The further commercialization of renewable energy conversion and storage technologies requires heterogeneous electrocatalysts that meet the exacting durability target. Studies of the stability and degradation mechanisms of electrocatalysts are expected to provide important breakthroughs in stability issues. Accessible in situ/operando techniques performed under realistic reaction conditions are therefore urgently needed to reveal the nature of active center structures and establish links between the structural motifs in a catalyst and its stability properties. This review highlights recent research advances regarding in situ/operando techniques and improves the understanding of the stabilities of advanced heterogeneous electrocatalysts used in a diverse range of electrochemical reactions; it also proposes some degradation mechanisms. The review concludes by offering suggestions for future research.

1. Introduction

Heterogeneous electrocatalysis is crucial for the efficient interconversion of electrical and chemical energy, allowing for the storage and use of renewable energy to drive electrochemical electron-transfer reactions for energy provision and the production of various valuable chemicals.[3–5] To ensure effective electrocatalytic reactions (e.g., cathodic oxygen reduction reaction (ORR), anodic oxygen evolution reaction (OER), and photochemical water splitting), it is therefore desired.

In situ/operando characterization is a powerful and informative approach in catalysis research.[12] As judicious tools for the knowledge-based design of electrocatalysts, in situ/operando optical, X-ray, and electron-based techniques can provide important experimental evidence during genuine catalytic operation, which can be used to address the experimental uncertainties introduced by ex situ measurements.[13,14] Representative in situ/operando characterization methodologies (e.g., X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy, transmission electron microscopy, Raman, infrared spectroscopy, X-ray diffraction/scattering (XRD), and other recently emerging methods) can capture meticulous details of the operating catalyst and enable better real-time understanding of the methods by which the stability mechanisms of a specific electrocatalytic reaction are catalyzed by the catalyst.[15,16] Each advanced in situ/operando technique has unique capabilities and methodologic limitations that determine the specific
properties of the target catalytic materials. For example, simple and accessible optical-based techniques have largely succeeded in the clear identification of intermediate species, while their limitations related to the limited spatial resolution and low sensitivity to changes on the catalyst surface can be complemented by X-ray-based techniques. The combination of several in situ/operando approaches, which exhibit multiple temporal and spatial resolutions, may enable the discovery and development of highly active and stable catalysts. Thus far, there has not been a systematic and critical overview of in situ/operando techniques for understanding the stability and degradation mechanisms of state-of-the-art heterogeneous electrocatalysts.

In this review, we focused on the current status and recent advances regarding the use of in situ/operando techniques to understand the stability and degradation mechanisms of the operating heterogeneous electrocatalysts, highlighting the relationships between the deactivation and disintegration of catalytic active-site structure. First, aspects of the strong associations between stability issues and catalytic active-site evolution are briefly summarized (Section 2). Then, we present a series of illustrative examples of recent in situ/operando characterization techniques applicable for ORR (Section 3), OER (Section 4), HER (Section 5), CO₂RR (Section 6), and NRR (Section 7); we highlight how these techniques can help to address stability issues. Finally, we consider the future outlook and challenges for in situ/operando studies of stability mechanisms.

2. A Brief Summary of the Strong Correlations Between Stability Issues and Catalytic Active-Site Evolution

Stability issues lead to inefficient energy conversion. Heterogeneous model electrocatalysts often exhibit substantial performance losses. Addressing the challenging stability issues requires a detailed understanding of the mechanism by which catalytic active site degradation occurs. For example, an operando analysis disclosed two distinct Fe₃N₄ sites (a high-spin Fe₃N₄C₁₂ moiety, denoted as S₁ and a low- or intermediate-spin Fe₃N₄C₁₀ moiety, denoted as S₂) embedded in different manners in as-prepared nitrogen-coordinated iron–carbon (Fe–N–C) catalysts. The analysis identified that the initial S₁ site with a high intrinsic activity for the ORR was rapidly and reversibly converted to inactive iron oxides during initial cycling, while the S₂ site with a comparatively low intrinsic activity was durable. The loss of the S₁ site was responsible for the rapid initial mitigated catalyst stability; the S₂ site was critical for performance maintenance after initial degradation. Increasing the site density of the stable S₂ site and/or stabilizing S₁ site would improve the catalyst’s durability. These insights into Fe₃N₄ site degradation have improved the understanding of the stability mechanisms and deactivation of Fe–N–C materials in the ORR; moreover, they have enabled the rational design of innovative electrocatalysts with improved durability. An additional important implication of the study was that understanding the underlying science behind the evolution of catalytic active sites under real operating conditions resulted in a conclusive understanding of stability issues. Overall, revealing the real-time and dynamic changes of active sites can considerably aid in addressing the durability issue.

3. Oxygen Reduction Reaction

The ORR is a complex and notoriously kinetically sluggish process that commonly occurs through either a 2H⁺/2e⁻ reduction to H₂O₂ or a 4H⁺/4e⁻ reduction to 2H₂O; this reaction directly determines the energy efficiencies of metal-air batteries and fuel cells. The desirable platinum (Pt)- (e.g., Pt₁₋₃, Pt alloys) and non-Pt C-based catalysts (e.g., N-coordinated transition metal-C materials (M=N=C, M = Fe, Co, Ni, Mn, etc.) and metal-free N-containing C-based (CNₓ) materials) drive the catalytic activation of oxygen (O₂) and accelerate the kinetics of ORR. These materials are critical in high-performance energy conversion and storage devices. A multiobjective optimization of surface active centers is essential to ensure the rational design of effective ORR electrocatalysts. This approach would enable the redox potential of a desired catalyst to be tuned to approach the thermodynamic potential at a specific pH with high stability.

3.1. Platinum-Based Catalysts

3.1.1. Platinum

The limited durability of Pt operated at high voltages is a challenge for the deployment of proton-exchange membrane fuel cells. Promoting the stabilities of Pt catalysts requires a comprehensive understanding of the dynamic evolution of the electrocatalytic active-center structure through the use of newly developed operando site-specific techniques. Volcano-type activity and coordination-activity plots have revealed that Pt with a low-index (111) surface exhibits strong ORR activity, with substantially enhanced catalytic performance because of the highly coordinated sites located at concavities. For reliable operando measurements of Pt sites, several modified versions of an electrochemical cell have been used in operando X-ray studies, especially studies using XAS because of its ability to provide atom- and element-specific examinations. For example, a modified cell introduced by Sasaki et al. allowed for the transmission and fluorescence modes of X-ray operation; it revealed a detailed understanding of the oxidation/dissolution mechanisms of Pt in C-supported Pt-nanoparticle (Pt/C) catalysts. In the catalysts, Pt degradation was associated with the oxidation transformation of metallic Pt to α-PtO₂-type oxide at potentials below 1.5 V only in the top layer of nanoparticles. This was accompanied by the dissolution of α-PtO₂-type oxide, which induced a loss of Pt sites at potentials above 1.9 V (Figure 1a–e). Recently, a well-established setup that combines small angle X-ray scattering and XAS in one configuration, thus allowing optimal acquisition and corresponding data quality for both techniques, validated the Pt dissolution-induced performance loss for Pt/C electrodes (Figure 1f,g). The major degradation pathways of non-C-supported Pt nanoparticles may differ from the above mechanisms. For example, in situ high energy XRD and small angle X-ray scattering analyses have
been used to infer the structural and morphological evolution of Pt; the results suggest that Pt poisoning caused by partial In/Sn redeposition and concomitant surface decoration of Pt particles (rather than Pt dissolution) is the likely origin of the significantly declined catalytic ORR activity exhibited by indium tin oxide-supported Pt particles. This has improved the understanding of the fundamental processes associated with the degradation behavior of Pt-based ORR electrocatalysts.

3.1.2. Platinum-Alloys

Alloying Pt with transition metals M (M = Co, Fe, Ni, Mn, V, Ti, etc.) may empower electrocatalysts with unique ORR properties. The catalytic stabilities of Pt-bimetallic nanoparticles (with clear composition-, morphology-, and size-dependent atomic arrangements and electronic structures) are commonly higher than the catalytic stabilities of their Pt counterparts. Here, emphasis is placed on in situ X-ray techniques that can be used to provide direct environmental evidence to understand the variations in stability caused by the effects of alloying Pt with transition metals. As a representative case, in situ synchrotron high-energy XRD analysis substantiated the structural origin of a twisted nanowire-shaped PtFe alloy with the highest durability among all PtFe-based ORR catalysts, in which increased (111) facets and compressive strain stabilized the alloy structure, thus producing remarkable durability (Figure 2a). A PtNi octahedra enclosed by (111) facets is commonly required post-synthesis by thermal treatment to unfold the fully optimized catalytic stability. Beer-mann et al. investigated the underlying heat-induced surface chemical processes of binary PtNi alloys using in situ heating transmission electron microscopy and in situ high temperature XRD. They found that annealing at an elevated temperature may result in the formation of a Ni-rich PtNi alloy and the incorporation of Ni-rich alloys into neighboring formerly octahedral particles, which had a positive impact on stability. Higher activity can correspond to higher stability in the ORR through the multiobjective optimization of surface active center structures, in contrast to the oxygen evolution reaction (OER) that is discussed in Section 4.

3.2. Platinum Group Metal-Free Catalysts

The inherent instabilities of platinum group metal-free ORR catalysts in acidic environments constitute major limitations of proton-exchange membrane fuel cells. The promising automotive applications of drop-in platinum group metal-free technology for proton-exchange membrane fuel cells are regarded as the main reasons for specific emphasis on the ORR in an acidic medium, rather than an alkaline medium. However, no clear relationships of the hypothesized degradation mechanisms (i.e., micropore flooding, demetallation, C oxidation, active-site protonation, and anion adsorption) with stability and intrinsic Moieties are the most likely predominant source of ORR activity in M–N=C catalysts. Model in situ/operando studies that have directly tracked the dynamic evolution of M–N=C moiety active sites may eventually lead to an in-depth understanding of the possible underlying prevailing degradation mechanisms that resulted in a loss of activity in the well-known ORR M–N=C catalysts, with a strong emphasis on Fe–N=C catalysts.
Figure 2. a) In situ fuel cell setup for HE-XRD characterization to determine the structural and compositional stability of the Pt$_{42}$Fe$_{58}$ and Pt$_{24}$Fe$_{76}$. b) Schematic of electrochemical TERS apparatus for operando characterization of FePc deactivation during ORR catalysis. c) The obtained in situ electrochemical TERS spectra providing direct experimental evidence of a reversible change (top) followed by an irreversible degradation (bottom) of FePc during ORR catalysis. d) Illustration of the operando $^{57}$Fe Mössbauer apparatus. e) The obtained operando $^{57}$Fe Mössbauer spectra for $^{57}$Fe-enriched Fe-NC-S recorded at an open-circuit voltage (OCV) of 0.9, 0.7, and 0.5 V (vs RHE), and after ORR (AFT, measured with removal of the potential after recording at 0.5 V vs RHE). f) Electrochemical flow cell configuration used for operando X-ray measurement. g) Schematic of soft XAS (fluorescence mode) cell. h) Schematic illustration of the thin film electrochemical cell and the sample configuration. (a) Adapted with permission.[43] Copyright 2020, ACS Publications. (b,c) Reproduced with permission.[59] Copyright 2019, ACS Publications. (d,e) Reproduced with permission.[65] Copyright 2020, Elsevier. (f) Reproduced with permission.[68] Copyright 2017, AIP Publishing. (g) Reproduced with permission.[79] Copyright 2014, American Association for the Advancement of Science. (h) Reproduced with permission.[84] Copyright 2016, ACS Publications.
Recently, operando tip-enhanced Raman spectroscopy, involving the combination of real-time measurements with Raman spectroscopy and scanning probe microscopy, has been implemented to provide fingerprinting-type information regarding Fe–N–C catalyst deactivation during operation in liquid electrochemical conditions (Figure 2b,c).\[39\] New unambiguous evidence for the exponential decay in ORR activity of a model iron(II) phthalocyanine (FePc) catalyst supports the direct deactivation of FeNx sites through the loss of Fe\(^{3+}\), rather than the destruction of CN\(_x\) sites through C corrosion. Importantly, the empirical association between progressive demetallation of FePc and loss of ORR activity further affirms the direct role of Fe-containing FeNx active sites in the ORR activity of Fe–N–C catalysts. By combining a tip with the confocal arrangement of an existing Raman spectroscopy setup, the tip-enhanced Raman spectroscopy technique offers the improved intensity and spatial resolution of Raman spectroscopy, enabling potential active sites to be revealed, while identifying the induced molecular reorientation and nanoscale redox behavior via electrochemistry.\[60–62\]

Mössbauer spectroscopy, which describes the recoilless absorption of \(\gamma\)rays in solids, is capable of capturing details of the chemical nature of FeNx sites and following the fate of such sites during operating conditions for typical ORR Fe–N–C catalysts.\[63,64\] It has proven difficult to devise an in situ strategy that allows an ORR to occur in an \(\text{O}_2\) saturated electrolyte, while satisfying the operando Mössbauer spectroscopy measurement condition requirements. Figure 2d displays an excellent operando Mössbauer spectroscopy electrochemical cell setup, in which \(^{57}\)Fe-enriched catalysts were connected in parallel with carbon-fiber electrodes as the working electrode and the width of the anode compartment restricted to ≤5 mm to enhance the Mössbauer signal (Figure 2e).\[65\] Offering iron-containing site-sensitive probing capabilities, the newly developed operando \(^{57}\)Fe Mössbauer technique has the potential to identify the exact structures of active FeNx moieties and shed light on the underlying degradation mechanisms of the potential-relevant electronic and structural dynamic cycles of Fe-centered sites under working conditions. Additionally, operando \(^{59}\)Co and \(^{119}\)Sn Mössbauer spectroscopy can provide important experimental evidence for cobalt- and tin-containing electrocatalysts. More recently, operando \(^{57}\)Fe Mössbauer spectroscopy has been used to identify two distinct FeNx sites in a working Fe–N–C catalyst comprising a high-spin Fe\(_{2}\)N\(_{10}\)C\(_{13}\) and a low or intermediate-spin Fe\(_{2}\)N\(_{10}\)C\(_{2}\) moiety; the Fe\(_{2}\)N\(_{10}\)C\(_{13}\) site was responsible for the rapid initial mitigated catalyst stability, while the Fe\(_{2}\)N\(_{10}\)C\(_{2}\) site with higher stability contributed substantially to the ORR activity after 50 h of operation in an acidic medium.\[20\] The improved understanding of Fe–N–C operando degradation mechanisms has enabled a rational approach to be developed toward improving the durabilities of Fe–N–C cathodes in acidic fuel cells.

The actualization of operando synchrotron-based XAS is a recent breakthrough in the XAS examination of the ORR; it has provided unique insights into atom-specific structural information and subtle details regarding the electronic properties of Fe–N–C electrocatalysts.\[66,67\] In a recently presented operando X-ray electrochemical flow-cell setup, the catalysts were deposited onto an X-ray transparent support and signals were obtained through a spectrometer or measured in a fluorescence yield counter (Figure 2f).\[68\] The XAS signals of most Fe–N–C catalysts shifted monotonically with the applied potential because of the Fe\(^{3+}/\text{Fe}^{2+}\) transition and adsorption/desorption of the oxygen adsorbate (denoted as O(H)), which were generated from the ORR and/or water activation.\[69,70\] Most studies based on in situ XAS analysis of the ORR have yielded direct evidence of the redox transition Fe\(^{3+}/\text{Fe}^{2+}\) and \(\text{O}_2\)-based structural-switching between the off- and in-plane configuration of Fe–N\(_4\) moieties, in which the switched in-plane configuration of the pyrolyzed Fe–N\(_4\) moieties has enhanced the ORR kinetics.\[67,69\] This may provide a new perspective concerning the reinterpretation of the demetallation process.

### 3.3. Metal-Free N-Containing C-Based Material Catalysts

Metal-free N-containing C-based material catalysts have received considerable interest as a class of acceptable low-cost ORR electrocatalysts that can substitute Pt for renewable energy technologies. Recently, there have been reports of the importance of nonmetal dopants (e.g., N, S, P, and B) and defect sites for the creation of active centers and transformations of inert pristine carbons into active electrocatalysts. However, conflicting knowledge of the complex active sites hinders an in-depth understanding of the stability mechanism. Selected in situ/operando techniques are chosen to capture a specific degree of complexity for the above key issues.

#### 3.3.1. Nonmetal Dopants

Recently, doping strategies for modulating the charge distribution over a C skeleton have been shown to impart enhanced ORR activities to a large family of C allotropes.\[73\] Since the first CNx material was developed for efficient ORR catalysis by Gong et al. in 2009,\[74\] various dopant species (e.g., B, I, N, S, P, and B) have dominated the research literature concerning C-based metal-free catalysts.\[75,76\] However, the mechanisms of doping-induced stability and doping-property diversity are not well understood; doped C-based metal-free catalysts have been created solely by trial and error. Very few operando techniques have been developed to identify the real-time dynamic evolution and deactivation mechanism of doped C-based metal-free catalysts electrocatalysis because the smaller cross-section of electron/phonon interaction events for light atoms (e.g., C, N, O, and S) hampers the accurate extraction of targeted material information (e.g., hard-XAS).\[77\] Specific characterization techniques with the ability to examine doped nonmetal atoms (e.g., soft-XAS and X-ray photoelectron spectroscopy) are limited because of either their low penetrating power in liquid
media or the requirement for a vacuum environment in which measurements can be made.\textsuperscript{[74,78]} A soft-XAS transmission cell (Figure 2g) operated in a fluorescence mode has been developed for operando studies, whereby an \( \approx 100\text{-nm} \) Si\(_3\)N\(_4\) film separates the liquid water from the high vacuum environment.\textsuperscript{[79]} The design criteria may inspire the electrocatalysis community to develop innovative C-based metal-free catalysts operando characterization techniques.

### 3.3.2. Defects

The intrinsic C defect sites of C-based metal-free catalysts are known to contribute to enhanced ORR activity;\textsuperscript{[80,83]} however, there has not been an in-depth exploration and clarification of the actual role of intentionally introduced C defects on ORR stability performance using operando techniques. Incoherent observations of minor intrinsic defects often use ex situ scanning transmission electron microscopy or high-angle annular dark field scanning transmission electron microscopy with aberration correction. Both techniques can visualize the honeycomb-like construction of the C framework.\textsuperscript{[82]} However, these techniques are typically operated under a high vacuum, interfering with real-time operando observations. The design concept incorporating a separation of the vacuum/liquid chambers may bypass the experimental hurdles in future operando studies. Another potential application of an operando technique is X-ray photoelectron spectroscopy, which can be operated under the equilibrium vapor pressure of water at room temperature; the C defect information can be indirectly analyzed based on the fitted bonds.\textsuperscript{[83,84]} As shown in Figure 2h, a 20–30-nm electrolyte film (meniscus) forms on the catalyst-containing working electrode, enabling X-ray photoelectron spectroscopy signals to be collected in operando.\textsuperscript{[84]}

### 4. Oxygen Evolution Reaction

The OER is an efficiency-limiting half-reaction that involves water splitting, which is inherently slower by over four orders of magnitude, compared with \( \text{H}_2 \) generation.\textsuperscript{[85]} The enhanced catalytic activity of a modified OER electrocatalyst always produces limited long-term operative stability; therefore, OER stability is negatively associated with its activity.\textsuperscript{[86–88]} Presently, Ir\(_2\)O\(_3\) and RuO\(_2\) display benchmarking OER activity,\textsuperscript{[89]} and the natural scarcity and exorbitant cost of the precious elements have served as a driving force in the remarkable progress made with OER electrocatalysts, with reasonably small overpotential and cost-efficient current densities. As promising substitutes, 3d transition metal-based (hydro)oxides have been reported to exhibit OER activity approaching (and sometimes outperforming) the activities of the benchmark catalysts, with comparatively good durability (catalytic lifetimes generally do not exceed several hundred hours) in less corrosive alkaline media.\textsuperscript{[90–92]} For example, Ni-based catalysts have been widely used in commercial alkaline water electrolysis technologies. Their derivatives (e.g., layered double hydroxides,\textsuperscript{[93,94]} amorphous/crystalline multimetallic oxides,\textsuperscript{[95,96]} perovskite-type oxides,\textsuperscript{[97,98]} and spinel-type oxides\textsuperscript{[99,100]} have attracted much attention as suitable OER catalysts. Various forms of transition metal-based non-oxide catalysts (e.g., nitrides, borides, sulfides, phosphides, selenides, tellurides) have demonstrated excellent OER performance with low overpotential and high stability, although they are prone to oxidation and hydrolysis under OER conditions.\textsuperscript{[101–104]} The limited operational stability in alkaline media remains a technical challenge.

The stability problem becomes more severe when OER electrocatalysts are used under harsh acidic proton-exchange membrane operating conditions despite the importance of a proton-exchange membrane electrolyzer. Only Ir-based oxides (e.g., IrO\(_2\)) are reportedly tolerated in highly corrosive acidic conditions; they represent the best available compromise between catalytic stability and OER activity in acidic media,\textsuperscript{[105]} while RuO\(_2\) is less stable (i.e., it is easily dissolved and leached out in acid electrolyte conditions). Thus, the commercialization of proton-exchange membrane electrolyzers will initially rely on the IrO\(_2\) catalyst. To reduce the use of noble metals, some noble-metal-reduced, acid-compatible, and noble-containing complex oxides (e.g., perovskites, pyrochlores, and fluorite-like compounds) have been developed as alternatives to IrO\(_2\) or RuO\(_2\).\textsuperscript{[106,107]} These materials commonly have multi-metal oxide forms, as well as high structural and compositional flexibility, enabling the modulation of electronic structure through composition- and structure-engineering and increasing the mass activities of noble metals (output current per Ir or Ru mass, unit: \( \text{A} \text{g}^{-1} \text{Ir or Ru} \)).\textsuperscript{[108,109]} Identifying the active sites and unraveling their structural and chemical evolution in real time is critical for the development of improved OER catalysts with balanced catalytic activity and stability.

#### 4.1. Mixed NiFe-Oxide-Based Electrocatalysts for Alkaline OER

Mixed NiFe-based heterobimetallic (oxy)(hydro)oxides are among the most active alkaline OER electrocatalysts, although the true active sites remain unconfirmed and several reported reaction mechanisms in such systems remain controversial.\textsuperscript{[110–113]} The current limited understanding of the characteristics that affect long-term stability under harsh conditions further restricts the potential commercial applications of alkaline water electrolyzers. To fully understand the activity and degradation mechanisms, a detailed analysis of the structural evolution and the progressive variation of OER active centers under real operating conditions, with respect to the as-synthesized state, requires the application of advanced in situ/operando characterization tools.

Surface structural reconstruction affects the intrinsic properties of OER electrocatalysts, thus influencing their catalytic stabilities.\textsuperscript{[114,115]} Most self-reconstruction processes triggered by electro-oxidation during the OER are comparatively slow. Very recently, a rapid and deep self-reconstruction process for a new class of NiFe-based electrocatalysts (i.e., NiFe/NiFeO\(_x\) nanoparticles anchored on NiMoO\(_4\) in amorphous carbon (NiMoFeO@NC)) with a core-shell structure has been developed through electrochemical etching.\textsuperscript{[116]} In situ Raman spectra have been used to directly demonstrate the self-reconstruction process (Figure 3a–c). These consist of fast etching of MoO\(_4^{2-}\) from NiMoO\(_4\) cores and synergistic incorporation of Fe in the
Ni-(oxy)hydroxide shells; the resulting catalyst exhibits extraordinary long-term stability, with negligible deactivation after 24 h of OER electrolysis at 100 mA cm$^{-2}$. The current understanding of the structural transformation of NiFe-based electrocatalysts during the OER process is also quite limited. Operando XAS analysis has revealed the detailed structural transformation process of a metal–organic framework (MOF) electrocatalyst (i.e., pristine Ni$_{0.9}$Fe$_{0.1}$-MOF $\rightarrow$ Ni$_{0.9}$Fe$_{0.1}$(OH)$_2$/MOF $\rightarrow$ Ni$_{0.9}$Fe$_{0.1}$(OOH)/MOF) and the nearly synchronous structural evolution of the Ni and Fe nodes, thus producing excellent stability (Figure 3d).$^{[117]}$ The potential-induced two-step reconstruction may be reversible, although this has not been reported in the literature.$^{[103,118-120]}$

Phase segregation is presumably responsible for the lack of catalyst durability.$^{[121,122]}$ The fundamental question concerning elimination of phase segregation during the OER requires investigation. Operando X-ray fluorescence microscopy measurements have been used to directly track the evolution of phase segregation. They have revealed a dynamic metal (Fe) dissolution–redeposition process, which accelerates the NiFe-based electrocatalyst deactivation; they have also confirmed that phase segregation is reversible for low-temperature OER electrocatalysts (Figure 3e–h).$^{[123]}$ By manipulating reversible phase segregation through modulation of the water oxidation and catalyst reduction potentials, an in situ electrochemical reduction strategy has been developed to recover degraded...
electrocatalysts; this enhances long-term OER electrocatalyst stability. The deactivation caused by evolution of various adverse active-phase microstructures during OER is also a non-negligible stability problem. The first direct atomic-scale evidence of catalytically active phase transitions under OER conditions has recently been obtained through the use of an operando XAS technique to rationalize the stabilities and activities of NiFe layered double hydroxides (LDHs) (Figure 3i,j).[124] Operando XAS spectra have shown that NiFe LDH transforms from the as-prepared α-phases to OER active γ-phases, with an approximately 8% contraction of the lattice spacing induced by the oxidation of Fe(III)/Ni(II) and anion-to-cation switching of intercalated ions.[124] The catalytic active-phase evolutions may be stability-affecting factors that explain the experimentally observed lack of durability in the alkaline OER. Additionally, the layered structure makes bulk NiFe LDH intrinsically unstable in an OER. Recently, in situ XRD was used to confirm the expansion of bulk NiFe LDH interlayers during an OER, which contributed to the OER deactivity (Figure 3k,l).[125] The observed changes suggested the dissolution of NiFe LDH during an OER, which was caused by an OH\(^-\) diffusion-induced local acidic environment and was detrimental to its stability. The elaborate strategy of delaminating bulk NiFe LDH into atomically thin nanosheets improved the diffusion of proton acceptors and effectively improved the OER stability of bulk NiFe LDH.

4.2. Non-Oxide-Based Electrocatalysts for Alkaline OER

4.2.1. Metal Chalcogenides

Transition metal-based chalcogenides (e.g., sulfides, selenides, tellurides) and pnictides (e.g., phosphides, nitrides, borides) have been extensively reported to exhibit superior apparent OER activity, but they generally exhibit poor stability because of potential-induced structural transformation. Complex structure-transformation processes commonly result in the generation of their corresponding oxides/(oxy)hydroxides, which may be the electrocatalytically active metal species that execute the OER because the post-oxidized non-oxide-based electrocatalysts often exhibit better catalytic activities.[126,127] For example, operando Raman spectra have revealed the transformation of electrocatalytically active species from an initial cobalt sulfide to a subsequent OER active cobalt oxyhydroxide, which contributed to its OER activity and stability.[128] Among the various metal chalcogenides, transition metal sulfides with two distinct classes of structure (i.e., nonlayered M\(_x\)S\(_y\) (M = Co, Ni, Fe, Cu, etc.) and layered MS\(_2\) (M = Mo, W) have attracted considerable attention as promising OER catalysts.[129,130] However, materials-based solutions are necessary to address the stability issues. The stability is commonly caused by systematic optimization of geometric structure and chemical composition. Recently, in situ XAS spectra confirmed the compositional origins of the long durabilities of Fe, Co, and Ni-based hybrid polymetallic sulfide nanotube arrays (FeCoNi-HNTAs) (Figure 4a,b), in which the improved phase stability of 1T' MoS\(_2\) (induced by the protection of a FeCoNi-HNTAs hybrid system) and the crystal-field coordination of Co ions (tuned by the participation of Fe) resulted in a synergetic effect that provided remarkable long-term durability.[131]

4.2.2. Metal Phosphides

Because of their tunable electronic structures and various phases, transition metal phosphides (TMPs) have emerged as efficient electrocatalysts for OERs. TMPs are also thermodynamically less stable under OER oxidation potentials and may gradually transform to metal oxide/(oxy)hydroxide phases as an activation step in the enhancement of their OER activities.[132,133] For example, in situ XAS and transmitted XRD can dynamically detect the active phase in Fe-doped cobalt

![Figure 4](https://example.com/figure4.png)

**Figure 4.** In situ EXAFS characterization showing phase stability of 1T' MoS\(_2\). a) Normalized in situ XANES spectra and b) the corresponding \(k^3\)-weighted FT profiles in R-space from EXAFS with different voltages. c) In situ XRD patterns for cobalt-based phosphides, with an incident X-ray wavelength of 0.7749 Å. Stability-number plotted versus d) mass-specific current density for powders and e) geometric current density for sputtered films. (a,b) Adapted with permission.[131] Copyright 2018, Springer Nature. (c) Reproduced with permission.[134] Copyright 2019, ACS Publications. (d,e) Reproduced with permission.[142] Copyright 2018, Springer Nature.
phosphides during an OER, confirming rapid bulk phase conversion into iron-doped cobalt oxyhydroxide rather than surface reconstruction boosted OER activity (Figure 4c).\[144\] Compared with TMP-based electrocatalysts protected by other materials (i.e., TMP-protected heterostructures), the OER stabilities of Ru-based electrocatalysts supported by other materials (i.e., TMP-exposed heterostructures) is limited because of the easier oxidation of TMP during long-term operating conditions.\[135–137\] In a TMP-exposed heterostructure, extra corrosion-resistant materials (e.g., cocatalysts\[138,139\] and C-based materials\[140,141\]) must be coupled as the protective layer for long-term stability.

### 4.3. Iridium-Based Electrocatalysts in Acid Media

In acidic media, numerous strategies for thriving Ir usage and optimizing catalytic stability/activity have made complex Ir-based oxides attractive as efficient and affordable OER electrocatalysts. There is a trade-off between stability and activity in an acidic OER. To verify the stabilities of Ir-based oxides, the stability number has been proposed as a metric to enable a reasonable comparison of stability properties and determine activity–stability relationships. The stability number is expressed as the ratio of the amount of oxygen evolved to the amount of dissolved Ir, which is independent of surface area, catalyst loading, or number of active sites involved (Figure 4d,e).\[142\] A similar activity–stability factor has also been expressed to propose the activity–stability dependence of catalysts; it is measured simultaneously using an in situ inductively coupled plasma mass spectrometry method.\[143\] There is a critical need to determine the mutual activity–stability determinant properties through integrated consideration of catalyst stability and activity. For example, combined operando small angle X-ray scattering and XAS measurements have been used to monitor the dynamic changes of a high surface area Ir-based oxide and its heat-treated derivative. The results revealed the relative contributions of different instability mechanisms (i.e., surface oxidation, Ir-dissolution, and agglomeration) to the overall performance decay of Ir-based catalysts.\[144\] The operando information has enabled unified activity–stability determinant properties to be established and has simplified the identification of Ir-based oxides with the right activity–stability balance.

### 4.4. Ruthenium-Based Electrocatalysts in Acid Media

Compared with Ir-based oxides, Ru-based oxides (e.g., RuO\(_2\)) usually exhibit comparatively higher catalytic activity, although they normally demonstrate poor stability (dozens of hours) because of the potential-induced Ru-oxidation, which results in the formation of water-soluble high valence Ru oxides (e.g., RuO\(_4\)) in an acidic OER.\[97,145\] The construction of Ru-based mixed oxides,\[7,146\] establishment of advanced heterostructures,\[147,148\] and design of Ru–C composites,\[149,150\] are feasible approaches to improve the long-term stabilities of Ru-based catalysts without affecting their OER activity; however, these approaches remain insufficient. Recently, operando XAS was used to examine single-atom Ru confined in an acid-resistant C nitride-derived N–C support. A strong Ru–N bond improved the structural stabilities of Ru-based catalysts by reducing the rate of Ru dissolution in acidic media. The analysis also identified dynamic oxygen pre-adsorption on an Ru site in the formation of the O–Ru–N structure, which was responsible for the high OER stability and activity.\[151\] Although Ru-based oxides exhibit instability issues, their stability may be enhanced through an in-depth understanding of the nature of the active sites and underlying deactivation mechanisms via multiple advanced in situ techniques.

### 5. Hydrogen Evolution Reaction

The electrocatalytic HER is crucial in the large-scale production of hydrogen, an environmental-friendly fuel with high mass-energy density (142 MJ kg\(^{-1}\), upper heating value).\[152\] Currently, Pt and Pt-based materials are considered state-of-the-art electrocatalysts for HERs because they possess optimal hydrogen binding energy.\[153,154\] Developing cost-effective, active, and stable electrocatalysts to decrease Pt usage is the ultimate goal in the successful deployment of hydrogen-based alternative energy technologies. Earth-abundant catalysts (e.g., dichalcogenides,\[155,156\] phosphides,\[157,158\] carbides,\[159,160\] and nitrides\[160,161\]) have been extensively exploited. Because of the commercialization of hydrogen generation, long-term stability is a ubiquitous and urgent concern. Although various effective heterostructured electrocatalysts are known,\[162,163\] there have been few attempts to apply in situ/operando analysis to assess the stability issues in the HER because it is widely assumed that the stabilities of electrocatalysts are superior in a HER, compared with stabilities in harsh OER conditions.

#### 5.1. Platinum-Based Catalysts

Although Pt and Pt-alloys are considered thermodynamically stable during HERs based on the Pourbaix diagram, potential-induced dissolution, migration, and agglomeration occur in electrolyte solutions.\[164,165\] For example, in situ transmission electron microscopy analyses have provided insights into gas bubble-induced migration and the successive agglomeration of Pt nanoparticles during the HER process, which triggers cathode degradation and deactivation.\[166\] However, it remains difficult to apply in situ analyses to identify the dynamic structures of Pt-based electrocatalysts at the atomic level in catalytic stability studies. Uncovering the nature of Pt single-atom catalysts under real HER working conditions, which acts as a model system, is important for understanding stability issues. Recently, in situ/operando XAS results provided direct experimental evidence that the weakened Pt–N bonding in single-atom Pt anchoring on the N–C substrate induced the structural reconstruction of single-atom Pt under HER-relevant potentials. This demonstrated that the formation of small Pt clusters in the resulting catalysts was responsible for improved HER stability (Figure 5a,b).\[167\] By applying operando XAS, Fang et al. revealed that the interactions and charge transfer between single-atom Pt and a N–C substrate tended to be weakened under an electrochemical HER, leading to a near-free state of Pt, which exhibited favorable bonding energies with the...
reactants (Figure 5c). This resulted in long-term stability over a wide range of electrolyte pH values.

5.2. Transition Metal Dichalcogenides

Some transition metal dichalcogenides (e.g., 2D MoS$_2$, WS$_2$, MoSe$_2$, and WSe$_2$) exhibit structure-related HER catalytic properties that are comparable with the catalytic properties of platinum group metals. For most transition metal dichalcogenides, the actual catalytically active species during HER processes comprise the reduced metallic state (M$^0$). For example, Tran et al. reported that the elimination of the terminal S$_2^{2−}$ ligand of amorphous MoS$_x$ at HER-relevant potentials generated Mo–H moieties, which behaved as the actual catalytic centers. With regard to electrochemical stability, in situ/operando analyses of structure–stability relationships have rarely been reported. Zhai et al. conducted advanced operando synchrotron X-ray powder diffraction characterization to capture the phase transformation from cubic NiSe$_2$ to hexagonal NiSe in real time (Figure 5d). The resulting phase was attributed to the enhanced stability during an alkaline HER.

5.3. Transition Metal Phosphides

TMPs are cost-effective, highly active, and non-noble metal HER electrocatalysts that can tolerate a wide pH range and have received substantial attention because of their unique physicochemical properties. Zhang et al. conducted a detailed electrochemical and spectroscopic characterization, which revealed no significant pH-dependent stability mechanisms of Co$_2$P in either acidic or alkaline electrolyte solutions. They concluded that Co$_2$P stoichiometrically dissolved in acid electrolyte solutions and tended to transform into hydroxides under alkaline electrolysis conditions during the HER process.

Figure 5. a) Corresponding Fourier-transformed extended X-ray absorption fine structure (FT-EXAFS) fitting in R-space of Pt$_{SA}$/N–C, showing the weakened Pt–N bonding and strengthened Pt–Pt bonding during repeated LSV scanning. b) Schematic illustration of the dynamic structure reconstruction of Pt$_{SA}$/N–C to form a few small Pt clusters during continuous HER. c) 3D profile plot of successive operando Pt L$_3$-edge XANES spectra acquired at different applied potentials, indicating a higher 5d occupancy of Pt when the applied potential was negatively shifted to +0.15 and to −0.07 V. d) Chronoamperometric curve of NiSe$_2$ at −0.18 V for 6 h and the corresponding operando SXRD patterns (λ = 0.49547 Å), revealing the dynamic structural and compositional transformation from cubic NiSe$_2$ to hexagonal NiSe under a series of reductive conditions. (a,b) Adapted with permission. Copyright 2021, Wiley-VCH. (c) Reproduced with permission. Copyright 2020, Springer Nature. (d) Reproduced with permission. Copyright 2020, ACS Publications.
5.4. Transition Metal Carbides

Transition metal carbides have no restrictions in the position of active sites,\(^{184,185}\) whereas active sites commonly exist at the edge in transition metal dichalcogenides. Transition metal carbides also have no penalty for the phase control, whereas TMPs have a limit for tuning the intrinsic catalytic activity according to the phase control (e.g., the P content, which greatly influences the chemical stabilities and electrochemical conductivities of TMPs).\(^{157,160}\) As a typical model, molybdenum carbides (Mo\(_x\)C) with four main crystal phases (i.e., \(\alpha\)-Mo\(_x\)C\(_{\gamma}\), \(\beta\)-Mo\(_x\)C, \(\eta\)-Mo\(_x\)C, and \(\gamma\)-Mo\(_x\)C) have distinct HER properties; \(\gamma\)-Mo\(_x\)C exhibits optimal stability in acidic solution.\(^{159}\) Furthermore, Ta\(_x\)C and Nb\(_x\)C have an excellent HER performance because of the absolute values of the Gibbs free energy for hydrogen adsorption (\(\Delta G^{\mathrm{ads}}\)).\(^{186,187}\) Although 2D transition metal carbides (MXenes) have shown promise as HER catalysts, few studies have applied in situ/operando analyses to examine the complicated stabilities of MXenes. In a representative work conducted by Jin et al., density functional theory calculations were carried out for 24 MXenes to comprehensively investigate their thermodynamic stabilities under HER-relevant conditions. The results suggested that stability and HER performance were closely related to the outermost metal; moreover, the HER performance of MXenes could be further optimized by tuning the C\(^2\)-O bond strength, C\(^2\) species, and O-termination charge (M\(^2\) = Cr, V, Ti, or Nb).\(^{188}\)

5.5. Transition Metal Nitrides

Transition metal nitrides are an exciting class of materials for HER processes because of their valuable physical and chemical properties that originate from the nitride anion (N\(_3^-\)), which imparts unique electronic and bonding characteristics.\(^{189,190}\) However, incorporation of N into a transition metal lattice is thermodynamically unfavorable, and therefore most transition metal nitrides are deficient in N.\(^{191,192}\) Additionally, high corrosion resistance is attractive for HERs in acidic media. In 2013, Cao et al. examined the structural polytypes of novel C\(_{\gamma}\)Mo\(_x\)N\(_2\)\(_x\)\(_2\) material under acidic conditions. The Co ions in bulk octahedral sites containing a mixture of divalent Co and trivalent Mo were protected from acid exposure by the Mo ions present within the octahedral layer, which supported good acid stability.\(^{193}\) With the assistance of X-ray absorption near edge structure and calculations of the electron density state, Jin et al. obtained detailed information regarding newly developed atomically thin N-rich Mo\(_x\)N\(_6\) nanosheets, then revealed that the resulting high valence state of Mo atoms made these nanosheets unsusceptible to active site poisoning, leading to impressive HER stability in a wide range of electrolyte solutions.\(^{194}\)

6. Carbon Dioxide Reduction Reaction

The conversion of CO\(_2\) to value-added chemicals and fuels through electroreduction has been recognized as the ideal approach toward carbon-neutral renewable energy storage and utilization.\(^{195,196}\) However, the limited long-term stabilities of active and selective electrocatalysts have restricted the move toward applied systems. Compared with the number of studies regarding activity/selectivity issues, there have been fewer catalytic stability studies involving model catalysts for the CO\(_2\)RR. Currently, solid-state noble metal-based, transition metal-based, and metal-free materials are major CO\(_2\)RR heterogeneous electrocatalysts.\(^{197,198}\) In the following section, in situ/operando analysis of the complicated CO\(_2\)RR stability issues for the above three categories of catalysts will be reviewed and discussed, with a particular focus on the stability and degradation mechanisms that could explain catalyst failures.

6.1. Noble Metal-Based Catalysts

Empirically, noble metals can be placed into two main groups according to the main CO\(_2\)RR products that they form: H\(_2\) and CO.\(^{199}\) Under standard operating conditions, the noble metal Pt binds the primary intermediate, *CO, too strongly to release or allow further reduction of CO after its formation, resulting in the generation of H\(_2\) as the primary product.\(^{200,201}\) The strong CO binding and high competing HER activity have restricted the potential applications of Pt as CO\(_2\)RR catalysts. In contrast, Au and Ag bind *CO weakly, which triggers CO release upon generation; this prevents further reduction.\(^{202,203}\) It is now understood that the intrinsic physical and chemical properties of the metals, especially through d-band theory and their differing abilities to bind specific chemical intermediates, yield the enhanced selectivity and activity of CO\(_2\)RR production. Compared with Pt, Au and Ag are well known for their preferential CO\(_2\) electroreduction into CO, recording over 90% of Faradaic efficiencies for the CO production and enabling high selectivity for CO evolution.\(^{204,205}\) Compared with carbon monoxide dehydrogenase,\(^{206}\) a high reaction potential is needed for Au to provide sufficient multielectron-transfer driving-force for the activation of thermodynamically stable CO\(_2\); optimal binding configurations for *COOH are needed for improvements in CO generation. Although Au is a highly selective CO\(_2\)RR catalyst, the size stabilities of Au nanoparticles (AuNPs) under CO\(_2\)RR conditions are critical for the maintenance of reaction selectivity. Trindell et al. utilized scanning transmission electron microscopy to track the size ranges of three ligand-stabilized AuNPs from the working electrodes after 15 min of electrolysis (Figure 6a–c).\(^{207}\) They revealed the size distribution of AuNPs, in which the sizes of citrate-stabilized AuNPs and AuNPs encapsulated within sixth-generation, hydroxyl-terminated, poly(amineamine) dendrimers (G6-OH DENs) grew substantially; in contrast, the size of G8-OH analogue-stabilized AuNPs increased slightly. Their results also revealed the distinct catalytic selectivities for electrocatalytic CO\(_2\) reduction, in which the stable ~2 nm G8-OH analogue stabilized AuNP electrocatalysts exclusively yielded H\(_2\) as a product. Silver is a promising candidate as a CO\(_2\)RR electrocatalyst because of its economic viability compared with Pd and Au, as well as its high selectivity for the CO\(_2\)RR to produce CO.\(^{208,209}\) Notably, the shapes, morphologies, crystal facets, particle sizes, and electronic structures of Ag-based catalysts may play critical roles in influencing their activities, selectivities,
Several design strategies have been proposed to optimize the stabilities of Ag-based catalysts during electrolysis, including the construction of Ag single-atom structures,\textsuperscript{[211]} alloying with other metals,\textsuperscript{[212,213]} and construction of defect structures.\textsuperscript{[214]} For example, Ag single-atom catalysts exhibit high electrocatalytic stability toward CO$_2$RR.\textsuperscript{[211]} Using in situ environmental transmission electron microscopy and XRD (Figure 6d,e), Zhang et al. obtained detailed information regarding the thermal treatment and surface reconstruction of the MnO$_2$-induced evolution of Ag nanoparticles (AgNP) to single atoms, indicating that the presence of single Ag atoms as the only active sites promoted CO$_2$RR stability. Using a fast operando XAS technique to determine the time-dependent composition and structural evolution of an Ag$_2$O precatalyst during catalysis, Wu et al. reinvestigated the structure–activity relationships and revealed that the massive defect structures generated during operando electrochemical reduction led to significant stability enhancement, highlighting the critical role of defect structures for outstanding CO$_2$RR performance.\textsuperscript{[214]}

### 6.2. Transition Metal-Based Catalysts

Transition metals may be categorized into three main groups based on the major products that they form: CO, H$_2$, and hydrocarbons. The transition metals that primarily generate CO (e.g., Zn) bind the primary intermediate (e.g., *CO) weakly to allow CO release upon generation.\textsuperscript{[215,216]} In contrast, metals that generate H$_2$ most effectively in CO$_2$RR catalysis (e.g., Fe and Ni) bind *CO too strongly to release or allow further reduction of CO after its formation.\textsuperscript{[215,217]} Copper and oxide-derived Cu comprise a unique class of catalysts that can selectively reduce CO$_2$ to substantial amounts of hydrocarbons because of optimal *CO binding strength.\textsuperscript{[218]} Assessments of relationships...
between products and catalysts indicate that Fe and Ni are poor CO₂RR catalysts, which mostly produce H₂. The uniqueness of Cu makes it a competitive monometallic catalyst, enabling efficient electrochemical reduction of CO₂ into hydrocarbons and alcohols. The stability mechanisms and deactivation of state-of-the-art Cu-based catalysts for CO₂RR have been recently reviewed and are well understood.⁴²⁹

Non-noble metal Zn-based catalysts (e.g., porous Zn, hexagonal Zn, Zn foam, and dendritic Zn) exhibit promising properties for the electrochemical conversion of CO₂-to-CO.⁴²⁰⁻⁴²² By means of in situ Raman spectroscopy analysis, the relationships between CO₂RR performance and the structural features of oxide-derived Zn centers have been revealed; Zn(0) (rather than ZnO) has been identified as the active site at CO₂RR-relevant potentials.⁴²³ When using the vulnerable transition metal Zn catalyst, there is a need for caution regarding its long-term stability. Only a few studies have reported the use of in situ/operando techniques to investigate the stabilities of Zn-based catalysts. Rosen et al. conducted the first in situ/operando XAS analysis to capture the detailed real-time structural evolution of a Zn dendrite catalyst under realistic CO₂ electrolysis conditions. The Zn catalysts exhibited severe chemical oxidation to Zn²⁺ at potentials less negative than −0.7 V, whereas they exhibited good stability at potentials more negative than −0.7 V, which is likely the origin of the stability issues associated with Zn catalysts.⁴²⁶

6.3. Metal-Free Materials

Because of the strong covalent bonding between C atoms and the availability of various graphitic allotropes with changeable electronic properties, C-based metal-free catalysts have recently emerged as a promising option for the stable selective conversion of CO₂ to CO.⁴²⁴⁻⁴²⁵ C-based metal-free materials have better stabilities than do bulk metal catalysts because aggregation, pulverization, and structure reconstruction are not expected in catalysts such as N-doped C materials. Spectroscopic analyses have shown no changes in the peak intensities of corresponding N 1s peaks before and after the CO₂RR, demonstrating that positively charged C atoms (rather than N groups) behave as catalytically active sites for C-based catalysts, while basic N groups are presumably anchoring sites for CO₂ capture.⁴²⁶⁻⁴²⁷ The underlying catalytic mechanism behind C-based CO₂RR catalysis is the reduction–oxidation cycling between positively charged C atoms and the absorbed intermediate complex.⁴²⁶⁻⁴²⁸ There have been few in situ/operando studies of CO₂RR stability for C-based metal-free catalysts.

7. Nitrogen Reduction Reaction

Recently, electrocatalytic N₂ reduction into ammonia (NH₃) in the aqueous phase under mild conditions has become an attractive alternative to the well-established Haber–Bosch process for industrial NH₃ production, which requires high temperatures (300–550 °C), high pressures (200–350 atm), and natural gas for high-purity H₂ production.⁴²⁹⁻⁴³⁰ This has resulted in large energy consumption and substantial CO₂ emissions. The electronic and surface structures of catalysts potentially play crucial roles in achieving green NH₃ synthesis. According to the nature of catalysts used for NRRs, they may be classified into three major categories: homogeneous, heterogeneous, and biological. Various types of heterogeneous catalysts have been reported (e.g., transition metals, nitrides, oxides, sulfides, carbides, phosphides, hybrid metals, and metal-free catalysts) with diverse geometric and chemical structures. With the main focus on heterogeneous catalysts, the next section provides a summary of recent progress in understanding the stability mechanisms using in situ/operando techniques.

7.1. Metal Catalysts

Earth-abundant nonprecious transition metals (e.g., Fe, Mo, and Co) and noble metal catalysts (e.g., Rh, Ru, Pd, Pt, and Au) have the potential to efficiently synthesize NH₃ from N₂ and H₂O through direct electrochemical conversion.⁴³¹⁻⁴³⁸ Theoretical calculations indicate that Mo, Fe, Rh, and Ru should provide the highest catalytic activity to drive the N₂ reduction to NH₃.⁴³⁹ However, alongside the inert N₂ activation and reduction process, the reduction of H adatoms on the surfaces of metals at a negative applied bias into H₂ serves as a parasitic competing reaction. To achieve better selectivity for NH₃ synthesis, the stronger binding strength for N adatoms (rather than H adatoms) may be manifested as suppression of H₂ evolution relative to NH₃ synthesis. For example, early transition metals on the left side of volcano plots promote NH₃ generation, compared with late transition metals on the right side of volcano plots.⁴³⁹ Although Pd and Pt are not recommended for electrocatalytic NRRs because they are theoretically predicted to be highly active toward competing HER processes, several experimental studies have reported Pd- and Pt-based electrochemical NH₃ synthesis. In these processes, Pd exhibited a much higher NH₃ formation rate and Faradaic efficiency in the phosphate buffer solution mainly because of its higher barrier for mass- and charge-transfer, which resulted in the suppression of H₂ evolution; the activity of Pt toward N₂ reduction was low partially because of the endothermic nature of the binding energy of N adatoms on Pt surfaces.⁴³⁶ Gold catalysts have also been experimentally demonstrated to achieve efficient NH₃ production, in which the abundant high-index facets, sharper edges and corners, and amorphous nature may lead to higher catalytic activity.⁴³⁸⁻⁴⁴⁰⁻⁴⁴⁵

The stabilities of metal catalysts during NRRs remain poorly investigated and discussed throughout the literature. Operando XAS studies performed by Peng et al. showed that using single-atom Ru distributed on Mo₅CTₓ MXene nanosheets (Ru SAS/Mo₅CTₓ) N₂ electroreduction can be realized with high Faradaic efficiency and excellent stability.⁴⁴⁶ Operando XAS analysis captured the changes in the atomic structure of the rich Mo-deficit defect site-stabilized single-atomic Ru catalyst during electrochemical NRRs, revealing that metal Ru played an important role in providing active sites for catalytic intermediate adsorption and electron back-donation centers for efficient and stable N₂ activation. In addition, Wang et al. utilized operando XAS to track the real-time evolution of the adsorption
edge of single-atom Fe under standard operating conditions, revealing that X-ray absorption near edge structure and extended X-ray absorption fine structure profiles obtained after NRRs remained almost identical to the profiles obtained during and before these reactions (Figure 7a), thereby confirming the stability of single-atom Fe. [243]

7.2. Nitrides, Oxides, Sulfides, Carbides, and Phosphides

7.2.1. Transition Metal Nitrides

Theoretical calculations have suggested that transition metal nitrides comprise a family of promising candidates for electrochemical NRRs in ambient conditions, especially for VN, ZrN, NbN, and CrN. This has been credited to their distinct Mars–van Krevelen reaction mechanism, whereby surface N atoms incorporated in the outermost surface layer of transition metal nitrides are initially protonated and released as NH₃, followed by replenishment of the lattice N-vacancy involving adsorption of gaseous N₂ molecules to form a complete catalytic cycle. [244–246] This mechanism requires lower overpotentials and fewer energy inputs for catalytic turnover in NRRs than do dissociative and associative N₂ activation mechanisms involving pure transition metals. As mentioned previously, little is known regarding the details of the underlying stability mechanisms. Yang et al. conducted an operando XAS measurement to monitor the phase evolution of the as-prepared VN nanoparticles, in which the identified VN₀.7O₀.45 behaved as the active phase. The gradual conversion of the active VN₀.7O₀.45 phase to VN during NRRs was confirmed to be responsible for the reduced ammonia yield rate during the long-term reaction, explaining the rapid deactivation of the VN electrocatalyst at an applied potential of −0.2 V (Figure 7b). [247]

7.2.2. Transition Metal Oxides

In terms of noble-metal-free transition metal oxides, most investigations have focused on iron oxides (e.g., Fe₂O₃ [248] and Fe/Fe₃O₄ [249]) because they have been widely used industrial ammonia synthesis catalysts for more than a century. Over the years, other transition metal oxide catalysts with meticulously designed structures and compositions have been improved and optimized; Faradaic efficiencies close to or higher than 10% have been achieved. [250–252] However, because of the existence of the competing HER, the Faradaic efficiencies of most heterogeneous electrochemical NRR systems typically remain below 1%.
Alternative strategies in the design of potential heterogeneous electrocatalysts have required the combined optimization of dinitrogen adsorption and proton addition thermodynamics with sufficient suppression of HER, as well as careful experimental work to examine the reaction and degradation mechanisms. Recently, Luo et al. applied an in situ electrochemical quartz-crystal microbalance, which can accurately measure the mass change of the working electrode during the long-term NRR process; this was the first demonstration of the deactivation mechanism of a Y-stabilized ZrO$_2$ catalyst. As shown in Figure 7c, the mass of the ZrO$_2$ catalyst progressively increased after long-term stability tests, with a substantial decrease in catalytic activity. This was ascribed to the presence of O species that refilled O vacancies in the nanocomposite, eventually leading to catalyst deactivation.

7.2.3. Transition Metal Sulfides

Transition metal sulfides possess higher conductivities than do their oxide counterparts; they also exhibit unique electronic properties. Various transition metal sulfides have been explored as NRR catalysts for potential applications in the N$_2$ electroreduction to NH$_3$. Their performance follows the order of ZnS > NiS > CdS > CuS > Bi$_2$S$_3$ > FeS > MoS > Sb$_2$S$_3$ > SnS > MnS > PdS > PbS > AgS > CoS. Following the initial investigations, there have been few experimental studies concerning the use of transition metal sulfides to catalyze electrochemical NRR. Theoretical calculations have revealed the possible associative and dissociative mechanisms of electrochemical NH$_3$ formation for stable transition metal sulfides. The above mechanisms have not been quantitatively validated because in situ/operando measurements of N$_2$ versus H coverage changes during the NRR are difficult, thus hindering the understanding of deactivation and stability mechanisms. There have been very few in situ/operando investigations of the deactivation and stability mechanisms for transition metal sulfides catalyzing electrochemical NRR.

7.2.4. Transition Metal Carbides

For transition metal carbides, density-functional theory calculations have helped to illustrate how MXenes (a typical type of 2D transition metal carbides, with the general formula M$_3$C$_2$ from the d$^5$, d$^6$, and d$^7$ series) are promising catalysts for electrocatalytic N$_2$ reduction to NH$_3$. The chemisorption of N$_2$ has been identified as a spontaneous process because of the negative change in Gibbs free energy. Preferred N$_2$ coverages on the surfaces of MXenes containing d$^5$ or d$^6$ transition metals block the adsorption of CO$_2$ and H$_2$O, thus motivating their use in N$_2$ electroreduction. Typically, V$_2$C$_2$ and Nb$_3$C$_2$ exhibited respective overpotentials as low as 0.64 and 0.90 V, compared with the standard hydrogen electrode. Another computational study revealed the influence of the crystallographic surfaces of MoC on the electrochemical NRR, in which MoC(111) was the only surface with higher affinity for N adsorption than for H adsorption. This resulted in suppression of the HER on the MoC(111) surface, compared with all other MoC surfaces on which there was competition between N- and H-atom adsorption. Furthermore, through the application of in situ Fourier-transform infrared spectroscopy spectra, Qu et al. provided direct experimental evidence that electrocatalytic N$_2$ reduction on oxygen-containing MoC (O-MoC) embedded in nitrogen-doped carbon layers (N-doped carbon) proceeded through an associative reaction pathway; high structural and electrochemical stabilities were obtained (Figure 7d).

7.2.5. Transition Metal Phosphides

TMPs have been investigated as efficient electrocatalysts for HERs, while a few studies have demonstrated NH$_3$ production from the electrochemical reduction of N$_2$, albeit at low production rates. Negatively charged phosphorus may induce an electron cloud density deviation of metals, resulting in electron density modulation of TMPs, thus impacting reaction dynamics in the electrocatalytic NRR. By meticulous tuning of the structure and composition, the NRR performance of TMPs might achieve further validation. TMPs (e.g., MoP, Ni$_2$P, FeP, FeP$_3$, Cu$_3$P, CoP, and CoP$_3$) have demonstrated sufficient activity to drive N$_2$ electroreduction to NH$_3$ under ambient conditions. TMPs with higher P content commonly achieve better stability. Thus far, in situ/operando techniques have not been used to investigate these stability mechanisms.

7.3. Metal-Free Catalysts

Because of their potential environmentally friendly nature, low cost, high conductivity, and good resistance to corrosion, some representative metal-free catalysts (e.g., C and its derivatives, B and its compounds, polymeric carbon nitride, and black phosphorus) have shown impressive NRR performance that is comparable with the performances of many metal-based electrocatalysts. Because of the chemical natures of most transition metals, the weak adsorption strengths of N$_2$ molecules on the electrocatalyst surface usually give rise to low Faradaic efficiencies due to the existence of parasitic competing HER. For example, heteroatom N-doped C nanoporous membranes with a hierarchical structure achieved respective Faradaic efficiency and NH$_3$ formation rate of 5.2% (~0.2 V) and 0.08 g h$^{-1}$ cm$^{-2}$ (~0.3 V compared with reversible hydrogen electrode). However, N-doped carbon materials may degrade during the NRR, resulting in the generation of NH$_3$ from the N source in catalysts as contamination of labeled NH$_3$. For B-doped C-based materials (especially for B-doped nanostructured diamond/Ti electrodes), electron-deficient B may induce the buildup of surface charges and NRR active sites in carbon lattices, thus facilitating a back-donation process with striking durability over 8 days and no obvious decay in activity. Polymeric carbon nitride obtained by post annealing under an Ar atmosphere contains sufficient and homogeneously distributed nitrogen vacancies, which allows for electron redistribution to C atoms near those nitrogen vacancies; it also facilitates electron transfer to the adsorbed N$_2$, resulting in strong N$_2$ activation, with an NH$_3$ formation rate and Faradaic efficiency of 8.09 µg h$^{-1}$ cm$^{-2}$ (~0.2 V compared with reversible hydrogen...
Despite oxidative degradation (especially in the presence of water), the stability mechanisms and deactivation of metal-free catalysts remain unclear. Song et al. conducted an in situ Fourier-transform infrared spectroscopy measurement to capture the cleavage process of the $\text{N=N}$ bond on the surface of N, P co-doped hierarchical porous carbon, in which the N$_2$H$_4$ species clearly formed in the electrocatalytic process, thus confirming the NRR mechanism on the surface of the catalyst follows an associative pathway.\[270\]

### 7.4. Other Heterogeneous Catalysts

Hybrid catalysts could combine the merits of various components to harness the benefits inherent to each. For example, a synthetic FeNi bimetallic catalyst composed of the catalytically active but unstable Fe, and stable but inert Ni, exhibits substantial synergistic effects such that catalyst efficiency and stability are obviously improved, compared with either component alone. This performance is markedly better than the performance of a Pt/C electrocatalyst.\[271\] For MOFs (e.g., Co-based ZIF-67, Fe-based MIL-100(Fe), and Cu-based HKUST-1), poor stability toward water and acid/base solutions has hindered their direct use in the electroreduction of N$_2$ into NH$_3$. The proposed mitigation strategy to enhance durability involves the assembly of electrolyte-sensitive MOFs into membrane electrodes to prevent direct contact with aqueous solutions. Future investigations of the MOF-promoted electrochemical NRR will continue to focus on improved water stability. Perovskite (general formula of ABO$_3$), spinel (AB$_2$O$_4$), pyrochlores (A$_2$B$_2$O$_7$), and ion liquid-based catalysts have also been reported to exhibit electrocatalytic activity toward NRR. However, few in situ/operando studies have been carried out involving the above catalysts; therefore, the stability mechanisms remain unclear.

### 8. Conclusion: Remarks and Perspectives

The stability-relevant collective property is an omnipresent and pressing concern in the development of industrial catalysts, especially when they will be used in a harsh corrosive reaction environment. Critical breakthroughs in stability issues are often the result of an improved understanding of material structures, surface sites, and reaction mechanisms. In situ/operando techniques have been invaluable for achieving better understanding of the underlying microscopic processes of working catalysts; simultaneous measurements of catalytic structure and surface species are performed in a structurally and kinetically relevant manner, while providing important experimental evidence to address stability issues. In situ/operando characterization techniques provide an opportunity to understand the catalytic structure and stability properties. In this review, recent important in situ/operando characterization studies were summarized, with a focus on the structural and chemical microenvironment evolution of catalytic active sites that impact the stabilities of typical heterogeneous electrocatalysts. The aim of this review was to identify the stability and degradation mechanisms that are critical for the development of efficient and robust electrocatalysts. Future studies to address the challenging durability issue through the use of powerful in situ/operando techniques should be directed toward the following three topical areas:

#### 8.1. Establishing an “In Situ/Operando Probing Map”

Heterogeneous electrocatalysis is complex because it involves a multidimensional interface and various subtle structural evolutionary processes, together with the transfer of multiple protons and electrons. Furthermore, each in situ/operando technique has its own unique capabilities and limitations, implying that an in-depth understanding of the corresponding stability and degradation mechanisms through a single in situ/operando method may be difficult to achieve. For example, optical characterization techniques (e.g., surface-enhanced infrared absorption spectroscopy and tip-enhanced Raman spectroscopy) are suitable for identifying intermediate species and bond formation because the wavelength range of inelastically scattered light is relevant to the vibrational frequency of the intermediates; however, it is difficult to offer element-, orientation-, and state-sensitive probing capabilities because of the limited spatial resolution. The limitations of optical characterization techniques can be complemented by X-ray techniques. Combining complementary in situ/operando methods will allow for systematic tracking of the dynamic structure and reveal the underlying science of catalytic active sites, providing an in-depth understanding of the stability mechanisms. Therefore, an “in situ/operando probing map” should be established by combining complementary in situ/operando approaches to address the challenging stability issue.

#### 8.2. Designing Suitable Operando Cells Applicable for Real Devices

An operando analysis often requires considerable complexity in device design. Currently, most operando cells reported in the literature cannot fully mimic real operating conditions, thus causing “inappropriate” interpretation or understanding of structure/stability relationships, as well as the application of “inappropriate” design principles to optimize electrocatalysts. This has led the designed catalysts to sometimes differ from the expected durabilities of practical devices. Special care is needed in the design of suitable operando cells to minimize the experimental gap in measurement conditions between electrocatalytic reactions and instrumental requirements. Further improvements and optimizations in device design must be made to enable fully effective operando research.

#### 8.3. Accelerating Durability-Related Tests for Stability Assessments

Despite the great emphasis placed on stability-related studies, the reported studies have not conducted sufficient tests for
stability assessment. To significantly shorten the testing time and reduce testing costs, more efficient highly accelerated durability-related tests may provide extraordinarily valuable experimental data concerning degradation processes. However, simulating long-term stability through accelerated tests is challenging because of the existence of various degradation factors that influence stability. This has prevented data comparison and subsequent identification of the relative importances of those factors that influence stability.

Thus, there is a need for standardized accelerated durability-related tests for heterogeneous electrocatalytic energy conversion. Thus, there is a need for standardized accelerated durability-related experiments and unified stability evaluation procedures.

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Conflict of Interest
The authors declare no conflict of interest.

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