Detection of Superoxide Anion Oxygen Reduction Reaction Intermediate on Pt(111) by Infrared Reflection Absorption Spectroscopy in Neutral pH Conditions

Valentín Briega-Martos, William Cheuquepán, and Juan M. Feliu*

ABSTRACT: In this work, in situ external infrared reflection absorption spectroscopy (IRRAS) is successfully employed for the detection of intermediate species in the oxygen reduction reaction (ORR) mechanism on a flat and well-defined Pt surface. Superoxide anion species (O$_{2^-}$) are detected on the Pt(111) surface in an O$_2$-saturated solution with a NaF/HClO$_4$ mixture with pH 5.5 by the observation of a O−O vibration band at ca. 1080 cm$^{-1}$. The observation of O$_{2^-}$ without the use of any other additional method of signal enhancement is possible because in these experimental conditions O$_{2^-}$ is the main ORR-generated intermediate and its reactivity is limited in this pH. This leads to the accumulation of O$_{2^-}$ near the Pt surface, facilitating its identification.

The oxygen reduction reaction (ORR) is the electrocatalytic reaction that takes place in the cathode of proton-exchange membrane fuel cells (PEMFCs), the efficiency and cleanliness of which make them one of the most promising technologies for distributed power generators and electric vehicles. The sluggish kinetics of the ORR even for Pt, the best pure metal for this reaction, is one of the main drawbacks of fuel cell technology and hinders its commercialization. Hence, it is necessary to develop new electrode materials with improved electrocatalytic activity toward the ORR and high durability in order to make this technology suitable for commercial uses. In order to achieve this goal, a deep knowledge of the ORR mechanism obtained through fundamental studies is essential for the rational development of new electrocatalysts suitable for practical electrodes.

The ORR is a complex electrochemical reaction than requires the transfer of four electrons to yield water as the final product. As a consequence, several different intermediates can take part in the mechanism of the ORR, such as O$_{ads}$, OH$_{ads}$, O$_2$H$_{ads}$/H$_2$O$_{2ads}$/O$_{2ads}$, O$_{2ads}$/O$_{2^-}$, H$_2$O$_{2ads}$/H$_2$O$_2$ or HO$_2^-$/HO$_2$$_{ads}$. The high number of previous computational and experimental studies about the ORR evidence that the reaction occurs through a set of parallel reactions with a similar rate. Within this reaction mechanism, small changes in the experimental conditions could modify the relative rates of the different parallel steps, giving rise to a significant change in the global reaction mechanism. Therefore, it is mandatory to experimentally identify the nature of the ORR intermediate species in order to unambiguously establish which reaction mechanism is taking place at certain experimental conditions.

However, the short lifetime and the low coverage of most of the intermediates, as well as the possible influence by other coadsorbed species, make necessary the use of new experimental techniques and strategies with very high surface sensitivity.

Apart from the use of the rotating ring-disk electrode (RRDE) that has allowed detecting H$_2$O$_2$ as a final product of the ORR under different conditions, several spectroscopic techniques with special configurations have been employed in order to identify other reaction intermediates during the last 15 years. Teliska et al. assigned the oxygen adsorption sites for O and OH species by near-edge X-ray adsorption spectroscopy (XANES) in combination with ab initio theoretical calculations in ORR conditions. Shao et al. identified experimentally for the first time O$_{2ads}$ as an ORR intermediate in alkaline media at pH 11 on a Pt thin film by surface-enhanced infrared reflection absorption spectroscopy with attenuated total reflection (ATR-SEIRAS). Friebel et al. were able to differentiate the chemisorbed oxygen-containing species on Pt from the different platinum oxides by XANES. Casalongue et al. observed using ambient pressure X-ray photoelectron spectroscopy (APXPS) that during the ORR on a fuel cell
cathode composed of Pt nanoparticles the nonhydrated OH species are the dominant species, and with the assistance of DFT calculations they showed that the reduction of these species requires less overpotential than that of hydrated OH. More recently, the HO\textsubscript{2,ads} intermediate has been identified on a Pt(111) single-crystal electrode in 0.1 M HClO\textsubscript{4} by shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS), while O\textsubscript{2,ads}\textsuperscript{−} was detected on the three Pt basal planes in alkaline solution at pH 10. In the same year, Nayak et al. observed by multibounce attenuated total reflection infrared (ATR-IR) spectroscopy bands attributed to HO\textsubscript{2,ads} and H\textsubscript{2}O\textsubscript{2,ads} on Pt nanoparticles in 0.1 M HClO\textsubscript{4}. HO\textsubscript{2,*} soluble species was previously suggested by Gómez-Marín et al. as an intermediate in the ORR mechanism by cyclic voltammetry on Pt(111) and polycrystalline Pt in 0.1 M HClO\textsubscript{4} varying different experimental conditions. The existence of HO\textsubscript{2,*} intermediate as a bifurcation point in the ORR mechanism was proposed by Staszak-Jirkovský et al. from experiments with Au–Pd\textsuperscript{14} and by Ruvinskiy et al. by experiments with Pt nanoparticles supported on different carbon nanomaterials.\textsuperscript{15} ORR and hydrogen peroxide reduction reaction (HPRR) cyclic voltammetry experiments on different Pt single crystals in solutions with pH values ranging from acidic to neutral values in the absence of anion-specific adsorption also suggest that HO\textsubscript{2,*} constitutes a bifurcation point in the ORR mechanism previous to the formation of H\textsubscript{2}O\textsubscript{2.}\textsuperscript{17–20} The latest works presenting spectroscopic evidence of ORR intermediates comprise the work by Dong et al. in which OOH\textsubscript{ads} and OH\textsubscript{ads} Raman bands are observed with different intensity on Pt(211) and Pt(311) surfaces in 0.1 M HClO\textsubscript{4} by the SHINERS technique\textsuperscript{21} and the work by Kukunuri and Noguchi, who attribute to the O\textsubscript{2,ads} intermediate an infrared band observed at ca. 1100 cm\textsuperscript{−1} in 0.1 M HClO\textsubscript{4} by SEIRAS with a Pt/Au/ZnSe surface and spectral analysis under O-isotope and D\textsubscript{2}O conditions.\textsuperscript{22}

Figure 1. Polarization curves for the ORR on Pt(111) in O\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} (black line) and in O\textsubscript{2}-saturated NaF/HClO\textsubscript{4} mixture solution with pH 5.5 (red line) with a rotation rate of 2500 rpm (A) and in nonhydrodynamic conditions (B). The cyclic voltammograms in absence of O\textsubscript{2} are also included. Scan rate: 50 mV s\textsuperscript{−1}.
In the present work, in situ external infrared reflection absorption spectroscopy (IRRAS) in a NaF/HClO₄ mixture solution with pH 5.5 is employed to identify O₂⁻ads intermediate on Pt(111). These pH conditions and the absence of anion adsorption have allowed the detection of an ORR intermediate on a flat surface by infrared spectroscopy without the use of any other system to enhance the spectroscopic signal.

Figure 1 shows the voltammetric results for the ORR on Pt(111) in 0.1 M HClO₄ and in a NaF/HClO₄ mixture with pH 5.5 in both hydrodynamic conditions with a rotation rate of 2500 rpm (panel A) and in nonhydrodynamic conditions (panel B). On the one hand, an improvement in the current density near the onset potential can be observed for pH 5.5, in agreement with previous results. On the other hand, the main difference between both pH values is the diminution of the limiting current density (j_{lim}) in the case of pH 5.5. This was also observed in the previous works and was attributed to the existence of a bifurcation point in the ORR mechanism before H₂O₂ formation, because this diminution of j_{lim} is not observed when the HPRR is investigated in the same conditions. The decrease of j_{lim} for pH 5.5 was explained in terms of the inability for O₂H⁺ intermediate, or its basic form, O₂⁻, to react at the interface and its necessary diffusion to the bulk solution, with the subsequent loss of Faradaic efficiency. The fact that this decrease is observed only for pH > 3 and is larger as the pH increases was rationalized by considering that, below the pKₐ value of 4.8 for the O₂H⁺/O₂⁻ equilibrium, the O₂H⁺ species would be the main species and it would be easily reduced, while at higher pH values the major species should be O₂⁻, which could not be easily reduced and would diffuse to the bulk solution. The shape of the polarization curve is different in the absence of hydrodynamic conditions because in this case the concentration of the reactant, O₂⁻, is not well-maintained near the surface. In the case of pH 5.5, a small peak or overshooting is observed at high potentials because, added to the fact that in pH 5.5 the limiting current densities are much lower, in this case the kinetic activity is higher than at pH 1.1. Moreover, there is a progressive slight increase of the current density as the potential is swept to more negative values for both pH values. The remarkable consequence from the different electrochemical behavior at neutral pH in the presence of anion-specific adsorption is that it could lead to differences in the concentration of the ORR intermediates near the Pt surface, and therefore, it is interesting to perform in situ infrared spectroscopy measurements in these experimental conditions.

The electrochemical interface between the Pt(111) surface and the NaF/HClO₄ solution with pH 5.5 has been studied by in situ IRRAS in ORR conditions. The resulting infrared spectra presented in Figure 2 show the appearance of a band at ca. 1080 cm⁻¹ from 0.5 V vs RHE to 0.2 V vs RHE. Nakamura et al. noted a band at 1080 cm⁻¹ in their previous work using SHINERS to detect the ORR intermediates in alkaline media, a band centered at 1080 cm⁻¹ was observed for pH 1.1, as inferred from Figure 1. Therefore, the intermediate species responsible of the band at 1080 cm⁻¹ observed in this work should be different than adsorbed OH. A band at ca. 1095 cm⁻¹ was observed by Kukunuri et al. from SEIRAS measurements on a Pt/Au/ZnSe in 0.1 M HClO₄. With the aid of additional experiments in O-isotope conditions, they ascribed this band to the O–O stretching vibration of O₂⁻ intermediate species. They explain the possibility of detecting this intermediate because of the use of NaF buffer at pH 5.5, the formation of O₂H⁺ is negligible in front O₂⁻. In this way, the lifetime of O₂⁻ near the Pt surface increases at potentials above 0.7 V vs RHE would increase, allowing its detection. In the previous work using SHINERS to detect the ORR intermediates in alkaline media, a band centered at ca. 1150 cm⁻¹ was observed for the three Pt basal planes, and a calculated frequency of 1182 cm⁻¹ was obtained from DFT calculations. The value for the observed band in this work is close to these wavenumbers, and the little differences could be explained by differences in the coverage of O₂⁻ intermediate or the different surface charge because the difference between the studied pH values (5.5 and 10.3) is important. In our work, because of the use of NaF buffer at pH 5.5, the formation of O₂H⁺ is negligible in front O₂⁻. In addition, because a buffer solution is used, the local pH near the surface is better maintained, close to the nominal value of the bulk solution. In these conditions the reduction of O₂⁻ would be inhibited at the whole studied potential range because the measured current density is practically half of the current density measured for pH 1.1, as inferred from Figure 1. Therefore, the apparition of the band at ca. 1080 cm⁻¹ could be related to O₂⁻ and its lower reactivity in these conditions, which would favor the accumulation of O₂⁻ intermediate at the Pt surface. The fact that this band appears noticeably from 0.5 V vs RHE to
more negative values could be due to the lack of controlled hydrodynamic conditions in the IRRAS setup, because the O2 concentration near the surface would be low and an additional overpotential would be needed to generate the required surface concentration of the detected intermediate (see the comments above regarding Figure 1B). In conclusion, the detection of O2− in the flat surface of the Pt single-crystal electrode by IRRAS spectroscopy in these conditions is possible because of the predominance of O2− intermediate and its limited reactivity at pH 5.5, which increase its lifetime at the Pt surface.

In order to discard that the observed band corresponds to H2O2 species, in situ IRRAS experiments for Pt(111) in the same solution with pH 5.5 saturated in Ar and in the presence of 1.7 mM H2O2 were carried out. The spectra in Figure 3 show the appearance of a negative band at ca. 1150 cm−1 when potential is swept from positive to negative values. This band corresponds to the O=O vibration for H2O2, which is consumed as the potential is increased, and therefore, the band observed in ORR conditions cannot be ascribed to the H2O2 species, because it is located at ca. 1080 cm−1.

To summarize, one of the ORR intermediates, O2−, has been identified for the first time without using any signal enhancement configuration on Pt(111) by means of an infrared spectroscopy. This has been achieved because for the selected working solution, a NaF/HClO4 mixture with pH 5.5, the pH near the Pt surface is buffered at a value in which O2− is the predominant intermediate and cannot be further reduced. Therefore, O2− species can accumulate at the electrode surface, allowing its detection by the IRRAS technique. This study opens the door to new strategies that can facilitate the detection of ORR intermediate on well-defined surfaces in order to obtain new information about the mechanism of this reaction.

■ EXPERIMENTAL METHODS

The single-crystal electrode with Pt(111) well-defined orientation was prepared from a Pt bead ca. 6 mm in diameter and cleaned according to the methodology described by Clavilier et al.28,29 The counter electrode and reference electrode were in both electrochemical and spectroelectrochemical measurements a Pt electrode cleaned by flame-annealing and 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 scale.

Electrochemical experiments were carried out in the hanging meniscus configuration following the general procedure described in ref 30. The in situ infrared spectroscopy experiments were carried out in the thin-layer configuration according to the IRRAS methodology described in refs 31 and 32 using a BaF2 window and employing the subtractively normalized interfacial Fourier transform infrared reflectance spectroscopy (SNIFTIRS) procedure.33–35 Further experimental details are described in the Supporting Information.

■ ASSOCIATED CONTENT

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcl.0c03510.

Detailed experimental procedures and IRRAS measurements in absence of O2 (PDF)

■ AUTHOR INFORMATION

Corresponding Author
Juan M. Feliu — Instituto de Electroquímica, Universidad de Alicante, E-03080 Alicante, Spain; orcid.org/0000-0003-4751-3279; Email: juan.feliu@ua.es

Authors
Valentin Briega-Martos — Instituto de Electroquímica, Universidad de Alicante, E-03080 Alicante, Spain;
orcid.org/0000-0001-8407-2260
William Cheuquepán — Instituto de Electroquímica, Universidad de Alicante, E-03080 Alicante, Spain

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcl.0c03510

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work has been financially supported by MCINN (FEDER) (Spain) through project PID2019-105653GB-100.

■ REFERENCES

(1) Norskov, J. K.; Rossmeisl, J.; Logadottir, A.; Lindqvist, L.; Kitchin, J. R.; Bligaard, T.; Jonsson, H. Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. J. Phys. Chem. B 2004, 108, 17886–17892.
(2) Sharma, S.; Branco, C. M. Noble Metal Electrocatalysts for Anode and Cathode in Polymer Electrolyte Fuel Cells. In Nanostructured Materials for Next-Generation Energy Storage and Conversion:
Fuel Cells; Li, F.; Bashir, S.; Liu, J. L., Eds.; Springer-Verlag GmbH: Berlin, 2018; pp 171–198.

(3) Fantauzzi, D.; Zhu, T.; Mueller, J. E.; Fiot, A. W. F.; Hensen, E. J. M.; Jacob, T. Microkinetic Modeling of the Oxygen Reduction Reaction at the Pt(111)/Gas Interface. Catal. Lett. 2015, 145, 451–457.

(4) Gómez-Marín, A. M.; Felu, J. M. New Insights into the Oxygen Reduction Reaction Mechanism on Pt(111): A Detailed Electrochemical Study. ChemSusChem 2013, 6, 1091–1100.

(5) Yeager, E. Electrocatalysts for O2 Reduction. Electrochim. Acta 1984, 29, 1527–1537.

(6) Markovic, N. M.; Gasteiger, H. A.; Ross, P. N. Oxygen Reduction on Platinum Low-Index Single-Crystal Surfaces in Sulfuric-Acid-Solution - Rotating Ring-Pt(hkl) Disk Studies. J. Phys. Chem. 1995, 99, 3411–3415.

(7) Markovic, N. M.; Gasteiger, H. A.; Ross, P. N. Oxygen Reduction on Platinum Low-Index Single-Crystal Surfaces in Alkaline Solution: Rotating Ring Disk(Pt(hkl)) Studies. J. Phys. Chem. 1996, 100, 6715–6721.

(8) Teliska, M.; O’Grady, W. E.; Ramaker, D. E. Determination of O and OH Adsorption Sites and Coverage in Situ on Pt Electrodes from Pt L23 X-Ray Absorption Spectroscopy. J. Phys. Chem. B 2005, 109, 8076–8084.

(9) Shao, M.-h.; Liu, P.; Adzic, R. R. Superoxide Anion Is the Intermediate in the Oxygen Reduction Reaction on Platinum Electrodes. J. Am. Chem. Soc. 2006, 128, 7408–7409.

(10) Friebel, D.; Miller, D. J.; O’Grady, C. P.; Anniyev, T.; Barg, J.; Bergmann, U.; Ogasawara, H.; Wikfeldt, K. T.; Pettersson, L. G. M.; Nilsson, A. In Situ X-Ray Probing Reveals Fingerprints of Surface Platinum Oxide. Phys. Chem. Chem. Phys. 2011, 13, 262–266.

(11) Casalongue, H. S.; Kaya, S.; Viswanathan, V.; Miller, D. J.; Friebel, D.; Hansen, H. A.; Norskov, J. K.; Nilsson, A.; Ogasawara, H. Direct Observation of the Oxygenated Species During Oxygen Reduction on a Platinum Fuel Cell Cathode. Nat. Commun. 2013, 4, 6.

(12) Dong, J.-C.; Zhang, X.-G.; Briega-Martos, V.; Jin, X.; Yang, J.; Chen, S.; Yang, Z.-L.; Wu, D.-Y.; Felu, J. M.; Williams, C. T.; Tian, Z.-Q.; Li, J.-F. In Situ Raman Spectroscopic Evidence for Oxygen Reduction Reaction Intermediates at Platinum Single-Crystal Surfaces. Nat. Energy 2019, 4, 60–67.

(13) Nayak, S.; McPherson, I. J.; Vincent, K. A. Adsorbed Intermediates in Oxygen Reduction on Platinum Nanoparticles Observed by in Situ IR Spectroscopy. Angew. Chem., Int. Ed. 2018, 57, 12855–12858.

(14) Gomez-Marín, A. M.; Felu, J. M.; Edson, T. On the Reaction Mechanism for Oxygen Reduction on Platinum: Existence of a Fast Initial Chemical Step and Soluble Species Different to H2O2. ACS Catal. 2018, 8, 7931–7943.

(15) Staszak-Jirkovský, J.; Ahlberg, E.; Panas, I.; Schiffrin, D. J. The Bifurcation Point of the Oxygen Reduction Reaction on Au-Pd Nanoclusters. Faraday Discuss. 2016, 188, 257–278.

(16) Ruvinovsky, P. S.; Bonnefont, A.; Pham-Huu, C.; Savinova, E. R. Using Ordered Carbon Nanomaterials for Shedding Light on the Mechanism of the Cathodic Oxygen Reduction Reaction. Langmuir 2011, 27, 9018–9027.

(17) Briega-Martos, V.; Herrero, E.; Felu, J. M. Effect of pH and Water Structure on the Oxygen Reduction Reaction on Platinum Electrodes. Electrochim. Acta 2017, 241, 497–509.

(18) Briega-Martos, V.; Mello, G. A. B.; Arias-Ais, R. M.; Climent, V.; Herrero, E.; Felu, J. M. Understandings on the Inhibition of Oxygen Reduction Reaction by Bromide Adsorption on Pt(111) Electrodes at Different pH Values. J. Electrochem. Soc. 2018, 165, J3045–J3051.

(19) Briega-Martos, V.; Herrero, E.; Felu, J. M. Hydrogen Peroxide and Oxygen Reduction Studies on Pt Stepped Surfaces: Surface Charge Effects and Mechanistic Consequences. Electrocatal. Acta 2020, 334, 135452.