On the Lattice Oxygen Evolution Mechanism: Avoiding Pitfalls

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**Thermodynamics & activity of lattice oxygen evolution**

\[
\eta_{\text{LOER}} = f([\text{M}^{4+}]_{\text{solution}})
\]

@ \( U = 1.23 \) V vs. RHE
The oxygen evolution reaction (OER) is often designated as the enigma in water electrolysis because the development of active and stable OER catalysts is a challenging and formidable task. While ab initio theory in the density functional theory approximation initially focused on the mechanistic description via the OH, O, and OOH adsorbates, in recent years the lattice oxygen evolution reaction (LOER) mechanism attracted increasing attention, given that the LOER is seen as the main reason for catalyst instability under anodic potential conditions. The present concept article critically analyzes the LOER and indicates pitfalls in the interpretation of this mechanistic pathway. A method to assess the energetics of the LOER in relation to conventional OER mechanisms by the compilation of free-energy diagrams is introduced, which may contribute to enhance our understanding of the competing LOER and OER on the atomic scale. Further works are urgently needed to comprehend the interrelationship for the evolution of gaseous oxygen from the electrolyte or the crystal lattice.

1. Introduction

Development of energy storage systems to capture energy produced from renewables is vital for the progress of a sustainable energy economy. One opportunity is electrochemical splitting of water by electrolysis to produce the energy vector $\text{H}_2$. The water splitting consists of the hydrogen (HER) and oxygen (OER) evolution reactions at the cathode and anode, respectively. The HER is a simple two-electron process, which is best catalyzed by platinum (Pt). Despite the scarcity of Pt, the HER is not identified as a bottleneck, given that already low Pt loadings of about (0.5–1.0) mg/cm$^2$ at the cathode reveal reasonable HER activity.$^{[1]}$ A different situation is encountered with the anodic OER, the enigma in water electrolysis.$^{[2]}$ Here, $\text{IrO}_2$ corresponds to the best catalyst when taking both activity and stability into account, while $\text{RuO}_2$ is more active but less stable than $\text{IrO}_2$. Both Ir and Ru are critical elements due to their price and natural abundance, but even more precarious is the fact that the most active OER catalysts are significantly less effective compared to the performance of Pt in the HER. While the HER can be catalyzed by low Pt loadings at applied overpotentials of about 50 mV (to reach a current density of about 10 mA/cm$^2$), the OER overpotential for 10 mA/cm$^2$ is in the order of 300 mV, that is, a factor of six higher.$^{[3]}$ Given that the HER is a two-electron process, whereas the OER corresponds to a four-electron process, the factor of two relating to the different amount of electrons transferred does not fully account for the low OER activity. On the atomic scale, the humble OER activity is traced to a scaling relation ($\Delta G_3 + \Delta G_4 = \text{const.}$) in the so-called mononuclear OER mechanism,$^{[4]}$ which reads (Eqs. (1)–(4)):

$$M + \text{H}_2\text{O} \rightarrow M - \text{OH} + \text{H}^+ + e^- \quad \Delta G_1$$
$$M - \text{OH} \rightarrow M - \text{O} + \text{H}^+ + e^- \quad \Delta G_2$$
$$M - \text{O} + \text{H}_2\text{O} \rightarrow M - \text{OOH} + \text{H}^+ + e^- \quad \Delta G_3$$
$$M - \text{OOH} \rightarrow M + \text{O}_2(g) + \text{H}^+ + e^- \quad \Delta G_4$$

In the above equations, $M$ refers to the catalytically active surface site, e.g., an undercoordinated metal surface atom. The formation of $\text{O}_2$ requires stabilization of the intermediate species $\text{OH}$, $\text{O}$, and $\text{OOH}$ on the active site [cf. Eqs. (1)–(4)]. The observed scaling relation affects the $\text{OH}$ and $\text{OOH}$ adsorbates, rendering that the adsorption free energies $\Delta G_3$ and $\Delta G_4$ cannot be tuned independently.$^{[5]}$ Consequently, breaking the $\text{OH}$ vs. $\text{OOH}$ scaling relation is seen as a universal remedy to enhance OER activity.$^{[6]}$ However, so far, no major progress could be achieved following this strategy, which is backed up by the fact that the breaking of the $\text{OH}$ vs. $\text{OOH}$ scaling relation has been identified as a mandatory, yet insufficient criterion for high OER activity.$^{[7]}$ While a discussion about the implications of breaking this scaling relation can be found elsewhere,$^{[8]}$ the present concept article does not address OER activity and scaling relation, but rather sets stability, and thus the intimate interplay between the adsorbate and lattice oxygen evolution mechanisms in the foreground. In the following, the interrelationship between the adsorbate and lattice oxygen evolution is discussed, and how the competition between these two pathways can be captured by the construction of free-energy diagrams on the atomic scale. It is concluded that the current implementation of the oxygen evolution from the lattice by ab initio theory is insufficient, thus rendering the necessity of further theoretical studies to gain a fundamental understanding of the lattice OER and its correlation to the formation of gaseous oxygen from the electrolyte.

2. Results and Discussion

2.1. Lattice oxygen evolution reaction (LOER)

The lattice oxygen evolution reaction (LOER) is commonly viewed as the main reason for the lacking long-term stability of electrode materials in the OER,$^{[9]}$ particularly reported for acidic electrolyte solutions.$^{[10]}$ Besides the mononuclear pathway [cf.
LOER. A potential opportunity to monitor the evolution of gaseous oxygen from the lattice refers to online electrochemical ship between catalyst stability under OER conditions and the mass spectrometry (OLEMS). Yet, there is a discrepancy in the literature on the relation-ship between catalyst instability and the LOER pathway, with prolongated operational time. This argument may substantiate the correlation between the LOER and catalyst instability, though, that this thermodynamic analysis does not provide any information on the potential occurrence of the LOER because the LOER kinetics in relation to the adsorbate evolving kinetics [cf. Eqs. (1)–(4)] remains elusive. Therefore, it would be incorrect to assume that the higher driving force for the LOER compared to the adsorbate OER renders the LOER feasible for any electrocatalyst.

Starting from scratch, the OER from the electrolyte, i.e. water splitting, as well as the LOER from the metal oxide’s lattice are given by Equations (9) and (10), respectively:

\[ 2 \text{H}_2\text{O}_{(aq)} \rightarrow \text{O}_2(g) + 4 \text{H}^+ + 4 \text{e}^- \]  
\[ \frac{2}{n} \text{M}^{2n+} + \text{O}_2^-_{(s)} \rightarrow \frac{2}{n} \text{M}^{2n+}_{(aq)} + \text{O}_{2(g)} + 4 \text{e}^- \]  

The Nerst equation for the two processes at \( T = 298.15 \text{ K} \) reads:

\[ U_{\text{OER}} = U_{\text{OER}}^0 + \frac{25.7 \text{ mV}}{4} \cdot \ln \left( \frac{\alpha (\text{O}_2) \cdot \alpha^n (\text{H}^+) \cdot \alpha^{2n} (\text{M}^{2n+})}{\alpha (\text{H}_2\text{O})} \right) \]  
\[ U_{\text{LOER}} = U_{\text{LOER}}^0 + \frac{25.7 \text{ mV}}{4} \cdot \ln \left( \frac{\alpha (\text{O}_2) \cdot \alpha^{2n} (\text{M}^{2n+})}{\alpha^n (\text{M}^{2n+} \text{O}_2^-)} \right) \]  

In Equations (11) and (12), \( U_{\text{OER}}^0 \) denotes the standard equilibrium potential of the OER, that is, 1.23 V vs. SHE (standard hydrogen electrode) at pH = 0, and \( \alpha \) indicates the activity of reactants and products. The activity of water can fairly be assumed as constant, \( \alpha (\text{H}_2\text{O}) = 1 \), and the pH value is fixed to 0, that is, \( \alpha (\text{H}^+) = 1 \). Similarly, the activity of the metal oxide, \( \text{M}^{2n+} \text{O}_2^-_{(s)} \), can be anticipated to be 1. Therefore, Equation (11) can be rewritten as follows [Eq. (13)]:

Eqs. (1)–(4)], also denoted as adsorbate evolution mechanism in the literature, gaseous oxygen can be produced by removing oxygen from the crystal lattice, giving rise to the so-called LOER pathway. Different LOER mechanisms are discussed in the literature,\(^{[11,12]} \) and the most prominent one is given by Equations (5)–(8):

\[ \text{O}_{\text{lat}} + \text{H}_2\text{O} \rightarrow \text{O}_{\text{lat}} - \text{OH} + \text{H}^+ + \text{e}^- \]  
\[ \text{O}_{\text{lat}} - \text{OH} \rightarrow \text{V}_0 + \text{O}_{2(g)} + \text{H}^+ + \text{e}^- \]  
\[ \text{V}_0 + \text{H}_2\text{O} \rightarrow \text{O}_{\text{lat}} - \text{H} + \text{H}^+ + \text{e}^- \]  
\[ \text{O}_{\text{lat}} - \text{H} \rightarrow \text{O}_{\text{lat}} + \text{H}^+ + \text{e}^- \]  

In Equations (5)–(8), \( \text{O}_{\text{lat}} \) and \( \text{V}_0 \) indicate an oxygen atom from the lattice and an oxygen vacancy, respectively. As evident from the mechanistic description, the formation of an oxygen vacancy is critical because it could stimulate degradation processes, such as the detachment of metal ions into the electrolyte solution, causing mass loss of the electrode material with prolonged operational time. This argument may substantiate the correlation between the LOER and catalyst instability, but in the further course I am going to critically assess the correlation between catalyst instability and the LOER pathway described by Equations (5)–(8).

Yet, there is a discrepancy in the literature on the relationship between catalyst stability under OER conditions and the LOER. A potential opportunity to monitor the evolution of gaseous oxygen from the lattice refers to online electrochemical mass spectrometry (OLEMS).\(^{[13,14]} \) While OLEMS data for RuO\(_2\) indicated that the OER proceeds without lattice exchange,\(^{[13]} \) the LOER has been quantified for the formation of gaseous oxygen over IrO\(_2\),\(^{[15]} \) which was confirmed by a theoretical study in the density functional theory (DFT) approximation.\(^{[12]} \) This outcome is in direct contrast to the fact that IrO\(_2\) is more stable than RuO\(_2\),\(^{[16]} \) and that the LOER is assumed to render instability of electrode materials.\(^{[9]} \)

2.2. Thermodynamic analysis of the LOER

Given the above contradiction, it appears imperative to critically analyze the correlation between the adsorbate and lattice oxygen evolution mechanisms as well as catalyst stability. In 2015, Binninger et al. reported that any metal oxide cannot be stable under oxygen evolution conditions.\(^{[9]} \) Using thermodynamic considerations, the authors demonstrated that the applied overpotential for the LOER, \( \eta_{\text{LOER}} \), is always larger than that for the OER, \( \eta_{\text{OER}} \), at a fixed electrode potential: \( \eta_{\text{LOER}} \geq \eta_{\text{OER}} \). As a direct consequence, the bulk phase of any metal oxide is thermodynamically unstable at applied electrode potentials exceeding the oxygen evolution equilibrium potential.\(^{[9]} \)

The work of Binninger et al. provides thermodynamic reasoning that the LOER is energetically preferred over the adsorbate evolving mechanism. I would like to emphasize, though, that this thermodynamic analysis does not provide any information on the potential occurrence of the LOER because the LOER kinetics in relation to the adsorbate evolving kinetics [cf. Eqs. (1)–(4)] remains elusive. Therefore, it would be incorrect to assume that the higher driving force for the LOER compared to the adsorbate OER renders the LOER feasible for any electrocatalyst.

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Comparing Equations (13) and (14), it becomes evident that these formulas differ in a single term only, namely the activity of dissolved metal ions in the electrolyte solution. Only if \( a(M^{n+}) \) amounts to 1, the equilibrium potential of the LOER equals that of the OER. However, particularly at the beginning of electrolysis, no metal ions are expected to be present in the electrolyte solution so that, correspondingly, \( a(M^{n+}) \ll 1 \). As a consequence, the equilibrium potential of the LOER is lower than that of the OER, and as such the applied overpotential for the LOER, \( \eta_{\text{LOER}} = U - U_{\text{LOER}} \), exceeds that of the OER, \( \eta_{\text{OER}} = U - U_{\text{OER}} \), in agreement with the somewhat more tedious derivation by Binninger et al.\(^{[9]} \)

The qualitative discussion above motivates to have a quantitative look on the thermodynamics for the OER and LOER. Assuming that the metal corresponds to a tetravalent ion \((n = 2)\), such as encountered with the prominent metal oxides RuO\(_2\) or IrO\(_2\), as OER catalyst, the equilibrium potential for the LOER is calculated for different activities of \( a(M^{n+}) \), adopting \( a(O^2-) = 1 \) for simplicity. The outcome is compiled in Table 1. In this case, the OER equilibrium potential, \( U_{\text{OER}} \) [cf. Eq. (13)], amounts to 1.23 V vs. RHE (reversible hydrogen electrode). It should be noted that \( a(M^{n+}) > 0 \) is a precondition to analyze equation (14), and thus \( a(M^{n+}) = 10^{-9} \) is used as smallest activity value in the analysis.

Table 1 illustrates that at a fixed applied electrode potential of \( U > 1.23 \) V vs. RHE, the applied overpotential for the LOER, \( \eta_{\text{LOER}} \), is about \((0.0-0.13) \) V higher than that of the OER, \( \eta_{\text{OER}} \), depending on the activity of the metal ion in solution, which is experimentally unknown in experiments. Two different scenarios are conceivable, namely a) the LOER does not proceed for a given electrode material, or b) the LOER is operative. In case a), the activity of \( M^{n+} \) can assumed to be constant, and thus the equilibrium potential of the LOER does likely not change with prolonged operational time. In case b), however, the LOER causes an increasing concentration of \( M^{n+} \), and thus a rising activity in the course of electrolysis. Therefore, at constant potential conditions, the applied overpotential for the LOER, \( \eta_{\text{LOER}} \), is decreasing with prolonged operational time as long as the electrolyte solution is not exchanged during electrolysis. This could potentially cause a smaller activity for a given electrocatalyst over the course of electrolysis, particularly if the LOER is the dominating mechanistic pathway. Experimentally, long-term measurements would be needed to monitor the dynamic behavior of OER electrocatalysts, whereas many research labs restrict such measurements to a few hours only.\(^{[16]} \)

### 2.3. Kinetic analysis of the LOER and OER: free-energy diagrams

While so far, the discussion addressed the thermodynamics of the LOER and OER, in the following I am going to outline how this thermodynamic information is related to the kinetics of these oxygen evolving processes. Following Parsons’s seminal work on the free-energy diagram and rate-determining step,\(^{[17]} \) the kinetics of an electrocatalytic reaction is governed by the transition state with highest free energy, \( G_{\text{rds}} \), in the free-energy landscape. Taking the mononuclear OER mechanism [cf. Eqs. (1)–(4)] as representative example, the definition of \( G_{\text{rds}} \) is pictured in Figure 1.

In the same fashion to the OER, the mechanistic processes of the LOER can be summarized in a free-energy diagram. The adsorbate and lattice oxygen evolution mechanisms are compared at \( U = 1.23 \) V vs. RHE in Figure 2. Please note that at \( U = 1.23 \) V vs. RHE, the LOER already feels an overpotential due to \( a(M^{n+}) < 1 \). Therefore, the LOER product state is energetically lower than that of the OER. For both mechanisms, the rate-determining term \( G_{\text{rds}} \) is marked, and three different cases can be observed: a) \( G_{\text{rds}}^\text{rds,LOER} > G_{\text{rds}}^\text{rds,OER} \), b) \( G_{\text{rds}}^\text{rds,LOER} \approx G_{\text{rds}}^\text{rds,OER} \), c) \( G_{\text{rds}}^\text{rds,OER} \approx G_{\text{rds}}^\text{rds,LOER} \) (cf. Figure 2). The situation in a) or c) suggests that either only the lattice oxygen evolution or the adsorbate mechanism is operative, respectively. In case b), the OER and LOER are competitive and may occur both.

The construction of free-energy diagrams for the OER is commonly based on ab initio theory in the density functional theory (DFT) approximation.\(^{[18]} \) Yet, the majority of DFT studies evaluates the adsorption free energies of the reaction intermediates OH, O, and OOH only while the reaction kinetics in terms of transition states is ignored.\(^{[19]} \) The main reasons are that computational methods to compute transition states in an electrochemical environment are still in its infancy, and that the application of sophisticated grand-canonical approaches, relying on a constant electrode potential but varying charge as encountered with the situation in experiments, is prohibitively expensive.\(^{[19]} \) Given that only the thermodynamic information in Figure 2 is available, a descriptor is needed to approximate electrocatalytic activity in terms of \( G_{\text{rds}}^\text{rds,LOER} \) and \( G_{\text{rds}}^\text{rds,OER} \). This can be achieved by the notion of \( G_{\text{max}}(\eta) \),\(^{[20]} \) which is an overpotential-dependent activity descriptor that mimics kinetic effects due to the correlation with the Tafel slope in the analysis (cf. Figure 3).\(^{[21]} \) The concept of \( G_{\text{max}}(\eta) \) relies on the free-energy span model, as introduced by Shaik and Kozuch.
in the field of homogeneous catalysis,[22] and evaluates the free-energy difference between the intermediate with smallest and highest free energy in dependence of the applied overpotential.[22] The descriptor \( G_{\text{rds}}(\eta) \) is also useful for the analysis of selectivity ratios,[23] but here this concept is applied to the study of competing mechanistic pathways for the evolution of gaseous oxygen. For the case \( G_{\text{rds}}^{\text{LOER}} \geq G_{\text{rds}}^{\text{OER}} \) (cf. Figure 2a), the idea of \( G_{\text{rds}}(\eta) \) is illustrated in Figure 3.

While also other activity descriptors have been suggested to analyze the energetics of reaction intermediates in the OER, most notably the thermodynamic overpotential (\( \eta_{\text{TD}} \)) and the electrochemical-step symmetry index (ESSI),[7] it is noteworthy that \( G_{\text{max}}(\eta) \) is the only descriptor that contains a measure for sensitivity in the analysis: only if the \( G_{\text{max}}(\eta) \) values differ by at least \( \pm 0.2 \) eV, it can be fairly concluded that the mechanistic pathway with the smallest \( G_{\text{max}}(\eta) \) value is the dominating reaction channel.[24] Otherwise, the other mechanisms with slightly higher \( G_{\text{max}}(\eta) \) values cannot be fully excluded. Actually, application of \( \eta_{\text{TD}} \) or ESSI for the evaluation of the adsorbate and lattice oxygen evolution mechanisms is not feasible since both descriptors rely on a zero-overpotential analysis, that is, the adsorption free energies are analyzed at \( \eta_{\text{rds}} = \eta_{\text{OER}} = 0 \) V.[21,24] As evident from the above discussion, \( \eta_{\text{LOER}} \) and \( \eta_{\text{OER}} \) correspond to different applied electrode potentials due to the different equilibrium potentials of the LOER and OER, and thus comparison of the energetics at \( \eta_{\text{LOER}} = \eta_{\text{OER}} = 0 \) V is not practicable; rather comparison at the same applied electrode potential should be conducted.

While Figure 3 introduces a method to conceptually analyze the competition between the OER and LOER for a given electrocatalyst based on the application of the descriptor \( G_{\text{max}}(\eta) \), it would be additionally required to evaluate different cases relating to the activity of the metal ion, \( \alpha(M^{n+}) \), in solution. As evident from Table 1, the equilibrium potential of the LOER shifts with increasing activity of \( M^{n+} \) so that, correspondingly, low-activity, medium-activity, and high-activity scenarios (e.g., \( \alpha(M^{n+}) = 10^{-7}/10^{-9}/10^{-3} \)) should be compared. This aspect is shown in Figure 4, illustrating that the activity of the metal ion may influence the energetics significantly, and thus impacts the competition between the LOER and OER pathways.

2.4. Modeling the LOER by DFT

In the previous section, the free-energy landscapes of the OER and LOER are discussed, including subtleties relating to the activity of the metal ion, \( M^{n+} \). While I was pointing out that the reaction intermediates for the OER, denoted by (i) to (v) in the above figures, refer to the mononuclear mechanism (cf. Eqs. (1)–(4)) or any other reported pathway, so far I did not clearly specify the meaning of (i) to (v) in the free-energy diagrams for the LOER. Given that the most prototypical mechanistic LOER path is indicated in Equations (5)–(8), one may suspect that the specified intermediates O\(_{\text{ad}}\), O\(_{\text{ad}}\)-OH, V\(_{\text{ad}}\), and O\(_{\text{ad}}\)-H are meant.[11,12,25] This misconception is the major point that caused my motivation to write this concept article. The interpretation of the LOER mechanism appears to be an apparent community or communication gap between experimentalists and theoreticians in electrocatalysis. Let me go more into detail.

If we inspect the commonly modeled LOER mechanism from the literature (cf. Eqs. (5)–(8)), it becomes clear that lattice oxygen, O\(_{\text{ad}}\), is involved in the mechanistic processes of oxygen evolution, but in Equation (7) the oxygen vacancy, V\(_{\text{ad}}\), is re-filled by an oxygen atom that originates from the aqueous solvent, water. Additionally, no metal ion is dissolved into the electrolyte when comparing this LOER mechanism to the thermodynamic analysis by Binninger et al.[29] Therefore, the mechanistic descrip-

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**Figure 1.** Free-energy diagram of the OER according to the mechanistic description in equations (1)–(4) at \( U = 1.23 \) V vs. RHE. The reaction intermediate (RI) with lowest free energy (active surface configuration) and the transition state (TS) with highest free energy are indicated by turquoise and violet colors, respectively. \( G_{\text{rds}}^{\text{max}} \) marks the corresponding TS free energy for the transition from the active surface to the TS with highest free energy, governing the kinetics. Brown arrows specify the overpotential dependence of each RI and TS, and \( \alpha(j = 1, 2, 3, 4) \) denotes the transfer coefficient of each TS. The free energies of the RIs and TSs in the figure are arbitrarily chosen. Adapted with permission.[24] Copyright 2020, American Chemical Society.
tion in Equations (5)–(8) corresponds to an OER pathway, in which formally both oxygen atoms originate from the electrolyte [cf. Eqs. (5) and (7)]. In other words, the prototypically modeled LOER mechanism refers to a conventional OER description that simply takes place on a different surface site in that an oxygen lattice atom is reconciled with the active center. As such, the same rules as for the mononuclear mechanism [cf. Eqs. (1)–(4)] hold true, that is, the mechanistic description in equations (5)–(8) is independent of the metal-ion activity, $a(M^{4+})$. Therefore, no additional driving force for this pathway is encountered compared to the LOER description by Binninger et al.\cite{9} and thus it is not feasible to correlate this mechanistic description with catalyst stability.

I would like to emphasize that to my opinion it is erroneous to relate the occurrence of the LOER description of Equations (5)–(8) to catalyst instability. Even if this mechanistic pathway is kinetically preferred over the mononuclear mechanism [cf. Eqs. (1)–(4)], it does not directly imply that the given electrocatalyst is unstable under anodic potential conditions because no direct mass loss of the electrode is observed. This finding should actually be a trigger for further theoretical considerations in the DFT approximation to model catalytic pathways, in which the evolution of gaseous oxygen is accompanied with the dissolution of a metal ion into the electrolyte, thereby referring to the analysis of Binninger et al.\cite{9} to understand the correlation of the additional thermodynamic driving force (cf. Section 2.1) to the kinetic response.

I would like to remind that in this case the mechanistic processes feel an additional overpotential due to $a(M^{4+})$ (cf. Figure 4). A potential strategy to evaluate the LOER including dissolution of a metal ion into the solution is illustrated in Figure 5.

In Figure 5, a six-fold coordinated metal site, $M$, is displayed, such as encountered with rutile IrO$_2$ and RuO$_2$. Modeling the LOER combines the evolution of gaseous oxygen with the dissolution of $M^{4+}$ into the electrolyte, thereby dividing the overall process into the elementary steps to capture the energetics in the form of a free-energy diagram.\cite{26} The suggested procedure could provide atomic-scale insight whether the LOER including metal-ion dissolution is a reason for catalyst instability under anodic potential condition, given that for the process in Figure 5 an additional driving force depending on the metal-ion activity, $a(M^{4+})$, in solution has to be considered (cf. Figure 4).

While the outlined model in Figure 5 goes beyond previous theoretical considerations on the LOER in the literature,\cite{9,16,25,26} I would like to note that the computational protocol for the...
description of the elementary steps may be challenging. This manifests in the occurrence of charged species, namely the vacant active site and the metal ion in solution. Given that the positive and negative charges compensate each other, it appears plausible to pull the metal cation from its active site stepwise into the electrolyte by replacing all removed oxygen species subsequently with solvating water molecules. On the other hand, ab initio molecular dynamics is a promising technique to elucidate in the presence of explicit water molecules whether the dissolution of the metal ion into solution takes place when the local environment of the active site is stepwise altered.\cite{30,32}

Finally, I would like to note that, so far, the discussion focused on single-site OER and LOER mechanisms. In the literature, also multi-site pathways have been reported,\cite{30} and the above discussion may also hold true for these multi-site mechanisms, which, however, are not further illustrated in this concept article.

2.5. LOER and catalyst stability

In this final section, I am going to comment on the interrelationship of the LOER and catalyst stability. This concept article was motivated by the finding that the LOER was reported for the case of IrO$_2$ rather than for RuO$_2$, but RuO$_2$ is distinctly less stable than IrO$_2$ under anodic potential conditions.\cite{12–14} As I elaborated in the previous sections, one possible answer to this obvious misunderstanding refers to the fact that the occurrence of the conventionally considered LOER does not directly imply catalyst instability. In ab initio studies, the LOER is discussed as a mechanistic pathway that consumes lattice oxygen and restores it with oxygen atoms from the solvent water so that no direct conclusions on the stability under anodic potential conditions can be made. Even if the LOER pathway of equations (5)–(8) is operative for IrO$_2$, IrO$_2$ is highly stable under the anodic potential conditions because the LOER description including dissolution of a metal ion into the electrolyte, albeit thermodynamically preferred, is kinetically suppressed for IrO$_2$.\cite{30} This could be reconciled with the situation in Figure 2c.

Relating to RuO$_2$, it was reported that one major side product under OER conditions refers to the formation of rutheniumtetroxide, RuO$_2$\cite{31}, which was also confirmed theoretically by means of ab initio MD simulations.\cite{32} This finding should be a reminder that the LOER including dissolution of a metal ion into the electrolyte is not the only process that may contribute to degradation of an electrode under OER conditions. The formation of side products under OER conditions can be monitored experimentally by the application of inductively coupled plasma mass spectrometer (ICP-MS).\cite{30} Yet, the present concept article does not aim to discuss the OER over RuO$_2$ and IrO$_2$ in great detail, as encountered with a recent overview article in the field,\cite{30} but rather to resolve the occurring discrepancies in the interpretation of the LOER on the atomic scale. I am confident that the clarification of the conventional LOER modeling in relation to the thermodynamic study of Binninger et al.\cite{9} may initiate further theoretical studies that aim to comprehend the interrelationship for the evolution of gaseous oxygen from the electrolyte or the crystal lattice for various electrode compositions.

3. Conclusions

In this concept article, the lattice oxygen evolution reaction (LOER) mechanism and its implications on activity and stability in the evolution of gaseous oxygen are critically discussed. Referring to the thermodynamic analysis of
Binninger et al., the LOER feels an additional driving force compared to the conventional oxygen evolution reaction (OER) via the OH, O, and OOH adsorbates, but only if the LOER is accompanied with the dissolution of a metal ion into solution. The additional overpotential for the LOER, however, strictly depends on the activity of the metal ion in the solution, which experientially is unknown and may change in the course of electrolysis, thus impacting the long-term activity of this material in case that the LOER is the dominating mechanistic pathway.

A potential strategy to elucidate the impact of the LOER on the activity and stability for a given electrocatalyst refers to the prototypical modeling of the LOER in the literature relies on a mechanistic description via an oxygen lattice atom, in which, however, no additional driving force for the elementary processes is encountered since the dissolution of a metal ion into the solution is not taken into account. Therefore, an advanced model is suggested (cf. Figure 5), which considers both the evolution of gaseous oxygen from the lattice in conjunction with the dissolution of a metal ion. This framework appears to be a plausible approach to assess whether the LOER, due to its increased thermodynamic driving force, is a reason for catalyst instability under anodic potential conditions, and thus may enhance our understanding in the evolution of gaseous oxygen on the atomic scale.

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**Conflict of Interest**

The authors declare no conflict of interest.

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