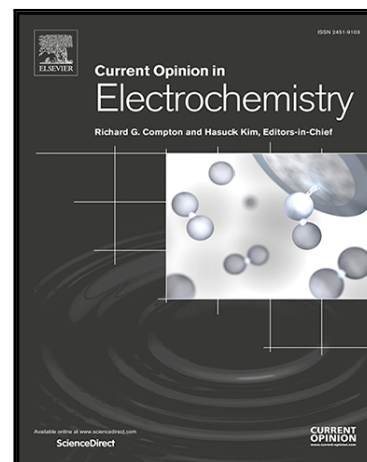


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**Highlights**

- Recent works regarding the ORR at Pt are reviewed.
- The possibility of a soluble ORR intermediate is discussed.
- The effect of the adsorption strength of oxygenated species on the ORR is analyzed.
- The role of the water structure close to the surface on the ORR is highlighted.

*Oxygen reduction at Platinum electrodes: The interplay between surface and surroundings properties*

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### Abstract

In this work, recent progress in the understanding of the mechanism of the oxygen reduction reaction at Pt surfaces is shortly reviewed. Specifically, the presence of a soluble and short-lived intermediate different to H<sub>2</sub>O<sub>2</sub> in the ORR reaction path and the interrelated effect between the surface arrangement, adsorption of oxygen-containing species and water structure in the ORR reactivity in acid environments are discussed. Besides, the influence of the proton concentration on the ORR product distribution, the existence of a chemical step and the possible role of the soluble intermediate as a bifurcation point in the mechanism are also analyzed.

**Keywords:** Scan rate study, mass-transport effects, rotating disk electrodes, hydroperoxyl radical, water structure, Volcano curves.

### Introduction

The sustainable commercialization of fuel cell and advanced metal-air power sources depends on, among other things, the development of better electrocatalysts for the oxygen reduction reaction (ORR). For this goal, it is fundamental to identify the underlying dynamics that governs the ORR mechanism. However, even for platinum, the best pure metal electrocatalyst for the reduction of oxygen, the molecular-level details of this reaction are not well understood.

In this short review, recent studies of the ORR at Pt surfaces, but mainly at Pt(111) single crystal, are discussed. These works have evidenced the complexity of this reaction that takes place through several interconnected chemical and electrochemical steps, but at the same time, given new valuable information into the details of the ORR mechanism.

### **ORR at Pt(111): A soluble and short-lived, intermediate species different to H<sub>2</sub>O<sub>2</sub>**

A few years ago, ORR studies at Pt(111) electrodes in acid reported indirect evidences for the existence of a soluble intermediate, with a short lifetime, formed at potentials close to the reaction onset,  $E_{onset}^{ORR}$  [1-4]. It was first noted that the value of ORR peak currents,  $j_p^{ORR}$ , in linear sweep voltammograms (LSVs) at the same scan rate,  $\nu$ , was lower at stationary relative to rotating disk electrodes (RDEs) under non-steady state conditions, and it increased with the rotation rate,  $\omega$ , as it is shown in Figures 1A and 1B. Besides, it was also noted that when the potential was held at a value,  $E_h$ , close to  $E_{onset}^{ORR}$ , for a certain time,  $\tau_h$ , at stationary electrodes,  $j_p^{ORR}$  continuously increased until reaching a limiting value, Fig. 1C [3]. This increase in  $j_p^{ORR}$  was measured even if  $E_h$  is chosen to be a potential where oxygen is being reduced, but close to  $E_{onset}^{ORR}$ , for which a continuous increase in the diffusion layer thickness is expected, as it is depicted by curve *a* in Fig. 1C where  $E_h = 0.95$  V.

After a careful analysis of experimental and theoretical works, the hydroperoxyl radical, HO<sub>2</sub><sup>\*</sup>, was proposed to be the most probable species responsible of current-potential, *j*-*E*, dynamics in Fig. 1. Here, because of the lack of a parallel oxidation peak if, instead of a negative-, a positive-going scan is measured, it was concluded that hydrogen peroxide could not be responsible of the unusual *j*-*E* responses. If H<sub>2</sub>O<sub>2</sub> accumulates close to the electrode surface to produce the increase in  $j_p^{ORR}$  in Fig. 1, an equivalent increase, but in oxidation currents, should have been measured when the positive-going scan was recorded, because both the reduction and oxidation of H<sub>2</sub>O<sub>2</sub> on Pt surfaces only are controlled by the mass transport [5,6]. In addition, spectroscopic studies have already identified adsorbed superoxide ion, O<sub>2</sub><sup>-</sup><sub>ads</sub>, as an intermediate species in the ORR on Pt(poly) [7-9].

The formation of a soluble and short-lived intermediate, or an adsorbed one that desorbs and goes to the solution, different to H<sub>2</sub>O<sub>2</sub>, was not envisioned before. Indeed, the fact that a soluble species is formed close to the reaction onset strongly suggests that

at those potentials the dissociative adsorption of oxygen is not the preferential reaction path for the ORR in these surfaces, putting an end to a long-standing dilemma regarding this possibility [10]. Nevertheless, it could be still possible that at potentials lower than  $E_{onset}^{ORR}$ , the initial dissociation of oxygen could become the dominant route, because of the decrease in the surface coverage of oxygen-containing species.

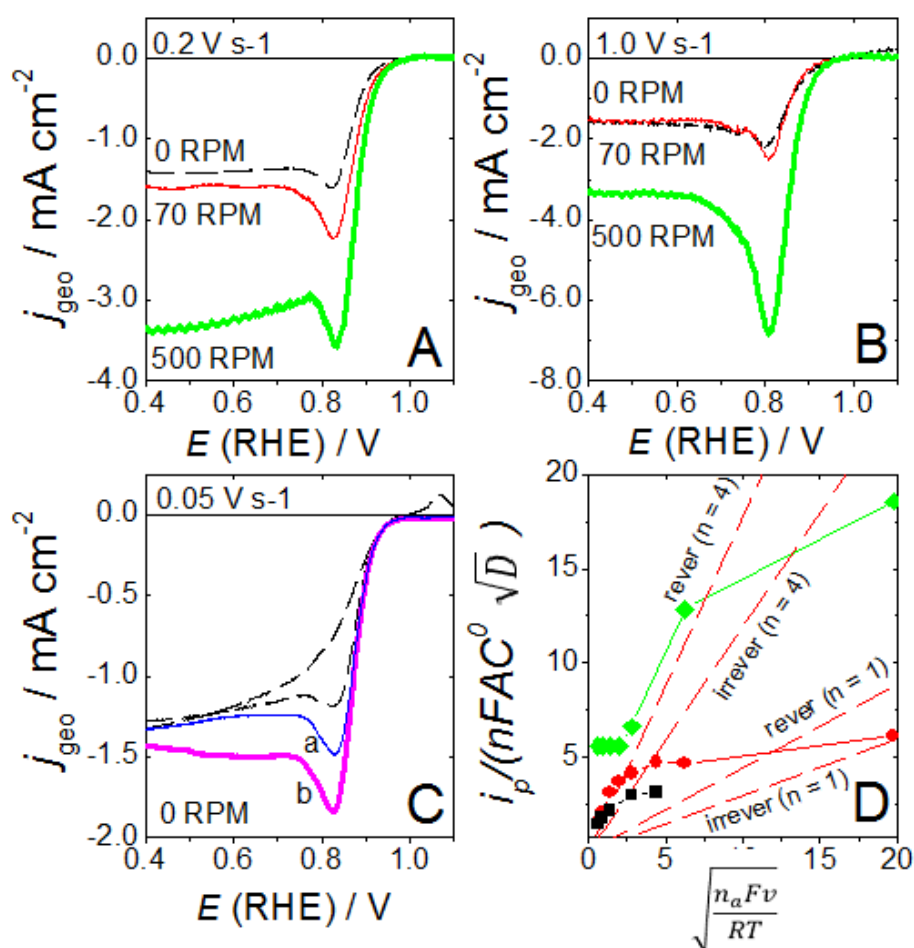


Figure 1: Negative-going linear sweep voltammograms for the oxygen reduction in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> on stationary and rotating Pt(111) electrodes at different scan rates. (A) and (B) LSVs at 70 (thin line), 500 rpm (thick line) and stationary electrodes (dashed line). (C) LSVs after holding the potential at  $E_i = 0.95 \text{ V}$  for 120 s (thin line),  $E_i = 1.20 \text{ V}$  for 30 s (thick line) and for the cyclic voltammogram (dashed line). (D). Normalized peak currents against the square root of the normalized scan rate at stationary (■) and rotating disk electrodes at 70 (●), 500 (◆). For the sake of comparison, theoretical curves for single four ( $n = 4$ ), and one ( $n = 1$ ) total charge

transfers with a first fast and slow ( $\alpha = 0.5$ ) electron transfer are also given in D (dashed lines).

### A chemical step inside the ORR mechanism

From the theory for single fast, Eqn. (1a), or slow, Eqn. (1b), electron transfers at both stationary and rotating electrodes,  $j_p$  should increase proportional to  $\sqrt{v}$ , regardless the rotation rate [11-13], according to,

$$j_p = 0.446nFAC_o^0\left(\sqrt{\frac{n_aFDv}{RT}}\right) \quad (1a)$$

$$j_p = 0.496nFAC_o^0\left(\sqrt{\frac{\alpha n_aFDv}{RT}}\right) \quad (1b)$$

where  $n$ ,  $n_a$ ,  $F$ ,  $A$ ,  $C_o^0$ , and  $D$ ,  $\alpha$ ,  $R$  and  $T$  have the usual meaning.

These equations are also valid for  $n$ -electron processes with the first electrochemical step as rate-determining step (RDS) [11], and thus, in principle they should have been also valid for measured  $j_p^{ORR}$  during the ORR at Pt at different  $v$  [1,4,10]. However, this was not the case, not only because of the  $\omega$ -dependence of  $j_p^{ORR}$  in Fig. 1, indicating the presence of a soluble intermediate, but also due to the levelling of  $j_p^{ORR}$ , first at stationary electrodes and RDEs at slow  $\omega$ , at increasing  $v$ 's [1,2]. This last dynamics is easier to note when changes in the normalized  $j_p^{ORR}$ ,  $i_p^{ORR}/nFAC_o^0\sqrt{D}$ , are plotted against the square root of the normalized scan rate,  $\sqrt{\frac{n_aFv}{RT}}$ , as in Fig. 1D, and suggests the existence of a chemical step in the ORR mechanism [11,12,14].

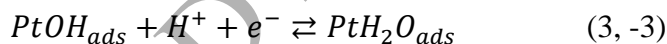
Additional evidences of a chemical step in the mechanism, probably involving the transference of protons, are provided by ORR studies at microelectrodes [15], sparse arrays of nanoparticles (NPs) [10,14], and planar Pt surfaces in buffer solutions with  $2.8 < pH < 5.6$  [16]. In these cases, lower limiting currents,  $j_{lim}$ , relative to the expected ones from the Levich equation [11] were reported, despite a proton flux to the surface high enough to support a four-electron transfer [10,14-16]. At  $2.8 < pH < 5.6$ ,  $j_{lim}$ 's still follow a linear relation with  $\omega^{1/2}$  but with a smaller slope than the expected one from the Levich equation for a 4-electron transfer, which would indicate that less electrons were transferred [11], although no increase in ring currents in a rotating ring-disk setup (RRDEs) were measured. This apparent contradiction between the change in  $j_{lim}$  with  $\omega^{1/2}$  and the lack of change in the product distribution, since there was no increase in the production of  $H_2O_2$ , is compatible with the existence of a fast surface chemical reaction,

involving the transference of protons, with a high equilibrium constant [17]. At higher  $pH$ s the total concentration of the product of the chemical reaction decrease because of the decrease in the proton concentration,  $[H^+]$ , which in turns affects the total amount of oxygen reduced to water.

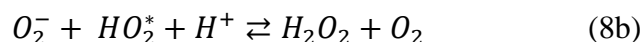
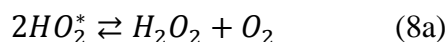
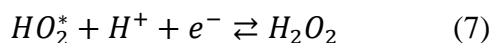
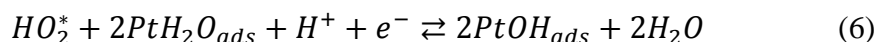
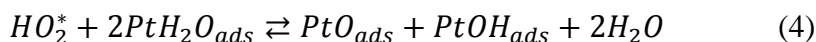
From available data, the production of  $HO_2^*$  by means of a concerted oxidation of the Pt surface, in a non-electrochemical reaction was proposed as first step [1-3,18], Eqn. (2). However, considering that apparently  $O_2$  does not directly accept protons during reduction steps [18,19], Eqn. (2) could possibly take place through the formation of adsorbed superoxide anion,  $O_2^{\cdot-}_{ads}$  followed by fast protonation. The influence of the surface on the  $pKa$  of adsorbed species would stabilize  $O_2^{\cdot-}_{ads}$  on the surface at  $pH = 1$  [20]. This step would explain the increased amount of adsorbed O-containing species at Pt, surfaces in  $O_2$ -saturated relative to  $O_2$ -free solutions [21-23], without a total charge transfer [1,2,12,18]. Note also that peroxo-like and superoxo-like two-dimensional (2D) surface oxides are already formed in  $O_2$ -free solutions [24], and thus the ORR could occur through similar intermediate structures.



Then, the first electron transfer would come from the immediate reduction of adsorbed hydroxyl,  $OH_{ads}$ , Eqn. (3), formed in Eqn. (2),



Regardless the exact mechanism, the formation of the  $HO_2^*$  radical opens the possibility of at least four, parallel subsequent reactions. It could dissociate into one adsorbed oxygen species, namely  $O_{ads}$  and  $OH_{ads}$ , or two  $OH_{ads}$ , in either I) a chemical process, Eqns. (4) or (5), or II) a electrochemical reaction, Eqn. (6). Also, III)  $HO_2^*$  could reduce to  $H_2O_2$  in a proton-coupled electron transfer (PCET), Eqn. (7), or IV) dismutate into oxygen and  $H_2O_2$ , Eqns. (8). Figure 2 depicts a simplified reaction mechanism, proposed to take place close to  $E_{onset}^{ORR}$  following the ideas exposed above [12].



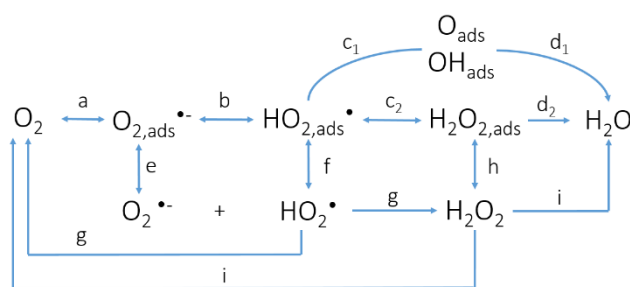


Figure 2. Simplified reaction mechanism proposed to occur close to ORR reaction onset at Pt surfaces [12].

The flexibility of  $\text{HO}_2^*$  to generate water, following either a direct route without the formation of  $\text{H}_2\text{O}_2$ , Eqns. (4) to (6), or a serial path through the formation of  $\text{H}_2\text{O}_2$ , Eqns. (7) and (8), is the reason why this radical was suggested to be a bifurcation point in the ORR at Au-Pd Nanoalloys [25]. In this sense, from what it has been exposed here, it appears that the same could apply at Pt surfaces, and probably at other non-precious (Cu) electrocatalysts [26]. Moreover, similar initial steps during the ORR at Pt in aqueous electrolytes have been also reported in aprotic solvents [27], which strongly suggests a unified initial ORR pathway, regardless the solvent and the electrode. The influence of these latter parameters would be reflected on the nature of final product and the magnitude of the ORR activity.

On the other hand, it has been recently reported that while the  $\text{H}_2\text{O}_2$  reduction at Pt(111) is inhibited between  $1.0 < pH < 5.4$  at potentials lower than the potential of zero free charge (PZFC) [5], an equivalent inhibition for the ORR only occurs at  $pH \leq 1.0$ , but not at  $3.0 < pH < 5.4$  [16]. This fact indicates a dependence of the product distribution during the ORR,  $\text{H}_2\text{O}_2$  or  $\text{H}_2\text{O}$ , on  $[\text{H}^+]$ . This result would open the possibility to control the main ORR product through a quantitative control of the proton transport kinetics to the catalyst, as it has been already demonstrated at non-precious (Cu) electrocatalysts [26], and it could guide the design of new Pt-based catalysts.

### **From ordered to polycrystalline electrodes: Effect of the surface arrangement, water structure and adsorption of oxygen-containing species on the ORR activity**

Studies at polycrystalline platinum, Pt(poly), also evidenced similar  $j$ - $E$  dynamics to those shown in Fig. 1 [12]. Hence, the formation of a soluble species with a short



lifetime, generated close to  $E_{onset}^{ORR}$ , is not an unique feature for the Pt(111) surface but, instead, it is a common step during the ORR in acid media. The consequences of these findings in the design of new materials and the durability of Pt-based catalysts are discussed elsewhere [12]. Nevertheless, the ORR activity at Pt(poly) is lower than the one at Pt(111) and its vicinal surfaces, despite the presence of defects at Pt(poly) surfaces. It is known that steps and defects at {111} and {110} terraces promotes the activity of Pt(111) and Pt(110) vicinal surfaces in acid [1,28-34], which it has been explained by considering the {111} terrace edges (bottom of the steps), also denominated concave defects [34], as the ORR active sites at high index planes [33,35]. Figures 3A and 3B illustrate ORR polarization curves at Pt(poly), Pt(100), Pt(111) and Pt(331) in both the positive- and negative-going LSVs.

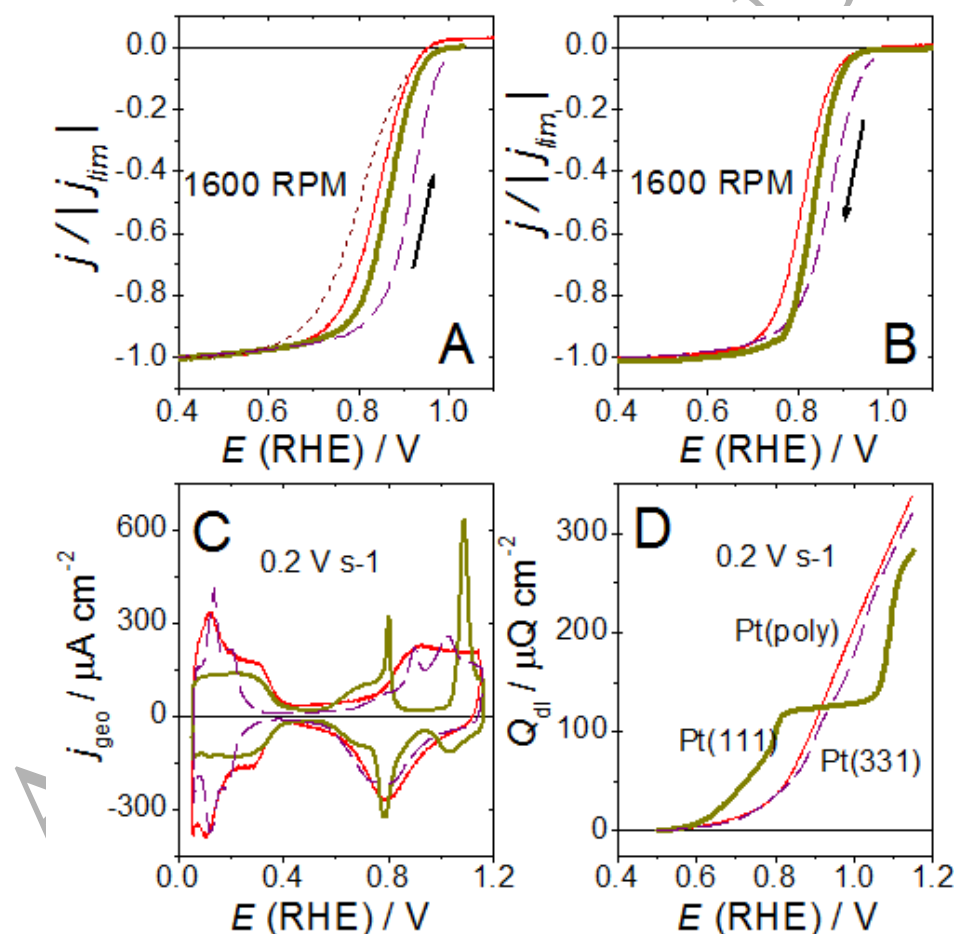


Figure 3: (A) Positive- and (B) Negative-going linear sweep voltammograms, normalized by the limiting current density, for the oxygen reduction in O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub> at Pt(poly) (thin line), Pt(100) (dotted line), Pt(111) (thick line) and Pt(331) (dashed line) electrodes. (C) Voltammetric profiles for Pt(poly), Pt(111) and Pt(331)

electrodes in Ar-saturated solutions. (D) Total integrated transferred charge from the double layer region to 1.15 V during the positive-going scan for CVs given in (C).

Contrarily to the ORR in acid, the most active surface in alkaline electrolytes is the Pt(111) basal plane, and the ORR activity decreases in Pt(111) and Pt(110) vicinal surfaces, with the lower activity at Pt(110) and Pt(100) electrodes [1,4,36]. This activity trend can be well explained by differences in the oxygen adsorption energy,  $\Delta G_{\text{Oads}}$ . It is known that less close-packed, as Pt(100) and Pt(110), and lower-coordinated facets, as steps and defects, of fcc metals generally bind O-containing species more strongly than the (111) facet [37,38]. Thus, the catalyst's ORR activity versus  $\Delta G_{\text{Oads}}$  should result in a volcano-type plot, as for any dissociative reaction [37,39], with the most close-packed surface, the (111) plane, located at the top of the curve. The question, then, is why steps and defects at {111} and {110} terraces show higher ORR activities relative to the basal planes in acid environments [1,4].

It has been proposed that the activity trend in acid can be explained by considering the hydroxyl binding energy,  $\Delta G_{\text{OH}^{\text{T}}_{\text{ads}}}$ , at terrace sites as the ORR activity descriptor, estimated from blank cyclic voltammograms (CVs) [31,34], as in Fig. 3C, or from infrared measurements [38,40]. Inside this framework, a theoretical volcano-plot for the ORR activity vs.  $\Delta G_{\text{OH}^{\text{T}}_{\text{ads}}}$  that qualitatively follows the experimental results can be calculated [29]. Hence, the destabilization of all related adsorbed ORR intermediates with the decrease in the terrace width, due to a decreased solvation, increases the ORR reactivity in acid [23,28,29,31,40-43]. A similar interpretation, but including geometric arguments in terms of the generalized coordination number, GCN, has been also proposed with equivalent conclusions [34]. In this case, only surfaces with high relative abundance of surface sites with a GCN > 7.5, and a  $\Delta G_{\text{OH}}$  ca. of 0.1 to 0.15 V weaker than Pt(111) have higher ORR activity than this basal plane [34].

However, not always a decrease in  $\Delta G_{\text{OH}}$  implies higher ORR activities [35,44,45], as it is clear from Figs. 3C and 3D. In this figure, the ORR activity at Pt(poly) and Pt(331) is notably different, being less and more active than Pt(111), respectively, though the onset for the adsorption of O-containing species at those surfaces is practically the same. Similar conclusions are drawn if the same analysis is performed for data in alkaline media [36], especially in terms of the GCN, which depends on the surface geometry but not on the nature of the electrolyte. Then, the higher activity of steps and defects at {111} and {110} terraces in acid cannot be simply explained by

only considering differences in  $\Delta G_{\text{OH}^{\text{T}},\text{ads}}$  and solvation effects, or the GCN, between these surfaces.

Other studies have suggested that, besides the adsorption strength of O-containing species, the interfacial water structure near the surface also influences the ORR activity [1,16,18,35,36,46,47], because its effect on solvation entropies, or the water dipole polarization at the electric double layer, affects the mobility and/or reactivity of participating non-adsorbed species [46,47]. It has been shown that the ORR occurs only at a potential cathodic enough to deplete the interface of hydrogen-up oriented water, H-up (oxygen-down) [47], and that an increase in the stability of the water structure slightly inhibits the ORR [46]. A theoretical study has also predicted a destabilization effect on  $O_{\text{ads}}$  by an H-up, but not a hydrogen-down water orientation [41]. This is because  $O_{\text{ads}}$  repels an adjacent water molecule in an H-up orientation and changes its structure to an H-down (oxygen-up) configuration [41]. The complex ORR activity trend reported in presence of alkali metal cations both in acid [48] and in alkaline electrolytes [49] could also be explained by the effect of the water structure on the ORR activity.

In this sense, the higher activity of steps and defects at {111} and {110} terraces in acid, but not alkaline, arrives because of differences on the water structure surrounding the intermediates at those  $pH$ s [1,16], evidenced on the ORR operation potential with respect to the PZFC of the electrode. For Pt(111) the PZFC changes from 0.34 V to 1.05 V vs. RHE, when going from  $pH = 1$  to 13 [50]. Therefore, during the ORR the surface is positively charged at  $pH = 1$  but negatively at  $pH = 13$ . This difference in the surface charge implies a different orientation of water molecules [1,16,41,42,50]: while water molecules are organized following an H-up structure in acid, they are arranged in an H-down orientation in alkaline electrolytes. Now, since the presence of steps increases the stability of the H-up orientation [41], the destabilization effect on  $O_{\text{ads}}$  by the H-up structure is smaller at Pt(111) relative to the one at stepped surfaces, increasing the ORR activity in these latter electrodes [1]. This destabilization does not appear in alkaline electrolytes due to the H-down configuration of the interfacial water at this  $pH$ .

Therefore, increasing the step density promotes the ORR in acid because of two main reasons. i) it decreases the stability of the structured H-bond network on, and near, the surface and ii) it stabilizes the H-up orientation of interfacial water molecules [41]. These combined effects decrease the adsorption energy of O-containing species

[28,29,31,41-43], and increase the electrode mobility/reactivity of soluble species [46,47]. So, why is Pt(poly) less active than Pt(111)? Possibly because of the presence of {100} domains on the Pt(poly) surface [51], as its reactivity should be an average of the activity of different surface sites [34]. As it is appreciated in Fig. 3A, Pt(100) is the least active surface in non-adsorbing acid electrolytes [1,4], and the presence of steps does not significantly increase its activity [1,4]. This idea could also be applied to explain the ORR activity of Pt NPs with different sizes and shapes [34,52].

It is important to highlight, however, that despite the promoting role of low coordinated sites in the ORR activity in acid, it would be rather difficult successfully to employ this result in designing more active and stable Pt-based catalysts. It has been shown that carefully designed Pt NPs would rapidly evolve to thermodynamically equilibrated shapes and sizes with similar activities, regardless the initial shape or size, because of the potential induced dissolution/re-deposition of Pt atoms at potentials close to  $E_{onset}^{ORR}$  [32,52-55]. Apparently, this process is not modified by the presence of oxygen in the electrolyte [56-58], and then, it would be inherent to the nature of the electrolyte and the electrode. Hence, strategies are needed to increase the stability of these NPs, such as the approaches already effectively attempted on metal-Pt alloys [32,53,59,60], and Pt stepped surfaces by modifying the surface by selective deposition of stable adatoms [61], which have increased the stability of these surfaces.

### Concluding remarks

This review briefly summarizes recent progress regarding the ORR at Pt surfaces, but mainly at model Pt(111) electrodes. In this sense, the possible formation of a soluble species close to the reaction onset different to hydrogen peroxide, the essential role of the proton concentration and the possible existence of a chemical step inside the mechanism are discussed. It is also shown that the ORR dynamics is dominated by a complex interplay of different factors. In addition to the strong effect of specifically adsorbed anions as spectator species and the adsorption strength of O-containing species, recognized long time ago [1,32,62,63], the arrangement of surface atoms and the PZFC, which in turns determines the interfacial water structure close to the surface, have an important contribution to the electrode activity, especially in acid. It is concluded that although these studies have

provided new evidence, many questions remain open and more work is still necessary to unravel the ORR mechanism on Pt surfaces.

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In this work, recent results regarding the oxygen reduction at Poly(Pt) electrode are summarized and analyzed in light of possible criteria design of new Pt-based electrocatalysts with improved activity and durability. In this sense, the role of the hydroperoxyl radical and hydrogen peroxide in the ORR mechanism are discussed. In addition, results regarding a chemical-electrochemical-chemical-electrochemical sequence for the initial reaction path is also reviewed.
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This study reported the ORR at Pt single crystals and Pt(poly) in slightly acid buffered solutions. Results evidenced a decrease in the limiting current between  $3.0 < pH < 5.6$  without an increase in the production of  $H_2O_2$ , and despite a proton flux high enough to support a four electron transference process. This fact clearly suggests the existence of a chemical reaction involving the proton in the ORR mechanism.

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