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# VIP Universality in Oxygen Evolution Electrocatalysis on Oxide Surfaces

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Trends in electrocatalytic activity of the oxygen evolution reaction (OER) are investigated on the basis of a large database of HO\* and HOO\* adsorption energies on oxide surfaces. The theoretical overpotential was calculated by applying standard density functional theory in combination with the computational standard hydrogen electrode (SHE) model. We showed that by the discovery of a universal scaling relation between

## Introduction

Electrochemical water splitting has attracted substantial interest in the recent years as a key process in hydrogen production from sunlight and other sources of electricity.<sup>[1]</sup> The clean, renewable conversion of solar radiation into fuels can be done directly by photons exciting electrons in a semiconductor in which the energy level of the valence band is sufficiently low. The conversion could also be done, in an indirect way, by electrolysis using a potential difference obtained from a photovoltaic cell or from a wind turbine. In both cases, effective catalysis for water oxidation to molecular oxygen, that is, the oxygen evolution reaction (OER), is needed. There are, however, several challenges that have to be solved for the process to become economically attractive. One of them is associated with the substantial overpotential and thereby energy losses at the anode, where oxygen is evolved, according to the following overall reaction, involving four electron transfers [Eq. (1)]:<sup>[2]</sup>

$$2 H_2 O(I) + 4 \times 1.23 \text{ eV} \rightarrow O_2 + 4 H^+ + 4 e^-$$
 (1)

Substantial effort has been devoted to find more effective catalysts for the oxygen evolution reaction and to elucidate the reaction mechanism.<sup>[3]</sup> Two excellent reviews describing the development in this field can be found in Ref. [4].

To improve upon current electrocatalysts, it is important to develop a fundamental understanding of the reactions on different materials.  $^{\scriptscriptstyle [3f-h]}$  The electrocatalytic activity is to a large extent determined by the binding strength of the reaction intermediates to the electrode surface. Plotting the activity as a function of binding energy can give rise to a volcano plot. This concept has been previously successfully applied to the oxygen evolution reaction.<sup>[3a,c,h]</sup> As the binding energies are difficult to measure, other descriptors believed to correlate with the reactivity, have been used. An example is the use of the

the adsorption energies of HOO\* vs HO\*, it is possible to analyze the reaction free energy diagrams of all the oxides in a general way. This gave rise to an activity volcano that was the same for a wide variety of oxide catalyst materials and a universal descriptor for the oxygen evolution activity, which suggests a fundamental limitation on the maximum oxygen evolution activity of planar oxide catalysts.

standard enthalpy of lower to higher oxide transformation  $(MO_x \rightarrow MO_{x+1})$ .<sup>[3b, d-g]</sup>

Advances in density functional theory (DFT) calculations make it possible to accurately determine surface binding energies that can hence be used as activity descriptors.<sup>[3h]</sup> The reverse reaction, the oxygen reduction reaction (ORR) in which molecular oxygen is reduced to water, involves the same general reaction intermediates as the OER. Recently, new alloy electrocatalysts for the ORR have been suggested on the basis

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of computational studies, in which the values of the activity descriptor are calculated, followed by identification of promising candidates.  $^{\rm [5]}$ 

Previously, the OER has been studied using computational methods on two classes of materials: metals<sup>[6]</sup> and rutile oxides.<sup>[7]</sup> A similar computational approach has been used for the OER which is in competition with chlorine evolution on rutile oxides.<sup>[8]</sup> In these studies, the proposed reaction mechanism consists of four consecutive proton and electron transfer steps. Considering the OER intermediates to be HO\*, O\*, and HOO\*, free energy diagrams have been constructed and the oxygen evolving activity has been estimated using O\* binding energies as a descriptor. Our previous studies<sup>[6, 7]</sup> have shown that scaling relationships can be established between the binding energies of HO\*, HOO\*, and O\* species on oxide surfaces. The scaling relations suggest that there is only one free parameter that determines the free energy diagram and thereby the activity. In other words, the activity can be plotted as a function of only one parameter, for example, the oxygen binding energy. The result is a volcano-shaped relationship between catalytic activity and the calculated oxygen adsorption energy. We found that on the surfaces that bind oxygen too strongly, the potential is limited by the formation of HOO\* species, whereas for surfaces that bind oxygen too weakly, the potential is limited by the oxidation of HO\*.  $^{[6,\,7]}$ 

Herein, we revisit the origin of the overpotential for oxygen evolution on the basis of an extensive database of calculated binding energies on oxide surfaces. We include rutile, perovskite, spinel, rock salt, and bixbyite oxides in our calculations. The scaling relationship between HO\* and HOO\* is found to be universal for all the studied materials. We introduce a new descriptor, the energy of a reaction step, which gives rise to a universal description of oxygen evolving activities on the studied materials. Excellent agreement was found in terms of trends, between the calculated overpotentials and the experimental results reported in literature.

### **Results and Discussion**

#### Free energy diagram

We consider the following four electron reaction paths in Equations (2)-(5):

$$H_2O(I) + * \rightleftharpoons HO^* + H^+ + e^-$$
(2)

$$\Delta G_1 = \Delta G_{\rm HO*} - \Delta G_{\rm H_2O(I)} - eU + k_{\rm b}T \ln a_{\rm H^+}$$

$$HO^* \rightleftharpoons O^* + H^+ + e^- \tag{3}$$

$$\Delta G_2 = \Delta G_{\text{O}*} - \Delta G_{\text{HO}*} - \text{eU} + k_{\text{b}} T \ln a_{\text{H}^+}$$

$$O^* + H_2O(I) \rightleftharpoons HOO^* + H^+ + e^-$$
(4)

$$\Delta G_{\rm 3} = \Delta G_{\rm HOO*} - \Delta G_{\rm O*} - {\rm eU} + k_{\rm b} T \ln a_{\rm H^+}$$

$$HOO^* \rightleftharpoons {}^*+O_2(g)+H^++e^-$$
(5)

$$\Delta G_4 = \Delta G_{\rm O2} - \Delta G_{\rm HOO*} - eU + k_{\rm b} T \ln a_{\rm H^+}$$

We applied a method previously developed for modeling the thermochemistry of electrochemical reactions based on density functional calculations.<sup>[4b,7,9]</sup> The derivation of relations 2-5 is in the Supporting Information. The effect of liquid water was implicitly taken into account as we used liquid water as reference. However, the interaction of water with the intermediates at the surfaces has been neglected. The reason is that on the oxidized surface, there was no room for water molecules at the surface, where the interactions would have been the largest.<sup>[7]</sup> We calculated  $\Delta G_{1-4}$  using the computational standard hydrogen electrode (SHE) allowing us to replace a proton and an electron with half a hydrogen molecule at U =0 V vs SHE.<sup>[9]</sup> The theoretical overpotential is independent of the pH or the potential values, because the free energies obtained by using Equations (2)-(5) vary in the same way with pH and U, thereby the potential determining step remains the same. Therefore, the analysis performed for the free energies is at standard conditions (pH=0, T=298.15 K) and U=0:  $\Delta G_{1-4}^{0}$ . Since the barriers between the intermediates are not included, the free energy diagrams we have produced represent a first step towards a complete picture of the reaction path. We expect that the thermodynamic analysis presented here will capture trends in activity, due to cancellation of errors when similar surfaces are compared; however, absolute activities are not obtained at this level of modeling.

A very important parameter which can be deduced from the free energy diagram is the size of the potential-determining step. This concept was developed in other previous papers for OER and ORR<sup>[6-7,9-10]</sup> and reviewed in two other recent papers.<sup>[4]</sup> More precisely, the catalytic performance was estimated by the magnitude of the potential-determining step for the OER,  $G^{OER}$ . This was the last step to become downhill in free energy as the potential increased, that is, the specific reaction step in the four-step mechanism with the largest  $\Delta G$  [Eq. (6)]:

$$G^{\text{OER}} = \max \left[ \Delta G_1^{\ 0}, \ \Delta G_2^{\ 0}, \ \Delta G_3^{\ 0}, \ \Delta G_4^{\ 0} \right]$$
(6)

For which  $\Delta G_{1-4}^{0}$  is  $\Delta G_{1-4}$  at U=0 (pH 0 and T=298.15 K).

The theoretical overpotential, which is independent of pH, at standard conditions is then given by Equation (7):

$$\eta^{\text{OER}} = (G^{\text{OER}}/e) - 1.23 \text{ V}$$
 (7)

The energy diagram for the ideal (but nonexistent) oxygen evolution catalyst is shown in Figure 1a. This ideal catalyst should be able to facilitate water oxidation just above the equilibrium potential. This requires all the four charge transfer steps to have reaction free energies of the same magnitude at zero potential (4.92 eV/4 = 1.23 eV). This is equivalent to all the reaction free energies being zero at the equilibrium potential, 1.23 V (Figure 1a). The catalyst that fulfills this requirement is thermochemically ideal. Real catalysts do not show this behavior. The calculated free energy diagrams at standard conditions of the OER on the surfaces of LaMnO<sub>3</sub> (strong binding), SrCoO<sub>3</sub> (intermediate binding), and LaCuO<sub>3</sub> (weak binding) are shown in Figure 1a,c,d. The most representative potentials are at U =



**Figure 1.** Standard free energy diagram for the OER at zero potential (U=0), equilibrium potential for oxygen evolution (U=1.23), and at the potential for which all steps become downwards at pH 0 and T=298 K over: a) the ideal catalyst, b) LaMnO<sub>3</sub>, c) SrCoO<sub>3</sub>, and d) LaCuO<sub>3</sub>. Standard free energies at U=0 for e) the ideal catalyst, f) LaMnO<sub>3</sub>, g) SrCoO<sub>3</sub>, and d) LaCuO<sub>3</sub>. For all three cases,  $\Delta G_{HOO^*} - \Delta G_{HO^*}$  (vertical dashed lines) is approximately constant with an average value of 3.2 eV, whereas the optimum value is 2.46 eV. The variation of  $\Delta G_{O^*}$  between  $\Delta G_{HOO^*}$  and  $\Delta G_{HOO^*}$  differs for each one. For the ideal case,  $\Delta G_{HO^*}$  is 1.23 eV,  $\Delta G_{HOO^*}$  is 3.69 eV, and  $\Delta G_{O^*}$  is in the middle at 2.46 eV.

0 V for which all steps are uphill, at standard equilibrium potential for oxygen evolution at U=1.23 V, when some of the steps become downhill but some still remain uphill, and at the  $G^{\text{OER}}$  potentials when the potential-determining step becomes downhill. Accordingly, LaMnO<sub>3</sub> had a rather large overpotential due to  $\Delta G_3^{0}$ . For SrCoO<sub>3</sub>,  $\Delta G_2^{0}$  and  $\Delta G_3^{0}$  were almost the same value and the overpotential was small, whereas for LaCuO<sub>3</sub>,  $\Delta G_2$  was the potential-determining step.

### Scaling relations

Figures 1g,f,h show that the bond strength of all the intermediates decreases from left to right (LaMnO<sub>3</sub>, SrCoO<sub>3</sub>, LaCuO<sub>3</sub>). Note that the levels of the intermediates moved together, that is, if one reaction energy changed, the others did too. This correlated energy phenomenon has been observed on metal and metal oxide surfaces as a result of the scaling relations between the intermediates.<sup>[6-7,11]</sup> An example is the linear relation between the binding energy of HO\* and O\*, for which the slope of one half reflects that oxygen has two bonds to the surface, whereas HO\* has only one bond. The intercept is determined by the type of binding site, meaning that there are different intercepts for HO\*(ontop) vs O\*(ontop) scaling compared to the HO\*(hollow) vs O\*(hollow) scaling. This gives rise to different intercepts for metals and oxides because the binding sites are different. Figures 1e-h show that the free energy difference between HO\* and HOO\* is almost constant, independent of the binding strength to the surface. It was pointed out in a recent review by M. Koper<sup>[4b]</sup> that the bindings of HO\* and HOO\* are related to each other by a constant of approximately 3.2 eV both for metals and oxide surfaces regardless of the binding site, which implies that there is a universal scaling relation between HO\* and HOO\*.

Figure 2 shows that the binding energies of HOO\* and HO\* species on the various oxide surfaces were linearly correlated, with a slope of approximately 1, and an intercept of 3.2 eV. The mean absolute error (MAE) of the linear fit was 0.17 eV, in-

Here, we established the formal scaling relationship between

HO\* and HOO\* binding energies over a wide range of oxides.



**Figure 2.** Adsorption energy of HOO\* plotted against the adsorption energy of HO\* on perovskites, rutiles, anatase,  $Mn_xO_y$ ,  $Co_3O_{4x}$  and NiO oxides. They were calculated using the relations (10) and (11) and do not include zero point energy and entropy corrections. Hollow symbols represent the adsorption energy on the clean surfaces: perovskites ( $_{\bigcirc}$ ), rutiles ( $_{\triangle}$ ),  $Mn_xO_y$  ( $_{\square}$ ), anatase ( $_{\diamond}$ ),  $Co_3O_4$  (+), NiO. The solid symbols represent the adsorption energies on high coverage surfaces, with oxygen atoms representing nearest neighbors. The best fit of all the points is  $\Delta E_{HOO*} = \Delta E_{HO*} + 3.20$  eV and with 68% of the points within  $\pm 0.2$  eV and 95% within  $\pm 0.4$  eV. The red star indicates the point at which the binding energies need to be for an ideal electrocatalyst. The relation for the perfect catalyst is:  $\Delta E_{HOO*} = \Delta E_{HO*} + 2.44$  eV.

dicating an extremely strong correlation between the two species.

The slope of unity in the correlated binding energies of HO\* and HOO\* reflects the fact that both species have a single bond between an O atom and the surface. The constant intercept implies that HO\* and HOO\* normally prefer the same type of binding site. From the point of view of the surface, HO\* and HOO\* look very similar. This results in the approximately constant difference of  $\Delta E_{\rm HOO*} - \Delta E_{\rm HO*}$  of 3.2 eV for all the oxides considered. Notably, this difference is also observed on metal surfaces.<sup>[6]</sup> Furthermore,  $\Delta E_{\rm HOO*}$  and  $\Delta E_{\rm HO*}$  are independent of potential and they only describe the interaction between the intermediates and surface oxides. However,  $\Delta G_{1-4}$ changes with potential, pH, and temperature.

Interestingly, the constant difference between the adsorption energies of HO\* and HOO\* of 3.2 eV, regardless of the binding energy of O\*, defines a lower limit for the OER overpotential.<sup>[4b]</sup> Since two proton and electron transfer steps separate the two intermediates, the perfect separation in terms of energy should be 2.46 eV, as illustrated in Figure 1 e. The difference in the energetic of these two steps between actual catalysts and an ideal one (3.2-2.46 eV)/2 e gives a minimum overpotential of 0.4-0.2 V, even if we could find a material in which the O\* level is placed optimally between those of HO\* and HOO\*, as shown in Figure 1 g (with the value -0.2 V that comes from standard deviation of the population from 3.2 eV value:  $2\sigma = \pm 0.4 \text{ V}$  with 95% of the values expected to lie within this confidence interval). The thermochemically ideal catalyst is characterized by having  $\Delta G_1^0 = \Delta G_2^0 = \Delta G_3^0 = \Delta G_4^0 =$ 1.23 eV at standard conditions, which can only be achieved at a specific binding of all intermediates indicated by the red star in Figure 2. It is seen that this point clearly falls outside the general trends and there is no oxide-based material in the classes considered here that provides an optimum binding of both HO\* and HOO\*. In this picture, the challenge is to find a way to modify oxide surfaces or the electrochemical interface, such that the relative stability of HOO\* and HO\* changes.

#### Descriptor and activity volcano

Given the constant difference between the HOO\* and HO\* levels, the variation in the overpotential,  $\eta^{OER}$  from one oxide surface to the next is determined by the O\* adsorption energy. This means that, either step (2) or step (3) is potential determining [Eq. (8):

$$\begin{aligned} G^{\text{OER}} &= \max[\Delta G_{2'}^0, \Delta G_{3}^0] = \max[(\Delta G_{O*}^0 - \Delta G_{HO*}^0), (\Delta G_{HOO*}^0 - \Delta G_{O*}^0)] \\ &\approx \max[(\Delta G_{O*}^0 - \Delta G_{HO*}^0), 3.2 \text{ eV} - (\Delta G_{O*}^0 - \Delta G_{HO*}^0)] \end{aligned}$$

$$\tag{8}$$

The difference  $(\Delta G_{O*}^0 - \Delta G_{HO*}^0)$  is therefore a unique descriptor for the OER activity, and the theoretical overpotential at standard conditions is given by Equation (9):

$$\eta^{\text{OER}} = \{\max[(\Delta G^{0}_{\text{O}}* - \Delta G^{0}_{\text{HO}}*), \ 3.2 \text{ eV} - (\Delta G^{0}_{\text{O}}* - \Delta G^{0}_{\text{HO}}*)]/e\} - 1.23 \text{ V}$$
(9)

Plotting  $\eta^{\text{OER}}$  as function of  $\Delta G^0_{O*} - \Delta G^0_{HO*}$  for the classes of materials considered here will therefore lead to a universal volcano relationship independent of the catalyst material. For clarity, the trends are shown separately for perovskites (Figure 3 a) and rutiles (Figure 4 a), and the points represent the calculated value for each oxide.



**Figure 3.** a) Activity trends towards oxygen evolution plotted for perovskites. The negative theoretical overpotential was plotted against the standard free energy of the  $\Delta G_{0*}^0 - \Delta G_{HO*}^0$  step. The low coverage regime was considered and the calculated values were used to show the activity of each oxide. The volcano curve was established by using the scaling relation between  $G_{HOO*}^0 - G_{O*}^0$  and  $G_{O*}^0 - G_{HO*}^0$ . b) Theoretical overpotential vs the experimental overpotential in alkaline media. Experimental data were adapted from the study of O. M. Bockris and T. Otagawa.<sup>[3a,12]</sup> All experimental values were recorded at 10 mA cm<sup>-2</sup>, room temperature, and pH 14.

This theoretical analysis leads to the following ordering of catalyst activities for the following perovskites:  $SrCoO_3 > LaNiO_3 > SrNiO_3 > SrFeO_3 > LaCoO_3 > LaFeO_3 > LaMnO_3$ . The trend agrees well with experimental findings by Bockris et al. and Y. Matsumoto et al.<sup>[3a, 12]</sup> under alkaline conditions (Figure 3 b). All experimental overpotentials were reported at 10 mA cm<sup>-2</sup>, because a large database of overpotentials are reported at this current density. Ideally, the comparison should be made with potentials obtained on single crystals. Even



**Figure 4.** a) Activity trends towards oxygen evolution, for rutile, anatase,  $Co_3O_4$ ,  $Mn_xO_y$  oxides. The negative values of theoretical overpotential were plotted against the standard free energy of  $\Delta G_{HOY} - \Delta G_{OY}$  step. The effect of interaction with the oxygen from the neighboring site is considered: rutile oxides ( $\blacktriangle$ ),  $Mn_xO_y$  ( $\blacksquare$ ). For NiO<sub>b2</sub>, PbO<sub>b2</sub>, and SnO<sub>b2</sub>, cus sites (see Figure 5 a,b) are empty, and the reaction takes place on the bridge sites (a complete picture of the surface is given in the Supporting Information). Hollow triangles ( $\triangle$ ) represent the low coverage regime. b) Theoretical overpotential vs the experimental overpotential in acidic media ( $\bigcirc$ ) and in alkaline media ( $\bigcirc$ ). Experimental data were taken from Y. Matsumoto and E. Sato.<sup>(12)</sup> All experimental values were considered at 10 mA cm<sup>-2</sup> and room temperature.

then, the quantitative comparison between theoretical and experimental overpotentials remains difficult. The theoretical overpotential is not directly comparable to experimentally determined values because the activation barriers were neglected. Furthermore, the experiments were performed using electrodes with oxide nanoparticles, for which the effective surface area is often unknown or not reported. Hence, the current per geometric area is not directly available. In addition, the experimentally measured overpotential depends on the current density at which it is measured. Despite these uncertainties, it should be possible to compare trends in overpotentials for a set of different oxides.

The comparison to the experiments can be seen in Figure 3 b for the perovskites. According to our calculations, SrCoO<sub>3</sub> has a  $\Delta G^0_{HO*} - \Delta G^0_{O*}$  of 1.48 eV, close to the very top of the volcano. The high activity of SrCoO<sub>3</sub> was also predicted theoretically by Y. Matsumoto et.al.,<sup>[13]</sup> however, the main problem lies in the experimentally determined value and is related to how to obtain SrCoO<sub>3</sub> with perovskite-type structure, since experimentally SrCoO<sub>3</sub> was obtained under a non-perovskite type structure and exists as SrCoO<sub>2.5</sub> in composition.

For the other oxides such as rutiles (anatases), Mn oxides, and Co oxides, the activity order given by the theoretical calculations was extracted from Figure 4a:  $Co_3O_4 \approx RuO_2 > PtO_2$ -rutile phase  $\approx RhO_2 > IrO_2 \approx PtO_2$   $\beta$ -phase(CaCl<sub>2</sub>)  $\approx$  Mn<sub>x</sub>O<sub>y</sub>  $\approx$  NiOb<sub>2</sub>  $\approx$  RuO<sub>2</sub> and IrO<sub>2</sub> anatase phase  $> PbOb_2 \gg$  Ti, Sn, Mo, V, Nb, Re oxides. The anatase phases with crystallographic orientation 001, such as RuO<sub>2</sub> and IrO<sub>2</sub>, showed approximately the same activity as the rutile phases. A similarly good agreement between the theoretical and experimental values of overpotentials on oxides other than perovskites is illustrated in Figure 4b.

Even the comparisons between different experimental values were difficult to establish, due to many factors that affect the potential, such as pH, effective surface area, and particle size. A slight discrepancy exists between the calculated and measured Co3O4 activity. DFT calculations showed that Co<sub>3</sub>O<sub>4</sub> was slightly more reactive than RuO<sub>2</sub>, whereas most of the experimental studies suggest that Co3O4 has a higher overpotential than RuO<sub>2</sub> by 0.2–0.25 V.<sup>[12]</sup> It was shown that  $Co_3O_4$ is nonstoichiometric with an excess of oxygen and that the size of crystallites vary with the calcination temperature.<sup>[3g]</sup> Recently, Singh et al. synthesized a spinel type of Co<sub>3</sub>O<sub>4</sub> thin film which showed a low overpotential<sup>[14]</sup> in agreement with our calculations. It has also been reported that the overpotential on Co-oxide nanoparticle electrocatalysts is size-dependent with lower overpotentials on smaller particles.<sup>[15]</sup> Other Co oxide structures with a low overpotential have been reported as well.<sup>[16]</sup> In Figure 4b, we compared for Co<sub>3</sub>O<sub>4</sub>, three experimental overpotentials from the literature to the computed overpotential. Starting from left to right, the most active was the value reported by Singh et al., [14] followed by three values reported by Esswein et al.<sup>[15a]</sup> A slight discrepancy was also obtained in the case of NiO, however, the theoretical value was calculated for a perfect single crystal NiO, whereas in reality, NiO is expected to have a more complicated composition, including species in higher oxidation states.<sup>[3g, 17]</sup>

We emphasize that the reaction mechanism is more flexible for the oxides close to the top of the volcano at which point the intermediates have a better compromise in interaction strength, which could be the case for  $Mn_xO_y$  oxides (detailed results will be discussed in a future manuscript). However, at the top of the volcano, the overpotential is small and other reaction paths could be relevant if their overpotential is smaller than the values reported in this study. This flexibility of reaction mechanism might result in a slight variation in the theoretical overpotentials, and the details of this matter are out of the scope of this paper.

The actual surface of an oxide catalyst can experience oxidation and/or dissolution in the highly corrosive OER environment. For example, some oxides such as NbO<sub>2</sub>, ReO<sub>2</sub>, VO<sub>2</sub>,

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 $MoO_2$ , and  $CrO_2^{[17a]}$  are not stable. Still, the theoretical values may be interesting as a guide in designing mixed oxides that could show improved activity.<sup>[18]</sup>

Given the robustness of this theoretical model as applied to oxide materials of well-defined stoichiometry and crystal structure, one can also potentially apply these methods to nonstoichiometric oxide catalysts.

## Conclusions

First principles periodic DFT calculations have been used to revisit the origin of the overpotential for oxygen evolution for a wide range of oxides including rutile, perovskite, spinel, rock salt, and bixbyite. A universal scaling relationship between the binding energy of HOO\* and HO\* was identified. The scaling relation led to an approximately constant difference between the binding energies of HOO\* and HO\*, which in turn defined the lowest possible theoretical overpotential for the OER on a wide variety of oxides. Few catalyst materials operate at this minimum theoretical overpotential, and the remaining hundreds of catalyst materials are further burdened by an additional overpotential arising from a suboptimal O\* binding

energy. Thus, the origin of the overpotential for oxygen evolution catalysis has been elucidated, whereby a single descriptor ( $\Delta G_{O^*} - \Delta G_{HO^*}$ ) was introduced, which resulted in a universal description of oxygen-evolving activities. Experimental trend studies from the literature could be described and understood within the model.

This study provides an understanding of the fundamental limitations for the OER activity on oxide-based electrocatalysts. Our results showed that for the classes of structures considered here, the OER activity could not be significantly improved beyond RuO<sub>2</sub> by tuning the binding between the intermediates and the catalyst surface.

To avoid the limitations defined by the universal scaling relation, one must find ways to stabilize HOO\* compared to HO\*. It is possible that three dimensional structures, such as rough surface structures, zeolites or co-adsorbates on the surface could achieve this relative stabilization of HOO\*. Effects such as these are likely present in enzymes that catalyze water oxidation very effectively in nature.<sup>[19]</sup> We calculated the binding energies of the intermediates  $O^*$ ,  $HO^*$ , and  $HOO^*$  on the rutile, perovskite, Mn, Co, and Ni oxide surfaces [Eqs. (10)–(12)]:

$$\Delta E_{\rm HO*} = E(\rm HO^*) - E(^*) - (E_{\rm H_2O} - 1/2 E_{\rm H_2})$$
(10)

$$\Delta E_{\text{HOO}*} = E(\text{HOO}^*) - E(^*) - (2 E_{\text{H}_2\text{O}} - 3/2 E_{\text{H}_2})$$
(11)

$$\Delta E_{O*} = E(O^*) - E(^*) - (E_{H_2O} - E_{H_2})$$
(12)

For which E(\*),  $E(HO^*)$ ,  $E(O^*)$ , and  $E(HOO^*)$  are the ground state energies of the clean surface and the surfaces with HO\*, O\*, and HOO\* adsorbed, respectively.  $E_{H_2O}$ ,  $E_{H_2}$  are the calculated DFT energies of H<sub>2</sub>O and H<sub>2</sub> molecules in the gas phase.

The surface structures together with the unit cells we used are shown in Figure 5. The stoichiometric surfaces were considered for rutile oxides, with the exception of PbO<sub>2</sub>, SnO<sub>2</sub>, and NiO<sub>2</sub>, on which the binding of intermediates are thermodynamically favored on nonstoichiometric surfaces (denoted by the subscript b, Figure 5). The results presented here, were obtained using DFT,<sup>[20]</sup> with the RPBE<sup>[21]</sup> exchange-correlation functional, and using the Dacapo plane-wave implementation.<sup>[22]</sup> Using RPBE functional will give better adsorption properties.<sup>[21]</sup> This level of theory has previously



**Figure 5.** Visualization of the considered surface structures of metal oxides. The dashed lined squares indicate the unit cells used in the calculations. The reaction takes place only on one site at a time. a) Rutile-like stoichiometric surface (110) for MO<sub>2</sub> with M=Ti, V, Cr, Mn, Nb, Mo, Ru, Rh, Re, Ir, Pt, Sn. Red and light blue spheres represent O and metal atoms, respectively. Positions 1 and 2 represent the active sites (cus). Positions 3 and 4 represent the in-active sites (BRIDGE) and are covered with oxygen with (1 × 2) unit cell. b) Rutile-like reduced surface (110) for MO<sub>2</sub>. Positions 3 and 4 represent the active position (BRIDGE) and positions 1 and 2 represent the inactive sites (BRIDGE) and are covered with oxygen with (1 × 2) unit cell. b) Rutile-like reduced surface (110) for MO<sub>2</sub>. Positions 3 and 4 represent the active position (BRIDGE) and positions 1 and 2 represent the inactive position (cus) with M=Ni, Pb, Sn. Red, and light blue represent O and metal atoms, respectively with (1×2) unit cell. c) Perovskite structure for LaMO<sub>3</sub> and SrMO<sub>3</sub> (100) surface with M=Ti, V, Mn, Fe, Co, Ni, Cu. Red, dark blue, and light blue spheres represent O, La(Sr), and metal, respectively. Sr and La are in the subsurface. The active sites/ unit cell are represented by (1,2,3,4) and the subsurface atom is represented by 5, with (2×2) unit cell, d) Mn<sub>2</sub>O<sub>3</sub> (110) surface structure. (2×1) unit cell was used in the calculations, e) Mn<sub>3</sub>O<sub>4</sub> (001) surface structure. (2×1) unit cell was used in the calculations, e) (1×1) unit cell was used in the calculations, e) Mn<sub>3</sub>O<sub>4</sub> (001) anatase-like surface with (1×2) unit cell, and h) MO(100) surface with M=Mn, Ni. The (1×1) unit cell is indicated.

predicted trends in formation energy of  $\mathsf{rutile}^{\scriptscriptstyle[23]}$  and perovskite oxides.<sup>[24]</sup> We therefore expected that it also correctly captured trends on adsorption energies. The Kohn-Sham equations were solved using a plane wave basis with a cutoff of 350-400 eV for kinetic energy and a cutoff of 500 eV for density. The ionic cores and their interaction with valence electrons were described by ultrasoft pseudopotentials.<sup>[21]</sup> The exchange and correlation effects are described using RPBE functional (a gradient approximation GGA for these effects) because they describe well the absorption properties. The occupancy of the one-electron states was calculated using an electronic temperature of  $k_{\rm B}T = 0.1 \, {\rm eV}$  for surfaces and 0.01 eV for molecules in vacuum. All energies were extrapolated to T = 0 K. The ionic degrees of freedom were relaxed using the guasi-Newton minimization scheme until the maximum force component was smaller than 0.05  $e^{A^{-1}}$ . Spin-polarization calculations were carried out for CrO2, Mn, Ni and Co oxides, and for perovskites when appropriate. More about the surfaces and other computational details can be found in the Supporting Information.

Instead of using the RPBE-generalized gradient correction self consistency,<sup>[21]</sup> we could have used other approaches for self-interaction corrections, such as GGA+ $U^{[25]}$  for some of the oxides (Co<sub>3</sub>O<sub>4</sub> and manganese oxides). This method presents its own limitations in terms of different *U* values that have to be chosen for each system and thereby the results could not be directly compared. As any functional, does not necessary gives better results.<sup>[26]</sup> These will make subject for each oxide separately. For the study of some oxides like Mn<sub>3</sub>O<sub>4</sub>, Mn<sub>2</sub>O<sub>3</sub>, and CoO<sub>4</sub>, other approximations for the exchange and correlations effects could be imposed, such as DFT+U.<sup>[24]</sup> This choice imposes limitations, because each system needs different values of *U* and finally the values cannot be compared.

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