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Investigating the Mechanism and Intermediates of the Oxygen Reduction Reaction

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ABSTRACT

The Oxygen Reduction Reaction (ORR) plays a crucial role in corrosion mechanisms and the operation of electrochemical energy devices, affecting both stability and efficiency. Despite extensive research, the exact mechanisms and intermediates involved in ORR continue to be subjects of study. The literature reports a range of intermediates and mechanisms, which can be complex and, at times, contradictory. This paper conducts a comprehensive literature review with a primary focus on ORR mechanisms on steel, while also examining platinum, gold, and carbon electrodes. Recent advancements in experimental techniques and theoretical modeling have improved our understanding of ORR, which is essential for corrosion science and energy conversion technologies.

This review compiles and analyzes the existing literature on the ORR, focusing on its behavior across different electrodes, including platinum, gold and steel/iron. The study identifies key intermediates such as HO_2^-, O_2^-, H_2O_2, OOH, and OH through electrochemical measurements and in situ spectroscopic methods, mapping their formation and consumption. Understanding these ORR pathways and their interactions with other corrosion processes contributes to the refinement of predictive corrosion models.

Keywords: oxygen reduction reaction (ORR), corrosion mechanisms, intermediates, electrochemical measurements.

INTRODUCTION

Oxygen is an important factor in the oil and gas sector even though it’s a common assumption that these systems are devoid of oxygen. While hydrocarbon reservoirs do not contain any oxygen[1], oxygen can be introduced in these systems as a contaminant. Oxygen ingress into these systems can occur due to several reasons such as leaks, maintenance procedures, equipment failures, chemical injections, and improper operating protocols[1]. Oxygen can be introduced into these systems at levels from parts per billion (ppb) to parts per million (ppm), building up in stagnant areas and causing localized corrosion. The presence of oxygen becomes a concern because it corrodes the infrastructure and might alter the hydrocarbon composition.[2] To understand the implications of oxygen in these systems is key for asset integrity, which helps to make sure operations are safe, improving production efficiency. The oxygen reduction reaction (ORR) and its mechanisms are of importance, as they determine the corrosion rate and formation of potential byproducts.

The oxygen reduction reaction (ORR) plays a key electrochemical reaction in various applications, including fuel cells, metal-air batteries, and corrosion processes. In aqueous solutions under standard conditions, the ORR has a reversible potential of 1.23 V compared to the standard hydrogen electrode (SHE) as shown in Equation (1).[3] To improve energy efficiency in fuel cells and mitigate material degradation, understanding and optimizing the ORR is crucial.

$$\mathbf{O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-} \qquad \mathbf{E_{rev} = 1.23V\ vs\ SHE} \tag{1}$$

This study outlines the mechanisms and intermediates reported across various electrode materials such as steel, platinum, gold, and carbon. Findings of this study have direct implications for understanding corrosion, energy technologies, and identifying areas for future research. As an important electrochemical process, the oxygen reduction reaction (ORR) also plays a key role in corrosion in pipeline systems. The ORR becomes relevant and needs to be addressed in pipeline systems which are susceptible to oxygen ingress. Since steel is the main component in these systems, its corrosion can be driven by oxygen reduction. Insights into the mechanisms and intermediates of this reaction are crucial to assessing pipeline integrity, and corrosion behaviors, leading to effective mitigation strategies.

Recent advancements in testing methods such as spectroscopic techniques and precise electrochemical measurements, have brought new insights to the ORR process.[4] Improvements in theoretical models and computational chemistry have made it possible to predict reaction paths and intermediate species more accurately.[5] This review brings together these latest findings offering a thorough understanding of the ORR mechanisms across various electrode materials.

BACKGROUND

The oxygen reduction reaction has been studied using many different experimental and theoretical methods. ORR mechanisms have been investigated on various electrode materials, like stainless steel[6–11], platinum[4,5,12,13], and gold.[12,14–16] Electrochemical methods such as cyclic voltammetry (CV) and rotating disk electrode (RDE) measurements, are used to figure out reaction kinetics and intermediate species. Research has also been reported on the effect of various parameters like pH[4] and electrolyte composition on ORR kinetics. Theoretical studies, including density functional theory calculations[5], are used to elucidate reaction energy barriers and the rate determining steps. Effect of catalysts with nanostructures[16] and specific crystal faces[14] on the efficiency of the ORR have been studied. These different approaches aim to provide a full mechanistic understanding of the ORR, aiding in fabrication of efficient catalysts for fuel cells, metal-air batteries, and mitigating corrosion.

Electrochemical Techniques

Cyclic voltammetry (CV), rotating disk electrode (RDE) measurements, and rotating ring-disk electrode (RRDE) measurements, play a crucial role in ORR research. These methods have a strong impact on the study of oxygen reduction reactions. Rotating Disk Electrode (RDE) measurements play a key role in ORR kinetic studies. RDE helps separate kinetic and diffusion effects by allowing precise control of mass transport. Researchers can use various techniques with the RDE to examine various materials and conditions:

Linear Sweep Voltammetry (LSV) with RDE (similar to Potentiodynamic Polarization):

This method scans the potential starting from the OCP in one direction (typically cathodic for ORR) while the electrode[4,6,8–10,12–16] rotates at set speeds. The rotation creates a laminar flow of electrolyte ensuring steady-state mass transport of oxygen to the electrode surface. The polarization curve allows to extract key factors like corrosion potential (E_{corr}) and corrosion current density (i_{corr}) using Tafel extrapolation. For materials such as stainless steel potentiodynamic polarization can show passivation areas and breakdown potentials.

Koutecky-Levich Analysis:

LSV at different rotation speeds (400-3600 rpm) yield the Koutecky-Levich plots. These help to determine the kinetic current density, which doesn't depend on mass transfer effects, and the number of electrons that are transferred during the ORR.[6,8,11,12,15]

Tafel Analysis:

This approach plots the log of current density against overpotential. The resulting plot's slope (Tafel slope) gives insights into the rate-limiting step and the reaction's mechanism.[7,8,11]

Cyclic Voltammetry (CV)

Cyclic Voltammetry (CV) sweeps the electrode potential back and forth between two limits while measuring the resulting current[6,9,12,16]. This technique helps to understand reaction kinetics and mechanisms by analyzing current-potential relationships, identifying redox peaks, and examining the reversibility of electron transfer processes.

Rotating Ring Disk Electrode (RRDE)

The rotating ring disk electrode (RRDE) technique, builds on RDE, proves useful to study the ORR.[6,7,11,12] The RRDE has a central disk electrode with a concentric ring electrode around it. This setup helps to detect intermediate species that form at the disk as they move outward to the ring. It allows the measurement of the disk current (total ORR current) and the ring current (peroxide oxidation) to figure out how much the 4-electron and 2-electron pathways contribute. This gives key information about the mechanism that RDE alone can't provide.

Electrochemical techniques are commonly used for these studies and have many benefits; however, they have some shortcomings. In solutions with low conductivity, solution resistance can cause IR drop, which might skew voltametric results. These methods yield information about the reaction kinetics, but to gain mechanistic insight, these methods need to be backed up with spectroscopy or theoretical models. RRDE has limitations, including the need for perfect alignment of the disk and ring electrode as potential interactions between the ring and disc electrodes might affect the readings. RRDE technique assumes that all the intermediate products formed at the disk electrode reach the ring electrode, which might not always be the case. Oxygen solubility, diffusion coefficients, changes in water chemistry, and temperature fluctuations can potentially alter the Koutecky-Levich analysis leading to skewed kinetic and mechanistic analysis. Despite these shortcomings, researchers have managed to utilize these methods for studying ORR on different materials. These studies have provided key insights on kinetics, electron transfer number, effect pH and electrolyte on the ORR mechanism.

Theoretical Calculations

Density Functional Theory (DFT) calculations, as used by Nørskov et al.[5], have an influence on understanding ORR mechanisms and molecular interactions at the atomic level. These theoretical computational methods help researchers to predict reaction intermediates, calculate out binding energies, and identify rate-determining steps. The key advantage of using DFT is that it can probe the reactions that are often difficult or impossible to measure via experimental methods. However, the accuracy of DFT calculations is greatly influenced by the chosen functional and model system. These calculations might not always accurately represent the actual catalytic surfaces or electrolytes interactions.

Surface Analysis and Characterization

Surface analysis methods have been used to characterize electrode materials and correlate surface features to ORR activity. For example, Awad et al. used X-ray diffraction (XRD) and SEM to investigate gold electrodes modified with copper nanoparticles.[16] Le Bozec et al. used X-ray photoelectron spectroscopy (XPS) to examine the composition and oxidation states of surface oxides on stainless steel demonstrating how surface treatments can influence the ORR. [6] These methods yield insights into the surface morphology, makeup, and structure. This information is key to understanding catalyst properties and their influence on ORR performance. However, these methods often need specialized equipment and extensive sample preparation and may not accurately represent the electrode surface under the actual reaction conditions.

Kinetic Analysis

Research has used kinetic analysis to study ORR reaction mechanisms and reaction rates. Ge et al. used Tafel slopes and Koutecky-Levich plots to determine the electron transfer number and rate-determining steps of ORR on different catalysts.[12] Alexander et al. and Awad et al. also used Tafel analysis to investigate the effects of overpotential and current density relationship yielding key insights on the activation-controlled and mass-transfer-controlled regions of the reaction.[8,16] Wang et al. applied kinetic models to examine reaction pathways and identify rate-limiting steps.[13] Kinetic analysis can measure reaction rates and identify rate-determining steps, however the results from these analyses depend on how well the chosen model fits and the quality of the experimental data. This analysis can also misrepresent complex multi-step reactions as simple elementary reactions without adequate information about the mechanism.

Each of the methods discussed above has its advantages and shortcomings, to gain a comprehensive understanding of the ORR, often several approaches are used together. When experimental data is paired with theoretical work, a more comprehensive mechanistic understanding can be obtained, helping to overcome the limitations of individual techniques.

DISCUSSION

ORR on Steel Electrodes

Mechanisms of Oxygen Reduction Reaction on Steel

The oxygen reduction reaction (ORR) on steel surfaces can occur through several mechanisms, primarily categorized as four-electron and two-electron reduction pathways.

1. Four-electron reduction pathway: This pathway serves as one of the main mechanisms seen on steel surfaces[6–11]. This pathway directly reduces oxygen to hydroxide ions in alkaline media or water in acidic media. The overall reactions can be represented as:
   Equation (21) in alkaline media:[8,9]

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH^- \qquad (2)$$

   Equation (22) in acidic media [6]:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{3}$$

Literature has reported different types of mechanisms and different intermediates ranging from peroxide (O_2^{2-})[6,8] to superoxide (O_2^-)[11,12] for the four-electron reduction pathway. The exact pathways and intermediates are discussed later in this paper.

2. Two-electron reduction pathway: This pathway results in the creation of hydrogen peroxide (H_2O_2) or its ionic form (HO_2^-) as an intermediate or final product.[6–8,11]The overall reactions can be represented as:

   Equation (4) in alkaline media:[9]

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \tag{4}$$

   Equation (5) in acidic media:[6,8]

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{5}$$

3. Mixed two- and four-electron pathway: Research has shown a combined pathway where both the four-electron and two-electron reductions happen at the same time. For example, studies on polished 904L stainless steel revealed that 10-20% of the oxygen goes through partial reduction to hydrogen peroxide, while the rest follows the four-electron pathway to hydroxide ions.[6]

Conditions for the Proposed Mechanisms

Experimental conditions greatly influenced ORR mechanisms on steel surfaces. Researchers observed four-electron pathways in various pH ranges and NaCl concentrations for different steel types.[7–9] Both four-electron and two-electron pathways were reported in alkaline conditions.[7] Pre-reduced 904L stainless steel showed a four-electron pathway in seawater.[6] These findings emphasize the importance of water chemistry, pH, and fluid dynamics in ORR processes.

Surface Effects

Steel surface conditions significantly impact ORR mechanisms and kinetics. Key effects include:

- Chromium-rich oxide layers on AISI 304: Alters ORR kinetics.[9]
- Pre-passive oxide on SAE 1006: Favors two-electron reduction pathway.[7]
- Pre-reduced surfaces on 904L: Promotes four-electron reduction pathway.[6]
- Fe/Cr oxide films on 304L/316L: Enhances ORR activity.[8]
- Polished surfaces on 904L: Supports multiple reduction pathways.[6]

These findings emphasize the importance of surface characterization and preparation in ORR studies on steel.

Kinetics

ORR kinetics on steel surfaces depend on various factors. Key findings include:

- First-order reaction with mixed activation-diffusion control.[9,10]
- Tafel slopes: -115 to -180 mV/decade for AISI 304;[9] 135-170 mV/decade for 304L/316L.[8]
- Levich behavior for diffusion layers >20 μm.[8]

These observations provide insights into factors affecting ORR on steel surfaces. Complete understanding of these effects is essential to predict and control corrosion on steel in different conditions. Steel is a common material used in oil and gas infrastructure construction; however it has a tendency to form oxides, which can impact ORR behavior. Noble metals like Gold and platinum don't oxidize at standard conditions and serve as benchmarks for ORR studies. Studying these metals provides better insights into potential ORR pathways that otherwise would’ve been studied due to the nature of the steel’s surface.

Table 1
Detailed outlined experimental conditions for ORR studies on steel

Reference paper	6	7	8	9	10	11
Test Type	ORR on stainless steel in seawater	ORR on steel in alkaline solutions	ORR on stainless steel in chloride media	ORR on stainless steel	ORR on stainless steel	ORR on iron in borate buffer
Temperature (°C)	20°C	Room temperature	25 ± 1°C	20°C	30°C	25°C
pH	~8 (seawater)	pH 10-14	Not mentioned	4 to 10	pH 4-10	pH 7 to pH 9.4
O2 Concentration	Air-saturated	Oxygen-saturated	Oxygen-saturated	Oxygen-saturated	O_2-saturated	O_2-saturated, 0 to 1 atm
Total Pressure	Not specified	1 atm	Not specified	Not specified	Not specified	1 atm
Gas Mix	Oxygen in seawater	Oxygen	Air, oxygen-saturated	Oxygen	Oxygen	O_2 and N_2
Metal Specimen	904L, 316L stainless steel	SAE 1006 steel	304L, 316L stainless steel	AISI 304 stainless steel	AISI 316 stainless steel	99.99% pure iron (Fe)
Liquid phase Brine	Seawater	1 M NaOH	NaCl solutions	0.5 M NaCl	0.5 M NaCl solution	Borate buffer (0.0375 M $Na_2B_4O_7$ + 0.15 M boric acid)
Mass transfer specification	RDE, 100-2000 rpm	RDE, 700-4900 rpm	RDE, diffusion layer varied	RDE, 1000-4000 rpm	RDE, 1000-4000 rpm	RDE, RRDE
Experimental techniques used	CV, LSV, RRDE, XPS	RRDE, LSV	RDE, potentiodynamic, Tafel slopes	Polarization, CV, Levich	Polarization, Levich, Tafel	Steady-state polarization, Tafel plots, disk-ring analysis

ORR on Gold Electrodes

Mechanisms

The oxygen reduction reaction (ORR) on gold surfaces can proceed through multiple paths pathways. These pathways differ in the number of electrons transferred and the intermediates formed. The literature points to two main mechanisms: the four-electron reduction and the two-electron reduction.

1. Four-Electron Reduction

The four-electron reduction pathway is more evident for ORR on gold[12,14–16], it reduces oxygen to hydroxide ions in alkaline solutions or water in acidic solutions. On gold surfaces, this mechanism has been represented by Equation (21) in alkaline media[12,16] and Equation (22) in acidic media.[12,15]

Literature has reported superoxides (O_2^-) as the main intermediates for the four-electron reduction pathway.[12] The exact pathways and intermediates are discussed later in this paper.

2. Two-Electron Reduction

The two-electron reduction path results in hydrogen peroxide (H_2O_2) or its ionic form (HO_2^-) as the main product.[12,14–16] This pathway isn't ideal for energy conversion applications as it's not as efficient. This mechanism has been represented as Equation (4) in alkaline media [12,16] and Equation (5) in acidic media.[12,15]

3. Four-Electron Reduction with Two Parallel Pathways

Studies on Au(111) surface by Nørskov et al. (though their study focused more on Pt) suggest that the ORR can proceed through two parallel pathways, either a dissociative or an associative mechanism.[5]

For the dissociative mechanism:

a) O_2 dissociates into adsorbed atomic oxygen,

$$O_2 + * \rightarrow 2O* \tag{6}$$

b) Then adsorbed oxygen is reduced to hydroxyl,

$$O* + H^+ + e^- \rightarrow OH* \tag{7}$$

c) And hydroxyl is further reduced to water,

$$OH* + H^+ + e^- \rightarrow H_2O \tag{8}$$

For the associative mechanism:

a) molecular oxygen adsorbs intact,

$$O_2 + * \rightarrow O_2* \tag{9}$$

b) formation of hydroperoxide intermediate,

$$O_2* + H^+ + e^- \rightarrow HO_2* \tag{10}$$

c) further reduction to hydroxyl,

$$HO_2* + H^+ + e^- \rightarrow 2OH* \tag{11}$$

d) reduction of hydroxyl to water.

$$OH* + H^+ + e^- \rightarrow H_2O \tag{12}$$

Where * represents an active site on the surface.
These mechanistic details provide a better idea of the possible intermediate steps in the reaction and how adsorbed species play a part in the ORR process on gold.

Conditions for the Proposed Mechanisms

Researchers studied ORR on gold surfaces under various conditions, with detailed experiments with parameters listed in Table 2. Adzić et al. investigated Au(100) and Au(311) in acidic and alkaline solutions, observing the four-electron pathway.[14] Awad et al. used O_2-saturated 0.5 M KOH for copper-modified gold, enhancing the four-electron process.[16] Ge et al. employed O_2-saturated 0.1 M NaOH at pH 13, reporting both four-electron and two-electron pathways.[12] Gotti et al. explored neutral solutions mimicking blood composition, noting a transition from two-electron to four-electron pathways.[15]

Table 2
Detailed outlined experimental conditions for ORR studies on gold

Reference paper	14	16	15	12
Test Type	ORR on gold single crystals	ORR using cyclic and RDE	ORR on gold and glassy carbon	ORR on various catalysts
Temperature (°C)	~25°C	25 ± 1°C	~20°C	25°C
pH	Acidic/alkaline	Alkaline (0.5 M KOH)	Neutral (pH 7.4)	Alkaline (pH 11-14)
O2 Concentration	Not mentioned	O2-saturated	O2-saturated	O2-saturated
Total Pressure	Not mentioned	Not mentioned	Not specified	1 atm
Gas Mix	O2 in electrolyte	O2	O2	Pure O2
Metal Specimen	Gold single crystals	Nano-Cu on polycrystalline gold	Gold, glassy carbon	Pt, Au, Pd, Ag, others
Liquid phase Brine	0.05 M H2SO4, 0.1 M NaOH	0.5 M KOH	NaCl/NaHCO3 solution	0.1 M KOH, NaOH
Mass transfer specification	RDE, 1600 rpm	RDE, 800 rpm	RDE, 500-3000 rpm	RDE, RRDE
Experimental techniques used	CV, RRDE, Tafel analysis	CV, RDE, RRDE, XRD, SEM	CV, LSV, RDE, Koutecky-Levich	CV, RDE, RRDE, XRD, TEM

Surface Effects

Gold's surface state is crucial in determining the activity of the oxygen reduction reaction (ORR). The four-electron pathway is considered to be more efficient and, as seen in the literature, most studies are focused on enhancing the four-electron pathway by modifying the surface:

- Crystal orientation of gold surface;[14] Au(100) enhanced four-electron pathway compared to Au(311).
- $AuOH^-$ adsorption on Au(100) surfaces;[14] Promoted four-electron reduction by lowering activation energy.
- Copper nanoparticles deposited on Au(100);[16] Accelerated four-electron process, activity comparable to platinum.
- Surface polishing of gold electrodes;[15] Facilitated electron transfer, showing distinct reduction peaks.
- Interactions between gold surface and oxygen species;[12] Influenced pathway selectivity and lowered ORR overpotential.

The ability to modify gold's catalytic activity by modifying its surface and controlling reaction conditions enables ways to develop more efficient ORR catalysts to use in fuel cells, sensors, and other electrochemical devices.

Kinetics

The kinetics of oxygen reduction reaction (ORR) on gold surfaces vary depending on surface structure and reaction conditions.

- First-order kinetics with respect to oxygen concentration on Au(100) and Au(311).[14]
- Tafel slope: -120 mV/decade for four-electron reduction; first electron transfer rate-determining step.[14]
- Cathodic transfer coefficient (βn): 0.25-0.49 in neutral solutions.[15]
- Electron transfer: $n=2$ for $O_2 \rightarrow H_2O_2$, $n \approx 4$ for $O_2 \rightarrow H_2O$.[15]
- Copper-modified gold: ORR at 20-65 mV more positive potentials than platinum.[15]

ORR on Platinum Electrodes

Mechanisms

Several mechanisms have been proposed for the oxygen reduction reaction (ORR) on platinum surfaces. The most commonly discussed pathways are the four-electron reduction and the two-electron reduction, with some studies suggesting a mixed pathway or parallel mechanisms.

1. Four-Electron Reduction: The four-electron reduction is considered the primary pathway for ORR on platinum surfaces.[4,5,12,13] This mechanism involves the complete reduction of oxygen to water or hydroxide ions, depending on the pH of the electrolyte. The overall reaction can be represented as Equation (21) in alkaline media[4,5,12,13] and Equation (22) in acidic media.[4,12] Although precise reaction pathways and intermediates for ORR on platinum differ from what previously was reported for golden and steel electrodes, which will be discussed later in the paper.

2. Two-Electron Reduction: The two-electron reduction pathway involves the formation of hydrogen peroxide (H_2O_2) as an intermediate or final product [4,12]. The overall reaction can be represented as Equation (4) in alkaline media [4,12] and Equation (5) in acidic media [4,12]. While this pathway is less common on platinum surfaces, Strbac et al. noted that it could occur under certain conditions, particularly at intermediate potentials and in specific pH ranges.[4]

3. Mixed or Parallel Pathways: Some studies suggest that both the four-electron and two-electron pathways can occur simultaneously or in parallel on platinum surfaces. Nørskov et al. proposed two parallel pathways for the four-electron reduction.[5]

    a. For the dissociative mechanism, it follows Equation (6), Equation (7), and Equation (8) the same as ORR on Gold Electrodes.

    b. For the associative mechanism, Nørskov et al. give priority to the proton-electron interaction on the left hand sides of Equation (13) and Equation (14) which involves a new product on the platinum surface:

        i. formation of hydroperoxide intermediate

$$O_2^* + (H^+ + e\text{-}) \rightarrow HO_2^* \qquad (13)$$

        ii. further reduction to water and adsorbed oxygen

$$HO_2^* + (H^+ + e\text{-}) \rightarrow H_2O + O^* \qquad (14)$$

where * represents an active site on the platinum surface.

Conditions for the Proposed Mechanisms

The conditions under which these mechanisms were studied varied across the literature, with detailed experiments with parameters listed in Table 3.

- Platinum oxide (PtOH) formation/reduction: Affects reaction kinetics, particularly at negative potentials.[4]
- Strong O and OH adsorption on Pt(111) at high potentials: Inhibits reaction rate, stabilizes O* and OH* intermediates.[5]
- Adsorbed O* and OH* on Pt(111) surface: Inhibits reaction, especially at high potentials; OH desorption is rate-limiting.[13]
- Sulfate ion (HSO_4^-) adsorption on polycrystalline Pt: Impacts reduction rates, promotes $2e^-$ pathway at intermediate potentials, pH-dependent.[4]
- Surface quality and pH on polycrystalline Pt: Can shift between $4e^-$ and $<2e^-$ pathways depending on conditions.[4]

Table 3
Detailed outlined experimental conditions for ORR studies on platinum

Reference paper	13	5	4	12
Test Type	ORR on Pt(111)	ORR on Pt(111) using DFT	ORR, HPRR on Pt(poly)	ORR on various catalysts
Temperature (°C)	~23°C	25°C	23 ± 2°C	25°C
pH	Acidic, 0.1 M $HClO_4$	pH 0 (standard hydrogen electrode)	pH 1-13	Alkaline (pH 11-14)
O2 Concentration	Oxygen-saturated	Assumed oxygen-saturated	Oxygen-saturated	Oxygen-saturated
Total Pressure	1 atm	1 atm	Not specified	1 atm
Gas Mix	O_2	O_2 and H_2	O_2 for ORR, H_2 for HPRR	Pure O_2
Metal Specimen	Pt(111)	Pt(111)	Pt(poly)	Pt, Au, Pd, Ag, others
Liquid phase Brine	0.1 M $HClO_4$	Not specified	0.05 M K_2SO_4 with H_2SO_4/KOH	0.1 M KOH, NaOH
Mass transfer specification	RDE, 1600-2500 rpm	Not specified	RDE, 1600 rpm	RDE, RRDE
Experimental techniques used	Polarization, kinetic modeling, Tafel slopes	DFT, free-energy, kinetic modeling	CV, RDE, Koutecky-Levich, Tafel plots	CV, RDE, RRDE, XRD, TEM

Surface Effects

The surface properties of platinum play a crucial role in determining the ORR mechanism and kinetics.

- Polycrystalline Pt: PtOH formation/reduction influences reaction; oxide reduction at negative potentials affects kinetics.[4]
- Pt(111): Strong O and OH adsorption at high potentials inhibits reaction rate; O* and OH* are stable intermediates.[5]
- Pt(111): Strong O and OH adsorption inhibits reaction at high potentials; OH desorption is rate-limiting.[13]

Kinetics

The kinetics of ORR on platinum surfaces exhibit complex behavior.

- Polycrystalline Pt: First-order kinetics; Tafel slope ~120 mV/decade for $4e^-$ pathway.[4]
- pH 3.0-6.0: Two Tafel slopes observed (~120 and ~175 mV/decade).[4]
- Pt(111) DFT: First electron transfer rate-determining; barrier ≥0.45 eV.[5]
- Pt(111) double-trap model: OH desorption rate-limiting step.[13]

Reaction Pathway Elementary Steps and Intermediates

Four-Electron Pathway for Oxygen Reduction Reaction

According to all literature reviewed, the overall reaction can be written as Equation (21) for alkaline media[4,8,9,12,16] and Equation (22) for acidic media.[4–6,12,13,15]

1. Superoxide as an Intermediate

Researchers have reported superoxide (O_2^-/HO_2) serves as an intermediate for the 4 electron ORR pathway. Formation of superoxide intermediate has been proven through methods like rotating ring-disk electrode (RRDE) and spectroscopy. Jovancicevic et al. noted superoxide's to be the most likely intermediate with minimal formation peroxide species using electrochemical tests in neutral solutions.[11] Formation of superoxide was determined to be the rate-determining step (RDS) in the four-electron pathway[11] in the following reaction sequence steps:

I. First electron transfer (RDS):

$$O_2 + e^- \rightarrow O_2^- \tag{15}$$

II. Superoxide reacts with water:

$$O_2^- + H_2O \rightarrow OH^{ad} + O^{ad} + OH^- \tag{16}$$

III. Alternative reaction: Superoxide reacts with water:

$$O_2^- + H_2O \rightarrow HO_2^{ad} + OH^- \tag{17}$$

IV. Reduction of absorbed hydroperoxide:

$$HO_2^{ad} + H_2O + e^- \rightarrow 2OH^{ad} + OH^- \tag{18}$$

V. Adsorbed oxygen reduction:

$$O^{ad} + H_2O + e^- \rightarrow OH^{ad} + OH^- \tag{19}$$

VI. Reduction of adsorbed hydroxide:

$$OH^{ad} + e^- \rightarrow OH^- \tag{20}$$

In this sequence, the superoxide (O_2^-) and other intermediates have a high reactivity and can change the pathway based on conditions like pH, oxygen partial pressure, electrode surface composition, or other chemical species. Intermediates are sensitive to these changes and shifts in conditions can result in different reaction pathways or the production of alternative intermediates such.[11]

2. Peroxide as an Intermediate

In some cases, the ORR has an intermediate step with formation of peroxide ($O_2^{2-}/HO_2^-/H_2O_2$) forms. Research using rotating ring-disk electrode (RRDE) and linear sweep voltammetry has demonstrated the existence of peroxide under specific conditions. For example, Jovancicevic et al. noted that on passive iron surfaces, the two-electron reduction pathway leading to hydrogen peroxide takes over.[11] However, hydrogen peroxide can also appear as an intermediate in the four-electron pathway under specific conditions.[6] Scientists confirmed this by looking at the current at both the ring and disk electrodes.[6] Literature has also pointed out that electron transfer can take place in a single step as well (Equation (21) and (22) without any intermediates).[11,16]

The reaction step for the formation of hydrogen peroxide is the same as Equation (5), but the peroxide in the sequence has a high reactivity as an intermediate for the formation of water:

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \tag{23}$$

This reaction can change the pathway depending on the conditions in the environment like pH, electrode material, oxygen concentration and influence by other chemical species. Also, changes in the conditions of the electrode surface such as surface oxides being present or pre-reduction treatments, can change the stability of peroxide intermediates.

Two-Electron Pathway for Oxygen Reduction Reaction

The two-electron oxygen reduction reaction produces peroxide ($O_2^{2-}/HO_2^-/H_2O_2$) as its final product. The two-electron pathway is favorable when the surface state of the substrate allows peroxide to exist as a stable species.[11] Jovancicevic et al. found that superoxide can serve as an intermediate before hydrogen peroxide forms as the final product.[11] Methods like rotating ring-disk electrode (RRDE) and cyclic voltammetry have been used to support the existence of superoxide and peroxide during this process.[11,16] Wroblowa et al. spotted the generation of hydrogen peroxide as the end product in their RRDE research on steel surfaces.[7]

The overall reactions can be written as Equation (4) in alkaline media[4,9,12,16], and Equation (5) in acidic media [4,6,8,12,15], but the reaction sequence steps involve adsorbed species:[10,11]

I. Oxygen is first adsorbed onto the surface (RDS):

$$O_2 \longrightarrow O_2^{ad} \tag{24}$$

II. Formation of adsorbed superoxide species:

$$O_2^{ad} + H_2O + e^- \rightleftharpoons O_2H^{ad} + OH^- \tag{25}$$

III. Reduction of superoxide species:

$$O_2H^{ad} + e^- \rightleftharpoons O_2H^- \tag{26}$$

IV. Formation of hydrogen peroxide:

$$O_2H^- + H_2O \rightleftharpoons H_2O_2 + OH^- \tag{27}$$

Superoxide and peroxide play a role as reactive intermediates in this sequence. Note that Equation (25), Equation (26), and Equation (27) are given as reversible reactions. The pH and catalytic properties of the electrode surface have an impact on the formation and stability of these species. In some cases, hydrogen peroxide might break down or interact further, based on the reaction environment.[6]

Alternative Pathways for Oxygen Reduction Reaction (ORR)

Besides the usual two- and four-electron pathways, literature reports other pathways for ORR. These pathways occur at very specific conditions and have been discussed in previous sections of the paper (on Pages 4, 6, 9). One example shows a mix of two- and four-electron pathways where oxygen reacts to form hydrogen peroxide (10-20%) and the reminder undergoes complete oxidation to water on polished stainless steel in seawater.[6] Another pathway involves variable electron transfer where less than two electrons are transferred on polycrystalline platinum depending on the pH and ion adsorption.[4] Also, theoretical DFT models of Pt(111) and Au(111) surfaces reveal two 4-eletron pathways in parallel, with associative and dissociative steps, demonstrating adsorbed intermediates such as O and OH.[5]

Comparative Analysis of ORR Across Electrode Materials

Findings on different oxygen reduction reaction (ORR) pathways and mechanisms across various substrates, techniques, and conditions have been summarized in Table 4. This table provides a comprehensive understanding of both two- and four-electron ORR pathways. It includes information on substrates, reaction conditions, surface effects, intermediates, and kinetics. The table sums up key findings from published research.

Table 4
Summary of oxygen reduction reaction (ORR) pathways, substrates, techniques, conditions, surface effects, kinetics, and intermediates.

Overall Reaction	**Reaction Pathway Scheme**	**Substrate Material**	**Techniques Used**	**Conditions for this Mechanism**	**Surface Effects**	**Kinetics**	**Intermediates**	**References**
4-electron reduction	$O_2 + 4e^- + 2H_2O \rightarrow 4OH^-$	Steel, Gold Platinum, Cu-modified Au	CV, RDE, RRDE, LSV, XRD, SEM, EDS	pH 4-14, 0.5-1 M NaCl, NaOH, seawater, 100-4000 rpm	Oxide films influence, AuOH species	First-order; Tafel slopes: -115 to -180 mV/dec	Peroxide, Superoxide	4–16
2-electron reduction	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	SAE 1006, 304L stainless steel, Au, Pt-based catalysts, Fe	LSV, CV, RDE, RRDE, Tafel plots, SEM	Alkaline and neutral solutions, pH 7-14, borate buffer, 0.5 M KOH	Surface oxides, passive films	First-order; Tafel slope ~110 mV/dec	Peroxide, Superoxide	4,6–8,11,12,14–16
Alternate ORR pathways	Mixed 2- and 4-electron pathway	904L stainless steel, Pt	RDE, RRDE, LSV, CV, Koutecky-Levich plots	Natural seawater, 0.05 M K2SO4, pH 3-10, 400-4900 rpm	Polished surfaces	Tafel slope ~120 mV/dec	Peroxide, Superoxide	6
	Dissociative mechanism: Associative mechanism	Pt(111), Au(111)	DFT, Free Energy Calculations	Simulated fuel cell conditions	Adsorbed O* and OH* intermediates	First electron transfer rate-determining	O*, OH*, HO_2*, H_2O_2 * represents an active site on the platinum surface	5
	Double-trap model: $O_2 \rightarrow O_{ads} \rightarrow OH_{ads} \rightarrow H_2O$	Pt(111)	LSV, Kinetic modeling, Free energy diagrams, DFT	0.1 M $HClO_4$, acidic media	Strong O and OH adsorption	Desorption of OH is rate-limiting	O_{ads}, OH_{ads}	13

CONCLUSIONS AND IMPLICATIONS

Understanding the oxygen reduction reaction (ORR) and its mechanisms have real-world implications and uses in various fields. In energy conversion technologies like fuel cells, this insight enables optimization of reactions for better efficiency and longevity. In the oil and gas industry, identifying ORR intermediates like O^{2-} and H_2O_2 improves corrosion models and improves corrosion inhibition chemistries, both of which are used to mitigate equipment failure that can lower operational costs.

As discussed in this study, different intermediates are involved in the oxygen reduction reaction, and thus they can have implications on localized corrosion mechanisms. Localized corrosion is a major threat to pipeline integrity and the understanding of localized corrosion mechanisms requires of the intermediates involved, especially in systems with oxygen contamination. In such cases of oxygen ingress in pipeline systems, the intermediates and pathways of the ORR are especially relevant to the localized corrosion issues experienced in pipeline systems.

After a thorough review of the oxygen reduction reaction, the following conclusions can be made:

- Electrochemical techniques such as rotating ring disc electrode (RRDE) and cyclic voltammetry (CV) proved essential in identifying key mechanisms and intermediates
- The four-electron reduction pathway was the most predominant mechanism defined.
- The two-electron pathway becomes more relevant in the presence of passive or oxide layers on the substrate surface, due to the stability of peroxide species on these surface states.
- The most common intermediates were superoxide (O_2^-, HO_2) and peroxide (HO_2^-, H_2O_2) species.
- Alternative pathways under specific conditions were also identified and reviewed.

The ORR pathways and intermediates on various materials are reviewed in this study, especially their significance to the corrosion pathways in pipelines which mainly consists of steel. Knowledge and understanding of these pathways and intermediates, can prove useful on developing and enhancing corrosion mitigation strategies. Using this knowledge, improved coatings, corrosion inhibitors, and cathodic protection systems can be designed, aiding in the integrity of pipelines.

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