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## Review

# Stability challenges of electrocatalytic oxygen evolution reaction: From mechanistic understanding to reactor design

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## SUMMARY

**The electrochemical synthesis of chemicals and fuel feedstocks has been demonstrated to be a sustainable and "green" alternative to traditional chemical engineering, where oxygen evolution reaction (OER) plays a vital role in coupling with various cathodic reactions. While tremendous attention, involving both research and review topics, has been focused on pushing the limit of OER catalysts' activity, the long-term stability of OER catalysts, which may play an even more important role in large-scale electrolysis industrialization, has been much less emphasized. Until this point, few systematic strategies for developing OER catalysts with industrially relevant durability have been reported. In this review, critical mechanisms that could influence OER stability are summarized, including surface reconstruction, lattice oxygen evolution, and the dissolution-redeposition process of catalysts. Moreover, to bridge the gap between lab-scale OER tests and large-scale electrocatalysis applications, stability considerations in electrolyzer design for long-term operation are also discussed in detail. This review provides catalyst and reactor design principles for overcoming OER stability challenges and will focus more attention from the field on the great importance of OER stability as well as future large-scale electrocatalysis applications.**

## INTRODUCTION

At present, humanity is facing serious energy and environmental challenges, including a rise in the global population with an increased demand on energy resources, global warming and climate change, and heavy industrial pollution.[1–6] Renewable electricity, which can be generated from renewable sources such as solar panels, wind farms, hydropower, etc., will play a significant role in providing sustainable energy supplies for the world and thus help to mitigate the exacerbation of global climate change.[1–3,7] Due to the continuously decreasing cost of renewable electricity, utilizing these cheap, abundant, and "green" electrons for the synthesis of basic chemical/fuel feedstocks via electrochemistry is becoming not only environmentally friendly but also economically attractive.[8–10]

To date, a wide range of electrochemistry technologies have received extensive attention in both academia and industry.[11–19] These include hydrogen evolution reaction (HER) via water splitting,[18–21] $CO_2/CO$ reduction reaction ($CO_2$/CORR) to chemicals and fuels,[14,22–24] $2e^-$-oxygen-reduction reaction ($2e^-$-ORR) to $H_2O_2$,[16,25,26] and nitrogen reduction reaction (NRR) to ammonia.[27–29] While it is these half-cell reduction reactions that generate the desired products and therefore

### Context & scale

Recently, clean energy conversion through electrocatalysis is evolving rapidly as a promising alternative to fossil-fuel energy systems. However, electrolyzers have always suffered from long-term stability challenges, especially for the anodic oxygen evolution reaction catalysts. So far, other than high-cost noble-metal catalysts such as $IrO_2$, no catalysts with industrially relevant stability for oxygen evolution process in acidic and neutral conditions have been demonstrated. Thus, mechanisms that lead to catalytic instability require further investigation and deep understanding to guide future catalyst design.

In order to explore both the origins of and solutions to the stability challenges, this review provides a comprehensive overview and analysis on mechanistic studies of OER catalytic stability. Surface reconstruction of catalysts under oxidation potential during oxygen evolution is one of the causes of catalyst degradation. In addition, lattice oxygen can sometimes participate in the reaction pathway and induce structural instability of catalysts. In addition, redeposition of dissolved ions onto the catalyst surface is a process that gains less attention

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attract extensive attention in our research field, we would like to emphasize that most of these cathodic reactions will be coupled with oxygen evolution reaction (OER) as the anodic reaction to supply protons and balance the charge.[1,3,10] It is because OER only requires water as a source and could be more easily applied for large-scale electrolysis compared to other anodic reactions. Therefore, in the prospect of the electrochemical energy conversion landscape (Figure 1), OER electrocatalysis is an indispensable component and stepping stone for a wide range of electrochemistry technologies. Developing OER catalysts with low-cost materials, industrially relevant activity, and long-term durability is highly desired but still challenging at the current stage.

Activity, stability, and cost are three critical merits that need to be considered when designing OER electrocatalysts for practical applications (Figure 2A). To date, most OER catalyst studies have mainly focused on improving the OER catalytic activity and decreasing the materials' cost,[7,30–34] while only very few of them have systematically focused on developing strategies to improve the catalytic stability of OER catalysts, especially in acidic conditions.[20,35] This might be due to limited catalyst candidates that are stable under harsh acidic conditions. That said, while improving the catalysts' OER activity is scientifically interesting and technologically important, OER stability could be an even more important factor to consider in real applications and thus requires more attention.

Here we use two representative model catalysts to illustrate the importance of stability in practical scenarios. As shown in Figures 2B and 2C, we assumed two types of catalysts with different activity and stability performances: one starts with higher OER activity (200 mV overpotential at 1 A cm$^{-2}$) but degrades faster (0.5 mV h$^{-1}$), while the other one is less active (300 mV) but remains more stable (0.1 mV h$^{-1}$). As a result, although the latter catalyst presents a much lower initial OER activity, compared to the former catalyst, it saves 43% of the energy cost caused by OER overpotentials after 2,000 h continuous operation and will save even more with longer operation time. This example clearly demonstrates that the long-term stability of OER catalysts in practical applications could carry even more weight than the consideration of their activity, which, however, has been much less emphasized in current OER studies.

To date, IrO$_2$-based noble-metal catalysts are the only catalysts that can meet the stability requirement under a local acid environment on a commercial-scale proton exchange membrane (PEM) electrolyzer.[18,36] Unfortunately, Ir is one of the rarest and most expensive elements, with global production of less than nine tons per year.[37] Therefore, developing more catalysts with higher durability together with good activity and low cost for practical applications is an urgent need in this field. In contrast, transition-metal catalysts under alkaline environments in traditional alkaline water electrolyzers (AWE) show a relatively higher stability, but due to the electrolyzer design, AWE has more operating limitations and requires higher power consumption.[38,39] Anion exchange membrane electrolyzer, a recently emerging technique, has the potential to resolve these challenges, but more understanding in electrolyzer designs and applicable catalysts are still required.[40–42] Previous reviews on OER topics have systematically summarized the recent developments of OER catalysts with good activities and earth-abundant elements.[7,10,30,31] In this review, we will instead focus on the importance of OER stability by summarizing recent mechanistic studies on OER catalyst degradation as well as electrolyzer design considerations, which we believe will attract more attention to this research direction and also provide more insights for future design of long-term OER catalysis.

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but can greatly influence the catalytic stability. Besides the catalyst consideration, critical elements of electrolyzers are also discussed in this review to provide insights in electrolysis operation under more realistic conditions. Based on the studies summarized in this article, we also provide potential strategies to design stable OER catalysts. By appropriately tuning the components, structures, dissolution, and redeposition rates of catalysts, we believe that the development of catalysts with long-term stability for oxygen evolution reaction can be achieved in the near future.

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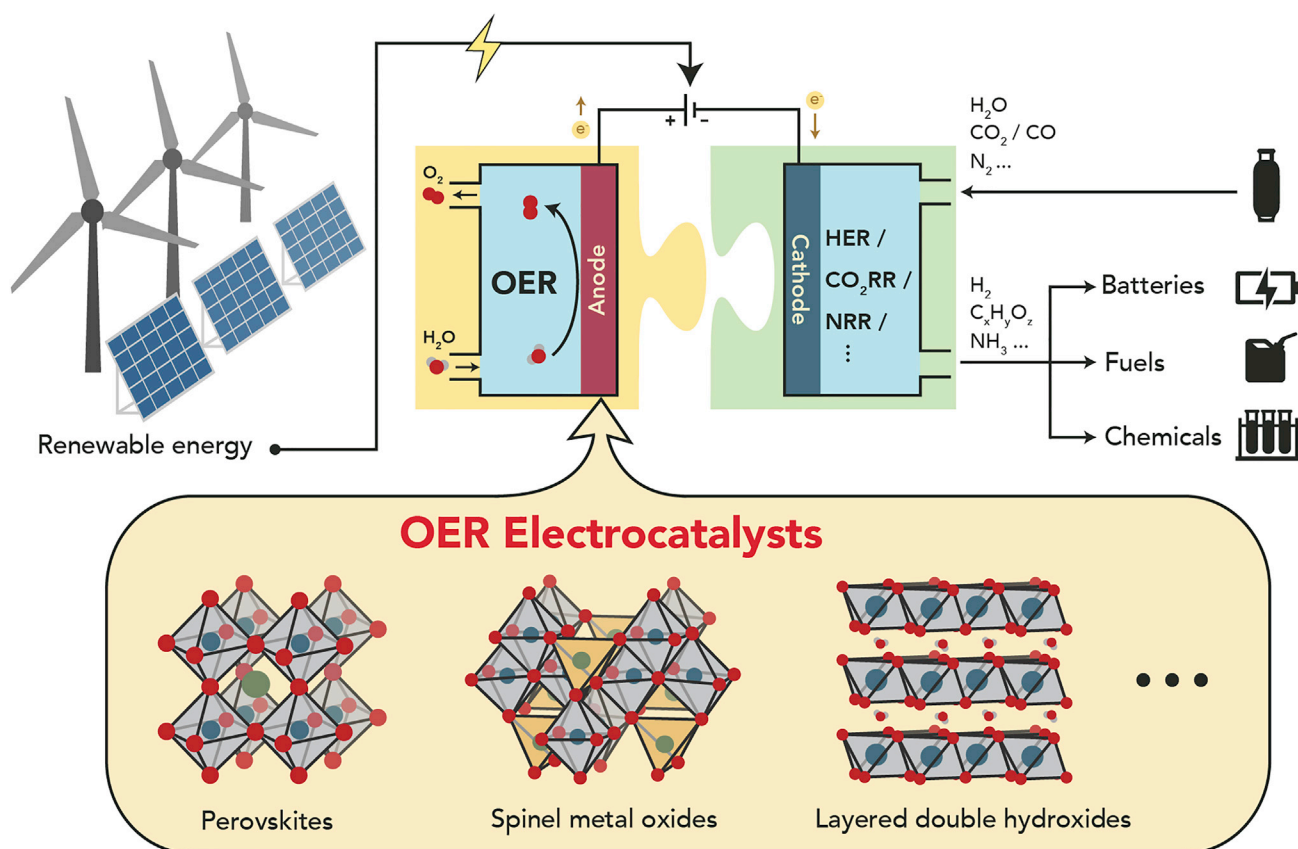
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**Figure 1. Schematic of the electrochemistry energy conversion landscape and the role of OER electrocatalysts**

A thorough understanding of the degradation mechanism of OER catalysts holds the key to designing stable electrocatalysts for long-term use. In this review, we aim to summarize the mechanisms of catalyst reconstruction, OER pathway, dissolution, and redeposition that would affect the stability of the catalysts during the OER process. At the initial stage of OER, some catalysts undergo significant surface reconstructions due to the high oxidation potentials, which can alter the true OER active sites and may also lead to catalytic instability. Additionally, the surface lattice oxygen in catalysts may participate in OER catalysis processes via different oxygen evolving pathways, causing performance degradation. During electrolysis, catalysts may also undergo a dissolution-redeposition process that will either reconstruct the catalytic surface or lead to a dynamically stable OER status. These are the critical phenomena that can affect OER catalytic stability from different aspects and they will be discussed in detail in this review. Finally, to bridge the gap between lab-scale measurements and practical applications, we will summarize how different factors or components in electrolyzers can affect stability in practical water-splitting applications. We believe this review can provide a different perspective as well as rational guidelines, with emphasis on the stability issue, for the future development of OER catalysts for practical applications.

## SURFACE RECONSTRUCTION

### Catalyst reconstruction under different conditions

It is well known that during the OER process, metal catalysts can undergo a surface reconstruction process to form metal oxides or (oxy)hydroxides due to the high
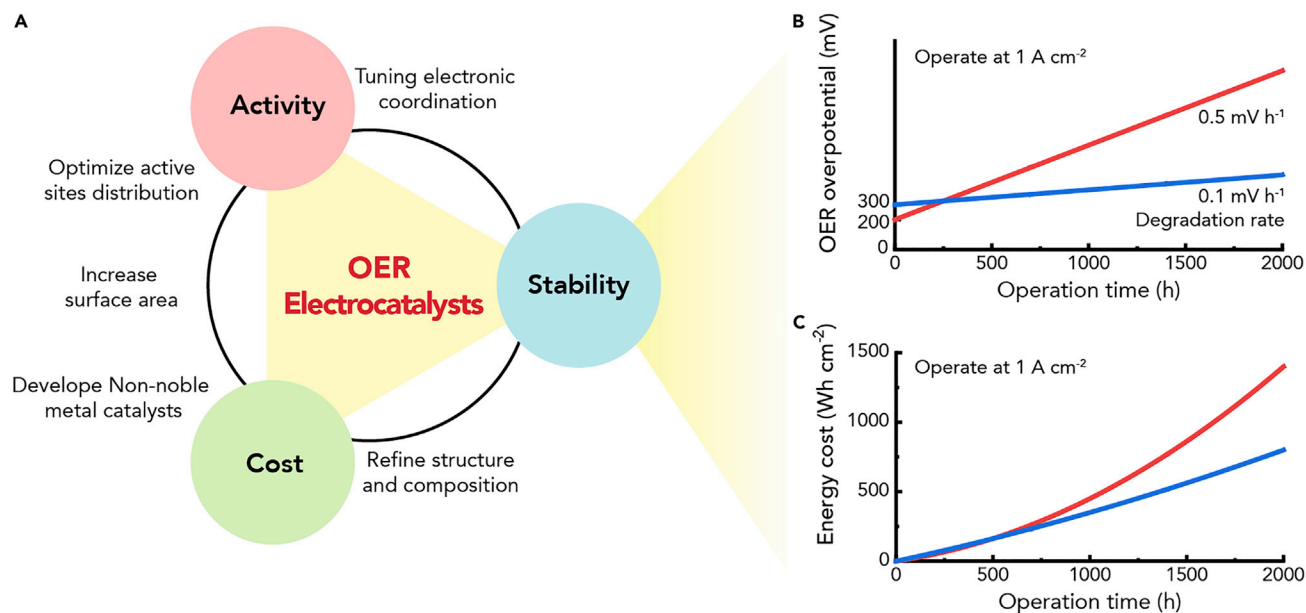
**Figure 2. The importance of OER catalytic stability**

(A) Important merits and general strategies for designing OER catalysts.

(B) Proposed schematic stability test of two different catalysts: one with good initial activity but a higher degradation rate (red curve) and vice versa for the other catalyst (blue curve).

(C) Energy costs of OER overpotential under a current density of 1 A cm$^{-2}$ based on the performances of the two different catalysts in (B). The blue curve saves 43% energy compared to the red curve after a 2,000-h operation period.

oxidation potentials.[43] Early studies have found that catalysts including transition-metal sulfides, selenides, nitrites, and phosphides demonstrate good OER activities under alkaline conditions. However, it was later revealed that these catalysts were oxidized through a reconstruction process during the reaction.[44–49] High-resolution transmission electron microscopy (HRTEM) images showed that corresponding metal (oxy)hydroxides were formed on the surface or even in bulk. Catalysts such as transition-metal-based alloys can also transform into (oxy)hydroxides under this anodic potential.[50,51] These results indicate that these pristine catalytic materials are not stable during the oxygen evolution process. Instead of the pristine catalysts, their derived metal (oxy)hydroxides actually serve as the true catalytically active species and stable phases for OER (Figure 3A). In fact, transition-metal-based (oxy)hydroxides such as NiFe-based (oxy)hydroxides, one of the most efficient OER catalysts under alkaline conditions, can be developed through this surface reconstruction process.[52,53]

In contrast, surface reconstruction can also occur on OER catalysts under acidic conditions. Due to the harsh conditions of OER in acidic media, only a few catalysts remain stable during the oxidation process and nearly all of them are noble-metal-based catalysts.[35] Among these candidates, Ir- and Ru-based catalysts are two of the well-known materials that show promising catalytic activity and stability for acidic OER. Studies have shown that surface of the bulk Ir and Ru metal would be oxidized into $IrO_2$ and $RuO_2$ during the catalytic process.[56,57] These transformation processes have been observed through atom probe tomography (APT) (Figure 3B).[55] Under the anodic current during oxygen evolution, the first few atomic layers of the pure Ir film will gradually transform into non-stoichiometric Ir–O species and finally into $IrO_2$ as the stable phase for this electrocatalytic reaction. These findings revealed that
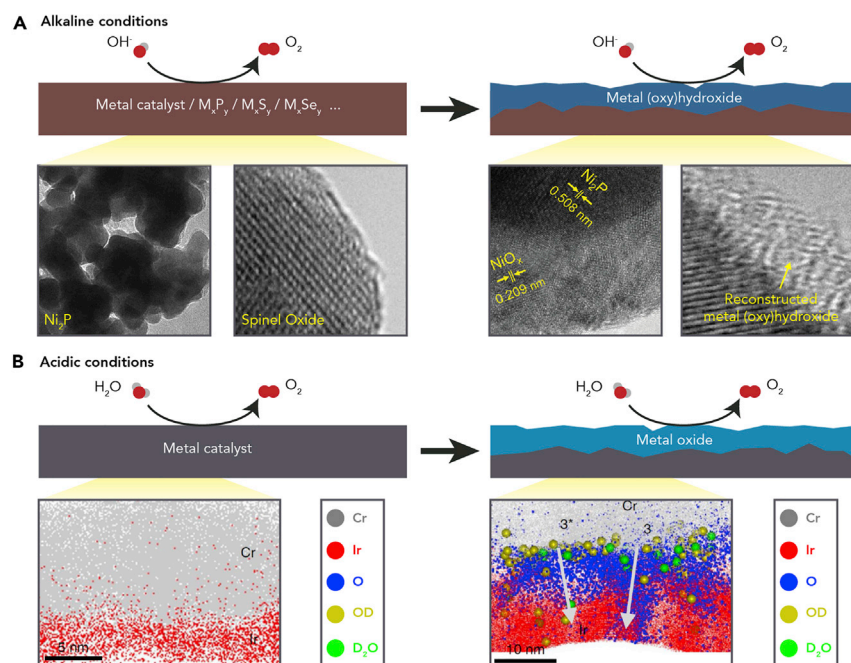
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**Figure 3. Catalysts go through surface reconstruction during the OER process under alkaline and acidic conditions**

(A) Under alkaline conditions, catalysts including transition metals, metal phosphides, sulfides, and selenides can be reconstructed into metal (oxy)hydroxides. HRTEM images of $Ni_2P$ and spinel oxide $CoFe_{0.25}Al_{1.75}O_4$ (left) being reconstructed into corresponding metal (oxy)hydroxides (right) are demonstrated as examples. Adapted from Stern et al.,[48] and Wu et al.,[54] with permission; copyright 2015, Royal Society of Chemistry, and 2019, Springer Nature, respectively.

(B) Under acidic conditions, metal-based catalysts (left) can be reconstructed into metal oxides. APT images of Ir (left) being reconstructed into $IrO_2$ (right) are demonstrated as an example. Adapted from Li et al. with permission;[55] copyright 2018, Springer Nature.

pristine catalysts are not necessary the real active species nor the stable phase under the electrocatalytic environment due to the possible surface reconstruction process. In Figure 3, we summarize several examples and demonstrate a general schematic of catalysts surface reconstruction under both acidic and alkaline conditions, with metal oxides and (oxy)hydroxides as the most common active sites after reconstructions.

## Thermodynamic stability and Pourbaix diagram

The above-mentioned surface reconstruction processes can be further explained from a thermodynamic point of view. Compared to catalysts such as metal chalcogenides and pnictides, it is well accepted that for most metal elements, metal oxides are the thermodynamically stable endpoint of most chemical processes under strongly oxidative aqueous environments.[58,59] Furthermore, Pourbaix diagrams created through theoretical studies can provide a deeper understanding. By modeling the surface stability, Pourbaix diagrams explain how metal-based catalysts would go through surface reconstruction or dissolve under specific pH and voltage during OER. For example, a recent study proposed Pourbaix diagrams of Sr, Ti, Ru, and Ir metals to predict their thermodynamically favorable surface terminations and further extended the calculation to predict the stability of perovskite oxides based on these metals.[60] Studies have also screened metal oxides for their computational aqueous stabilities to predict potential acid-stable candidates[61] or have combined theoretical Pourbaix diagram analysis and experimental results to propose a Ru-based OER catalyst with improved performance.[62,63] Therefore, thermodynamically
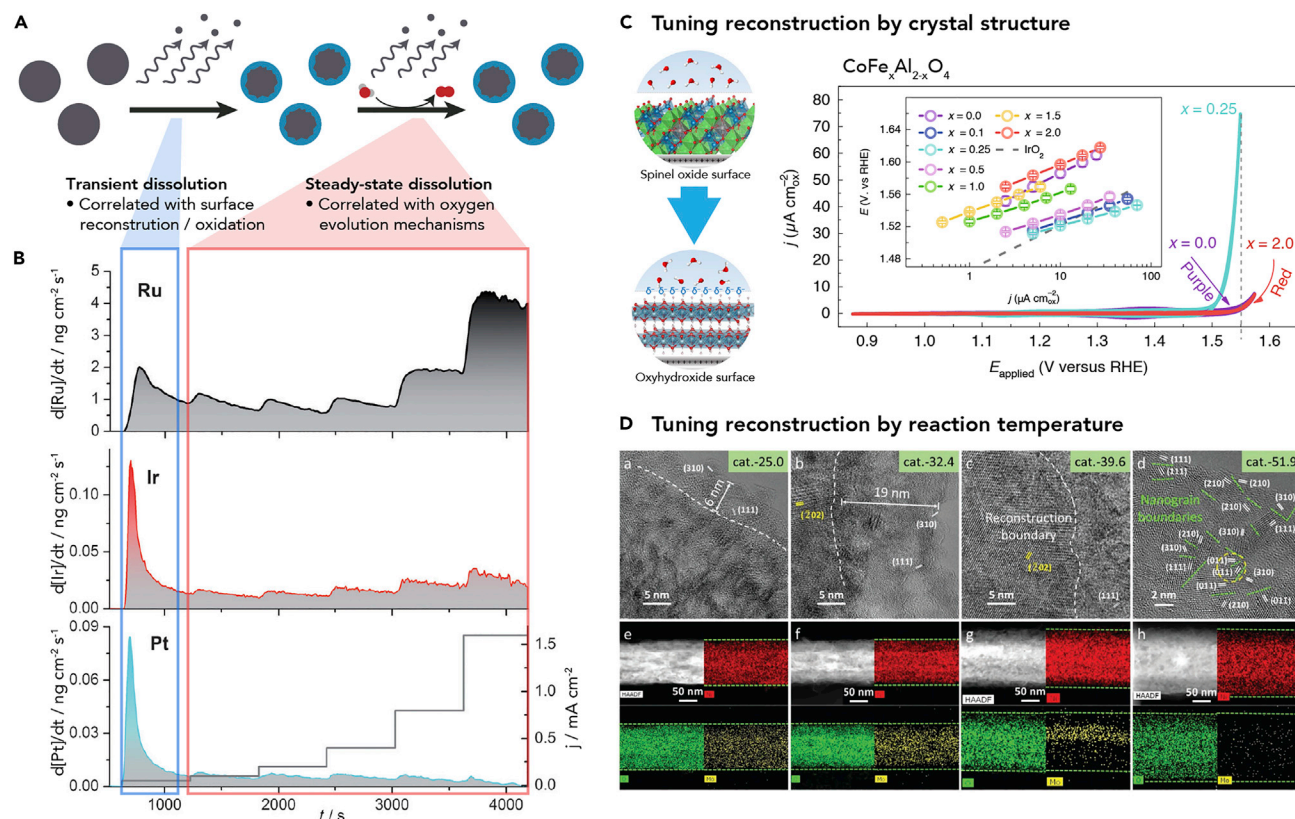
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**Figure 4. Dissolution processes during OER and strategies for tuning surface reconstruction**

(A) Schematic of catalysts undergoing transient dissolution during surface reconstruction, and steady-state dissolution during OER process.

(B) Dissolution rate of Ru, Ir, and Pt under the applied anodic current profile in 0.1 M $H_2SO_4$. Adapted from Cherevko et al. with permission;[56] copyright 2014, John Wiley and Sons Ltd.

(C) Reconstruction process from spinel $CoFe_{0.25}Al_{1.75}O_4$ into oxyhydroxide (left), and CV curves and corresponding Tafel plots (inset) of $CoFe_xAl_{2-x}O_4$ in 1 M KOH with different component ratios, x (Right). Adapted from Wu et al. with permission;[54] copyright 2019, Springer Nature.

(D) HRTEM (a–d) and HAADF-STEM images with corresponding elemental mappings (e–h) of $NiMoO_4$ after performing OER in 1 M KOH under different temperatures (T = 25.0°C, 32.4°C, 39.6°C, or 51.9°C, accordingly). Adapted from Liu et al. with permission;[67] copyright 2020, John Wiley and Sons.

analysis and Pourbaix diagrams can be useful tools to help us predict and explain experimental surface reconstruction products and will provide critical information for OER stability studies.

**Transient dissolution induced by surface reconstruction**

One of the challenges of surface-reconstruction reactions is that it could accompany a high catalyst dissolution rate and thus lead to catalytic instability, which is the so-called "transient dissolution mechanism."[56] Comparatively, the dissolution process of the stable-phase catalysts during OER is sometime referred to as steady-state dissolution.[64] A schematic of different dissolution types is presented as Figure 4A. To investigate how different polycrystalline noble metals show distinct performances and stabilities under acidic OER environments, Cherevko et al.[56] tested the transient and steady-state dissolution rate of noble-metal candidates, including Ru, Ir, and Pt; they found that their dissolution profiles could be quite different. For example, Ru has a high steady-state dissolution rate, while Ir and Pt have a low steady-state dissolution rate but a relatively high transient dissolution rate (Figure 4B). These results are also consistent with the finding that $RuO_2$ and $IrO_2$ exhibit an order-of-magnitude lower dissolution rate than their metallic analogs.[57,55,65,66] In

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addition, for certain catalysts such as Ru- and Ru-oxide-based catalysts, transient dissolution has also been observed at the potential lower than the OER potential (1.23 V).[65,66] This indicates that the catalytic instability can be induced by the surface oxidation and reduction processes of the catalysts but not necessary only by the oxygen evolving process.

### Tuning surface reconstruction

Therefore, studying how catalyst surface reconstruction can be induced, tuned, and terminated plays a key role not only in enhancing catalytic activity but also in prolonging long-term durability of catalysts. Recently, Wu et al.[54] proposed that the inactive spinel $CoAl_2O_4$ could be induced to perform surface reconstruction by substituting Al with a certain amount of Fe. After the reconstruction was induced, OER activity of the catalyst was promoted. *In situ* characterizations suggested that just within two cyclic voltammetry (CV) cycles, Fe species in $CoFe_{0.25}Al_{1.75}O_4$ will facilitate the pre-oxidation of Co with the subsequent surface reconstruction into oxyhydroxide as the active sites. This newly formed surface layer has an improved activity, which lowered the OER overpotential by $\sim$70 mV, while neither $CoAl_2O_4$ nor $CoFe_2O_4$ showed such an improvement (Figure 4C). This reconstruction process would co-occur with Al leaching, which could alter the local electronic structure to prevent further reconstruction and therefore terminate the process at a stable oxyhydroxide phase. This finding indicated that the surface reconstruction could possibly be tuned by altering the crystal structure and metal components of the catalysts.

Moreover, Liu et al.[67] have demonstrated that the surface reconstruction can also be driven by the reaction temperature. They used $NiMoO_4$ as the pre-catalyst and performed OER under different temperatures. Only $\sim$6 nm surface layers of the $NiMoO_4$ were reconstructed when operated under 25.0°C, while reconstruction degree was deepened and the whole structure was transformed into NiOOH under 51.9°C (Figure 4D). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images revealed that Mo species were leached out during the reconstruction and the stable oxyhydroxide phase, NiOOH, showed an improved OER activity. The thermally induced complete reconstruction in this work may be related to the changes in the oxidation environments at different temperature, which could tune the redox states of the catalysts. These clues suggest that reaction potential, crystal structure, and metal oxidation state of the catalysts are all critical to controlling the surface reconstruction.

### State-of-the-art characterization techniques for catalyst structure analysis

As a result, identifying the real active species and stable phase could provide important information for OER stability. Here, several characterization techniques are recommended for analyzing the targeted catalysts before and after OER process. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) can provide general physical and chemical information of the catalysts before and after catalytic tests. HRTEM can be employed to determine the surface reconstruction boundary and the crystal structure changes, and combined with electron dispersive X-ray spectroscopy (EDS) elemental mapping can further demonstrate the elemental composition changes after reaction.[48,67] Moreover, APT can provide atomic-scale information for the bulk catalyst analysis.[55]

In addition, *in situ* characterization would be preferred to investigate the OER mechanism.[59] Previous studies have used *in situ* HRTEM assisted by *in situ* Fourier transform infrared spectroscopy (FTIR) to analyze the evolution of $CoS_x$ into alpha phase

CoOOH.[45] *In situ* X-ray absorption spectroscopy (XAS) is also a powerful tool to characterize electronic structure and chemical bond of the catalysts, which has been employed to study the electron states and active phases of oxyhydroxides and layered double hydroxides (LDH).[68,69] Only through these detailed characterizations can researchers reveal the detailed mechanism of surface reconstruction during OER.

### Perspectives of catalysts design strategies

A deeper understanding of the mechanism of surface reconstruction can also provide hints for the design strategies for stable OER catalysts. As discussed above, metal oxides are the thermodynamically favorable endpoint for most of the metals under oxidative environments such as OER.[58,59,70] Therefore, metal oxides or (oxy) hydroxides would be good starting candidates for stable OER electrocatalysts. Preparing metal oxide as catalysts instead of bulk metal can also decrease the transient dissolution, which can potentially avoid the structural changes and instability during OER.[57] Some studies also purposefully prepared transition metal chalcogenides,[52,71] phosphides,[72] or alloys[51,73] as precursors and transformed them into (oxy)hydroxide under anodic electrochemical conditions. This suggests an alternative strategy that we can use pre-catalysts as scaffolds and go through surface reconstruction to form a more active and stable OER catalyst. However, in order to properly adopt this strategy, further understandings in tuning surface reconstruction are required.

### OXYGEN EVOLUTION PATHWAY

OER pathways also play a key role in catalytic stability. A mechanistic understanding of the reaction pathways can provide explanations of how catalysts dissolve during the oxygen evolution process. In general, the oxygen evolution mechanism can be mainly classified into the conventional adsorbate evolution mechanism (AEM) and the lattice oxygen oxidation mechanism (LOM).[74] In AEM, the OER activity is highly correlated to adsorption energies of the adsorbed intermediates. The scaling relation of these adsorption bonds suggests that there is a theoretical limitation of the OER activity.[75,76] On the other hand, LOM has attracted increased research interest and has recently been widely discussed due to its potential to surpass the limitation of AEM.[77–79] In the reaction pathway of LOM, lattice oxygen of the catalysts, particularly metal oxides, can participate in the oxygen evolution and involve the direct O-O coupling. Since LOM provides a distinct reaction pathway for O-O coupling, its reaction energy will not be limited by the adsorption energy scaling relationship of the AEM pathway. In spite of the potential of LOM to enhance OER activity, participation of the lattice oxygen could also lead to catalyst instability from thermodynamic considerations.[80] Therefore, unveiling the enigma of LOM is now crucial for the development of efficient and stable OER catalysts. Here, by summarizing previous studies, we propose a possible reaction pathway for AEM and LOM in Figure 5A and suggests how the lattice oxygen participates in OER through LOM.

### LOM under different conditions

Lattice oxygen participation in OER under acidic conditions has been revealed in early studies by isotope labeling together with differential electrochemical mass spectrometry (DEMS).[82–84] It was found that the lattice oxygen in the oxide layer of $RuO_2$ will take part in OER, and the formation of soluble $RuO_4$ species can be detected as the corrosion product. Meanwhile, no oxygen exchange was observed for Pt-oxide-based catalysts during OER. These findings were further supported by a later study through screening the dissolution rates and activity of 6 different noble-metal catalysts including Ru-, Au-, Ir-, Rh-, Pt-, and Pd-based catalysts in acidic electrolyte (Figure 5B).[56] Among
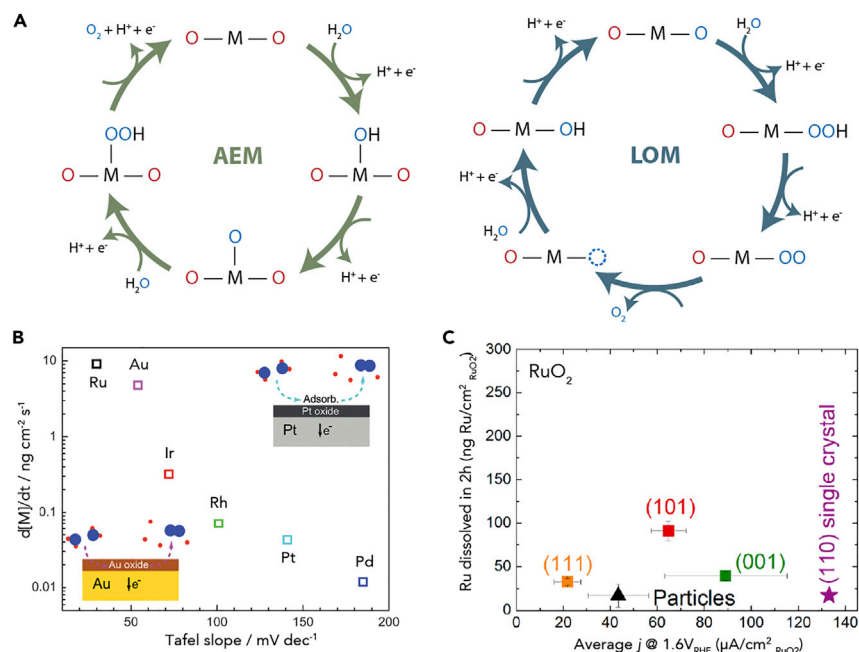
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**Figure 5. OER reaction pathways and catalytic activity-stability relationship**

(A) Reaction pathways of OER. $H_2O$ and four electron transfers are involved to evolve one $O_2$ in both AEM (left) and LOM (right) reaction pathways. M stands for metal active site and the dashed circle represents the lattice oxygen vacancy.

(B and C) Debate between activity-stability relationship of OER catalysts.

(B) Correlation between Tafel slope and dissolution rate of six noble-metal catalysts measured in 0.1 M $H_2SO_4$. Inset schematics suggest catalysts with high and low activities would go through LOM and AEM pathways, accordingly. Adapted from Cherevko et al. with permission;[56] copyright 2014, John Wiley and Sons.

(C) Normalized current density and dissolution of different $RuO_2$ catalysts in 0.5 M $H_2SO_4$ for a 2 h potentiostatic test at 1.6 $V_{RHE}$, showing no direct correlation between activity and stability. Adapted from Roy et al. with permission;[81] copyright 2018, American Chemical Society.

these noble-metal catalysts, Ru has a low Tafel slope but a high steady-state dissolution rate. The steady-state dissolution rate of Ru is strongly correlated to the operation current (Figure 4B), therefore the dissolution here is likely to be triggered by the oxygen evolution process, which could be attributed to Ru's reaction pathway preference for LOM.[82,85] In contrast, noble metals such as Pt and Pd have higher Tafel slopes but lower dissolution rates and are believed to go through AEM during oxygen evolution. This is also consistent with another study that compared several monometallic oxides.[86] It showed that these monometallic oxides have inverse trends for activity (Au < Pt < Ir < Ru) and stability (Au > Pt > Ir > Ru). This can be explained from the thermodynamic viewpoint that oxygen anion in the metal oxide lattice accompanying LOM will serve as the basic driving force for metal ions dissolution or structural change.[80] Based on this viewpoint, metal oxides will eventually become unstable under oxidation environment through LOM.

Besides LOM under acidic conditions, lattice oxygen participation has also been observed under alkaline conditions recently. Grimaud et al.[78] tested a series of perovskite OER catalysts by in situ isotope labeling mass spectrometry. They found that for some highly active catalysts, the $O_2$ generation during OER could come from the lattice oxygen. Candidates with lattice oxygen exchange such as $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ and $SrCoO_{3-\delta}$ exhibited pH-dependent OER activities, while those without

lattice oxygen exchange such as $LaCoO_3$ showed pH-independent OER activity. This could be attributed to the mechanistic difference between LOM and AEM.[87] Density functional theory (DFT) calculations further demonstrated that perovskites with higher activities tend to have stronger metal-oxygen covalency and to be more exact, enable the non-concerted proton-electron transfer steps in LOM. This viewpoint is supported by a recent study by Pan et al.[88] in which perovskite-based electrocatalysts with more extensive LOM were designed that showed enhanced activities. Activity volcano plots for AEM and LOM of perovskite systems have been established by a simulation work, which showed that LOM is preferred for several candidates to achieve higher OER activity.[79] Similar trends have also been demonstrated in spinel oxide[89,90] and oxyhydroxide[91,92] systems. Besides acidic and alkaline conditions, lattice oxygen emigration has also been observed in neutral OER.[93] Overall, lattice oxygen participation in OER has been observed under different environments for a wide range of catalyst systems.

### Activity-stability relationship

The studies mentioned above demonstrate a trend that LOM can promote OER activity but can also lead to lattice structural instability, which is in contrast with the catalytically stable but less active AEM pathway. If this activity-instability correlation of LOM is robust and universal, it will hinder researchers in this field from pursuing OER catalysts with both high activity and durability. Therefore, it is an urgent challenge to elucidate the detailed mechanism of OER.

Recently, the relationship between AEM and LOM has been widely discussed, and whether activity and stability are directly correlated is still under debate.[81,94,95] For example, in contrast to most of the previous works that believed LOM was the main oxygen evolution pathway of $RuO_2$, a study has demonstrated that no lattice oxygen exchange was observed on well-crystalline $RuO_2$.[96] It was valid on the surfaces including rutile (110), (100), (101), and (111) orientations under both acidic and alkaline conditions. The results were also supported by their simulation works, showing that the removal of the –OO group on the coordinatively unsaturated ruthenium ($Ru_{CUS}$) site and the neighboring oxygen site plays a critical role.[97,98] This indicated that the high OER activity of Ru-based catalysts could be attributed to the ideal binding energy on the $Ru_{CUS}$ site but not necessarily due to the LOM reaction pathway. Another work by Roy et al.[81] also studied the activities and dissolution rates of different $RuO_2$ facets and found that, in contrast to previous belief,[94,95] activity and stability do not necessarily have direct correlation (Figure 5C). For instance, in this study, the more active $RuO_2$ (110) facet with a higher oxygen-evolution-current density does not show a higher dissolution rate than other facets. Another example from perovskite system $BiSrCoO_3$ also suggests that, based on the proposed non-concerted proton-electron transfer mechanism, high activity does not necessarily correlate with LOM or instability.[99,100] Overall, the true mechanism of OER is still under intense debate, but these results indicate that by properly tuning the facets and active sites, catalysts with both high activity and stability can possibly still be reached. Therefore, more fundamental investigations into OER mechanism on different catalysts are still urgently required.

### Crystallinities and metal vacancies

These diverse observations on lattice oxygen exchange may be related to the crystallinities and oxygen vacancies of the catalysts, which are attributed to the different catalyst preparation processes. This viewpoint can be supported by several studies on Ir-based catalysts. Although $IrO_2$-based catalysts are currently known as the only stable catalysts for the commercial-scale electrolyzer under acidic conditions,[36,101] some studies still observed lattice oxygen exchange and high dissolution rate on $IrO_2$.[102,103] To elucidate the reaction and dissolution mechanism, Kasian et al.[104] compared hydrous iridium oxide
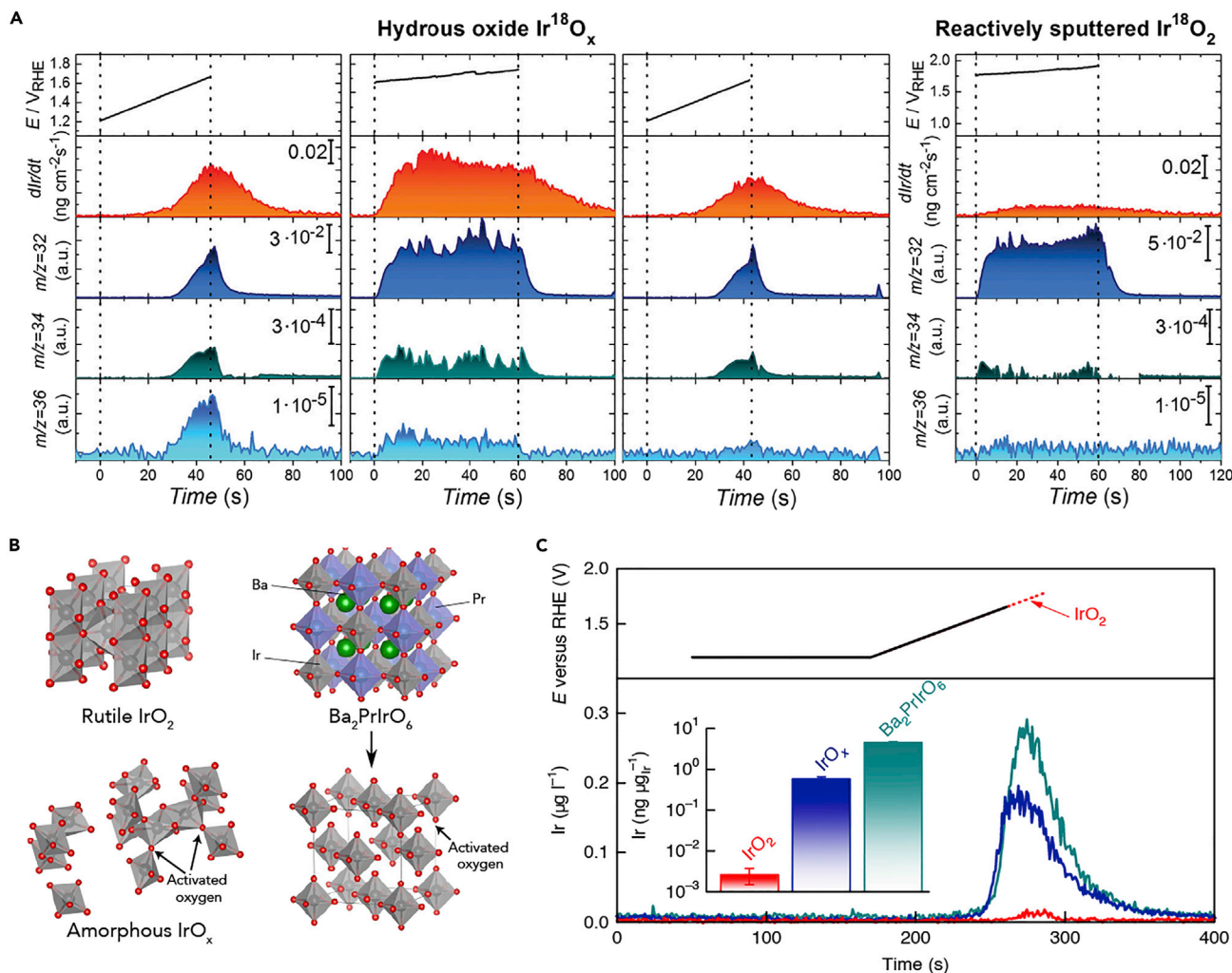
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**Figure 6. Correlation between lattice structure and OER stability**

(A) Dissolution rate and lattice oxygen exchange (shown as isotope-labeled $^{16}O^{18}O$, $^{18}O^{18}O$ signal) of hydrous $Ir^{18}O_x$ (left) and rutile $Ir^{18}O_2$ (right) during OER in 0.1 M HClO$_4$. Reprinted from Kasian et al. with permission;[104] copyright 2019, Royal Society of Chemistry.

(B and C) Assumed crystal structures of Ir-based catalysts (B) and their dissolution rate during OER in 0.1 M HClO$_4$ (C). Inset in (C): integrated and normalized Ir dissolution. Adapted from Geiger et al. with permission;[105] copyright 2018, Springer Nature.

and rutile IrO$_2$ catalysts through isotope labeling combined with APT and online mass spectrometry. It was revealed that Ir hydrous oxide with –Ir$^{III}$OOH species could contribute to a higher extent of LOM and thus lead to faster Ir degradation, while rutile IrO$_2$ is more stable and no significant lattice oxygen exchange was observed (Figure 6A). More comprehensive studies have also been conducted to investigate the dissolution processes of various iridium-based oxides, and they found that the formation of amorphous iridium oxide could trigger the LOM and show high activity accompanied by a high Ir dissolution rate.[105–107] For instance, Figures 6B and 6C show that IrO$_x$-based catalysts with more defects and vacancies can lead to a higher dissolution rate,[105] presumably because these metal vacancies can introduce more lattice oxygen exchange and cause instability of the crystal structure.

More recently, a simulation study proposed that dopants or metal vacancies could promote the LOM over AEM for well-structured surfaces.[108] The authors chose

$RuO_2$ as the model. The results showed that AEM is preferred for well-crystalline $RuO_2$, while adding dopants such as Ni and Co or creating surface defects on $RuO_2$ surface could lead to LOM pathway. These results all suggest that the preference of the OER pathway is not simply determined by catalyst elements. In fact, the degree of crystallinity, defect, and vacancies are all critical for the reaction pathway during OER and thus will all influence the catalytic stability. This also provides a possible explanation for the previous debate and diverse observations of lattice oxygen exchange on different metal oxides catalysts, such as $RuO_2$.

### State-of-the-art characterization techniques for LOM and dissolution

More explorations and characterizations in oxygen evolution mechanisms are still required to provide more clues toward a durable catalyst design. Techniques such as combining isotope labeling and differential/online electrochemical mass spectrometry (DEMS/OLEMS) can effectively investigate whether there is lattice oxygen exchange during OER. Combining these techniques with online inductively coupled plasma mass spectrometry (ICP-MS)[104,105,109,110] or electrochemistry-mass spectrometry (EC-MS)[111] can further explore the relation between lattice oxygen participation and dissolution rate. In addition, the dissolution products from the catalysts should be carefully considered to avoid any measurement error. Pourbaix diagrams discussed in the previous section can provide useful information. For example, soluble $RuO_4$ has been identified as one of the products for Ru-based catalyst dissolution,[84] and formation of gaseous $IrO_3$ has been identified as a possible route for Ir-based catalyst dissolution.[106] Recently, *in situ* Raman spectroscopy and XAS were used to study the OER mechanism of Co oxyhydroxide.[92] Characterization results revealed that Co(IV) species, $CoO_2$, was detected as the dominating resting state, while the cobalt superoxide species was identified as an active intermediate and was formed concurrently with the oxidation of CoOOH to $CoO_2$ during OER. This observation provides a new mechanistic perspective of how lattice oxygen between two metal active sites evolves through the LOM route during OER.

### Perspectives of catalysts design strategies

Moreover, it remains a great challenge to apply these mechanistic understandings in the design of stable catalysts. Some studies have demonstrated that stability can be enhanced by tuning the alloy structures of Ru and Ir oxides to alter their reaction pathway;[112–115] except for $IrO_2$-based catalysts, there are still no catalysts that result in long-term stability under acidic conditions. According to the previous observations on $IrO_2$-based catalysts prepared from different methods, metal oxides with high crystallinity could be a good target for better stability.[104–107] In addition, a recent study proposed a different strategy by atomically dispersing Ru onto different $PtCu_x/Pt_{skin}$ core-shell structures.[116] This strategy effectively mitigates the degradation of the Ru-based catalyst, potentially because the dispersed Ru atom on the surface can switch the reaction pathway from the originally dominant LOM to AEM. Although AEM was believed to show lower catalytic activity than LOM in general, this designed Ru-$PtCu_x$ catalysts still perform with promising activities due to the ideal electronic structure of the Ru atom, which is well tuned by the ratio of $PtCu_x$ core-shell structures. The design strategies summarized here could provide some inspirations, but in order to pursue a long-term durable catalyst, there is still an urgent need to comprehensively elucidate the real OER mechanism.

## DISSOLUTION-REDEPOSITION PROCESS

Dissolution of catalysts is usually the main cause of performance degradation. Catalyst dissolution can be triggered by harsh conditions during OER, including strong acidic or alkaline environments and oxidation environments. In the previous sections we have

discussed that dissolution can also be caused by surface reconstruction and lattice oxygen participation. In fact, the dissolution under oxidation environments during electrochemical reaction can be quite complicated. Studies have shown that different catalytic facets, support substrates, and reaction potentials can all lead to distinct dissolution pathways.[117,118] Thus, further studies are required to unravel the complex dissolution mechanisms. In addition to the intrinsic stability of the catalysts, dissolved catalysts or ions in the electrolyte could also influence catalysis performances or even go through a redeposition process during the electrochemical reactions. This mechanism has received less attention comparatively but it is believed to critically affect the catalytic activity and stability under long-term operations.[119–121] Therefore, in this section, the redeposition process and the ion effect in electrolyte will be discussed in detail.

### Anodic electrodeposition

It is well known that by introducing metal ions in the aqueous solution, the electrodeposition of the metal can be performed under cathodic currents through a reduction process. However, it is lesser known that metal-based materials can also be electrodeposited onto the electrode under anodic currents. In fact, the anodic current deposition strategy has been applied to prepare various types of OER catalysts with good activities. An early study found that by performing an anodic CV scan in phosphate-buffered water with cobalt (II) ions, an oxidation wave could be observed near the OER onset potential. This oxidation wave is actually the electrodeposition process of the Co-based catalysts formed in situ.[122] In addition, this cobalt-ion-containing solution was used as the electrolyte with indium tin oxide as the electrode to perform electrolysis at the OER potential. It exhibited a rising current density and reached a peak value and Co-based catalysts coated on the electrode were observed. This indicates that electrodeposition of the catalysts and oxygen evolution processes could co-exist under the oxidation potential, which provides an inspiration in OER catalyst preparation. Several later studies have demonstrated that several OER catalysts such as Ir-based catalysts can be prepared through such anodic electrochemical deposition, including $IrO_x$, Ir clusters, and Ir single-atom catalysts.[123–125] All of which show good OER activity under alkaline conditions. During these depositions, anion complexes such as $Ir(OH)_6^{2-}$ were suggested to be the possible depositing species, and thus explains why metal-based catalysts could also be electrodeposited under anodic current.

In addition to catalysts that were prepared and had performed OER under neutral or alkaline solutions, an anodic deposition strategy has also been applied in the preparation of catalysts under corrosive acidic conditions.[126] In the study, $Co^{2+}$, $Fe^{3+}$, and $Pb^{2+}$ ions were intentionally added into acidic solutions as electrolytes. During the electrooxidation of the electrolytes under constant potential, $CoFePbO_x$ catalyst would continuously deposit onto the electrode surface and oxidative current would gradually increase until reaching a quasi-steady state. It is expected that these non-noble metals are likely to dissolve in acidic solutions, and thus the balance between dissolution and electrodeposition processes here provide a new route to dynamically enhance catalytic stability. In fact, $PbO_x$ matrix has long been known to be stable in acidic media,[127] so the idea presented in this work can also be applied to other transition-metal complexes in the design of stable acidic OER catalysts.[128,129]

### Active phase reconstruction

From the electrodeposition examples above, we notice that under the voltage of OER operation, not only oxygen evolution could happen but this anodic condition can also trigger deposition of metal species. This phenomenon is less recognized in conventional OER studies but can strongly impact the catalytic mechanisms of
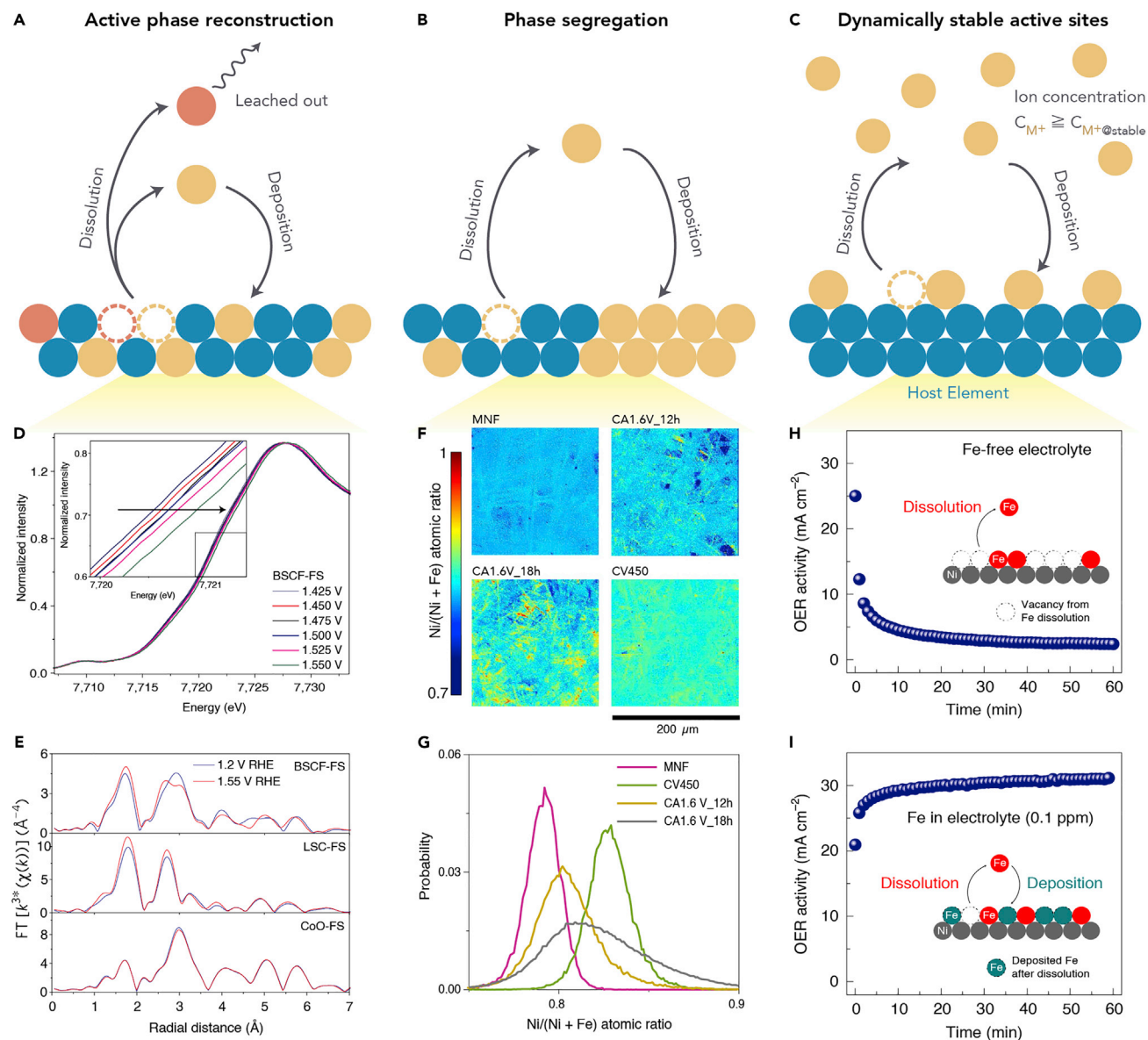
**Figure 7. Types of dissolution-redeposition processes during OER**

(A–C) Schematic diagram of how dissolution-redeposition processes influence catalytic stability through active phase reconstruction (A), phase segregation (B), and dynamically stable active sites (C).

(D and E) *Operando* Co K-edge XANES during OER in 0.1 M KOH indicates an increase in the Co oxidation state as voltage increase (D), and Fourier transform of the EXAFS indicates that BSCF-FS has a significant structural change (E). The splitting peak at ~2.5–2.7 Å corresponds to Co–Co edge-sharing polyhedral of Co (oxy)hydroxide. Adapted from Fabbri et al. with permission;[119] copyright 2017, Springer Nature.

(F and G) XFM images of Ni/(Ni + Fe) atomic ratio mapping of pristine MNF, after 12 h CA, 18 h CA, and 450 cycles CV measurements in 1 M KOH, accordingly (F) and their atomic ratio distribution (G). Adapted from Kuai et al. with permission;[120] copyright 2020, Springer Nature.

(H and I) OER activity of FeNi (oxy)hydroxide during CP measurements at 1.7 V in Fe-free purified 0.1 M KOH (H) and in 0.1 M KOH with 0.1 ppm Fe (I). Adapted from Chung et al. with permission;[121] copyright 2020, Springer Nature.

OER. For example, a self-reconstruction process of perovskite nanocatalysts during OER has been proposed to be attributed to this dissolution and redeposition phenomenon.[119] Flame-sprayed perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF-FS) was tested in this study, and *operando* X-ray absorption near-edge structure (XANES) spectra of Co K-edge revealed that metal (oxy)hydroxide active surface layers were formed during OER in alkaline solutions (Figures 7A and 7D). It was proposed

that after the dissolution of this perovskite, $Ba^{2+}$ and $Sr^{2+}$ cations would easily leach out while rather insoluble $Co^{2-3+}$ and $Fe^{2-3+}$ cations would go through a redeposition process and form (oxy)hydroxide layers on the surface, as shown in the schematic diagram in Figure 7A. Extended X-ray absorption fine-structure (EXAFS) spectra of BSCF-FS, flame-sprayed $La_{0.2}Sr_{0.8}CoO_{3-\delta}$ (LSC-FS), and CoO (Figure 7E) further revealed that only BSCF-FS has a significant electronic structural change. This indicates the dissolution-reposition process is also highly related to catalyst components and structures. Similar observations can be found in a work for delafossite analog synthesis.[130] They intercalated Ag into CoFe (oxy)hydroxide layers by anodic electrodeposition through a self-reconstruction process to prepare the desired catalysts for alkaline OER.

Additionally, the redeposition process has also been observed in acidic media in a perovskite system.[131] A series of $Ir^V$-based perovskite-like materials were tested as OER catalysts. The study found that these materials would all reach similar activities after several CV cycles. To elucidate the reason, Ir dissolution and deposition under different conditions were then further studied. It was revealed that these perovskites were not stable under acidic conditions and would dissolve into the electrolyte. Subsequently, these Ir ions redeposited and precipitated as IrOx on the surface of the catalysts under OER operation potential and thus acted as the true active sites. For this reason, these perovskite-like materials will eventually reach similar OER activities. In general, surface reconstruction in neutral, alkaline, or acidic conditions through the dissolution-redeposition process have all been demonstrated to be possible and thus further indicate the importance of identifying the true catalytic active site.

### Phase segregation

Dissolution and redeposition can be critical to long-term durability of catalysts. In another aspect, properly manipulating the catalytic operating conditions to control the dissolution-redeposition process could also prolong the OER catalyst lifetime. A recent study noted that mixed Ni–Fe hydroxide (MNF) has completely different performances under CV and chronoamperometry (CA) stability tests.[120] Inspired by this finding, the authors did mechanistic research under these operation conditions. They used X-ray fluorescence microscopy (XFM) to reveal that the surface of pristine MNF would go through a phase segregation process after a continuous 12 and 18 h CA operation. In contrast, even after 450 CV cycles there was no obvious phase segregation (Figures 7B, 7F, and 7G). Phase segregation reportedly causes the loss of activity,[132] and was proposed to be attributable to the dynamic dissolution-redeposition process of the metal ions that caused cation redistribution.[120] The study further found that this phase segregation for NiFe hydroxide is reversible at the potential between the OER operation potential and catalysis reduction potential. Based on this idea, an intermittent reduction method was developed to revive the NiFe hydroxide by performing catalyst reduction for 2 min at 1.33 V after every 1 h of oxygen evolution at 1.63 V under continuous CA test. It was shown that this method could greatly enhance the catalytic stability. This result indicates that the dissolution and redeposition process can be controlled by tuning the voltage and that the complicated redox reaction of catalysts itself can be sensitive to the potential.

Here, we would also like to emphasize that CV test for thousands of cycles could mimic the start-up and shutdown cycles of electrolyzer operation. However, as the above example study demonstrates, it is not rational to justify the long-term durability of the catalysts only by CV test, due to the complex real-time redox process

under different potentials. In fact, different oxidation potential, reduction potential, and scan rate could all lead to different stability profiles.[133] CA or chronopotentiometry (CP) tests with desired operation conditions for at least hundreds of hours combined with dissolution species measurement are thus recommended to demonstrate the long-term stability of OER catalysts.

### Dynamic stability

The dissolution-redeposition process can also be tuned by the metal ions in the electrolyte. From the anodic electrodeposition phenomenon introduced above, we can expect that with an ideal substrate, operation voltage, and amount of metal ions in electrolyte, it is possible to reach a dynamic equilibrium between metal dissolution and redeposition to accomplish long-term stability. Recently, this idea has been demonstrated on the transition-metal (oxy)hydroxide system by introducing 0.1 ppm of Fe ion into alkaline electrolyte and using (oxy)hydroxide clusters as hosts, such as $NiOOH$, $CoOOH$, $NiCuOOH$, etc.[121] It was found that dynamically stable Fe active sites were formed on the surface through balancing the dissolution and redeposition rates of Fe, which greatly enhanced the catalytic stability relative to that in the test in which metal ions were not introduced into the electrolyte (Figures 7C, 7H, and 7I). According to the previously mentioned study, $[Fe(OH)_4]^-$ is likely to be the adsorbed species, in this case, for the anodic redeposition.[134] The adsorption energy between Fe and the metal host has been suggested to be the key descriptor for the dissolution-redeposition process and could be highly related to the catalytic stability in this system.[121] Intentionally adding different ions has also been demonstrated to alter the OER pathway and promote the activity.[135] Therefore, the metal-ion effect in the electrolyte could provide a new design route for dynamically stable long-term operation and enhanced performance of OER.

### Practical guidance and perspectives

In general, the redeposition effect has received less attention in previous OER studies, but it is critical to both surface reconstruction and durability of catalysts. Therefore, we believe there is a need to elucidate the complicated mechanism of the dissolution-redeposition process. Figures 7A–7C summarizes how the dissolution-redeposition process can affect the catalyst structure and stability in different ways. In addition, we would also like to reiterate the importance of the effect of metal ions in the electrolyte. An early study has emphasized that even a small amount of electrolyte impurities can cause completely different electrocatalysis performances.[136] The study mentioned above further indicated that as little as 0.01 ppm of Fe ion in electrolyte could alter both catalytic activity and stability by deposition effect.[121] Therefore, electrolyte impurities should always be carefully checked to reveal the true intrinsic performance of catalysts. Furthermore, if the dissolution-redeposition phenomenon is also widely applicable to different catalysts discussed in the previous sections, then the mechanisms of surface reconstruction and LOM should be reconsidered. For example, the isotope-labeled lattice oxygen exchange observed in previously mentioned experiments could potentially not all be due to the LOM pathway but could also come from dissolved and redeposited metal oxides. Overall, these mechanistic studies provide a great insight for reaching long-term OER stability, but there are still more enigmas in the complicated OER mechanisms left for us to explore.

## OER STABILITY IN PRACTICAL ELECTROLYZERS

Although most OER activity and stability studies in recent literature were performed with standard, lab-scale three-electrode setups, the ultimate goal is to bridge the gap between lab-scale testing systems and practical electrolyzers and apply these

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catalysts to commercial-scale electrolysis.[137] It is well known that catalyst stability in three-electrode measurements might not necessarily translate into practical electrolyzer stability.[138,139] For example, the rotating-disk electrode (RDE) technique has been widely used for lab-scale measurement but the micro-bubbles formed on the electrode actually cannot be completely removed by the rotation and can result in an experimental artifact for the stability performance test.[140] In contrast, in a practical electrolyzer, the operation conditions could be more intense than the lab-scale test, and there are many more factors that can affect stability performance.

When applying the lab-scale mechanistic understanding discussed in the previous sections to practical electrolyzers, these mechanisms can act differently due to the distinct reaction environments. To link the lab-scale understanding and real electrolyzer application, we would like to provide some points for consideration. First, in commercial-scale operation, which is usually under high current density and voltage, the preferred surface reconstruction product of the catalyst could be different. Pourbaix diagrams can suggest how thermodynamically favorable terminal species of metal-based catalysts would be different under low and high operation voltage. In addition, the oxygen evolution pathway could be altered due to potential morphology or electronic structural changes on the catalysts in the electrolyzer. Membranes and ionomers that can affect local pH environments, as well as different catalyst supports, can all influence the charge density distribution on the catalysts. In addition, the dissolution-redeposition process might have a more significant effect in batch systems or systems with recyclable electrolyte; however, in an electrolyzer under a flow system, the dissolved metal-ion concentration might be lower, thus reducing the ion influence. So far, very few studies have focused on connecting lab-scale and commercial-scale stability performances. Therefore, we encourage more investigations in the future to bridge this gap. Recently, a study provided a detailed examination between lab-scale three-electrode cells and commercial-scale electrolyzers.[141] The results indicated that $IrO_x$ are more stable in commercial-scale electrolyzers. An overestimated local acidity on the catalyst as well as stabilization processes over time in the electrolyzers have been identified as the main reasons for this difference. These results also indicate the importance of combining knowledge of OER stability from different systems and show that more information on electrolyzer design is required.

Current leading electrolyzer designs, taking water electrolysis as an example, include conventional AWE and two other promising designs, proton exchange membrane water electrolyzers (PEMWE) and anion exchange membrane water electrolyzers (AEMWE; Figures 8A–8C). Compared to the traditional AWE, PEMWE and AEMWE can benefit from compact design with low ionic resistance and low ohmic loss (iR) of membrane electrode assembly (MEA), which could significantly lower the energy cost.[36,142] Due to the membrane properties and local pH effect, the anodic reaction in PEMWE and AEMWE can be attributed to acidic OER and alkaline OER, respectively. The development of PEMWE is relatively mature and PEMWE has been demonstrated in commercial-scale water electrolysis for long-term operation.[18,40] However, due to the local acidic environment, development of durable OER catalysts other than Ir-based noble-metal catalysts remains a great challenge.[18,36] In contrast, recently emerging AEMWE technology has the advantage that more OER catalysts are applicable for its local alkaline environment, but the membrane stability and electrolyzer design still need improvements in order to meet long-term electrolysis requirements.[40] In these electrolyzers, elements including membranes, binders, supports, operation conditions, local pH effect,
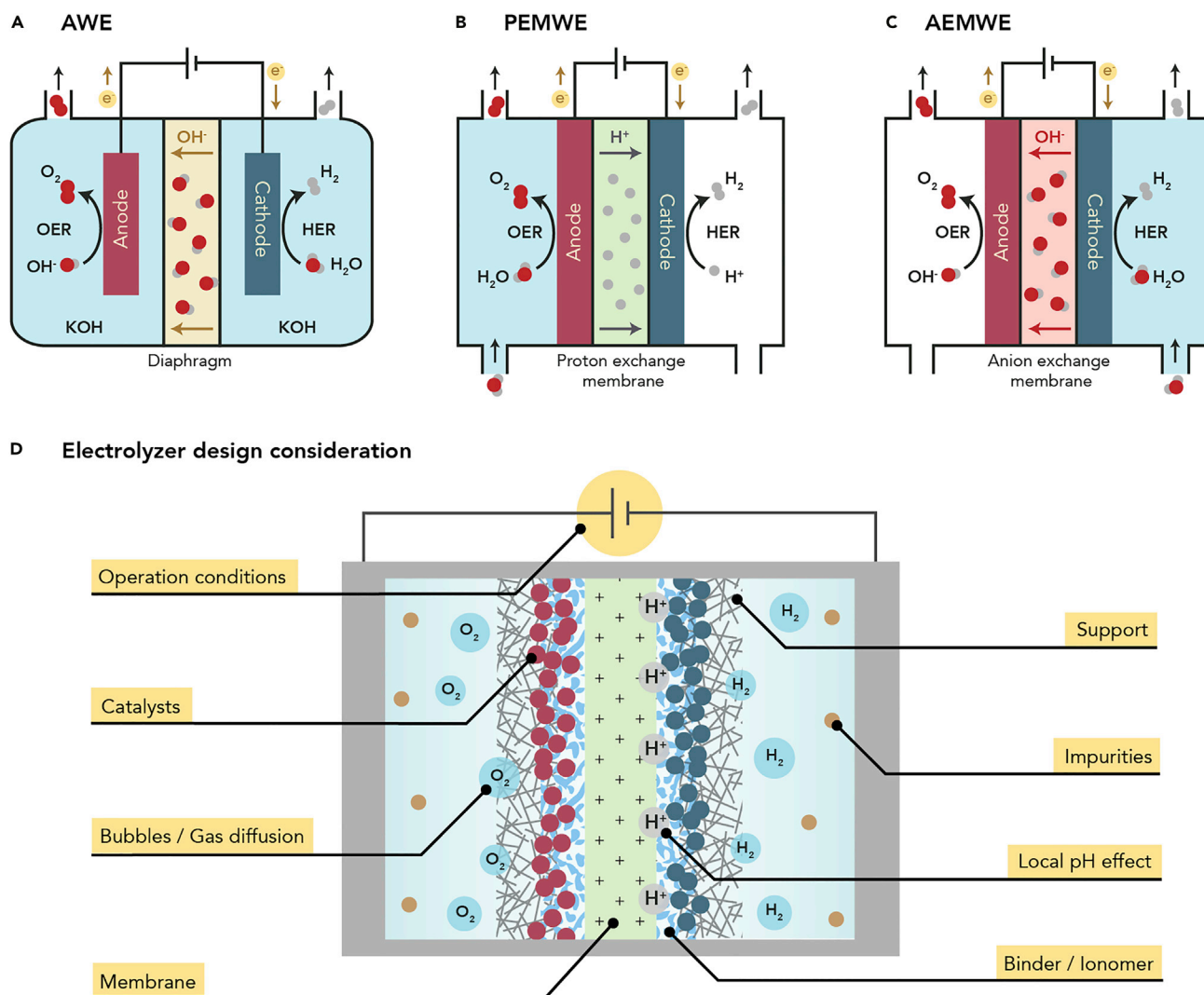
**Figure 8. Leading configurations of current water electrolyzers and design considerations for long-term stability**
(A) AEM with diaphragm membrane and KOH electrolyte.
(B) PEMWE with water flow on anode side as electrolyte. Water supply is not required on cathode side in most cases. Proton exchange membrane allows proton migration for cathodic reaction.
(C) AEMWE with water flow on cathode side. Based on different configurations, anode side can work either with or without water supply. Anion exchange membrane allows OH⁻ migration for anodic reaction.
(D) Critical elements that need to be considered for fabricating electrolyzers with long-term stability.

bubbles, and impurities (Figure 8D) could all contribute to the stability of practical operation, and they will thus be discussed in the following sections.

### Membrane and ionomer

The membrane is one of the key points for stable electrolyzer design. The development of proton exchange membranes has met the commercial durability standard. Currently, the mechanically stable Nafion membrane is been widely used in PEMWE devices, but it should be noted that operation conditions such as temperature and current density could still cause membrane thinning and degradation.[143] This observation was explained by the oxygen crossover to the cathode side with the subsequent formation of peroxide and free radicals, which would lead to membrane degradation under certain current densities and temperatures. In contrast, for anion

exchange membranes, different membranes have been developed and have demonstrated minor degradation over thousands of hours, but further improvement is still needed to fabricate a durable AEMWE device.[41,42] Reduction of the hydroxide conductivity in the anion exchange membrane is one of the challenges for long-term operation. A recent study has proposed a strategy for MEA fabrication that involves introducing an electrical contact pathway connecting the membrane with aqueous electrolyte, which serves as an additional OH⁻ transport pathway.[144] Through this method, conductivity of the anion exchange membrane can be regenerated. Investigations into other effects such as functional group degradation of the polymer, blocking of the ion exchange pathway, and the effects of temperature and electrolyte on membranes are also needed in order to extend membrane durability.

Ionomers are another important factor for electrolysis stability. It serves as the binder as well as ion conductor for catalyst particles on the electrode. Low ionomer content can lead to high ionic resistance, while an excess ionomer content can lead to electrode blocking and mass diffusion limitations.[145,146] Thus, the amount of ionomer should be optimized under different catalysts and operation conditions. Compared to the relatively stable Nafion ionomer for PEMWE, a durable ionomer design for AEMWE remains challenging. Recently, a new ionomer has been proposed, which demonstrates an enhanced stability in AEMWE operation.[40] It was proposed that by removing phenyl groups from the polymer backbone, the formation of acidic phenol, which would lower the electrolyte pH and reduce catalyst performance, could effectively be prevented. This new ammonium-enriched ionomer also provides higher ion-exchange capacity, thus enhancing the performance of AEMWE. A deeper understanding of the polymers including membranes and ionomers is still required to increase the stability of MEA fabrication.

### Electrode and support materials

Selecting a proper support material to fabricate the electrode is also critical for long-term electrolysis. A study has shown that the electronic structure of the catalyst can be altered by the catalyst-support interaction and can further influence the catalytic stability.[147] In this study, $IrO_x$ nanoparticles were separately loaded onto carbon black and antimony-doped tin oxide. It was revealed that the oxidation states of Ir and stability performances for acidic OER were completely different on these distinct supports, which could be contributed to the metal/metal oxide support interactions. A related study also proposed that the stability of Ir could be quite different on glassy carbon, gold, or boron-doped diamond supports.[148] A similar phenomenon was observed in NiFe oxyhydroxide systems under alkaline conditions, which showed different redox states and catalytic activities for catalysts with and without carbon support.[149] The differences in electronic structure and catalyst-support interaction also explain why optimizing the loading amount of the catalyst is also critical for reaching a stable operation condition.[146,149] Moreover, since the support or gas diffusion layer usually contains carbon-based materials, carbon corrosion or carbon oxidation should also be taken into account when evaluating catalytic stability. This is not only true for practical electrolyzers[150] but also for the lab-scale experiments[151] because the morphology and electronic structure changes or simply degradation of the carbon support can have a big impact on catalytic stability. From another aspect, regenerating catalytic electrodes and decomposing the impurities on the electrodes are also required for commercial electrolyzer operation, and it was recently proposed that this could be achieved by high-temperature pulse annealing.[152] Overall, these studies all provided further insights into fabrication of durable electrodes for long-term OER electrolysis.

### Operating conditions and local environment

Operating conditions should always be taken into consideration when applying lab-scale testing results of the catalysts to commercial-scale electrolyzers. From the mechanistic studies mentioned in the previous sections, we can find that the catalyst corrosion mechanisms are strongly correlated with the applied voltage and current density, which can lead to different dissolution pathways. Therefore, we can expect that there would be a certain potential window for stable OER operation depending on different catalysts. The catalysts with stable performances in lab-scale testing are not necessarily stable under industrial operating conditions at high current densities and high production rates.[36,153] To explain this point further, first, the local pH might not be identical between lab-scale three-electrode-cell measurements and MEA electrolyzers operating at high current densities. Unlike lab-scale measurements in which the local pH is mostly dependent on aqueous electrolytes, the ion transfer rate in the membrane, the reactant diffusion rate, and the surface coverage of the products are all critical factors that could alter the real local pH of MEA. In MEA electrolyzers, different types of membranes with distinct ion transfer properties can lead to harsh local pH environments in different manners,[154] such as more acidic environments in PEMWE or alkaline environments in AEMWE.

In addition, gas bubbles evolving from OER under high current densities can show distinct physical properties compared to lab-scale tests. For example, higher $O_2$ bubble evolution rates can cause interfacial supersaturation, higher catalytic surface coverage, larger ohmic resistance, etc., which could all lead to instability of the operation process.[155] Moreover, it has been directly observed by *in situ* TEM that the structural oscillations of the catalysts can be induced by the formation and collapse of gas bubbles during OER.[156] Such structural oscillation can be attributed to water uptake in the catalysts and the oxygen evolution inside the oxides. All the evidence suggests that the operating conditions of electrolyzers, especially under high potential and current densities, can trigger catalytic instability from different aspects and thus should be carefully monitored.

### Impurities

Last but not least, electrolytes and operation environments in practical applications are not necessarily the same as lab-scale measurements. In lab-scale tests, catalytic performance is typically measured in pure water, acidic, or alkaline electrolytes. The selectivity of the OER often does not need to be taken into rigorous consideration in these pure electrolytes. However, water feeds with impurities, or even saline water might be used in practical electrolyzers in order to enhance energy transformation efficiencies, and thus, the effects including OER selectivity, blocking of the catalytic sites, and blocking of ion transfer pathways on the membranes should be considered in these practical applications.[157] For selectivity, NiFe-(oxy)hydroxide-based catalysts have been shown to have good performance in seawater splitting and have also been directly applied in alkaline AEMWE with reasonable stability.[158,159] In contrast, impurity deposition on the catalysts or membrane is still a critical challenge for practical electrolyzer applications, thus requiring more attention. In general, electrolytes and impurities, as well as other elements including membranes, ionomers, supports, electrodes, local pH, bubbles, and operating conditions mentioned above should all be taken into consideration when designing a practical electrolyzer for long-term operation.

### SUMMARY AND PERSPECTIVES

Reaching long-term stability of OER is a critical challenge, and a more detailed understanding of catalytic mechanisms is needed to reach this goal. Mechanistic
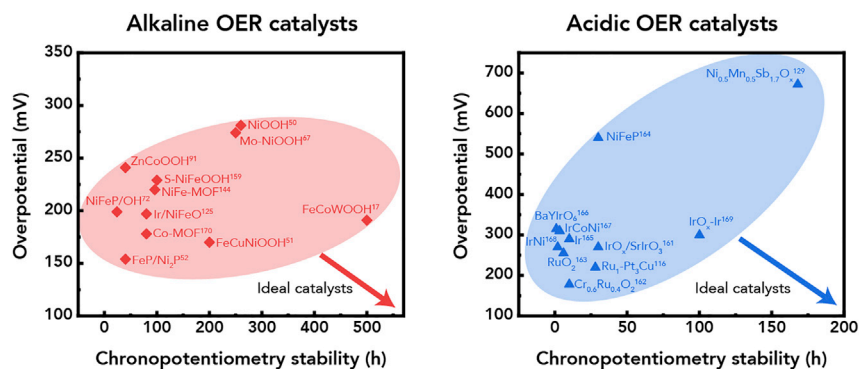
**Figure 9. Activity and stability performances of recently reported OER catalysts**
Performances of recently proposed catalysts under alkaline and acidic conditions, with the main catalyst components and references number labeled. y axis: catalyst overpotential under lab-scale OER test at 10 mA cm$^{-2}$, which represents the catalytic activity. x axis: CP stability test duration under at least 10 mA cm$^{-2}$, which represents the catalytic stability. In acidic solutions, no catalysts except Ir-based catalysts have yet reached good activity (<300 mV) with fair stability (>50 h). In contrast, catalysts under alkaline conditions have reached relatively decent stability, but applying these catalysts to practical electrolyzers for stable operation remains challenging.[17,50–53,67,72,91,116,124,125,129,144,159–169]

studies summarized in this review may provide clues to overcoming the stability challenges. Surface reconstruction of the catalysts under oxidation environments is one of the important processes that can lead to transient dissolution and cause catalytic instability during the initial stage of electrolysis. In addition, LOM is a promising reaction pathway that can reach higher OER activities but can also cause structural instability of the catalysts due to the lattice oxygen participation. Furthermore, although the dissolution-redeposition effect is a less discussed phenomenon, it can not only cause catalyst reconstruction and phase segregation but can also help with reaching a dynamically stable OER process. After all, the goal in this field is to bring the OER catalysts to practical applications, therefore the interactions between catalysts and the elements of electrolyzers also require further investigations in order to reach the long-term electrolysis goal.

In Figure 9 we have summarized the OER overpotential and CP operation time of selected catalysts that have been developed in recent years. In general, transition-metal (oxy)hydroxides are the major types of catalysts with promising performance reported under alkaline conditions. In contrast, nearly all catalysts with reportedly decent activities under acidic conditions are Ir- or Ru-oxide-based noble-metal catalysts. Non-noble-metal catalysts still suffer from high dissolution rates in acid. Moreover, only a few of these catalysts can remain stable and many require extremely high overpotential.

In addition, catalysts developed for alkaline OER show relatively good stability compared with acidic OER catalysts but applying these catalysts to practical electrolyzers such as AEMWE for long-term use remains challenging. Therefore, we look forward to future studies to bridge the gap between lab-scale performance and commercial-scale operation for these catalysts. In contrast, although development of electrolyzers in acidic environments such as PEMWE is relatively mature, from Figure 9 we can see that development of a catalyst with both good activity and stability in acid remains an urgent challenge.

### Future perspectives and strategies to improve OER stability
To facilitate future OER stability studies, we would like to recommend several metrics to compare the stability of catalysts. CV tests with thousands of cycles have been
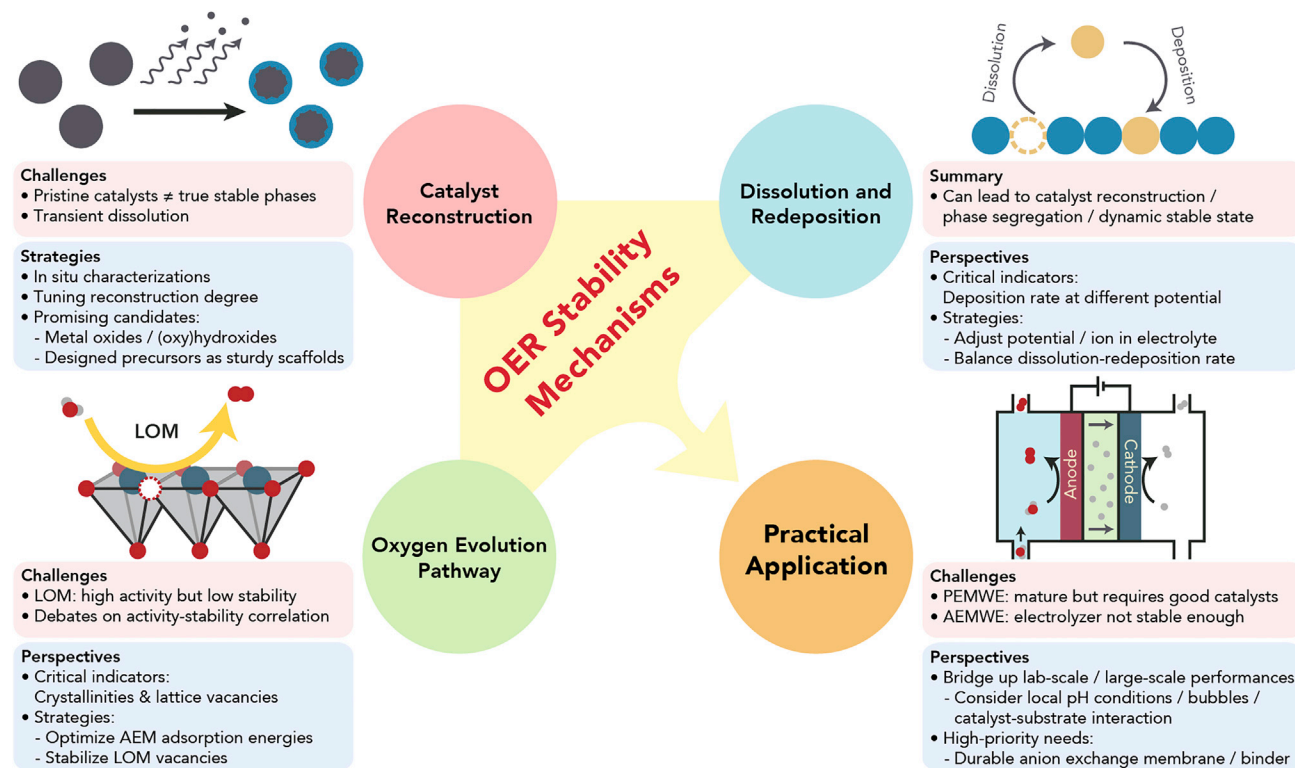
**Figure 10. Summary of challenges and future perspectives to improve OER stability**

used to mimic the start-up and shutdown cycles of electrolyzer operation; however, CA or CP tests are always the recommended and straightforward way to demonstrate the long-term stability. This can serve as the direct indicator for the real-time electrolyzer application. A CA test under 10 mA cm$^{-2}$ has been suggested as a testing condition to benchmark the OER stability under lab-scale test.[35,170] To be more specific, reporting current density based on geometric area (mA cm$^{-2}_{geo}$) can provide meaningful information for commercial-scale application, while reporting current density based on surface area of the catalysts (mA cm$^{-2}_{cat}$) is also important for intrinsic stability comparison. Furthermore, measuring the amount of dissolved catalyst by characterization methods such as ICP-MS is also critical to stability studies. For example, Geiger et al.[105] have proposed the stability number (S-number) as a metric to compare the stability. S-number is defined as the ratio between the amount of evolved oxygen (calculated from the total measured charge $Q_{total}$) and the amount of dissolved catalyst. The stability metrics discussed here can serve as suggested guidelines for future studies in reporting performances.

In addition, based on the mechanistic studies and challenges summarized in this review, we would like to propose several future perspectives and potential strategies for developing catalysts with improved stability. In Figure 10, we summarize the stability challenges and future perspectives proposed in this review. First, from the aspect that catalysts can undergo surface reconstruction, one of the critical challenges now is that pristine OER catalysts are not necessarily the true active phase during reaction. This will hinder us from understanding what the true species is that can remain stable during OER. Therefore, we recommend performing post-catalysis or *in situ* characterizations. These characterizations can provide important information to the field regarding the stable catalytic structure. Studies have

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demonstrated that surface reconstruction can be tuned by catalyst components or reaction temperature,[54,67] thus the next step would be to investigate more methods to control the reconstruction. Through this route, we can control the reconstruction degree and terminate the process at the desired point to stabilize the catalysts. Since surface reconstruction can also trigger transient dissolution, metal-oxide-based catalysts would be good starting candidates to avoid severe reconstruction during OER. Alternatively, preparing sturdy precursors as scaffolds that can stabilize the catalysts after surface reconstruction could also be a good strategy in maintaining catalyst structure.

Considering the oxygen evolution mechanisms, the LOM pathway provides a possible route for a further breakthrough in OER activity, although it can also lead to instability. In fact, the correlation of activity, stability, AEM, and LOM is still under intense debate, and it is a critical question that needs to be solved next. We believe the crystallinities, lattice oxygen, and metal vacancies are the critical indicators to solve this question. The lattice oxygen exchange and catalytic instability observed in some studies might be triggered by the defects but not the preference of the intrinsic catalyst elements, so the performances could be contradictory to other studies with higher catalyst crystallinity. Therefore, how we can normalize these factors in order to understand the real mechanism might be the next challenge. Besides, based on the current understanding of OER mechanism, there are different directions and strategies to improve catalyst stability. There is no lattice exchange in the AEM pathway, thus further optimization of electronic structures and adsorption energies of the catalysts that go through AEM can achieve both good stability and activity. In contrast, in order to stabilize the catalysts that undergo the LOM pathway, tuning the coordinate structures under an active surface layer to stabilize the lattice oxygen would be a potential strategy.

Redeposition is a critical process that needs to be further considered in the future. This is because the dissolution-redeposition process can not only provide new explanations on catalyst surface reconstruction but can also lead to different explanations of the lattice oxygen exchange phenomenon from previous isotope-labeling results. The mechanism(s) of how metal ions deposit under anodic current, how segregation occurs on different substrates, and how we can tune the deposition rate are the critical questions that need to be elucidated next. Based on the similar concept of electrocatalytic selectivity under different reactions, deposition rate is presumably strongly connected to the operating potential and the ion concentration in electrolyte, dependent on different metal catalysts. Therefore, these factors would be a good starting point for further investigation. Once we have a comprehensive understanding of the deposition rate under different conditions, we can then balance the dissolution and redeposition rates as desired to reach dynamic OER stability. If we can balance and control the redeposition rate for catalyst recovery, then the goal of infinite OER operation time could potentially be achieved.

With a thorough mechanistic understanding, the ultimate goal is to apply OER catalysts to practical application. To bridge the gap between lab-scale and large-scale performances, reaction environments of catalysts need to be further considered. To be more specific, under large-scale current densities in MEA operation, conditions such as local pH and bubble evolution rate would be more extreme, which might often be neglected during lab-scale tests. Therefore, catalysts should be designed according to these environments to reach long-term stability. As discussed in Figure 9, to improve the acidic OER performance, developing non-noble-metal catalysts with high activity and stability is the next critical step. In contrast, for improving

the catalyst performance in alkaline OER, more attention should be given to developing the electrolyzer, especially the development of a durable anion exchange membrane and ionomer. In conclusion, we believe that the summarized mechanistic studies and catalyst design strategies in this review will provide important clues to overcoming the stability challenges and push the stability of OER to the next stage.

## DECLARATION OF INTERESTS

The authors declare no competing interests.

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