The inhibition of hydrogen peroxide reduction at low potentials on Pt(111): hydrogen adsorption or interfacial charge?

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Abstract

The hydrogen peroxide reduction reaction (HPRR) on Pt(111) has been studied for the first time in acid to neutral pH values in the absence of anion specific adsorption using the HMRDE configuration. The onset for the reduction is ca. 0.95 V (RHE) for the Pt(111), irrespective of the pH value. At more negative potential values, the reduction is inhibited. It has been found that the diminution of the activity on Pt(111) occurs at the same potential value in the SHE scale for the different pH values. This indicates that this deactivation is not dependent on hydrogen adsorption process, as has been previously suggested. However, it should be related to the interface water reorganization and the potential of zero free charge of the metal surface. In addition, studies in alkaline conditions suggest that the presence of adsorbed OH species promotes the total conversion of hydrogen peroxide to water.

Keywords

Oxygen reduction reaction

Hydrogen peroxide reduction

Pt(111)

Platinum single crystal

Hydrogen adsorption

Interfacial charge

Potential zero free charge

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1. Introduction

Oxygen reduction reaction (ORR) is probably the most important electrocatalytic reaction because of its applications is several fields such as in fuel cells, lithium-air batteries or corrosion processes. The study of hydrogen peroxide reduction and oxidation reactions (HPRR/HPOR) has a strategic importance in electrotalaysis since H_2O_2 is one of the possible intermediates in the ORR mechanism. Despite the important number of theoretical and experimental investigations carried out during the last years, the mechanism of the ORR on metal surfaces is not totally clear yet. It has been proposed that OOH intermediate species (adsorbed or as a soluble radical) could constitute a bifurcation point in the mechanism at certain conditions [1-5]. This intermediate could diffuse to the bulk solution and disproportionate [4], or dissociate directly into O and OH adsorbed intermediate species [1] or be reduced to H_2O_2 [4-7]. In turn, hydrogen peroxide could be the final reaction product in a 2 e$^-$ pathway:

$$(1) \quad O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$$
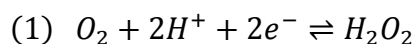
or it could be further reduced to water (Eq. 2).

$$(2) \quad H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$$
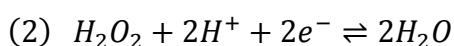
Considering the last possibility, H_2O_2 has an active role and the study of its electrocatalytic behavior could shed light on the ORR mechanism and is the main species in this paper because its change of reactivity at low potentials on Pt(111) electrodes.

In this respect, hydrogen peroxide has been detected during the ORR on metal surfaces in several works [8-13]. Damjanovic et al. observed the formation of H_2O_2 at low potentials on a Pt surface in sulfuric acid solution by using rotating-disk electrode (RRDE) and they provided the first explanation for this behavior [9]: unpaired d-electrons of the surface atoms would be a requirement for O_2 reduction to H_2O, and these d-electrons would be paired by interaction with adsorbed hydrogen. Therefore, they proposed that oxygen would no longer be able to

dissociate when hydrogen is adsorbed, being reduced then to H_2O_2 rather than to H_2O. In later works by Markovic et al. [11, 14], hydrogen peroxide was also detected at low potentials during ORR at the basal planes of platinum single crystal electrodes by using the RRDE technique, both in acid and alkaline solutions. They observed that the inhibition of the ORR at low potentials is surface sensitive, being stronger at Pt(111). In Pt(110) the current deactivation and the corresponding hydrogen peroxide detection at low potentials are almost negligible. Because of this, the explanation given by Damjanovic et al. was discarded. They proposed that the change from a 4 electrons pathway to a 2 electrons pathway was due to the adsorption of hydrogen occupying the μ-peroxo adsorption O_2 sites. Thus, the scission of the O-O bond was prevented and hydrogen peroxide was formed instead of water.

The explanation given by Markovic et al. in [11] has been accepted and used during the last years [5, 15-19], but the direct study of hydrogen peroxide reduction could help to get more information about this situation. When the HPRR is studied in acid media, the behaviour is consistent to that observed in ORR, and current drops to almost zero at potentials close to 0 V vs. RHE for Pt(111), while there is almost no current inhibition for Pt(110) [11, 20, 21]. Strbac studied the pH effect on the oxygen and hydrogen peroxide reduction reactions, but this work was performed with polycrystalline Pt and in the absence of buffering conditions [22]. Investigations with well-oriented surfaces in buffered conditions could be crucial in order to get more information about the inhibition process of the HPRR at low potentials. Recent works have demonstrated that the use of buffer solutions based on HF/F⁻ species allows working at pH values close to neutral conditions avoiding the anion specific adsorption [23, 24]. It has been demonstrated that these solutions can be used for the study of electrocatalytic reactions such as the ORR and the HPRR/HPOR in valid buffering conditions [4, 25]. In this work, $HClO_4$/NaF mixtures have been used to study the HPRR on Pt model surfaces at more neutral values. The results presented here point out that there must be other

causes for the inhibition of H_2O_2 reduction to water apart from the blocking of active sites by adsorbed hydrogen. The comparison of the obtained results for the HPRR at different pH values with the voltammetric profiles for the ORR could help to clarify the mechanism for oxygen reduction because similar molecular interactions are expected between oxygen and hydrogen atoms.

2. Experimental

Experiments were performed following the general procedure described in [26]. The working electrode, a Pt(111) single crystal surface, was prepared from small Pt beads ca. 2 mm in diameter, following the method described by Clavilier et al. [27]. The counter electrode was in all cases a platinum coiled wire cleaned by flame annealing. The reference electrode was a Ag/AgCl, KCl (saturated) electrode in contact with the working solution through a Luggin capillary. All potential values have been converted into the RHE or SHE scales.

The working solutions were prepared using concentrated $HClO_4$ (Merck, for analysis), NaF (Sigma-Aldrich, 99.99%), NaOH·H_2O (Merck, Suprapur, 99.99%), $KClO_4$ (Merck, Suprapur) and $\geq$ 30 % H_2O_2 solution (Fluka, TraceSELECT® Ultra, for trace analysis). Ar and H_2 (N50, Air Liquide) were used. Ultrapure water (Elga PureLab Ultra, 18.2 MΩ cm) was employed for glassware cleaning and preparing the solutions.

A signal generator EG&G PARC and eDAQ EA161 potentiostat with an Edaq e-corder ED401 recording system were used for the electrochemical measurements. All the experiments were performed with the hanging meniscus rotating disk electrode (HMRDE) configuration using an EDI101 rotating electrode. Rotation rate was controlled by a Radiometer CTV 101. All experiments were carried out at room temperature.

3. Results and discussion

The HPRR/HPOR voltammetric profiles for Pt(111) in the different pH solutions prepared with NaF/HClO$_4$ mixtures are shown in Fig. 1A and 1B in the RHE and SHE scales, respectively. The H$_2$O$_2$ concentration has been selected in order to give rise to a half of the theoretical limiting current density for the ORR in an O$_2$ saturated solution. For the sake of comparison, the obtained results have been normalized to the limiting current density values.
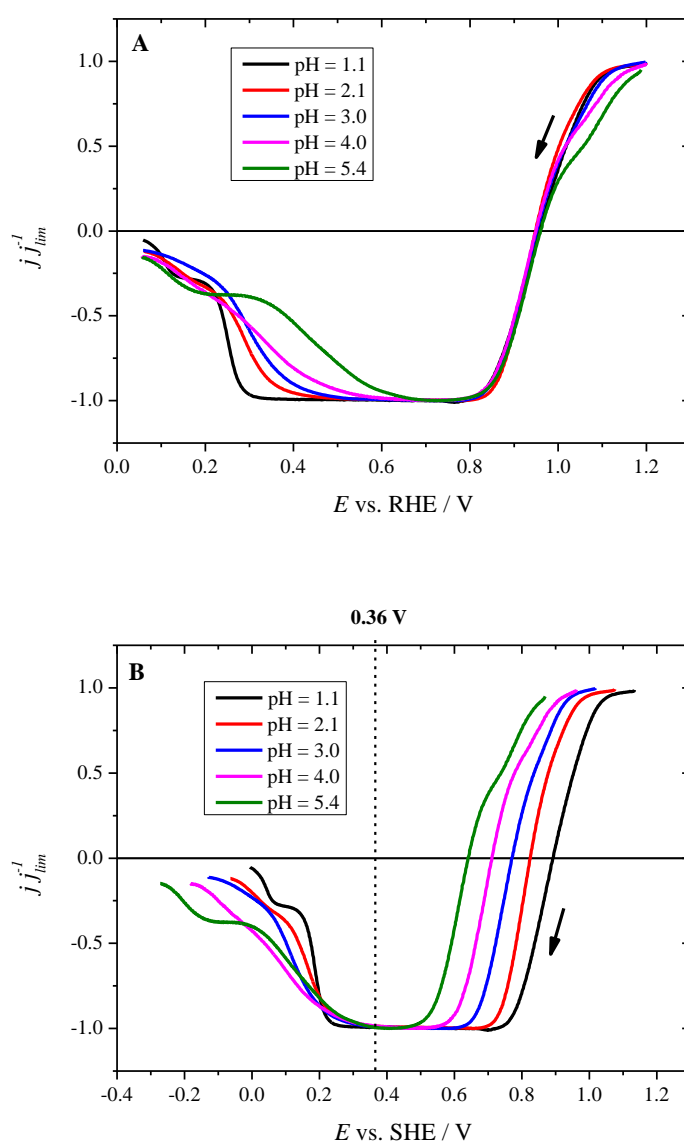

Fig. 1: Normalized polarization curves for the HPRR and HPOR on Pt(111) in 1.7 mM H$_2$O$_2$ with pH < 5.4 prepared with NaF/HClO$_4$ mixtures in the RHE scale (A) and in the SHE scale

(B); scan rate: 50 mV s^{-1}, rotation rate: 2500 rpm. The dotted line marks the potential vs SHE at which the first current drop starts for the different pH values.

The polarization curve for HPRR and HPOR in 0.1 M HClO$_4$ corresponding to the pH value 1.1 agrees well with the previously reported ones [20, 21]: the limiting current is obtained between 0.3 and 0.8 V vs RHE, and two current drops at 0.3 V and 0.15 V vs RHE are observed. The potential value at which the first deactivation is observed coincides with the onset potential for the hydrogen adsorption at this pH value . However, as the pH of the solution is increased, the higher the pH value is, the more positive starting potential for the current drop in the RHE scale becomes. As the hydrogen adsorption/desorption processes lies in the same potential region in this scale for the different pH values [4], the current deactivation for these pH values cannot be related to the onset of H$_{ads}$ and, therefore, should depend on other factors.
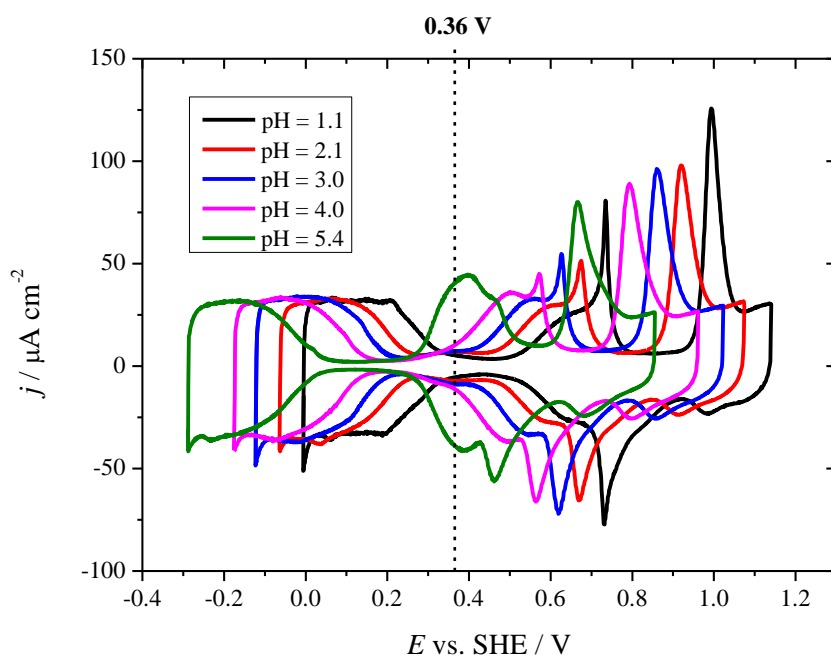

Fig. 2: Voltammetric profiles in Ar-satured solutions with pH < 5.4 prepared with NaF/HClO$_4$ mixtures in the SHE scale; scan rate: 50 mV s^{-1}. The dotted line indicates the current maximum for the reversible feature observed between ca. 0.2 and 0.5 V vs SHE.

Fig. 2 shows the corresponding blank profiles in the supporting electrolyte. It is important to highlight the presence of a reversible broad peak in the blank profiles around 0.35 V vs SHE, which is independent of the pH value. This feature has a maximum at 0.36 V vs SHE and is very close to the potential of zero free charge of the Pt(111) electrode (ca. 0.28 V vs SHE) [23, 28]. Iwasita and Xia reported a sudden change in the IR vibrational spectra of interfacial water at this potential region in $HClO_4$ solutions, and they proposed that water molecules change their orientation from hydrogen down to oxygen down [29]. A change in the orientation of the water layer re-orientation was also put forward from laser heating experiments by the observation of a maximum in the interfacial entropy at these potentials [30]. Therefore, this peak has been previously attributed to the re-orientation of the water dipole layer at the interface [31, 32]. It can be seen that the first current drop starts at the same potential value, ca. 0.36 V vs SHE, for all pH values above 2.0 (Fig. 1B). In any case, a detailed correspondence is difficult because the shape of the water reorganization feature is pH dependent and non-symmetrical especially in the most acidic solution [32]. In conclusion, it seems that the first deactivation of hydrogen peroxide reduction can be attributed to changes in the interface water structure, which is related to the potential of zero free charge of the interface, rather than the beginning of the hydrogen adsorption. The explanation given in [11] cannot be extended to higher pH values. It has been previously pointed out that the interfacial charge and water structure have an influence in the onset potential of the ORR [4]. In conclusion, these results clearly indicate that water in the interface plays a relevant role in the oxygen reduction reaction, and it is necessary to take this into account for further advances in the investigation of this reaction.

The HPRR on Pt(111) has been also investigated in 0.1 M NaOH. The comparison with the case of pH 5.4 is shown in Fig. 3. It should be stressed that the first current density drop starts around the same potential value at RHE scale for both cases. In the comparison

with the corresponding blank profile in alkaline media, the drop in the reduction current takes place at the same potential at which OH is completely desorbed from the (111) surface, which suggests that the presence of adsorbed OH species does not disfavor the reduction of H_2O_2 to water although the potentials are much more negative than the potential of zero charge in the SHE scale. It looks like HPRR behavior is similar to that observed in laser heating pulsed experiments in which the potential of maximum entropy (pme) values are buffered by OH adsorption and thus do not follow the same trend as in acidic solutions [24].
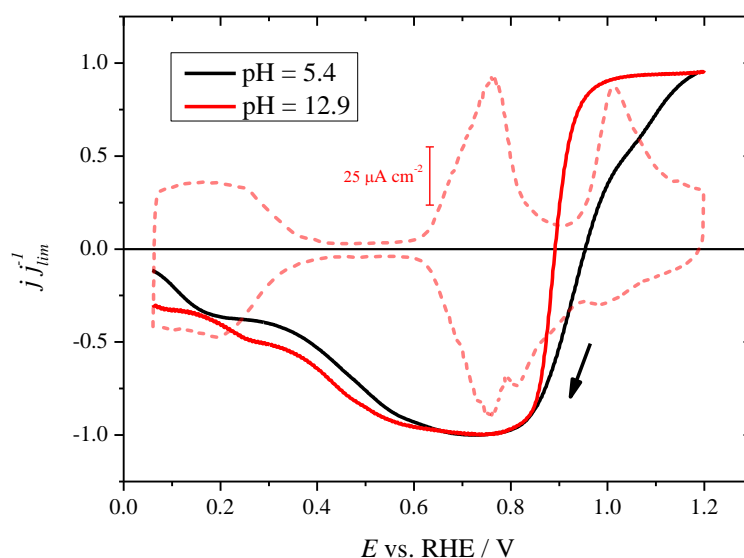

Fig. 3: Polarization curves for the HPRR and HPOR on Pt(111) in 1.7 mM H_2O_2 with pH = 5.4 prepared with a NaF/HClO₄ mixture and pH = 12.9 (0.1 M NaOH) in the RHE scale. Scan rate: 50 mV s^{-1}, rotation rate: 2500 rpm. The dotted line corresponds to the blank voltammetry for 0.1 M NaOH.

4. Conclusions

The study of the hydrogen peroxide reduction reaction at different pH values on Pt(111) has revealed that the deactivation observed at low potentials occurs at more positive potentials in the RHE scale as the pH value is increased. In other words, this deactivation starts at the same potential value in the SHE scale (ca. 0.36 V) for the different pH values

above 2. This indicates that there should be more factors apart from the hydrogen adsorption that produce this current inhibition. The re-orientation of the water interface layer and the potential of zero charge of the metal surface are likely to be related with this behavior. Studies in alkaline solution indicate that the presence of adsorbed OH is also an important factor, since it allows the reduction of H_2O_2 at more negative potentials in the SHE scale in comparison with the observed at more neutral pH values. Future works in combination with studies of the ORR in these conditions could help to obtain more information about the oxygen reduction mechanism and the influence of interfacial water on this reaction. In this sense, more studies on other well-oriented platinum surfaces are being carried out.

5. Acknowledgements

6. References

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