Discerning Activity and Inactivity in Earth-Abundant Molecular Water Oxidation Catalysts

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Most computational studies on the oxygen evolution reaction (OER) focus on systems which are known to catalyze this process experimentally. This work computationally examines a number of earth-abundant metal (M=Mn, Fe, Co, Ni) complexes with tetradentate coordinating anionic ligands which, subject to the same experimental conditions, either evolve or do not evolve oxygen. We offer an account for the inactivity of catalysts and develop an effective thermodynamic descriptor to describe the activity of those catalysts that do evolve oxygen. Additionally, we describe how the functionalization of certain Fe OER catalysts can boost activity. Finally, to allow for the rapid evaluation of homogeneous OER catalysts within this family of complexes, high-level heuristics to computationally screen these catalysts are detailed.

A primary issue with the electrocatalytic production of hydrogen from water is the inherent capital investment required for the oxygen evolution reaction (OER) catalyst at the anode. Industrial OER catalysts are based on expensive rare-earth metals,^[1] driving research on cost-efficient molecular catalysts based on first-row transition metals which are orders of magnitude more abundant, namely manganese,^[2,3] iron,^[4–8] cobalt,^[9,10] nickel^[11] and copper.^[12]

The set of molecular OER catalysts investigated in this work is based on experimental studies from Lloret-Fillol and co-workers,^[4] wherein a family of iron complexes with tetradentate nitrogen-based ligands with two active sites in *cis*-positions were identified to be active. Therein, the authors also reported the thwarted attempts to promote the OER using first-row transition metal complexes under identical experimental reaction conditions (*i.e.* catalyst concentration, oxidant concentration, oxidant type and pH). Subsequent experiments have shown that substituting electron withdrawing groups (EWG=NO₂, CO₂Et, Cl) in the *para* position of the pyridine ligand in one such catalyst, [Fe(OTf)₂(Pytacn)]²⁺ (Pytacn = 1-(2'-pyridyl-methyl)-4,7-dimethyl-1,4,7-triazacyclononane), greatly improved the OER activity, while the substitution of a fluorine and methyl in

the α -pyridine position led to reduced performance, which was posited to be due to increased catalytic degradation.^[13]

In this contribution, we outline the results of a detailed mechanistic study into the aforementioned family of earth-abundant complexes, depicted in Figure 1, including functionalizations which have been tested experimentally. Interestingly, these catalysts display varying levels of OER activity under the same experimental conditions, with initial turnover frequency (TOF) ranging from 0 to 838 h⁻¹, making them ideally suited to direct comparisons to allow for the rationalization of the origins of catalyst efficacy. This task is highly amenable to inspection via density functional theory (DFT) because hypothetical reaction mechanisms can be examined exhaustively to unveil the factors determining catalytic activity. Furthermore, DFT can help to verify the nature of a given catalyst while facilitating the formulation of key heuristics and descriptors for rational catalyst design.^[14,15] Indeed, such descriptors have been used to discover state-of-the-art earth-abundant heterogeneous OER catalysts.^[16]

While previous theoretical works investigating subsets of these catalysts from Lloret-Fillol *et al.* have focused on the exploring the mechanism of the O–O bond formation step, an account of the inactivity shown by the Co, Ni and Mn catalysts which were presented originally, a direct comparison of the activities of the iron-based active catalysts, and a detailed rationalization of the effects of the catalyst functionalization is still lacking. Our approach reported herein focuses on these issues by modelling the intermediate steps – beginning from M^{II}(H₂O)(H₂O) – towards the [M^V(O)(OH)]²⁺ intermediate of both active and inactive complexes. This final intermediate, [M^V(O)(OH)]²⁺, has been chosen since experimental and computational studies strongly suggest that [Fe^V(O)(OH)]²⁺ is the only species which can promote the O–O bond formation at room temperature, which we denote as the oxygen evolving intermediate (OEI).^[17,18] Proton coupled electron transfer (PCET) and electron transfer (ET) steps were modelled for every intermediate starting from the metal oxidation state M(II) to M(V). Proton transfers were not considered due to the large computational costs involved in the required consideration of explicit solvent for reliable pK_a values.^[18,19] While our methodology does not include kinetic barriers, it provides essential insight into the redox potential at which electrochemical steps are expected to occur prior to the formation of the OEI. We also considered isomeric complexes where the catalyst geometry was asymmetric with respect to the position of the active site. Each of the catalysts examined, along with their associated experimental TOFs, are shown in Figure 1.

In Figure 2 we present the Gibbs energy profile of potential routes toward the OEI for the 1 M catalysts calculated at

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Figure 1. Complexes modelled in this work with accompanying labels and experimental initial TOF values (in h^{-1}) from Refs. 4,13

Figure 2. Calculated Gibbs energy diagrams (at $U = 1.61 \text{ V}$ vs NHE) of potential OER pathways for **1M** complexes featuring different metals: Co (blue lines), Ni (green lines), Mn (yellow lines), and Fe (red lines). Solid lines between OER intermediates represent a PCET step, while dashed lines represent electron transfers (ETs). Accompanying oxidation states are shown along the x-axis. Each intermediate is labelled corresponding to one of the geometries indicated along the top of the energy diagrams. Color code: metal center (orange), O (red), N (blue), C (grey) and H (white).

ambient conditions and at an applied potential (U) of 1.61 V versus the normal hydrogen electrode (NHE). This potential corresponds to the redox potential of cerium ammonium nitrate (CAN),^[20] the sacrificial oxidant used in the experiments. Each reaction intermediate in Figure 2 is labelled as **1M-A/B**, where *A* denotes the active site *trans* to the methyl-substituted

amino group, and *B* denotes the active site co-planar with the pyridine ligand.

The calculated energies in Figure 2 illustrate clearly the well-documented large 'oxo-wall' for Co and Ni complexes,^[21] showing no exergonic paths for **1Co** or **1Ni** in going from Co(III) to Co(IV), or from Ni(IV) to Ni(V). While we find that **1Mn** does have exergonic paths between each oxidation state under

reaction conditions, the most stable Mn(IV) intermediate, the symmetric $1\text{Mn}-\text{OH}/\text{OH}$ isomer, is more stable than the proposed OEI for 1Fe , $1\text{Fe}^{\text{V}}-\text{O}/\text{OH}$ or $1\text{Fe}^{\text{V}}-\text{OH}/\text{O}$. More specifically, this $1\text{Mn}^{\text{IV}}-\text{OH}/\text{OH}$ complex is calculated to be 0.35 eV lower in energy than the $1\text{Mn}^{\text{IV}}-\text{O}/\text{OH}_2$ complex, which can undergo a PCET to the OEI in oxidation state Mn(V). Moreover, UV-vis and Raman spectroscopy experiments indicated that $2\text{Fe}^{\text{IV}}-\text{O}/\text{OH}_2$ complexes are the necessary precursors to an electrophilic oxygen evolving iron-oxo-cerium intermediate in 2Fe .^[4,22] Our results support this observation as we reproduce this iron species to be the resting state until an applied potential of *ca.* 1.5 V (Figure S1a). In the case of 1Mn , however, these $1\text{Mn}^{\text{IV}}-\text{O}/\text{H}_2\text{O}$ and $1\text{Mn}^{\text{IV}}-\text{H}_2\text{O}/\text{O}$ intermediates are the least stable of the Mn(IV) complexes.

For the oxygen evolving 1Fe catalyst, while there is no downhill path from $1\text{Fe}^{\text{III}}-\text{H}_2\text{O}/\text{H}_2\text{O}$, we note that the Gibbs energy difference between that intermediate and $1\text{Fe}^{\text{III}}-\text{H}_2\text{O}/\text{OH}$ is only 0.08 eV, which can undergo an exothermic PCET step to the intermediates $1\text{Fe}^{\text{IV}}-\text{OH}/\text{OH}$, $1\text{Fe}^{\text{IV}}-\text{O}/\text{H}_2\text{O}$ or $1\text{Fe}^{\text{IV}}-\text{H}_2\text{O}/\text{O}$. These latter intermediates are very close in energy (within *ca.* 0.08 eV), and all of them exhibit exergonic routes to the OEI. Using the same analysis, the activity of the remaining iron catalysts can be rationalized, as shown in Figures S1, S2 and S3.

Having distinguished active and inactive catalysts, we now turn our attention to distinguishing the most active catalysts. The precursor species to oxygen evolution, the OEI, has been rigorously shown to be $\text{Fe}^{\text{IV}}-\text{O}/\text{H}_2\text{O}$ in 2Fe . Assuming each Fe catalyst shares the same essential oxidative intermediates, we have investigated the predicted potential for the PCET step from the lowest energy $\text{Fe}^{\text{IV}}-\text{O}/\text{H}_2\text{O}$ to the most stable topological $\text{Fe}^{\text{V}}-\text{O}/\text{OH}$ isomer for each active iron catalyst, hereafter referred to as the *predicted potential to OEI*. Interestingly, the representation of the experimental activity and that predicted potential (Figure 3) appears to be linearly correlated.

Figure 3. Plot of the relationship between the reported experimental TOFs and the predicted potential to OEI in OER active Fe *cis*-labile catalysts. The blue-shaded region represents the 95% confidence interval of the linear model, with correlation coefficient of -0.58 . When potential outliers are removed, the correlation coefficients are -0.72 for Set A (excluding $1\text{Fe}-\text{Cl}_\text{H}$) and -0.87 for Set B (excluding $1\text{Fe}-\text{NO}_2\text{H}$ and 2Fe).

Given that this analysis only considers the thermodynamic Gibbs energy change for one possible step in a complex reaction such as the OER, this is a noteworthy result, suggesting that oxidation to $\text{Fe}^{\text{V}}-\text{O}/\text{OH}$ is a common potential limiting step. This finding ultimately indicates that O–O bond formation is not rate limiting for these complexes, which would not be without precedent as this has been confirmed to be the case for 2Fe ^[4,22] as well as heterogeneous $\alpha\text{-Fe}_2\text{O}_3$ OER catalysts.^[23] We attribute this correlation to the nature of the rate determining step and Brønsted-Evans-Polanyi relations between reaction and activation energies, which indirectly account for the kinetics and thereby TOF, to distinguish active from inactive catalysts. There are, however, a few deviations from the line of best fit (black line in Figure 3), which can be interpreted in different ways. For example, the relative difference between the predicted potentials are within previously reported inherent DFT errors for PCETs.^[15] However, since the coordination environment of these complexes are all the same, one may expect qualitatively correct trends despite slight errors in the absolute values. Another possibility is that there are two sets of outliers to the linear model. This is illustrated in Figure 3, where we plot the linear fit after removing $1\text{Fe}-\text{Cl}_\text{H}$, with the remaining set of catalysts labelled Set A, or both $1\text{Fe}-\text{NO}_2\text{H}$ and 2Fe , with the remaining catalysts denoted as Set B. Obviously we would not expect increased TOFs to continue indefinitely at continuously lower predicted potential to OEI, as O–O bond formation may become limiting, for instance, which could also explain the deviation for $1\text{Fe}-\text{Cl}_\text{H}$. Additionally, because the $1\text{Fe}-\text{Cl}_\text{H}-\text{OH}/\text{OH}$ intermediate is more stable relative to the $1\text{Fe}-\text{Cl}_\text{H}-\text{O}/\text{H}_2\text{O}$ and $1\text{Fe}-\text{Cl}_\text{H}-\text{H}_2\text{O}/\text{O}$ intermediates in the oxidation state Fe(IV) (Figure S3), from which the OEI is proposed to form, we posit that the outlier is $1\text{Fe}-\text{Cl}_\text{H}$ and stress that the linear relationship may even cease after 1.5 V. In all, we emphasize that while the mechanistic details of O–O bond formation are still unclear for these complexes, focusing only on barriers related to this step may obscure the full picture for homogeneous OER catalysts. Therefore, we propose that this descriptor is used along with an analysis of the relative stability of $1\text{M}^{\text{IV}}-\text{OH}/\text{OH}$ against $1\text{M}^{\text{IV}}-\text{O}/\text{H}_2\text{O}$, or $1\text{M}-\text{H}_2\text{O}/\text{O}$ to garner a cursory prediction of activity. Of course, this descriptor cannot account for competing reactions which may deactivate the catalyst. In the following, we describe a primary route towards catalyst deactivation.

Costas *et al.* have recently reported that the deuteration of specific hydrogen atoms in the catalyst leads to striking effects on the OER activity.^[24] In particular, the deuteration of the C atoms of the ethylene linker in 3Fe caused a five-fold increase in the turnover number (TON) without improving initial TOF, indicating that the bridging H atoms are deactivating the catalyst after a given number of cycles. For a separate Fe coordination complex, not studied in this work, the H-atoms of methyl groups were deuterated. This greatly increased the TOF of the non-deuterated species from *ca.* 10 to 200 h^{-1} , which was hypothesized to be due to the hydroxylation of the methyl group by the equivalent OEI intermediate for this catalyst. This was confirmed by DFT studies, which showed that the barrier heights involved for the C–H hydroxylation were accessible

under experimental conditions and that this deactivation was kinetically favored for the methyl group. Due to the pronounced effect of deuterating the methyl group on the reported TOF, we sought to investigate this competing reaction leading to catalyst deactivation. We present the results of this investigation for **1Mn**, **1Fe**, **1Fe-Cl-H** and **1Fe-NO₂-H** in Table 1, which includes the Gibbs energy barriers for the two hydroxylations possible from $M^V\text{-OH/O}$, reported as $\Delta G_A^\ddagger$ and $\Delta G_B^\ddagger$, and the one hydroxylation possible from $1M^V\text{-O/OH}$, reported as $\Delta G_C^\ddagger$. An illustration of these reactions is shown in Figure 4.

The results in Table 1 need to be interpreted with care, as the relevant barriers are the ones associated with the most stable isomer. Accounting for this, **1Mn** and **1Fe** both share the same isomeric stability (i.e. $1M^V\text{-OH/O}$), and therefore have comparable barriers. Here we can see that the Mn-O* moiety in the lowest energy $1M^V\text{-OH/O}$ is the most easily deactivated of the studied complexes, with a $\Delta G_{A,B}^\ddagger$ of 0.53 and 0.71 eV respectively, which are accessible under the experimental conditions and below the previously reported barriers for O-O bond formation.^[17] Furthermore, $\Delta G_C^\ddagger$ for **1Mn** exhibits an even lower barrier of 0.45 eV, although we expect this intermediate to be less easily accessible as the $1M^V\text{-O/OH}$ is not the most stable isomer. All of this implies that **1Mn** could be rendered active by deuterating methyl groups, provided C-H hydroxylation is what prevents oxygen evolution instead of the thermodynamic sink at the $1M^V\text{-OH/OH}$ or $1M^V\text{-OH/H}_2\text{O}$ intermediates (Figure 2). The similarity between the oxygen evolving complex in Photosystem II and the iron-oxo-cerium OEI has been noted previously,^[22] indicating that such *cis*-labile Mn catalysts could be possible. In the case of the Fe-based

complexes, energy barriers increase by ca. 0.1–0.2 eV. While the barriers of the functionalized complexes from $Fe^V\text{-OH/O}$ ($\Delta G_{A,B}^\ddagger$) are almost identical, we see a marked difference in the values of the barrier for hydroxylation of the $Fe^V\text{-O/OH}$ isomer ($\Delta G_C^\ddagger$), (*vide infra*). Previous DFT studies of this hydroxylation found similarly distinct barriers for a specific catalyst,^[24] although that analysis was less complex as it did not include a comparison of topological isomers or distinct catalysts.

Importantly, our studies on modified **1Fe** catalysts also shed light on the improved activity of the catalysts functionalized with EWG in the pyridine *para*-position (Figure 1). In particular, calculations indicate that the $Fe^V\text{-O/OH}$ intermediates are more stable than $Fe^V\text{-OH/O}$ for **1Fe-Cl-H** and **1Fe-NO₂-H** (Figure S3), whereas the reverse trend is observed for **1Fe** (Figure 2). Hence, this functionalization swaps the stabilities of the topological isomers of the OEI as compared with **1Fe**, making the functionalized catalysts more resistant to deactivation via C-H hydroxylation, since there is one less methyl group to deactivate the catalyst from the OEI. This effect could be investigated experimentally by selectively deuterating specific methyl groups for functionalized and non-functionalized catalysts presented in this study. A potential explanation for the observed difference in $\Delta G_C^\ddagger$ between **1Fe** and the functionalized catalysts is a slight increased distance of the metal-oxo moiety in the $Fe^V\text{-O/OH}$ intermediate to the nearest H-atom of the single methyl group – from 2.561 to 2.625 Å – which is reflected in a larger hydroxylation barrier (Table 1). In general, this underscores that homogeneous OER catalysts should be designed to maximize the distance to methyl groups. Furthermore, we propose that the slightly reduced $\Delta G_C^\ddagger$ value in **1Fe-Cl-H** may account for the observed deviation from the relationship shown in Figure 3.

With all the knowledge acquired above, we formulate the following high-level blueprint for future efficient evaluation of OER complexes with two *cis*-active sites using only absolute Gibbs energies: i) Calculate the predicted potential to the OEI; ii) assess the relative stability of $M^IV\text{-O/H}_2\text{O}$ vs. $M^V\text{-OH/OH}$; and iii) note the proximity of the O atom in the most stable OEI to neighboring methyl groups. If the predicted potential to OEI is less than 1.6 V, (all catalysts which satisfy this in Figure 3 exhibit a TOF greater than 100 h⁻¹), the $M^IV\text{-O/H}_2\text{O}$ intermediate is within 0.1 eV of $M^V\text{-OH/OH}$ (to avoid the unfavorable thermodynamic sink), and the electrophilic O atom within the OEI is at least 3.0 Å away from the nearest H-atom of a dangling methyl group.

In conclusion, in this work we presented a thorough investigation of experimentally reported active and inactive OER catalysts. We showed that straightforward considerations based on absolute thermodynamic energies are enough to explain the inactivity of Co and Ni complexes, while also coarsely distinguishing active catalysts via a simple thermodynamic descriptor. A primary advantage of molecular OER catalysts is their inherent tunability via functionalization, however, unraveling the effects of such adaptations can be challenging. This work establishes the site-selectivity for the OEI enforced by functionalizing **1Fe** with EWGs in the *para*-position, aiding the inhibition of the off-cycle hydroxylation of methyl

Table 1. Calculated Gibbs energy barriers (in eV) for the hydroxylation reaction shown in Figure 4.

Catalyst	$\Delta G_A^\ddagger$	$\Delta G_B^\ddagger$	$\Delta G_C^\ddagger$
1Mn ^[a]	0.53	0.71	0.45
1Fe ^[a]	0.72	0.85	0.34
1Fe-Cl-H ^[b]	0.70	0.82	0.98
1Fe-NO₂-H ^[b]	0.72	0.83	1.11

[a] The most stable OEI is $M^V\text{-OH/O}$. [b] The most stable OEI is $M^V\text{-O/OH}$.

Figure 4. Possible competing C-H hydroxylation reactions from the two OEI isomers OH/O and O/OH. The associated calculated barriers are shown in Table 1.

groups. In all, this work demonstrates that DFT-calculated PCET and ET energies is an effective means of screening hypothetical transition metal catalysts. Our approach allows for a rapid and efficient evaluation of hypothetical Fe-based *cis*-active site OER complexes while highlighting the importance of studying and reporting inactive as well as active catalysts.

Computational Section

Computational details are provided in the Supporting Information along with the Gibbs energy profiles for each catalyst which is not depicted in Figure 2. All the data underlying this work, including the cartesian coordinates and energies of the modelled structures are available at the following ioChem-BD online dataset: <https://doi.org/10.19061/iochem-bd-6-38>.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: oxygen evolution reaction • water splitting • first-row transition metals • reaction descriptor • density functional theory

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COMMUNICATIONS

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Discerning Activity and Inactivity
in Earth-Abundant Molecular
Water Oxidation Catalysts

Take the plunge: A number of Fe-based water oxidation catalysts with two cis-labile active sites have been shown to be active. Herein, we present a theoretical approach which explains why Fe is active where other metals are inactive in the same condi-

tions. We also show that the activity of Fe catalysts can be rationalized using a simple reaction descriptor along with other key considerations. In all, these results lead to a blueprint for rational catalyst design.

Michael John Craig and Max García-Melchor share their work on discerning activity and inactivity in earth-abundant molecular water oxidation catalysts @TCD_Chemistry @CCEM_Group @Michael_Craig_ @MGarcia_Melchor

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