

Review Article

Mechanistic understanding of electrode corrosion driven by water electrolysis

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Abstract

Corrosion is one of the most complicated phenomena in physical chemistry. In electrocatalysis, including water electrolysis and fuel cells, corrosion of electrodes is often triggered by catalyzed interfacial reactions. However, researchers are only now beginning to unravel the mechanistic interplay between electrocatalytic activity and electrochemical stability of electrode materials. Here, we review recent efforts in the area of computational electrocatalysis of water splitting to obtain atomic-scale insights into the degradation pathways of anode and cathode materials. This knowledge is crucial for the rational design of corrosion-resistant catalysts for both fresh- and seawater electrolysis, as well as for the choice of operating conditions. We also stress that computational modeling of elementary steps of electrode corrosion is pertaining not only to materials stability, but also to electrocatalytic behavior since activity and stability of catalysts are intimately but nontrivially coupled.

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Water splitting, Electrocatalysts, Activity, Stability, Reaction mechanisms.

Introduction

Corrosion is a classic problem in electrochemistry. In electrocatalytic applications, either to convert environmentally relevant small molecules such as H₂O, CO₂, O₂, and N₂ into energy carriers and value-added

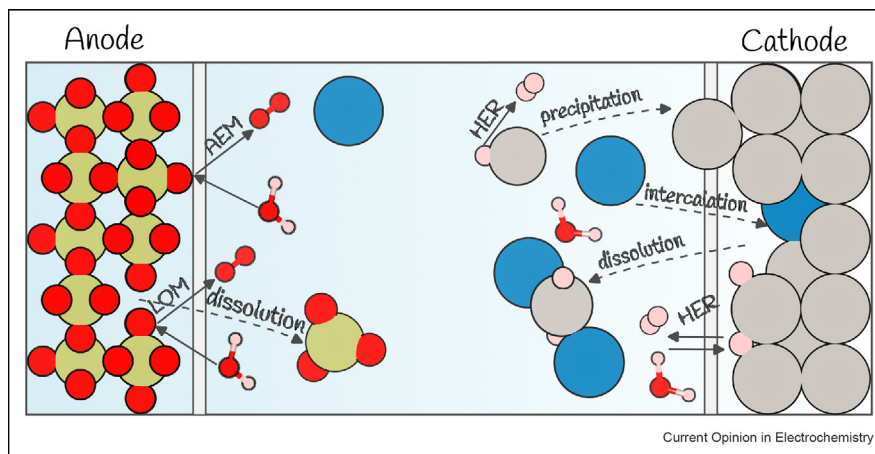
chemicals or to carry out more complex organic electrosynthesis, electrodes are known to corrode [1–4]. Previous experimental studies have provided a great deal of knowledge about electrocatalytically driven corrosion under both reductive and oxidative reaction conditions. However, it is only recently that we have started building atomic-scale connections between activity and corrosion of electrocatalysts. In this regard, quantum-mechanical based simulations are well poised to bring complementary mechanistic insights.

While corrosion is clearly not limited to electrochemical water splitting systems, water is the most common media for a variety of reactions in electrocatalysis. Therefore, it is typical that electrochemical reduction reactions would compete with the hydrogen evolution reaction (HER) at the cathode, whereas oxidative processes would compete with the oxygen evolution reaction (OER) at the anode. Given the significance of electrochemical splitting of water as a promising energy conversion technology, most research efforts so far have focused on unveiling degradation mechanisms for this process. Therefore, in this opinion we will focus on electrode corrosion driven by water electrolysis, especially discussing recent theoretical progress in developing our basic understanding of associated reaction mechanisms.

Figure 1 schematically illustrates a multitude of the interfacial processes occurring during electrocatalytic water splitting at both anode and cathode sides. These include surface oxidation/hydrogenation, metal dissolution/precipitation, surface restructuring, and catalyzed reactions along different reaction pathways. Their interrelated nature and nontrivial dependences on control parameters such as electrode potential and solution pH make simulations a formidable task and require consideration of model subprocesses such as a specific OER mechanism or a single-species dissolution event. However, recent progress in coupling first-principles simulations with machine learning approaches is bringing a better understanding of the collective behavior of complex catalytic interfaces [5–8].

One of the reasons for a limited theoretical understanding of electrocatalytically triggered corrosion mechanisms is that the majority of computational

Figure 1



Schematic illustration of possible interfacial processes, occurring during water splitting at the anode (left) and cathode (right). Dark yellow, red, gray, and pink colors stand for Ir, O, Pt, H, respectively. Dark blue represents the alkali metal cation. Abbreviations AEM, LOM, HER are used for the adsorbate evolving mechanism, lattice oxygen mechanism, and hydrogen evolution reaction, accordingly. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

studies so far has focused on evaluating the OER activity rather than stability. Moreover, this has been almost exclusively done for model surfaces neglecting structural and chemical evolution of the catalyst's surface during the OER. However, it is established that dynamic surface-state changes, including corrosion, during catalyzed reactions largely determine both the mechanism and kinetics of the overall catalytic processes [4,9–14]. From an experimental perspective, the challenge is to detect highly reactive and thus short-lived reaction intermediates at complex electrode/electrolyte interfaces. Therefore, it is important to perform dedicated theory-experiment investigations to interrogate corrosion mechanisms that will also shed light on the catalytic activity of materials. It is also worth pointing out that currently there are no universal theoretical frameworks for evaluating electrochemical stability except Pourbaix diagrams. While this approach, based solely on equilibrium thermodynamics, can be used to analyze thermodynamic driving forces of materials instability, it is however far from sufficient and cannot provide atomistic information about electrode corrosion mechanisms under electrocatalytic conditions.

In this opinion, we will review recent progress in the area of computational first-principles modeling aimed to unveil atomic-scale mechanisms of electrode corrosion triggered by electrocatalytic water splitting reactions. These computational efforts will be discussed in close connection with available experimental investigations. Here, we are primarily concerned with noble metal-based materials as most active and stable water-splitting catalysts. In what follows, we will first concentrate on anodic corrosion occurring under

oxidative reaction conditions and then cathodic corrosion will be discussed. In the end, we will provide some conclusions and outlook.

Anodic corrosion

Electrode corrosion under oxidative reaction conditions has been the primary focus of prior investigations. As a result, anodic corrosion is much better studied than cathodic corrosion that will be discussed in the next section. Nevertheless, our basic understanding of the mechanistic relationship between electrocatalytic surface processes and corrosion mechanisms remains rather limited even for anodic processes. Under anodic polarization the metal electrode becomes oxidized forming a metal-oxide surface layer that promotes metal dissolution into the electrolyte in the form of positively charged ions. However, how the mechanism and kinetics of this process depend on the magnitude and the nature (constant, dynamic) of electrode polarization, and the composition of the electrode and electrolyte is the subject of ongoing research.

In the context of oxygen electrocatalysis, a recent thermodynamic analysis revealed a fundamental and universal correlation between the OER activity and the corrosion of metal oxides [15]. Specifically, it was demonstrated that any metal oxide becomes thermodynamically unstable under the OER conditions irrespective of solution pH due to instability of the oxygen anions in the metal oxide lattice. It was shown that under OER conditions, the thermodynamic driving force for the OER via the lattice oxygen mechanism (LOM) is equal or even more negative than that for the oxygen evolution from the electrolyte at a fixed electrode

potential. It should be pointed out that the participation of lattice oxygen atoms in the OER is not taken into account in purely equilibrium Pourbaix stability diagrams. In previous years, the LOM has been mostly analyzed as an alternative to the conventional adsorbate evolving mechanism (AEM) in light of the OER activity [16,17]. To this end, the established computational hydrogen electrode (CHE) approach is employed to estimate theoretical OER overpotentials [18]. However, the mechanistic role of the LOM in electrochemical stability of OER catalysts remains unclear.

Although the LOM does lead to the breaking of lattice metal-oxygen bonds, this mechanism does not automatically imply catalyst degradation. This is because other factors including the kinetics of lattice oxygen participation and metal dissolution should also be analyzed [2,19]. For instance, by employing isotope labelling with atom probe tomography, online electrochemical and inductively coupled plasma mass spectrometry, it was revealed that the LOM results in faster degradation and dissolution of Ir species in electrochemically formed hydrous IrO_x catalysts than in rutile IrO_2 under OER conditions [20]. In the SrIrO_3 OER electrocatalyst, amorphization was found to be initiated by the lattice oxygen redox that promotes coupled Sr^{2+} and O^{2-} diffusion facilitating further structural reorganization [21]. The involvement of lattice oxygen in the OER was also proposed to be a source of structural reorganization triggering metal dissolution in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ [22]. On the other hand, despite experimentally detected substantial dynamic lattice oxygen exchange during the OER for epitaxial LaNiO_3 thin films, no significant deterioration of surface crystallinity was observed [23].

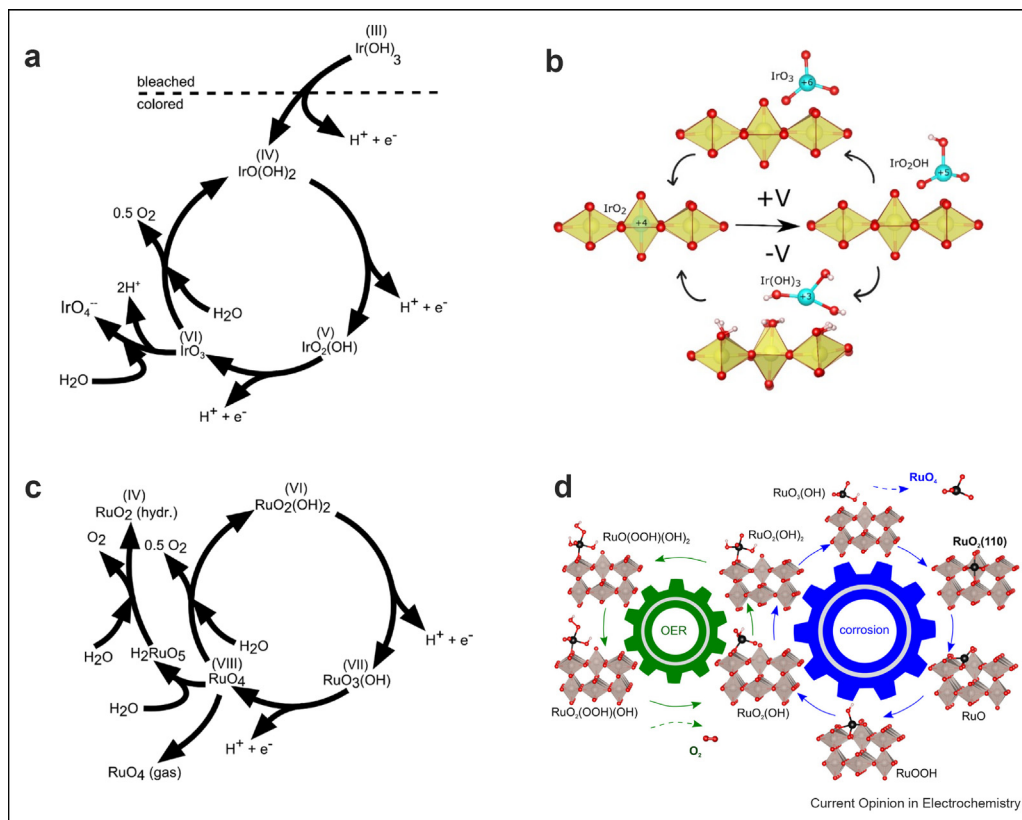
In a recent concept article, Exner critically discussed the correlation between the AEM and LOM pathways, and catalyst instability [19]. Given that the theoretical work of Binniger *et al.* is purely thermodynamic [15], the main emphasis was put on the role of OER kinetics. To this end, the free-energy diagram approach involving an overpotential-dependent activity descriptor $G_{\text{max}}(\eta)$ was applied. The purpose of $G_{\text{max}}(\eta)$ is to mimic kinetic effects by evaluating the free-energy difference between the intermediate with smallest and highest free energy as a function of the applied overpotential [24]. The suggested approach, however, also requires the knowledge of the activity of the metal ions as a result of metal dissolution into the solution during the LOM. This can significantly influence the competition between the LOM and AEM pathways. It was conceptually demonstrated that although the LOM is competitive with the AEM at low activities of dissolved M^{4+} , the AEM should become energetically more favorable (i.e., lower $G_{\text{max}}(\eta)$) as the concentration of metal ions in the electrolyte increases. It should be noted, however, that the AEM pathway may also trigger

dissolution of metals, e.g., at defective sites [25]. Therefore, it is likely that the concentrations of metal ions in solution due to both OER mechanisms should be considered when constructing a more complete model of metal-oxide instability.

It is also worth briefly discussing recent studies focusing on identification of the overall mechanism of metal dissolution that is triggered by the OER. For example, a series of experimental investigations aimed to unveil transition-metal dissolution pathways in the state-of-the-art Ir- and Ru-based OER electrocatalysts. As early as in 1984, Kötter *et al.* employed *ex situ* X-ray photoelectron spectroscopy (XPS) to examine IrO_2 films and proposed a reaction path for O_2 evolution and corrosion of IrO_2 as schematically depicted in Figure 2a [26]. More recent studies based on inductively coupled plasma mass spectrometry (ICP-MS) have been especially instrumental in pinpointing the mechanistic correlation between the OER and metal dissolution pathways [20,27,28]. This approach enabled observation of common intermediates of oxygen evolution and dissolution products during water electrolysis [27]. On the basis of the obtained data, at least three possible dissolution pathways of Ir-based catalysts were proposed depending on the nature of the electrode material (metallic Ir and its oxides) and applied potential.

To complement these experimental efforts, a number of studies employed DFT calculations to monitor the formation of reaction intermediates during the dissolution of transition metals from the metal-oxide surface into the aqueous solution. For instance, in a recent study [29] Ir dissolution at the $\text{IrO}_2(110)/\text{water}$ interface was investigated using *ab initio* molecular dynamics (AIMD) simulations in conjunction with thermodynamic integration. It was revealed, in agreement with prior experiments [27], that the adsorbed IrO_2OH dissolution intermediates are thermodynamically stable in a relatively broad potential range transforming into either Ir(VI) as IrO_3 species at higher potentials or Ir(III) as $\text{Ir}(\text{OH})_3$ species at lower anodic potentials, respectively. The found dissolution mechanism is illustrated in Figure 2b. Similar first-principles simulations were undertaken to model Ru dissolution from rutile RuO_2 surfaces [32–34]. For example, the Ru dissolution mechanism from $\text{RuO}_2(110)$ facet derived from DFT simulations [32] turned out to be consistent with a previously proposed mechanism [30,35] involving the transformation of the surface-bound $\text{RuO}_2(\text{OH})_2$ intermediate via RuO_3OH into aqueous RuO_4 as the final dissolution product (see Figure 2c,d). Overall, it appears that despite a number of approximations involved in these modeling studies, they provide extremely valuable information about dissolution mechanisms that is not available from thermodynamic Pourbaix diagrams. This includes critical insights into the formation, evolution, stability and reactivity of metastable dissolution

Figure 2



Proposed electrochemical cycles for the OER and corrosion of the IrO₂ (upper panel) and RuO₂ (lower panel) electrodes. Figures (a) and (c) represent experimentally hypothesized mechanisms, while figures (b) and (d) show the pathways with corresponding reaction intermediates as obtained from first-principles simulations. Reprinted with permissions from Kötz et al., Zagalskaya et al., Kötz et al., Klyukin et al. [26,29–31].

intermediates [29,32–34,36,37]. Future studies should go beyond single-event analyses based on enhanced sampling techniques by incorporating coupled interfacial processes during the OER such as surface oxidation, restructuring and metal dissolution. In this regard, recent advancements in the area of deep machine learning tools capable of efficient sampling multiple rare events in many-body systems hold great promise [8,38].

Materials doping is a common strategy to modify the properties of electrocatalysts. Doping can be employed not only to tune catalytic activity of an electrode, but also to enhance its electrochemical stability. For example, it was experimentally demonstrated that mixing IrO₂ with TiO_x in a wide composition range results in much improved electrochemical stability under the OER conditions [39]. The underlying reason for this result is that TiO₂ is thermodynamically stable under highly acidic and oxidizing conditions of the OER [40]. Importantly, it was found that mixtures containing 40–50 at.% of Ir exhibit OER reactivity comparable to thermally prepared IrO₂ with very low metal dissolution as indicated by the ICP-MS measurements. Specifically,

the S-number of $1.5 \cdot 10^6$ for Ir_{0.5}Ti_{0.5}O_x is close to $9.2 \cdot 10^5$ reported for thermally grown IrO₂. Qualitatively similar results for the activity-stability characteristics were obtained for Ti-doped RuO₂ [41]. It was found that Ti substitution of up to 20 at.% improves stability and lowers Ru dissolution. DFT calculations showed that the AEM on Ru sites is the most favorable reaction pathway. By using AIMD simulations it was also demonstrated that Ru dissolution becomes less favorable (higher kinetic barriers) as the concentration of Ti dopants increases, in agreement with experimental observations.

Recently, the role of electrolyte chemistry including the effects of redox-inactive “spectator” species on electrocatalytic activity has been gaining growing attention. However, modeling studies taking into account the effects of solution pH, electrolyte composition and solvent dynamics in materials degradation pathways are not that common. For example, it was previously demonstrated that the competition between surface restructuring and reoxidation kinetics as a response to the ongoing OER process should play an important role in

the electrochemical stability of electrodes [36,42]. The mechanistic role of electrolyte chemistry in electrode corrosion becomes of central practical significance in applications such as seawater electrolysis.

Given the scarcity of freshwater resources in the world, direct electrolysis of seawater, which is one of the most abundant resources on Earth, represents an appealing strategy for green hydrogen production [43,44]. However, this technology faces a number of challenges among which are severe electrode corrosion, the competition between the oxygen and chlorine evolution reactions at the anode, and precipitation of insoluble alkali-earth hydroxides and carbonates. It is established that abundant Cl^- species in seawater solutions can lead to the undesired formation of metal-chloro complexes on both the cathode and anode accelerating electrode corrosion [45]. Recent computational efforts brought some valuable information about the Cl^- -induced initiation of materials corrosion. For example, a series of theoretical works focused on unveiling fundamental mechanisms responsible for the breakdown of some passivating oxide layers such as Al_2O_3 and Cr_2O_3 [46–48]. In the case of Al_2O_3 interfaces, it was shown through DFT thermodynamics calculations that electrochemical insertion of Cl^- from solution into pre-existing oxygen vacancies could be energetically favorable depending on the oxide structure, the presence of grain boundaries and applied voltage [47]. However, such modeling studies focusing on water-splitting electrocatalysts are still quite rare. Nevertheless, these mechanistic investigations are necessary for the rational design of corrosion-resistant electrodes and development of corrosion-mitigation strategies in seawater electrolysis. For instance, it was experimentally demonstrated that in situ-generated polyanion-rich passivating layers formed at the $\text{NiFe/NiS}_x/\text{Ni}$ anode are responsible for repelling of Cl^- anions thus enhancing corrosion resistance of the electrode [43]. Overall, strategies that impede adsorption of Cl^- appear to hinder the destructive Cl^- ingress into the electrode structure [49]. Yet, recent DFT calculations revealed a strong correlation between the O and Cl chemisorption enthalpies indicating a fundamental challenge for the design of stable and selective seawater electrocatalysts. The existence of this scaling relationship complicates the decoupling of water and chlorine oxidation processes [50,51].

Cathodic corrosion

Corrosion of electrodes occurring under reductive potentials is much less understood than anodic corrosion. This is in part due to the phenomenon of cathodic protection observed by H. Davy back in 1824. The idea behind cathodic protection is to avoid metal oxidation by making it thermodynamically unfavorable via reducing the electrochemical potential of the metal.

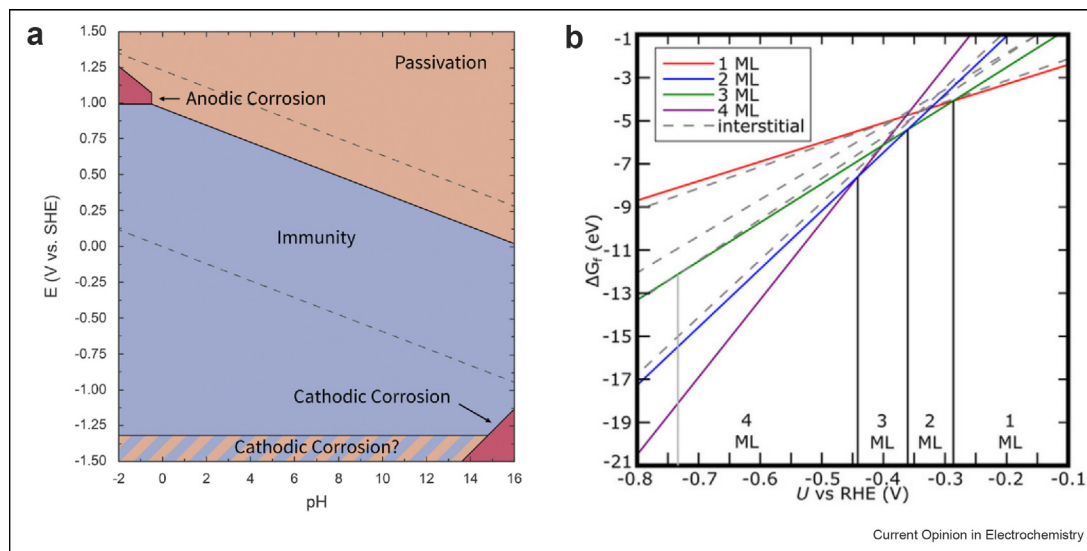
This can be achieved, e.g. by connecting the metal to be protected to a more electropositive sacrificial metal that will undergo preferential corrosion. Nevertheless, at sufficiently negative electrode potentials the protected metal will still suffer from cathodic corrosion.

While being known for more than a century since its first observation by F. Haber in 1898, cathodic corrosion has started attracting an increasing attention only in the past decade. This interest has been driven by both fundamental reasons and interesting practical applications of cathodic corrosion such as synthesis of nanocatalysts with highly controlled morphology. Here, we refer to a nice recent overview of the topic [52]. In this section, we aim to briefly discuss recent theoretical progress in understanding the atomic-scale mechanisms underlying cathodic corrosion.

It was revealed in experiments that not only the electrode nature, but also the electrolyte composition have substantial effects on the cathodic corrosion rates and the resulting morphologies of nanoparticles [52–55]. For example, it was demonstrated that corrosion of Pt, Rh, and Au in LiOH, NaOH, and KOH solutions becomes more pronounced at higher cation concentrations and when changing the electrolyte from LiOH to KOH [56]. Therefore, it was suggested that electrolyte cations should play an important role in cathodic corrosion phenomenon. In addition, since cathodic corrosion was not observed in the absence of water, it was proposed that both cations and hydrogen species may adsorb on the metal surface and possibly form ternary metal hydrides as metastable dissolution intermediates [52,56].

In a previous DFT study, it was determined that alkali metal cations can indeed compete with hydrogen species from water for adsorption sites at sufficiently negative electrode potentials [58]. For example, it was found by computing cation adsorption equilibrium potentials across a number of fcc metals that specific cation adsorption is most favorable on Pt(111) but may also occur on other metals with the overall order of $\text{Pt}(111) > \text{Pd}(111) > \text{Ni}(111) > \text{Ag}(111), \text{Au}(111)$. In a more recent DFT investigation, cathodic corrosion of Pt was modeled in a more direct way by simulating Pt dissolution into the electrolyte from the (111) surface covered by both H and Li species under constant-potential conditions [59]. To this end, constant Fermi-level AIMD simulations in conjunction with the thermodynamic integration method were employed. This approach enabled the observation of how cathodically dissolving Pt species are evolving at the electrode/electrolyte interface under experimentally relevant conditions of constant potential. The study revealed the formation of metastable Pt hydrides stabilized by alkali cations at the interface as cathodic corrosion intermediates. These Pt dissolution intermediates were

Figure 3



a) Modified Pourbaix diagram for platinum, including the cathodic corrosion region. **b)** Computational phase diagram for surface platinum hydrides. Reprinted with permissions from Hersbach et al., Hanselman et al. [52,57].

found to be stabilized in the uncommon for Pt aqueous chemistry negative oxidation state making them extremely reactive. Indeed, it was shown that these intermediates can discharge at the interface by reacting with solution H_2O molecules to yield H_2 . It was also shown that at more cathodic potentials the oxidation state of Pt atoms of the dissolving intermediates becomes more negative and the thermodynamic driving force to produce H_2 gets much greater. It should be pointed out, however, that this study employed a model Pt(111) surface considering only underpotential deposited hydrogen (H_{upd}). It was sufficient to demonstrate conceptually that ternary Pt hydrides can form under cathodic polarizations, but the study could not provide insights into how the chemical composition of these corrosion intermediates can vary depending on reaction conditions.

In another DFT based investigation the formation of multilayer (sub)surface hydride structures on Pt(111) was analyzed from a thermodynamic point of view [57]. Such high-density Pt surface hydride phases are indeed expected to form under strongly reducing conditions of cathodic corrosion. However, experimentally it is challenging to decipher the level of surface hydrogenation since cathodic corrosion starts at more negative potentials than the onset of the HER. In this work, thermodynamic stability of a variety of possible Pt surface hydride structures up to 4 ML of hydrogen as a function of electrode potential was analyzed based on DFT calculated stability diagrams (see Figure 3b). Onset potentials for their formation from clean Pt(111) were obtained using the computational hydrogen electrode

(CHE) method. To make the model more tangible, the authors had to ignore a few key factors such as the presence of adsorbed alkali cations, dynamic H-driven surface restructuring and the role of explicit electrode potential. Nevertheless, the study provided further atomistic insights into the mechanism of cathodic corrosion. For instance, the formation of a remarkably stable phase containing 3 ML of atomic hydrogen was suggested as a possible precursor for cathodic corrosion. Further investigations are necessary to fully disentangle various factors affecting cathodic corrosion mechanisms from both thermodynamic and kinetic points of view.

Conclusions and outlook

In this contribution, we discussed a series of recent investigations aimed to gain mechanistic insights into corrosion of cathode and anode materials under the conditions of electrocatalytic fresh- and seawater splitting. Although such studies, both experimental and computational, fall far behind current efforts focusing on catalytic activity, they are critical for our fundamental understanding of the complex interplay between mechanisms of corrosion and electrocatalytic reactions. We would like to stress that despite widespread use of Pourbaix diagrams for the analysis of thermodynamic stability of electrode materials, further atomic-scale insights are necessary for a comprehensive understanding of aqueous corrosion from both thermodynamic and kinetic standpoints. In this regard, first-principles based computational techniques offer a way to examine such reactions by modeling elementary steps at electrocatalytic interfaces under well controlled conditions. We

also suggest that future computational investigations should go beyond modeling of isolated reaction events and account for the collective dynamic nature of reacting/corrosion interfaces. This will help uncover complex interrelationships between various interfacial sub-processes. Recent advances in combining DFT and machine learning methods, for example, to overcome limitations related to efficient sampling of multiple metastable states, show particular promise in this respect. Also, we believe that more studies should be devoted to understanding the effects of electrolyte chemistry on electrochemical stability of electrodes similar to recent investigations focusing on how electrolyte species modify electrocatalytic activity.

Declaration of competing interest

The authors declare the following financial interests/personal relationships that may be considered as potential competing interests: Vitaly Alexandrov reports financial support was provided by University of Nebraska-Lincoln.

Data availability

No data was used for the research described in the article.

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