to approximately 15 mV/pH unit in the RHE scale or 45 mV/pH unit in the SHE scale. Such displacement parallels the shift of the peaks in the blank voltammogram, that moves with the pH nearly with the same slope. This anomalous pH-shift (smaller than the expected Nernstian shift of 59 mV/decade) has been reported for (110) steps in the past [39]. As the adsorption processes strongly decrease as the pH increases, the multiple peaks observed on surfaces cooled in CO are less visible at more alkaline pHs.



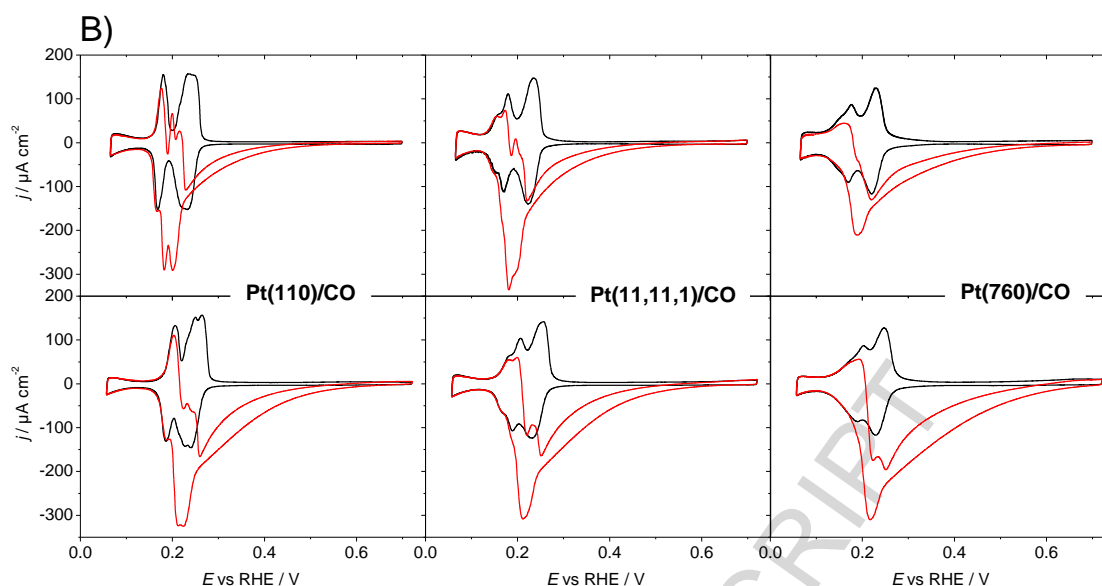


Figure 8. PDS reduction on Pt(110), Pt(11,11,1) and Pt(760) cooled in H<sub>2</sub>/Ar (A) and CO (B) at pH 3 (upper panel) and pH 5 (lower panel). NaF + HClO<sub>4</sub> mixtures (0.1 M total concentration). 50 mV/s

### 3.3.2 (100) pole

Figure 9A and B shows the PDS reduction on stepped surfaces vicinal to the (100) pole cooled in H<sub>2</sub>/Ar and CO at pH 3 and 5. At pH 3, the PDS reduction on Pt(100) and vicinal surfaces cooled in H<sub>2</sub>/Ar show similar behavior to that described for pH 1. For the basal plane, only one reduction peak at 0.448 V vs RHE is observed. For Pt(15,1,1) and Pt(710), two reduction peaks are observed. One reduction peak is at a similar potential to that found in Pt(100) and another one emerges around 0.345 V vs RHE. This means approximately 15mV/pH unit in the RHE scale for the step. A similar shift is found for the peak that belongs to the terrace. On surfaces cooled in CO the behavior is similar. Two reduction peaks are observed for stepped surfaces, while only one peak is observed for the basal plane. Again, the reduction current around 0.34 V is lower in surfaces cooled in CO than those cooled in H<sub>2</sub>/Ar. At pH 5 the PDS reduction is completely inhibited on Pt(100) cooled in both atmospheres. On stepped surfaces the

reduction is not completely inhibited and some reduction currents are observed, mainly in the sites associated to terrace border. For example, on Pt(710)/H<sub>2</sub> the reduction current is significant around 0.37 V vs RHE; the current for the same surface cooled in CO is less important.

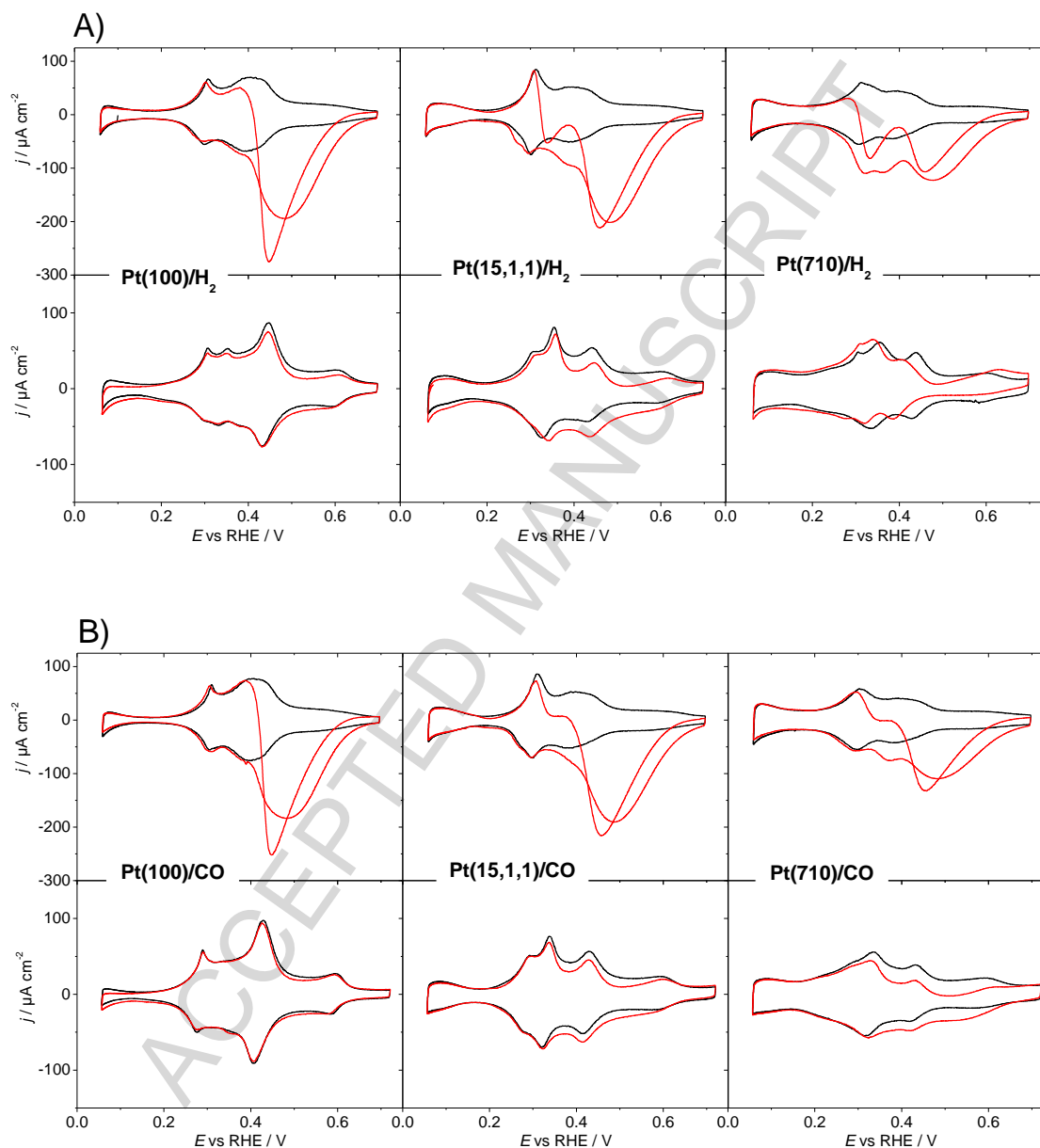


Figure 9. PDS reduction on Pt(100), Pt(15,1,1) and Pt(710) cooled in hydrogen (A) and CO (B) at pH 3 (upper panel) and pH 5 (lower panel). NaF + HClO<sub>4</sub> mixtures (0.1 M total concentration). 50 mV/s

#### 4. Discussion

PDS reduction has often been taken as a model anionic reduction reaction taking place, particularly on mercury, at very large negative overvoltages, in a region of potentials where the electrode surface is negatively charged [40, 41]. The influence of double layer effects on such reactions becomes very important. In particular, the variation of the potential in the diffuse part of the double layer leads to what has been called the Frumkin effect [42]. For this reason, PDS reduction has been extensively investigated in a broad range of cathode materials [38, 40, 41, 43-46]. This reaction is often described as taking place through several parallel pathways that can be grouped in two extreme situations [42, 46]. In the outer sphere pathway, the PDS anion situated at the OHP receives the electron transferred from the surface through a weak coupling interaction with the electrode. In this situation, the rate of the reaction should be independent of the electrode material and, on the other hand, very sensitive to double layer effects, such as the depletion of anionic species due to the electrostatic interaction with a negatively charged electrode surface. For this reason, the reaction becomes sensitive to the pzc of the electrode, since this affects the charge at a particular potential. A different reaction pathway would involve the formation of adsorbed intermediates. This pathway is expected to be sensitive to the surface structure given the influence of the latter on the adsorption isotherm of adsorbed intermediates. In particular, if PDS needs to be adsorbed before the electron transfer, the inhibition of the reaction is expected at negative charges. Also, competition with other adsorbed species such as hydrogen, hydroxyl or anions will have a great influence on the rate of the reaction. In agreement with previous studies [27, 29] the reaction on platinum seems to proceed through the second pathway mentioned above, involving adsorbed intermediates. Comparison with data on different cathodic materials [40] suggest that the outer sphere pathway would take place at more negative polarization, in a potential range that is precluded due to the presence of hydrogen evolution. Besides, according to the classical equations describing the Frumkin effect [40], the outer sphere pathway is inhibited due to the relatively high pzc values of



platinum surfaces in comparison with mercury or other investigated cathodic materials. For Pt(111) and its vicinal surfaces, PDS reduction takes place in a relatively narrow potential range, being inhibited both at the low and at the high potential ranges [27, 29]. The inhibition at low potentials is more puzzling since, when the reaction is studied at higher pHs, the current drop takes place in a potential range where the surface is expected to be free of adsorbed species. This led us to propose that the free charge on the electrode is the main parameter governing the position of the current drop [27, 29]. As a result, the reaction becomes a sensitive probe to interrogate the position of the pzfc of platinum electrodes. Moreover, the existence of several reduction peaks for stepped surfaces suggests that the reaction is sensitive to the local properties of the surface, i.e., to the local values of pzfc of terrace and step sites [29]. The observed trends for the variation with the step density of the characteristic potential values extracted from the PDS reduction curves turned out to be consistent with the variation of pme values measured with the laser induced temperature jump method, giving support to this hypothesis [29].

Similar to the strategy followed in our previous works [27, 29], we can use the inhibition potential ( $E@j=0$ ) for the different surfaces studied here to get an estimation of the location of the pzfc. The  $E@j=0$  for Pt(110) can be read from the CVs of figure 2 by looking for the potential where the current for PDS reduction coincides with the current in the blank. The values are 0.138 V and 0.152 V, for the electrode cooled in  $H_2/Ar$  and CO respectively. Comparison with the values of pztc coming from CO-displacement experiment shows that the trend is the same (surface cooled in hydrogen has a lower value than that cooled in CO) but, the actual values are different. On the other hand, if the value of  $E@j=0$  is compared with pme values, a good agreement is obtained. The pme value for Pt(110)/ $H_2$  is around 0.145 V vs RHE [33] and 0.150 V for Pt(110)/CO (unpublished result). These values are near to the values obtained from the PDS reduction approach. The  $E@j=0$  for Pt(100) cooled in hydrogen or CO is around

0.375 V vs RHE. Comparison with the pzfc value, 0.415 V [2], or the pme, 0.345 V [33] reported in the past for the surface cooled in hydrogen point out the effectiveness of the PDS reduction to get information about the charge state. We have previously proposed that pme values can be taken as a good indication of the location of the pzfc if the orientation of interfacial water is dominated by electrostatic interactions [33]. The only case where independent measurements of pzfc and pme can be obtained is Pt(111) in non-adsorbing electrolyte solution, where hydrogen and anion adsorption are well separated [33, 47]. In this case, good correspondence between pme and pzfc supports the correspondence between both parameters. For Pt(110) and Pt(100), the pzfc values obtained from CO charge displacement lie in the hydrogen region. Since hydrogen adsorption gives a negative contribution to the total charge, it is clear that at the pzfc the free charge should be positive to compensate the hydrogen charge. Consequently, the pzfc should be at negative potentials relative to the pztc. Indeed, pme values for Pt(110) and Pt(100) are more negative than pztc values [33]. The good coincidence between pme and the  $E_{@j=0}$  for Pt(110) demonstrates once more the consistency between the different approaches.

Regarding the values of  $E_{@j=0}$  for stepped electrodes with (110) terraces, a value around 0.14 V is obtained that remains constant with the step density. Within the framework presented in previous paragraphs, this value can be taken as indicative of the pzfc of (110) terraces. This approach fails to give a value for the local pzfc of (111) or (100) steps, since no characteristic feature can be attributed to these step sites in the PDS reduction profile. Only for the turning point on both crystallographic zones, a peak in the PDS reduction profile can be associated to step sites. For Pt(331)/H<sub>2</sub> (figure 3C) the shoulder around 0.60 V can be attributed to (111) steps and for Pt(210) a peak at 0.32 V can be attributed to (100) steps.

Regarding the results for electrodes vicinal to the (100) pole, the similarity between peak potential (0.42 V, decreasing with the step density and 0.30 V,

increasing with the step density) suggests a restructuring breaking the nominal structure of step sites. In this regard, STM results have shown that steps in Pt(S)[n(100)x(110)] surfaces evolve into a zig-zag structure changing the step symmetry from (110) to (111) [4]. Similar restructuring could also take place on the n(110)x(100) surfaces, as evidenced from the lack of (100) response in this case (figure 4). In relation to the peaks observed for (100) vicinal surfaces, the peak at 0.41 V likely belongs to the reduction of PDS on (100) terraces, whereas the nature of the reduction peak at 0.3 V is more elusive. The first hypothesis is that the peak at 0.3 V corresponds to the reduction on (110) step sites since these are the nominal ones and also the current density increases as the step density increases. However, a comparison with the basal plane, Pt(110), reveals that the response at 0.3 V must correspond to sites of a different geometry. Therefore, the response at 0.3 V could correspond to the first row of (100) sites on the terrace adjacent to the step or to the (111) step.

Another remark worth noting is that, contrary to the result reported for (111) terraces [29] where the peak potential for the PDS reduction on terraces moves to more positive potentials as the terrace width decreases, the peak potential for the (110) or (100) terraces remains constant. The potential where reduction current drops to zero remains also constant with the step density on the crystallographic zones investigated in this paper.

## 5. Conclusions

	$E_{\text{peak}}$ (V vs RHE)	$E_{@j=0}$ (V vs SHE)	pH-dependence in RHE scale ( same electrode)	Step density dependence (the same pH, different value of $n$ )
<b>Basal planes</b>				
Pt(111)	0.52 (pH 1) 0.62 (pH 3) 0.72 (pH 5)	0.29 pH 1 0.28 pH 3 0.27 pH 5	$\approx 53\text{mV/pH}$	The $E_{\text{peak}}$ and the $E_{@j=0}$ move to more positive potentials as the terraces become shorter
Pt(110)	0.19 (pH 1) 0.22 (pH 3) 0.24 (pH 5)	0.08 pH 1 -0.03 pH 3 -0.11 pH 5	$\approx 15\text{mV/pH}$	The $E_{\text{peak}}$ and $E_{@j=0}$ remain approximately constant
Pt(100)	0.40 (pH 1) 0.43 (pH 3) N/A (pH 5)	0.32 pH 1 0.21 pH 5 N/A pH 5	$\approx 15\text{mV/pH}$	The $E_{\text{peak}}$ and $E_{@j=0}$ remain approximately constant
<b>Stepped surfaces</b>				
Steps (111) on terraces (100)	0.328 (pH 1)	0.249 pH 1	$\approx 5\text{mV/pH}$	The $E_{\text{peak}}$ and $E_{@j=0}$ remain

<b>Pt(15,1,1)</b>	0.335 (pH 3)	0.137 pH 3		approximately constant
Steps (111) on terraces (110)	No current observed	————	————	————
Steps (110) on terraces (111) <b>Pt(775)</b>	0.156 pH 1 0.200 pH 5	0.086 pH 1 -0.08 pH 5	$\approx 12\text{mV/pH}$	The $E_{\text{peak}}$ and $E_{@j=0}$ remain approximately constant
Steps (110) on terraces (100) <b>Pt(710)</b>	0.308 pH 1 0.334 pH 3	0.210 pH 1 0.119 pH 3	$\approx 13\text{mV/pH}$	The $E_{\text{peak}}$ and $E_{@j=0}$ remain approximately constant
Steps (100) on terraces (111) <b>Pt(755)</b>	0.318 pH 1 0.343 pH 3	0.23 pH 1 0.07 pH 5	$\approx 13\text{mV/pH}$	The $E_{\text{peak}}$ and $E_{@j=0}$ remain approximately constant
Steps (100) on terraces (110)	No current observed	————	————	————

**Table 1:** Summary of the most important parameters characterizing the PDS reduction on platinum stepped surfaces.

We have shown that the peroxodisulfate reduction can be used to investigate the surface properties of complex platinum stepped surfaces by a simple methodology, just employing cyclic voltammetry. In the present manuscript, we have applied this approach to study Pt stepped surfaces vicinal to the (110) and (100) poles. The dependence of characteristic potential values (peak potential and potential where current drops to zero,  $E_{@j=0}$  values) with step density, cooling atmosphere and pH has been carefully investigated. In general, our previous hypothesis about the (approximate) coincidence of  $E_{@j=0}$  values and  $p_{\text{me}}$  is supported by the new data. Regarding the local contribution of terraces and step sites, where  $E_{@j=0}$  values cannot always be obtained, peak potential can be taken as indicative of the local properties of the surface.

Table 1 presents a summary of the most important parameters extracted from the study of the PDS reduction on platinum single crystals electrodes from references [27, 29] and from the present study. It is clear that a significant difference exists between the behavior of (111) sites and the (110) and (100) sites. First, the peak and inhibition potential of (111) terraces closely follows Nernstian behavior with pH whereas the dependence found in the other crystallographic symmetries is non-Nernstian. In general, step sites also show non-Nernstian behavior with pH. Regarding the effect of step density, both the peak and inhibition potential for the (111) site shifts to more positive potentials as the width of the terrace decreases, whereas for sites with (110) and (100) symmetry, the peak potential remains invariant with the step density. In the case of

(111) terrace, disruption of the water network was taken as a tentative explanation of the observed trend [29]. The fact that for (110) and (100) surfaces this behaviour differs may point out the particular interaction of the water network with (111) surfaces given the better matching of the water network with the hexagonal distribution of atoms on the surface. Another important finding extracted from table 1 is the observation of only one reduction peak for surfaces with (110) terraces. The reason for this behavior is likely associated to the particular morphology of this kind of surfaces, since (110) sites can themselves be considered as stepped sites composed of two (111) unit cells. An open question that remains is why the PDS reduction on (100) symmetry is completely inhibited as pH is more alkaline.

The effect of the cooling atmosphere (either H<sub>2</sub>+Ar mixture or CO) has also been examined. In particular, for surfaces cooled in CO a better long range ordered surfaces are obtained. It is not always clear, however, that the result will be consistent with the nominal structure predicted from the hard sphere model of the surface.

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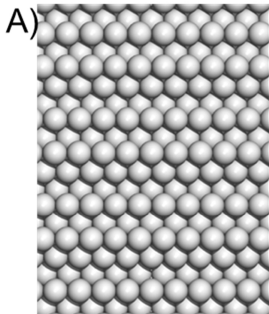
## Highlights

- Peroxodisulfate reduction is investigated on platinum stepped single crystals vicinal to (110) and (100).
- The surface structure depends on the cooling atmosphere after flame annealing.
- CO atmosphere appears to produce the most ordered surface.
- The peroxodisulfate reduction magnifies the differences on the surface structure caused by the cooling atmosphere.
- The pH dependence of the peroxodisulfate reduction reveals a non-Nernstian behavior.

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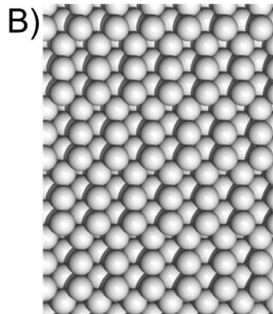
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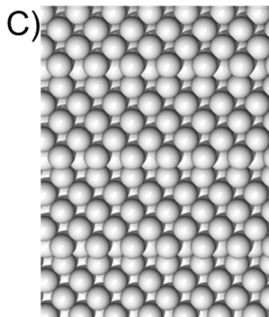
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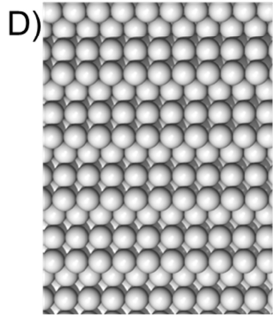


Figure 1

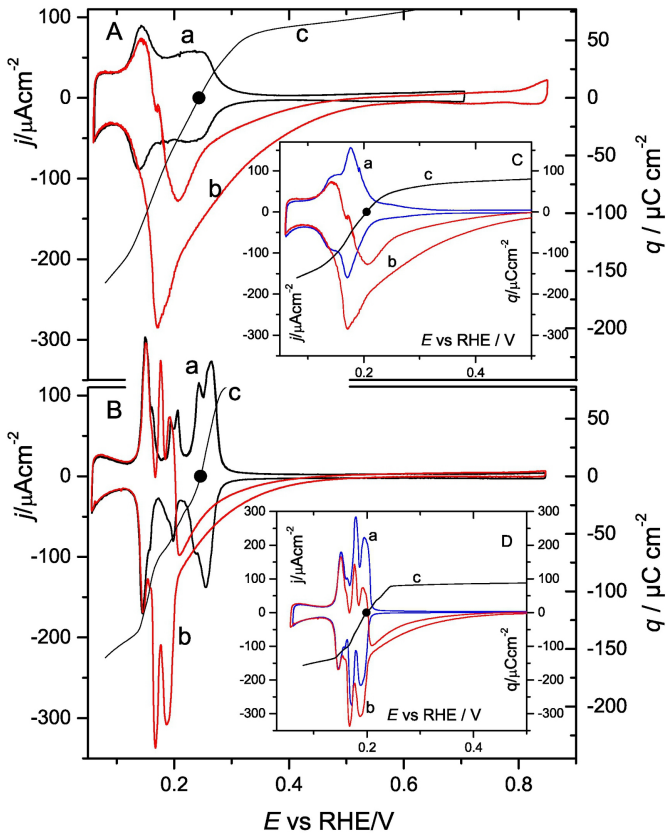


Figure 2

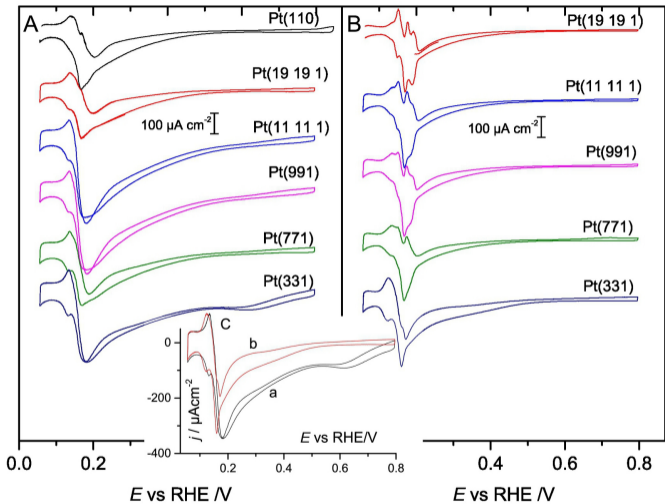


Figure 3

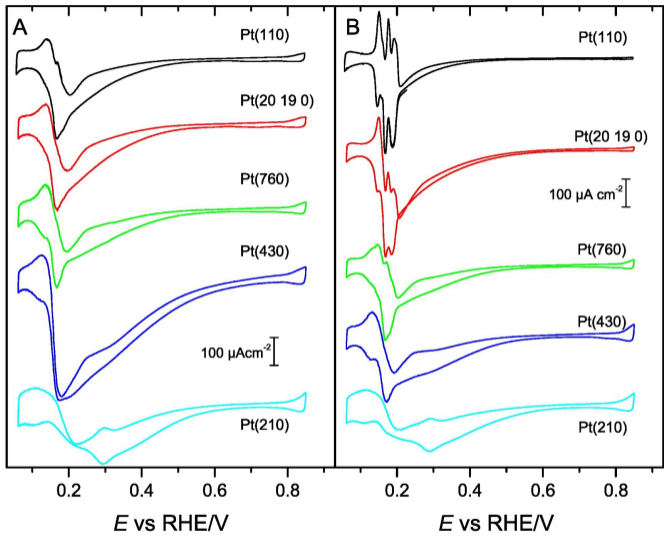


Figure 4

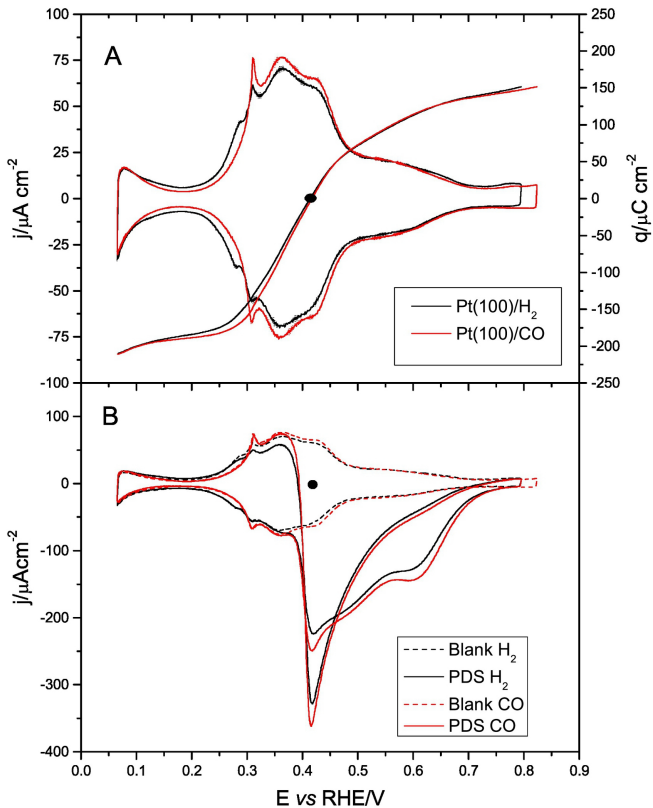


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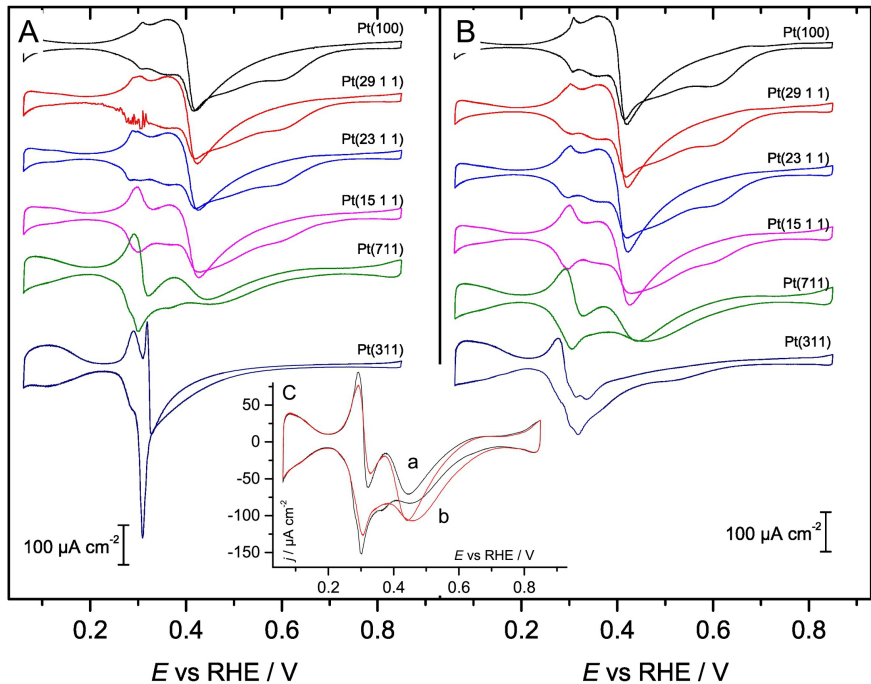


Figure 6

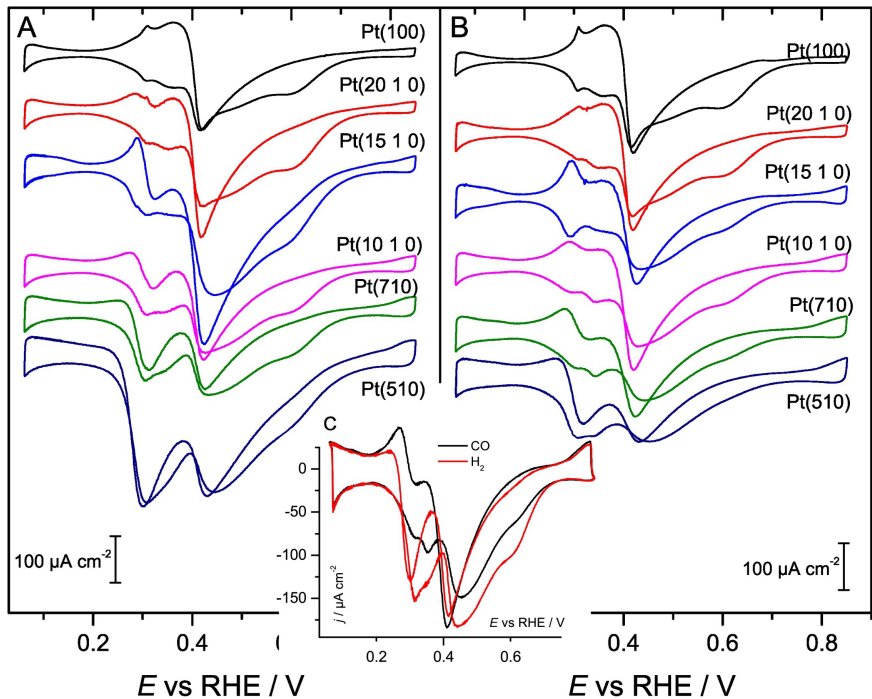


Figure 7



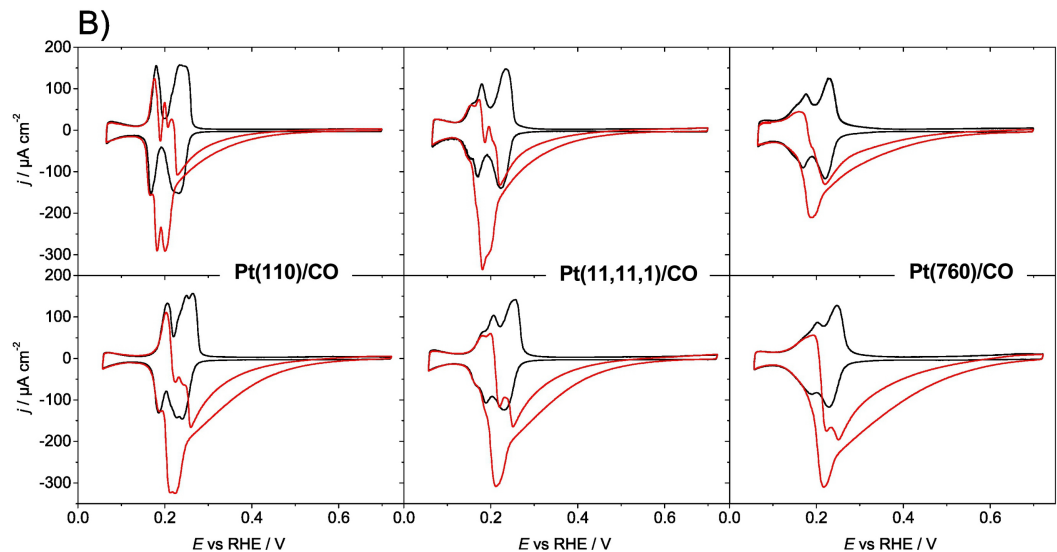
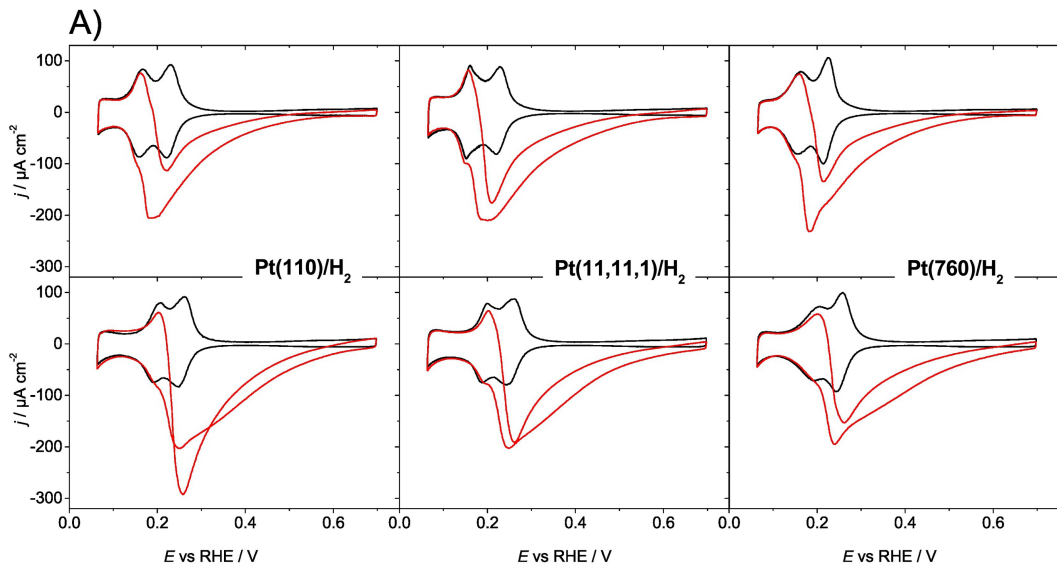
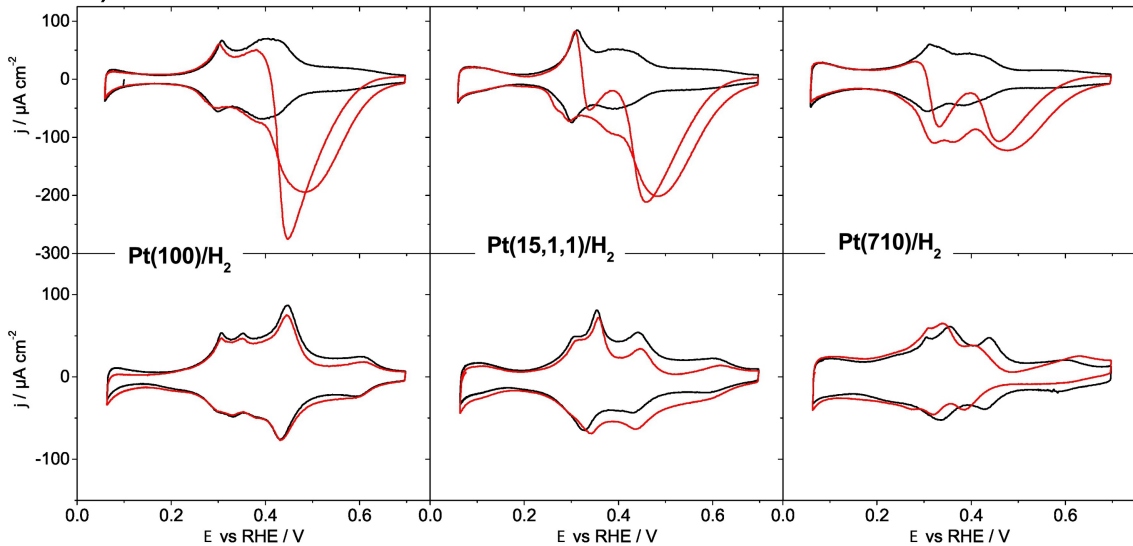


Figure 8

A)



B)

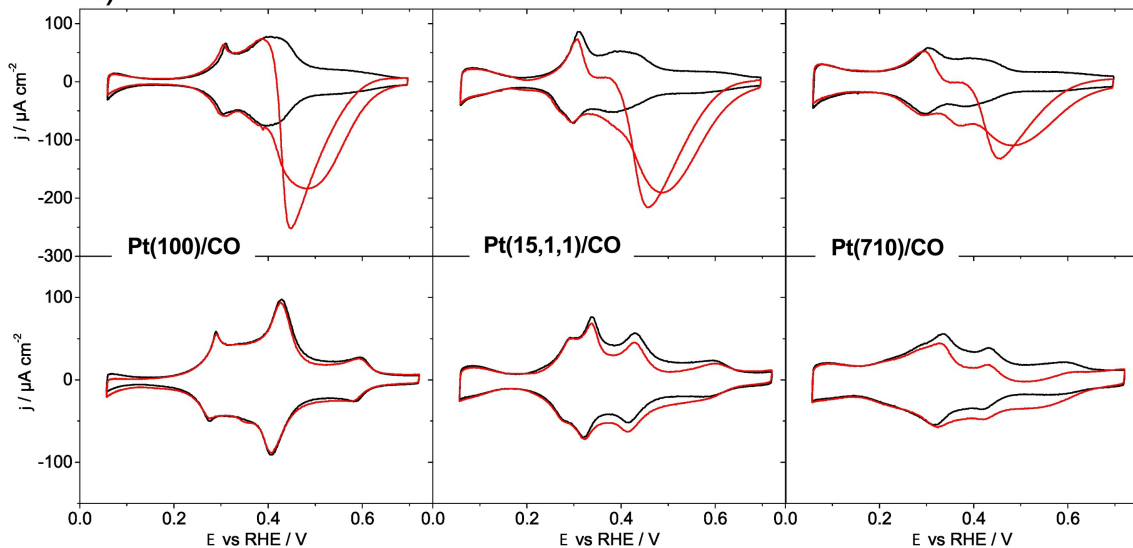


Figure 9