

Chapter

Function of Catalyst-Material Phases in Low-Temperature Electrolysis

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Abstract

Low-temperature electrolysis driven by renewable energy sources has emerged as a vital route for sustainable chemical production, carbon cycle closure, and the realization of a circular economy. Central to the advancement of this technology is the development of efficient and stable electrocatalyst materials, which govern both the thermodynamics and kinetics of electrochemical reactions. The catalytic phase—specifically whether the material exists as a metal, oxide, or hydroxide—is decisive in determining key performance metrics such as activity, selectivity, stability, and product distribution. Each phase exhibits unique physicochemical attributes, including variations in crystal structure, electronic properties, and surface affinity, affecting adsorption behavior, charge transfer dynamics, and corrosion resistance. This chapter provides a detailed exploration of the roles of metal, oxide, and hydroxide phases in electrocatalysis, focusing on their mechanistic contributions in critical reactions like the electrochemical CO₂ reduction (ECR) and alkaline oxygen evolution reaction (OER). In addition to discussing the intrinsic properties of each phase, the chapter highlights the significance of phase evolution, particularly in situ transformations and induced transitions, as a promising strategy to enhance catalytic performance. These dynamic processes often lead to increased surface area and grain boundary density, which can substantially boost reactivity and durability. By combining structural insights with mechanistic understanding, this chapter aims to offer a cohesive framework for designing next-generation electrocatalysts optimized for high-performance electrolysis applications.

Keywords: electrochemistry, CO₂ reduction, low-temperature electrolysis, electrocatalyst, oxygen evolution reaction, OER, alkaline electrolysis

1. Introduction

Low-temperature electrolysis, particularly when powered by renewable energy sources, is rapidly emerging as a cornerstone technology in the transition to a circular and decarbonized economy. By facilitating the transformation of plentiful and readily accessible feedstocks—including water and captured carbon dioxide (CO₂)—into chemical fuels and valuable industrial products, it provides a direct pathway to reduce greenhouse gas emissions, enhance energy security, and close the anthropogenic

carbon cycle. The process is underpinned by two electrochemical reactions: the electrochemical reduction of carbon dioxide (ECR) at the cathode and the oxygen evolution reaction (OER) at the anode. Collectively, these elements facilitate the generation of storable and transportable energy carriers, including hydrogen and carbon-based fuels, thereby addressing the mounting demand for flexible, distributed energy systems [1–3].

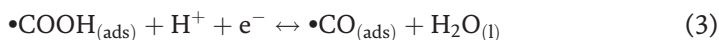
In recent years, ECR has attracted significant attention as a method of storing excess renewable electricity in the form of chemical bonds. The process has the potential to yield a range of valuable products, including carbon monoxide (CO), formate, methane, ethanol, and other C₂+ compounds, with the particular product depending strongly on the catalyst used. Among these, CO and formate are regarded as particularly promising due to their relatively high selectivity and favorable technoeconomic profiles. More complex products, such as ethanol or hydrocarbons, offer high energy density and are therefore desirable for liquid fuel applications. However, their large-scale production remains challenging due to competing reaction pathways and low Faradaic efficiencies [4–7]. In parallel, water electrolysis continues to serve as the most mature and direct route to green hydrogen production. In this process, the cathodic half-reaction, otherwise known as the hydrogen evolution reaction (HER), is relatively facile, while the anodic half-reaction, otherwise known as the OER, remains kinetically sluggish due to its complex four-electron mechanism [8]. Consequently, the OER is widely regarded as the limiting step in overall water-splitting efficiency and is a key focus of catalyst development efforts. The advancement of both ECR and OER is contingent on the design and implementation of effective electrocatalyst materials [9–11]. The catalyst's properties determine the energy required to drive the reaction and also influence reaction kinetics, intermediate stabilization, product selectivity, and long-term system durability. With regard to the reduction of CO₂, the composition of the catalyst dictates the favored pathways. For example, copper uniquely facilitates C–C coupling and the formation of C₂ + products, while silver and bismuth favor simpler products such as CO and formate [12]. In the context of the OER, traditional benchmarks such as IrO₂ and RuO₂ offer excellent performance in acidic and alkaline environments. However, they are constrained by scarcity and cost, rendering their large-scale application unsustainable. This has given rise to a significant increase in the level of interest in transition metal oxides and hydroxides, particularly those based on nickel, iron, and cobalt, which have demonstrated competitive activity and are more abundant. However, these alternatives frequently exhibit limited durability under prolonged operation, undergoing structural transformations or dissolution under oxidative electrochemical conditions [13–16].

The development of electrocatalysts capable of achieving high activity, selectivity, and stability simultaneously remains a central challenge in electrolysis research. Achieving product specificity in ECR is a particularly complex process due to the numerous competing multi-electron pathways, each of which is sensitive to changes in catalyst morphology, surface structure, and local reaction environment. It is imperative to consider stability, particularly in the context of OER catalysts, which are required to demonstrate resilience to harsh oxidative potentials, fluctuating pH levels, and corrosive electrolytes over the course of their operational lifetimes. A considerable number of materials that show great promise in laboratory settings often demonstrate significant degradation when subjected to industrial conditions. Moreover, the overall system efficiency is closely associated with the overpotential required to initiate and sustain the reactions. It is imperative to reduce these energy inputs while preserving elevated current densities to ensure economic viability and facilitate scale-up [17–21].

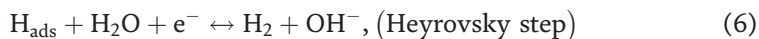
In order to address these interconnected challenges, it is necessary to develop a more profound mechanistic understanding of the behavior of catalysts under operating conditions. This includes phase transitions, active site restructuring, and interfacial dynamics. As electrochemical systems move toward practical deployment, these efforts will be instrumental in bridging the gap between fundamental materials science and applied electrochemical engineering. It is therefore vital to acknowledge the potential of low-temperature electrolysis to play a pivotal role in the development of a resilient, low-carbon energy infrastructure.

2. Fundamentals of electrocatalysis in electrolysis

The ECR is a complex, multistage process that encompasses the transfer of multiple electrons [1–3]. It involves several crucial steps, including CO₂ adsorption, electron transfer, and product desorption occurring at the electrode's surface. Extensive research has revealed that the current density, the specific electrochemical species involved, and the selectivity of the ECR are predominantly influenced by the choice of electrode material and the reduction potential applied [22–24]. The initial step of the ECR is the diffusion of CO_{2(g)} over the catalyst layer, followed by one e[−]-transfer for the formation of the •CO_{2(ads)}[−] intermediate, Eq. (1). The following protonation of the •CO_{2(ads)}[−] Eq. (2), aided by the water molecule, is proposed to happen rapidly, forming the transition •COOH species [25]. A subsequent step involves both an electron and a proton transfer, Eq. (3), forming the adsorbed •CO_(ads). Finally, the •CO_(ads) desorbs from the catalyst's surface, yielding the CO_(g) Eq. (4) [26–28].



The electrochemical CO₂ reduction (ECR) process follows the Eley-Rideal mechanism, where only one species undergoes adsorption [29, 30]. Initial Tafel analysis data suggested that Eqs. (1) and (2) could be the possible rate-determining steps (RDS) for ECR. However, recent work by Deng et al. [31] has shown that the RDS for CO formation is equation Eq. (1), while the RDS is independent of the catalyst material used and the reaction environment. The Eq. (1) is a composite step that encompasses the crucial processes of CO_{2(g)} diffusion over the catalyst layer and electron transfer. At lower current densities, the rate of electron transfer in Eq. (1) is the critical factor influencing the rate of ECR. At higher levels of polarization, of more than 200 mA cm^{−2}, the diffusion of CO_{2(g)}, as seen in Eq. (1), toward the active surface of the catalyst becomes the limiting factor for the ECR rate. Given the strong correlation between the catalyst's properties and the ECR performance, the Sabatier principle emerges as a crucial tool for predicting a catalyst's activity and product selectivity [32]. It asserts that for high catalytic activity, the interactions between the catalyst and the reaction species should exhibit an intermediate intensity for the reaction to be favored. The parasitic hydrogen evolution reaction (HER) progresses at the cathode in parallel with the ECR. The generally accepted HER mechanism in alkaline and neutral media is exhibited below:



The splitting of a water molecule and the adsorption of hydrogen on the surface of the electrode or catalyst is described by the Volmer step, Eq. (5), which always consists of the initial step of the HER. This is then followed by the production of hydrogen through either an electrochemical process, the Heyrovsky step, Eq. (6), or a chemical process, as in a Tafel step, Eq. (7). Numerous studies have exhibited that at low η , lower than -0.15 V, the HER goes through the Heyrovsky step, while the Tafel step follows in parallel. However, at a high η of more than -0.25 V, the electrode is considered overwhelmed by H_{ads} . The Tafel step becomes negligible, with the HER progressing through the Heyrovsky step, owing to its high rate constant [33–35]. The low thermodynamic potential of the HER, summarized in **Table 1**, and its faster overall kinetics strongly favor the reaction at the expense of ECR (**Figure 1**).

At lower polarization, the reactions' kinetics are mainly determined by the e-transfer. The function of a selective and efficient catalyst for the ECR is to successfully redirect the majority of the total current of the electrolyzer toward the ECR instead of the HER. It is worth noting that at a high current density of more than 300 mA cm^{-2} , both the ECR, Eq. (4), and HER, Eq. (6), rates are primarily governed by species desorption, with additional limitations imposed by mass transfer of the reactants. Considering the significantly higher diffusion coefficient of H_2 , D_{H_2} , compared to the

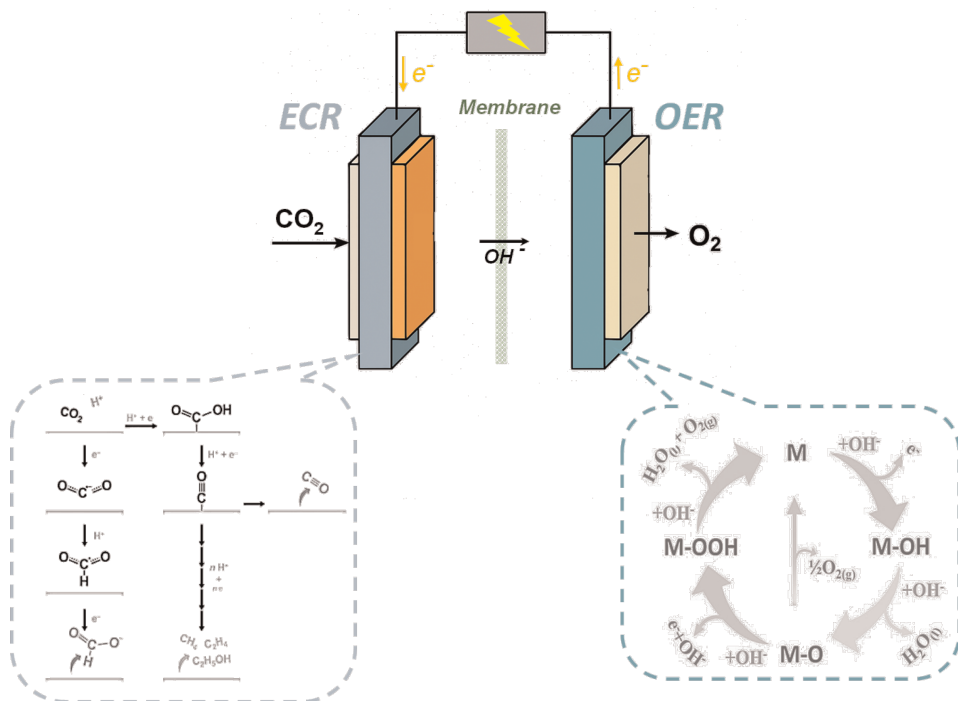


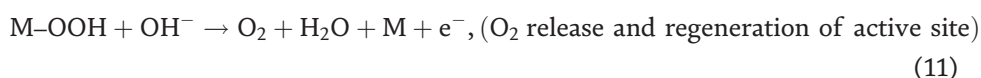
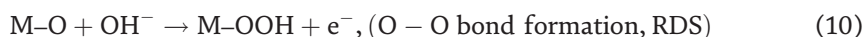
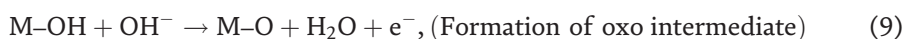
Figure 1. Schematic representation of a typical electrolyzer, utilized for the cathodic CO_2 valorization (ECR) and the anodic oxygen production (OER) at alkaline conditions.

Product (Reaction)	Equation	E _o (V vs. SHE, 25°C)
Hydrogen (HER, acidic)	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0
Carbon monoxide (ECR)	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.104
Formic acid (ECR)	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.171
Methanol (ECR)	$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	0.016
Methane (ECR)	$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	0.169
Ethylene (ECR)	$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	0.085
Oxygen (OER, alkaline)	$4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	0.401
Hydrogen (HER, alkaline)	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.828

Table 1.
Half-reaction potentials of the main low-temperature electrolysis paths [36].

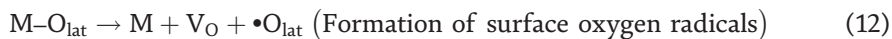
CO_2 one, D_{CO_2} , and CO one, D_{CO} [37], the faster mass transfer of the H_2 will inevitably favor the HER at high current densities. At lower reaction rates, ECR is favored by the catalyst's active centers so that the partial current density for the ECR, j_{CO} , is always larger than that for HER, j_{H_2} . While at higher currents, due to the effect of mass-transfer limitations on the reactions' species, HER takes over, imposing the opposite condition [38–40]. Three key figures of merit determine the preference for either ECR or HER. The Faradaic Efficiency, $\text{FE} (\%) = \frac{Q_{\text{pr}}}{Q_{\text{th}}}$, quantifies the ratio of the theoretically calculated charge spent on product formation Q_{th} , calculated by the total charge passed, to the actual amount Q_{pr} , quantified by analytical techniques. The partial current density j_i signifies the rate of product formation ($j_i = j \cdot \text{FE}$), derived from the total current density flowing through the electrolyzer j and the FE for the specific product (i) formation. Evaluating the viability of the reaction, the energy efficiency, $\text{EE} (\%) = \frac{E_o}{E_{\text{cell}}} \text{FE}$ of the electrolyzer for a specific product (i), offers valuable insights. It articulates the thermodynamic efficiency of product formation, as expressed through the relation $\frac{E_o}{E_{\text{cell}}}$, relative to its kinetic efficiency (FE).

The oxygen evolution reaction (OER) in alkaline media, found in **Table 1**, follows complex yet distinct mechanistic pathways as reaction pathways [41, 42]. The two primary mechanistic pathways have been identified for the OER in alkaline media as either the Adsorbate Evolution Mechanism (AEM) or the Lattice Oxygen Mechanism (LOM). The AEM is the traditional surface-mediated pathway where OER proceeds through proton-coupled electron transfers (PCETs) involving adsorbed intermediates [2, 43]. These steps typically occur on transition metal active sites (M), with oxygen forming via a sequence of reactions involving $^*\text{OH}$, $^*\text{O}$, and $^*\text{OOH}$ surface species, as seen below:



The AEM activity is closely tied to the binding energies of these intermediates. However, the adsorption energies of $^*\text{OH}$ and $^*\text{OOH}$ are linearly correlated, with a

typical energy difference of ~ 3.2 eV. This imposes a theoretical overpotential limit of ~ 370 mV. To overcome this bottleneck, recent strategies focus on optimizing intermediate adsorption via doping, vacancy engineering (V_O), strain modulation, and electronic structure tuning, according to the Sabatier principle [44]. In contrast, the LOM introduces an alternative pathway in which the lattice oxygen (O_{lat}) of the catalyst itself participates in the OER. This mechanism circumvents the *OOH intermediate and breaks the linear scaling constraints of AEM, potentially enabling lower overpotential and faster kinetics, as seen:



While LOM offers the advantage of enhanced activity by overcoming the adsorption energy limitations of AEM, it may compromise catalyst stability due to irreversible lattice oxygen loss and the formation of oxygen vacancies. Nevertheless, it has been shown that tuning metal-oxygen co-valence can modulate lattice participation, with lower Tafel slopes (~ 43 mV dec $^{-1}$) serving as an experimental fingerprint for LOM pathways [45, 46].

Overall, it is evident that the catalyst material plays a pivotal role in shaping both the reaction pathway and the overall efficiency of the electrochemical process, with its properties directly influencing performance and selectivity.

3. Electrocatalytic phases

Catalyst-material phases—namely metals, oxides, and hydroxides—play crucial and often complementary roles in governing electrocatalytic performance in low-temperature electrolysis, especially for the ECR and the OER. These phases influence key factors such as electron conductivity, adsorption energetics, intermediate stabilization, and structural stability, which in turn define activity, selectivity, and durability [47].

3.1 Metal phases in electrocatalysis

Metallic phases serve as highly conductive active sites, promoting efficient electron transfer and the adsorption of reactants. Their electrocatalytic performance is fundamentally influenced by their intrinsic properties, including electronic structure, binding energies, and the position of the d-band center. The electronic structure dictates the distribution of electronic states in the vicinity of the Fermi level, which in turn affects the ability of the catalyst to adsorb and activate reactants. The binding energies of the key intermediates must be optimized to ensure their stability during the reaction while also allowing for the desorption of the product. A pivotal descriptor in this context is the d-band center, whose position relative to the Fermi level is indicative of the adsorption strength of reaction intermediates. Metals with a higher d-band center have been observed to bind adsorbates more strongly, which has the potential to

enhance activation. However, this binding may also impede product release. These properties have been shown to influence the overall activity, selectivity, and stability of metal catalysts [48].

The selectivity of ECR is governed by the adsorption energies and reaction pathways of key intermediates on the catalyst surface. For instance, the formation of $^*\text{COOH}$ and $^*\text{OCHO}$ intermediates leads to CO and formate products, respectively. The binding strength of these intermediates is influenced by the electronic structure of the catalyst, particularly the d-band center. A higher d-band center is generally associated with enhanced adsorption, which can stabilize intermediates but concurrently impede product desorption. Conversely, a lower d-band center leads to weaker adsorption, facilitating desorption but potentially destabilizing intermediates. It is notable that copper (Cu) is distinguished by its capacity to yield multicarbon (C_2^+) products, including ethylene and ethanol. This phenomenon is attributed to its moderate binding strength for $^*\text{CO}$ intermediates, which facilitates C-C coupling steps. The formation of C-C bonds is a critical step in the generation of C_2^+ products, and it requires a delicate balance in the adsorption energies of intermediates to proceed efficiently. Conversely, silver (Ag) and gold (Au) exhibit high selectivity toward CO production due to their weaker binding of $^*\text{CO}$ intermediates, which promotes desorption before further reduction can occur. Tin (Sn) has been observed to promote the formation of formate, a process that is believed to be the result of its strong affinity for the $^*\text{OCHO}$ intermediate. The aforementioned trends in product selectivity are closely tied to the metal-dependent adsorption energetics of intermediates such as $^*\text{COOH}$, $^*\text{CO}$, and $^*\text{OCHO}$ [49]. A key addition from Ringe et al. [50] is the recognition of the role played by electrochemical double-layer (EDL) effects and field-driven adsorption in ECR kinetics, particularly for metals like gold. Their multiscale modeling and experimental analysis demonstrated that the rate-limiting step for CO formation on Au shifts with overpotential, from $^*\text{COOH}$ to $^*\text{CO}$ at low overpotential to CO_2 adsorption at intermediate potentials, and eventually to CO_2 mass transport at high overpotential. This underscores the significance of EDL-induced surface charge effects on $^*\text{CO}_2$ stabilization and the recognition that reaction kinetics are not solely dictated by thermodynamics or static binding energies but also by field-mediated interactions with dipolar intermediates. In a similar manner, the alloying of metals has been demonstrated to modulate the electronic structure and binding properties of the active surface, thereby exerting a consequential influence on ECR selectivity. For instance, Cu-Ag alloys have been demonstrated to enhance C_2 product formation by stabilizing $^*\text{CO}$ and $^*\text{OCCO}$ intermediates while suppressing formate pathways. This synergistic effect is attributable to the electronic interactions between Cu and Ag atoms, which adjust the d-band center and, consequently, the adsorption energies of key intermediates. In the same context, Cu-Sn alloys have been observed to exhibit selectivity toward CO or formate production, depending on the composition. The incorporation of Sn into Cu modifies the electronic environment, affecting the binding strength of intermediates and altering reaction pathways. It is possible to design catalysts with tailored selectivity for desired ECR products by carefully controlling the alloy composition and structure [51, 52].

Transition metal materials in their metallic phases (e.g., Ni, Co, Fe, Cu, or their alloys) are typically characterized by high electrical conductivity and structural robustness. These properties enhance OER efficiency by lowering energy barriers and accelerating intermediate transformations (e.g., $\text{M-OH} \rightarrow \text{M-O} \rightarrow \text{M-OOH}$) [53, 54]. However, as OER catalysts, their direct activity is generally limited. Metallic phases frequently function as precursors or conductive supports, forming the backbone

structure that undergoes in situ transformation into more catalytically surface-active oxide or oxy-hydroxide phases under OER operating conditions. This process maintains mechanical stability and prevents degradation, as evidenced by the NiFe/NiFeOx core-shell structure [55]. Transition metals dynamically shift oxidation states (e.g., $\text{Ni}^0 \rightarrow \text{Ni}^{3+}$, $\text{Fe}^0 \rightarrow \text{Fe}^{3+}$), optimizing adsorption energies of OER intermediates ($^*\text{O}$, $^*\text{OH}$, $^*\text{OOH}$) and fine-tuning reaction pathways [56]. The combination of metals with differing oxidation states, such as NiFe alloys with Fe^{3+} and Ni^0 , has been shown to yield synergistic effects, thereby reducing the overpotential to 160 mV at 10 mA/cm². This is achieved by leveraging Fe^{3+} for OER activity and Ni^0 for charge transfer. In the context of OER, metallic surfaces oxidize to form active oxyhydroxides (e.g., NiOOH, CoOOH), with the metallic core ensuring the continuous supply of electrons to these catalytic sites [57]. Strategies such as doping (e.g., Fe into Ni) or hybridization with conductive supports further enhance performance by modifying electronic structures, stabilizing intermediates, and increasing surface area. Collectively, these mechanisms ensure the balance of conductivity, active site availability, and stability, thus enabling transition metal-based catalysts to demonstrate comparable OER efficiency to that of noble metal systems [58].

3.2 Oxide phases in electrocatalysis

Oxide phases, typically transition metal oxides (e.g., NiO, Co_3O_4 , Cu_2O), offer tunable redox chemistry and rich surface chemistry. Their electrocatalytic functionality is governed by a combination of their electronic conductivity and surface reactivity, both of which are highly dependent on their composition and structural features. Metal oxides exhibit a wide spectrum of electronic conductivities, ranging from insulating to semiconducting to metallic, rendering them versatile platforms for catalytic applications. Transition metal oxides exhibit high intrinsic conductivity, facilitating efficient charge transfer during reactions such as the ECR or the OER [59]. The surface reactivity of metal oxides is influenced by surface terminations, lattice defects, and the presence of hydroxyl groups, complementing their bulk properties. The surface features of the material under investigation create active sites that enhance the adsorption and activation of reactant molecules. It is noteworthy that oxygen vacancies can function as electron-rich sites, thereby promoting CO_2 adsorption and facilitating the formation of key intermediates during reduction. Furthermore, the acid-base character of the oxide surface has been demonstrated to modulate the adsorption strength and stability of intermediates, thereby directing reaction pathways and influencing product selectivity. Collectively, these intrinsic and tunable properties render metal oxides as highly adaptable materials for electrocatalytic systems [60].

For the ECR, metal oxides fulfill a vital function by stabilizing key reaction intermediates, thereby significantly influencing both catalytic activity and product selectivity. In the context of reductive electrochemical conditions, metal oxides frequently undergo partial reduction, resulting in the generation of distinctive surface characteristics that diverge significantly from their metallic counterparts. These features include the formation of oxygen vacancies, the emergence of mixed-valence states, and the retention of metastable oxide phases. Each of these contributes to the catalytic behavior observed in oxide-containing electrocatalysts [61]. One of the most critical contributions of partially reduced metal oxides is the stabilization of key reaction intermediates through the presence of oxygen vacancies (VO). These electron-rich defects function as active adsorption sites, thereby facilitating the binding and activation of CO_2 molecules. The enhancement of the formation and stabilization of

intermediates such as $^*\text{COOH}$ and $^*\text{OCHO}$ is influenced by oxygen vacancies, which in turn impact the subsequent formation of CO and formate. To illustrate this point, consider the case of SnO_2 -based catalysts. The deliberate generation of oxygen vacancies in these catalysts has been shown to correlate with an enhancement in formate selectivity. This is due to the stabilization of the $^*\text{OCHO}$ intermediate, which occurs preferentially over competing pathways [62]. Similarly, ZnO surfaces have been demonstrated to exhibit high CO selectivity, even in their partially reduced states. This finding suggests that active oxide sites persist under operational conditions and contribute directly to catalytic performance [63].

Furthermore, partially reduced metal oxides often exhibit a mixture of oxidation states on their surfaces, as exemplified by oxide-derived copper catalysts that feature Cu^0 , Cu^+ , and Cu^{2+} species [64]. This heterogeneity creates a dynamic and flexible surface environment where various intermediates can be stabilized through different adsorption configurations. The presence of Cu⁺ sites has been shown to be specifically correlated with enhanced C-C coupling, a critical step in the formation of multicarbon products such as ethylene and ethanol. In addition to stabilizing intermediates, the surface characteristics of partially reduced oxides have been shown to suppress competing reactions, notably the HER. The utilization of catalysts that exhibit a preference for the adsorption and conversion of CO_2 -derived species over protons has been demonstrated to enhance the Faradaic efficiency toward the formation of desired carbon-based products. The capacity of non- and partially reduced metal oxides to provide tailored active sites, facilitate multi-electron reaction pathways, and mitigate undesired side reactions positions them as highly effective and tunable materials for selective and efficient ECR.

In addition to pristine metal oxides, composite heterostructured oxide-based catalysts have demonstrated considerable application potential as efficient ECR catalysts. A variety of metal-oxide interfaces are of significance in this regard, not only as structural foundations but also as contributors to the overall catalytic performance [65]. At these junctions, electronic and structural synergies arise that modify the adsorption energies of CO_2 and its intermediates, enhance local electric fields, and tune the d-band center of the metallic phase. These interfacial phenomena create energetically favorable pathways for key reaction steps such as $^*\text{COOH}$ or $^*\text{CO}$ stabilization, C-C coupling, and proton-electron transfer [66]. Besides promoting direct catalytic activity through interfacial synergy, metal oxides serve a crucial function as catalyst supports for the ECR. Oxides like Cr_2O_3 and CeO_2 offer excellent chemical and electrochemical stability under the reductive potentials typically applied during CO_2 reduction. These materials are capable of maintaining their structural integrity and surface composition while enabling the uniform dispersion and anchoring of ECR active metallic nanoparticles (e.g., Ag) [67]. The stability of these supports under reaction conditions is essential for preventing nanoparticle aggregation and maintaining high electrochemical surface area throughout long-term operation.

Beyond their structural role, these oxides can also influence the local electronic environment at the metal-support interface. A characteristic example is the CeO_2 , known to possess oxygen storage capacity and a reversible $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple, which enables it to participate in dynamic surface charge transfer processes during catalysis. This can influence the electronic density of deposited metal particles, leading to modified intermediate binding and potentially altered product selectivity [21]. These oxide-supported systems offer several strategic advantages: (i) improved dispersion of supported catalytic sites, (ii) enhanced CO_2 adsorption at oxide-metal boundaries, and (iii) the suppression of side reactions (e.g., HER) through surface

polarity tuning. In addition, these supports often contribute to a more favorable electrochemical environment by affecting local ion distributions and double-layer capacitance, both of which are known to impact ECR kinetics [68].

Transition metal oxides (TMOs) have been identified as a class of materials with considerable potential for use as OER catalysts, particularly within an alkaline environment. The appeal of these materials can be attributed to three key factors. Firstly, their structural diversity plays a significant role in their appeal, as do their tunable electronic properties. Secondly, their ability to host a variety of oxidation states is a crucial factor. Transition metal oxides (TMOs) have the capacity to adopt a variety of crystal structures, including spinel (e.g., Co_3O_4), perovskite (e.g., LaNiO_3), and layered (e.g., NiO). These structures offer distinct catalytic sites and pathways for oxygen evolution. A significant development in the field of TMO-based OER catalysis is the emergence of mixed metal oxides, where the amalgamation of two or more transition metals results in a synergistic effect. For instance, NiFe oxides have repeatedly exhibited superior OER activity in comparison to their single-metal counterparts. The incorporation of Fe into NiO or $\text{Ni}(\text{OH})_2$ matrices has been demonstrated to increase the number of active sites while concomitantly modulating the electronic structure, thereby optimizing the adsorption energies of OER intermediates such as $^*\text{OH}$, $^*\text{O}$, and $^*\text{OOH}$ [69–71]. Similarly, the doping of other metals can introduce additional active sites, create oxygen vacancies, and enhance charge transfer. Cu-doped Co oxides have also demonstrated reduced overpotential and improved stability, attributed to lattice distortions and enhanced surface reactivity [72].

Defect engineering is another powerful strategy for boosting the OER performance of TMOs. Introducing oxygen vacancies, cation deficiencies, or lattice strain can significantly alter the electronic structure and increase the density of active sites [73]. For example, porous $\text{NiO}/\text{NiCo}_2\text{O}_4$ nanotubes with abundant oxygen vacancies have been shown to facilitate a four-electron OER pathway, achieving low Tafel slopes and high current densities [74]. The presence of defects not only enhances intrinsic activity but also improves conductivity, which is often a limiting factor for oxide catalysts. Morphology control, such as the synthesis of aerogels, nanowires, or hollow structures, further amplifies the catalytic performance by maximizing surface area and exposing more active facets. NiFe oxide aerogels, for instance, combine the benefits of high porosity and interconnected networks, leading to rapid mass transport and efficient charge separation [75]. Oxide phases offer a versatile platform for OER catalysis, with their performance tunable through compositional, structural, and morphological modifications. The ongoing development of mixed metal oxides, defect-rich materials, and hybrid structures continues to push the boundaries of OER efficiency and durability.

3.3 (Oxy)-hydroxide phases in electrocatalysis

Metal hydroxides represent a distinct and functionally versatile class of electrocatalytic materials, particularly in alkaline media, where they often serve as active phases or dynamic precursors to catalytically competent species. Their layered structures, rich in hydroxyl groups ($-\text{OH}$), enable reversible proton and electron transfer, thereby conferring remarkable electronic and chemical adaptability. These characteristics render them particularly pertinent in both the OER and the ECR contexts.

The emergence of hydroxide phases as critical components in ECR has been particularly pronounced in alkaline and near-neutral pH environments. The function of these elements extends beyond the provision of structural support, as they contribute directly to key aspects of the catalytic process, including intermediate stabilization,

interfacial charge modulation, and promotion of multicarbon product pathways. These materials frequently manifest as surface layers or discrete domains in hybrid systems, exhibiting distinctive electrochemical and chemical properties that enhance both activity and selectivity. A pivotal mechanism through which hydroxide phases promote ECR is through the modification of the local pH near the catalyst surface. This effect is especially significant when hydroxide species are formed or accumulated *in situ* during electrochemical operation. As demonstrated in the research conducted by Xiao et al., the development of hydroxide-rich layers on Cd-based catalysts has been shown to significantly increase the local pH level. This, in turn, has been observed to impede the competing hydrogen evolution reaction (HER) and to encourage the formation of carbon monoxide (CO) with Faradaic efficiencies that exceed 99% across a wide range of potential ranges [76]. The catalytic enhancement can be mechanistically attributed to several factors. First, the elevated local pH favors the deprotonation and activation of CO₂ molecules, facilitating the formation of key intermediates such as *COOH and *CO. These intermediates benefit from hydrogen bonding interactions with surface hydroxyls, which stabilize their adsorption and lower the energy barrier for subsequent reaction steps. In particular, *CO stabilization is crucial for efficient CO desorption or further reduction into multicarbon products on metal centers such as Cu. Secondly, hydroxide phases actively participate in forming dynamic and adaptive surface structures. Under ECR conditions, many metal catalysts can develop surface-reconstructed layers consisting of mixed metal-oxide-hydroxide domains. These layers serve as electron-rich interfaces, which alter the local electric field and improve the adsorption energetics of intermediates. For instance, in Cu-based catalysts, the presence of hydroxide has been linked to enhanced C-C coupling due to increased *CO coverage and stabilization of *OCCO intermediates—critical steps in the formation of C₂ + products [77, 78]. Additionally, hydroxide-containing interfaces such as metal-hydroxide junctions have been shown to enhance charge redistribution and interfacial electric fields, tuning the binding energy of intermediates. These properties enable not only improved CO₂ activation but also selective pathway steering by inhibiting proton adsorption and HER, enhancing the ECR. The structural and chemical flexibility of hydroxides under operating conditions allows them to function as dynamic catalytic components. They can regenerate or reconfigure during operation in response to potential changes, thereby maintaining active sites and suppressing deactivation phenomena observed in other oxide or metallic systems [79–81].

While oxide phases have traditionally been regarded as the primary OER catalysts, recent *in situ* and *in operando* studies have revealed that, under OER operating conditions, many TMOs and metallic precursors undergo surface reconstruction to form oxy-hydroxide phases (e.g., NiOOH, CoOOH, FeOOH). These oxyhydroxides have emerged as the true active phases responsible for the highest OER activity, particularly in alkaline media. The formation of oxy-hydroxide phases is a dynamic process, often initiated by the application of anodic potentials during OER. For example, Ni(OH)₂ is oxidized to NiOOH, while Co(OH)₂ transforms into CoOOH [82]. The presence of Fe is especially beneficial; Fe-doped NiOOH (NiFeOOH) exhibits dramatically enhanced activity compared to pure NiOOH. Fe incorporation induces lattice strain, modulates the electronic structure, and optimizes the adsorption energies of OER intermediates, resulting in lower overpotential and higher turnover frequencies [83, 84]. Recent *in operando* X-ray absorption and Mössbauer spectroscopy studies have identified high-valent Fe⁴⁺ species as key active sites in NiFe oxyhydroxides, persisting even after prolonged OER operation [85, 86]. Introducing chromium (Cr)

into the phase transition of metal (Fe, Co, or/and Ni) hydroxides creates an FeCoNiCr multimetal hydroxide phase to enhance the active OER phase, oxy-hydroxide, [87] by stabilizing high-valent $\text{Co}^{3+}/\text{Ni}^{3+}$ states, according to recent research. This synergistic effect surpasses the enhancements observed in Fe-doped systems alone. The presence of Cr promotes the formation of a more active $\beta\text{-NiOOH}$ phase, leading to improved OER kinetics. Furthermore, Cr can regulate the crystallization and phase homogenization of NiFe and CoFe oxide/hydroxides, inducing the formation of smaller, more homogenous nanodots [87–89].

Layered double hydroxides (LDHs) are recognized as highly effective pre-catalysts for the OER in alkaline water electrolyzers due to their unique structural and electronic properties. The layered structure of LDHs, composed of edge-sharing metal-hydroxide octahedra with intercalated anions, allows for significant compositional flexibility and the incorporation of multiple metal ions. This versatility enables LDHs to undergo dynamic surface reconstruction under OER conditions, transforming into catalytically active metal oxy-hydroxide phases such as NiOOH or FeOOH . To illustrate this point, consider the example of NiFe-LDHs, which can reconfigure into highly active NiFeOOH phases. This process results in low overpotential and enables expeditious redox cycling of the metal centers [90, 91]. Additionally, the high surface area of LDHs, especially when exfoliated into single-layer nanosheets, greatly increases the number of accessible active sites, leading to significantly enhanced OER activity compared to bulk materials and even surpassing benchmark catalysts like IrO_2 [92, 93]. The compositional flexibility of LDHs also allows for synergistic interactions between different metal ions, such as Ni and Fe in NiFe-LDHs, where Ni promotes charge transfer and Fe optimizes the adsorption energies of OER intermediates. This synergy results in catalytic performance that is outstanding, with LDHs demonstrating low overpotential at high current densities. In addition, the hierarchical and porous architectures frequently observed in LDH-based materials enhance mass transport and stability, thereby ensuring efficient operation even at industrially relevant current densities. It is evident that the aforementioned characteristics collectively render LDHs a versatile and powerful platform for the development of next-generation OER catalysts in water electrolyzers [94].

Oxy-hydroxides are characterized by higher electrical conductivity than their oxide counterparts, owing to the presence of hydrated layers and proton intercalation. This facilitates rapid transport and efficient electron transfer during OER. The electronic and structural properties of oxyhydroxides can be further tuned through doping, defect engineering, and the creation of heterostructures. For example, Mo-doped NiFeOOH has been reported to follow a heterogeneous diatomic oxygen mechanism, achieving exceptional activity in alkaline media [95–97]. While oxyhydroxides are highly active in alkaline environments, their stability in acidic media remains a challenge due to the dissolution of transition metal ions. Overall, oxy-hydroxide phases are now widely recognized as the true active catalysts for OER, with their formation and stability being key determinants of long-term performance. The dynamic interplay between oxide and oxy-hydroxide phases underscores the importance of *in situ* and *in operando* characterization techniques in understanding and optimizing OER catalysts.

4. Phase transitions and in situ catalyst evolution

Electrocatalytic systems frequently undergo dynamic phase transitions (Figure 2a) between metallic, oxide, and hydroxide states, thereby significantly

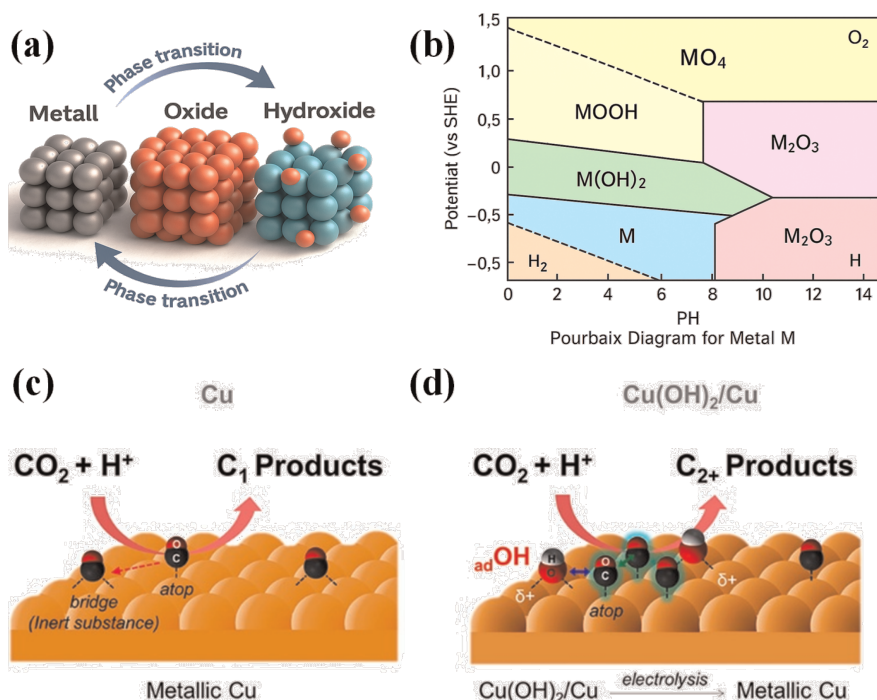


Figure 2. (a) Schematic representation of the main phase transitions to be observed in redox reactions for the different material phases. (b) Generic Pourbaix diagram for a metal (M) indicating the various phase transitions induced by overpotential and pH. (c) ECR reaction pathway over metallic Cu. (d) ECR reaction pathway over metallic-Cu(OH)₂ and its parallel non-Faradaic reduction to metallic-Cu; both figures (c and d) were reprinted after permission from Iijima et al. [98].

influencing catalytic activity, selectivity, and stability. The electrochemical environment is a driving force behind these transformations and is fundamental to key processes such as water splitting, nitrogen reduction, and carbon conversion. The Pourbaix diagram (**Figure 2b**) provides a thermodynamic framework for predicting the stable phase of a material as a function of pH and electrode potential.

4.1 Phase transitions in CO_2 reduction electrocatalysis

Phase transitions among metal, oxide, and hydroxide states play a crucial role in governing catalytic behavior during the ECR. These dynamic transformations, strongly influenced by parameters such as applied potential, electrolyte composition, and pH, can significantly alter the catalyst's surface composition, electronic structure, and reactivity [99]. One of the most impactful transitions is the reduction of metal oxides and hydroxides to their metallic state (**Figure 2c** and **d**) under cathodic conditions. This process gives rise to oxide-derived metals (OD-Ms), a class of catalysts that exhibit distinct physico-chemical properties compared to their pristine metallic counterparts. The formation typically begins with the electrochemical or thermal reduction of an oxide-based material, acting as the pre-catalyst [100]. This principle is applied to both pristine metal-oxide materials and composite oxide pre-catalysts. Leading to the formation of either single-phase OD-Ms or OD-metal alloys [101, 102]. This redox cycling results in the partial or complete removal of lattice oxygen, generating defects such as vacancies, dislocations, and grain boundaries. These structural features enhance the density of active sites and

alter the local electronic environment, while residual subsurface oxygen or oxide species may persist and further influence catalytic behavior [103, 104]. The transformation is often incomplete due to kinetic limitations, particularly in thicker oxide layers or under mild reduction conditions. The result is a mixed-phase surface composed of metallic, oxide, and/or hydroxide domains. These interfacial regions create a heterogeneous and highly active catalytic landscape, enabling alternative reaction pathways and offering a broad spectrum of binding sites not present on clean metal surfaces. Oxide-derived metals possess several key characteristics that make them particularly effective for ECR. Their defect-rich morphology, high surface area, and high grain boundary (GB) concentration improve CO₂ adsorption and intermediate stabilization, and overall, the ECR activity [105, 106]. The modified electronic structure—often reflected in shifts in the d-band center due to embedded oxygen species—alters the binding energies of crucial intermediates such as *COOH, *CO, and *OCHO, thus tuning both activity and product selectivity [107]. Furthermore, metal-oxide interfaces present in these materials contribute to intermediate stabilization via local electric fields and spatial confinement. Importantly, the partially reduced and defective surfaces also suppress the competing HER, thereby enhancing Faradaic efficiency for carbon-based products.

In addition to oxide-to-metal transitions, the reversible transformation between metal oxides and hydroxides plays an equally crucial role in tuning catalytic behavior for the ECR. The electrolyte pH has a significant influence on the stability and restructuring of these phases [81]. Under alkaline conditions, metal oxides readily convert to hydroxides due to the abundance of OH[−] ions, whereas acidic environments favor re-oxidation or dehydroxylation back to oxide phases. These phase transitions significantly affect the surface speciation and electronic properties of the catalyst, directly impacting the adsorption energies of key intermediates and, consequently, the activity and selectivity of the ECR. Notably, the formation of hydroxide layers during ECR is not a passive or inert phenomenon but a dynamic, in situ process that creates highly reactive surface states [98]. Hydroxide-rich layers have been shown to elevate the local pH, suppress the competing HER, and stabilize critical intermediates such as *CO and *OCCO—key precursors in C-C coupling pathways. These effects collectively promote the formation of valuable multicarbon (C₂⁺) products such as ethylene and ethanol, especially under alkaline electrolysis conditions. Hydroxide-derived metals (HD-Ms), obtained via electrochemical reduction of pre-formed metal hydroxides, exhibit catalytic properties distinct from their pristine metallic counterparts [108]. The reduction process introduces a high density of surface defects, such as vacancies, grain boundaries, and amorphous regions, that serve as catalytic hot spots. These structural features facilitate CO₂ adsorption and activation, while residual hydroxyl or subsurface oxygen species can modulate the electronic structure, finely tuning the binding strength of reaction intermediates. This is particularly evident in copper-based systems, where surface-adsorbed hydroxyls (OH_{ad}) can either enhance *CO adsorption and C-C coupling when optimally present or hinder activity by blocking active sites and promoting HER if in excess [76]. The hydroxide-to-metal transformation, therefore, is not merely a preparative step but a functional transition that defines the catalyst's performance. The structural and electronic complexity resulting from this transition enables enhanced selectivity toward C₂⁺ products by facilitating multistep reaction pathways and intermediate stabilization [109].

4.2 Phase transitions in oxygen evolution reaction (OER)

The OER in water electrolysis requires efficient electrocatalysts to overcome its inherently sluggish kinetics. LDHs have emerged as promising pre-catalysts due to

their ability to undergo in situ structural transformation into active metal oxyhydroxide phases under OER conditions. LDHs, with their general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}]_{x/n} \cdot mH_2O$, feature tunable metal cations (e.g., Ni, Fe, Co) and interlayer anions (e.g., NO_3^- , CO_3^{2-}) that enable dynamic reconstruction during electrochemical activation. Under anodic potentials, LDHs transition from their as-synthesized α -phase to catalytically active γ -phase oxyhydroxides (MOOH), characterized by $\sim 8\%$ lattice contraction and interlayer cation exchange (e.g., K^+ replacing anions). This structural evolution enhances electrical conductivity and exposes redox-active metal sites, as observed in NiFe-LDHs that form γ -NiFeOOH with optimized Ni^{3+}/Fe^{3+} coordination environments [110].

The phase transformation is driven by oxidative deprotonation and metal oxidation, facilitated by defects and dopants. For instance, Cr doping in FeCoNi hydroxides reduces the free energy barrier for $M(OH)_2 \rightarrow MOOH$ conversion by 10–22%, enabling faster activation [111]. Similarly, oxygen vacancies in $Sr_{1-x}Ca_xFe_2O_{6-\delta}$ perovskites boost conductivity by two orders of magnitude compared to defect-free analogs. *In situ* electrochemical atomic force microscopy reveals that strain-induced cracking and wrinkling in NiCo-LDH nanosheets during OER correlate with partial oxidation to $NiCoO(OH)_x$, highlighting the interplay between structural dynamics and activity [112]. These reconstructed oxyhydroxides follow a Mars-van Krevelen mechanism, where lattice oxygen participates in O-O bond formation via O-bridged Fe-M reaction centers ($M = Ni, Co$), lowering the energy barrier for *OOH deprotonation [113].

The effectiveness of LDHs as pre-catalysts originates from their layered structure, which ensures uniform distribution of metal cations and provides efficient ionic diffusion pathways. Dynamic interlayer anions such as NO_3^- disrupt the layered framework during electrochemical activation, generating structural disorder that produces highly defective interfaces. These defect-rich surfaces exhibit optimized electronic configurations and coordinative unsaturated sites, which directly boost catalytic performance by lowering activation barriers for intermediate adsorption [114]. Post-transformation, the resulting oxyhydroxides exhibit exceptional stability (e.g., FeCoNiCr hydroxide maintains 150-hour OER activity with a 224 mV overpotential) [111]. This *in situ* activation mechanism highlights the adaptability of LDHs as customizable frameworks for advancing high-efficiency OER catalysts.

The dynamic transformation between metal oxides and oxyhydroxides plays a key role in determining the performance and stability of OER electrocatalysts. Under anodic potentials, oxides such as NiO and Co_3O_4 transform into active oxyhydroxide phases (e.g., γ -NiOOH, CoOOH), which possess hydrated layered structures that facilitate efficient proton-coupled electron transfer and expose more active sites [115]. The stabilization of these oxyhydroxide species can be enhanced through doping and strain engineering; for example, Fe incorporation in NiOOH improves redox cycling and durability, while interstitial Si doping in RuO_2 suppresses unwanted lattice oxygen activity and enhances stability in acidic media [116]. Cation leaching and surface restructuring also play crucial roles. Controlled leaching, such as Mo from NiFe sulfides, can generate defect-rich, highly active surfaces and extend catalyst lifetime, but excessive leaching leads to structural degradation and loss of activity. Therefore, balancing reconstruction and leaching is key to achieving both high activity and long-term stability in OER catalysts. These findings underscore the importance of tuning oxide-hydroxide transformations and surface chemistry to design robust, efficient water-splitting electrocatalysts. These degradation pathways are exacerbated in acidic media, where lattice oxygen participation in OER (Mars-van Krevelen mechanism) induces crystalline phase collapse and irreversible surface amorphization [117].

4.3 Comparative analysis of phase interplay and stability

In the ECR, the stability and performance of catalysts are intricately linked to phase transformations occurring during operation, particularly in oxide-derived and hydroxide-transformed metal systems. Oxide-derived metals, such as copper, undergo partial reduction (e.g., $\text{Cu}_2\text{O} \rightarrow \text{Cu}^0$) under cathodic conditions, creating highly defective surfaces enriched with grain boundaries and undercoordinated sites that enhance activity and C-C coupling efficiency. However, these features also introduce vulnerabilities, such as structural coarsening, surface atom migration, and residual oxide instability, which compromise long-term durability under sustained operation [118–120]. Phase transitions between hydroxides and metallic copper (e.g., $\text{Cu}(\text{OH})_2 \rightarrow \text{Cu}^0$) also yield catalytically favorable morphologies but can suffer from dynamic reconstruction and uncontrolled subsurface oxidation or re-oxidation, especially at fluctuating potentials. Additionally, electrolyte-driven restructuring, including carbonate formation or cation exchange (e.g., K^+ or Na^+ adsorption), can lead to loss of active phase, catalyst delamination, and suppression of multicarbon product pathways [121, 122].

To address these degradation pathways, recent strategies have focused on controlling redox transformations and interfacial composition. Pre-conditioning oxide catalysts under reducing potentials enables the formation of thermodynamically stabilized defect sites while minimizing over-reduction or collapse of active regions [123]. Doping approaches have been shown to modulate electronic structures and maintain surface roughness essential for C-C coupling while simultaneously mitigating agglomeration and phase collapse. Composite catalyst systems, particularly metal-oxide and metal-hydroxide hybrids (e.g., Cu-CeO_2 , $\text{Cu-Ni}(\text{OH})_2$), further enhance operational robustness by offering lattice strain buffering and dual-functionality in CO_2 activation and proton management. These heterojunctions facilitate charge redistribution and stabilize reactive intermediates like $^*\text{CO}$ or $^*\text{CHO}$ through synergistic interfacial fields. Operando studies reveal that maintaining partial oxide features under bias—rather than a complete reduction—is critical for preserving selectivity toward C_2 + products [124–126].

The interplay between oxide and oxy-hydroxide phases during OER directly impacts catalytic stability and degradation pathways. In operational conditions, catalysts are subject to dynamic structural transformations, including hydroxylation of metal oxides (e.g., $\text{NiO} \rightarrow \gamma\text{-NiOOH}$) and sulfur-oxygen exchange in sulfides. These processes expose active sites and concomitantly trigger destabilizing processes, such as cation leaching and phase over-oxidation [127].

Strategies to stabilize active phases focus on modulating reconstruction pathways. Doping high-valent cations (e.g., Mo in NiFeOOH) strengthens metal-oxygen bonds, suppressing over-oxidation and maintaining γ -phase integrity under high potentials [128]. Similarly, strain engineering in perovskites like $\text{SrCo}_{0.9}\text{Fe}_{0.1}\text{O}_{3-\delta}$ stabilizes metastable phases with optimal oxygen vacancy densities, enhancing conductivity while resisting segregation [129]. For layered double hydroxides (LDHs), Cr doping promotes homogeneous cation distribution, delaying phase separation during OER and enabling 150-hour stability [130]. These approaches highlight the balance required between activity-enhancing phase transitions and structural preservation, guiding the design of catalysts that reconcile high performance with operational durability [131, 132].

5. Conclusion

The ECR is highly sensitive to the structural and electronic properties of the catalyst, which are governed by dynamic phase transformations. Oxide-derived metals (O-DMs) have emerged as highly effective electrocatalysts due to their defect-rich surfaces and altered electronic structures resulting from oxide-to-metal reduction. These structural features stabilize key intermediates such as $^*\text{CO}$ and $^*\text{OCCO}$, thereby promoting multicarbon (C_{2+}) product formation. Subsurface oxygen residues and grain boundaries in O-DMs have been shown to shift the d-band center, thereby tuning the adsorption energies of intermediates and enhancing reaction selectivity. Furthermore, in situ studies demonstrate that such catalysts are not static but undergo dynamic restructuring under operating conditions, thereby continuously regenerating active sites. Furthermore, the integration of oxides such as CeO_2 or ZnO within composites has been demonstrated to enhance CO_2 activation through the introduction of synergistic effects and oxygen vacancies, thereby facilitating enhanced electron transfer. While contemporary strategies have considerably enhanced selectivity and activity, challenges persist in the domains of long-term stability control and atomic-level phase behavior comprehension.

The catalytic performance of transition metal-based materials for the OER is intricately linked to their phase composition and dynamic transformations under operating conditions. Metallic phases function as conductive precursors, thereby facilitating the formation of catalytically active surfaces. Oxide phases offer structural versatility and tunable electronic properties, with their performance further enhanced by defect engineering, morphology control, and compositional tuning. In conclusion, it is the oxy-hydroxide phases that are formed in situ during OER that host the most active sites and drive the reaction with the highest efficiency, particularly when doped synergistically with elements such as Fe or Cr.

Recent advances in in situ and in operando characterization have enhanced the understanding of dynamic phase transitions in electrocatalysts, enabling more rational and targeted design strategies. Recent research has focused on the use of doping, defect engineering, and strain modulation to direct surface reconstruction and optimize active site exposure and electronic structure. In future research, the focus should be on enhancing the stability of oxy-hydroxide phases, particularly in acidic environments. Future efforts should also focus on developing hybrid materials with tunable interfaces, leveraging computational modeling, and applying machine learning to predict and control phase behavior. The integration of real-time diagnostics to monitor structural evolution under operating conditions has the potential to further accelerate the development of efficient, stable, and earth-abundant catalysts, thereby advancing the deployment of sustainable electrochemical energy technologies.

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