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## TiO<sub>2</sub>-coated rutile oxide catalysts for acidic oxygen evolution: a design principle

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Green hydrogen production through water electrolysis under acidic conditions is limited by the efficiency of the anodic oxygen evolution reaction (OER). In this study, we outline a design principle for developing active and potentially stable rutile oxide electrocatalysts for acidic OER. Using density functional theory, we find that the adsorption energies for Ti, Sn, and Zr active sites correlate with the position of the Fermi level relative to the oxygen 2s states as the surrounding oxide composition is varied. This trend is not observed for platinum-group elements. We attribute this difference to the inability of Ti, Sn, and Zr active sites to access oxidation states above the 4+ of the rutile structure, according to changes in geometry and charge. Ti emerges as an adsorption site of special interest, since varying the composition of the surrounding rutile oxide allows titanium sites to reach theoretical overpotentials as low as 0.14 V. We then demonstrate tunable activity for TiO<sub>2</sub>-coated conductive rutile substrates. Based on literature evidence that TiO<sub>2</sub> coatings improve stability under acidic OER conditions without substantially compromising activity, we suggest that a TiO<sub>2</sub> overlayer can serve as both an active site and corrosion protection. We propose a composition-based model that successfully finds Ir and Ru free compositions (W<sub>x</sub>Pt<sub>1-x</sub>O<sub>2</sub>, W<sub>0.46</sub>Pd<sub>0.54</sub>O<sub>2</sub>) that can activate the applied TiO<sub>2</sub> overlayer.

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### Broader context

Proton-exchange membrane water electrolyzers offer significant advantages over alkaline water electrolyzers in the production of green hydrogen, including higher current densities, a high-purity hydrogen gas and a compact device design. As catalysts for the anodic oxygen evolution reaction (OER), oxides based on Ir offer the best compromise between activity and stability, however, the scarcity of Ir limits the industrial scalability of this technology. Earth-abundant alternatives are usually either active but unstable under acidic conditions, or stable but not sufficiently active. This work outlines a design principle for the fabrication of active and stable TiO<sub>2</sub>-coated rutile oxide catalysts for the acidic OER. Our calculations demonstrate that the activity of a Ti site correlates with the position of the Fermi level of the surrounding oxide. By choosing the right surrounding oxide composition, Ti sites can be activated to achieve low OER overpotential. The same principle is found to apply for TiO<sub>2</sub> overlayer(s) which can then act as both active site and corrosion protection. The Fermi level energy of the host oxide can be predicted based on the composition, making it possible to construct Ir- and Ru-free catalysts with predicted high OER activity.

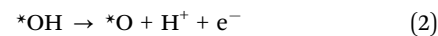
## Introduction

Practical strategies for storing electricity from renewable energy sources, *e.g.* in the form of chemical fuels, are crucial to reduce dependence on fossil fuels. Molecular hydrogen is a suitable fuel in this context, since it can be efficiently generated through water electrolysis (WE).<sup>1</sup> Alkaline WE is a well-established technology relying on transition metal based catalysts,<sup>2,3</sup> however proton exchange membrane water electrolysis (PEMWE), which operates under acidic conditions, offers several

advantages over the alkaline setup, including higher current densities, purer product gas and more compact devices.<sup>4</sup> The oxygen evolution reaction (OER), occurring at the anode, is recognised as the kinetic bottleneck in both alkaline and acidic water electrolysis.<sup>5</sup> The limitation arises because the OER consists of four proton-coupled electron transfer steps, *e.g.* for the conventionally assumed adsorbate evolution mechanism (AEM, see Section S1 in the SI for illustration):



$$\Delta G_1 = \Delta G_{* \text{OH}} - eU_{\text{RHE}}$$



$$\Delta G_2 = \Delta G_{* \text{O}} - \Delta G_{* \text{OH}} - eU_{\text{RHE}}$$

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$$\Delta G_3 = \Delta G_{*OOH} - \Delta G_{*O} - eU_{RHE}$$



$$\Delta G_4 = \Delta G_{O_2} - \Delta G_{*OOH} - eU_{RHE}$$

where \* denotes the active site and  $U_{RHE}$  is the potential of the electrode relative to the reversible hydrogen electrode (RHE). Ideally, the free energy of all four steps ( $\Delta G_1$ ,  $\Delta G_2$ ,  $\Delta G_3$ , and  $\Delta G_4$ ) should be equal to the thermodynamic potential of 1.23 V, but in practice the universal scaling relations relate the adsorption free energies of \*OH and \*OOH ( $\Delta G_{*OOH} \approx \Delta G_{*OH} + 3.2$  eV), which implies that a minimum potential of 1.6 V must be applied for all steps to have a negative free energy.<sup>6,7</sup>

Within this limitation, oxides based on Ir and Ru are the most efficient catalysts for acidic OER.<sup>8–14</sup> IrO<sub>2</sub> is less active than RuO<sub>2</sub>, but IrO<sub>2</sub> is substantially more stable.<sup>8,10</sup> Both IrO<sub>2</sub> and RuO<sub>2</sub> are metallic conductors,<sup>15</sup> facilitating electron transport in the anode catalyst and offering low electronic resistance. However, the low abundance of Ir and Ru precludes industrial upscaling of this technology.<sup>16</sup> Materials based on earth-abundant elements are usually either stable but inert or active but unstable under acidic OER conditions. Research on catalysts based on earth-abundant elements has therefore often followed one of two approaches: activating stable materials or stabilising active materials.<sup>17,18</sup>

Stable materials that are based on low-cost elements have been doped to enhance their OER activity. For example, TiO<sub>2</sub> is stable in acid,<sup>19</sup> but it is a poor OER catalyst because it is a semiconductor.<sup>20</sup> Both experimental and theoretical studies have demonstrated that the catalytic activity can be enhanced by doping.<sup>21–24</sup> The dopant introduces new states in the band gap, which determine the Fermi level. In particular, introducing one or two subsurface layers of SrRuO<sub>3</sub> into inert SrTiO<sub>3</sub> enhanced the experimentally measured OER activity under alkaline conditions, which was attributed to new electronic states introduced by the dopant.<sup>25</sup> In a later computational study, this concept was extended by introducing a single subsurface layer of different transition metals into SrTiO<sub>3</sub>, SrZrO<sub>3</sub>, TiO<sub>2</sub>, and ZrO<sub>2</sub>, and a correlation between the Fermi level and catalytic activity was established.<sup>26</sup> Since the catalytic activity is influenced by the energy position of the dopant states in the band gap, it is desirable to be able to tune these states, which is difficult to achieve with a single dopant. Co-doping with both n-type (electron-donor) and p-type (electron-acceptor) dopants has therefore been investigated, demonstrating that the OER activity of TiO<sub>2</sub> and SrTiO<sub>3</sub> can be tuned.<sup>20,21</sup> As an extreme case of the co-doping strategy, Ti atoms incorporated in a conducting high-entropy oxide (HEO), *i.e.* an oxide containing five different metals, were theoretically predicted to be highly active.<sup>27</sup>

Protecting active but unstable catalysts by coating or enriching them with a stable oxide such as TiO<sub>2</sub> is an alternative strategy for improving catalyst performance. Dimensionally

stable anodes (DSAs), used in the commercial production of chlorine, employ this strategy.<sup>28</sup> DSAs consist of a mixture of active precious-metal oxides such as RuO<sub>2</sub> and IrO<sub>2</sub>, together with TiO<sub>2</sub>, which offers stability. Such mixtures have therefore been extensively studied, and it has been shown that the formation of an ultrathin TiO<sub>2</sub> coating on oxide nanoparticles consisting of Ru, Ti, and Nb resulted in improved stability during chlorine evolution.<sup>29</sup> Thin TiO<sub>2</sub> coatings have also been formed on active catalysts such as MnO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub>, resulting in improved stability without significant loss of activity.<sup>30,31</sup> Such coatings can be readily made by atomic layer deposition (ALD),<sup>30,32</sup> thermal diffusion,<sup>29</sup> sputter deposition,<sup>31</sup> and electrodeposition.<sup>33</sup>

The catalytic activity for OER on oxides can be estimated computationally by calculating the free energies of the individual steps along the reaction pathway (eqn (1)–(4)). Correlations between catalytic activity and the adsorption energies of reaction intermediates are often represented by volcano plots.<sup>34,35</sup> In particular,  $\Delta G_2$  has been proposed as a universal descriptor of OER activity.<sup>7</sup> It is attractive to relate these adsorption energies to electronic properties of the material to provide an understanding of the adsorption process and reduce the effort required to predict the catalytic activity of new materials.<sup>36</sup> A range of electronic descriptors have been widely studied in the literature, inspired by the success of the d-band model from Hammer and Nørskov. They showed that the binding energy on metal surfaces is linearly dependent on the energy difference between the center of the metal d-band and the Fermi level of the material.<sup>37,38</sup> This approach has been less successful in describing the adsorption energies on oxides. In contrast, the positions of the O<sub>2p</sub> band, t<sub>2g</sub> band, the occupancy of the e<sub>g</sub> orbital, and the vacuum level relative to the Fermi level have all been identified as alternative descriptors for different systems.<sup>22,26,39–43</sup>

Here, guided by the fundamental ideas from these previous efforts, we outline a new design principle for developing active and potentially stable electrocatalysts for the OER under acidic conditions. We first study Ru, Rh, Ir, Os, Pd, Pt, Ti, Sn, and Zr “guest” atoms substituted at surface sites in rutile oxide slabs (“host”) with a range of element compositions. Using density functional theory (DFT), we show how the adsorption energies of \*OH and \*O intermediates on these guest sites change as the host composition, and therefore its Fermi level, is varied. For Ti, Sn, and Zr guests, the adsorption energies show a pronounced variation that correlates with the host Fermi level, whereas Ru, Rh, Pd, Pt, Os, and Ir guests show only low variations, which are independent of the Fermi level. By studying changes in the geometry and the charge at the adsorption site, we show that this difference is related to the inability of the Ti, Sn, and Zr guest elements to access oxidation states higher than the 4+ oxidation state of the rutile structure. Ti is particularly interesting, as it spans binding energies corresponding to OER overpotentials as low as 0.14 V. Motivated by this, we further extend the concept from single Ti sites to TiO<sub>2</sub> overlayers applied as coatings on conductive rutile oxides (substrates). The overpotentials on TiO<sub>2</sub> overlayers coating



substrates of various compositions showed trends similar to those for single Ti sites. Finally, we show that a simple linear model can successfully predict the Fermi level of the  $\text{TiO}_2$ -coated system from the composition of the underlying substrate oxide. Thus, substrate oxides with a Fermi level that optimally activates the  $\text{TiO}_2$  overlayer for the OER can be designed from combinations of metal oxides that are not necessarily active or stable by themselves, making it possible to avoid Ru and Ir entirely. As an example, our model accurately predicts  $\text{W}_x\text{Pt}_{1-x}\text{O}_2$  and  $\text{W}_{0.46}\text{Pd}_{0.54}\text{O}_2$  substrate compositions that, when coated with  $\text{TiO}_2$ , exhibit calculated OER overpotentials as low as 0.39 V.

## Methodology

DFT (*cf.* Section S2 in the SI for computational details) is used to calculate the adsorption energies of the reaction intermediates  $^*\text{OH}$ ,  $^*\text{O} + \text{Hb}$ ,  $^*\text{O}$ ,  $^*\text{OOH}$ ,  $^*\text{O}_2 + \text{Hb}$ , and  $\text{O}_2(\text{g}) + \text{Hb}$ , where Hb is a hydrogen atom adsorbed on a bridging oxygen atom adjacent to the adsorption site (\*). These calculations are carried out for a range of adsorption site elements (guests) and surrounding oxide compositions (hosts), as illustrated in Fig. 1a. More specifically, Ru, Rh, Ir, Os, Pd, Pt, Ti, Sn, and Zr have been considered as guests, while both pure oxides of these

elements (except for  $\text{ZrO}_2$ , which does not have a rutile polymorph),<sup>44,45</sup> and high entropy oxides have been employed as hosts. More details and structural illustrations of this dataset are provided in Sections S2 and S4 of the SI.

We focus on the (110) surfaces of rutile structures because  $\text{RuO}_2$ ,  $\text{IrO}_2$ ,  $\text{RhO}_2$ ,  $\text{OsO}_2$ ,  $\text{PdO}_2$ ,  $\text{PtO}_2$ ,  $\text{SnO}_2$ , and  $\text{TiO}_2$  are all known to form a rutile polymorph.<sup>15,46,47</sup> Rutile is the preferred crystal structure for  $\text{TiO}_2$ ,<sup>48</sup>  $\text{RuO}_2$ ,  $\text{IrO}_2$ ,  $\text{OsO}_2$ ,<sup>49</sup> and  $\text{SnO}_2$ ,<sup>50</sup> under standard conditions.  $\text{PtO}_2$  prefers a distorted rutile structure,<sup>51</sup> rutile  $\text{RhO}_2$  is possibly only a high-pressure phase,<sup>52</sup> while  $\text{PdO}_2$  appears to have been synthesised by only one group and is unstable under standard conditions.<sup>47</sup> The (110) surface is the rutile facet that preserves the highest coordination number for surface atoms, and for  $\text{TiO}_2$  it is calculated to have the lowest surface energy.<sup>53</sup> Furthermore, corrosion measurements on  $\text{RuO}_2$  single crystals<sup>54</sup> and  $\text{IrO}_2$  crystalline films<sup>55</sup> demonstrate low dissolution rates from the (110) facets, which indicate increased stability compared to other facets.

In our analysis, we included previously published adsorption energies for  $^*\text{O}$  and  $^*\text{OH}$  on the rutile (110) surface of near-equimolar HEOs consisting of Ru, Ti, Ir, Os and Rh (details about the HEOs dataset are provided in Sections S3 and S4 in the SI).<sup>27</sup> Similar HEOs in the  $\text{IrOsPdPtRu}$ ,  $\text{IrOsPtRhRu}$ ,



**Fig. 1** (a) Schematic representation of the host-guest data, illustrating the two parts of the structure; the element of the adsorption site (guest) and the composition of the surroundings (host). Ru, Rh, Ir, Os, Pd, Pt, Ti, Sn, and Zr were studied as guests. For the host compositions, pure rutile oxides of these elements (except for  $\text{ZrO}_2$ ) along with high entropy oxides were examined. (b) Top and side view of the rutile (110) surface model utilised in this study. (c) Illustration of the Fermi level calculated by DFT ( $E_{\text{Fermi,DFT}}$ ), relative to the oxygen 2s band on the DOS of pure  $\text{RuO}_2$ . The blue line corresponds to the  $E_{\text{Fermi,DFT}}$ , the red peak corresponds to the projected DOS of the oxygen 2s band of the oxygen atoms, and the black dashed line corresponds to the centroid of this band ( $E_{\text{Center,O2s}}$ ). Occupied levels are shaded.



AuOsPdPtRu, and AuIrOsPdPtReRhRu composition spaces have been prepared as nanoparticles using microwave solvothermal synthesis, and their OER activities were studied under acidic conditions.<sup>56</sup>

The surface model (Fig. 1b) consists of three coordinatively unsaturated sites (cus). One of these is the adsorption site and the other two are either bare or occupied with a pre-adsorbed oxygen, depending on the O\* affinity of the adsorbing metal element (details are provided in Section S2 in the SI).

The adsorption free energies of the catalytic intermediates ( $\Delta G_{\text{intermediate}}$ ) are calculated as:

$$\Delta G_{\text{intermediate}} = \Delta E_{\text{DFT}} + \Delta \text{ZPE} - T\Delta S \quad (5)$$

where  $\Delta E_{\text{DFT}}$  is the DFT calculated adsorption energy (computational details are provided in Section S2 in the SI),  $\Delta \text{ZPE}$  and  $T\Delta S$  account for changes in zero-point energy and entropy upon adsorption, respectively, and are taken from ref. 6. From the adsorption free energies, we can then calculate  $\Delta G_1$ ,  $\Delta G_2$ ,  $\Delta G_3$ , and  $\Delta G_4$  at  $U_{\text{RHE}} = 0$  V and employ the computational hydrogen electrode (CHE)<sup>35</sup> to evaluate the overpotential,  $\eta$ :<sup>57</sup>

$$\eta = \frac{\max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}}{e} - 1.23 \text{ V} \quad (6)$$

$\eta$  represents the additional potential beyond the thermodynamic 1.23 V that is required to make all four reaction steps thermodynamically downhill ( $\Delta G_i \leq 0$ ). We plot  $-\eta$  such that higher positions on the volcano correspond to lower overpotentials (higher activity).

As a descriptor for the adsorption free energies, we investigate the Fermi level, which was previously observed to correlate with the adsorption energies of OER intermediates for doped SrTiO<sub>3</sub> and TiO<sub>2</sub>.<sup>26</sup> In that study, the vacuum level was used as a reference to compare DFT-calculated Fermi levels ( $E_{\text{Fermi,DFT}}$ ) across different oxides; here, we adopt the approach in ref. 58, where  $E_{\text{Fermi,DFT}}$  values are aligned using a sharp low-energy peak in the density of states (DOS) as a reference. In our case the oxygen 2s band centroid ( $E_{\text{center,O2s}}$ ) is used as the reference point, because it is common to systems studied, lies at relatively low energies (approximately  $-18$  eV), and generally exhibits a sharp, non-interacting peak as illustrated in Fig. 1c for RuO<sub>2</sub> (see Section S5 in the SI for the DOS of all pure oxides studied). In the case of RuO<sub>2</sub>, the  $E_{\text{Fermi,DFT}}$  relative to the oxygen 2s band center is 18.6 eV ( $E_{\text{Fermi,RuO}_2}$ ) and we use this value to normalise the Fermi level energies of all systems in this study

$$E_{\text{Fermi}} = [E_{\text{Fermi,DFT}} - E_{\text{center,O2s}}] - E_{\text{Fermi,RuO}_2} \quad (7)$$

All the  $E_{\text{Fermi}}$  are calculated on the bare surface of each structure.

In addition to the host-guest dataset described above, we studied TiO<sub>2</sub> overlayers applied as coatings on conductive rutile oxides (substrates). We modelled pure RuO<sub>2</sub>, RhO<sub>2</sub>, IrO<sub>2</sub>, OsO<sub>2</sub>, PdO<sub>2</sub>, and PtO<sub>2</sub> substrates, as well as substrates containing 89%, 78%, and 56% of each oxide, with the remainder being a random mixture of the other five oxides. To study the effect of increasing the coating thickness, the substrate oxides were

investigated with both one and two TiO<sub>2</sub> overlayers. We also studied TiO<sub>2</sub>-coated rutiles of  $W_x\text{Pt}_{1-x}\text{O}_2$  ( $W =$  tungsten,  $x = 0.04, 0.08, 0.12, 0.17, 0.21$ , and  $\text{WO}_2$ ) and  $W_{0.46}\text{Pd}_{0.54}\text{O}_2$ , as Ir and Ru free OER candidates. For each  $W_x\text{Pt}_{1-x}\text{O}_2$  composition, we construct two distinct rutile slabs covered with one TiO<sub>2</sub> overlayer and calculate adsorption energies at all six Ti cus sites. The lattice constants of all TiO<sub>2</sub>-coated doped structures were set to the composition weighted averages of the lattice parameters of the constituent pure oxides. More details on the TiO<sub>2</sub>-coated dataset are provided in Sections S2 and S4 of the SI.

GGA functionals such as RPBE are known to over-delocalise electrons and to underestimate band gaps. To assess how this affects our  $E_{\text{Fermi}}$  descriptor and the band gaps of the systems in our study, we benchmarked the  $E_{\text{Fermi}}$  (as defined in eqn (7)) and the band gaps using the HSE06 hybrid functional.<sup>59</sup> We perform non self-consistent calculations, which have shown good agreement with self-consistent hybrid calculations<sup>60</sup> and are widely used,<sup>61–63</sup> while avoiding the computationally too demanding self-consistent HSE06 calculations for large surface slabs.

The HSE06  $E_{\text{Fermi}}$  values calculated for the TiO<sub>2</sub>-coated systems are on average 0.08 eV lower than the RPBE  $E_{\text{Fermi}}$  values, although there are significant outliers (Fig. S9 in the SI). We also compared the band gaps between HSE06 and RPBE for the bare surface slabs of the pure oxides (Table S4). HSE06 band gaps remain in the metallic, near-metallic regime for RuO<sub>2</sub>, IrO<sub>2</sub>, OsO<sub>2</sub>, RhO<sub>2</sub>, and WO<sub>2</sub>, in agreement with resistivity measurements.<sup>15</sup> PdO<sub>2</sub> is also calculated to be metallic, and ref. 64 shows that Pd doping in RuO<sub>2</sub> improves OER activity, suggesting that Pd incorporation is unlikely to severely diminish electronic conductivity. TiO<sub>2</sub> and SnO<sub>2</sub> show much larger HSE06 band gaps than RPBE, consistent with the known GGA underestimation on semiconductors. In Fig. S8, the RPBE band gaps of the bare surface slabs for the mixed oxides studied in this work indicate metallic or near-metallic behaviour (band gap range around 0–0.15 eV).

We also studied the D3 dispersion correction<sup>65</sup> in the RPBE calculations for the TiO<sub>2</sub>-coated systems. D3 introduces an approximately constant shift of 0.25 eV in  $\Delta G_2$  but the  $E_{\text{Fermi}} - \Delta G_2$  trend remains essentially unchanged (Fig. S16 in the SI).

## Results and discussion

The adsorption free energies of \*OH ( $\Delta G_{\text{*OH}}$ ) and \*O ( $\Delta G_{\text{*O}}$ ) intermediates on the pure oxides as a function of the  $E_{\text{Fermi}}$  of the bare surface slabs are shown in Fig. 2a and b, demonstrating clear linear correlations. Looking at the individual guest elements in the host-guest systems, two significantly different trends in the adsorption free energies are observed (Fig. 2c–f). For Ti, Sn, and Zr guests, a notable variation in the adsorption free energies that correlates with the variation in  $E_{\text{Fermi}}$  is observed (Fig. 2c and d), indicating that the adsorption energy is primarily determined by the host composition. In contrast to this, the adsorption energies for the other guest elements (Ru, Rh, Ir, Os, Pd, Pt) span a much smaller energy range and are not correlated with  $E_{\text{Fermi}}$  (Fig. 2e and f), indicating that, in these



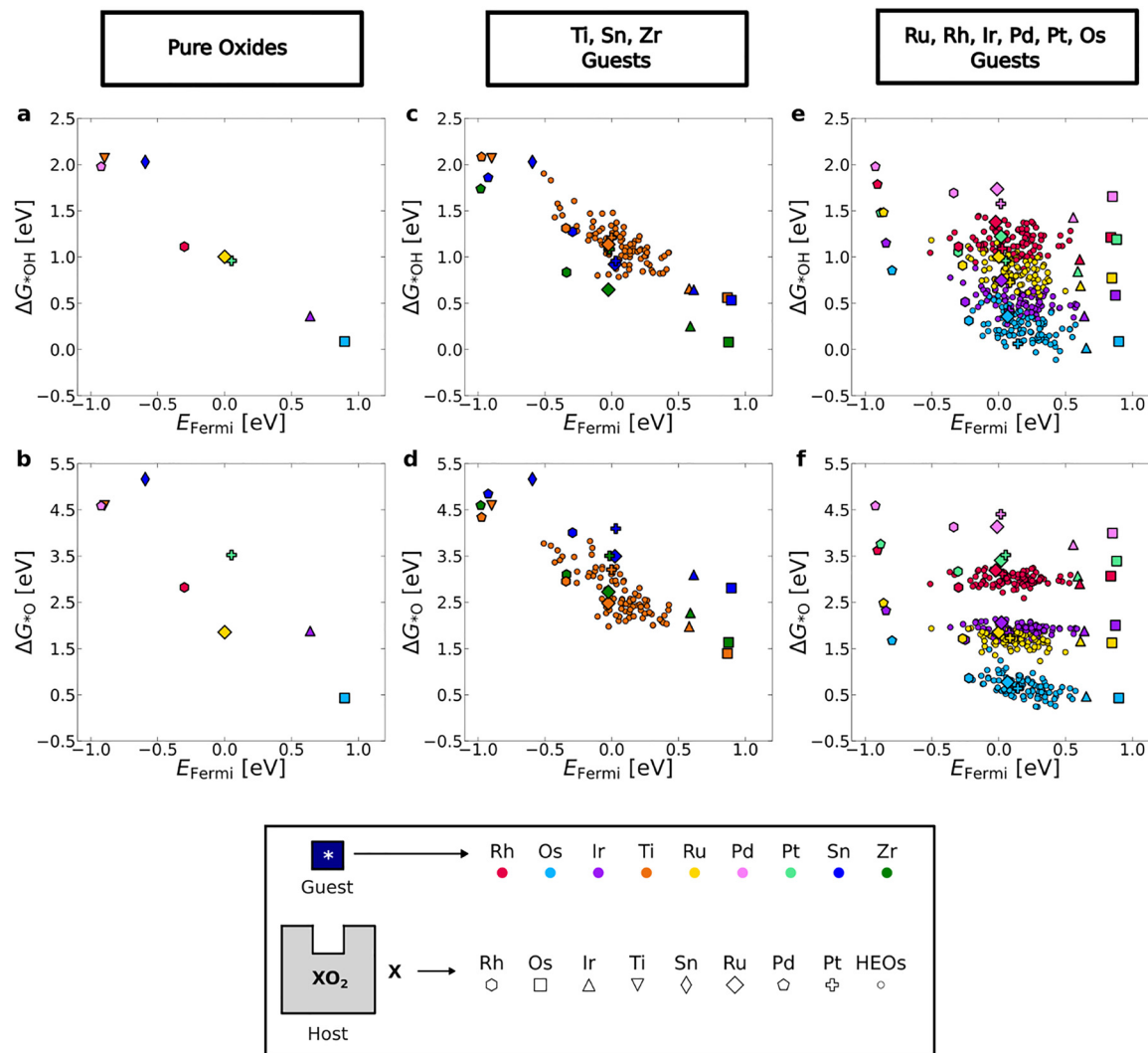


Fig. 2 Correlation between adsorption energies of the  $^*OH$  and  $^*O$  intermediates and the  $E_{Fermi}$  of the bare surface slabs for the pure oxides (a) and (b), the Zr, Ti, and Sn guests data (c) and (d), the Ru, Rh, Os, Ir, Pd, and Pt guests data (e) and (f). Markers represent different host compositions and colours correspond to different guest elements, as described in the legend.

systems, the adsorption energy is primarily determined by the guest element. We note that the data corresponding to  $SnO_2$  and  $TiO_2$  hosts are excluded from Fig. 2e and f, because their semiconducting electronic structure leads to a significantly different behaviour. Analysis of the trends in  $\Delta G_{^*O}$  and  $E_{Fermi}$ , as the guest element is varied for each pure-host composition (including data where  $TiO_2$  and  $SnO_2$  are hosts) can be found in Section S6 in the SI.

In ref. 27, a model based on the local atomic environments could predict  $\Delta G_{^*OH}$  and  $\Delta G_{^*O}$  adsorption energies. The model worked very well for Ru, Rh, Ir, and Os sites, but less well for Ti sites. We now know that  $^*OH$  and  $^*O$  adsorption on Ti sites depend strongly on  $E_{Fermi}$ , which was completely missing from the developed model.

To further understand the interactions between the adsorbates and the surface, we derived the scaling relation  $\Delta G_{^*O} = a\Delta G_{^*OH} + b$ , where  $a$  is the slope and  $b$  is the intercept,

for each of the guest elements under study (see Section S7 in the SI). Ti, Sn, and Zr exhibit strong correlations ( $R^2 = 0.85\text{--}0.99$ ) with slopes approaching 2 ( $a = 1.5\text{--}1.9$ ). A relationship between OH and O adsorption energies with a slope of around 2 has been observed on metals,<sup>66</sup> which have multiple electrons at the Fermi level, and on oxides, except when the computational cell only contains one dopant,<sup>67</sup> *i.e.* when there is only one electron at the Fermi level.

To investigate the origin of the two different trends in the adsorption energies, we conducted Bader charge analysis<sup>68</sup> on the structures before and after the adsorption of  $^*OH$  and  $^*O$ . The Bader charge difference of the adsorption site atom upon adsorption of A ( $\Delta q_{^*A}$ , A = OH or O) is calculated as the difference between the Bader charge of that atom in the bare surface ( $q_*$ ) and the charge when the adsorbate is added ( $q_{^*A}$ ):

$$\Delta q_{^*A} = q_{^*A} - q_* \quad (8)$$





**Fig. 3** Probability distributions of the Bader charge difference ( $\Delta q_{*A}$ ) at the adsorption site atom in the RuRhIrOsTi high entropy oxides dataset after (a)  $*OH$ , and (b)  $*O$  adsorption. (c) Probability distributions of the change in the distance ( $\Delta d_{*A}$ ) between the adsorption site atom and the oxygen atom underneath after  $*OH$  and (d)  $*O$  adsorption. Data for Ru, Rh, Ir, and Os adsorption sites are aggregated into a single distribution for comparison with the distribution based on data for Ti sites. (e) Schematic figure of the proposed explanation for the different adsorption energies trends observed for Ti, Sn, and Zr guests and Ru, Rh, Ir, Os, Pd, and Pt guests.

Using the HEO dataset, we collected the  $\Delta q_{*A}$  and  $\Delta q_{*O}$  values of Ru, Rh, Ir, and Os adsorption sites in one distribution and the corresponding values for the Ti adsorption sites in another distribution. Each set was plotted as a probability histogram, normalising each by the number of data points so that its total area equals one. The resulting plots, shown in Fig. 3a and b, demonstrate that the Ti sites exhibit a small change in charge upon OH and O adsorption. This suggests that the charge transferred to the adsorbate is supplied by the surrounding oxide rather than by the Ti adsorption site itself. This behaviour is consistent with Ti already occupying its highest oxidation state (4+) in the rutile structure. Therefore, further oxidation of the Ti site is unfavourable, and the additional charge must be supplied by the host. In contrast, Ru, Rh, Ir, and Os sites show larger changes in charge upon adsorption, indicating that electrons are, to a large extent, taken locally from the adsorption site. This is consistent with these platinum group elements being able to access oxidation states higher than 4+, making further oxidation of the metal center feasible. The trends observed for Sn, Zr, Pd and Pt adsorption sites are consistent

with these conclusions, *i.e.* Sn and Zr, which also have a maximum oxidation state of 4+, behave like Ti, while Pd and Pt behave more like the other platinum group elements (see Section S8 in the SI for details).

To further elucidate the distinct trends in adsorption behaviour, we calculated the change in the distance between the adsorption site atom and the oxygen atom underneath it upon adsorption of A ( $\Delta d_{*A}$ , A = OH or O):

$$\Delta d_{*A} = d_{*A} - d. \quad (9)$$

Again, the results for Ru, Rh, Ir, and Os are combined, while the Ti data are collected separately. The normalised distributions are shown in Fig. 3c and d, demonstrating that the Ti atoms are significantly displaced from their original position when an adsorbate is added. This observation qualitatively shows that Ti cannot form additional bonds, and to create a new bond (with the adsorbate) it therefore must weaken the bond with the oxygen atom underneath. In contrast, Ru, Rh, Ir, and Os show smaller displacement, indicating that the increased number of bonds and the associated increase in the oxidation state can be



accommodated. The observed trends for Sn, Zr, Pd, and Pt in the host-guest data generally align with these findings (see Section S9 in the SI for details). Fig. 3e summarizes that Ru, Rh, Ir, Os, Pd, and Pt sites can offer charge locally to the adsorbate, whereas Ti, Sn, and Zr sites cannot, and therefore draw charge from the surrounding oxide, while the bond between the adsorption site and the oxygen atom underneath weakens.

To evaluate the impact of the different adsorption behaviour on the OER activity, the theoretical overpotential ( $\eta$ ) for OER has been calculated using eqn (6). We have considered both the adsorbate evolution mechanism (AEM) given in eqn (1)–(4), along with alternative pathways which have previously been studied for rutile oxides, where the proton of the  $^*OH$  and  $^*OOH$  intermediates is transferred to a neighbouring bridging oxygen atom to form  $^*O + Hb$  and  $^*O_2 + Hb$  (eqn (S1)–(S4)).<sup>27,69–72</sup> Additionally, we considered the pathway in which molecular oxygen desorbs from the surface already in the third step, represented as  $O_2(g) + Hb$ . Further details of the reaction

pathways and illustrations of the intermediates can be found in Section S1 in the SI.

Volcano plots of the calculated theoretical overpotential based on the minimum energy pathway as a function of  $\Delta G_2$  are shown in Fig. 4. Ti, Zr, and Sn guests (Fig. 4a) exhibit a significant variation in the overpotential compared to the Ru, Rh, Ir, Os, Pd and Pt sites (Fig. 4b) in accordance with the corresponding trends in the adsorption energies. The Ti ensemble is particularly remarkable, because it includes the high-activity region near the peak of the volcano plot. Notably, many Ti sites demonstrate activities beyond the conventional volcano (as low as  $\eta = 0.14$  V), due to the absence of the known scaling relation  $\Delta G_{^*OOH} \approx \Delta G_{^*OH} + 3.2$  eV (see Fig. S14b). In particular,  $O_2(g) + Hb$  and  $^*O_2 + Hb$  intermediates are found to be thermodynamically more stable than  $^*OOH$ . Meanwhile, high catalytic activity is only marginally achieved at Zr sites, and not at all at Sn sites, due to the weak binding of the  $^*O$  intermediate across the entire  $E_{Fermi}$  range. Among the platinum group elements,



Fig. 4 Negative theoretical overpotentials ( $-\eta$ ) of the Ti, Sn, and Zr guests (a) and the Rh, Ru, Ir, Os, Pd, and Pt guests (b) as a function of the free energy of the second catalytic step ( $\Delta G_2$ ) of the OER. The volcano plot line is generated by employing the known scaling relation  $\Delta G_{^*OOH} \approx \Delta G_{^*OH} + 3.2$  eV. Markers represent different host compositions and colours correspond to different guest elements, as described in the legend.



the Os guest data covers the widest activity range. This could be attributed to OsO<sub>2</sub> having the highest  $E_{\text{Fermi}}$  among the studied oxides (Fig. 2), resulting in electrons donated by Os adsorption sites having similar energies to the electrons at the  $E_{\text{Fermi}}$ .

Inspired by the tunable activity observed for Ti guest sites across different host compositions (Fig. 4a), we now extend this single-site concept to a more advantageous catalyst design by considering TiO<sub>2</sub> coatings on conductive rutile oxide substrates. Previous studies have shown that a TiO<sub>2</sub> coating can be applied on conductive oxides, often with a minor decrease in the activity and improvement of the stability under acidic OER conditions.<sup>30–32</sup> The feasibility of producing TiO<sub>2</sub> coatings of one or two monolayers is supported by ref. 29, where an ultrathin protective TiO<sub>2</sub> layer was formed by annealing RuO<sub>2</sub> nanoparticles on a Nb-doped TiO<sub>2</sub> support. The thickness of the TiO<sub>2</sub> layer was  $\sim 4.4$  Å, compared with  $\sim 4.0$  Å for a single TiO<sub>2</sub> monolayer. Moreover, the atomic layer deposition (ALD) technique has demonstrated exceptional control for fabricating TiO<sub>2</sub> coatings on IrO<sub>2</sub>, RuO<sub>2</sub>, and F-doped SnO<sub>2</sub> films.<sup>32</sup> In ref. 32, the average growth rate of TiO<sub>2</sub> was estimated *via* profilometric and scanning electron microscopy measurements to be 0.50–0.65 Å per ALD cycle. It is also possible that thicker TiO<sub>2</sub> coatings can be used for OER catalysis without strongly compromising activity, since ref. 30 reports that TiO<sub>2</sub> coatings up to 5.5 nm on Co<sub>3</sub>O<sub>4</sub> increase durability without significantly affecting the activity relative to bare Co<sub>3</sub>O<sub>4</sub>.

To investigate whether TiO<sub>2</sub> coatings exhibit tunable activity, as observed for Ti guest sites, we calculated the adsorption energies and overpotentials on TiO<sub>2</sub>-coated rutile oxides composed of the conductive elements studied above, namely Ru, Rh, Ir, Os, Pt, and Pd (see Methodology section). The  $\Delta G_2$  of these systems is plotted against the  $E_{\text{Fermi}}$  in Fig. 5a and b. A strong correlation is demonstrated ( $R^2 > 0.8$ ), with the linear fit showing a consistent slope of around  $-0.8$  for one TiO<sub>2</sub> and two TiO<sub>2</sub> overlayers, close to the slope obtained for the single Ti sites ( $-0.92$ ). This demonstrates the robustness of the  $E_{\text{Fermi}}$  as a descriptor for the adsorption energies on both single Ti sites and TiO<sub>2</sub> overlayers. More details and illustrations of the slab structures in this dataset are provided in Sections S2 and S4 of the SI.

The theoretical overpotential based on the minimum energy pathway is directly compared to the  $E_{\text{Fermi}}$  for these systems in Fig. 5c and d. From these plots, it is evident that TiO<sub>2</sub>-coated oxides can be highly active if they have a suitable  $E_{\text{Fermi}}$ . Notably, a system with a  $E_{\text{Fermi}}$  close to 0 eV (compared to the  $E_{\text{Fermi}}$  of RuO<sub>2</sub>), can yield low overpotentials beyond the conventional volcano (Fig. 5c). The shape of these distributions suggests a volcano-type activity trend. Adding a second TiO<sub>2</sub> overlayer increases the overpotential (Fig. 5d), consistent with experimental observations that thicker TiO<sub>2</sub> coatings on Co<sub>3</sub>O<sub>4</sub> progressively decrease OER performance.<sup>30</sup> Scaling relations of the adsorption energies and conventional volcano plots for the TiO<sub>2</sub>-coated oxides data can be found in the Section S11 of the SI.

To further expand the use of the  $E_{\text{Fermi}}$  as a descriptor, we propose a model ( $E_{\text{Fermi,model}}$ ) which predicts the  $E_{\text{Fermi}}$  of TiO<sub>2</sub>-coated oxides based on the composition of the substrate oxide (excluding the TiO<sub>2</sub> overlayer). Specifically, this model is a weighted average of the  $E_{\text{Fermi}}$  of the pure oxides,

$$E_{\text{Fermi,model}} = \frac{1}{N_{\text{total}}} \sum_i (N_i \cdot E_{\text{Fermi},i}) \quad (10)$$

where  $E_{\text{Fermi},i}$  is the Fermi level of the bare surface slab of the pure oxide of the element  $i$ ,  $N_i$  is the number of atoms of the element  $i$  and  $N_{\text{total}}$  is the total number of the metal atoms (we do not count the oxygen atoms) in the surface slab.

In Fig. 6a,  $E_{\text{Fermi,model}}$  values predicted by eqn (10) are plotted against the  $E_{\text{Fermi}}$  (calculated from eqn (7)) for the TiO<sub>2</sub>-coated oxides with one TiO<sub>2</sub> overlayer. A strong correlation is observed ( $R^2 = 0.98$  and MAE = 0.04 eV), showing that the composition of the substrate oxide is a straightforward way to engineer the  $E_{\text{Fermi}}$  of TiO<sub>2</sub>-coated oxides. We note that while the model is clearly successful for mixtures primarily consisting of platinum-group elements, it may be too simplistic for some combinations of elements, for example, when mixing results in changes in oxidation states.

Based on the observation that the activity of TiO<sub>2</sub>-coated rutile oxides can be tuned through the substrate oxide  $E_{\text{Fermi}}$  (Fig. 5), and that the  $E_{\text{Fermi}}$  of the TiO<sub>2</sub>-coated systems can be predicted from the substrate oxide composition using the linear model in eqn (10) (Fig. 6a), we now apply this to predict Ir- and Ru-free OER candidates. We also exclude Rh and Os, because they are equally or even more scarce and expensive than Ru and Ir.<sup>16</sup> Instead, we select TiO<sub>2</sub>-coated PtO<sub>2</sub> as a representative system, whose activity is not yet optimal, and dope it with tungsten (W) to tune  $E_{\text{Fermi}}$ .

In Fig. 6b, we show that the model (eqn (10)) successfully predicts the  $E_{\text{Fermi}}$  of the TiO<sub>2</sub>-coated W<sub>x</sub>Pt<sub>1-x</sub>O<sub>2</sub> data. The two distinct rutile slabs for each composition are found to have similar  $E_{\text{Fermi}}$ , indicating that  $E_{\text{Fermi}}$  is largely controlled by composition rather than the specific arrangement of metal atoms in the slab. In Fig. 6c, we see that the adsorption energies vary almost linearly with the  $E_{\text{Fermi}}$ , and the trend is shifted smoothly from the TiO<sub>2</sub>-coated PtO<sub>2</sub> towards the TiO<sub>2</sub>-coated WO<sub>2</sub> direction, as the amount of W increases. The observed scatter arises from an inequivalent local coordination environment associated with the distinct atomic configurations at the three different Ti-cus sites sampled on each composition. This indicates that  $E_{\text{Fermi}}$  is not a perfect descriptor, since all six adsorption sites (three Ti sites for each of the two atomic configurations) experience similar  $E_{\text{Fermi}}$ . In Fig. 6d, it is evident that these systems follow the expected volcano trend. The largest improvement in overpotential is observed for W<sub>0.12</sub>Pt<sub>0.88</sub>O<sub>2</sub> and W<sub>0.17</sub>Pt<sub>0.83</sub>O<sub>2</sub> (as low as 0.55 V), compared with the PtO<sub>2</sub> substrate composition (0.73 V), indicating that higher activity can be achieved while reducing precious-metal content. Increasing the W content further to 21 at% reduces the activity, indicating that the W<sub>x</sub>Pt<sub>1-x</sub>O<sub>2</sub> substrate composition is optimal at  $x = 12$ – $17$  at%.

We applied the same design principle to predict active Pd-based catalysts. In Fig. 6, we show TiO<sub>2</sub>-coated W<sub>0.46</sub>Pd<sub>0.54</sub>O<sub>2</sub>



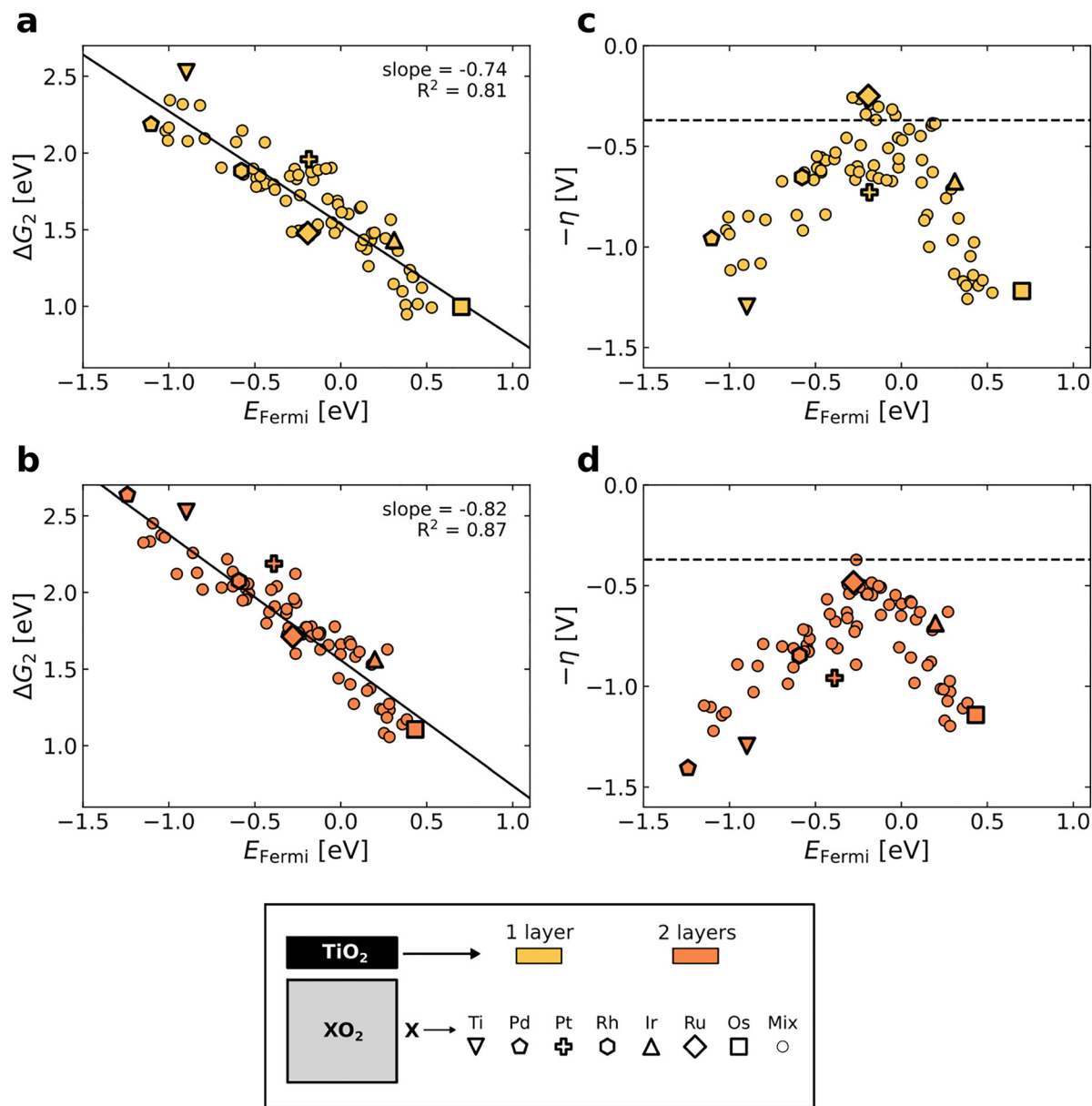


Fig. 5 Correlation between  $E_{\text{Fermi}}$  and  $\Delta G_2$  for rutile oxides coated with one overlayer (a) and two overlayers (b) of  $\text{TiO}_2$ . Black lines correspond to the best linear fits. Negative theoretical overpotentials ( $-\eta$ ) as a function of the  $E_{\text{Fermi}}$  for the rutile oxides covered with one overlayer (c) and two overlayers (d) of  $\text{TiO}_2$ . The dashed horizontal line indicates the value of the overpotential at the apex of the activity volcano defined by the conventional scaling relation  $\Delta G_{\text{H}_2\text{O}} \approx \Delta G_{\text{OH}} + 3.2$  eV. Markers represent different substrate oxide compositions and colours correspond to different number of  $\text{TiO}_2$  overlayers as described in the legend.

(purple star), which has a significantly lower overpotential ( $\eta = 0.39$  V) than the  $\text{TiO}_2$ -coated  $\text{PdO}_2$  ( $\eta = 0.96$  V). Together with the  $\text{TiO}_2$ -coated  $\text{W}_x\text{Pt}_{1-x}\text{O}_2$  results, this demonstrates that tuning the substrate  $E_{\text{Fermi}}$  provides a robust route to designing Ru and Ir free catalysts.

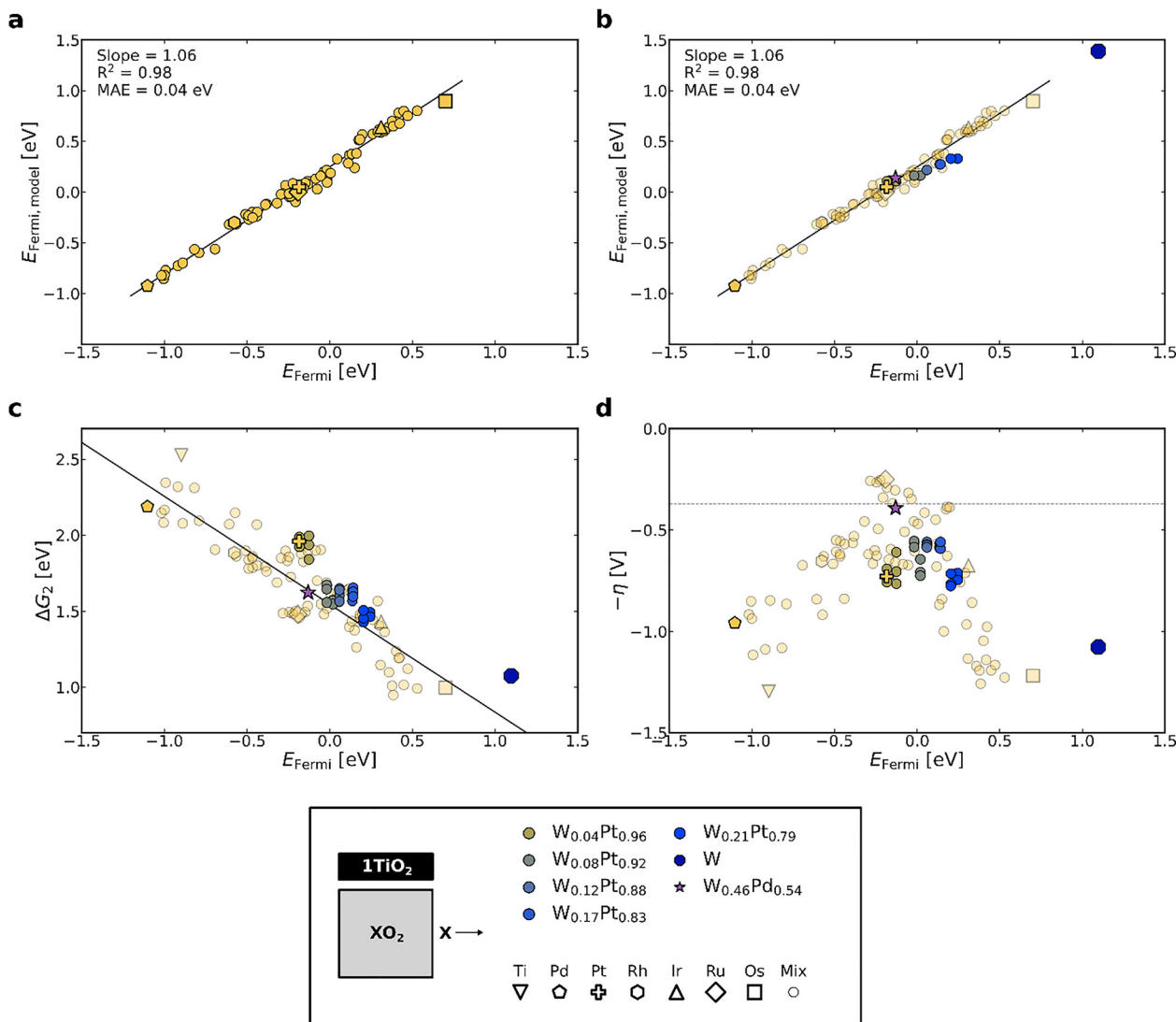
## Conclusions

In summary, our work presents a theoretical design principle for active and potentially stable OER electrocatalysts under

acidic conditions. We find that elements which cannot be oxidised beyond the 4+ oxidation state in the rutile structure (Ti, Sn, and Zr) exhibit adsorption energies and activities that are correlated with the  $E_{\text{Fermi}}$  of the surrounding oxide, whereas this behaviour is not observed for Pt, Pd, Ir, Os, Ru, and Rh sites. Among these, Ti is found to be particularly special, as it spans a wide range of adsorption energies, many of which correspond to very low overpotentials ( $\eta = 0.14$  V).

We then show that these observations on single Ti sites can be transferred to a more advantageous catalyst design by





**Fig. 6** (a) Correlation between the composition-based model (eqn (10)) and the real  $E_{\text{Fermi}}$  data obtained from DFT (eqn (7)) for oxides covered with one  $\text{TiO}_2$  overlayer. The black line corresponds to the best linear fit. (b) The  $W_xPt_{1-x}O_2$  and  $W_{0.46}Pd_{0.54}O_2$  substrate compositions have been predicted based on the model (eqn (10)). (c) Correlation between  $E_{\text{Fermi}}$  and  $\Delta G_2$  for the  $W_xPt_{1-x}O_2$  and  $W_{0.46}Pd_{0.54}O_2$  substrate oxides. The semi-transparent data points and the linear fit (black line) correspond to the data shown in Fig. 5a. (d) Negative theoretical overpotentials ( $-\eta$ ) as a function of the  $E_{\text{Fermi}}$  for the  $W_xPt_{1-x}O_2$  and  $W_{0.46}Pd_{0.54}O_2$  substrate oxides. The semi-transparent points correspond to the data shown in Fig. 5c. The dashed horizontal line indicates the value of the overpotential at the apex of the activity volcano defined by the conventional scaling relation  $\Delta G_{\text{OOH}} \approx \Delta G_{\text{OH}} + 3.2$  eV.

studying  $\text{TiO}_2$  coatings on conductive rutile oxide substrates. For these systems, a volcano-type relationship is observed between activity and  $E_{\text{Fermi}}$ , demonstrating that a  $\text{TiO}_2$ -coated oxide with a suitable  $E_{\text{Fermi}}$  can be highly active and potentially stable under acidic OER conditions, consistent with experimental reports that  $\text{TiO}_2$  coatings can preserve activity while improving stability in acid.<sup>19,29–32</sup> Furthermore, we show that a simple linear model can accurately predict the  $E_{\text{Fermi}}$  of  $\text{TiO}_2$ -coated oxides based on the composition of the substrate oxide. Using this model, we identify Ir and Ru free substrate compositions,  $W_xPt_{1-x}O_2$  and  $W_{0.46}Pd_{0.54}O_2$ , with  $E_{\text{Fermi}}$  values that can activate the  $\text{TiO}_2$  overlayer, illustrating a practical route to designing Ir and Ru free acidic OER catalysts.

## Author contributions

J. R. supervised the whole project. G. K. S. performed the DFT calculations and data analysis supervised by K. L. S., H. H. K., and J. R. G. K. S., H. H. K., and K. L. S. wrote the manuscript. All authors discussed the results, provided insights and suggestions, and helped improve the manuscript.

## Conflicts of interest

The authors have submitted a patent application (European application under number EP 25387103.2) covering this work.



## Data availability

The data and analysis that support the findings of this study are openly available at <https://www.erda.dk/archives/f73eb5ea1d7a1897bfa54659f714b3cd/published-archive.html>.

Supplementary information (SI): reaction pathways for the OER; DFT calculations setup; RuRhIrOsTi high entropy oxide dataset; description of the model structures; Fermi level alignment using O 2s band centroid; trends in  $\Delta G_{\text{O}}$  and EFermi; scaling relations between adsorption energies; Bader charge differences in pure oxide hosts; change in distance between adsorption site and oxygen atom beneath in pure oxide hosts; conventional volcano plots for TiO<sub>2</sub>-coated metal oxides; and D3-corrections. See DOI: <https://doi.org/10.1039/d5ee07605f>.

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