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Does the breaking of adsorption-energy scaling relations guarantee enhanced electrocatalysis?

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Abstract: The adsorption energies of numerous species on homogeneous and heterogeneous catalysts scale linearly with each other. Such linear dependence lowers the degrees of freedom in multistep reactions, greatly simplifying computational electrocatalysis models. The downside of scaling relations is that they limit the efficiency of electrocatalytic reactions. For instance, the scaling relation between *OOH vs *OH supposedly limits the oxygen evolution and reduction reactions (OER, ORR): while the energetic separation of these intermediates should ideally be 2.46 eV, on most catalysts it is ~3.20 eV. Thus, it is currently assumed that breaking such scaling relation might lead to significant enhancement of OER/ORR electrocatalysis. In this review, we evaluate this hypothesis using literature data. The analysis suggests that breaking the *OOH vs *OH scaling relation is a necessary yet insufficient condition to optimize OER/ORR electrocatalysts. Alternatively, we define a new descriptor: the electrochemical-step symmetry index (ESSI), the optimization of which effectively corresponds to low calculated overpotentials.

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Brief introduction to scaling relations

Since their discovery [1], adsorption-energy scaling relations have immensely contributed to the fields of catalysis and surface chemistry [2,3]. As they have been shown to exist between a broad range of adsorbates on homogeneous and heterogeneous catalysts, their insights have been extraordinarily useful in computational catalysis to rationalize

activity trends [2,3]. Remarkably, they have also been used to build Sabatier-type activity plots, which guide experiments toward the discovery of new catalyst materials [4,5]. On facet i of a given set of materials, adsorption-energy scaling relations between species 1 and 2 are defined as:

$$\Delta G_2^i = A_{1,2} \Delta G_1^i + B_{1,2}^i \quad (2)$$

While some authors attribute scalability to bond-order conservation theory [2,6], we explain it based

on the connection between the electronic and geometric structure of materials and their adsorption behavior [7-9]. If ΔG_1^i and ΔG_2^i scale with each other and depend on a set of structural parameters $\{\omega_j\}$ as $\Delta G_1^i = g^i(\{\omega_j\}) + \beta_1^i$, $\Delta G_2^i = f^i(\{\omega_j\}) + \beta_2^i$, then:

$$f^i(\{\omega_j\}) = A_{1,2} g^i(\{\omega_j\}) \quad (3)$$

$$B_{1,2}^i = \beta_2^i - A_{1,2} \beta_1^i \quad (4)$$

According to Equation (2), if two species scale with each other, their adsorption energies are proportionally modulated by the same parameters and $A_{1,2}$ is the proportionality constant. $A_{1,2}$ is a dimensionless, surface independent slope, calculated applying electron-counting rules to the adsorbates [7,8]. For instance, the *OH vs *O scaling has $A_{O/OH} \approx \frac{1}{2}$, as the O atom in *OH lacks one electron to reach the octet and *O lacks two. However, scaling relations are not limited to species bound via the same atom, so that e.g. *O scales well with *S [8].

Recently, Su et al [7] identified several parameters belonging to $\{\omega_j\}$: outer electrons, work function, excess charge, d-band center, integrated crystal orbital overlap population, integrated crystal orbital Hamilton population. They also showed that while $A_{1,2}$ is typically positive, negative slopes are observed between covalent and ionic adsorbates [7].

In Equation (3), the offset $B_{1,2}^i$ depends on the slope, β_1^i and β_2^i . Based on structure-energy relationships [9-15], one can conclude that β_1^i , β_2^i and the offset depend on the coordination of facet i [9,14]. A particular case is $A_{1,2} = 1$, as a single offset describes the data for all facets and materials (the scaling of *OOH vs *OH in Figure 1 is a salient example, other examples include *CHO vs *CO and *Cl vs *F) [8,9,14,16]. Note in passing that there are also scaling relations between adsorption energies

and other types of energetics, namely bulk energies of formation [17] or adsorption-site stability [18].

From a catalysis perspective, the existence of scaling relations entails a simple but far-reaching idea: if (at least some of) the adsorption energies are linearly dependent, the degrees of freedom available for optimizing catalytic sites are lower than the number of different adsorbed species [19,20].

From a modelling perspective this is an advantage, as models of catalytic reactions can, and have been, largely simplified [5,6]. However, this is considered to be a limitation for the design of enhanced materials, as linear dependence may preclude further optimization of catalytic activities [6]. In other words, the energetic connection between adsorbates is allegedly deleterious in catalysis.

Thus, it is believed that breaking scaling relations may lead to enhanced catalysts. This idea is extended in electrocatalysis, especially for CO₂ reduction [21], oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) [19,20]. For the latter two, it is considered that the scaling between the adsorption energies of *OOH and *OH might be the origin of the high overpotentials observed experimentally.

On the example of the OER catalyzed by a wide variety of materials, we show here that breaking the scaling between *OH and *OOH is a necessary yet insufficient condition to optimize catalytic active sites. As such, breaking it may not necessarily lead to high OER activities, and materials that do not break this scaling might as well be highly active. We will show that a more robust description of OER activity is provided by the electrochemical-step symmetry index (ESSI), an energetic descriptor defined and tested here, which can also be used for other reactions such as the ORR.

1. Scaling relations in oxygen evolution electrocatalysis

We assume that the OER ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, $E^0 = 1.23$ V) proceeds as [19,22]:

The calculated OER overpotential (η_{OER}) is:

$$\eta_{OER} = \max(\Delta G_4, \Delta G_5, \Delta G_6, \Delta G_7) / e - E^0 \quad (9)$$

Where e is the (positive) electron charge. Given the scaling relations between the adsorption energies of $*O$, $*OH$ and $*OOH$ (ΔG_O , ΔG_{OH} , ΔG_{OOH}) on numerous materials [1,9,19,20,23-29], only one of the three can be freely modified to optimize the reaction energies $\Delta G_4 = \Delta G_{OH}$, $\Delta G_5 = \Delta G_O - \Delta G_{OH}$, $\Delta G_6 = \Delta G_{OOH} - \Delta G_O$, $\Delta G_7 = 4.92 - \Delta G_{OOH}$ and thereby minimize η_{OER} . This is in line with the reduction in the degrees of freedom mentioned in the Introduction. Initially, it was proposed that a “fundamental” overpotential should arise from the scaling relation between ΔG_{OH} and ΔG_{OOH} [20]. This idea is based on four considerations:

(i) $*OH$ and $*OOH$ are separated by two proton-electron transfers (to verify that, sum Equations (4) and (7), or (5) and (6)).

(ii) For an ideal OER catalyst: $\Delta G_4 = \Delta G_5 = \Delta G_6 = \Delta G_7 = 1.23$ eV. Therefore, such catalyst has $\Delta G_O^{ideal} = 2.46$ eV, $\Delta G_{OH}^{ideal} = 1.23$ eV, and $\Delta G_{OOH}^{ideal} = 3.69$ eV.

(iii) The scaling relation of ΔG_{OOH} vs ΔG_{OH} should have a slope of 1 ($A_{OH/OOH} \approx 1$), as the oxygen atom bound to the surface in $*OH$ and $*OOH$

lacks an electron to reach the octet in both cases [9,19,20]. Note, however, that the slope is typically smaller as a result of the increasing covalence of the metal-OOH bond for late-transition metal active sites [25,27].

(iv) Because $A_{OH/OOH} \approx 1$, a single line includes all materials, regardless of their composition and coordination [9,19,20]. The offset of such line is

Figure 1. Adsorption-energy scaling relation between *OH and *OOH on various materials: LaMO₃ and SrMO₃ [17,19,27], monoxides MO [17,27], (un)doped TiO₂ [26]), porphyrins [25], and functionalized graphitic materials (FGMs) [24,29]. The best fit to the points is provided (black line) together with the prediction made by Koper [20] and Man *et al* [19] (red line). A band around the black line covers an area of ± 1.5 MAE around the best fit and contains 76% of the data. MAE: Mean absolute error, 0.17 eV in this case. ♦: ideal catalyst.

approximately 3.20 eV (Figure 1), where data are included for porphyrins [25], functionalized graphitic materials (FGMs) [24,29], and four families of transition metal oxides (perovskites LaMO₃ and SrMO₃ [17,19,27], monoxides MO [17,27] and (un)doped TiO₂ [26]). Note in Figure 1 that the ideal catalyst is ostensibly far from the main trend [19].

As the ideal separation between *OOH and *OH is 2.46 eV but the actual separation is nearly constant on most materials and equal to 3.2 eV, a minimal $\eta_{\text{OER}} = (3.20 - 2.46) \text{ eV} / 2e^- = 0.37 \text{ V}$ is suggested to result from scaling relations [19,20]. Note that this substantial overpotential adds at least an extra 30% requirement to the equilibrium potential of 1.23 V for water splitting.

Numerous works have confirmed such constant separation [1,9,19,20,23-27,29] and significant efforts have been directed toward identifying materials with $\Delta G_{\text{OOH}} - \Delta G_{\text{OH}} \approx 2.46 \text{ eV}$.

In this regard, various strategies have been proposed to stabilize *OOH preferentially over *OH: three dimensional sites [24,30], doping [31], introducing hydrogen donor/acceptor functionalities and ligands [32], confinement effects [33], and electrolyte modification [25,34]. However, few examples exist where superior experimental catalytic activity may be attributed to the breaking of the *OOH vs *OH scaling [31]. Therefore, it is important to assess whether screening studies should merely focus on identifying catalysts with $\Delta G_{\text{OOH}} - \Delta G_{\text{OH}} \approx 2.46 \text{ eV}$, or if other criteria should be considered.

2. Breaking the *OOH vs *OH scaling: panacea or partial solution?

If the unideal constant separation between *OH and *OOH were to blame for (part of) OER inefficiencies, a sizable departure from 3.20 eV to 2.46 eV should correspond to a decrease in η_{OER} . In other words, $(\Delta G_{\text{OOH}} - \Delta G_{\text{OH}} - 2.46 \text{ eV}) / 2e^-$ should tend to zero for the most active materials and be a large positive number for the least active ones.

Unfortunately, this is not observed in Figure 2, where there is no straightforward correlation between η_{OER} and the departure from 3.2 eV to 2.46 eV. Strikingly, a number of catalysts break the *OOH vs *OH scaling, as they display minimal deviations from 2.46 eV, but simultaneously possess high η_{OER} .

This is the case of Au FGMs [24,29], for which $\Delta G_{\text{OOH}}^{\text{Au-FGM}} - \Delta G_{\text{OH}}^{\text{Au-FGM}} = 2.49 \text{ eV}$ but $\eta_{\text{OER}}^{\text{Au-FGM}} = 1.49 \text{ V}$. Another example is CaO [17], which has $\eta_{\text{OER}}^{\text{CaO}} = 1.83 \text{ V}$ in spite of $\Delta G_{\text{OOH}}^{\text{CaO}} - \Delta G_{\text{OH}}^{\text{CaO}} = 2.72 \text{ eV}$. Based on the breaking of the *OOH vs *OH scaling relation, one would typically assume that these catalysts have negligible overpotentials, while those are in fact remarkably large. One can also find highly active materials that do not break the *OOH vs *OH scaling: consider

Figure 2. Calculated OER overpotentials (η_{OER}) for various electrocatalysts plotted as a function of their departures from the ideal *OOH vs *OH energetic separation of 2.46 eV. ♦: ideal catalyst.

Mo-doped TiO_2 (denoted TiMoO_2), which has $\Delta G_{OOH}^{\text{TiMoO}_2} - \Delta G_{OH}^{\text{TiMoO}_2} = 3.52\text{eV}$ and $\eta_{OER}^{\text{TiMoO}_2} = 0.53\text{V}$ [26].

All these data and several others included in the Supporting Information lead us to conclude that breaking the *OOH vs *OH scaling may not necessarily guarantee enhanced OER electrocatalysis. This is because what defines an ideal OER catalyst is not that the sum of two of its reaction energies be 2.46 eV but rather that all of them be 1.23 eV [19].

3. Electrochemical-step symmetry index (ESSI): a more robust descriptor of electrocatalytic activity

If breaking the *OOH vs *OH scaling relation is a necessary yet insufficient condition to optimize OER electrocatalysis, what else is needed? The ideal catalyst sheds light into this matter: $\Delta G_O, \Delta G_{OH}, \Delta G_{OOH}$ are such that all reaction energies of the electrochemical steps are numerically equal to the equilibrium potential [19]. Thus, one can hypothesize that a measure of the departures of all “suitable” steps from ideality might help distinguish

Figure 3. a) η_{OER} as a function of the electrochemical-step symmetry index (ESSI). The best linear fit is provided with a band around it covering an area of ± 1.5 MAE (MAE = 0.21 eV), which contains 86% of the data. The red line describes $\eta_{OER} = ESSI$, the lower bound of which is the ideal catalyst (♦). b) Selected data from (a) with range bars in the ESSI axis. Materials easy to optimize have null or wide bars, while narrow bars denote the opposite.

between high- and low-activity electrocatalysts. This is confirmed in Figure 3a, where ESSI and η_{OER} exhibit a good linear correlation. ESSI is defined in Equation (9) and applies only to steps for which $\Delta G_i \geq E^0$ (denoted ΔG_i^*), as only those can be potential-limiting:

$$ESSI = \frac{1}{n} \sum_i^n (\Delta G_i^* - E^0) \quad (10)$$

To exemplify the use of Equations (8) and (9), consider LaNiO_3 [17,19,27]: ΔG_4 to ΔG_7 are 1.54, 1.56, 1.52 and 0.30 eV. Therefore, $\eta_{\text{OER}}^{\text{LaNiO}_3} = (1.56 - 1.23) \text{ eV/e} = 0.33 \text{ V}$ from (6), and $ESSI^{\text{LaNiO}_3} = (0.31 + 0.33 + 0.29) \text{ eV} / 3e^- = 0.31 \text{ V}$ from (7). Figure 3b identifies LaNiO_3 as an active OER material because its ESSI and η_{OER} are small, although $\Delta G_{\text{OOH}}^{\text{LaNiO}_3} - \Delta G_{\text{OH}}^{\text{LaNiO}_3} = 3.07 \text{ eV}$.

There is an important feature of ESSI by construction (see Equations (8) and (9)): $ESSI \leq \eta_{\text{OER}}$. This is observed in Figure 3a in all cases. Materials for which $ESSI = \eta_{\text{OER}}$ are 21% of the data in Figure 3a and fall over the red dashed line. For those, only one step in (4) to (7) is larger than 1.23 eV. Importantly, the ideal catalyst belongs to the line and represents its lower bound. Close to the line are materials for which the energies of all steps larger than 1.23 eV are nearly identical.

As the best linear fit in Figure 3a has a slope close to 1 and an offset of 0.27 V, most catalysts possess at least two reaction energies larger than 1.23 eV and, in average, they are 0.27 eV less negative than the potential-limiting step. In fact, 64% of the data possesses two steps larger than 1.23 eV and only 14% possesses three.

4. Optimizing OER catalysts with ESSI guidelines

Figures 2 and 3 strongly suggest that catalyst optimization should not only focus on breaking the $^*\text{OOH}$ vs $^*\text{OH}$ scaling. Instead, the potential-determining steps for each material are to be considered. Since ESSI is defined as an average (Equation (9)), one can add bars to it showing the range they span, as depicted in Figure 3b. Materials with $ESSI = \eta_{\text{OER}}$, such as Mn-BH_2 (a porphyrin with BH_2 ligands and a Mn center), have null bars because only one of their steps, which is also the potential-determining step is larger than 1.23 eV. In principle, such materials are easy to optimize, as only one step

needs to be altered to lower η_{OER} . Materials close to $ESSI = \eta_{\text{OER}}$ are normally difficult to optimize, as they have two (CuO) or three (LaNiO_3) steps larger than 1.23 eV and rather similar in energy, so that their bars are narrow. Altering the potential-determining step might simply cause another step to become potential-limiting, leaving η_{OER} practically unaltered. Finally, materials relatively far from the line where $ESSI = \eta_{\text{OER}}$ have wide bars and are good candidates for optimization. This is the case of materials such as Co-BH_2 porphyrin, Rh_{FGM} (functionalized graphitic materials with Rh-N_4 centers) and LaGaO_3 . Although they have several steps larger than 1.23 eV, these steps differ appreciably, so optimizing the potential-limiting step may effectively result in an overpotential decrease.

In Figure 3a we observe that the statistical dispersion of the data increases alongside ESSI, so that good catalysts are usually highly symmetric and, thus, hard to optimize. It is then, when ESSI is close to zero, that scaling relations need to be broken.

5. Joint analysis of oxygen reduction and evolution by means of ESSI

Rossmeisl and co-workers [32] noticed that assuming the oxygen reduction reaction (ORR) mechanism to be the inverse of the OER ($\text{O}_2 \rightarrow ^*\text{OOH} \rightarrow ^*\text{O} \rightarrow ^*\text{OH} \rightarrow \text{H}_2\text{O}$), leads to a double volcano activity plot. Because of scaling relations, the OER and ORR activity summits are located at different adsorption energies [24,25,29,32]. This implies that a given surface site can hardly be simultaneously efficient for OER and ORR. This is observed in Figure 4, where ESSI for the OER is plotted against η_{OER} as in Figure 3, and ESSI for the ORR is plotted against $-\eta_{\text{ORR}}$.

As shown by Rossmeisl *et al* [32], there is a “forbidden region” around the ideal catalyst: the best-fit lines in Figure 4 have slopes close to 1, but the offsets differ by $0.27 + 0.34 = 0.61 \text{ V}$. If the OER

Figure 4. Correlation between ESSI and OER and ORR catalytic activity, defined as η_{OER} and $-\eta_{\text{ORR}}$, respectively. The MAE for the ORR is 0.18 eV and 84% of the data is contained within an area of ± 1.5 MAE. The red dashed line describes the points for which $\eta_{\text{OER}} = \text{ESSI}$ and $-\eta_{\text{ORR}} = \text{ESSI}$.

mechanism is indeed the inverse of the ORR, 0.61 V is the lowest possible overpotential sum (also known as bifunctionality index) as a result of the asymmetry of the electrochemical steps. This agrees well with the experimental fact that bifunctionality indices of ~ 0.8 V are observed for active ORR/OER catalysts (measured with linear sweep voltammetry at 10 and -1 mAcm^{-2} for the OER and the ORR, respectively) [35,36]. Note in passing that, as shown in Figure 5 and as a result of assuming inverse mechanisms, the ESSI for ORR and OER are linearly dependent and the slopes of the lines depend on the number of steps larger and smaller than 1.23 eV.

6. Additional considerations

Before concluding, we would like to emphasize that the analysis here can be influenced by certain additional factors.

First, there is growing awareness in computational electrocatalysis about the impact of solvation in scaling relations and volcano-type

Figure 5. Correlation between ESSI_{OER} and ESSI_{ORR} for the catalysts considered in this study. The slopes depend on the number of steps larger and smaller than 1.23 eV.

activity plots. Recent studies highlight the importance of solvation for the realistic modeling of electrocatalysts [14,25,28,34,37-42]. While regarding solvation as a constant shift to all data points within a trend is still the preferred method to account for solvent effects in electrocatalysis, we believe that catalyst-specific corrections [25,28,37], although computationally more expensive, are required for providing more accurate activity predictions. The same holds for models incorporating an explicit solvent description [37,39,42-46], which provide more accurate results than implicit schemes but are more computationally demanding.

Furthermore, the analysis here assumes that OER and ORR proceed through a single reaction mechanism on all types of materials [19,20,22]. While this is a convenient assumption frequently used in computational electrocatalysis to simplify screening studies, it may not be representative of real (electro)catalytic processes. This has recently been pointed out for CO hydrogenation during CO_2 reduction [14], and the OER [47]: if a certain material splits O_2 into 2^*O without prohibitive kinetic barriers, the formation of $^*\text{OOH}$ is avoided and the scaling between $^*\text{OOH}$ and $^*\text{OH}$ does not influence η_{OER} .

There are also some methodological concerns regarding the OER framework used here. For instance, RuO₂(110), an archetypal OER material, is not predicted to be active in a density functional theory (DFT) description at the GGA level. Using DFT+U [48,49] or including structural defects mitigate but do not completely suppress this artifact [50]. Using a new type of scaling relations (not made for several materials using identical simulation parameters, as conventionally done, but for a single material using different simulation parameters) [39], Briquet *et al* detected an anomaly among the adsorption energies of oxygenates on RuO₂(110), which is likely responsible for the poor prediction of its OER activity. Explicit solvation and exchange-correlation functionals including van der Waals interactions help in correcting the anomaly. Recently, Tripkovic *et al* have also shown that the OER activities of oxides modelled with DFT+U and hybrid functionals strongly depend on the values of U and exact exchange used, so the results should be obtained and interpreted with extreme precaution [51].

7. Summary and outlook

Here we have discussed the application and reaches of adsorption-energy scaling relations in the context of oxygen electrocatalysis. While substantial computational and experimental efforts have been directed toward identifying OER catalysts that break the *OOH vs *OH scaling, our analysis of literature data suggests that this is a necessary yet insufficient condition to design superior catalysts.

From a thermodynamic perspective, the criterion that guarantees efficient electrocatalysis is minimal deviation from the equilibrium potential of the reaction energies of all electrochemical steps [19]. In this regard, we pointed to recent OER computational studies that support this idea, and introduced a new descriptor, the electrochemical-step symmetry index (ESSI). Our analysis of ESSI values explains why high OER activity may be predicted on

materials that do not break scaling relations, and why low OER activity may as well be predicted on materials that break those. Furthermore, we extended the ESSI-based analysis to the ORR.

We suggest that future efforts directed to the design of enhanced OER and/or ORR catalysts focus not just on breaking the *OOH vs *OH scaling but on optimizing ESSI and finding material properties that correlate well with it. In particular, the range bars associated to ESSI and the number of steps larger than 1.23 eV indicate how easy or difficult it is to lower the overpotential of a given material.

Last but not least, note that our conclusions and the ESSI analysis may also be extended to other multistep electrocatalytic reactions such as CO₂ reduction, for which breaking the *CHO vs *CO scaling is considered paramount [16,21]. Recently, it was suggested that *CO hydrogenation is likely not the potential-limiting step of CO₂ reduction, implying that breaking the scaling between *CHO vs *CO might not suffice to enhance CO₂ reduction [14].

While adsorption-energy scaling relations are a powerful tool to understand trends and guide computational and experimental studies, we recommend that their exact role on designing superior catalysts be assessed with great caution.

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Supporting Information for:

Does the breaking of adsorption-energy scaling relations guarantee enhanced electrocatalysis?

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In Tables S1-S6 we provide all the data used to build Figures 1-3 in the main text. All energies are in eV, whereas $\Omega = (\Delta G_{OOH} - \Delta G_{OH} - 2.46 \text{ eV}) / 2e^-$, $ESSI_{OER}$, $ESSI_{ORR}$, η_{OER} and $-\eta_{ORR}$ are in V.

Table S1. OER data for (un)doped TiO₂ taken from [1].

Material	ΔG_O	ΔG_{OH}	ΔG_{OOH}	Ω	$ESSI_{OER}$	η_{OER}	$ESSI_{ORR}$	$-\eta_{ORR}$
TiO ₂	4.60	2.07	5.08	0.27	1.07	1.30	-1.07	-1.39
V-TiO ₂ (5cM)	2.35	1.38	4.50	0.33	0.53	0.91	-0.53	-0.80
V-TiO ₂ (5cM)	3.17	1.18	4.67	0.51	0.51	0.75	-0.51	-0.98
V-TiO ₂ (6cM)	2.76	0.38	3.97	0.56	1.14	1.02	-0.38	-0.84
V-TiO ₂ (6cM)	3.40	1.02	4.56	0.54	1.14	1.15	-0.38	-0.87
V-TiO ₂ (6cM)	3.46	1.12	4.63	0.52	1.11	1.11	-0.37	-0.94
Nb-TiO ₂ (5cM)	1.38	-0.08	3.39	0.51	0.44	0.76	-1.31	-1.31
Nb-TiO ₂ (5cM)	2.14	0.23	3.74	0.52	0.52	0.67	-0.52	-0.99
Nb-TiO ₂ (6cM)	2.33	0.10	3.61	0.52	0.37	1.00	-1.12	-1.12
Nb-TiO ₂ (6cM)	2.38	0.05	3.59	0.54	0.60	1.13	-0.60	-1.17
Nb-TiO ₂ (6cM)	2.69	0.29	3.80	0.54	1.17	1.19	-0.39	-0.93
Ta-TiO ₂ (5cM)	1.50	-0.51	3.04	0.55	0.58	0.78	-1.74	-1.74
Ta-TiO ₂ (5cM)	1.86	-0.024	3.52	0.54	0.42	0.65	-1.25	-1.25
Ta-TiO ₂ (6cM)	2.33	0.07	3.60	0.53	0.38	1.02	-1.15	-1.15
Ta-TiO ₂ (6cM)	2.17	-0.35	3.37	0.63	0.80	1.31	-0.80	-1.58
Ta-TiO ₂ (6cM)	2.55	0.125	3.64	0.53	0.62	1.20	-0.62	-1.10
Cr-TiO ₂ (5cM)	2.43	1.85	4.87	0.28	0.92	1.20	-0.92	-1.18
Cr-TiO ₂ (5cM)	3.44	1.61	5.14	0.53	0.48	0.59	-1.45	-1.45
Cr-TiO ₂ (6cM)	2.91	1.23	4.76	0.53	0.36	0.61	-1.07	-1.07
Cr-TiO ₂ (6cM)	4.14	1.72	5.23	0.52	0.84	1.20	-0.84	-1.54
Cr-TiO ₂ (6cM)	3.84	1.56	5.04	0.51	0.69	1.05	-0.69	-1.35
Mo-TiO ₂ (5cM)	0.49	0.42	3.72	0.42	2.0	1.99	-0.67	-1.17
Mo-TiO ₂ (5cM)	1.46	0.61	4.16	0.54	1.46	1.45	-0.49	-0.61
Mo-TiO ₂ (6cM)	0.86	0.28	3.83	0.54	1.74	1.73	-0.58	-0.94
Mo-TiO ₂ (6cM)	2.18	0.62	4.17	0.54	0.54	0.74	-0.54	-0.60
Mo-TiO ₂ (6cM)	2.35	0.58	4.10	0.53	0.53	0.53	-0.53	-0.64
W-TiO ₂ (5cM)	-0.33	-0.23	3.16	0.47	1.39	2.26	-1.40	-1.46
W-TiO ₂ (5cM)	0.42	0.34	3.90	0.55	2.25	2.34	-0.75	-1.16
W-TiO ₂ (6cM)	0.26	0.05	3.50	0.49	1.10	1.58	-1.10	-1.17

W-TiO ₂ (6cM)	1.16	0.05	3.60	0.55	0.65	1.20	-0.65	-1.17
W-TiO ₂ (6cM)	1.46	0.21	3.71	0.52	0.52	1.00	-0.52	-1.01
Mn-TiO ₂ (5cM)	3.38	1.92	4.82	0.22	0.38	0.69	-1.13	-1.13
Mn-TiO ₂ (5cM)	4.22	2.06	5.07	0.27	0.88	0.92	-0.88	-1.38
Mn-TiO ₂ (6cM)	4.20	1.94	5.09	0.34	0.87	0.92	-0.87	-1.40
Mn-TiO ₂ (6cM)	4.50	2.01	5.07	0.29	1.02	1.25	-1.02	-1.38
Mn-TiO ₂ (6cM)	4.48	2.01	5.10	0.31	1.01	1.24	-1.01	-1.41
Fe-TiO ₂ (5cM)	3.73	2.10	4.95	0.19	0.63	0.88	-0.63	-1.26
Fe-TiO ₂ (5cM)	4.31	2.16	5.10	0.24	0.93	0.93	-0.93	-1.41
Fe-TiO ₂ (6cM)	3.81	1.55	5.06	0.48	0.67	1.03	-0.67	-1.29
Fe-TiO ₂ (6cM)	3.98	1.55	5.06	0.52	0.76	1.20	-0.76	-1.37
Fe-TiO ₂ (5cM)	3.88	1.50	4.94	0.49	0.71	1.16	-0.71	-1.25
Ru-TiO ₂ (5cM)	2.15	1.05	4.19	0.34	0.81	0.80	-0.27	-0.50
Ru-TiO ₂ (5cM)	3.55	1.73	5.12	0.46	0.48	0.58	-1.43	-1.43
Ru-TiO ₂ (6cM)	2.98	0.49	4.53	0.79	0.79	0.74	-0.79	-0.84
Ru-TiO ₂ (6cM)	3.83	1.42	4.96	0.54	0.69	1.19	-0.69	-1.27
Ru-TiO ₂ (6cM)	3.90	1.47	4.95	0.51	0.72	1.20	-0.72	-1.26
Ir-TiO ₂ (5cM)	1.81	0.61	3.68	0.30	0.32	0.63	-0.33	-0.61
Ir-TiO ₂ (5cM)	3.45	1.75	4.68	0.23	0.45	0.53	-0.50	-0.99
Ir-TiO ₂ (6cM)	2.72	1.13	4.64	0.52	0.52	0.67	-0.52	-0.95
Ir-TiO ₂ (6cM)	3.78	1.44	4.94	0.52	0.65	1.11	-0.66	-1.25
Ir-TiO ₂ (6cM)	3.64	1.35	4.86	0.52	0.59	1.06	-0.59	-1.17
Ni-TiO ₂ (5cM)	4.55	2.03	4.80	0.15	1.04	1.29	-1.04	-1.10
Ni-TiO ₂ (5cM)	4.59	2.08	5.12	0.14	1.06	1.15	-1.06	-1.43
Ni-TiO ₂ (6cM)	4.27	2.03	5.31	0.41	0.90	1.01	-0.90	-1.62
Ni-TiO ₂ (6cM)	4.57	2.08	5.08	0.27	1.05	1.25	-1.05	-1.39
Ni-TiO ₂ (6cM)	4.47	2.04	5.06	0.28	1.00	1.19	-1.00	-1.37

Table S2. OER/ORR data for porphyrins taken from [2].

Metal center-ring ligand	ΔG_O	ΔG_{OH}	ΔG_{OOH}	Ω	ESSI _{OER}	η_{OER}	ESSI _{ORR}	$-\eta_{ORR}$
Cr-H	0.85	0.26	3.53	0.40	0.81	1.45	-0.81	-0.97
Cr-F	1.00	0.38	3.63	0.39	0.73	1.40	-0.73	-0.85
Cr-OH	0.76	0.22	3.49	0.40	0.85	1.50	-0.85	-1.01
Cr-CH ₃	0.61	0.18	3.33	0.35	0.92	1.49	-0.92	-1.05
Cr-BH ₂	0.94	0.36	3.58	0.38	0.76	1.41	-0.76	-0.87
Cr-NH ₂	0.60	0.10	3.33	0.38	0.92	1.49	-0.93	-1.13
Mn-H	0.93	0.27	3.53	0.39	0.76	1.36	-0.76	-0.96
Mn-F	1.13	0.46	3.70	0.39	1.34	1.34	-0.45	-0.77
Mn-OH	0.74	0.23	3.51	0.41	0.86	1.54	-0.86	-1.01
Mn-CH ₃	0.74	0.18	3.39	0.37	0.86	1.41	-0.86	-1.05
Mn-BH ₂	1.41	0.75	3.94	0.37	1.30	1.30	-0.43	-0.56
Mn-NH ₂	0.46	-0.05	3.18	0.38	1.00	1.49	-1.00	-1.28
Fe-H	1.19	0.63	3.77	0.34	1.36	1.36	-0.45	-0.67
Fe-F	1.37	0.68	3.85	0.36	1.26	1.26	-0.42	-0.55
Fe-OH	1.07	0.48	3.62	0.34	0.69	1.31	-0.69	-0.75
Fe-CH ₃	1.10	0.57	3.73	0.35	1.39	1.39	-0.46	-0.70
Fe-BH ₂	1.51	0.88	4.09	0.38	1.35	1.35	-0.45	-0.59
Fe-NH ₂	0.89	0.34	3.45	0.32	0.78	1.32	-0.78	-0.89
Co-H	2.30	1.21	4.09	0.21	0.56	0.56	-0.19	-0.40
Co-F	1.97	1.04	4.09	0.29	0.89	0.89	-0.30	-0.40
Co-OH	1.65	0.88	3.95	0.31	1.07	1.07	-0.36	-0.46
Co-CH ₃	2.14	1.00	4.07	0.30	0.69	0.69	-0.23	-0.38
Co-BH ₂	2.47	1.24	4.29	0.29	0.20	0.58	-0.60	-0.60
Co-NH ₂	1.26	0.77	3.86	0.31	1.37	1.37	-0.46	-0.74
Ni-H	3.66	1.82	4.85	0.28	0.60	0.61	-0.60	-1.16
Ni-F	3.43	1.85	4.93	0.31	0.41	0.62	-1.25	-1.25
Ni-OH	3.21	1.58	4.78	0.37	0.37	0.40	-1.10	-1.10
Ni-CH ₃	3.82	1.84	4.6	0.15	0.68	0.75	-0.68	-0.91
Ni-BH ₂	3.85	1.93	4.78	0.20	0.70	0.70	-0.70	-1.10
Ni-NH ₂	3.10	1.32	4.46	0.34	0.26	0.55	-0.77	-0.77
Cu-H	4.12	2.07	5.07	0.27	0.83	0.84	-0.83	-1.38
Cu-F	4.15	2.04	5.01	0.25	0.85	0.88	-0.85	-1.33
Cu-OH	3.69	1.62	4.94	0.43	0.42	0.84	-1.25	-1.25
Cu-CH ₃	3.76	1.83	4.89	0.30	0.65	0.69	-0.65	-1.20
Cu-BH ₂	4.61	11.77	4.98	0.37	1.07	1.61	-1.08	-1.30
Cu-NH ₂	2.69	0.92	4.48	0.55	0.55	0.56	-0.55	-0.80

Table S3. OER/ORR data for SrMO₃, taken from [3-5].

Material	ΔG_O	ΔG_{OH}	ΔG_{OOH}	Ω	ESSI _{OER}	η_{OER}	ESSI _{ORR}	$-\eta_{ORR}$
SrScO ₃	5.23	2.38	5.21	0.18	1.38	1.61	-1.39	-1.52
SrTiO ₃	3.91	1.61	4.90	0.42	0.72	1.07	-0.73	-1.22
SrVO ₃	-0.07	0.13	3.35	0.38	1.26	2.19	-1.27	-1.43
SrCrO ₃	0.92	0.75	3.99	0.39	1.84	1.84	-0.61	-1.06
SrMnO ₃	2.29	1.21	4.41	0.37	0.88	0.88	-0.29	-0.72
SrFeO ₃	2.98	1.67	4.70	0.28	0.33	0.47	-1.00	-1.00
SrCoO ₃	3.00	1.54	4.44	0.22	0.25	0.31	-0.76	-0.76
SrNiO ₃	3.84	2.17	4.92	0.15	0.69	0.94	-0.69	-1.24
SrCuO ₃	4.75	2.32	5.31	0.26	1.14	1.19	-1.15	-1.62
SrZnO ₃	5.16	2.56	5.40	0.19	1.35	1.37	-1.35	-1.72
SrGeO ₃	4.44	1.74	5.22	0.51	0.99	1.47	-0.99	-1.53
SrRuO ₃	2.26	1.11	4.09	0.26	0.59	0.59	-0.20	-0.40

Table S4. OER/ORR data for LaMO₃, taken from [3-5].

Material	ΔG_O	ΔG_{OH}	ΔG_{OOH}	Ω	ESSI _{OER}	η_{OER}	ESSI _{ORR}	$-\eta_{ORR}$
LaScO ₃	4.80	1.82	4.88	0.30	1.17	1.75	-1.17	1.75
LaTiO ₃	-1.82	-1.16	2.23	0.46	2.14	2.82	-2.14	2.82
LaVO ₃	-0.74	-0.22	2.95	0.36	1.60	2.48	-1.60	2.48
LaCrO ₃	0.69	0.56	3.69	0.33	1.76	1.76	-0.59	1.77
LaMnO ₃	1.39	0.65	3.85	0.37	1.23	1.24	-0.41	1.24
LaFeO ₃	2.74	1.25	4.55	0.42	0.29	0.57	-0.86	0.57
LaCoO ₃	2.22	1.49	4.50	0.27	0.66	1.05	-0.66	1.05
LaNiO ₃	3.09	1.54	4.61	0.30	0.31	0.32	-0.93	0.33
LaCuO ₃	4.92	2.42	5.39	0.26	1.23	1.27	-1.23	1.27
LaZnO ₃	5.18	2.48	5.27	0.17	1.36	1.47	-1.36	1.47
LaGaO ₃	4.88	1.95	5.02	0.30	1.21	1.70	-1.21	1.70
LaRuO ₃	1.87	0.74	3.74	0.27	0.64	0.64	-0.21	0.64

Table S5. OER/ORR data for MO, taken from [4,5].

Material	ΔG_O	ΔG_{OH}	ΔG_{OOH}	Ω	ESSI _{OER}	η_{OER}	ESSI _{ORR}	$-\eta_{ORR}$
CaO	5.38	2.32	5.04	0.13	1.46	1.82	-1.46	1.83
ScO	-0.90	-1.52	1.98	0.52	1.69	1.70	-1.68	1.71
TiO	-1.61	-1.05	2.32	0.46	2.03	2.71	-2.04	2.71
VO	-0.94	-0.71	2.56	0.41	1.70	2.27	-1.70	2.28
CrO	0.22	-0.13	2.90	0.29	1.12	1.44	-1.12	1.45
MnO	1.42	0.42	3.66	0.39	0.52	1.01	-0.52	1.01
FeO	1.76	0.38	3.75	0.45	0.45	0.76	-0.45	0.76
CoO	1.98	0.78	3.92	0.34	0.71	0.71	-0.24	0.71
NiO	2.49	1.03	4.12	0.31	0.31	0.40	-0.31	0.40
CuO	3.93	2.00	4.75	0.14	0.74	0.77	-0.74	0.77

Table S6. OER/ORR data for FGM [6,7].

Metal center	ΔG_O	ΔG_{OH}	ΔG_{OOH}	Ω	ESSI _{OER}	η_{OER}	ESSI _{ORR}	$-\eta_{ORR}$
Cr	0.89	0.35	3.60	0.40	0.78	1.49	-0.78	1.49
Mn	1.89	0.88	4.08	0.37	0.95	0.96	-0.32	0.96
Fe	2.11	1.03	4.11	0.30	0.76	0.76	-0.25	0.76
Co	2.93	1.22	4.11	0.21	0.48	0.48	-0.16	0.49
Ni	4.16	2.14	4.91	0.15	0.85	0.92	-0.85	0.92
Cu	4.52	2.31	5.11	0.17	1.03	1.08	-1.03	1.09
Ru	1.72	0.58	3.63	0.30	0.37	0.68	-0.37	0.68
Rh	2.84	1.23	4.19	0.25	0.17	0.37	-0.51	0.37
Pd	4.65	2.50	5.08	0.05	1.09	1.28	-1.10	1.28
Ag	4.77	2.52	5.12	0.07	1.16	1.30	-1.16	1.30
Ir	2.41	1.24	4.26	0.28	0.32	0.61	-0.32	0.62
Pt	4.61	2.42	5.11	0.11	1.08	1.19	-1.08	1.19
Au	4.84	2.62	5.11	0.01	1.19	1.40	-1.19	1.39

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