



## Understanding the electronic and structural effects in ORR intermediate binding on anion-substituted zirconia surfaces

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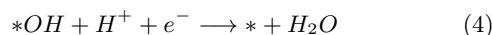
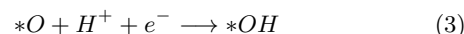
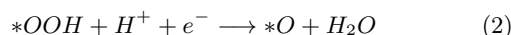
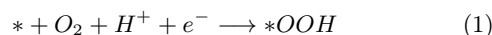
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# Understanding the Electronic and Structural Effects in ORR Intermediate Binding on Anion-Substituted Zirconia Surfaces

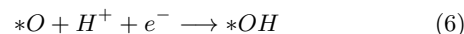
Sukanya Sinha,<sup>[a]</sup> Tejs Vegge,<sup>[a]</sup> Kirsten T. Winther,<sup>\*[b]</sup> Heine Anton Hansen<sup>\*[a]</sup>

For oxygen reduction reaction (ORR), the surface adsorption energies of O and OH\* intermediates are key descriptors for catalytic activity. In this work, we investigate anion-substituted zirconia catalyst surfaces and determine that adsorption energies of O and OH\* intermediates is governed by both structural and electronic effects. When the adsorption energies are not influenced by the structural effects of the catalyst surface, they exhibit a linear correlation with integrated crystal orbital Hamiltonian population (ICOHP) of the adsorbate-surface bond. The influence of structural effects, due to re-optimisation slab geometry after adsorption of intermediate species, leads to stronger adsorption of intermediates. Our calculations show that there is a change in the bond order to accommodate the incoming adsorbate species which leads to stronger adsorption when both structural and electronic effects influence the adsorption phenomena. The insights into the catalyst-adsorbate interactions can guide the design of future ORR catalysts.

the conventional platinum-based catalyst which constitute almost 55% of the total cost.<sup>[6]</sup> The cathodic oxygen reduction reaction (ORR) has sluggish kinetics and consequently high overpotential as compared to the swift kinetics of anodic hydrogen oxidation reaction (HER), hence the cathode requires higher catalyst loading than the anode. In order to accelerate PEMFC technology development, it is crucial to explore non-platinum ORR catalysts that are highly efficient as well is affordable. In the course of development of non-platinum based ORR catalysts, numerous candidates have been studied like polymer based catalysts, transition metal oxides, nitrides, oxynitrides, carbides, carbonitrides.<sup>[7–13]</sup> In the PEMFCs, oxygen reduction reaction can take place through two different pathways at the fuel cell cathode, the two-electron pathway and the four-electron pathway.<sup>[14]</sup> However, for the PEMFC cathodic catalyst, the two-electron pathway is not desirable; it is the four-electron pathway which is preferred for the long-term operation of PEMFC. Previous studies have demonstrated that the four-electron pathway can involve two different mechanisms.<sup>[15]</sup> One is the 'associative mechanism' which can be described as follows:



The other mechanism is called the 'dissociative mechanism' where the initial step is oxygen dissociation.



where \* denotes the active sites on the catalyst surface.<sup>[16]</sup> Previous studies have demonstrated O and OH intermediates are the key descriptors that can help in predicting the ORR activity of catalysts.<sup>[15,17,18]</sup> While there are a number of studies which has studied the relative binding energies of these two species in terms of scaling relations<sup>[19,20]</sup>, their underlying descriptors are not very well-understood.<sup>[18,21]</sup> Fung et al showed that the integrated crystal orbital Hamiltonian population (ICOHP)<sup>[22]</sup> of the bond between lattice metal and oxygen is a good descriptor for the adsorption energy of hydrogen on lattice oxygen in perovskites,<sup>[23]</sup> and recently Winther et al demonstrated that the O and OH adsorption energies on transition metal MO<sub>2</sub> surfaces is well

## Introduction

Among various alternatives for environmentally friendly energy conversion technologies, fuel cells offer a great deal of promise as a highly efficient device for the same. Polymer electrolyte membrane fuel cells (PEMFCs) are fuel cells where a fuel like hydrogen or methanol is oxidized at the anode and oxygen is reduced at the cathode to produce energy.<sup>[1]</sup> The interest in PEMFCs arise due to their varied applications, ranging from transportation in form of fuel cell electric vehicles (FCEV)<sup>[2]</sup> to potable and stationary power systems in form of auxiliary power units (APU).<sup>[3]</sup> There are several challenges associated with PEMFCs like lifetime,<sup>[4]</sup> component durability<sup>[5]</sup> and most importantly the cost of

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captured by the metal-oxygen ICOHP of the bulk oxide<sup>[24]</sup>. In this work, we are studying the trends in the adsorption energy of O and OH adsorbates on the surface of anion-substituted zirconia. We find that in the absence of structural reorganization in the zirconia slabs the adsorption energies are captured by the integrated COHP with a high accuracy.

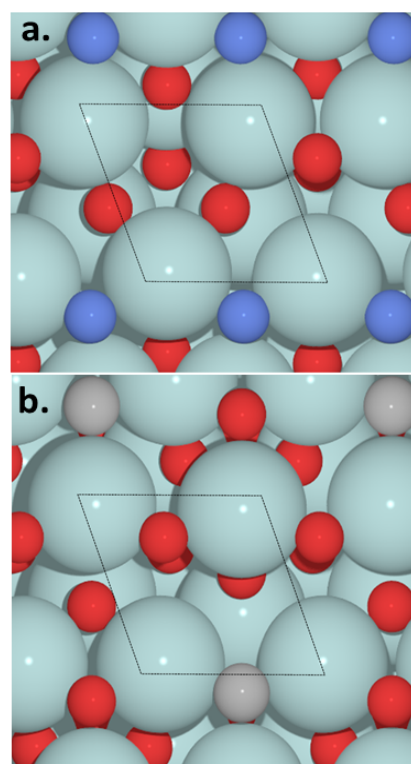
While a number of studies has previously reported zirconium oxynitride ( $Zr_2ON_2$ ) as an promising alternative to platinum based ORR catalysts<sup>[25,26]</sup>, the reason behind the favourable ORR activity of the same is not well understood. A number of transition metal-based ORR catalysts which show promising ORR activity<sup>[25,27,28]</sup> also exhibits deviations from standard scaling relations<sup>[29]</sup>. It is generally accepted that deviation from these scaling relations is the key to enhanced ORR electrocatalysis.<sup>[30]</sup> In our previous work we have explored the possibility of enhanced ORR activity due to bending of ORR scaling relations.<sup>[31]</sup> We concluded that the  $G_O$ - $G_{OH}$  scaling relation for ORR on  $Zr_2ON_2$  catalyst indeed shows deviation from the standard scaling relation, however, there was no indication that it necessarily results in enhanced electrocatalysis. Several electronic descriptors failed to capture the complexity of the  $Zr_2ON_2$  catalyst surface that arises from presence of two different anions i.e. oxygen and nitrogen in the anionic layers. Hence, in order to simplify the system, we have created model systems where we substitute one or two lattice oxygen for a carbon or two nitrogen atoms for this study. Further, we use ICOHP as an electronic descriptor for describing trends in the adsorption energies of the O and OH adsorbates as well as to gain insights into bonding configurations of the same.

## Results and Discussion

### Nitrogen and Carbon substituted Zirconia

Zirconia is a crystalline compound with polymorphic crystal structure and exhibits three different crystalline forms: monoclinic, tetragonal and cubic form.<sup>[32,33]</sup> Previous studies have demonstrated the tetragonal phase shows the highest ORR activity among all three, hence that is the phase we have selected for our study.<sup>[34]</sup> Our selected  $ZrO_2$  crystal belongs to space group  $P4_2/nmc$  (137) or according to the Fedorov notation has the Fedorov symbol of 67a.<sup>[35]</sup> In our study we are exploring adsorption of ORR intermediates on the (011) surface of a  $ZrO_2$  slab.<sup>[36]</sup> It has a hexagonal lattice structure with a total vacuum of 1.6 nm (with 0.8 nm on both sides of the slab). The model structures that has been studied in this work are two different types of anion-substituted zirconia; nitrogen substituted zirconia and carbon substituted zirconia slabs. In order to prepare the model structure for nitrogen substituted zirconia, two lattice oxygen atoms were substituted with two nitrogen atoms. The nitrogen atom has a formal oxidation state of -3 while oxygen has an oxidation state of -2. Therefore, to preserve the charge neutrality of the system an oxygen vacancy is introduced. For preparing the model structure of carbon substituted zirconia, a similar strategy is used, one lattice oxygen atom was substituted with a carbon atom. In order to maintain charge neutrality of the model system, since carbon has a formal oxidation state of -4 while oxygen has an oxidation state of -2, we introduced an oxygen vacancy.

The anionic substitutions were carried out on the surface and/or the sub-surface anion layers. However, the oxygen vacancy was introduced only in the sub-surface anion layer. This was done since our test calculations show surface vacancies are unstable. Hence, we have 8 lattice oxygen atoms in the surface and sub-surface anion layer, where potential anionic substitutions could be carried out and 4 lattice oxygen atoms, in sub-surface anion layer, where potential oxygen vacancies can be introduced. Different combinations of anionic substitutions and introduction of oxygen vacancy to the zirconia slab leads to creation of 84 different nitrogen-substituted slabs and 28 different carbon-substituted slabs. 1 illustrates two such anion-substituted zirconia structures, a nitrogen substituted zirconia and a carbon substituted zirconia slab. High throughput workflows were used to create and optimize the anion substituted zirconia slabs in addition to carrying out the adsorption calculations for the adsorption of the ORR intermediates. The structural and electronic trends for the adsorption of the O, \*OH and \*OOH intermediates on the anion substituted  $ZrO_2$  slab is evaluated systematically by studying the adsorption over all the Zr-top sites. The adsorption energies of the ORR adsorbates are calculated relative to the gas phase water and hydrogen in molecular form.

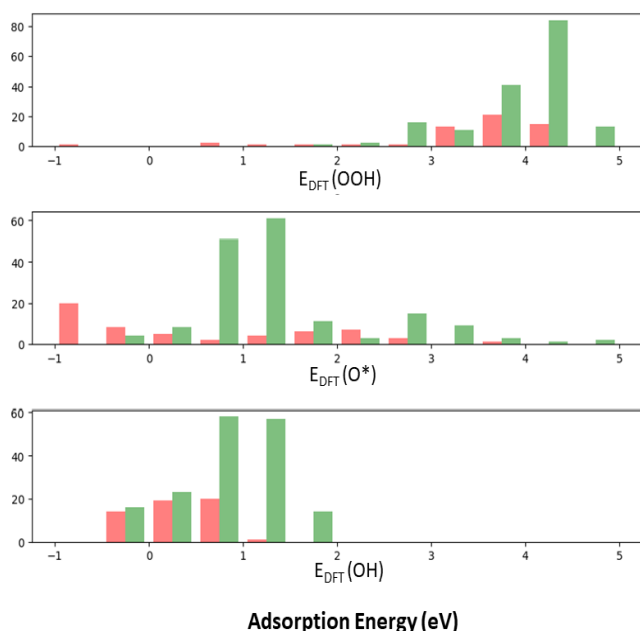


**Figure 1.** Geometries of anion substituted zirconia slab. a) Nitrogen substituted zirconia slab b) Carbon substituted zirconia slab. (The light cyan atom is Zr, red is O, blue is N and grey is C)

### Adsorption Energy and Limiting Potential Distribution

The range of distribution of adsorption energies can help us understand the adsorption configurations of ORR adsorbates (O, OH or OOH) on nitrogen or carbon substituted zirconia surface. From the histogram of O, OH and OOH

adsorption energies, shown in Figure 2, one can observe the OOH adsorption energies for both nitrogen and carbon substituted slabs are spread over a modest range of around 4 eV. The variation of OOH adsorption energy is largely due to variation in the alignment of the OOH adsorbate with the anion-substituted zirconia surface. The OH adsorption energy show a narrow range of 2 eV which is due to OH adsorption taking place mainly on the ontop zirconia site. However we noted the most surprising observation for O adsorption energy. For both nitrogen and carbon substituted slabs, they are spread over a large range of around 5 eV. We attribute the reason for this large range of adsorption energy to the wide variety of configurations of O adsorption. The O adsorbate adsorbs on ontop zirconia sites, bridge sites and in some cases forms a complex with the substituent anion, nitrogen or carbon. There are different ranges of adsorption energy associated with each adsorption configuration; the adsorption on ontop zirconia sites being the weakest followed by adsorption on the bridge sites and the strongest adsorption configuration being the anionic complex formation.

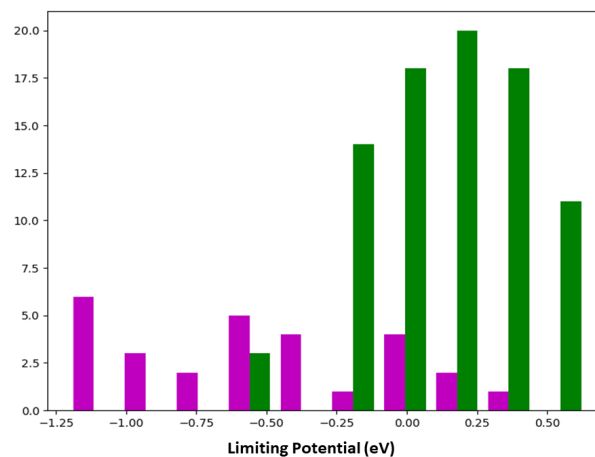


**Figure 2.** Histogram of adsorption energies of ORR intermediates i.e. OOH, O and OH. The red bars represent adsorption energies for carbon substituted slabs while green represents adsorption energies for nitrogen substituted slabs.

For most of the materials the adsorption of ORR intermediates are restricted by a linear scaling.<sup>[18,30,37]</sup> Hence we wanted to explore whether such scaling relations exist for the systems explored in this study. The OOH-OH and O-OH scaling relations are provided in the Supporting Information. From these plots of scaling relations, we can understand the adsorption energies do not scale well with each other for nitrogen and carbon substituted zirconia systems.

Within the CHE model the highest potential at which all the reaction steps are downhill in free energy is called the thermodynamic limiting potential, ( $U_L$ ). The  $U_L$  gives us

a measure of the activity of a catalyst. Higher  $U_L$  implies higher catalytic activity. A negative value of  $U_L$  implies catalytic inactivity. From the histogram of limiting potentials in 3, we can observe the  $U_L$  for most of the carbon substituted slabs is negative. On the other hand  $U_L$  for most of the nitrogen substituted slabs are positive and the peak is obtained at 0.25V with some of the values reaching upto 0.65V. Hence we can conclude that anionic substitution with nitrogen on zirconia is more favorable to ORR activity than that with carbon.



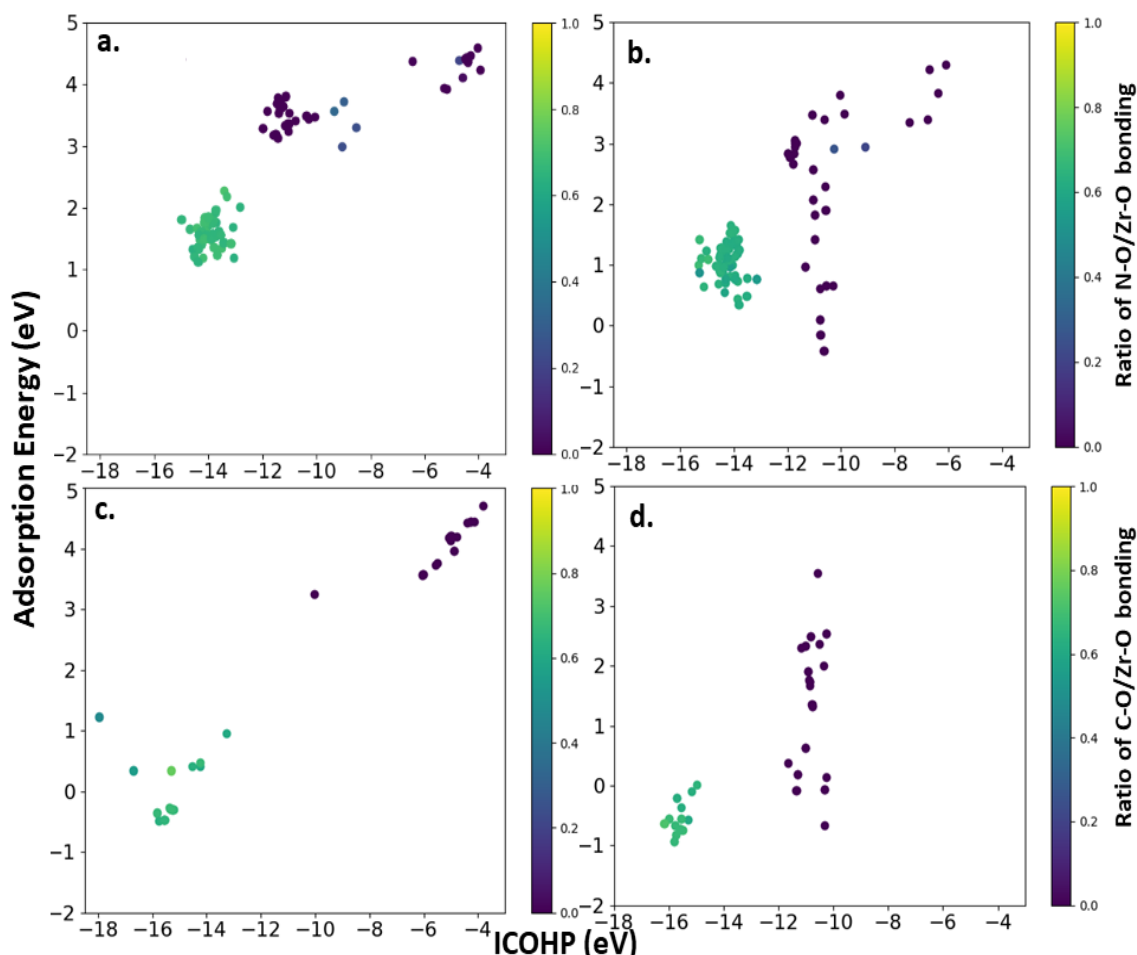
**Figure 3.** Histogram of limiting potentials for both carbon and nitrogen substituted zirconia slabs. The magenta bars represent limiting potentials for carbon substituted slabs while green represents limiting potentials for nitrogen substituted slabs.

We have also explored potential correlation between  $U_L$  and relative slab stability by plotting them in form of a scatter plot. It has been provided in the Supporting Information. From the plot, we can conclude that the  $U_L$  does not show any correlation with the relative slab stability of the anion substituted zirconia slabs.

### ICOHP as a Electronic Descriptor for O Adsorption

The bonding and anti-bonding interactions in a chemical system can be studied with a method known as crystal orbital Hamiltonian population (COHP).<sup>[38,39]</sup> In our study, we have found that the integrated crystal orbital Hamiltonian populations (ICOHP)<sup>[22]</sup> can provide valuable insights to the origin of adsorption energy variations. The calculation of ICOHP involves projection of plane wave basis sets solution, which is obtained from calculations carried out using ground state DFT method, into LCAO basis functions. We can calculate the Hamiltonian between two projected orbitals from the basis functions, which would indicate whether the net interaction is bonding or anti-bonding at a particular band energy.<sup>[22,40]</sup> Hence, the ICOHP can be considered as energy contribution from overlap of two orbitals. Such an energy contribution can be negative (bonding) or positive (anti-bonding).

One of the aims of our study is to gain an understanding of the structural and electronic effects on the adsorption of ORR intermediates on anion-substituted zirconia slabs. In order to achieve this, we create two types of structural models, the unconstrained model and the constrained model. In



**Figure 4.** ICOHP vs Adsorption energy plots a) Constrained Nitrogen substituted zirconia slab b) Unconstrained Nitrogen substituted zirconia slab c) Constrained Carbon substituted zirconia slab d) Unconstrained Carbon substituted zirconia slab

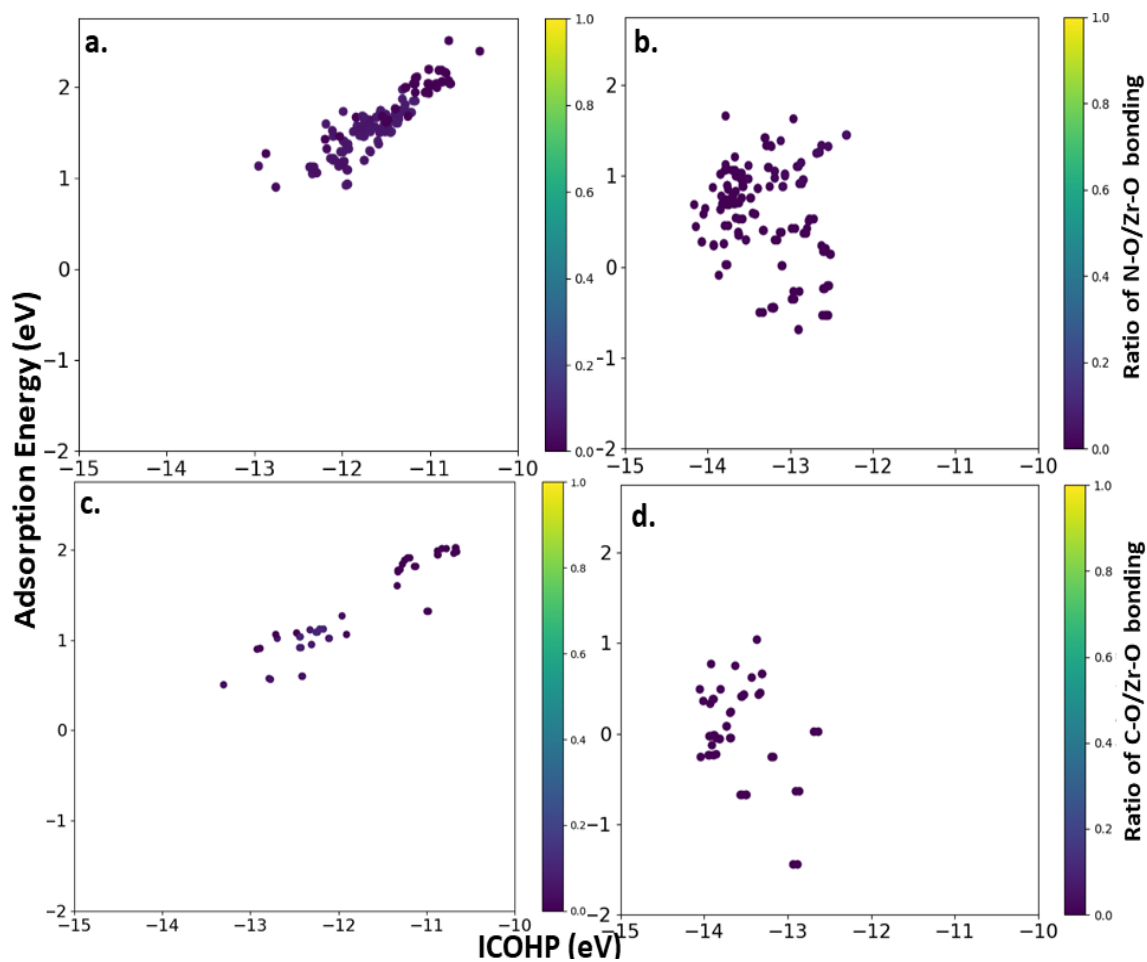
the unconstrained model, the top two layers of the slab and the adsorbate is relaxed during the optimisation calculations (the bottom layer is constrained) while in the constrained model, the entire slab is constrained during the optimization calculation with only the adsorbates being free to move (where the two top layers of the slab are relaxed for the slab without adsorbates).

The adsorption of O species is carried out on the ontop-Zr sites on nitrogen and carbon-substituted slabs (both unconstrained and constrained). Our adsorption calculations over the unconstrained slab reveal that the incoming adsorbates introduce significant structural changes in the anion-substituted slabs which implies that there are both structural and electronic effects that influences the adsorption energy. In terms of structural change, the displacement of lattice anions i.e. oxygen, nitrogen and carbon is much more significant than that of the zirconium. Previous studies report similar influence of structural and electronic effects on different electrocatalysts.<sup>[41–43]</sup> Fig 4a and 4c shows the correlation between the total ICOHP of the O adsorbate (considering bonds to all nearest Zr, N and C neighbours) and O adsorption energy over constrained slabs. Since the constrained slab cannot move during O adsorption, the adsorption energy in this case is affected by electronic effects

only. Thus, in the constrained case the adsorption energy is expected to be proportional to the O-surface bond energy, captured by the ICOHP. As such we can observe quite a linear dependence of adsorption energy on ICOHP, except for in the weak binding limit ( $\Delta E \approx 4.6$ )eV. However in the unconstrained case shown in fig 4b and 4d, we see a strong deviation from the linear trend. We therefore conclude that, in addition to electronic effects, structural reorganization effects in the zirconia slab play a major role in adsorption of O intermediate.

### ICOHP as a Electronic Descriptor for OH Adsorption

Similar adsorption calculations are carried out with OH adsorbate on ontop-Zr sites on the nitrogen and carbon substituted zirconia slabs (both unconstrained and constrained). Since adsorption of OH over the constrained slab is influenced only by the electronic effects, in the Fig 5a and Fig 5c we can observe a linear dependence of adsorption energy on ICOHP. Since ICOHP magnitude is an indicator of bond strength, higher ICOHP magnitude indicates a stronger bond. As higher adsorption energy also indicates stronger bond, ICOHP shows a strong correlation with adsorption energy in this case. However, when the slab is unconstrained, the adsorption energy is influenced not only by the electronic effects but also the structural effects. The structural effects are caused, mainly, by the reorganisation of the anion-substituted zirconia lattice caused by the incoming adsorbate species. The synergistic effect of the structural and electronic changes cause a deviation from the linear trend between the adsorption energy and ICOHP which can be observed in Fig 5b and 5d. This is similar to the deviation from the linear dependence of O adsorption energy on ICOHP we observe in figure 4b and 4d. We have quantified the effect of structural changes only on the adsorption energies by computing the differences in the adsorption energies of the constrained and unconstrained slabs and have presenting them in form of a histogram which is provided in the Supporting Information. From the histogram we can understand adsorption of O intermediate induces structural changes in the slab to a greater degree than the OH intermediate.

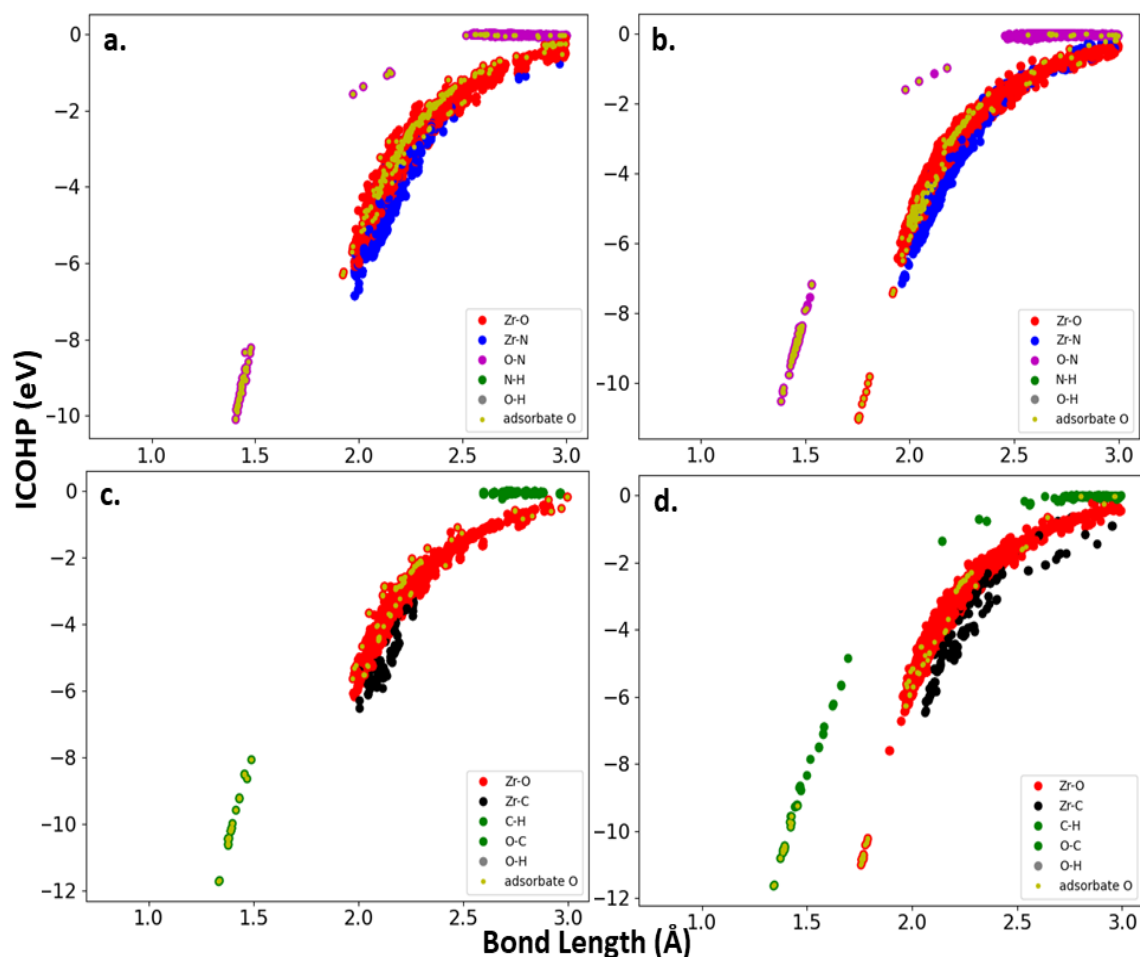


**Figure 5.** ICOHP vs Adsorption energy plots a) Constrained Nitrogen substituted zirconia slab b) Unconstrained Nitrogen substituted zirconia slab c) Constrained Carbon substituted zirconia slab d) Unconstrained Carbon substituted zirconia slab.

## Insights into Bond Configurations

As ICOHP is an indication of bond strength, there exists a correlation between bond length and ICOHP. Fig 6 gives us an overview of the relation between bond lengths between different pairs of atoms for O adsorption over nitrogen and carbon substituted zirconia slabs (unconstrained and constrained). Similar plots have been made for OH adsorption have been provided in the Supporting Information. The yellow overlay indicates the bonds that are formed between an atom (zirconia, nitrogen or carbon) and the adsorbate oxygen. The trend that we observe across the unconstrained system versus the constrained system is that the adsorbate oxygen and zirconium tend to bond more strongly in the unconstrained system as opposed to the constrained system. In order for the O adsorbate to adsorb over the unconstrained system, the lattice zirconium atoms have to rearrange themselves. This is so as to change the bond order to accommodate the incoming O species. If such a structural rearrangement is not possible or it does not change the bond order enough, then it is more favorable for the O adsorbate to adsorb over the lattice nitrogen or carbon. The change in bond order is also evident from the fact that for the unconstrained system, the ICHOP for the zirconium-adsorbate oxygen bond is distributed over a larger range than in the constrained system. From Fig 6 it is also clear that only ICOHP, as a descriptor, is not enough to capture the trend in the adsorption energies.





**Figure 6.** ICOHP vs bond length plots a) Constrained Nitrogen substituted zirconia slab b) Unconstrained Nitrogen substituted zirconia slab c) Constrained Carbon substituted zirconia slab d) Unconstrained Carbon substituted zirconia slab

## Conclusion

ICOHP is a very useful electronic descriptor for prediction of O and OH adsorption energies on zirconia-based catalytic systems. From our comparative study of constrained and unconstrained anion-substituted zirconia slabs, we understand both the structural as well as electronic effects of the slabs play a role in the adsorption of the O and OH intermediates. The incoming adsorbates introduce structural changes in the slab, the lattice Zr atoms get displaced to change the bond order in order to accommodate the adsorbate species on the surface of the slab. The structural reorganization of the nitrogen and carbon substituted zirconia slabs partially contributes to the bond strength between the active sites and the adsorbates.

Additionally, we can also state that anionic substitution on zirconia catalyst with nitrogen is a better choice than that by carbon in terms of ORR activity. We draw this conclusion from the values of limiting potential calculated for the anion-substituted zirconia slabs illustrated in figure 3. The predominantly positive values of  $U_L$  with the peak at 0.25V and values reaching as high as 0.65V is indicative of the same. However, there was no correlation found between the stability of the slabs and their ORR activity.

## Computational Details

All the DFT calculations have been performed using the Vienna Ab Initio Simulation Package (VASP)<sup>[44]</sup> and the core electrons are described with the projector augmented wave (PAW) method<sup>[45]</sup>. To describe the correlation and exchange energy the Perdew-Burke-Ernzerhof functional (PBE)<sup>[46]</sup> is used. The Atomic Simulation Environment (ASE)<sup>[47]</sup> is used to set up and analyse the structures, which are optimised with a plane wave cutoff of 500 eV and Brillouin-zone integration is performed with a Monkhorst-Pack k-point mesh<sup>[48]</sup> of 2x2x1. All the calculations were done with spin polarization. The self-consistent electron density loop is converged to  $10^{-6}$  eV and the structures are relaxed until all forces are below  $0.02 \text{ eV } \text{Å}^{-1}$ .

We have studied nitrogen and carbon substituted zirconia slabs. The model includes three cationic layers with the bottom layer fixed in its bulk position and the upper two layers are allowed to relax. A high throughput workflow was used to create the nitrogen and carbon substituted zirconia slabs. Another similar high throughput workflow was used to optimize the slabs and carry out the adsorption calculations for the different ORR intermediates. The workflow was interfaced with the Atomic Simulation Environment (ASE) and was managed with the workflow management software, MyQueue.<sup>[47,49]</sup>

The first step of the workflow consisted of relaxing all the anion substituted zirconia catalyst structures. The ORR intermediates were added to the on-top-Zr sites of the relaxed anion substituted zirconia structures and were allowed to adsorb on the said catalytic sites. The final optimized structures of the catalyst slabs with adsorbates are used to run single point VASP calculations with increased number of bands. The WAVECAR files from the single point calculations are used to finally carry the COHP calculations. The Lobster package<sup>[50]</sup> was used to perform COHP calcu-

lations. The calculations were started from re-converging electronic structure with symmetry being disabled. ICOHP between all pairs of atoms were included in the Lobster calculation up to a radial cutoff of  $3 \text{ Å}$  were investigated. More specifically we focus on the bond between the adsorbed oxygen, and the surface Zr, C and N atomic species.

For calculation of the limiting potential,  $U_L$ , the free energies of the ORR steps are calculated. The value of the ORR step with the lowest magnitude corresponds to the value of limiting potential.

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## Conflict of Interest

The authors declare no conflict of interest.

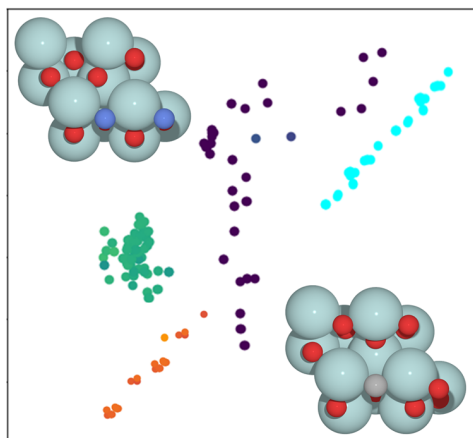
**Keywords:** Oxygen Reduction Reaction • Density Functional Theory • anion-substituted zirconia • non-PGM electrocatalyst • integrated crystal orbital Hamiltonian population

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## Entry for the Table of Contents



For oxygen reduction reaction (ORR), the surface adsorption energies of O and OH\* intermediates are key descriptors for catalytic activity. In this work, we investigate anion-substituted zirconia catalyst surfaces and come to understand that adsorption energies of O and OH\* intermediates is influenced by both structural and electronic effects. The insights into the catalyst-adsorbate interactions can guide the design of future ORR catalysts.