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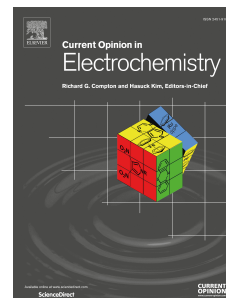
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On the nature of adsorbed species on Platinum Single Crystal electrodes.

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Abstract

The dependence of voltammetric currents on multiple parameters (concentration, pH, temperature, etc) has become a primary source of information in interfacial studies of noble metal electrodes. Peak potential, charge, and width are intimately related to surface structure and reactivity. However, this interpretation usually neglects the complexity of the redox processes involved. For the so-called hydrogen adsorption region in platinum, anion competitive adsorption plays an important role that is usually overlooked. While charge displacement already demonstrated decades ago the existence of anion adsorption contributions, only recently a combination of several surface-sensitive techniques has proven unambiguously the presence of OH adsorbed on step site at potentials much lower than usually considered. This information must not be neglected when analysing the properties of complex catalysts such as those composed of nanoparticles since it is of great importance for understanding its overall reactivity, for comparing with computational results, and for performing coulometric analysis.

Introduction.

Already in the very early studies that identified the existence of adsorption processes in the voltammetry of noble metal electrodes, it was soon realised the existence of a correlation between surface structure and voltammetric profile [1–3]. This correlation, which could be used to characterise the morphology of the electrode surface, elevated the cyclic voltammetry to the category of a surface characterization technique. The idea underlying this approach is the identification of certain voltammetric currents with adsorption processes that are highly dependent on the local nanoscopic environment surrounding the adsorption site. Adsorption energies depend on the distribution of atoms on the surface, the bonding mode of the adsorbing

molecule or adatom, and the lateral interactions between adsorbed species. Moreover, voltammetric peaks appear located at potentials directly correlated with the adsorption energies, with an area proportional to the number of adsorbed species and a width related to the nature of lateral interactions. In consequence, the voltammogram as a whole is often considered a fingerprint characteristic of the nanoscopic properties of the surface.

After the introduction of the flame annealing technique in the early 80s [4,5], the field of surface electrochemistry experienced a remarkable boom. Previous interfacial studies were mainly limited to mercury electrodes and results with solid metal electrodes were irreproducible and unreliable [1,6,7]. The flame annealing technique brought into play an inexpensive and broadly available method to achieve clean and ordered surfaces in electrochemistry [4]. Many laboratories turned their attention towards the interfacial studies with noble metal electrodes, mainly platinum and gold, and soon many relationships between surface structure and reactivity could be established. A huge amount of information has been acquired in the last decades, using a combination of multiple electrochemical and non-electrochemical techniques, including vibrational spectroscopies and scanning probe microscopies. Unfortunately, such wealth of information acquired with well defined surfaces is often overlooked by many researchers working with complex catalysts in real operating conditions, namely, dispersed nanomaterials. In this paper, we give a reflection about the importance of considering the true composition of the surface to understand reactivity and to correctly analyse integrated charges. In particular, we stress the importance of acknowledging the presence of anionic species, namely, hydroxyl or other anions on the most reactive sites on the surface.

Relationship between adsorption processes and surface sites.

Simple electrosorption isotherms, like Langmuir or Frumkin isotherms, predict a voltammetric peak for each adsorption process [8–13]. Then, the number of adsorbed species can be determined from the number of peaks and their surface concentration from the charge under each peak. The reality, however, is more complex, and real voltammograms contain a multiplicity of overlapping peaks, which are strongly dependent on the surface structure and composition of the solution. Therefore, although the idea of the voltammogram as a fingerprint is still valid, there is some uncertainty in the assignment of the charge under the different peaks to distinct species. Such assignment is usually based on the hard-sphere model of the surface that allows the calculation of the atomic density on the surface [14]. However, this model requires some arbitrary classification of available adsorption sites. For instance, in stepped

surfaces, adsorption sites are often classified as belonging to the terrace or the step although, in reality, there are more than two different kinds of atoms. A paramount example of such ambiguity is the $\text{Pt(S)}[n(111) \times (11\bar{1})]$ family of stepped surfaces since the step between (111) and $(11\bar{1})$ surfaces can be understood as either (111) or (110) steps (Figure 1a) [15]. When the (110) symmetry for the step is considered, the terrace has one fewer atom than in the other symmetry, which now belongs to the step site. For these surfaces, the voltammogram shows a clear peak at 0.12 V that grows as the density of step atoms increases (Figure 1b) that has been typically assigned to hydrogen adsorption on step atoms [15].

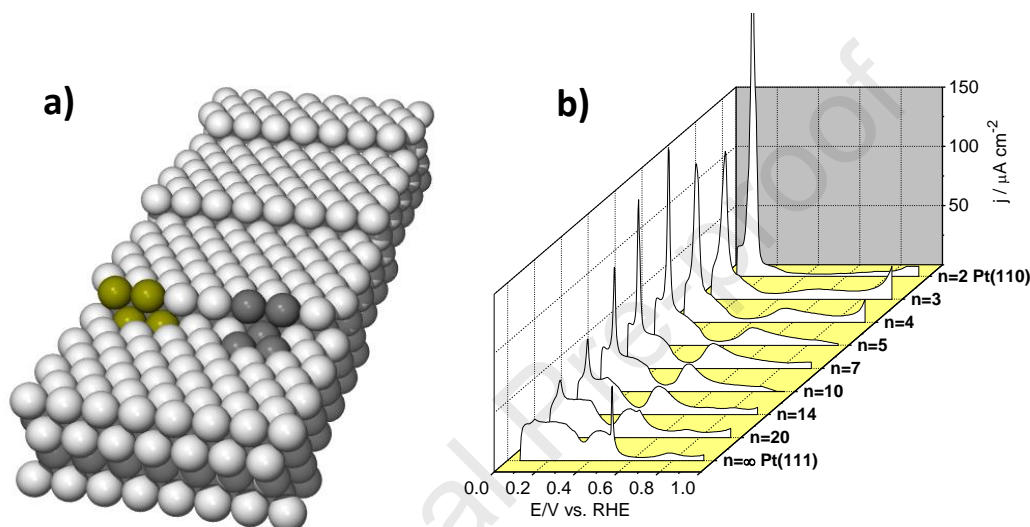


Figure 1. a) Schematic Illustration of a $\text{Pt(S)}[n(111) \times (11\bar{1})]$ surface. The green spheres represent a step considering a (111) geometry and the dark grey spheres highlight a step with a (110) geometry for the same surface. b) Cyclic voltammograms for a set of stepped surfaces belonging to the $\text{Pt(S)}[n(111) \times (11\bar{1})]$ series in $0.5 \text{ M H}_2\text{SO}_4$. Scan rate 50 mV s^{-1} (Adapted from ref.[15]).

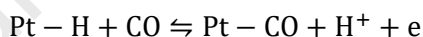
With this assumption in mind, it has been shown that the charge of this peak is consistent with the step density when the step is considered as belonging to the (110) symmetry. However, such an assignment has been questioned because it has been considered that anion adsorption may coexist with hydrogen adsorption in the same peak [16–18]. Such competitive coexistence of hydrogen and OH adsorption in a single voltammetric peak has been unambiguously demonstrated for the $\text{Pt}(110)$ basal plane [17,19]. Therefore, it is natural to think that similar competitive adsorption holds for the step sites with the same symmetry as the (110) basal plane. The specific influence of the nature of the cation on the so-called step peak has also been taken

as an indication that cations coadsorption takes place together with hydrogen and anion adsorption, possibly in the form of an adduct with the anion [20,21].

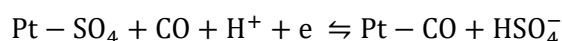
Identification of the adsorbed species involved in the voltammetric signals.

One strategy for the separation of different contributions contributing to the voltammetric charge, which has been used extensively in our group, is the potentiostatic charge displacement [22–25]. In this approach, a displacing agent that adsorbs strongly on the surface is introduced, displacing all the previously adsorbed species present at the potential of the experiment. To perform this experiment with Pt and Pt-group metals, CO is an excellent displacing agent, since it adsorbs very strongly, displacing almost any adsorbed species on the surface. Besides, being a gas, it can be easily introduced into the cell atmosphere, and its excess can be easily removed from the solution by bubbling Ar. Since the adsorbed CO can be eliminated from the surface through oxidation to CO₂, the recovery of the surface after the experiment can be assessed, ensuring the integrity of the process.

Described in chronological order, the first success of this technique was to demonstrate that the voltammogram of Pt(111) in sulphuric acid solution was composed of two regions: the hydrogen adsorption region below 0.3 V and the sulphate adsorption region above this potential value[26]. Hydrogen displacement leads to positive (oxidation) currents, according to:



On the other hand, sulphate displacement leads to negative (reduction) current, according to:



One limitation of the CO as a displacing agent is that it cannot be used at potentials where its oxidation takes place because it loses its character as a neutral probe. In acidic solutions, this means that it cannot be used above 0.5 V, while in alkaline solutions the range of potentials is even more restrictive since above 0.3 V it is readily oxidized. However, this is not a major problem because, given the charge conservation principle, the difference of displaced charge at two potentials should be equal to the charge required to voltammetrically transform the interphase from one potential to the other. In other words, the charge displaced at one potential can be combined with the voltammetric charge to recreate the complete charge vs potential curve. The validity of this assumption was tested for different electrode surfaces and solution compositions [23,27]. In this way, although it cannot be demonstrated directly with CO charge displacement, the adsorption states at high potentials in the voltammogram of Pt(111) in

perchloric acid solutions could be assigned to anion adsorption. This assignment was unambiguously proved using a second displacing agent, namely iodine [28,29]. Iodine is a much less convenient displacing agent than CO since it cannot be removed from the solution after each experiment, and it has a much narrower potential range of application because iodine is reduced to iodide at lower potentials and oxidised to iodate at higher potentials. Still, it could be used to displace the anion present on Pt(111) in perchloric acid solutions at 0.9 V, proving the consistency between voltammetric charges and displaced charges between both displacing agents.

Once the nature of these adsorption states was proved to be anionic, the nature of the adsorbed species still remained questionable. Some debate exists about whether perchlorate can adsorb specifically or not on platinum surfaces. The fact that exactly the same voltammogram was obtained with the three basal planes of platinum in perchloric acid and trifluoromethyl sulfonic acid was taken as proof that the adsorbed species should be the hydroxyl since the only anion present in both solutions is the hydroxide anion [30]. Moreover, similar adsorption states are also registered in hydrofluoric acid and in NaF/HF mixtures where no perchlorate is present [31,32].

Pt(111) is special among the different platinum surfaces because hydrogen and anion adsorption processes are well separated, as can be observed in Figure 2a: the hydrogen adsorption process takes place between 0.06 V and 0.40 V whereas the OH adsorption occurs between 0.55 V and 0.90 V [22]. The situation is more complicated for other platinum surfaces. For Pt(100) several peaks are observed in the voltammogram that can be assigned to hydrogen and anion adsorption. In perchloric acid solutions, a deconvolution has been proposed of the double-layer corrected voltammetric profile of Pt(100), showing the hydrogen adsorption and OH adsorption contributions overlapped from ca. 0.3 V (Figure 2b) [33]. However, the shape of two competing Frumkin isotherms is more complex than the simple deconvolution in figure 2b, as has been pointed out elsewhere [34].

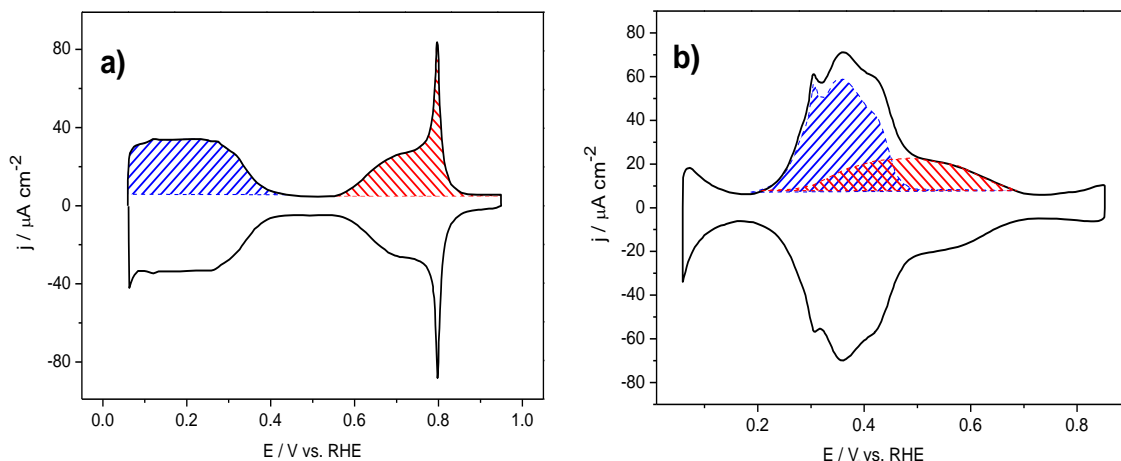


Figure 2. Cyclic voltammograms for a) Pt(111) and b) Pt(100) in 0.1 M HClO_4 at 50 mV s^{-1} . The region in blue corresponds to the hydrogen adsorption and the red one to the OH adsorption processes. The proposed deconvolution for the Pt (100) profile is adapted from ref [33].

Neglecting this relatively subtle effect, the voltammetric profile in this region can be fitted very well by a Frumkin isotherm with repulsive interactions [35]. Using this approach, a thermodynamic analysis of both the hydrogen and OH adsorption region could be done after such separation [36]. An additional complication with this surface is related to the presence of defects created after the elimination of the hexagonal reconstruction that takes place on the free surface prior to the contact with the solution [37,38]. In this way, different peaks and shoulders can be measured in the voltammogram associated with monodimensional (100) rows or (111) steps. Such defects are likely to adsorb hydroxyl at lower potentials. However, such local contributions cannot be separated using the charge displacement experiment since this technique only provide the overall charge on the surface and not the local contributions. Only in the case of relatively high step densities, a net contribution from the OH adsorption can be separated from the overall hydrogen adsorption on the terraces.

A similar situation happens with the Pt(110) surface. Again, the characteristic voltammetric features of this surface are determined, to a large extent, by the existence of a (1×2) reconstruction. In this structure, every second row of topmost atoms is lost in such a way that microfacets with (111) symmetry are formed (Figure 3a)[39].

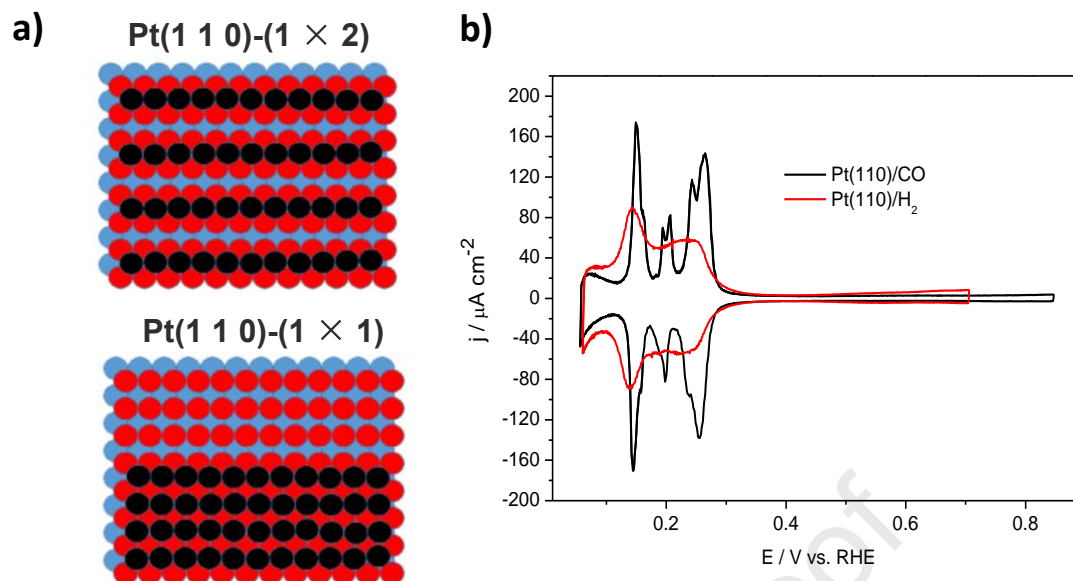
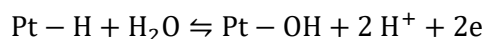


Figure 3. a) Schematic representation of the ordered (110)-(1x2) and (110)-(1x1) surfaces. Adapted from ref. [39] b) Cyclic voltammograms for the H₂ (red curve) and CO-cooled (black curve) Pt(110) surface in 0.1 M HClO₄ solution, Scan rate 50 mV s⁻¹.

In this case, the reconstruction is very sensitive to the rate of cooling after the flame annealing and the cooling atmosphere. Recent results have proposed that Pt(110) surfaces cooled in a reductive atmosphere created by mixing H₂ with Ar result in a partially reconstructed (1x2) surface [17,39]. In this case, the voltammogram contains two peaks, the one at lower potentials, mainly due to hydrogen adsorption, but the one at higher potentials more likely due to hydrogen desorption coupled to OH adsorption according to the reaction (Figure 3b, red curve):



It could be then said that OH adsorption is the driving force for hydrogen desorption at low potentials. The (1x2) reconstruction is lifted at high temperatures in the flame and, therefore, the surface is in the (1x1) structure at high temperatures after the flame annealing. If the cooling takes place very fast, the (1x1) structure is frozen, resulting in an unreconstructed surface. However, if the cooling ramp is slower (as would be the case with a larger electrode with a slower rate of heat transfer) patches of the (1x2) structure are formed as detected by X-ray scattering [40,41]. Finally, if the cooling is done in a CO atmosphere, CO adsorption stabilizes the (1x1) structure (Figure 3a)[39] and the reconstruction does not take place [17,39]. Allegedly, this is the most ordered surface that can be obtained by the flame annealing method. The voltammogram corresponding to this surface is composed of a series of peaks (Figure 3b, black

curve) that could be grouped in three sets, each one with a mean peak and a shoulder, that has been ascribed each one of them to hydrogen displacement by OH in sites of different geometry [39]. It has been demonstrated that coulometric considerations based on the deconvolution of the peaks lead to a correct estimation of the potential of zero total charge [17]. This reinforces two key ideas: First, that one peak is not necessarily ascribed to a single adsorbed species, but it can involve the cooperative/competitive coadsorption of multiple species[42,43], and, second, the important role that OH adsorption plays in the surface chemistry of platinum electrodes.

All the observations made above regarding well-defined single-crystal electrodes should be considered to explain the voltammetry of polycrystalline platinum electrodes and complex nanoparticle catalysts. In both cases, the heterogeneous surface can be understood in a first approximation as the addition of different contributions of sites of different geometry[44,45]. A more accurate description should also consider the electronic interactions between patches of different geometry. The voltammetry of polycrystalline platinum is composed of several peaks. Figure 4 depicts the cyclic voltammetry for the polycrystalline Pt surface plotted together with the voltammetric profiles for the Pt(111), Pt(110), and Pt(711) (Pt(S)[4(111) × (100)] step surface) surfaces. It shows how cyclic voltammetry for the polycrystalline surface results from a combination of all the different facets present at the surface. This correlation between the behaviour of single crystalline and polycrystalline surfaces is clearly observed in sulphuric acid solutions since the peaks for the different sites are better defined. Nevertheless, a similar situation is observed in the absence of specific anion adsorption, i.e., in perchloric acid or NaOH solutions[45]. In perchloric acid solutions, two peaks are typically observed in the voltammogram. The one at the lowest potentials, around 0.12 V, can be correlated with the first peak present in (110) surfaces and therefore ascribed mainly to hydrogen adsorption on local sites of this geometry. As mentioned above sites of this geometry involve also OH adsorption at potentials as low as 0.2 V. Such OH adsorption is usually neglected when the reactivity of platinum is considered, although it can imply important consequences for oxidation reactions that require a source of oxygen to be complete. Even more, OH is expected to adsorb on the (100) step sites that are typically correlated with the peak at 0.32 V.

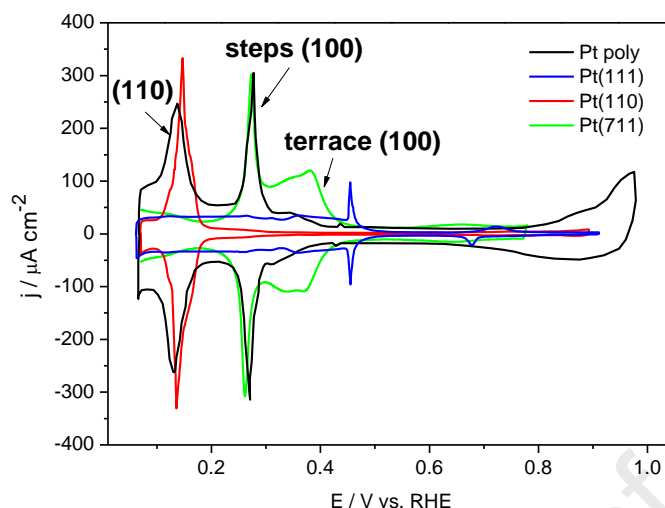


Figure 4. Cyclic voltammograms for Pt-polycrystalline, Pt(111), Pt(110) and Pt(711) surfaces in 0.5 M H₂SO₄ solution. Scan rate 50mVs⁻¹

To approach the study of complex real catalysts the study of stepped and kinked surfaces has been considered as an intermediate step to model such heterogeneous surfaces. We have recently combined electrochemical and spectroelectrochemical techniques to unequivocally identify the presence of OH-adsorbed species on a Pt(311) stepped surface, which contains two atom-wide (111) terraces and a monoatomic (100) step [24]. For this surface, the voltammetric profile is clearly divided into two different regions: the adsorption of hydrogen on the terrace sites takes place below 0.23 V and the step sites contributed at potentials above this value. Also, the step adsorption states are split into two peaks (figure 5a). CO displacement experiments were performed at three potentials (Figure 5b): at 0.24 V, the displaced charge was positive. At this potential, hydrogen on the terrace has been already desorbed and the positive charge indicates that hydrogen was adsorbed on the step. On the other hand, at 0.40 V, at the positive end of the peak, negative currents were measured in the transient, pointing out the presence of OH adsorption on the (100) steps. This finding was further confirmed by AC Voltammetry and Raman spectroscopy. Although postulated many times in the past from indirect observations [16–18,20,21], this is the first time in which several techniques have been combined to identify the presence of this important intermediate at the steps.

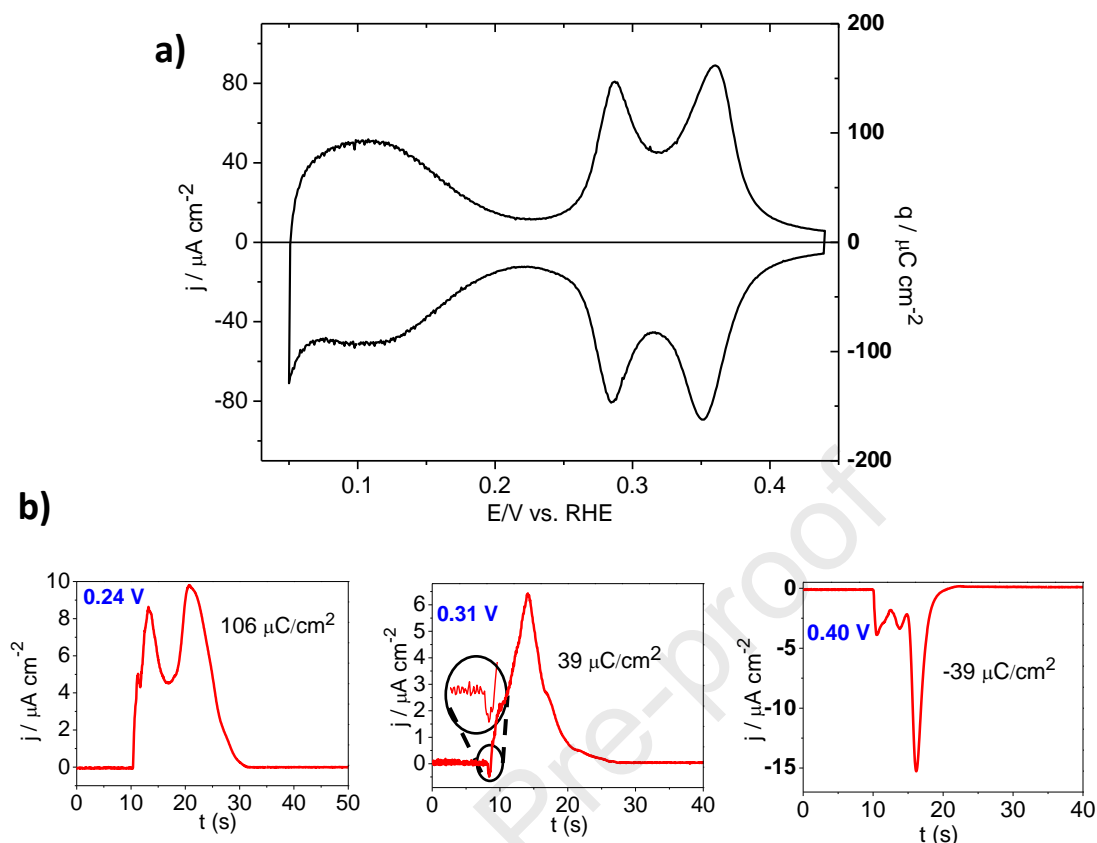


Figure 5. a) Cyclic voltammogram for Pt(311) surface and b) CO displacement experiments at different potentials in 0.1 M HClO_4 solution. Scan rate 50 mV s^{-1} Adapted from ref. [24]

Extending these studies to stepped surfaces with longer terraces is not an easy task since, while the local coverage of OH on the step can be significantly high, the overall coverage is low since the density of steps decreases as the length of the terrace increases. In general, the careful analysis of charge curves obtained from the combination of voltammetry and charge displacement shows the existence of positive net charges at potentials above the voltammetric peak that can be assigned to the step. The positive charge should be assigned to OH locally adsorbed on step sites.

Conclusions

Although the picture revealed in recent years about the adsorption processes taking place on noble metal electrodes is more complex than initially thought, still many publications simplify the interpretation. In this regard, it is common to find the expression “hydrogen peaks” when talking about the voltammetry of polycrystalline platinum. According to what has been discussed here, a significant contribution to the charge in the “hydrogen region” corresponds to

anion adsorption, either hydroxyl or any other anion present in the solution. This contribution can have important consequences in the interpretation of electrocatalytic phenomena such as oxidation of organic molecules, and oxygen reduction. Also, coulometric calculations from stripping voltammetry need to be adjusted to take into account the true nature of the adsorption processes. One iconic example is the calculation of CO coverage from its oxidation charge. This charge contains a significant contribution from the re-establishment of the anion adlayer that needs to be considered before the calculation of the coverage [46]. Although this idea was pointed out more than a decade ago, still many publications take an incorrect baseline for the calculation of the CO charge.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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