

Activity-Stability Relationships in Oxygen Evolution Reaction

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ABSTRACT: The oxygen evolution reaction (OER) is a critical process in various sustainable energy technologies. Despite substantial progress in catalyst development, the practical application of OER catalysts remains hindered by the ongoing challenge of balancing high catalytic activity with long-term stability. We explore the inverse trends often observed between activity and stability, drawing on key insights from both experimental and theoretical studies. Special focus is placed on the performance of different electrodes and their interaction with acidic and alkaline media across a range of electrochemical conditions. This Perspective integrates recent advancements to present a thorough framework for understanding the mechanisms underlying the activity–stability relationship, offering strategies for the rational design of next-generation OER catalysts that successfully meet the dual demands of activity and durability.



KEYWORDS: OER, activity, stability, activity-stability relationships, dissolution

1. INTRODUCTION

The oxygen evolution reaction (OER) has attracted considerable interest as it is coupled with essential industrial reduction processes like the hydrogen evolution reaction (HER), carbon dioxide reduction reaction (CO2RR), hydrogen peroxide production, and ammonia synthesis reaction (NRR).¹⁻⁶ Despite significant progress in developing OER catalysts, their practical use is still limited by two main challenges: achieving high catalytic activity^{7,8} and ensuring long-term stability during operation.9,10 Previously, research has concentrated on boosting the catalytic activity of the OER materials, aiming to reduce the energy required to start the reaction and speed up the process. However, highly active catalysts often have poor stability, breaking down quickly during extended use. This breakdown can occur through material loss, changes in structure, or surface alterations, leading to a decrease in the performance. As a result, there is growing awareness that finding the right balance between activity and stability is essential for developing OER catalysts suitable for commercial use.

Recent research has started to investigate the connection between catalytic activity and stability, exploring how these two properties are fundamentally linked. This emerging field aims to understand the mechanisms that control both activity and stability with the goal of designing catalysts that are not only efficient but also resilient under challenging conditions. By examining aspects such as electronic structure, surface chemistry, and surface changes over time, researchers hope to discover new ways to optimize both the activity and stability simultaneously.

In this Perspective, we explore a thorough overview of the current understanding of the relationship between activity and stability in the OER catalysts, with a focus on how these two critical properties are interconnected. Additionally, we discuss theoretical models and experimental methods that provide deeper insights into how these properties work together. By bringing together the most recent research, this review highlights key principles and suggests future pathways for the rational design of highly efficient and durable OER catalysts, ultimately supporting the progress of sustainable energy technologies.

2. CASE STUDIES ON THE RELATIONSHIP BETWEEN ACTIVITY AND STABILITY IN VARIOUS OER CATALYSTS

In acid media, ruthenium oxide is a well-known OER catalyst, exhibiting superior activity compared to other transition metal oxides.^{11–15} However, its low stability impedes its industrial application.^{16–19} As an alternative, iridium oxide catalysts have relatively lower performance, but adequate stability drawing

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Figure 1. Example of the inverse activity stability relationship in the OER. (a) Dissolved noble metal ions (ppb) and OER overpotential of different electrocatalysts prepared by thermal chemical (TC-, crystalline) and electrochemical (EC-, amorphous) methods. Reproduced from ref 24. Copyright 2014 American Chemical Society. (b) Dissolution rate and current density of monometallic hydr(oxy)oxides during alkaline electrolyte. Reproduced from ref 37. Copyright 2020 Springer Nature.

attention as promising OER catalysts in low pH conditions.²⁰⁻²³ In this context, several studies have demonstrated the relationships between the activity and stability of different noble metals under acid conditions. Danilovic et al. reported on the activity and stability trends of monometallic oxides produced by thermal and electrochemical methods at bulk metal rods.²⁴ Their analysis of osmium (Os), ruthenium (Ru), iridium (Ir), platinum (Pt), and gold (Au) in an acid electrolyte solution revealed that the OER overpotential order (Os \ll Ru < Ir < Pt < Au) is exactly transposed relative to the order of the amount of dissolved metal (Au < Pt < Ir < $Ru \ll Os$) measuring the electrolyte through an Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) (Figure 1a). Similarly, in sputtered samples, Ru metal achieved the highest OER current at the same overpotential, followed by Ir, RuO_{2} , and IrO_{2} , while the maximum amount of metal was dissolved.2

The inverse trend between activity and stability can be observed in the crystallinity and multimetallic oxide. Crystalline metal oxides generated by thermal methods show higher overpotential (low activity) and lower metal dissolution (high stability) than electrochemically generated amorphous metal oxides.²⁴ Similarly, the Mayrhofer group introduced an inverse relationship between the activity and stability of iridium oxides, which were prepared using either electron beam physical vapor deposition or electrochemical processes and annealed at different temperatures, which determine the degree of crystallinity.²⁶ Mom et al. also studied iridium oxides with different crystallinities and proposed that the inverse trend in activity and stability could be due to deprotonation processes, including μ_2 -OH and limited μ_1 -OH deprotonation.²⁷ The subsurface deprotonation observed in amorphous and semicrystalline IrO_x may explain the high activity of these materials. These deprotonation events lead to oxidation, affecting both oxygen and iridium atoms. This oxidation imparts an electrophilic character to the μ_1 -O atoms on the surface, making them more reactive for O-O coupling.

However, this subsurface deprotonation could also lower the barrier to Ir species dissolution. Together with the lower oxygen connectivity observed in less crystalline oxides, this might explain the correlation between crystallinity and stability. Moreover, the activity and stability relationships among diverse structures are present in multimetallic catalysts. The Markovic group prepared Ru–Ir oxides using various methods.²⁸ The assputtered Ru–Ir alloy sample had an identical composition in each layer, while iridium enrichment occurred in the annealed sample. Each metal alloy sample was treated with thermal and electrochemical processes to form oxide catalysts. The overpotentials and quantities of dissolved metal exhibited the same trends, highlighting the activity and stability relationships. Additionally, various studies have evaluated performance and stability based on the structure of oxides.^{29–32}

The relationship between the activity and stability is not limited to acidic electrolytes. Similar trends have been observed for noble metal catalysts in alkaline environments. A parallel relationship between activity and dissolution was noted for ruthenium metal, ruthenium oxide, iridium metal, and iridium oxide in 0.05 M NaOH.²⁵ Stoerzinger et al. also reported inverse trends between OER performance and stability for ruthenium and iridium oxides grown by pulsed laser deposition at pH 13.³³

This relationship is not limited to monometallic oxides but extends to perovskites, as well. Chang et al. compared ruthenium metal and SrRuO₃ (SRO), finding a correlation between catalytic activity and the amount of dissolved Ru in alkaline electrolytes.³⁴ Additionally, SRO single-crystal thin films with different facets demonstrated that stability is inversely proportional to activity. The transition from ordered Ru⁴⁺ to disordered Ruⁿ⁺ (n > 4), which is highly sensitive to the crystal structure, governs both the activity and stability of these catalysts, following an inverse relationship. SRO (111) is the most active but least stable single-crystal, while SRO (001) exhibits the opposite characteristics. Moreover, numerous studies have explored the relationship between activity and



Figure 2. Example of indirect activity stability relationship in OER. The first row indicates a 2 h CA measurement and dissolution of Ru for the stability of the RuO_2 particles and (111), (101), (110), and (001) surfaces. The second row indicates the relationship between the current of the OER and Ru dissolution. Reproduced from ref 39. Copyright 2018 American Chemical Society.

stability in relation to the exposed crystal facets.^{35,36} Similar to noble catalysts, earth-abundant transition-metal-based catalysts exhibit a trade-off between activity and stability. Chung et al. demonstrated that the dissolution of deposited Fe, Co, and Ni oxides aligns with the activity trend in alkaline solutions.³⁷ By removal of Fe impurities from a 0.1 M KOH solution, they were able to conduct a more accurate evaluation of the intrinsic properties of the catalysts. In these purified electrolytes, the stability trend observed was NiO_xH_y > CoO_xH_y ≫ FeO_xH_y, which is the exact opposite of the OER activity trend, where NiO_xH_y < CoO_xH_y < FeO_xH_y at 1.7 V, confirming the inverse relationship between activity and stability (Figure 1b).

To better understand the relationship between activity and stability in OER, as confirmed by experimental observations, Binninger and colleagues investigated the phenomenon theoretically.³⁸ Their focus was on how metal oxides under the OER conditions undergo significant corrosion, leading to structural changes and material dissolution. The study identifies a universal correlation between the OER activity and the instability of metal oxides, rooted in the thermodynamic properties of the oxygen anion within the metal oxide lattice. The authors demonstrate that under the OER conditions, all metal oxides are thermodynamically unstable, leading to the evolution of oxygen directly from the metal oxide lattice-a process termed lattice oxygen evolution reaction (LOER). The findings highlight that this thermodynamic instability is unavoidable, causing corrosion regardless of the pH value. The LOER mechanism is closely linked to the observed corrosion, with metal cations either dissolving in the electrolyte or participating in further reactions that contribute to structural changes.

Although many studies report an inverse relationship between activity and stability, there are also reports that question the clarity of this correlation. Some research groups have identified counterexamples that challenge the widely accepted understanding of this relationship. Roy et al. reported that the OER activity and dissolution of different facets of ruthenium oxide do not have clear correlations in 0.05 M H₂SO₄.³⁹ RuO₂ (001) performed the highest activity among the samples while experiencing the largest amount of metal dissolution in the first 2 h. Conversely, the dissolution amount of RuO₂ (001) decreased relative to other samples while maintaining high activity in the following 2 h. The RuO_2 (110) single crystal had the poorest OER activity during the initial 2 h but improved its activity without losing stability in the final 2 h (Figure 2). The authors suggested that dissolution exposes a new surface with distinct terminations compared to the asprepared surface and that the OER active sites are assumed to be decoupled from the vigorous dissolution sites. This statement denies a simple relationship between activity and stability. Cherevko et al. also accounted for various noble metal dissolutions in acid media, such as Ru, Ir, Rh, Pd, Pt, and Au, and some of them do not follow the expected relationships.⁴⁰ Specifically, Pd had the second highest amount of dissolution but ranked fourth in the level of OER activity. Au showed the most inferior OER onset potential, yet it was not the most stable noble metal. Similarly, studies on bimetallic samples have also provided counterexamples of the assumed relationship between activity and stability. Reier et al. investigated spin-coated Ir-Ni oxide catalysts with varying Ni proportions and found that the OER activity followed a volcano-shaped trend.⁴¹ The catalyst with 67 atomic% Ni exhibited the highest OER activity, yet the dissolution of Ir increased steadily as the

Ni content rose. This observation challenges the commonly held views on the relationship between activity and stability.

The electrolyte conditions where catalysts work, especially in alkaline conditions, inflict severe impact on activity, which hinders the commonly believed relationships. In this case, surface reconstruction through dissolution and redeposition frequently favors the activity of catalysts.^{42–46} Chung et al. unveiled the critical role of Fe impurities that are present in typical KOH electrolyte solutions.³⁷ The dynamic stability of Ni oxide catalysts, enhanced by the dissolution and redeposition of Fe ions in the solution, increases their activity—despite these catalysts initially displaying low activity and high stability in a purified solution. This finding suggests that external components, such as the electrochemical interface between the electrode and electrolyte, can disrupt the conventional relationship between the activity and stability.

The activity and stability of the OER catalysts are critical factors in their evaluation. As counterexamples to the traditional trade-off between activity and stability have emerged, several research groups have focused on designing catalysts that achieve both high OER activity and resistance to degradation. One strategy to enhance both properties involves modifying the atomic structure of the catalyst surface, particularly in highly unstable ruthenium oxides.^{47–55} Phase and structure engineering have also been proposed as methods to decouple the relationship between activity and stability.^{56–59} Additionally, some researchers have explored the incorporation of foreign cations to stabilize oxide catalysts while boosting OER activity.^{60–63} Furthermore, there are reports of achieving durability without sacrificing activity by employing sacrificial oxidation techniques.^{64–66}

3. BRIDGING THE GAP BETWEEN ACTIVITY AND STABILITY RELATIONSHIP AND PROPER EVALUATION

Controversial reports about activity and stability relationships stem from the varying interpretations and evaluation methods employed by different researchers. To begin with, various degradation mechanisms that hamper catalyst performance exist, which impede the understanding of catalyst stability and make fair comparisons between different samples difficult. The OER catalysts can degrade through various mechanisms, including catalyst reconstruction, dissolution, deposition, and lattice oxygen reactions.⁶⁷ Additionally, catalyst agglomeration, as reported in several studies, can impede the maintenance of activity.⁶⁸ The presence of multiple degradation pathways has made it challenging for researchers to determine which factors to prioritize and evaluate. Consequently, distinguishing specific degradation mechanisms in catalysts has been a significant challenge in electrochemical analysis. Therefore, it is crucial to thoroughly investigate each degradation pathway and its contribution to the overall catalyst degradation. Furthermore, accurately assessing the OER activity of the catalysts is a challenging task. Various studies have presented conflicting views on how to measure the true intrinsic activity of catalysts. A careful and unbiased evaluation of the catalytic activity is essential for understanding the relationship between activity and stability. Additionally, the choice of supports used in electrochemical measurements affects both the activity and stability. Selecting the appropriate backing electrodes is crucial for evaluating the performance of the catalysts themselves. In this context, we discuss three key steps for degradation analysis to help establish a functional link between activity and stability.



Figure 3. To bridge the functional link between activity and dissolution (stability) by a new metric. (a) S-number vs mass-specific current density for powder samples and geometric current density for sputtered films. Reproduced with permission from ref 100. Copyright 2018 Springer Nature. (b) Current and dissolution plots of Ir-based electrocatalyst and their activity stability factor. Reprinted or adapted with permission under a CC-BY 4.0 license from ref 62. Copyright 2017 Springer Nature.

3.1. Recommended Practice for Activity and Stability Analysis

First, selecting the appropriate substrates is crucial for an accurate assessment of the activity and stability. Substrates used in electrochemical measurements should be electrochemically inert with high electrical conductivity and stability. The glassy carbon electrode is commonly used in electrochemical procedures due to its durability across a wide potential range. However, carbon corrosion becomes a significant issue at the potential where OER occurs, limiting its long-term application.^{69,70} Geiger et al. compared four different substrates for OER and demonstrated that each backing electrode produces distinct results in terms of activity and stability.⁷¹ As an alternative, metal-based supports such as gold, titanium-based materials (e.g., Ti felt and TiONx), and nickel-based supports have been explored in numerous studies.⁷²⁻⁷⁵ Unfortunately, these options also have weaknesses in inertness, which can influence the OER activity.

Additionally, accurately measuring and evaluating the catalytic activity in the OER reactions is challenging. Extrinsic factors can significantly influence both activity and stability, making precise performance evaluation essential. One such factor is bubble formation, a common occurrence in electrochemical gas evolution reactions like OER.^{76–81} The formation of bubbles on the electrode surface can obstruct the mass transport of reactants, leading to an underestimation of the catalytic activity during electrochemical testing. Additionally, the choice of electrochemical methods can further distort the assessment of catalyst activity.⁸² Voltage–current characteristics are commonly used to compare catalytic activity, but the measured current can be influenced by nonfaradaic contributions and corrosion. For instance, nonfaradaic processes, such as the intercalation of species into catalyst layers, can

Purpose	Technique	Characteristics	Reference
Electronic structure	XANES (X-ray absorption near edge structure)	Oxidation state/local structure information (Easy for in situ)	27, 34, 110–118
	XPS (X-ray photoelectron spectroscopy)	Surface sensitive (High vacuum is needed)	27, 111–113, 119
	NEXAFS (Near edge X-ray absorption fine structure)	Sensitive to chemical neighbor (High vacuum is needed)	120
Crystal structure	XRD (X-ray Diffraction)	Bulk structure analysis	121, 122
	Raman	Applicable to Amorphous Sensitive to interfacial analysis	120, 123–127
	EXAFS (Extended X-ray absorption fine structure)	Local coordination analysis	110, 114, 115, 117
Particle size	SEM (Scanning electron microscopy)	Particle size and morphology	128
	TEM (Transmission electron microscopy)	Particle size and crystal analysis	45, 66, 128–130
	SAXS (Small angle X-ray scattering)	Particle size and distribution	110

Table 1. In Situ (or Identical Location) Analysis to Discuss Reconstruction during OER

contribute significantly to the current at low overpotentials,⁸² while bubble formation or mass transport limitations can complicate evaluations at high overpotentials.^{77,80} Therefore, electrochemical measurement techniques, such as Cyclic Voltammetry (CV), Linear Sweep Voltammetry (LSV), Chrono-Amperometry (CA), and Chrono-Potentiometry (CP), must be carefully chosen to minimize these extrinsic effects. It is also essential to select current and potential ranges thoughtfully to ensure fair comparisons among different samples. Detailed guidelines for OER evaluation procedures have been provided by various research groups.^{83–86}

Furthermore, side reaction, such as corrosion currents, can overlap with the OER current, making it challenging to accurately identify the "true" OER activity. In this context, product analysis becomes crucial. Techniques like gas chromatography $(GC)^{87-89}$ or mass spectrometry $(MS)^{90,91}$ during the OER process can confirm gaseous products, providing insights into the catalytic process. For example, the precise onset potential for OER can be determined when an O₂ signal is detected using online electrochemical mass spectrometry (OLEMS), which can also identify side reactions like carbon corrosion that simple electrochemical measurements might miss.⁹²⁻⁹⁴ Moreover, isotope labeling in MS analysis offers valuable insights into the OER mechanism, helping to confirm LOER in metal oxides by distinguishing between oxygen atoms from the lattice and those from the reactant using isotope labeling.^{82,95}

Finally, most of the studies discussed in this perspective focus on well-defined samples such as polycrystalline metal rods or single-crystalline deposited materials. While these studies have significantly contributed to understanding the relationship between activity and stability in OER catalysts, research on high surface area catalysts used in real industrial applications such as porous catalysts or nanoparticles remains relatively limited. Bridging the gap between controlled laboratory samples and real-world applications to better understand the activity and stability relationships is the primary challenge that remains in this field.

3.2. Consideration of Dissolution Analysis for Stability Analysis

Dissolution analysis, particularly in situ studies, plays a crucial role in understanding the relationship between the catalytic activity and stability. ICP-MS has been widely used to measure the amount of dissolved metal in electrolytes under reaction conditions.^{25,40,96–99} This measurement is important not only for assessing the extent of dissolution during electrochemical reactions but also for exploring the activity–stability relationship based on dissolution data. Since the value of catalysts must be evaluated from multiple perspectives, normalizing catalytic activity by the amount of dissolved metal is a wellestablished method for examining catalysts and quantifying the activity-stability relationship. Geiger et al. introduced the stability number (S-number) as an intrinsic parameter for catalysts, defined as the ratio between the amount of oxygen generated and the amount of metal dissolved (Figure 3a).¹⁰⁰ Similarly, Kim et al. introduced the Activity-Stability Factor (ASF), which is the ratio of OER activity, defined as the rate of oxygen production (OER current density), to the stability of oxide materials, measured as the rate of dissolution (equivalent dissolution current density) (Figure 3b).⁶² Following these studies, many researchers have confirmed the effectiveness of these metrics in evaluating the performance of catalysts.^{37,101-108} The approach of quantifying the activity-stability relationship is a valuable tool for understanding and assessing the effectiveness of OER catalysts.

While dissolution analysis is considered straightforward for assessing stability, there are several important factors to consider. Transient dissolution, which occurs during changes in the oxidation state, overlaps with steady-state dissolution related to the OER mechanism, both of which coexist in OER catalysts.⁴⁰ Furthermore, measuring "dissolution" is challenging, particularly during ex-situ analysis, where external factors like corrosion during cell disassembly or the lack of potential control in the initial stages can complicate results.¹⁰⁹ Careful consideration is needed when defining the catalyst stability and interpreting experimental data. Several studies have discussed the dissolution and redeposition cycles on OER catalyst surfaces.^{37,42-46} Dissolved catalysts can be redeposited quickly and are not collected during measurement of the dissolved catalysts. Moreover, active sites can be regenerated through redeposited catalysts, which leads to decent catalyst stability.^{37,42-46} Advanced consideration of the redeposition of dissolved metals is demanded in dissolution analysis.

3.3. Consideration of Reconstruction of Electrocatalyst by in Situ Analysis

In order to reveal the activity stability relationship when there is significant reconstruction during reactions, cutting-edge strategies have been developed and conducted to investigate the status of catalysts while the onset of the OER occurs. Especially, in situ analysis of material characterization including their oxidation state, size, crystallinity, etc. is highly demanded since the reconstruction occurs in "reaction conditions". Focusing on the purpose of reconstruction analysis, proper in situ method (or identical location analysis) can be helpful and a list of cases and their references are summarized in Table 1 for information.

4. CONCLUSION

The complex relationship between catalytic activity and stability continues to be a major challenge in the development

of high-performance OER catalysts. Traditionally seen as a trade-off, recent research has begun to reveal scenarios that question this conventional view. To fully understand these "functional relationships" and evaluate catalysts from both perspectives, several key steps are necessary. First, it is essential to identify the primary factors contributing to degradation, given its multifaceted nature. While metal dissolution is recognized as a significant degradation pathway in the OER, it is important to determine whether it alone provides a complete understanding of the process. Ongoing advancements in measurement techniques for both activity and stability are crucial and require further refinement. Cutting-edge strategies utilizing advanced equipment are gradually enhancing our understanding of these dynamics. Developing well-designed metrics that integrate both activity and stability is essential for the effective assessment of the quality of the OER catalysts. These efforts are expected to accelerate innovation in the OER field, leading to the development of more efficient and durable catalysts.

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Notes

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