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## Can dopants defend? Unraveling $\text{RuO}_2$ corrosion and reinforcement strategies for enhanced stability†

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To advance sustainable green hydrogen production through water electrolysis, where ruthenium dioxide ( $\text{RuO}_2$ ) is a promising catalyst for the oxygen evolution reaction (OER), we investigate the stability of  $\text{RuO}_2$ , focusing on corrosion resistance – a key challenge limiting its practical application. Using density functional theory (DFT), we analyze the thermodynamic stability and reaction pathways across various  $\text{RuO}_2$  surface orientations, with a primary focus on the (110) surface. Specifically, we assess the impact of doping with Ta, W, Re, Ir, Ti, and Pt on the thermodynamic stability of the  $\text{RuO}_2$ (110) surface against dissolution of Ru surface atoms in the form of  $\text{RuO}_4$ . Our findings reveal that dopants Ir, Ti, and Pt in low oxidation states significantly enhance the resistance of the  $\text{RuO}_2$ (110) surface against corrosion, while Ta, W, and Re in high oxidation states destabilize the surface, promoting degradation. We also identify specific dopant sites, such as those next to or directly underneath the dissolving Ru atom, that contribute significantly to surface stability, providing a roadmap for optimizing  $\text{RuO}_2$  catalysts. Additionally, we extend the investigation to reaction pathways towards the dissolution of the Ru atom by incorporating the effects of dopants, revealing that dopants not only alter the thermodynamic stability but also the reaction mechanism due to their different termination preferences. We establish a strong linear correlation between the Gibbs free energy of  $\text{RuO}_4$  formation ( $\Delta G_{\text{tot}}$ ) and the free energy of the highest intermediate ( $\Delta G_{\text{max}}$ ), proposing  $\Delta G_{\text{tot}}$  as a reliable descriptor for predicting the thermodynamic stability of doped  $\text{RuO}_2$  surfaces against Ru dissolution. This allows for efficient computational screening of surface modifications, including dopant selection and surface orientation tuning, without requiring detailed knowledge of the entire stepwise mechanism toward the formation and removal of  $\text{RuO}_4$ . This insight enables efficient computational screening of dopants and surface modifications, providing a framework for optimizing  $\text{RuO}_2$  catalysts to improve durability in electrochemical applications.

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## 1 Introduction

The transition towards sustainable energy sources has prompted intensive research into technologies capable of efficiently converting renewable electricity into storable and transportable forms. Among these technologies, water electrolysis is a promising avenue for producing green hydrogen, a clean and versatile energy carrier capable of decarbonizing various sectors, including transportation, industrial processes, and energy storage.<sup>1</sup> Polymer electrolyte membrane (PEM) electrolyzers (see Fig. 1), in particular, have gained traction due to their ability to catalyze hydrogen production at the cathode with high efficiency.<sup>2</sup> However, the sluggish kinetics of the oxygen evolution reaction (OER) at the anode pose a significant barrier to achieving optimal performance in water electrolysis systems.<sup>3</sup>

Addressing the challenges associated with the OER is paramount for advancing the commercial viability and widespread adoption of water electrolysis technology. Ruthenium dioxide ( $\text{RuO}_2$ ) has emerged as a promising catalyst for the OER, owing to its high activity and favorable electrochemical properties.<sup>4</sup>

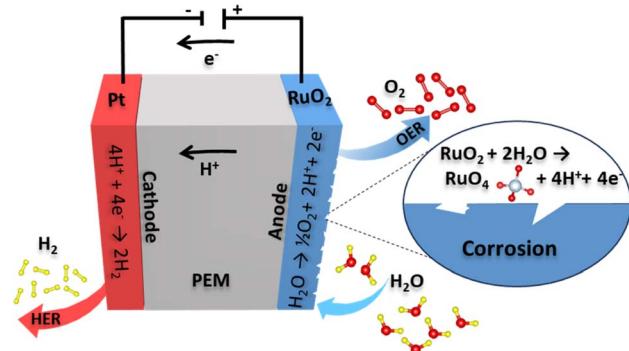


Fig. 1 A polymer electrolyte membrane (PEM) electrolyzer.

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Despite its potential, the practical application of  $\text{RuO}_2$  in water electrolysis is hindered by issues related to its stability under operating conditions.<sup>5</sup> The dissolution of Ru from the  $\text{RuO}_2$  structure leads to the formation of soluble  $\text{RuO}_4$  species, compromising the long-term stability and performance of  $\text{RuO}_2$ -based catalysts.<sup>6-8</sup> This instability is particularly pronounced at surface defect sites and undercoordinated Ru atoms, where dissolution is more likely to occur. Understanding the atomic-scale mechanisms of  $\text{RuO}_2$  degradation is therefore essential for developing more stable catalyst formulations.

Enhancing the stability of  $\text{RuO}_2$  requires a fundamental understanding of the mechanisms governing its degradation and the development of effective strategies to mitigate corrosion. One promising approach is heteroatom doping, where the incorporation of stable elements such as Ir, Ti, and Pt can modify the electronic structure of  $\text{RuO}_2$ , suppress Ru dissolution, and improve overall durability. For instance, a  $\text{Ru}_{0.5}\text{Ir}_{0.5}$  alloy achieves four times higher stability compared to other Ru-Ir OER materials by adjusting surface composition through segregation.<sup>9</sup> In Ir-Ru mixed oxides, Ru dissolves more rapidly than Ir, leading to activity loss, while the corrosion resistance of Ir contributes to overall stability.<sup>10</sup> Titanium substitution in  $\text{RuO}_2$  at low concentrations (12.5% and 20% Ti) enhances catalyst stability and reduces Ru dissolution.<sup>11</sup>  $\text{TiRuO}_2$  solid solutions improve selectivity towards cathodic electrochemical reactions (CER), such as the hydrogen evolution reaction (HER), rather than enhance OER activity.

Another approach involves oxygen vacancy engineering, where dopants such as W and Er increase the formation energy of oxygen vacancies, effectively improving the structural integrity of  $\text{RuO}_2$  and reducing dissolution in acidic PEM electrolyzers.<sup>12</sup> Furthermore, surface modifications, such as atomic layer deposition (ALD) of protective coatings and the formation of mixed-metal oxide layers, have been shown to enhance  $\text{RuO}_2$  stability, with submonolayer  $\text{IrO}_x$  on  $\text{RuO}_2$  significantly suppressing Ru dissolution and improving durability in PEM electrolyzers.<sup>13</sup> Meanwhile, Ru nanoparticles exhibit severe corrosion and instability during OER, whereas Ir nanoparticles show improved durability, indicating their potential as effective nanoscale OER catalysts.<sup>14</sup> Dispersing  $\text{RuO}_2$  over defective  $\text{TiO}_2$  enhances acidic OER performance by lowering the  $^*\text{OOH}$  formation barrier and improving stability.<sup>15</sup>

In this study, leveraging Density Functional Theory (DFT) calculations in the computational hydrogen electrode model,<sup>16,17</sup> we investigate the thermodynamic stability and reaction pathways of  $\text{RuO}_2$  catalysts in water electrolysis. We examine surface defects across various orientations, including (110), (100),  $c(2 \times 2)$ -reconstructed, and step edge configurations, to gain insights into the influence of surface morphology on  $\text{RuO}_2$  stability against corrosion. Additionally, we explore the effects of support materials like M = (Ta, W, Re, Ir, Ti, and Pt), selected based on their stability in oxidative environments, electrochemical properties, and structural compatibility with  $\text{RuO}_2$  due to their ability to form  $\text{MO}_2$  rutile structures, thereby potentially forming stable solid solutions and interfaces with  $\text{RuO}_2$ . These elements are known to influence corrosion resistance, making them ideal candidates for this study. Their

effects, either as a substrate or sublayer, on  $\text{RuO}_2$  surface composition and stability are examined. Finally, we investigate how doping with a selection of these elements influences the thermodynamic stability of the  $\text{RuO}_2(110)$  surface against corrosion.

In order to study the connection between thermodynamics and kinetics of corrosion, represented by the overall Gibbs free energy of  $\text{RuO}_4$  formation ( $\Delta G_{\text{tot}}$ ) and the free energy of the highest intermediate ( $\Delta G_{\text{max}}$ ), we delve into the reaction pathways of  $\text{RuO}_4$  formation at the bridge site of the (110) surface. Here, we focus on how different dopants alter the corrosion mechanisms and overall stability of  $\text{RuO}_2$  surfaces. By detailing these reaction pathways, we aim to identify opportunities for optimizing  $\text{RuO}_2$  catalysts to enhance their performance in water electrolysis. Finally, we demonstrate that  $\Delta G_{\text{max}}$  is highly correlated with  $\Delta G_{\text{tot}}$  for a large variety of modified surface structures, enabling the use of the Gibbs free energy of reaction as a descriptor in the optimization of the surface stability.

Ultimately, this study aims to advance sustainable energy technologies by developing robust and cost-effective catalysts for water electrolysis through knowledge-based proofing of the anode material against corrosion, facilitating the efficient use of renewable energy resources for green hydrogen production.

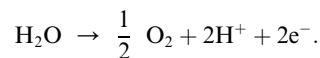
## 2 Computational details

Our investigation, grounded in DFT calculations, utilizes the Vienna *ab initio* simulation package (VASP)<sup>18,19</sup> employing the Perdew–Burke–Ernzerhof (PBE) functional.<sup>20</sup>

For surface computations, a  $(4 \times 2 \times 1)$   $k$ -point mesh is employed for  $(2 \times 2)$  superstructures of the (110) surface, with a constant  $k$ -point density in reciprocal space for larger surface configurations. These asymmetric slabs comprise five  $\text{RuO}_2$  trilayers, with two fixed and three fully relaxed trilayers. The relaxed bulk lattice parameters used in the calculations are optimized for  $\text{RuO}_2$ ,  $\text{IrO}_2$ , and  $\text{TiO}_2$ . Specifically, the lattice constants for  $\text{RuO}_2$  are  $a = b = 4.497 \text{ \AA}$  and  $c = 3.105 \text{ \AA}$ , for  $\text{IrO}_2$  they are  $a = b = 4.499 \text{ \AA}$  and  $c = 3.146 \text{ \AA}$ , and for  $\text{TiO}_2$  the parameters are  $a = b = 4.589 \text{ \AA}$  and  $c = 2.958 \text{ \AA}$ . A vacuum layer of  $17.359 \text{ \AA}$  is employed. An energy cutoff of  $450 \text{ eV}$  and convergence criteria of  $10^{-6} \text{ eV}$  for energy during structural optimization is specified. Pseudopotentials are utilized for various elements including Ru, Ti, Ir, W, Re, Pt, Ta, O, and H<sup>19,21</sup> designated as Ru\_sv, Ti, Ir, W, Re\_pv, Pt\_pv, Ta\_pv, O, H.

For Ti, a Hubbard coefficient  $U_H$  of  $8 \text{ eV}$  is implemented in the Generalized Gradient Approximation (GGA) calculation to accurately describe the localized nature of Ti d-electrons in the semiconductor, thereby improving the characterization of its electronic structure.<sup>22-24</sup> Other elements in the system did not require a  $U_H$  correction, as their electron interactions were sufficiently well-described by conventional DFT.

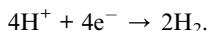
The reactions investigated in this study include the oxygen evolution reaction at the anode, represented by the following reaction:



The corrosion reaction at the anode is:



At the cathode, the hydrogen evolution reaction is represented by:



Our computational approach is based on the total free energy equation, following methodologies detailed in previous studies.<sup>16,17,25</sup> The free energy change for a particular configuration  $i$ , denoted as  $\Delta G_i(U_{\text{SHE},\text{pH}})$ , is calculated using the following expression:

$$\begin{aligned} \Delta G_i(U_{\text{SHE}}, \text{pH}) = & E_i^{\text{DFT}} - E_{\text{ref}}^{\text{DFT}} + n_{\text{RuO}_4} G_{\text{RuO}_4,\text{aq}} - n_{\text{e}^-,i} U_{\text{SHE}} \\ & - 0.059 \text{ eV} \cdot n_{\text{e}^-,i} \cdot \text{pH} - n_{\text{H}_2\text{O},i} G_{\text{H}_2\text{O},l} \\ & + \frac{1}{2} n_{\text{H}_2,i} G_{\text{H}_2} + n_{\text{O}_2} G_{\text{O}_2} \end{aligned} \quad (1)$$

The reason  $\text{RuO}_4$  was chosen in eqn (1) is that, at the potential corresponding to the dissolution threshold (around 1.21 V),  $\text{RuO}_4$  is typically the dominant solvated species. At higher potentials, ruthenium tends to stabilize in its higher oxidation state, often as  $\text{RuO}_4$ . In this equation,  $\Delta G_i(U_{\text{SHE},\text{pH}})$  represents the free energy change for configuration  $i$  as a function of the applied potential relative to the standard hydrogen electrode (SHE),  $U_{\text{SHE}}$ , and the pH of the environment. The term  $E_i^{\text{DFT}}$  is the electronic energy of the system in configuration  $i$ , while  $E_{\text{ref}}^{\text{DFT}}$  is reference energy, typically the energy of the initial state of the  $\text{RuO}_2$  system, obtained from density functional theory (DFT) calculations. The numbers  $n_{\text{RuO}_4}$ ,  $n_{\text{e}^-,i}$ ,  $n_{\text{H}_2\text{O},i}$ ,  $n_{\text{H}_2,i}$ , and  $n_{\text{O}_2}$  represent the number of  $\text{RuO}_4$  units involved in the reaction or transformation for configuration  $i$ , the number of electrons transferred in the electrochemical process associated with configuration  $i$ , the number of adsorbed water molecules involved, the number of hydrogen molecules, and the number of oxygen molecules, respectively. The constant 0.059 eV represents a unit conversion factor at room temperature.  $U_{\text{SHE}}$  is the applied potential relative to the standard hydrogen electrode.

$G_{\text{RuO}_4,\text{aq}}$  is the free energy of  $\text{RuO}_4$  in an aqueous solution, which can be determined using its entropy,  $S_{\text{RuO}_4,\text{aq}} \approx 104.55 \text{ J} (\text{K}^{-1} \text{ mol}^{-1})$ .  $G_{\text{H}_2}$  and  $G_{\text{O}_2}$  represent the free energies of hydrogen and oxygen molecules, respectively. The free energy of liquid water,  $G_{\text{H}_2\text{O},l}$ , is determined by the expression

$$G_{\text{H}_2\text{O},l} = E_{\text{H}_2\text{O},g}^{\text{DFT}} - T \cdot S_{\text{H}_2\text{O},g} + k_B T \ln(0.035) \quad (2)$$

where  $S_{\text{H}_2\text{O},g} = 188.8 \text{ J} (\text{K}^{-1} \text{ mol}^{-1})$  is the entropy of gaseous water, calculated at room temperature  $T = 298.15 \text{ K}$ , and 0.035 bar represents the vapor pressure of water.

At  $U_{\text{corr}}$ , which is the thermodynamic corrosion potential where the system is in dynamic equilibrium, and the net current of oxidation (corrosion) and reduction reactions on the surface is zero, indicating no net electron flow. When  $\text{pH} = 0$ ,

indicating an acidic environment, the total free energy at the corrosion potential is given by:

$$\begin{aligned} \Delta G_i(U_{\text{corr}}) = & E_i - E_{\text{ref}} + n_{\text{RuO}_4} G_{\text{RuO}_4,\text{aq}} - n_{\text{e}^-,i} U_{\text{corr}} \\ & - n_{\text{H}_4\text{O}} G_{\text{H}_2\text{O},l} + n_{\text{H}_2} G_{\text{H}_2} + n_{\text{O}_2} G_{\text{O}_2} = 0 \end{aligned} \quad (3)$$

This equation is essential for understanding the stability and reactivity of  $\text{RuO}_2$  under different electrochemical conditions, providing insights into the factors influencing its performance as an oxygen evolution reaction (OER) catalyst.

## 3 Results

Our results are structured into two main parts: overall thermodynamic stability of Ru sites at the surface against  $\text{RuO}_4$  formation and reaction pathways toward the dissolution of Ru in the form of  $\text{RuO}_4$ . This approach allows for a comprehensive analysis of  $\text{RuO}_2$  surface corrosion, exploring both the inherent stability of various doped configurations and the specific mechanisms through which corrosion occurs. Finally, we examine the suitability of  $\Delta G_{\text{tot}}$  as a descriptor for the stability of sites at the  $\text{RuO}_2(110)$  surface against corrosion by quantifying the correlation between  $\Delta G_{\text{tot}}$ , representing the overall thermodynamic stability of a specific site, and  $\Delta G_{\text{max}}$ , representing the least stable intermediate in the full corrosion mechanism.

### 3.1 Thermodynamic stability

In our investigation of the thermodynamic stability and corrosion susceptibility of various pure  $\text{RuO}_2$  surfaces, we examined different orientations (110, 100,  $c(2 \times 2)$ -reconstructed (100), and  $\text{RuO}_2(110)/\text{RuO}_2(100)$  step edge) to discern their relative stability against corrosion. Subsequently, we examine the influence of dopants, as well as the direct and indirect effects of the catalyst support.

**3.1.1 Different  $\text{RuO}_2$  surface facets.** The (110) surface of this material presents a nuanced picture with two distinct types of Ru atoms: coordinatively unsaturated sites (cus) and bridge sites (br). Fig. 2a and b show the free energy of corrosion as defined by eqn (3) as a function of the potential.

Positive free energies indicate that corrosion is not thermodynamically favored, implying that the surface is thermodynamically stable against corrosion. The potential at which the free energy turns negative will hereafter be referred to as the corrosion potential ( $U_{\text{corr}}$ ), which indicates the lowest potential at which corrosion is thermodynamically preferred. Examining the corroded potential as a stability metric reveals variations in the stability of both atom types. The  $\text{Ru}_{\text{br}}$  site involves the removal of one  $\text{Ru}_{\text{br}}$  atom and one of its  $\text{O}_{\text{br}}$  atoms, while the other  $\text{O}_{\text{br}}$  atom relocates to the top of the nearest  $\text{Ru}_{\text{br}}$  atom, which then becomes  $\text{Ru}_{\text{sf}}$ . The corrosion potential of 1.277 V for the  $\text{Ru}_{\text{br}}$  site is higher than the bulk corrosion potential of 1.21 V (the bulk corrosion potential refers to the total conversion of bulk  $\text{RuO}_2$  to  $\text{RuO}_4$ ), indicating that the site remains stable, as corrosion is not thermodynamically favored at this higher potential.



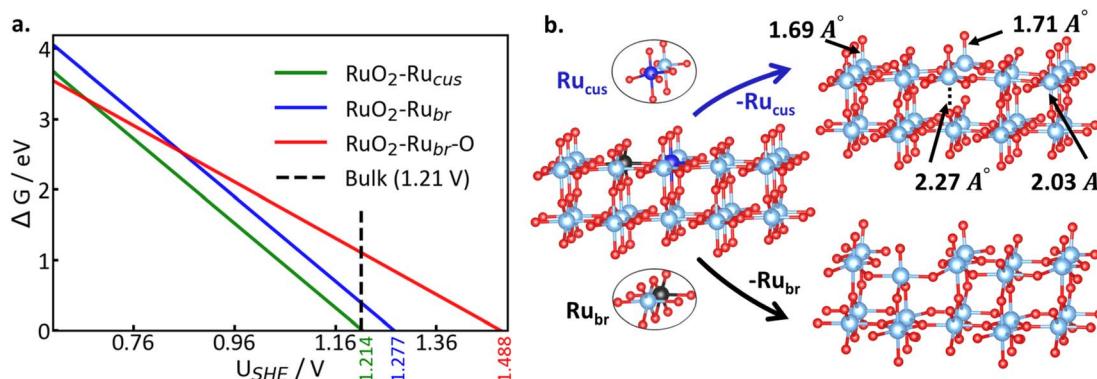


Fig. 2 Thermodynamic corrosion potentials and structures of (a and b) different Ru sites at the (110) surface. Corrosion potentials are 1.21 V, 1.277 V, and 1.488 V, calculated at pH = 0. Colors: sky blue: Ru<sub>bulk</sub>, blue: Ru<sub>cus</sub>, black: Ru<sub>br</sub>, red: O.

The Ru<sub>br</sub>-O site, formed by further removing the remaining O atom from the Ru<sub>br</sub> site (which previously moved to the nearest Ru<sub>br</sub> atom), transforms the nearest Ru<sub>br</sub> atom into a Ru<sub>4f</sub> atom without any termination on top. This site is identified as the most stable on the surface, with a corrosion potential of 1.488 V.

In contrast, the Ru<sub>cus</sub> site is the least stable, indicating a higher susceptibility to corrosion. Its stability is comparable to that of bulk material, with a corrosion potential of 1.21 V. However, the instability of the Ru<sub>cus</sub> site affects its neighboring Ru<sub>cus</sub> atom, leading to the elongation of the underlying bond after metal dissolution, from 2.03 Å to 2.27 Å, as shown in Fig. 2b (top). In this specific case, our analysis reveals that the neighboring Ru<sub>cus</sub> atom has a higher corrosion potential (1.291 V) compared to the initial Ru<sub>cus</sub> site (1.214 V), making it less susceptible to dissolution.

We uncovered distinct dissolution behaviors and stabilities by extending our analyses to the (100) surface and step edge

between the (100) and (110) facets. In each case, we examined the dissolution of different Ru sites with different oxygen terminations in the initial and final structures. Fig. 3 presents the summarized results, displaying the least stable site for each of the facets. Details for each of the facets can be found in Fig. S1–S3 in the ESI† for the (100), *c*(2 × 2)-reconstructed (100) and (100)/(110) step edge, respectively. For instance, Fig. S1 in the ESI† illustrates the dissolution behavior of the (100) surface, revealing the formation of a tetrahedral Ru<sub>4f</sub> structure post-dissolution and highlighting its comparatively lower stability: the least stable site on the (100) surface corrodes at a potential of 0.901 V, differing by 0.3 V compared to bulk RuO<sub>2</sub>.

Similarly, Fig. S2 in the ESI† elucidates the dissolution behavior of the (100)-*c*(2 × 2) surface, revealing corrosion potentials of 1.285 V for Ru<sub>4f</sub> (reported by Hess and Over)<sup>25</sup> and 1.255 V for Ru<sub>6f</sub> (according to our investigation). Ru<sub>4f</sub>, Ru<sub>5f</sub>, and Ru<sub>6f</sub> denote distinct Ru crystallographic sites with fourfold, fivefold, and sixfold coordination, respectively, affecting the material's electronic structure and bonding.

Moving on to the dissolution behavior of step edge surfaces, Fig. S3 in the ESI† reveals corrosion potentials and stability characteristics. Notably, the step edge surface exhibits decreased stability compared to the bulk material, particularly evident in the least stable site (Ru<sub>cus</sub>-O), with a corrosion potential of 0.858 V. The corrosion potentials for the least stable site on each facet are summarized in Fig. 3. This highlights the step edge as the least stable site among all examined, while the 110 surface emerges as one of the most stable surfaces. Consequently, we direct our further investigations towards the 110 surface.

**3.1.2 RuO<sub>2</sub>(110) surface with different dopants.** To explore the potential improvement in stability against the RuO<sub>2</sub>(110) surface corrosion, we investigated the impact of various dopants (Ta, W, Re, Ir, Pt, Ti) on its stability. The dopants were chosen based on their ability to form rutile-type structures, representing different groups of 3d and 5d transition metals. To isolate the effect of dopants from strain due to variation of the lattice parameter issues, we used the RuO<sub>2</sub> lattice parameter. Two models were constructed: (1) in the first model, a sublayer of dopants was placed in the middle of the RuO<sub>2</sub> layers, with the

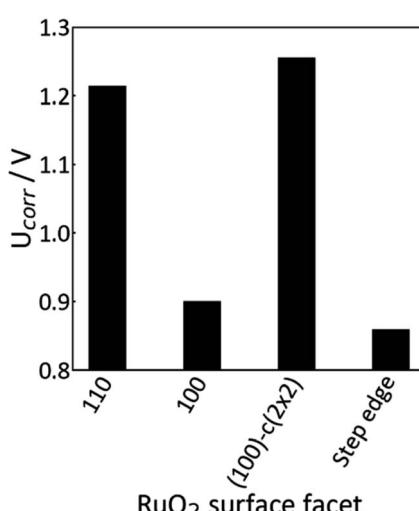


Fig. 3 Comparison of different RuO<sub>2</sub> surface facets based on potential calculations at pH = 0, identifying the least stable sites for each surface. The least stable sites are: 110: RuO<sub>2</sub>-Ru<sub>cus</sub>, 100: RuO<sub>2</sub>-Ru<sub>surf</sub>-O, 100-*c*(2 × 2): RuO<sub>2</sub>-Ru<sub>6f</sub> + O<sub>ot</sub>/Ru<sub>4f</sub>, and step edge: RuO<sub>2</sub>-Ru<sub>cus</sub>-O.



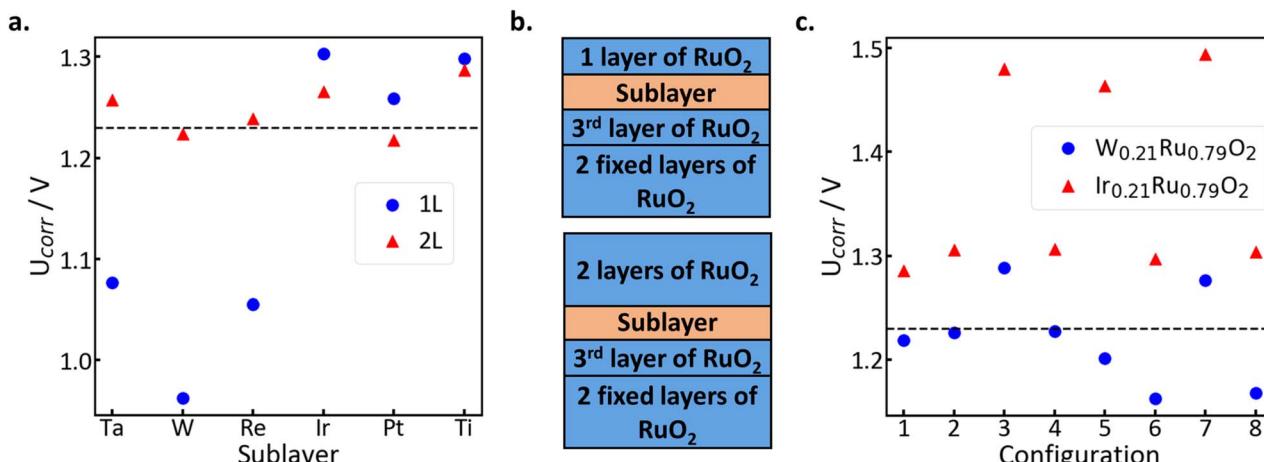


Fig. 4 (a and b) Influence of different dopant sublayers on RuO<sub>2</sub> corrosion with a varied thickness (1L or 2L) of RuO<sub>2</sub>; (c) influence of different M<sub>0.21</sub>Ru<sub>0.79</sub>O<sub>2</sub> (M = Ir, W) configurations on RuO<sub>2</sub> corrosion (cf. Fig. S4†). Potentials were calculated at pH = 0.

two bottom layers fixed (atoms in the vertical direction were constrained), while the remaining layers were allowed to relax in all directions, (cf. Fig. 4b), and (2) random arrangement of dopants M<sub>0.21</sub>Ru<sub>0.79</sub>O<sub>2</sub> (M = Ir, W) on the metal sites. This approach allows us to solely observe the influence of dopants on the corrosion of the RuO<sub>2</sub> surface without introducing strain.

Furthermore, to distinguish the direct and indirect effect of the sublayer in RuO<sub>2</sub> corrosion, we deposited 1 or 2 layers of RuO<sub>2</sub> atop the dopant sublayer. In the case of 1 layer (1L), the corroded Ru atom is bonded to the sublayer *via* a single O<sub>3f</sub> (direct effect), while with 2 layers (2L), only an indirect effect of the sublayer is probed, since surface Ru is not directly bonded to the sublayer. This approach enables us to investigate whether varying the thickness of the RuO<sub>2</sub> layer on the dopant sublayer affects the enhancement in stability against the RuO<sub>2</sub>(110) surface corrosion.

Fig. 4a and b illustrate the corrosion potential of the sublayer containing different dopants within the two models (1L, 2L). In the 1L model (direct effect), Ta, W, and Re destabilize the Ru top layer, whereas Ir, Pt, and Ti stabilize it against corrosion, as indicated by their decreased and increased corrosion potentials, respectively. The dopant is exposed after RuO<sub>4</sub> dissolution, resulting in different surface stabilities of the final surface: W strongly prefers a higher oxidation state, making it the least supportive dopant for RuO<sub>2</sub> surface stability against corrosion. Ta and Re prefer high oxidation states but not as strongly as W. In contrast, Ir, Pt, and Ti prefer lower oxidation states, with Ir and Ti being the most supportive dopants for RuO<sub>2</sub> surface stability against corrosion. The trends within the two groups persist in the 2L model, but the corrosion potentials for each of the dopants now scatter closely around the value for pure RuO<sub>2</sub>, with Ta, Ir, and Ti now causing a weak stabilization. For the others (W, Re, Pt), the effect on stability is negligible.

Continuing our investigation into the effect of doping on the stability of RuO<sub>2</sub> against corrosion, we selected W from the group (Ta, W, Re) and Ir from the group (Ir, Pt, Ti), mixing them randomly with RuO<sub>2</sub> to create eight configurations comprising

a mixture of M<sub>0.21</sub>Ru<sub>0.79</sub>O<sub>2</sub> (M = Ir, W). To maintain consistency and avoid lattice parameter issues, we fixed two layers of pure RuO<sub>2</sub> at the bottom, while three layers of (M<sub>0.21</sub>Ru<sub>0.79</sub>O<sub>2</sub> (M = Ir, W)) were allowed to relax (the considered dopant configurations are shown in Fig. S4†). Fig. 4c displays the corrosion potential of these configurations. In all configurations, Ir<sub>0.21</sub>Ru<sub>0.79</sub>O<sub>2</sub> consistently demonstrates superior stability against corrosion compared to W<sub>0.21</sub>Ru<sub>0.79</sub>O<sub>2</sub>. The observed variations in stability among configurations are fairly consistent between the two dopants, suggesting that the positions of dopant atoms influence the corrosion behavior of the Ru<sub>diss</sub> atom, particularly its nearest neighbors. The distribution of dopant atoms in the bridge atom sites of the surface significantly influences stability, particularly the nearest bridge atom of Ru<sub>diss</sub>, as observed in configurations (3, 5, 7), where the bridge site next to Ru<sub>diss</sub> is occupied with a dopant atom. The metal atom directly underneath the Ru<sub>diss</sub> plays a similarly strong role: configuration 7 in Ir<sub>0.21</sub>Ru<sub>0.79</sub>O<sub>2</sub>, where Ir is the metal atom underlying Ru<sub>diss</sub> atom, is identified as the most stable configuration. Conversely, configuration 3 in W<sub>0.21</sub>Ru<sub>0.79</sub>O<sub>2</sub>, where Ru acts as the underlying Ru<sub>diss</sub> atom, demonstrates the highest stability among W<sub>0.21</sub>Ru<sub>0.79</sub>O<sub>2</sub> configurations. This consistency aligns with sublayer results, where W and Ir in the sublayer destabilize and stabilize the surface Ru atom, respectively. This trend is equally observed in the random configurations. Conversely, configurations where the dopant is not located in the bridge position, such as configurations 6 and 8 in W<sub>0.21</sub>Ru<sub>0.79</sub>O<sub>2</sub>, which lack W bridge atoms, are the least stable. This analysis provides valuable insights into predicting the stability of the surface based on specific dopant sites.

Interestingly, while in the case of Ir, all configurations demonstrate a stabilization, W can provide both a stabilizing effect, if it is located directly at the surface, and a destabilizing effect, if it is located in the sublayer. The strong role of the dopant distribution is further emphasized if we further consider different dopant contents, only favoring the most stabilizing patterns identified from the above analysis: in this



approach, we can achieve a corrosion potential of 1.457 V for an Ir content as low as 8% in the slab, only placing one Ir atom in the bridge position next to, and another directly underneath (*cf.* Fig. S5†). This represents a significant enhancement compared to the bulk corrosion of 1.21 V. By adding more Ir dopants in favorable positions, the corrosion potential can be further raised to 1.492 V at 21% Ir in the slab. This result highlights that a significant degree of stabilization can theoretically be achieved by doping very little Ir in just the right positions; however, experimentally achieving such selective doping remains a significant challenge. This result is significant because the price of raw Ir metal has been over 10 times as high as that of Ru consistently over the past three years.<sup>26</sup> If Ir was used to stabilize RuO<sub>2</sub>-based anodes for OER, its content should be as low as possible to reduce the cost of raw materials. Our results presented herein enable a knowledge-based approach to achieve these goals, which remains to be tested by experimental model studies.

**3.1.3 Influence of strain and layer thickness in RuO<sub>2</sub>@IrO<sub>2</sub>(110) and RuO<sub>2</sub>@TiO<sub>2</sub>(110).** For further investigation, we selected Ir and Ti from the group (Ir, Pt, Ti) to create substrates of IrO<sub>2</sub> and TiO<sub>2</sub> (these being the most commonly used materials to modify RuO<sub>2</sub>), aiming to explore additional parameters influencing the stability of the RuO<sub>2</sub>(110) surface against corrosion. Here, we aim to elucidate the influence of a substrate on a pseudomorphically grown RuO<sub>2</sub> layer. In the substrate model, we focused on two aspects: first, the effect of RuO<sub>2</sub> thickness on its surface stability against corrosion of the RuO<sub>2</sub>(110) surface, and second, the impact of strain due to the different lattice parameters on the stability against the RuO<sub>2</sub>(110) surface corrosion. The lattice mismatch between RuO<sub>2</sub> and IrO<sub>2</sub> is approximately 0.839% along the [001] direction and -0.482% along the [110] direction. Meanwhile, the mismatch between RuO<sub>2</sub> and TiO<sub>2</sub> is approximately -4.910% along the [001] direction and 2.496% along the [110] direction, indicating that TiO<sub>2</sub> introduces a higher strain on RuO<sub>2</sub> compared to IrO<sub>2</sub>.

Using the lattice parameter of IrO<sub>2</sub>, Fig. 5a and b depict the corrosion potential of different thicknesses of RuO<sub>2</sub> on two IrO<sub>2</sub> substrate models consisting of either 3 or 4 layers (3L, 4L). We observe that there is a significant scatter in the  $U_{corr}$  for even and uneven numbers of RuO<sub>2</sub>(110) layers. Similarly, we observe slightly different corrosion potentials for 3 and 4 layers of IrO<sub>2</sub> substrate. Both models consistently show that odd layers of RuO<sub>2</sub> stabilize the surface more strongly against even layers, and the corrosion potential converges around 6–7 layers to around 1.23 V for both models. According to these calculations, odd layers of RuO<sub>2</sub> grown on the IrO<sub>2</sub> clearly show a higher stabilization. Still, this behavior is likely significant only for very thin epitaxially grown layers not exceeding 4–5 layers. However, the lattice strain introduced due to IrO<sub>2</sub> as a substrate led to an overall stabilization of the RuO<sub>2</sub>(110) surface by shifting the  $U_{corr}$  from 1.21 V (pure RuO<sub>2</sub>(110)) to 1.23 V.

Such odd-even oscillations have been described previously for TiO<sub>2</sub>(110),<sup>27,28</sup> and upon closer examination, we attribute it to the layer stacking in the (110) direction of the rutile lattice, which comprises two different types of atoms, Ru<sub>cus</sub> and Ru<sub>br</sub> stacked in an A–B–A–B sequence on the substrate. For odd and even layers, corrosion occurs in an A and B layer, respectively, which may explain the observed oscillation, although the exact reason for this behavior is still unknown. This observation prompted us to reinvestigate the (100) surface, composed solely of A layers, as depicted in Fig. S6.† In this model, the oscillation of the  $U_{corr}$  between odd and even layers is not observed. On a (100) surface, it is in steady observed that increasing thickness of strained RuO<sub>2</sub> on top of IrO<sub>2</sub>, destabilizes the surface against corrosion, from 1.13 V (1L) to 0.84 V (7L). This indicates that strain can introduce a significant stabilizing effect in an otherwise inherently unstable facet like (100) and may be employed in addition to targeted doping to enhance the durability of RuO<sub>2</sub>-based OER catalysts. On the other hand, in the more stable (110) facet, the effect of strain is negligible if IrO<sub>2</sub> is employed as a substrate.

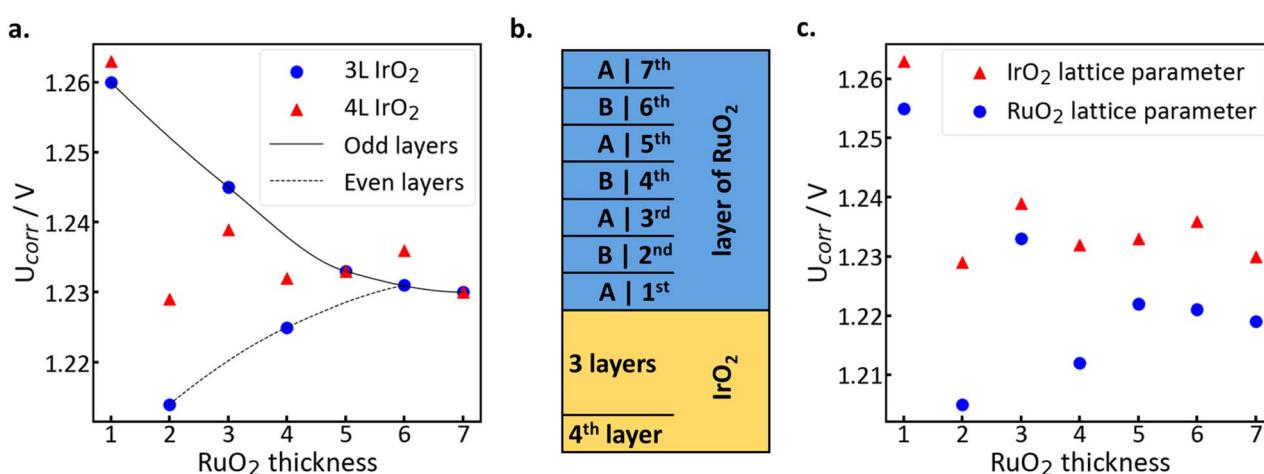


Fig. 5 (a and b) Influence of IrO<sub>2</sub>(110) substrate with different thicknesses of RuO<sub>2</sub> on the stability of RuO<sub>2</sub> against corrosion (calculated with IrO<sub>2</sub> lattice parameter). Configurations include 3 or 4 layers of IrO<sub>2</sub> with 1–7 layers of RuO<sub>2</sub>. (c) Influence of lattice parameters on the stability of RuO<sub>2</sub>(110) against corrosion. Potentials were calculated at pH = 0.



To validate these conclusions, the corrosion potentials for  $\text{RuO}_2$  layers grown on top of  $\text{IrO}_2$  without strain (*i.e.*, employing the  $\text{RuO}_2$  lattice parameter) are shown in Fig. 5c. Here, we observe the same odd-even oscillations; however, for thick  $\text{RuO}_2$  layers, the corrosion potential converges to the value of pure  $\text{RuO}_2(110)$ , confirming that the stability of the  $\text{RuO}_2$  surface is enhanced due to the strain introduced by the  $\text{IrO}_2$  substrate. The oscillations, on the other hand, are not a result of strain, but occur in thin  $\text{RuO}_2(110)$  layers regardless of strain. We emphasize that, despite these oscillations, the strain induced by the  $\text{IrO}_2$  substrate enhances stability of  $\text{RuO}_2(110)$ , regardless of thickness.

For the  $\text{TiO}_2$  substrate, we utilized the same model as for the 3L  $\text{IrO}_2$  model. Fig. S7† depicts the corrosion potential of different thicknesses of  $\text{RuO}_2$  on a 3L  $\text{TiO}_2$  substrate with varying lattice parameters. The odd-even oscillation behavior occurs here as well, but with a lower intensity. Interestingly, when using the  $\text{TiO}_2$  lattice parameter, the lattice strain leads to destabilization. Conversely, aligning with the  $\text{RuO}_2$  lattice parameter results in slight stabilization, consistent with Section 3.1.2. The different stabilization behavior of  $\text{IrO}_2$  and  $\text{TiO}_2$  substrates is likely due to the different magnitude of lattice mismatch, but also due to the different orientations of strain and stress.

The investigation reveals that  $\text{RuO}_2$  layers grown on  $\text{IrO}_2$  substrates exhibit enhanced stabilization due to minimal lattice mismatch, while  $\text{RuO}_2$  on  $\text{TiO}_2$  substrates faces destabilization due to greater overall lattice mismatch, with odd-even oscillations in corrosion potential observed for both substrates in (110) direction. The (100) direction does not display such

oscillations, but a significantly higher degree of stabilization due to the lattice mismatch.

### 3.2 Reaction pathways

In the second part of our investigation into the surface corrosion of the  $\text{RuO}_2(110)$  surface, we examine the corrosion at the  $\text{Ru}_{\text{br}}$  site, which exhibits six-fold coordination at typical OER operating potentials. We follow the mechanism proposed by Liu *et al.*,<sup>29</sup> consisting of a stepwise addition of  $\text{H}_2\text{O}$  from the electrolyte, followed by the removal of proton/electron pairs, resulting in the transformation of octahedral  $\text{RuO}_6$  into tetrahedral  $\text{RuO}_4$ , which subsequently detaches from the surface. Here, we investigate how a dopant sublayer, or quasi-random distribution of dopant atoms alter the energetics and reaction steps in the mechanism.

For the removal of  $\text{Ru}_{\text{br}}$ , we propose the following steps illustrated in Fig. 6, with the free energy profile depicted in Fig. 7:

Reconstruction step (a and b): this pivotal step initiates corrosion by lifting a  $\text{Ru}_{\text{br}}$  atom, forming two new Ru–O bonds with the neighboring  $\text{O}_{\text{ot}}$ . This Ru atom, now referred to as  $\text{Ru}_{\text{diss}}$ , requires +1.180 eV to accomplish this first, energetically uphill step.

First  $\text{H}_2\text{O}$  adsorption (c–g): in this step, an  $\text{H}_2\text{O}$  molecule is initially adsorbed on top of the new undercoordinated Ru site. This step is followed by the desorption of two-electron ( $e^-$ )-proton ( $\text{H}^+$ ) pairs. The process begins with  $\text{H}_2\text{O}$  adsorption and progresses until only terminal oxygen remains. Consequently, the newly formed  $\text{RuO}_6$  species undergoes a second reconstruction, transitioning into a tetrahedral  $\text{RuO}_4$  species. During

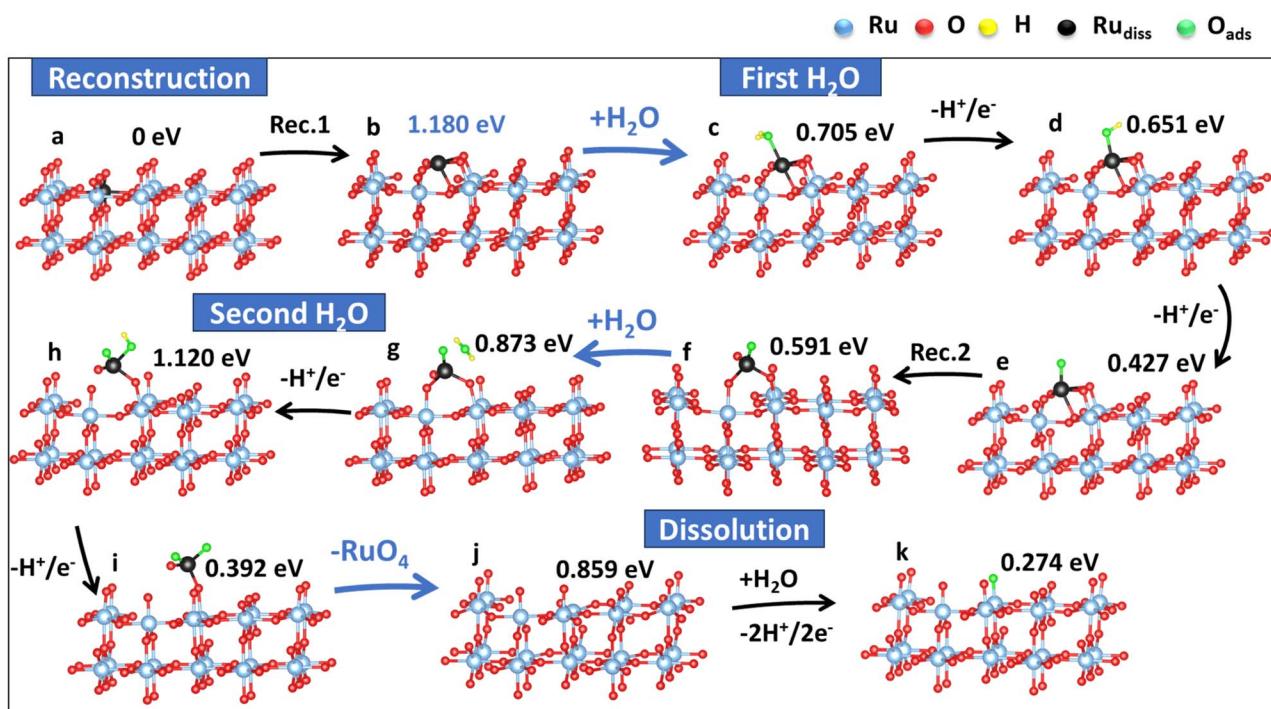


Fig. 6 The  $\text{Ru}_{\text{br}}$  corrosion mechanism on the  $\text{RuO}_2(110)$ . Colors: sky blue for  $\text{Ru}_{\text{bulk}}$ , red for O, yellow for H, black for  $\text{Ru}_{\text{diss}}$  (dissolution Ruthenium), and lime for  $\text{O}_{\text{ads}}$  (adsorbed oxygen).



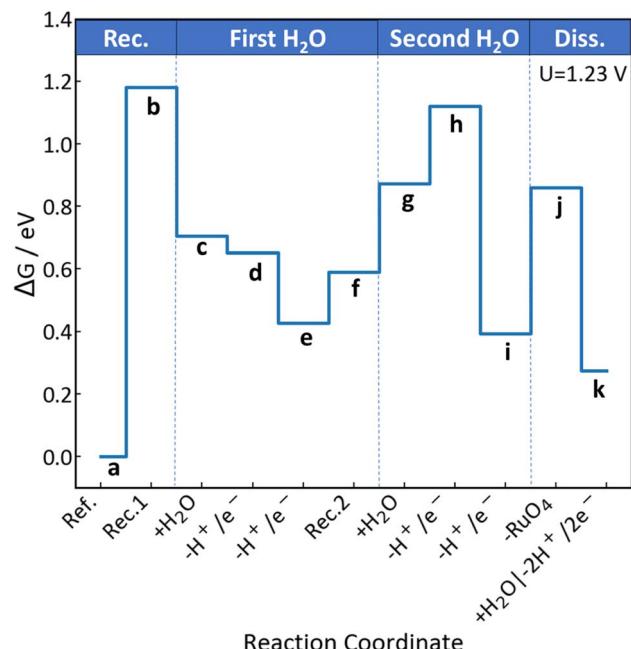


Fig. 7 The free energy profile of the  $\text{Ru}_{\text{br}}$  corrosion mechanism on the  $\text{RuO}_2(110)$  surface at an electrode potential  $U_{\text{SHE}} = 1.23$  V. Free energies were calculated at  $\text{pH} = 0$ .

this transformation, one of the  $\text{O}_{\text{br}}$  atoms detaches from the underlying Ru, becoming another terminal O. Simultaneously, the  $\text{Ru}_{\text{diss}}$  atom detaches from the underlying  $\text{O}_{\text{3f}}$  and one of the neighboring  $\text{O}_{\text{ot}}$  atoms. It is now connected to one  $\text{O}_{\text{ot}}$  and one  $\text{O}_{\text{br}}$ , establishing two terminal O atoms in a four-fold coordination ( $\text{Ru}_{\text{4f}}$ ).

Second  $\text{H}_2\text{O}$  adsorption (h and i): mirroring the preceding step, a second  $\text{H}_2\text{O}$  molecule adsorbs. Upon the removal of the first  $\text{H}^+/\text{e}^-$  pair, the  $\text{Ru}_{\text{diss}}$  atom severs its bond to the neighboring  $\text{O}_{\text{br}}$ , forming a  $\text{RuO}_3(\text{OH})$  complex attached only to  $\text{O}_{\text{ot}}$ . The final removal of  $\text{H}^+/\text{e}^-$  is exergonic and leads to the formation of a  $\text{RuO}_4$  species.

Dissolution step (j and k): in the final step, the  $\text{RuO}_4$  detaches from the surface, leaving an empty  $\text{Ru}_{\text{cus}}$  site behind. Subsequently, this site is saturated by the adsorption of the final  $\text{H}_2\text{O}$  molecule and the detachment of two  $\text{H}^+/\text{e}^-$  pairs.

The free energy profile of the  $\text{Ru}_{\text{br}}$  corrosion mechanism on the  $\text{RuO}_2(110)$  surface, as illustrated in Fig. 7, shows the free energy at each step. Notably, the initial reconstruction step (step b) presents the highest energetic threshold at 1.180 eV, indicating its unfavorable energetic characteristics. This chemical step is not influenced by the potential and likely represents the actual bottleneck under typical OER operating potentials.

Furthermore, removing the first  $\text{H}^+/\text{e}^-$  pair following the addition of the second  $\text{H}_2\text{O}$  (step h) is also quite high in free energy at 1.120 eV. This is the electrochemical step in nature, and its free energy can be lowered by increasing the applied potential. This indicates that the initially formed  $\text{RuO}_3(\text{OH})/\text{RuO}_4$  complexes may have a significant lifetime on the surface and may act as possible active sites in the OER, as proposed by Klyukin *et al.*<sup>30</sup>

We examined the influence of various dopants on the reaction pathway toward  $\text{RuO}_4$  formation to gauge the potential enhancement in stability against  $\text{RuO}_2(110)$  surface corrosion due to surface modification. Here, we distinguish between two possible modification strategies: (1) supporting  $\text{RuO}_2$  on a substrate of a different oxide, for which we only consider Ir, as it has a similar lattice parameter to  $\text{RuO}_2$ , thereby avoiding strain effects, and (2) doping, *i.e.*, the quasi-random substitution of Ru ions by other ions, and the respective influence on the reaction steps of the corrosion mechanism. Here, we consider Ti, Ir, and W, as representatives of the three groups favoring different oxidation states as identified in Section 3.1.2.

**3.2.1 Influence of substrate sublayer.** Initially, we scrutinized the mechanism of  $\text{Ru}_{\text{br}}$  removal over an  $\text{IrO}_2(110)$  support substrate, utilizing three layers of  $\text{IrO}_2$  with varying thicknesses of  $\text{RuO}_2$ . Based on our thermodynamic results (Fig. 5 and S7†), we selected a thickness of three layers to represent odd layers. Arguably, one layer shows a more pronounced change in stability due to the direct effect of the sublayer being exposed during the corrosion. This direct effect even changes the reaction mechanism in some cases, complicating the comparison. The direct effect of sublayer dopants will be considered separately in Section 3.2.2. Hence, we chose three layers to gauge the indirect effect of the support on the surface stability. Thermodynamically, we observed in Fig. 5 that odd and even layers lead to destabilization and stabilization compared to pure  $\text{RuO}_2(110)$ , respectively.

In Fig. 8, we illustrate the influence of the layer thickness on the free energy profile for the  $\text{Ru}_{\text{br}}$  corrosion mechanism on the  $\text{RuO}_2@\text{IrO}_2(110)$  surface with two models (2L, 3L) of  $\text{RuO}_2$ . We observed a significant correlation between the thermodynamic free energy of corrosion (represented by the free energy difference between the final state k and initial state a in Fig. 8) and reaction mechanisms, represented by the free energy of the highest intermediate ( $\Delta G_{\text{max}}$ ). The reaction steps of corrosion on the supported  $\text{RuO}_2(110)$  surfaces largely follow the same sequence as on pure  $\text{RuO}_2(110)$ , only the energies are shifted: The corrosion intermediates on odd layers exhibit higher free energies than their even-layer counterparts, indicating increased stability and reduced susceptibility to corrosion, both in terms of thermodynamics and in terms of thermodynamic barriers. However, the highest energetic threshold, *i.e.*, the reconstruction step (step b), remains unchanged for three layers of  $\text{RuO}_2$  (green line), standing at 1.197 eV. For two layers of  $\text{RuO}_2$  (orange line), the second  $\text{H}_2\text{O}$  adsorption, coupled with the removal of a proton/electron pair (step h) requires a free energy of 1.01 eV, which is not significantly different from the initial reconstruction step (step b), indicating a possible shift in the reaction pathway at this potential ( $U_{\text{SHE}} = 1.23$  V). However, at a potential typically applied during OER ( $U_{\text{SHE}} > 1.4$  V), the initial reconstruction step, being a purely chemical step, remains the highest energetic threshold.

**3.2.2 Influence of randomly distributed dopants.** Continuing our investigation into the effects of dopants (Ti, Ir, W) on the reaction mechanisms, we arranged our investigation based on the surface termination preferences of cus sites at  $U_{\text{SHE}} = 1.23$  V. Specifically, we examined the reactions



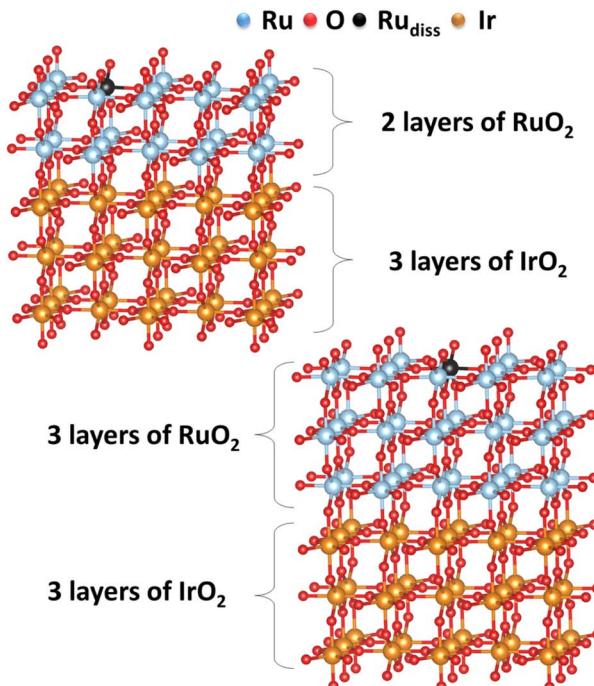
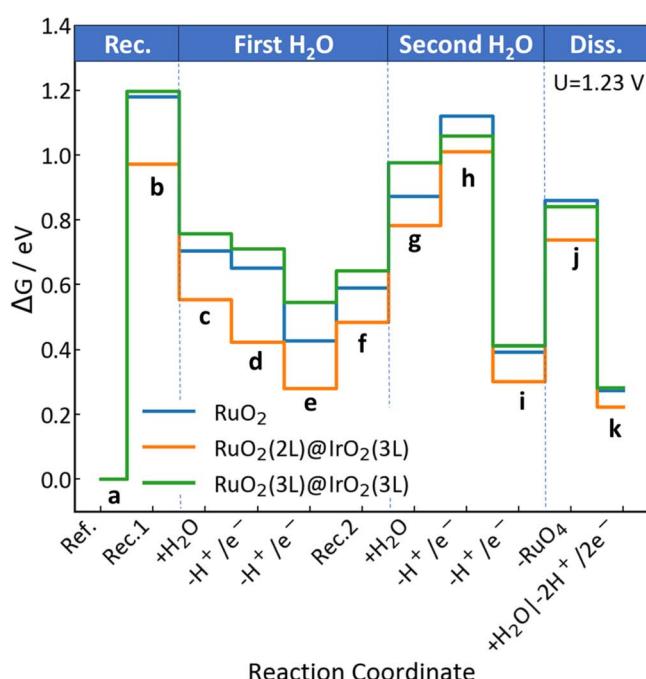


Fig. 8 Free energy profile at  $U_{\text{SHE}} = 1.23 \text{ V}$  for  $\text{Ru}_{\text{br}}$  corrosion mechanism on  $\text{RuO}_2@\text{IrO}_2(110)$  surface, comparing 2L and 3L  $\text{RuO}_2$  models. Free energies were calculated at pH = 0. Colors: sky blue for  $\text{Ru}_{\text{bulk}}$ , red for O, black for  $\text{Ru}_{\text{diss}}$ , and brown for Ir.

considering Ti, which favors termination without O; Ir, which favors termination with OH; and W, which favors O termination.

We initially focused on examining the  $\text{Ti}_{0.67}\text{Ru}_{0.33}\text{O}_2$  mixture, maintaining two fixed layers of  $\text{RuO}_2$  at the bottom while allowing three layers of  $\text{Ti}_{0.67}\text{Ru}_{0.33}\text{O}_2$  to relax. Fig. 9

focuses on the impact of Ti atom distribution on the free energy profile of the  $\text{Ru}_{\text{br}}$  corrosion mechanism on the  $\text{Ti}_{0.67}\text{Ru}_{0.33}\text{O}_2(110)$  surface. We consider two different configurations, each defining a specific neighborhood around the dissolving  $\text{Ru}_{\text{cus}}$  atom, to elucidate the influence on individual reaction steps. In configuration 1, the bridge atom next to the

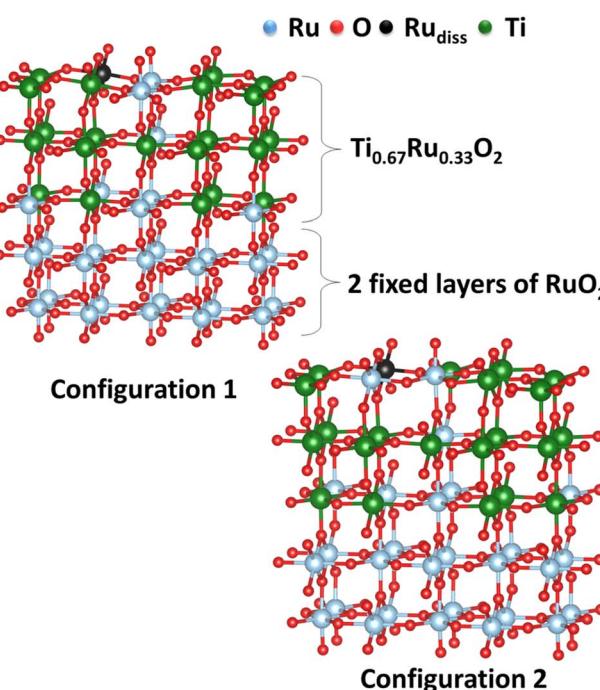
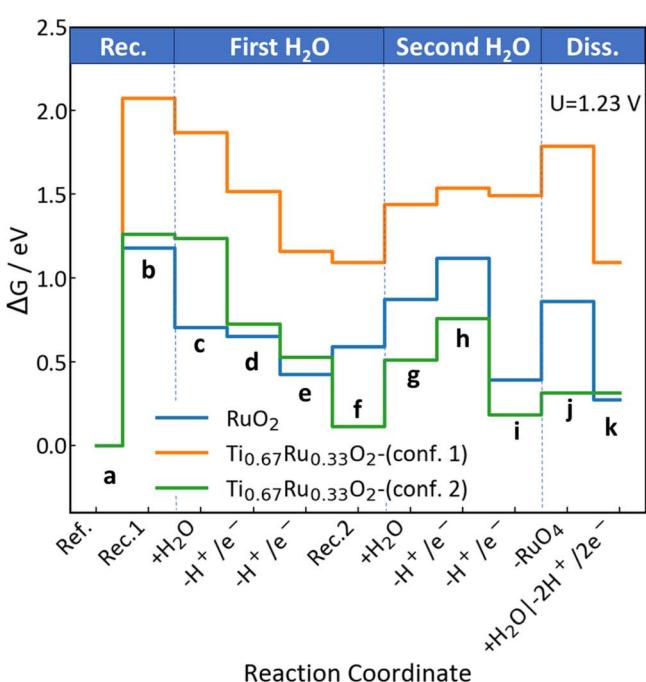


Fig. 9 The free energy profile at  $U_{\text{SHE}} = 1.23 \text{ V}$  illustrates the  $\text{Ru}_{\text{br}}$  corrosion mechanism on the  $\text{Ti}_{0.67}\text{Ru}_{0.33}\text{O}_2(110)$  surface in two configurations. Free energies were calculated at pH = 0. Colors: sky blue for  $\text{Ru}_{\text{bulk}}$ , red for O, black for  $\text{Ru}_{\text{diss}}$ , and green for Ti.



dissolving atom is replaced by Ti, while the neighboring cus atom participating in the dissolution mechanism remain Ru. In configuration 2, the neighboring bridge atom remains Ru, while the neighboring cus atom is replaced by Ti. We note that, on these doped surfaces, there are many possible realizations of the corrosion mechanism, involving the bridge and cus sites, and in some cases, different cus sites. We tested multiple configurations and bond-breaking sequences to identify the pathways with the lowest free energy. This comparative analysis, illustrated in Fig. S9,† highlights key differences between chosen and non-chosen configurations, revealing how dopants can alter the reaction mechanism compared to pure  $\text{RuO}_2(110)$ . The results shown below reflect the most favorable pathways identified.

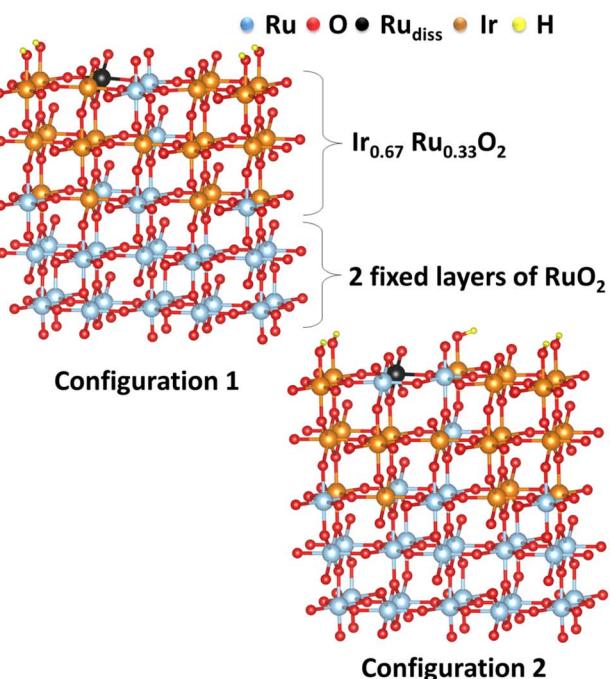
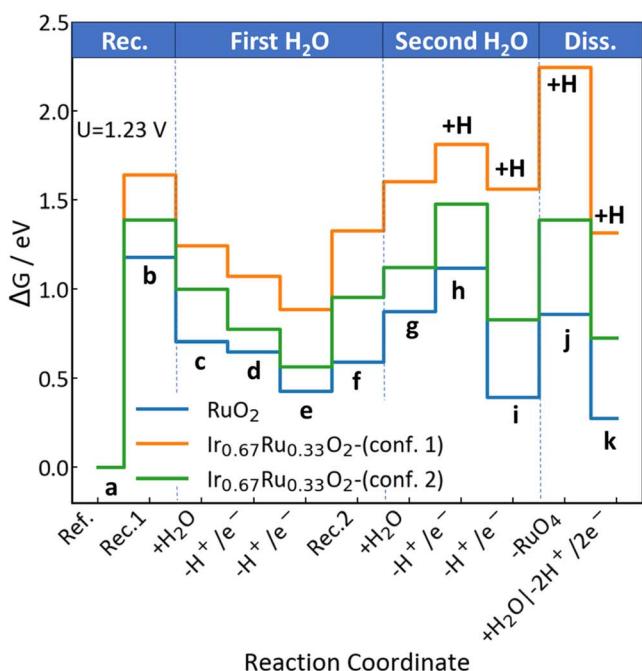
This specific modification of the environment alters the energetics of the reaction steps as follows: configuration 1 (orange line in Fig. 9) exhibits higher free energy and greater stability compared to pure  $\text{RuO}_2$  (blue line) and configuration 2 (green line). The free energy reaches its maximum value of 2.075 eV in configuration 1 (orange line in Fig. 9) during the reconstruction step (step b), while configuration 2 reaches a maximum of 1.264 eV during the same step. Notably, in configuration 1, the nearest bridge neighbor to  $\text{Ru}_{\text{diss}}$  is  $\text{Ti}_{\text{br}}$ . During the reaction steps, especially in the second  $\text{H}_2\text{O}$  adsorption step (step h), no proton/electron pair is removed, and the H adsorbs onto  $\text{O}_{\text{br}}$  (which is on  $\text{Ti}_{\text{br}}$ ). Then, in step j, the OH on  $\text{Ti}_{\text{br}}$  is removed.

In configuration 2, the nearest neighbor is another Ru<sub>br</sub>. The transition from step a to step b, due to the unfavorable terminal O at Ti<sub>cus</sub> in step a, involves three preparatory sub-steps (from b'' to b' shown in detail in Fig. S8†). These sub-steps include the

adsorption of  $\text{H}_2\text{O}$  on the  $\text{Ti}_{\text{cus}}$  atom. Upon the removal of the first  $\text{H}^+/\text{e}^-$  pair, the  $\text{Ru}_{\text{diss}}$  atom severs its bond to the neighboring OH of  $\text{Ti}_{\text{cus}}$ . The final removal of  $\text{H}^+/\text{e}^-$  is exergonic, resulting in the formation of the regular step b. Notably, we observed a significant drop in free energies, attributed to changes in the reaction mechanism compared to pure  $\text{RuO}_2(110)$ , starting from step f. Unlike pure  $\text{RuO}_2$ , where the tetrahedral  $\text{RuO}_4$  species is connected to neighboring  $\text{O}_{\text{br}}$  and  $\text{O}_{\text{ot}}$ , in configuration 2, the  $\text{RuO}_4$  species prefers being connected to two  $\text{O}_{\text{ot}}$ , resulting in an exergonic reaction step (e  $\rightarrow$  f). This is mainly because it is highly unfavorable for  $\text{Ti}_{\text{cus}}$  to be capped by terminal oxygen; moving the  $\text{RuO}_4$  species to the cus sites avoids this scenario. Similarly, upon the removal of the final  $\text{H}^+/\text{e}^-$  pair in the second  $\text{H}_2\text{O}$  adsorption step, the  $\text{Ru}_{\text{diss}}$  atom severs its bond with the neighboring  $\text{O}_{\text{ot}}$  of  $\text{Ru}_{\text{cus}}$  akin to the Walden inversion proposed by Hess *et al.*<sup>25</sup> This results in the formation of a  $\text{RuO}_4$  species attached only to the  $\text{O}_{\text{ot}}$  of  $\text{Ti}_{\text{cus}}$ , thereby avoiding the unfavorable terminal O at  $\text{Ti}_{\text{cus}}$ . In the final step,  $\text{RuO}_4$  detaches, leaving an empty  $\text{Ti}_{\text{cus}}$  site, as  $\text{Ti}_{\text{cus}}$  prefers termination without O.

Moving on to the  $\text{Ir}_{0.67}\text{Ru}_{0.33}\text{O}_2$  mixture, we adopted a similar methodology by fixing two layers of  $\text{RuO}_2$  at the substrate while allowing three layers of  $\text{Ir}_{0.67}\text{Ru}_{0.33}\text{O}_2$  to relax. The distribution of Ir atoms in configurations 1 and 2 of  $\text{Ir}_{0.67}\text{Ru}_{0.33}\text{O}_2$  mirrors that of Ti atoms in  $\text{Ti}_{0.67}\text{Ru}_{0.33}\text{O}_2$ .

Fig. 10 illustrates how the Ir distribution influences the free energy profile of the Ru<sub>br</sub> corrosion mechanism on the Ir<sub>0.67</sub>Ru<sub>0.33</sub>O<sub>2</sub>(110) surface. Like in Fig. 9, we explore two configurations: configuration 1 (orange line) shows a  $\Delta G_{\max}$  of 2.248 eV during the dissolution step (step j), whereas configuration 2 (green line) peaks at 1.479 eV during the second H<sub>2</sub>O



**Fig. 10** The free energy profile at  $U_{\text{SHE}} = 1.23$  V illustrates the Ru<sub>br</sub> corrosion mechanism on the Ir<sub>0.67</sub>Ru<sub>0.33</sub>O<sub>2</sub>(110) surface for two configurations. Free energies were calculated at pH = 0. Colors: sky blue for Ru<sub>bulk</sub>, red for O, yellow for H, black for Ru<sub>diss</sub>, and brown for Ir.

adsorption step (step h). Configuration 1 exhibits higher free energy and greater stability compared to pure  $\text{RuO}_2$  (blue line) and configuration 2. Notably, in configuration 1, the nearest neighbor to the  $\text{Ru}_{\text{diss}}$  is  $\text{Ir}_{\text{br}}$ . Starting from the second  $\text{H}_2\text{O}$  step (step h), upon the removal of the first  $\text{H}^+/\text{e}^-$  pair, the  $\text{Ru}_{\text{diss}}$  atom severs its bond with the neighboring  $\text{O}_{\text{br}}-\text{Ir}_{\text{br}}$ , resulting in the  $\text{Ir}_{\text{br}}$  being saturated by terminal OH. The subsequent steps take place exclusively on the  $\text{cus}$  sites. In configuration 2, the nearest neighbor is another  $\text{Ru}_{\text{br}}$ , and no changes in reaction mechanisms occur after step f, unlike configuration 2 of  $\text{Ti}_{0.67}\text{Ru}_{0.33}\text{O}_2$ .

Lastly, we investigated the  $\text{W}_{0.21}\text{Ru}_{0.79}\text{O}_2$  mixture, employing the same layer arrangement as in the previous mixtures. Similar to the previous examinations, we chose two configurations: configuration 1, where the neighboring bridge and  $\text{cus}$  atoms are W and Ru, respectively, and *vice versa*, in configuration 2. We selected a lower doping content in this case because W is the least similar to Ru, and addition of too much dopant may alter the properties in unpredictable ways; nevertheless, significant effects are observed here, because the specific doped sites have a larger effect on the corrosion behavior than the overall doping content, as shown in Section 3.1.2.

Fig. 11 depicts how the W distribution influences the free energy profile of the  $\text{Ru}_{\text{br}}$  corrosion mechanism on the  $\text{W}_{0.21}\text{Ru}_{0.79}\text{O}_2(110)$  surface. It explores two configurations relative to pure  $\text{RuO}_2$ . Notably, configuration 2 (green line) shows the highest free energy step at 1.144 eV during the final dissolution step (step j), while configuration 1 (orange line) peaks at 1.182 eV during the first reconstruction (step b).

The dramatic change in configuration 2 can be explained by the strong preference of  $\text{W}_{\text{cus}}$  to remain terminated by O at the

given potential: upon the removal of the final  $\text{H}^+/\text{e}^-$  pair in the second  $\text{H}_2\text{O}$  step, the  $\text{Ru}_{\text{diss}}$  atom severs its bond with the neighboring  $\text{O}_{\text{br}}$  of Ru, forming a  $\text{RuO}_4$  species attached only to the  $\text{O}_{\text{ot}}$  of W. While in the regular mechanism considered for all other cases,  $\text{RuO}_4$  desorbs, along with the  $\text{O}_{\text{ot}}$ ,  $\text{W}_{\text{cus}}$  requires to remain saturated. Therefore, before the dissolution step (step j), to lower this high free energy, a third  $\text{H}_2\text{O}$  molecule adsorbs, detaining two  $\text{H}^+/\text{e}^-$  pairs, as shown in Fig. S10.† This alteration in the mechanism akin to the Walden inversion proposed by Hess *et al.*<sup>25</sup> reduces the highest free energy step from 1.305 eV to 1.144 eV.

From the different behavior of the three dopants and their different termination preferences we learn that the choice of dopant can alter not only the free energies of the reaction steps, but also the nature of these steps. To avoid states that are too high in free energy due to unfavorable terminations of the metal sites next to  $\text{Ru}_{\text{diss}}$ , additional  $\text{H}_2\text{O}$  molecules may partake in the reaction toward  $\text{RuO}_4$ . On Ti-doped  $\text{RuO}_2$ , we observe that the initial reconstruction is complicated by the lack of terminal O at  $\text{Ti}_{\text{cus}}$ ; however, the final states involving the removal of  $\text{RuO}_4$  are simplified as they allow the  $\text{Ti}_{\text{cus}}$  to recover its vacant state. On the other hand, in W-doped  $\text{RuO}_2$ ,  $\text{W}_{\text{cus}}$  has such a strong preference to be capped with  $\text{O}_{\text{cus}}$  that additional steps are required late in the mechanism to detach  $\text{RuO}_4$  from the surface.

Close inspection of the data presented in Fig. 7–11 suggests that the thermodynamics of corrosion are highly correlated across a large variety of surface modifications. Based on all the data presented in this section, we quantitatively examined the correlation between the thermodynamic corrosion potential and the  $\Delta G_{\text{max}}$  of the full reaction energy profiles to assess the

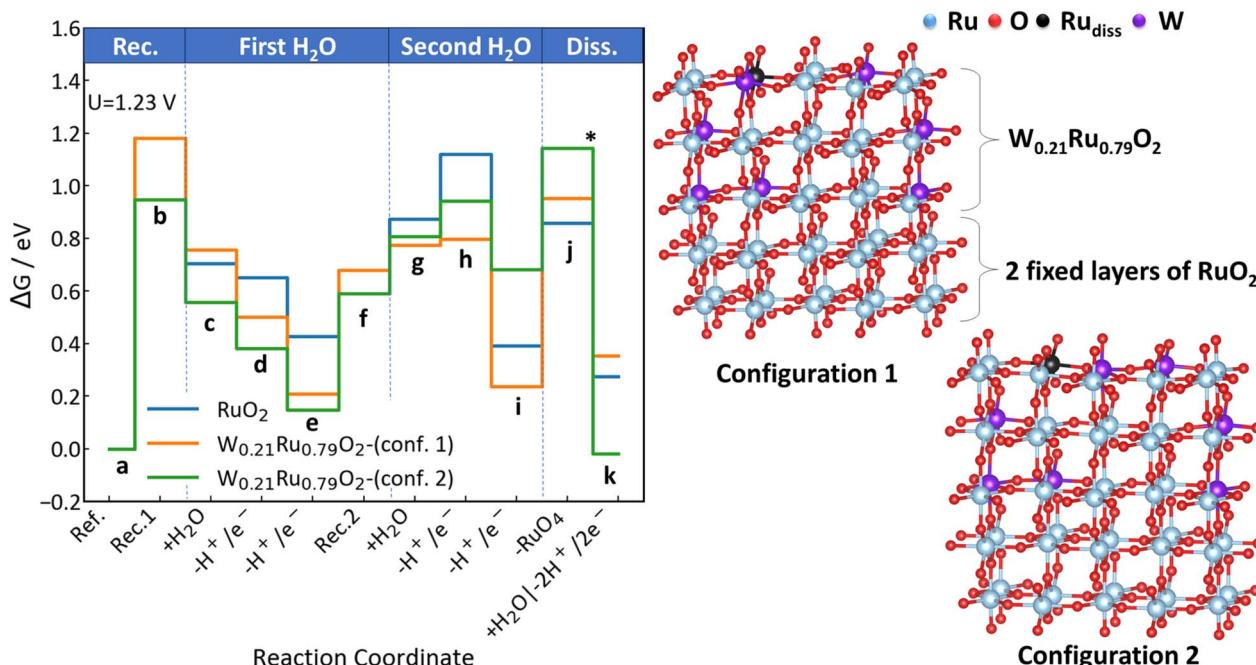


Fig. 11 The free energy profile at  $U_{\text{SHE}} = 1.23$  V illustrates the  $\text{Ru}_{\text{br}}$  corrosion mechanism on the  $\text{W}_{0.21}\text{Ru}_{0.79}\text{O}_2(110)$  surface for two configurations. Free energies were calculated at pH = 0. Colors: sky blue for  $\text{Ru}_{\text{bulk}}$ , red for O, black for  $\text{Ru}_{\text{diss}}$ , and violet for W. Note: step j consists of three steps represented by the highest free energy among them; please refer to Fig. S10† for details. \*



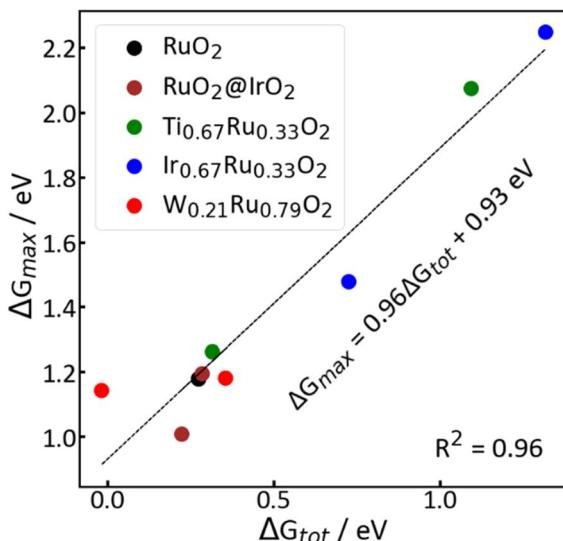


Fig. 12 Correlation between  $\Delta G_{\text{tot}}$  and  $\Delta G_{\text{max}}$  illustrates material stability interconnections across surfaces. Free energies were calculated at pH = 0 and  $U_{\text{SHE}} = 1.23$  V.

suitability of  $\Delta G_{\text{tot}}$  as a descriptor for screening studies. As depicted in Fig. 12, our correlation analysis reveals a robust positive relationship ( $R^2 = 0.96$ ) between the total free energy ( $0 \leq \Delta G_{\text{tot}} \leq 1.5$  eV) and the maximum free energy ( $1.0 \text{ eV} \leq \Delta G_{\text{max}} \leq 2.2$  eV). This finding provides compelling evidence of the inherent connection between these parameters, highlighting a fundamental relationship governing material stability across diverse surface configurations across a large range of free energies. The maximum free energy ( $\Delta G_{\text{max}}$ ) is particularly significant for kinetic studies as it often represents the potential-determining step of a reaction, thus influencing the overall reaction rate and, in the case of corrosion, stability. Since  $\Delta G_{\text{tot}}$  is a highly accessible quantity, requiring only the computation of initial and final state of the surface, we propose it as a descriptor suitable for screening the efficacy of different surface modifications *via* computation. Furthermore, this suggests that the stepwise corrosion mechanism does not need to be known in order to predict relative stabilities between similar surfaces.

Overall, our investigation into  $\text{Ti}_{0.67}\text{Ru}_{0.33}\text{O}_2$ ,  $\text{Ir}_{0.67}\text{Ru}_{0.33}\text{O}_2$ , and  $\text{W}_{0.21}\text{Ru}_{0.79}\text{O}_2$  mixtures unveils nuanced variations in reaction mechanisms and surface atom distributions. These findings underscore the critical role of dopant selection in optimizing  $\text{RuO}_2$  surface stability against corrosion. By elucidating the intricate interplay between dopants, surface terminations, and reaction pathways, our study provides valuable insights for the design and engineering of advanced materials exhibiting long-term stability for applications ranging from catalysis to energy storage.

## 4 Discussion

To begin our discussion, we contextualize our investigation into the thermodynamic stability of the  $\text{RuO}_2(110)$  surface within the broader scope of existing experimental and theoretical studies.

Our investigation corroborates those of Over *et al.*<sup>31</sup> who identified the  $\text{RuO}_2(110)$  surface as the most stable among various facets. Additionally, our results are consistent with Hess *et al.*<sup>25,32</sup> on  $\text{RuO}_2(100)$  and its  $c(2 \times 2)$  reconstructed facets as detailed in Fig. 3. Stoerzinger *et al.*<sup>33</sup> also examined the oxygen evolution reaction (OER) activity across different facets (100), (110), (101), and (111), confirming that the (110) facet is the most stable, while the (100) facet is the most active. Our study specifically targets the stability of the  $\text{RuO}_2(110)$  surface against corrosion and aims to enhance this stability.

Several studies have explored the incorporation of dopants into  $\text{RuO}_2$  to improve stability. Kasian *et al.*<sup>10</sup> focused on the stabilization effect of Ir in  $\text{RuO}_2$ , demonstrating that incorporating 25% Ir significantly enhances stability. Similarly, Escalera-López *et al.*<sup>34</sup> investigated the electrochemical activity–stability relationship of Ir–Ru mixed oxides ( $\text{Ir}_x\text{Ru}_{1-x}\text{O}_2$ ), finding that 20% Ir improves stability while maintaining high activity. Both studies indicated a significant positive effect on surface stability with a slight decrease in activity, which informed our chosen Ir concentration in Fig. 4c. Our results are consistent with these findings, showing a significant improvement in the stability of the  $\text{RuO}_2(110)$  surface. In studies exploring OER activity and electrocatalyst stability,  $\text{Ir}_x\text{Ru}_{1-x}\text{O}_y$  catalysts with Ir concentrations up to 70% were developed, achieving  $3 \text{ A cm}^{-2}$  at 1.8 V with strong stability in PEM electrolysis, though high turnover frequency altered Lewis acidity, impacting water oxidation.<sup>35</sup> Additionally, tuning the near-surface composition of Ru and Ir *via* surface segregation resulted in a  $\text{Ru}_{0.5}\text{Ir}_{0.5}$  alloy exhibiting four times higher stability than the best Ru–Ir OER materials, without compromising catalytic activity.<sup>9</sup> This is consistent with our investigation of the  $\text{Ir}_{0.67}\text{Ru}_{0.33}\text{O}_2$  mechanism, where the high Ir concentration contributes to one of the most stable surfaces, as shown in Fig. 10. We note that doping  $\text{RuO}_2$  with Ir poses an economic challenge, as the high cost of Ir may limit practical application. Our findings indicate that substituting specific Ru sites by Ir may result in significant enhancement, an insight that could be exploited to reduce the Ir content of mixed (Ru, Ir)  $\text{O}_2$  for OER applications.

Our study investigates the influence of lower cost doping elements, such as Ti and W, which have been proposed in the literature as potential dopants for  $\text{RuO}_2$ . Hao *et al.*<sup>12</sup> investigated the stability and activity of  $\text{RuO}_2$  with W and Er ( $\text{W}_{0.2}\text{Er}_{0.1}\text{Ru}_{0.7}\text{O}_{2-\delta}$ ). They found that adding W and Er significantly increases the catalyst's oxygen vacancy formation energy, improving durability and activity. This finding informed our chosen W concentration in Fig. 4c and 11 of the reaction mechanism investigation. Our predictions in Fig. 4c allow us to identify optimal dopant sites that enhance the durability and stability of the  $\text{M}_{0.21}\text{Ru}_{0.79}\text{O}_2(110)$  surface.

For  $\text{Ti}_x\text{Ru}_{1-x}\text{O}_2$ , Godínez-Salomón *et al.*<sup>11</sup> demonstrated that incorporating Ti (12.5–50%) enhances catalyst stability and reduces Ru dissolution, with low Ti concentrations (12.5–20 at%) significantly improving stability compared to pure  $\text{RuO}_2$ . Regarding  $\text{IrO}_2$  substrates, most studies focus on  $\text{RuO}_2$  substrates enhancing the surface activity of  $\text{IrO}_2$ . Our study uniquely examines the effect of  $\text{RuO}_2$  thickness on an  $\text{IrO}_2$



substrate, identifying the optimal thickness for maximal stability. Fig. 5 reveals a distinct odd-even layer behavior that suggests that uneven layers, such as 1 or 3, exhibit the highest stability.

Consistent with recent findings by Chaudhary *et al.*,<sup>36</sup> our study shows that tensile strain (as seen in RuO<sub>2</sub> on IrO<sub>2</sub>) enhances corrosion resistance, while compressive strain (as observed in RuO<sub>2</sub> on TiO<sub>2</sub>) leads to destabilization of the surface, highlighting the critical role of strain in influencing the corrosion behavior of RuO<sub>2</sub>.

In terms of reaction mechanism, while many studies have concentrated on the oxygen evolution reaction (OER) mechanism at RuO<sub>2</sub>(110), fewer have delved into the specifics of RuO<sub>2</sub> corrosion mechanisms. Klyukin *et al.*<sup>30</sup> proposed a concept wherein a defect-free surface undergoes transitions leading to RuO<sub>4</sub> formation and subsequent corrosion. Similarly, Liu *et al.*<sup>29</sup> introduced four potential initial reconstruction steps (chemical steps), focusing on one to elucidate a mechanism that results in RuO<sub>4</sub> formation and surface corrosion. We adopted and expanded upon this mechanism in our investigation.

Our study extends beyond merely detailing the corrosion mechanisms of the RuO<sub>2</sub> surface to examine the impact of doping on these mechanisms, as shown in Fig. 8–11. Our findings highlight how the termination of the cus atoms in dopants affects the reaction mechanism and the associated free energies. In contrast to Gong *et al.*,<sup>37</sup> who use metal–oxygen bond strength from MD simulations to predict dissolution rates of complex glasses, our study focuses on thermodynamic descriptors, specifically  $\Delta G_{\max}$  and  $\Delta G_{\text{tot}}$ , to assess corrosion resistance in RuO<sub>2</sub>. While Gong *et al.*<sup>37</sup> report  $R^2$  values of 0.80–0.92 for bond strength and dissolution rates, our study finds a strong correlation ( $R^2 = 0.96$ ) between  $\Delta G_{\max}$  and  $\Delta G_{\text{tot}}$ , demonstrating their effectiveness in predicting material stability. Similarly, Schwöebel *et al.*<sup>38</sup> use hydrogen bond acceptor strength as a descriptor for organic and inorganic compounds, demonstrating a high correlation ( $R^2 = 0.97$ ) with experimental data, while our study employs thermodynamic parameters to predict corrosion stability, highlighting the broad applicability of descriptor-based methods across different material types. The concept of 'maximum free energy' ( $\Delta G_{\max}$ ) as a descriptor for stability was first introduced by Exner and Over,<sup>39</sup> and our findings further support its utility in understanding reaction rates and mechanisms the trends of reaction rates and mechanisms upon altering the properties of the surface. Further work is required to understand the details of the kinetic processes governing the competition between the OER and the parasitic corrosion leading toward electrode dissolution. Kinetic studies are crucial for offering insights into activation energies, rate constants, and the effects of temperature and other reaction conditions.<sup>40–51</sup> Additionally, we plan to investigate the OER activity of various doped surfaces to compare their performance and stability relative to pure RuO<sub>2</sub>.

## 5 Conclusion

Through comprehensive DFT analyses, we elucidate the stability and reaction mechanisms of RuO<sub>2</sub> catalysts in water

electrolysis. Our investigation reveals the intricate interplay between surface orientations, dopants, and corrosion mechanisms, shedding light on key factors influencing RuO<sub>2</sub> stability against corrosion.

Our findings emphasize the critical role of understanding the intricate interplay between surface composition, dopants, and reaction mechanisms to optimize the stability of RuO<sub>2</sub> surfaces. Dopants such as Ir, Ti, and W exhibit diverse effects on stability, with Ir demonstrating superior stabilization compared to other elements. Specifically, Ti favors termination without O, Ir favors OH termination, and W favors O termination, each influencing distinct free energy profiles and reaction pathways, particularly evident in configuration 2 across all mixtures. Based on the correlation between the total change in Gibbs free energy ( $\Delta G_{\text{tot}}$ ) and the maximum Gibbs free energy ( $\Delta G_{\max}$ ) we propose  $\Delta G_{\text{tot}}$  as an accessible descriptor to predict the effect of different surface modifications on the stability of surface sites.

Overall, our study not only deepens our understanding of the complex behavior of RuO<sub>2</sub> surfaces but also offers valuable insights into designing tailored materials with enhanced stability for various applications, including catalysis and energy storage. These findings lay a solid foundation for future research aimed at optimizing the performance of RuO<sub>2</sub>-based materials in real-world applications, thereby advancing the field of materials science and engineering.

## Data availability

The Vienna *Ab initio* Simulation Package (VASP) code used in this study includes versions 5.4.4 and 6.4.2. Detailed information about VASP, including the latest updates and releases, can be found on the official VASP website: <https://www.vasp.at>.

## Conflicts of interest

There are no conflicts to declare.

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