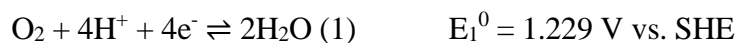


Recent progress on oxygen and hydrogen peroxide reduction reactions on Pt single crystal electrodes

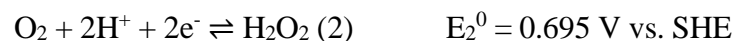
Valentín BRIEGA-MARTOS, Enrique HERRERO, Juan M. FELIU*

1. Introduction

The oxygen reduction reaction (ORR) is probably the most important cathodic process in electrocatalysis because of its universal role as comburent in life and key applications in several fields such as fuel cells, corrosion processes or lithium-air batteries. Despite many experimental and theoretical investigations that have been carried out during the last years and contributed to improve the knowledge about this reaction, the complete mechanism for the ORR is not elucidated yet [1]. The ORR involves the exchange of 4 electrons and 4 protons for the complete reduction of O₂ to water (Eq. 1). The reaction mechanism is complex and implies the formation of several intermediates involving O=O bond scission and O-H bond formation.



It was demonstrated that H₂O₂ is a reaction intermediate for this reaction under certain conditions [2-4]. H₂O₂ could be the final product in a 2-electron reduction process (Eq. 2), or it could be further reduced to water (Eq. 3).



The study of the hydrogen peroxide reduction and oxidation reactions (HPRR and HPOR) is therefore crucial for a better understanding of the ORR as it is a possible stable intermediate.

Previous theoretical studies taking into account the binding energy of OH intermediate indicated that Pt(111) is the most active surface towards the ORR [5]. However, the analysis of the electrocatalytic activity of the basal planes by extrapolation of experimental data for stepped surfaces pointed out that the stepped surfaces are more active than Pt(111) in acidic media [6-8], while in alkaline media experimental results and theory agree better [9]. This has been a controversial point during all the ORR research. The surface charge of the electrode can also have an influence towards the kinetics of the electrocatalytic reactions, but its specific effect has not been considered until recent works. The study of the ORR in different surface charge conditions can help to overcome the unsolved aspects for this reaction.

Other problems to elucidate the ORR mechanism are the difficulty for identifying the reaction intermediates. The traditionally available techniques are not able to detect all the reaction intermediates in the ORR [10]. Because of that it is important to compare theoretical calculations with the available experimental results in order to propose the possible intermediates [11, 12].

In this perspective paper, the most recent advances in the understanding of the ORR (and the HPRR) on well-oriented Pt surfaces are summarized in order to provide a general vision of what is known to date and the next strategies that could be employed.

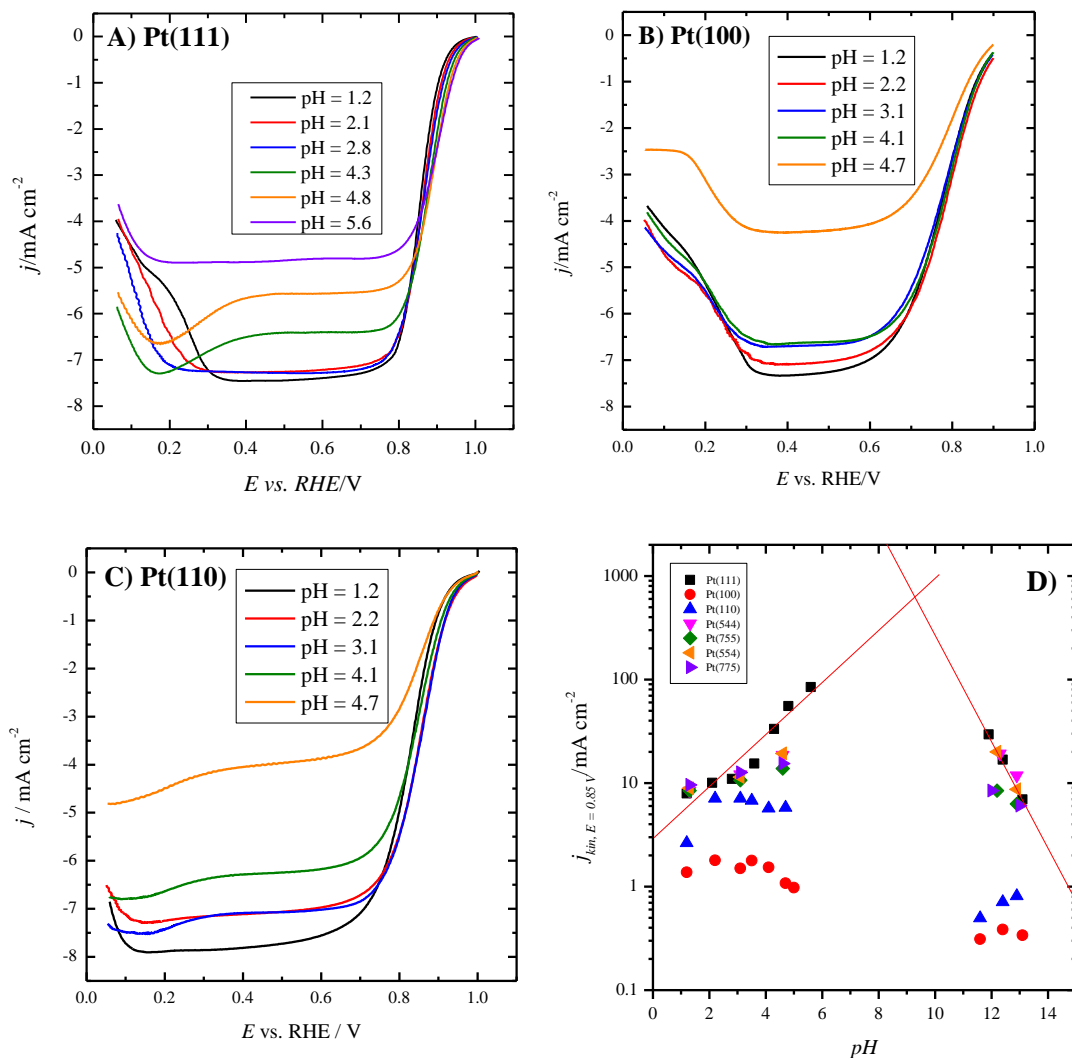
2. Effect of the surface charge on the ORR and the HPRR

The adsorption energy of the ORR intermediates is usually the descriptor used in kinetic investigations [5]. However, the electrode surface charge can also have a markedly influence on the electrocatalytic reactions [13]. For the study of the effect of surface charge to the electrocatalytic activity Pt electrodes is necessary to use working solutions without the presence of anions that adsorb specifically, since the latter ones can also modify the reactivity of the electrode [7]. The use of NaF/HClO₄ mixtures resulted to be suitable for this type of study at different pH because the pK_a of hydrofluoric acid is ca. 3 and F⁻ do not adsorb specifically on Pt [14]. This kind of electrolyte was used to study the ORR on Pt basal planes and different stepped surfaces in a pH range up to until 5.6 [15]. The cyclic voltammetry results for Pt(111) show that the onset potential moves to slightly more positive values as the solution pH increases (Figure 1A). The kinetic current densities at 0.85 V vs. RHE obtained by using the Koutecky-Levich equation are also improved as the pH is changed from acid to more neutral values (Figure 1B). The reaction was also studied in alkaline pH values from pH 11.9 to 13.1 using NaOH/KClO₄ mixtures, and in this case the higher the pH, the lower the kinetic current densities (Figure 1B). In conclusion, for Pt(111), the plot j_{kin} vs. pH shows a volcano trend with the maximum centered at pH ca. 9. The proposed explanation for this behavior was based on the fact that the potential of zero free charge (pzfc) for Pt(111) moves to more positive potentials in the RHE scale as the pH is increase from acidic values to pH = 6. Therefore, the onset potential for the ORR is closer to the pzfc for neutral pH values. The electrocatalytic activity would be maximum when the onset potential is close to the pzfc for the Pt(111) surface. When the pH is increased to alkaline values, the onset potential is gradually more negative than the pzfc, and thus the electrocatalytic activity decreases again. For Pt(100) and Pt(110) the situation is different (Figures 1B and 1C): the j_k values decreases slightly as the pH is increased in the whole potential range. This is because for Pt(111) the onset potential lies at potential values where OH species are adsorbed, but as the potential is swept to more positive values adsorbed OH desorbs at ca. 0.7. In the case of the other basal planes, however, the OH desorption takes place at much more negative values, and therefore at the relevant potential region for the ORR the surface always is covered by OH. The ORR is then mainly affected by the adsorbed OH and this is the reason for the almost constant observed behavior. The situation for the Pt(S)[(n-1)(111)×(110)] and Pt(S)[n(111)×(100)] is intermediate, since it can also be observed a volcano trend but with less pronounced slopes. This is because the fraction of (111) terraces is smaller as the step density is increased and may suggest that the overall reactivity depends on local contributions from terraces and steps. The possible effects of the surface charge on the ORR mechanism are discussed in sections 4 and 5.

The effect of surface charge was also studied for the HPRR [16]. The inhibition of the current density that takes place at low potentials for the ORR on Pt(111) was traditionally ascribed to the adsorption of hydrogen, which would hinder the scission of the O-O and yielding thus H₂O₂ instead of water [3]. However, measurements with NaF/HClO₄ mixtures at different pH values showed that this inhibition always occurs at the same potential in the SHE scale (Figure 1E) [16]. This potential is very near to the potential of maximum entropy (pme) for Pt(111). Consequently, the current density inhibition must be related to some change in the

interfacial water or to the surface charge of the electrode instead of the proposed hydrogen adsorption. The HPOR was also studied in alkaline media, but in this case the inhibition potential is determined by the OH adsorption/desorption potential [16].

Further studies have been carried out using Pt stepped surfaces (Figure 1F). On one hand, it can be observed that the current density inhibition potential shifts to more positive potential values with step density. This is in agreement with the variation of the local pme for terraces in stepped surfaces measured by laser-induced temperature jump experiments [17]. On the other hand, the intensity for the current density minimum observed at ca. 0.11 V vs. RHE increases as the step density is increased and this potential coincides well with the local pme for steps. In conclusion, there is a clear influence of the local surface charge properties towards the HPOR.



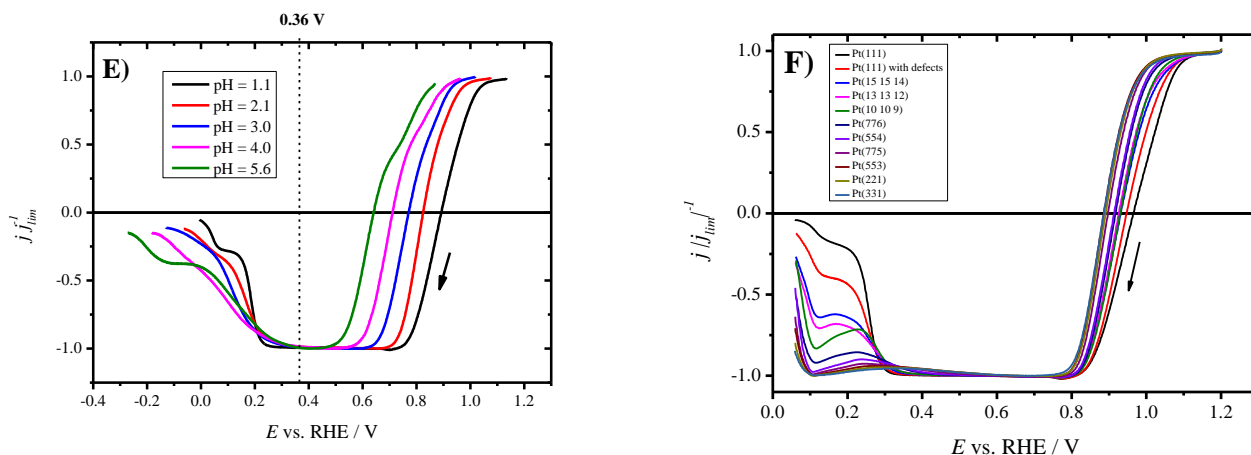


Fig. 1. Polarization curves for the ORR on Pt(111) (A), Pt(100) (B) and Pt(110) (C) in O_2 -saturated solutions with $pH < 5.6$ prepared with NaF/HClO₄ mixtures. Plot of the logarithm of j_k at 0.85 V on the different Pt single crystal electrodes as a function of pH. The straight lines correspond to Pt(111) (D). Normalized polarization curves for the HPRR and HPOR on Pt(111) in 1.7 mM H₂O₂ with $pH < 5.4$ prepared with NaF/HClO₄ mixtures in the SHE scale. The dotted line marks the potential at which the first current drops starts for the different pH values (E). Normalized polarization curves for the HPRR and HPOR on different Pt(S)[n(111)×(111)] stepped surfaces in 0.1 M HClO₄ and 1.7 mM H₂O₂ (F). Scan rate: 50 mV s⁻¹; rotation rate: 2500 rpm (for all the figures). Figures 1A, 1B, 1C and 1D are adapted from [15]. Figure 1E is adapted from [16].

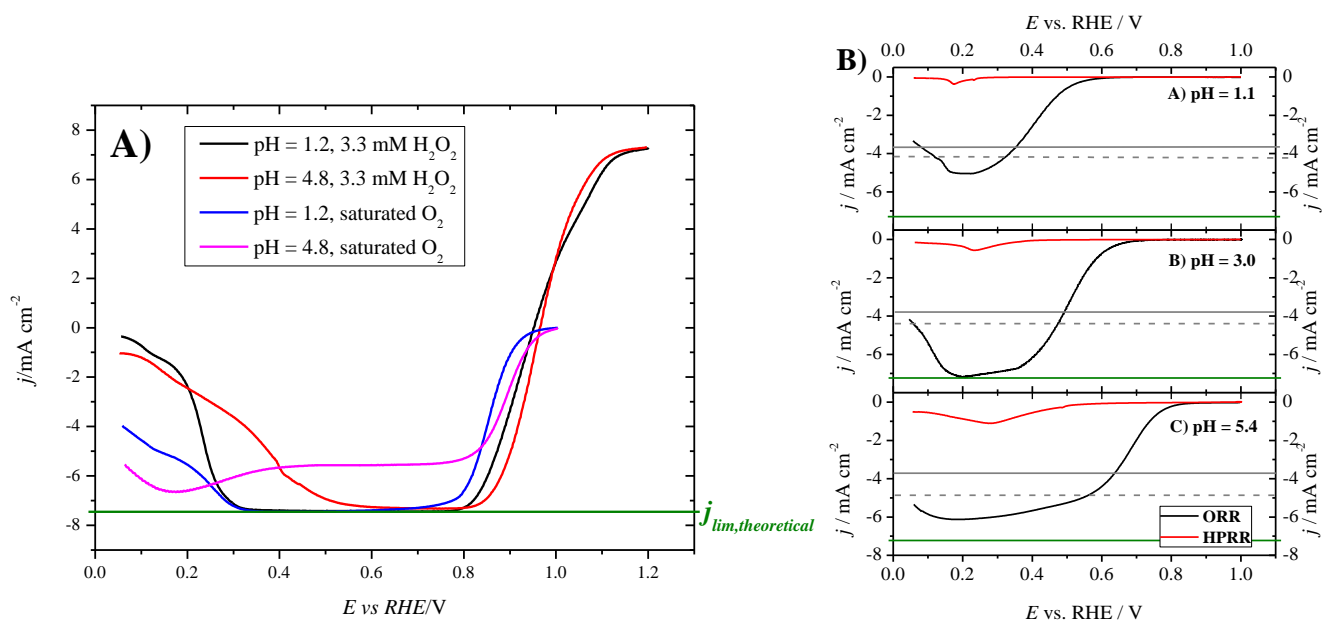
3. Experimental evidences of a bifurcation point in the ORR mechanism

Since the mechanism for the ORR involves several steps, there can exist bifurcation points from which, depending on the conditions, the reaction can follow different pathways. The OOH[•] species has been proposed previously in several works as a possible bifurcation point which could yield directly adsorbed O and OH or produce H₂O₂ [10]. It can be seen in Figure 1A that the limiting current densities for the ORR on Pt(111) decreases as the solution pH is increased from pH ca. 3. Analogous experiments for HPRR with a H₂O₂ concentration that would lead to the same limiting current densities were performed, but in this case no decrease of j_{lim} was observed (Figure 2A) [15]. It was proposed that this behavior for the ORR is due to the existence of a bifurcation point before the formation of H₂O₂. This previous intermediate would stop reacting electrochemically giving rise to a reduction in the faradaic efficiency. This intermediate was suggested to be OOH[•] soluble species in light of the results by Gómez-Marín et al. [15].

The mechanism of the ORR was also studied by investigating the effect of the presence of Br⁻ in working solutions with different pH values [18]. It was observed that at very acidic pH values (below pH = 1) the presence of Br⁻ reduces the j_{lim} to the half of its theoretical value. Therefore, the final product in these conditions is H₂O₂. However, as solution pH increases, the j_{lim} diminution is less drastic, and from pH = 3 the same j_{lim} values as those measured in absence of Br⁻ are obtained. Furthermore, the onset potential in the

presence of Br^- shifts to more positive potential values as pH increases. Additionally, measurements for the HP RR in the same conditions were carried out (Figure 2B) [18]. In all cases the j_{lim} measured for the ORR is higher than the sum of the theoretical j_{lim} for a 2-electron process and the measured current for the HP RR. This difference is especially important for $\text{pH} = 3$, where the j_{lim} for the ORR agrees well with the theoretical value (green line in Fig. 2B) while the HP RR is markedly inhibited. It is important to remark that the difference between the measured j_{lim} for the ORR and its theoretical value in Fig. 2B for $\text{pH} = 1.1$ is due to the presence of Br^- , while the difference in the case of $\text{pH} = 5.4$ is due to the solution pH and j_{lim} is the same in the presence and in the absence of Br^- (see ref. [18]). All these results indicate that the mechanism for the ORR does not follow a sequential scheme in which H_2O_2 is generated as an intermediate. There must be a bifurcation point that follows a pathway for producing water without the formation of H_2O_2 . This intermediate was also proposed to be OOH^\bullet species [18].

Gómez-Marín et al. also observed evidences of OOH^\bullet intermediate by carrying out experiments under non-steady-state conditions for polycrystalline Pt [19]. Linear sweep voltammetry (LSV) experiments in static conditions after holding the potential at 1.02 V vs. RHE during different resting times pointed out that the peak current density (j_p) is higher for the longest resting times (Figure 2C). In addition, measurements at different scan rates for the same resting time were also performed, and in all cases j_p is higher after holding the potential at the open circuit value during 150 s than the j_p value for the continuous LSV in steady state (Figure 2D). The authors suggested that OOH^\bullet soluble species are formed in a fast initial chemical reaction, and equilibrium is reached in such a way that no currents are measured at potentials higher than the onset potential. Once the onset potential is attained, this intermediate species would be reduced yielding the next reaction intermediates [19].



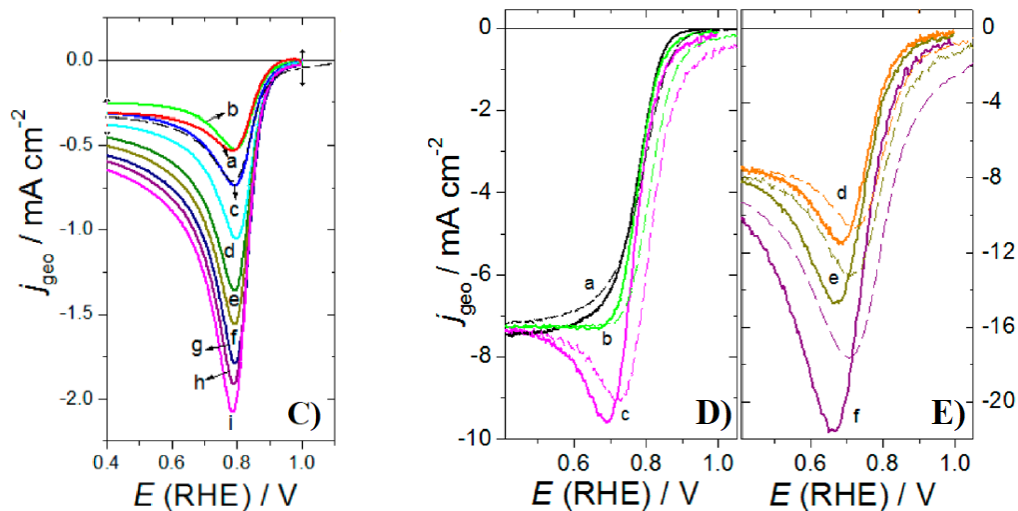


Fig. 2. Comparison between the ORR and the HPRR/HPOR at different pH values for the same limiting current density. The green line represents the theoretical value for j_{lim} . Scan rate: 50 mV s^{-1} ; rotation rate: 2500 rpm (A). Polarization curves for the ORR (black line) and HPRR (red line) on Pt(111) in the presence of 10^{-2} M KBr in the indicated pH values. Scan rate: 50 mV s^{-1} ; rotation rate: 2500 rpm. Grey line represents half ($2e^-$) of the theoretical j_{lim} for the ORR ($4e^-$) and the grey dashed line indicates the addition to this value of the experimental j_{lim} obtained for the HPRR. The green line represents theoretical j_{lim} for the ORR (B). Linear sweep voltammograms for the oxygen reduction in O_2 -saturated 0.1 M HClO_4 on stationary Pt(poly) electrodes after conditioning and holding at $E_i = 1.02 \text{ V}$ (OCP) for different resting times τ_h of (a) 0, (b) 1, (c) 5, (d) 15, (e) 30, (f) 45, (g) 60, (h) 90, and (i) 120 s and steady-state cycle for the continuous LSV (dashed line). Scan rate: 0.1 V s^{-1} (C). Linear sweep voltammograms for the ORR at Pt(Poly) in O_2 -saturated 0.1 M HClO_4 on RDEs at 2500 rpm after conditioning and holding the potential at $E_i = \text{OCP}$ a resting time $\tau_h = 150 \text{ s}$. The scan rate is (a) 0.1, (b) 0.8, (c) 2 (D), and (d) 3, (e) 5, (f) 10 V s^{-1} (E). For the sake of comparison steady-state cycles for continuous LSVs (dashed) are also given. Figures 2A and 2B are adapted from [18]. Figures 2C, 2D and 2E are adapted from [19].

4. Spectroelectrochemical and computational methods for intermediates identification

As mentioned in the Introduction section, on the most difficult challenges during the investigation of the ORR is the detection and identification of the reaction intermediates. The use of spectroelectrochemical methods together with theoretical studies is a common tool for determining these intermediates [11], but in the case of the ORR the detection limits of these techniques are usually too high. However, a recent study using the shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) with the Pt basal planes electrodes in acid and alkaline media proves the identification of ORR intermediates. This spectroelectrochemical technique consists on modifying the Pt surface with gold nanoparticles coated by an ultrathin and uniform silica shell. These nanoparticles are able to strongly enhance the Raman signal of molecules situated near the nanoparticle surface. By using this enhancing strategy the detection limits are suitable for the detection of ORR

intermediates.

Figure 3A shows the SHINERS spectra at different potential values for Pt(111) in 0.1 M HClO₄ O₂-saturated solutions. It can be seen that a band at 732 cm⁻¹ appears from 0.8 V vs. RHE when potential is changed from negative to positive values. The evolution of the band with the electrode potential and its comparison with the voltammetric results are shown in Figure 3B. The frequency for the O-O stretching vibration for OOH• species in the bridge configuration on Pt(111) (Figure 3C) was calculated by density functional theory (DFT) and the obtained result was 726 cm⁻¹. This value agrees well with the observed band for the SHINERS spectra, and therefore it was proposed that OOH• is a reaction intermediate for the ORR on Pt(111). This is the first case of an experimental evidence for the existence of OOH• intermediate. Analogous measurements were carried out for Pt(100) and Pt(110), and in these cases no band at ca. 730 cm⁻¹ was observed (Figures 3D and 3E). Therefore, OOH• would be an intermediate only for Pt(111). Instead, a band at ca. 1080 cm⁻¹ was observed for both electrodes (Figures 3D and 3E). By comparison with the DFT calculations results these bands were attributed to Pt-OH bending mode. In light of these results, they proposed a mechanism in which O₂ forms OOH• by a proton and an electron transfer. The dissociation energy for this intermediate to form adsorbed O and OH is 1.61 eV on Pt(111), while on Pt(100) this dissociation energy is 0.51 eV (no dissociation energy data is provided for Pt(110) but it is stated that it is also unstable in comparison with Pt(111) [12]. Therefore, OOH• intermediate would be more stable and would need a higher activation energy for dissociating into O and OH on Pt(111) than on Pt(100) or Pt(110). This is in agreement with previous theoretical works [20]. Therefore, it is possible to detect it on Pt(111) while in Pt(100) and Pt(110) the O-O breaks quickly making more difficult its observation. These differences between Pt(111) and the other basal planes could also be related with the specific effect of the surface charge. It has been pointed out in section 2 that a different electrocatalytic behavior with pH is observed for Pt(111) due to the fixed p_{zfc} from acid to neutral pH values and the more labile adsorbed OH layer. This could also determine the fact that OOH• in Pt(111) is more stable than in Pt(100) and Pt(110). Additional measurements in alkaline media (pH = 10) were performed and the superoxide species (O₂⁻) was detected for the three basal planes.

The adsorption behavior of oxygen and the reaction intermediates for the ORR has been extensively studied by theoretical calculations during the last years. The adsorption and dissociation processes of ORR intermediates on the three basal planes has been discussed recently in the work by Dong et al. [12]. DFT results point out the bridge configuration is the most stable adsorption mode for OOH• intermediate on Pt(111) (Figure 3C). As mentioned above, OOH• intermediate is less stable on Pt(110) and Pt(100). In the case of adsorbed O and OH intermediates on Pt(100) and Pt(110), it was proposed that OH species are adsorbed on top and the adsorbed O atom on the nearest neighbor contributes bending the H atom. The bridge adsorption mode was calculated to be more stable but the frequency did not correspond with the experimental value measured by EC-SHINERS. Calculations for H₂O₂ showed that a pathway through the formation of this intermediate would be hindered [20]. However, theoretical calculations may not take into account factors such as the surface charge or the surroundings which could alter the formed intermediates, as discussed in the next section.

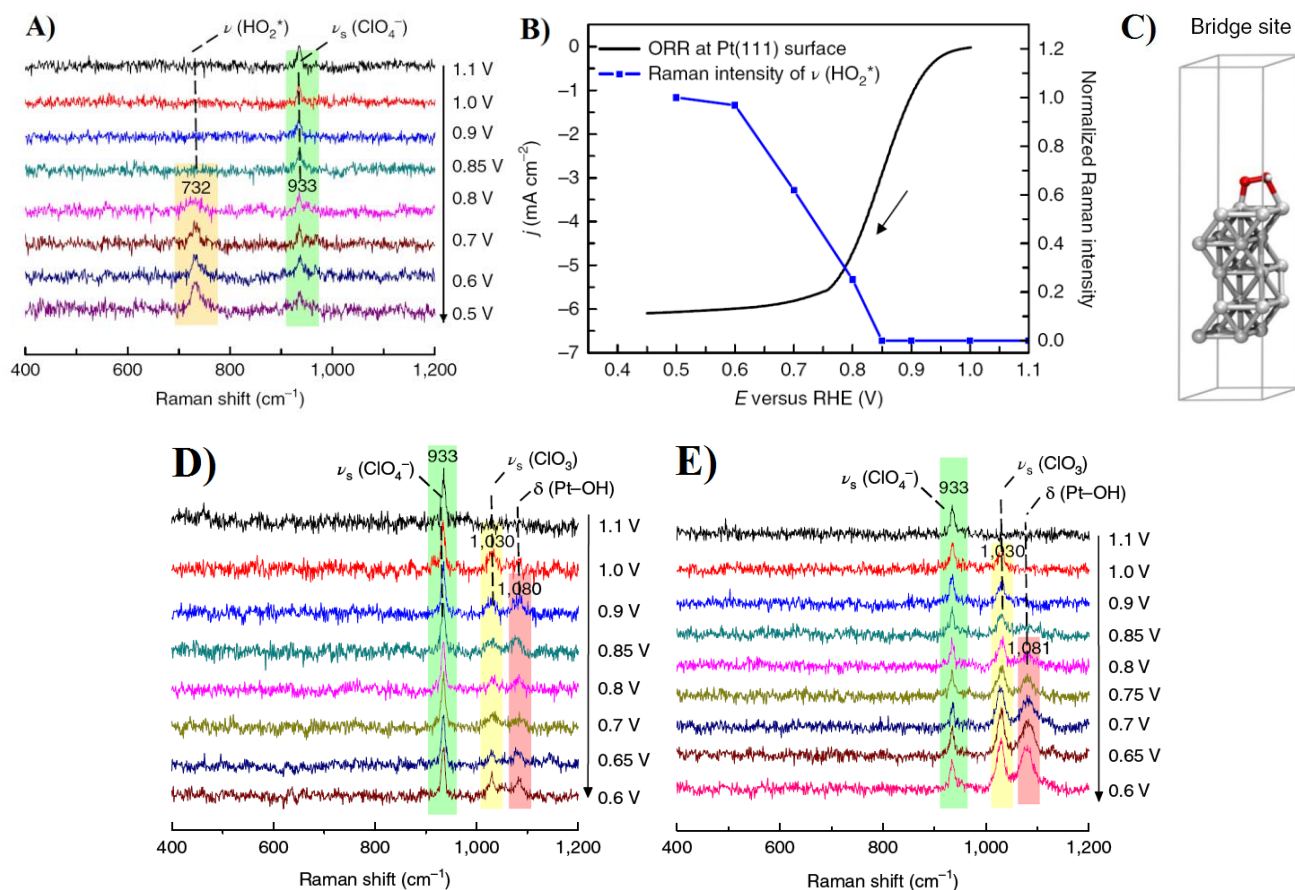


Fig. 3. EC-SHINERS spectra of the ORR system at a Pt(111) electrode surface in a 0.1 M HClO₄ solution saturated with O₂ (A). Normalized EC-SHINERS intensities of the stretching mode of O-OH around 732 cm⁻¹ at different potentials and polarization curve of the ORR process at the Pt(111) surface in a 0.1 M HClO₄ solution saturated with O₂. Scan rate: 50 mV s⁻¹; rotation rate: 1600 rpm (B). The arrows in both figures A and B represent the potential scanning direction and all potentials are relative to the RHE. Side-view illustrations of OOH• at a stable configuration at a Pt(111) surface on bridge site adsorption structure (C). EC-SHINERS spectra of the ORR system at Pt(100) (D) and Pt(110) (E) electrodes surface in a 0.1 M HClO₄ solution saturated with O₂. Adapted from [12].

5. ORR mechanism according to the recent results

In light of the previously described studies, the mechanism in Figure 4 is proposed. First, the initial chemical step can take at potential values more positive than the onset potential to form the soluble OOH• species. Once the onset potential is reached the O₂ molecule can be reduced also to the OOH• intermediate. There is an effect of the surface structure in the ORR mechanism: the OOH• intermediate is more stable in Pt(111) and therefore it can be detected by the EC-SHINERS technique, while in Pt(100) and Pt(110) its lifetime is smaller and cannot be detected. This could be due to the different adsorption energy of the intermediates on the basal plane orientations or to the effects of the surface charge. As has been already pointed out surface charge has an effect on the electrocatalytic activity, and therefore it can affect the mechanism. However, at more neutral pH the

decrease on j_{lim} can also be observed on Pt(100) and Pt(110), and this suggests that OOH^\bullet intermediate could be more stable on the latter surfaces in these conditions. On the other hand, the results from the ORR measurements in presence of bromides suggested that in very acidic solutions the path in which OOH^\bullet is reduced to H_2O_2 is preferred, while for more neutral pH values the mechanism follows a pathway in which H_2O_2 would not be formed. For solutions with low ionic strength, the H_2O_2 pathway is also favored. When Br^- anions are present in the solution the reduction of H_2O_2 is hindered and therefore the latter is the final product of the reaction. Lastly, when the solution pH is increased towards more neutral values the reduction of the OOH^\bullet intermediate is hindered and it goes to the bulk solution giving thus a decrease in the faradaic efficiency.

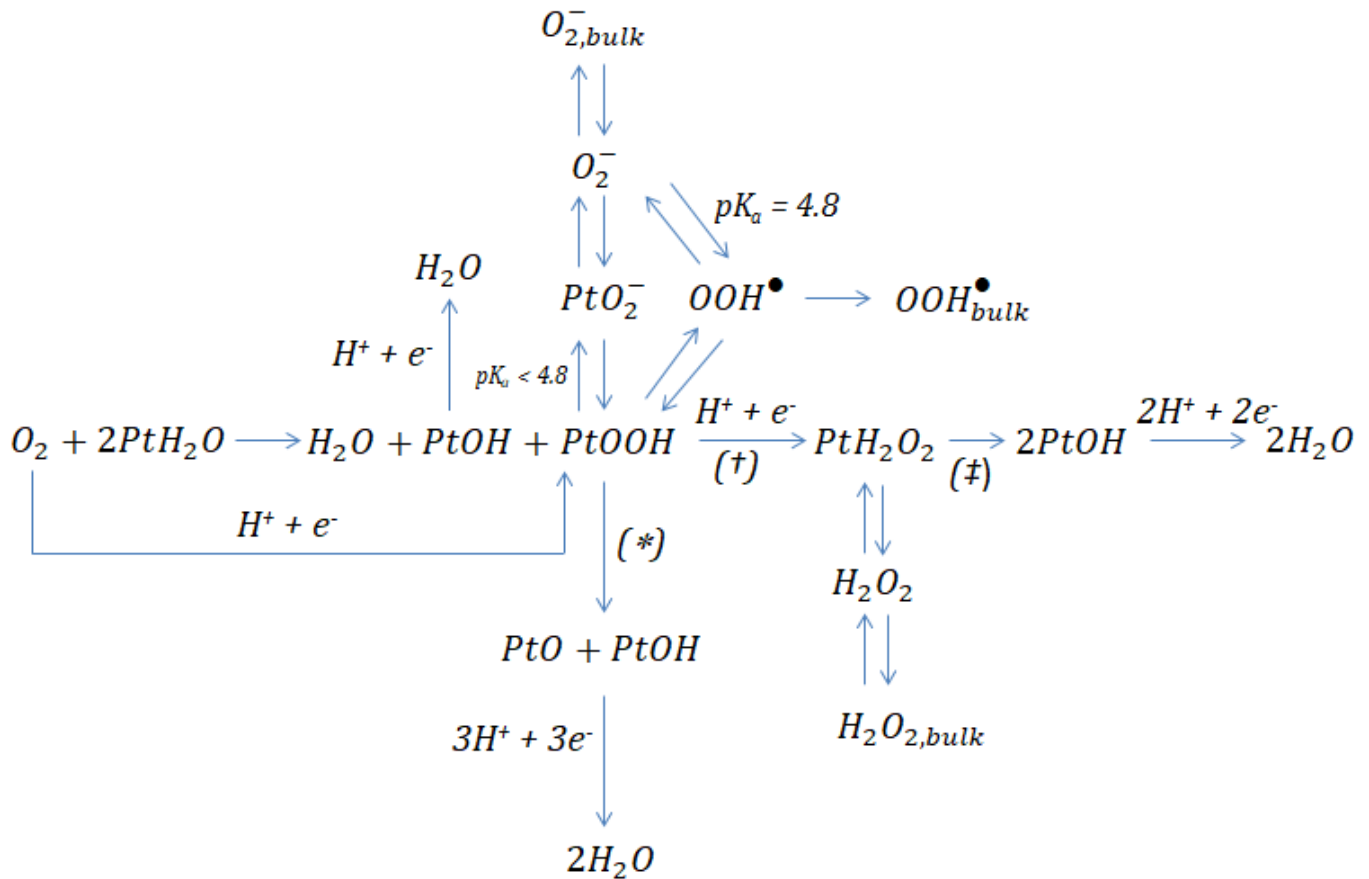


Fig. 4. Proposed scheme mechanism for the ORR on Pt electrodes. (*) Predominant at $2 < \text{pH} < 3$ and high ionic strength. Unaffected by Br_{ads} . This reaction is more favored in Pt(100) and Pt(110) than in Pt(111), and therefore the lifetime of OOH^\bullet is larger on Pt(111) in acidic media. (†) Favored at very acidic pH and low ionic strength. (‡) Hindered in presence of Br_{ads} .

6. Perspectives and conclusions

In this report the most recent advances for improving the knowledge on the ORR on Pt electrodes have been revised, especially in terms of the effect of the surface charge and the possible mechanism pathways. The electrode surface charge influences the kinetics for the ORR especially in the case of Pt(111), for which the maximum activity is expected to take place at $\text{pH} = 9$. For this pH value, the pzfc for this surface would be very close to the onset potential for the ORR. The dependence is different for Pt(100) and Pt(110) due to the

more rigid layer of adsorbed OH at low potentials, while for stepped surfaces the situation is intermediate. In the case of the HPRR, it was demonstrated that the inhibition that takes place at low potentials on Pt(111) is directly related to the pme of the surface, and therefore to the pzfc. Recent results point out that the HPRR is sensitive to the local pme of terraces and steps on Pt stepped surfaces.

It can be observed that the behavior of the ORR and the HPRR with pH is different: while for the HPRR the limiting current density is not affected, the latter decreases as the solution pH is increased for the ORR. In addition, when both reactions are studied in the presence of Br⁻ it can be seen that the HPRR is more inhibited than the ORR, especially at neutral pH values. The solution ionic strength also affects in a different way these reactions. All these results suggest that there exists a bifurcation point in the ORR mechanism prior the formation of H₂O₂. This bifurcation point has been proposed to be OOH[•] species. This intermediate could exist as a soluble species and it has been demonstrated that it can be formed from an initial chemical step. EC-SHINERS measurements and DFT calculations allowed the identification of the OOH[•] intermediate on Pt(111) in acidic media. This intermediate is more stable in Pt(111) than in Pt(100) and Pt(110) as indicated by the obtained dissociation energies and thus pointing out a surface structure effect.

The fundamental knowledge of the ORR is mandatory in order to develop electrode materials with the better performance from a rational strategy. Theoretical calculations are always carried out using model surfaces. The results derived from them cannot be compared with experiments performed with practical polyoriented surfaces. Direct relationships between the theoretical studies and the experimental measurements can only be established when well-oriented surfaces are used, and by this way it can be deduced which calculations are truly representative of the experimental situation. In this sense, the use of Pt single electrodes provides valuable information that can be extrapolated to nanoparticles and therefore electrocatalysts that can be used in practical applications. Therefore, although the use of single-crystals electrode cannot be used in practical applications, studies with well-oriented surfaces are important in order to achieve a complete fundamental knowledge of electrocatalytic reactions so that the best practical conditions are established. Further experiments with Pt stepped surfaces, which have step sites with a low coordination and a more similar behavior to the less coordinated sites in practical electrodes, and preferentially oriented Pt nanoparticles will be performed in order to obtain more information about how the surface charge affects the ORR and the HPRR and to gain more details about the mechanism of these reactions.

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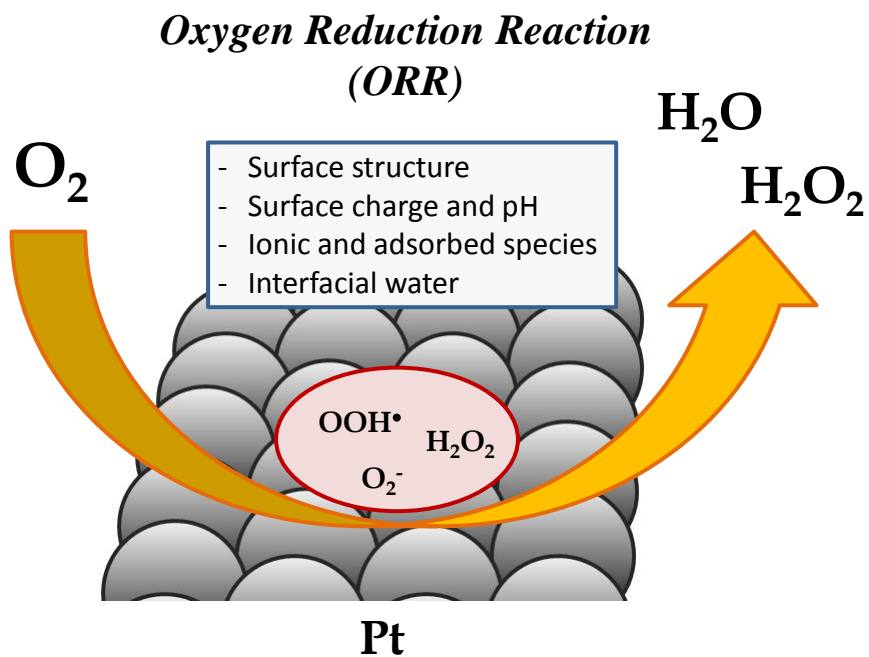
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Recent progress on oxygen and hydrogen peroxide reduction reactions on Pt single crystal electrodes

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In this perspective paper the most recent advances for the ORR in Pt single crystal electrodes are summarized. A mechanism for the reaction is presented in light of the recent results.