

# Machine-Learning Discovery of Highly Oxidized IrO<sub>x</sub> Phases

Raul A. Flores,<sup>\*,†</sup> Christopher Paolucci,<sup>\*,‡</sup> Ankit Jain,<sup>\*,¶</sup> Muratahan Aykol,<sup>\*,§</sup>  
Jens K. Nørskov,<sup>\*,¶</sup> Michal Bajdich,<sup>\*,||</sup> and Thomas Bligaard<sup>\*,||</sup>

<sup>†</sup> *SUNCAT Center for Interface Science and Catalysis, Department of Chemical  
Engineering, Stanford University, Stanford 94305, California, USA*

<sup>‡</sup> *Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia  
22903, United States*

<sup>¶</sup> *Department of Physics, Technical University of Denmark, Lyngby, Denmark*

<sup>§</sup> *Toyota Research Institute, Los Altos, CA 94022, USA*

<sup>||</sup> *SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator  
Laboratory, Menlo Park, CA 94025, USA*

E-mail: flores12@stanford.edu; cp9wx@virginia.edu;

temp\_temp\_ankits\_email\_address\_temp\_temp@dtu.dk; muratahan.aykol@tri.global; jkno@dtu.dk;

bajdich@slac.stanford.edu; bligaard@stanford.edu

## Abstract

Recent advancements in statistical methods, colloquially termed as machine learning, have revolutionized a tremendous number of fields due to the ease by which we can train models that are flexible enough to regress to data of interest while maintaining predictive power. Nowhere has this impact been felt as much as in the field of materials science, which had previously been bottle-necked by relatively computationally expensive methods. Herein, we report on a ML methodology to enumerate bulk

crystal structures in the  $\text{IrO}_2$  and  $\text{IrO}_3$  space.

## Introduction

The general problem of solving for the most thermodynamically stable crystal structure for an arbitrary inorganic system remains a prohibitive challenge in material science. Experimentally synthesized inorganic materials often conform to the globally minimum energy structure (or similarly stable meta-stable phases), therefore it is desirable from a computational perspective to know the corresponding crystal structure to conduct simulations on. This problem is theoretically challenging, as the number of possible crystal structures for a given stoichiometry is prohibitive. Iterative Active Machine Learning and unique prototype identification to discover stable new materials and catalysts. Motivation for  $\text{IrO}_x$ , low representation, longstanding controversy over oxidation states and topology, and demonstrates promise for OER and Li ion batteries.

Reported +6 oxidation state phases are achievable leading to high degree of structural variability, which is the highest for transition metals. High oxidation states (low pH high anodic voltage, harsh oxidizing conditions) unexplored, need very specific structures with precise oxygen connectivity (aka high pressure  $\text{SrIrO}_3$ ) that can exist. Machine learning is the efficient way to explore this exploring Antarctica for life sparse space. What we show here...

The two key features of our algorithm that make the exploration of an expansive space possible are its use of surrogate models and active learning framework. Because DFT calculations are prohibitively computationally expensive to carry out for large data sets, herein we train a Gaussian Process (GP) machine learning model to serve as a surrogate model. In general active learning applications, the requisite training data is not available. Active learning frameworks are a means by which to generate the most valuable training data set, on the fly.

# Results and discussion

## I. Active Learning Machine Learning Methodology

Our machine learning accelerated materials discovery method proceeds through the following steps First, the dataset of candidate materials is constructed. This data set will define the totality of materials that will be considered by the search algorithm, this is done because the search space of materials is not a continuous space but a discrete array of individual structures. Next, the dataset of materials is transformed into a vectorial representation by using a fingerprinting method that encodes the relevant chemical and structural information.

The structures that comprise the candidate data set were constructed by parsing for structurally unique systems in the OQMD and Materials Project DFT databases. The structural uniqueness was performed using a space-group symmetry classification scheme developed by Jain et al.,<sup>1</sup> which can classify a structure based on its composition and structure. (see SI for more details on the structural classification scheme). This structural classification scheme can directly serve as a structural fingerprint and has successfully been applied towards the prediction of formation energies of inorganic compounds<sup>1</sup> To focus the scope of the study, only AB2 and AB3 stoichiometries were parsed from the databases. The AB2 formula was chosen because it includes rutile-IrO<sub>2</sub>, the known most stable polymorph of IrO<sub>2</sub>. Importantly, AB3 was chosen to include high valency IrO<sub>3</sub> structures in our search. The results of the classification scheme resulted in a XYZ AB2 and XYZ AB3 structural prototypes for which iridium and oxygen were replaced for A and B sites, respectively. Finally, a coarse isotropic volume relaxation based on atomic radii was performed on the structures to accommodate the atomic radii of iridium and oxygen into the lattice. Finally, a Voronoi tessellation based fingerprinting scheme developed by Ward et al.<sup>2</sup> was used to encode the relevant chemical information for each structure into a vector quantity of length 271. The Voronoi based method was used because it is insensitive to volume relaxation. Separate, independent models were used for IrO<sub>2</sub> and IrO<sub>3</sub> to reduce the complexity of the space, this

has the additional effect of making a large number of the fingerprint descriptors redundant. As a result, the 271 length feature space is reduced to a TEMP length vector. PCA was used to reduce the dimensionality of the feature space from 271 to 20 features such that 99 % of the variance is captured.<sup>3</sup>

The active learning algorithm proceeds through iterative ML training, prediction, and acquisition steps and is visualized in figure TEMP. Although we could use practically any regression technique, we employed the Gaussian process (GP) regression model because it offers a high degree of flexibility and, most importantly, built-in error quantification. Error quantification on the predicted formation energies is important because its used in the acquisition criteria. Further details on the GP model, including hyper parameter information, is including in the SI. The acquisition is made by selecting the  $N$  systems with the lowest value of the acquisition function. The acquisition function is defined as the predicted formation energy minus the uncertainty,  $a = b + c$ . The value of  $N$  determines how many structures are selected for DFT calculations, and as such, determines the degree of parallelization of the routine. Small values of  $N$  result in an algorithm that is slow, as every DFT calculation is performed serially. Larger values of  $N$  speed up the algorithm, but potentially decreases the efficiency of the algorithm by TEMP TEMP. Here we chose a value  $N = 10$ . The acquired structures are initially volume relaxed, followed by a full relaxation of all of the atomic coordinates, see SI for additional details on the DFT methodology. The AL loop proceeds until convergence is achieved, which here is defined as the point at which the model has determined the lowest  $N$  structures and has achieved a degree of accuracy for the candidate space such that no structures have formation energies with a lower uncertainty bound lower than the most stable  $N$  structures.

1. Candidate space of structures is generated
2. Initial seed data is used to train a ML model
3. ML model predicts energy of entire candidate space

4. Most valuable calculation(s) is selected using acquisition function
5. DFT calculation(s) is(are) performed to obtain additional training data points
6. ML model is retrained with additional data
7. Repeat steps (TEMP) through (TEMP) until convergence criteria is reached

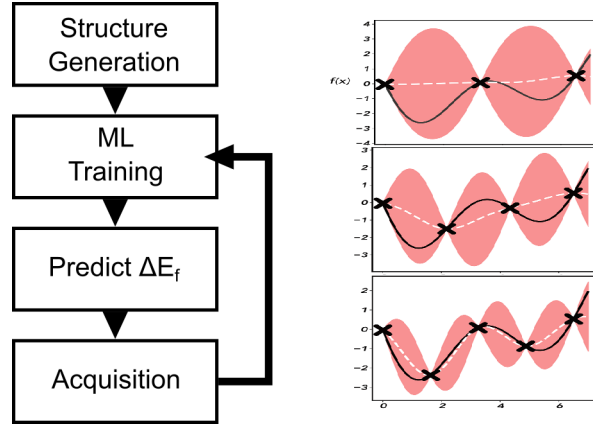


Figure 1: (a) Active learning algorithm diagram. First the candidate space of structures is generated, next, the machine learning model is trained on any available DFT formation energy data. The trained ML model is then used to predict the DE of the entire candidate space. Finally, an acquisition step is performed to pick the next most valuable calculation to perform an-initio DFT on (b) Toy model demonstrating a GP model converging with each subsequent iteration.

## II. Application of AL to stable polymorph discovery in the Ir-O space

- Describe relevant features - Physical intuition? - Describe convex hull plot (energy vs. Ir-O distance), computed amorphous phase to define synthesizability - While only 2  $\text{IrO}_2$  in MP/OQMD, we can compare our structures to other computed  $\text{IrO}_2$  not in open databases.

This is a citation example.<sup>4</sup>

- XYZ unique AB3 Structures, 259 unique prototypes. Substitute Ir and O, expand to minimum Ir-O distance ; XYZ - followed same procedure as in 3.1, Training Set of 35

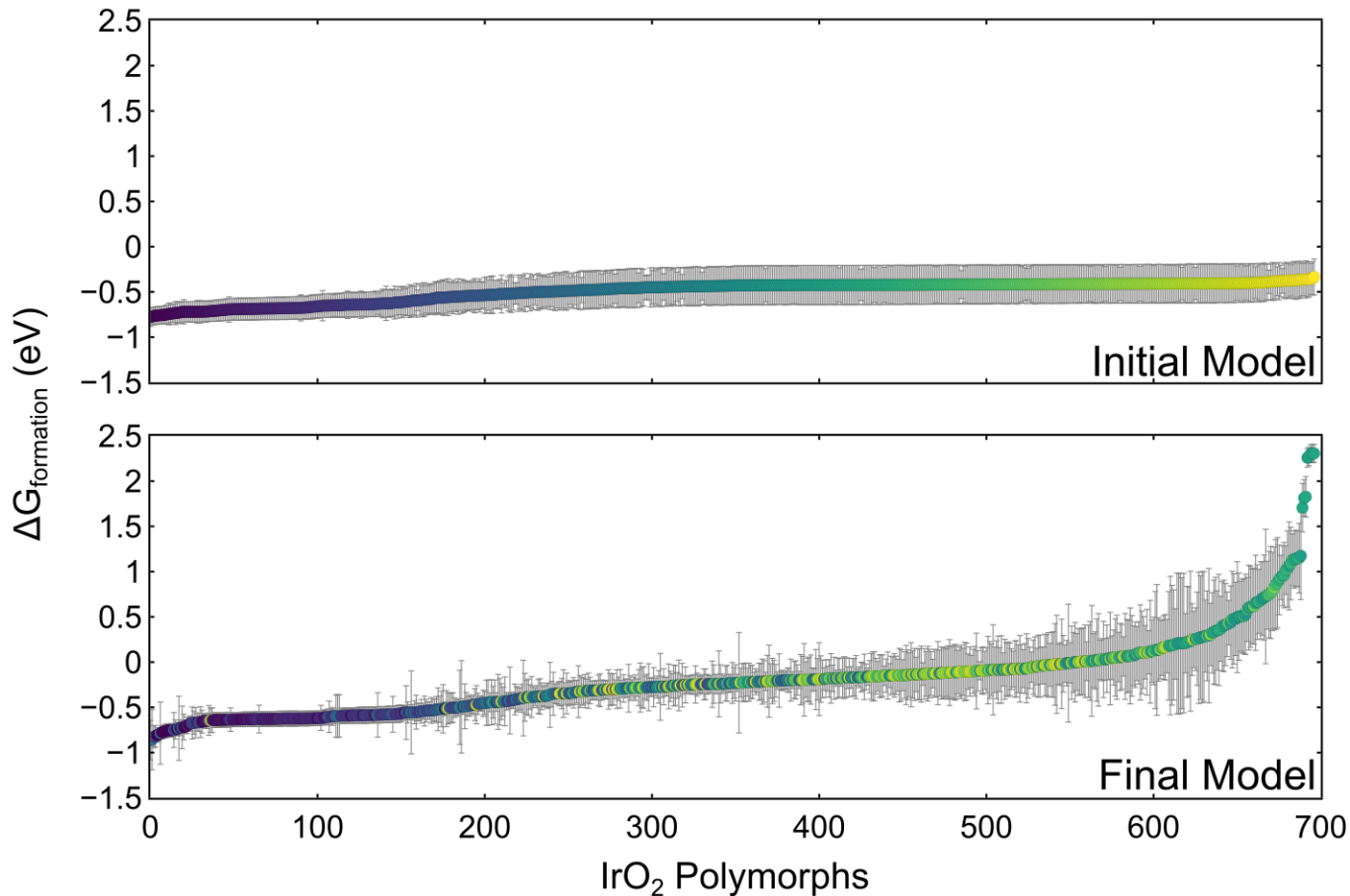


Figure 2: Gaussian process machine learning models trained initially on (a) publicly available DFT data for IrO<sub>2</sub> and (b) all of the acquired DFT calculations from the active learning algorithm. See SI for additional panels at intermediate iterations of the active learning algorithm. The Gibbs formation energy (either DFT derived or predicted from the GP model) and associated GP estimated error (2 sigmas or something TEMP) is plotted for each polymorph in the IrO<sub>2</sub> candidate space. The data points in each subset are ordered from most to least stable (lowest to largest DE formation). The individual markers are colored based on their ordering in the final converged GP model. Acquired structures are identified by their red borders and slightly larger size. The insets show the most stable TEMP structures, where several well known crystal structures are labeled.

structures, 8 of which are  $\text{IrO}_3$  - Describe initial training and training after first 10 DFT structures

- Describe convex hull, classes of structures ( $\alpha\text{-AlF}_3$  like, rutile like, and layered, should be segregated in hull plot) - briefly describe structures within each class, cite in literature where appropriate

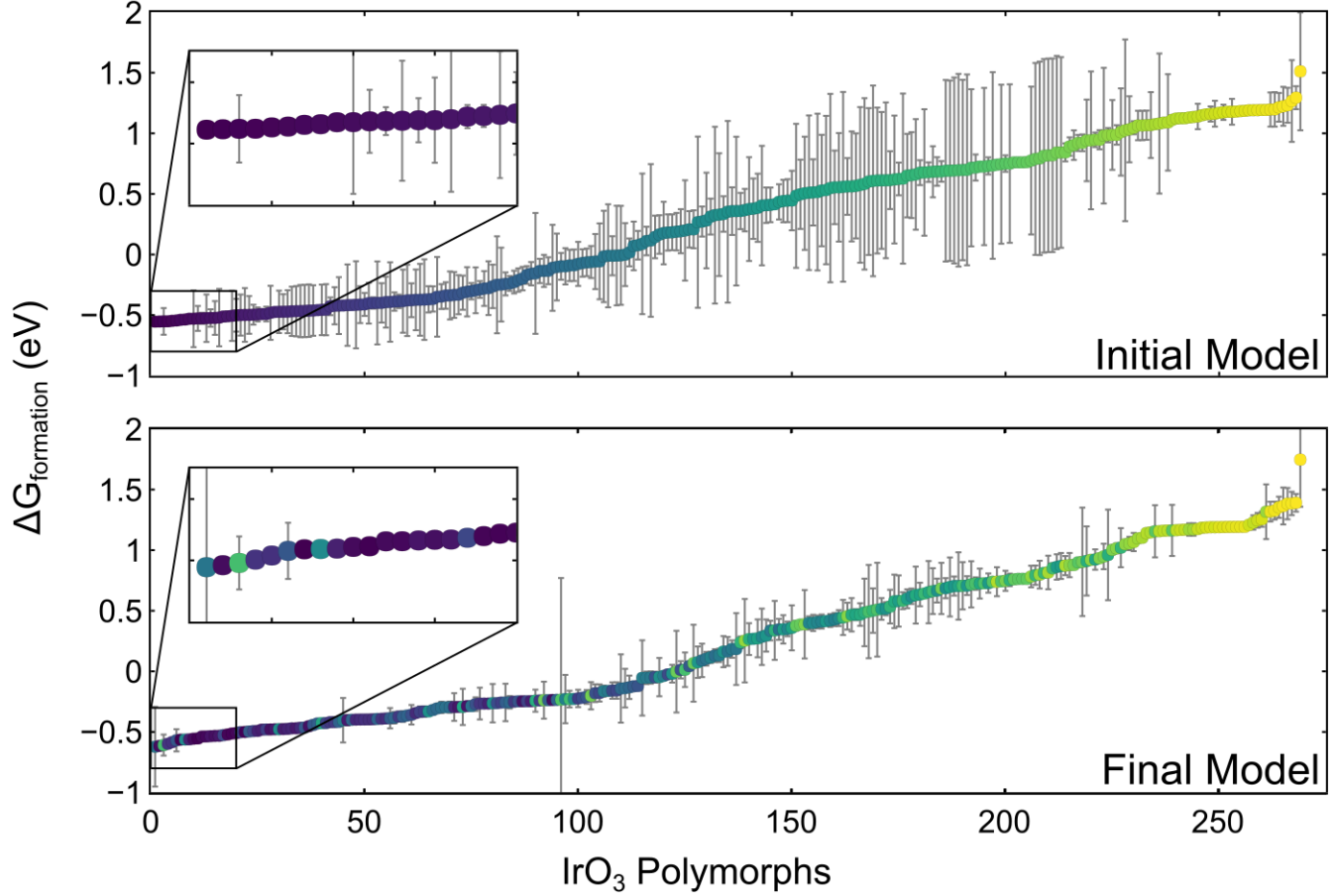


Figure 3: TEMP.

### III. Electrochemical OER Application

We next performed an ab initio thermodynamic and kinetic analysis to elucidate the electrochemical stability and OER activity of the four stable polymorphs (rutile- $\text{IrO}_2$ ,  $\alpha\text{-IrO}_3$ , rutile- $\text{IrO}_3$ , and  $\beta\text{-IrO}_3$ ) computed above (Fig. XYZ).

## Bulk Pourbaix

Fig. 4 reports the IrOx pourbaix diagram (E vs. pH) constructed with the following species: Ir, rutile-IrO<sub>2</sub>,  $\alpha$ -IrO<sub>3</sub>, rutile-IrO<sub>3</sub>,  $\beta$ -IrO<sub>3</sub>, and an aqueous dissolved IrO<sub>4</sub>[4-] species (See TEMP—SI for additional details).  $\alpha$ -IrO<sub>3</sub> is the most stable species under acidic conditions (pH <7) and in the bias region of interest for the OER (1.23 V vs. RHE). The stability regions of the metastable rutile-IrO<sub>3</sub> and  $\beta$ -IrO<sub>3</sub> phases are indicated by unfilled solid lines and appear stable in the OER relevant region of the diagram. The similar formation energies (SI XYZ) for all three IrO<sub>3</sub> species suggest some or all of these IrO<sub>3</sub> phases may be present and are stable under OER conditions.

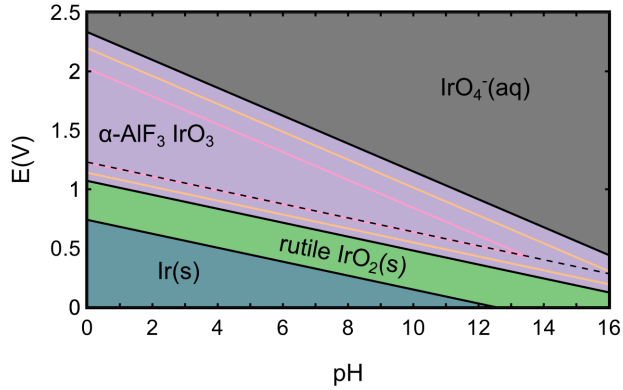


Figure 4: , Electrochemical bulk phase stability diagram (Pourbaix) of the Ir-O-H chemical space with respects to changes in potential and pH. We considered a bulk unoxidized Ir(s) (blue), a [+4] rutile-IrO<sub>2</sub> (green), and an aqueously dissolved IrO<sub>4</sub>[4-] (gray) phase. Additionally, we considered the three IrO<sub>3</sub> polymorphs,  $\alpha$ -IrO<sub>3</sub> (purple), rutile-IrO<sub>3</sub> (orange), and  $\beta$ -IrO<sub>3</sub> (pink). The water equilibrium line at 1.23 V vs RHE, which corresponds to a 0 overpotential catalyst, is shown by a dotted line.

## b. OER Surfaces and Activities

Fig. 5 summarizes the major results of the electrochemical activity and surface stability analysis, structure files and method details are reported in SI XYZ. Fig. 5 a.) reports the surface energy Pourbaix plots as a function of applied potential (at pH=0) for the four IrOx crystals of interest. The bulk phase limits of stability from figure TEMP are included at the bottom of each subplot. For each polymorph XYZ specific facets were chosen from



the highest intensity x-ray diffraction peaks from powder-diffraction spectra simulated in VESTA (TEMP insert vesta ref and ref SI xrd plot) and physical intuition. For each facet we computed the surface free energy for three coverages, bare, \*OH, and \*O. ~~shows the surface energy Pourbaix plots for the four IrO<sub>x</sub> crystals of interest. For each bulk system, the surface energy as a function of applied potential (pH=0), for various facets, and at various coverages (bare, \*OH, and \*O covered), are shown, see SI for more details.~~ At modest overpotentials ( $\eta = 0.3$  and potentials of  $1.5$  V vs RHE) the convex hull is populated solely by oxygen terminated surfaces. Consequently, we consider mainly oxygen terminated surfaces for the OER analysis.

The OER activity (expressed in terms of the limiting potential) for select oxygen terminated surfaces are shown in Fig. 5 as a function of the DGO-DGOH TEMP OER thermodynamic descriptor. The two rutile-IrO<sub>2</sub> surfaces (100, and 110) bind the OER intermediates strongly, locating them at a theoretical limiting potential of xyz. The predicted overpotentials of our rutile-IrO<sub>2</sub> systems are within the range of experimentally observed overpotentials found in literature. The three IrO<sub>3</sub> polymorph surfaces all have DGO-DGOH descriptor towards the top and right of the volcano, indicative of weaker binding energetics. This is evident from figure SI TEMP (scaling) which shows a clear distinction between the IrO<sub>2</sub> and IrO<sub>3</sub> polymorphs, with IrO<sub>3</sub> binding on average TEMP eV weaker than IrO<sub>2</sub>. The best performing systems, including the (100), (110), and (211) facets of a-IrO<sub>3</sub>, b-IrO<sub>3</sub> (101), and R-IrO<sub>3</sub> (110), have overpotentials of  $0.4$  V vs RHE, a  $0.2$  V vs RHE improvement over the rutile-IrO<sub>2</sub> system. We note that the computed overpotentials for our rutile-IrO<sub>2</sub> system differs from that reported in<sup>5</sup> by  $0.2$  V. This discrepancy is due to our use of spin-polarization, which was neglected in Seitz et al., which strengthens the binding of IrO<sub>2</sub>.

### c. OER Intermediate Scaling

Figure TEMP shows the scaling relations between the adsorption free energies of the OER intermediate species for the IrO<sub>x</sub> systems studied herein. It can be seen clearly that the data

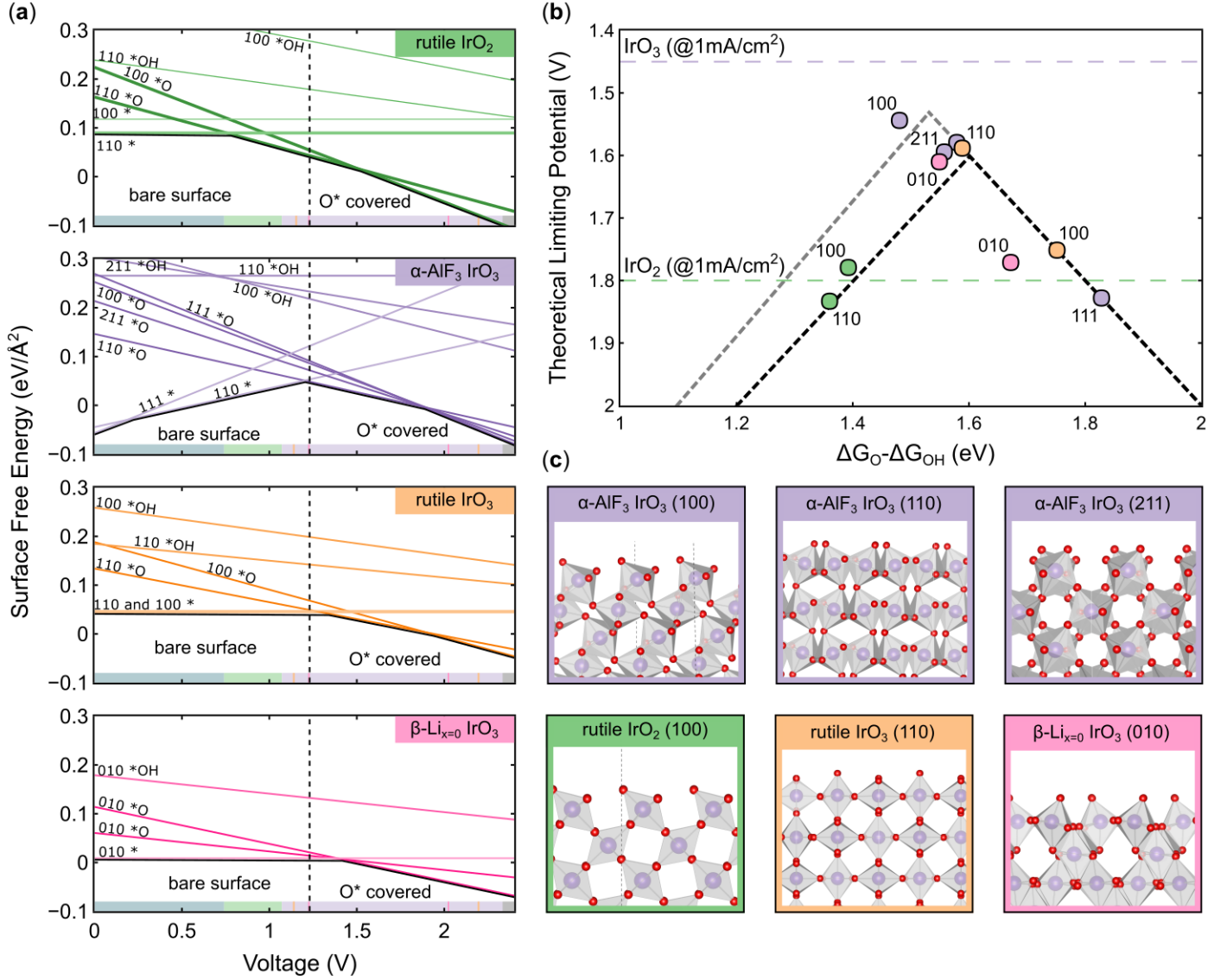


Figure 5: Summary of OER results for the four bulk structures of  $\text{IrO}_x$  considered: rutile- $\text{IrO}_2$  (green),  $\alpha\text{-IrO}_3$  (purple), rutile- $\text{IrO}_3$  (orange), and  $\beta\text{-IrO}_3$  (pink). (a) Surface energy Pourbaix diagrams for each structure, with the surface energy of various facets and coverages shown as a function of applied potential. The bulk Pourbaix diagram's bounds of stability at pH 0 are superimposed at the bottom of each subplot. (b) OER activity volcano for  $\text{IrO}_x$  systems considered utilizing the  $\Delta G_{\text{O}} - \Delta G_{\text{OH}}$  thermodynamic descriptor. The purple dotted line corresponds to the experimental limiting potential at  $10 \text{ mA cm}^{-2}$  for  $\text{IrO}_3$ ,<sup>5</sup> while the green band corresponds to the range of experimentally observed overpotentials for pristine  $\text{IrO}_2$  catalysts as reported in literature. (c) Select surface facets for the four  $\text{IrO}_x$  crystal systems considered.

points corresponding to the three  $\text{IrO}_3$  polymorphs are roughly 1 eV weaker binding than the rutile- $\text{IrO}_2$  points. This generally weaker binding of the  $\text{IrO}_3$  stoichiometry is responsible for the observed improvement in theoretical activity. The  $\Delta G_{\text{OOH}}$  vs.  $\Delta G_{\text{OH}}$  relationship is very close to the traditional “universal scaling relations”, demonstrating that our materials do not break the infamous  $\Delta G_{\text{OOH}}$  vs.  $\Delta G_{\text{OH}}$  scaling.

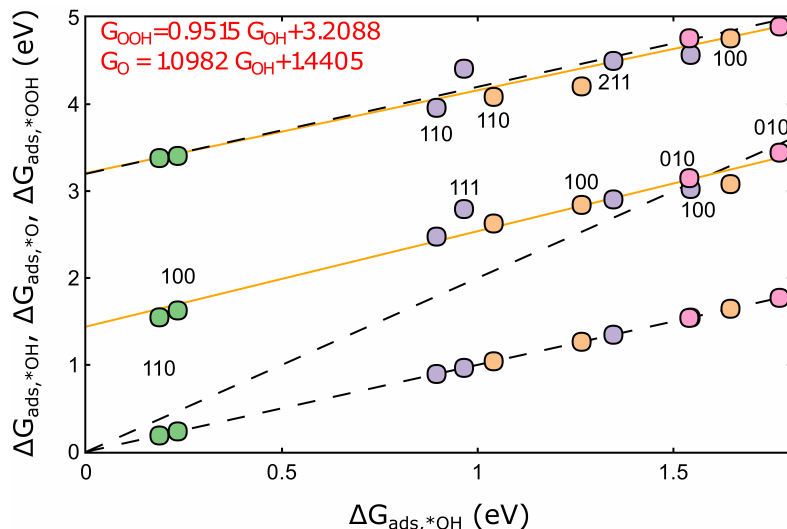


Figure 6: Relationship between the adsorption free energies of the three key OER intermediates (\*OH, \*O, \*OOH), with  $\Delta G_{\text{OH}}$  chosen as the dependent variable. Best fit lines are provided for  $\Delta G_{\text{OOH}}$  vs.  $\Delta G_{\text{OH}}$  and  $\Delta G_{\text{O}}$  vs.  $\Delta G_{\text{OH}}$ . Additionally, “universal scaling relations” for  $\Delta G_{\text{OOH}}$  vs.  $\Delta G_{\text{OH}}$  and  $\Delta G_{\text{O}}$  vs.  $\Delta G_{\text{OH}}$  are shown (black dotted lines) to emphasize our deviation from the traditionally reported scaling fits. The trivial  $\Delta G_{\text{OH}}$  vs.  $\Delta G_{\text{OH}}$  relationship is included for completeness.

## Conclusion

And in conclusion we presented work here...

## Acknowledgement

Organizations to acknowledge TRI SUNCAT Stanford NERSC etc.

JAGT and MB acknowledge the support by the U.S. Department of Energy, Office of

Science, Office of Basic Energy Science, via Grant DE-SC0008685 to the SUNCAT Center of Interface Science and Catalysis.

The authors would like to acknowledge the use of the computer time allocation for the Transition metal-oxide and metal surfaces: applications and reactivity trends in catalysis at the National Energy Research Scientific Computing Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

## **Supporting Information Available**

### **Machine Learning Algorithm Methods**

#### **Classifying unique prototypes in DFT databases**

TEMP

#### **Gaussian process regression model**

TEMP

#### **Gaussian process regression model**

Relevant details about the ML Gaussian process here

The Gaussian Process model utilized a rational quadratic kernel with variable length scales for each dimension of the feature space.

### **Electrochemical OER Computational Methods**

#### **Density Functional Theory Methods**

All OER calculations were performed using density functional theory (DFT) implemented via the Vienna ab-initio simulation package (VASP) and utilizing the PBE exchange-correlation functional. Dipole corrections were imposed on all non-symmetric slabs. A 4x4x3 k-point mesh with gamma-point centered Monkhorst-Pack was used for all slabs. The plane-wave energy cutoff was 500 eV.

All slab calculations maintained a vacuum spacing of 15 Å. All structures were relaxed utilizing a TEMP algorithm with a stop criteria being that all atoms satisfy a maximum force threshold of 0.02 eV/Å.

## OER Thermodynamic Methodology

### Surface Energy Pourbaix Methodology

Surface energy Pourbaix plots were constructed by calculating the surface energy of each slab by under standard conditions ( $V=0$  and  $\text{pH}=0$ ) and then utilizing the computational hydrogen electrode to compute the potential dependence of the surfaces.

Surface energy calculations were performed for various facets for slabs of increasing thickness. The bulk energy was then extracted by fitting the total energy of the slabs against the number of layers as explained in REF2. This was done to avoid common issues of surface energy divergence associated with using a separate bulk energy calculation.

The sensitivity of a given slab to an applied bias is dependent on the composition of the surface, in particular, the effect of coverage of electrolyte species which can deposit oxygen, hydrogen, and hydroxide species on the surface layers. These additional O and H atoms are not referenced to the atoms in the slab, but are instead referenced to the computational hydrogen electrode and water-splitting reaction. The equation for is as follows:

Procedure: - For the top/most stable bulk structures the following procedure was carried out

- \* Stable stoichiometric terminations were cut from the bulk Stable termination planes were guesstimated via intuition, and the x-ray diffraction pattern tool from Vesta

- \* Electrochemical surface coverage was elucidated via a surface Pourbaix analysis Need to know the coverage of surface under operating conditions ( $1.23 \text{ V RHE}$ )

- \* Thermodynamic/limiting potential analysis of the OER mechanistic pathway Volcano plot, limiting potentials, etc.

## References

- (1) Jain, A. PHYSICAL REVIEW B 98 , 214112 ( 2018 ) Atomic-position independent descriptor for machine learning of material properties. **2018**, *214112*, 1–7.

- (2) Ward, L.; Liu, R.; Krishna, A.; Hegde, V. I.; Agrawal, A.; Choudhary, A.; Wolverton, C. Including crystal structure attributes in machine learning models of formation energies via Voronoi tessellations. *Physical Review B* **2017**,
- (3) Tipping, M. E.; Bishop, C. M. Probabilistic principal component analysis. *Journal of the Royal Statistical Society. Series B: Statistical Methodology* **1999**,
- (4) Smith, A.; Smith, J. TEMP title. **9999**, *1*.
- (5) Seitz, L. C.; Dickens, C. F.; Nishio, K.; Hikita, Y.; Montoya, J.; Doyle, A.; Kirk, C.; Vojvodic, A.; Hwang, H. Y.; Norskov, J. K.; Jaramillo, T. F. A highly active and stable IrO<sub>x</sub>/SrIrO<sub>3</sub> catalyst for the oxygen evolution reaction. *Science* **2016**, *353*, 1011–1014.

## Graphical TOC Entry

