

# Machine-Learning Discovery of Highly Oxidized $\text{IrO}_x$ Phases

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## 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

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...

Crystallographic Discovery and Machine Learning. Current state of databases (OQMD, MP, CatHub, alflowlib). What parts of the database are missing (e.g.  $\text{IrO}_3$ ). Ankit - Condensed version of Ankit paper Prototyping databases to identify knowledge gaps. Deriving features from structures to describe heats of formation. What has been done (simple models) more recently using DFT+Machine Learning.

Oxides for batteries/fuel cells, Iridium Oxide, OER, Lithiated  $\text{IrO}_3$ . Highly oxidized phases of oxides for fuel cell and energy storage applications.

## Results and discussion

### I. $\text{IrO}_2$

For Structure Rendering Use: @Michal To Send example vesta files, font Avenir

Figures: Summary figure of found structures, - There are XYZ unique AB2 structures (or multiples, e.g.  $\text{A}_2\text{B}_4$ ) - Of those we found 697 unique AB2 prototypes (unique SG/Wyckoff

combination) in OQMD/MP - To generate our test set we substituted Ir for A and O for B, then isotropically expanded cell volume to constrain a minimum Ir-O distance of XYZ  
- Next translated each of the 697 structures to be described by 271 features (invariant to isotropic expansion/compression), then reduced to 30 using PCA, described in methods XYZ  
- To generate initial training data use existing DFT. Not enough on  $\text{IrO}_2$ , so used OQMD to generate initial training data from nearest structures in phase space, described in Methods XYZ. Training set of 30 structures in SI XYZ.

- Trained Gaussian Process, rational quadratic kernel, variable length scales. CV error of XYZ eV/atom, initial predictions in figure XYZ. - Selected 10 structures with lowest prediction-uncertainty for DFT. Structures were volume optimized, then fully relaxed, described in methods XYZ. - Model retrained with the 10 DFT computed structures ONLY, 271 features-110 features applicable to  $\text{IrO}_2$ -20 principle components for 99.9 percent variance. CV error - Repeat until XYZ, final predictions shown in Fig XYZ

- 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>1</sup> Without it I think stuff breaks.

## II. $\text{IrO}_3$

- XYZ unique AB<sub>3</sub> Structures, 259 unique prototypes. Substitute Ir and O, expand to minimum Ir-O distance 1 XYZ - followed same procedure as in 3.1, Training Set of 35 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

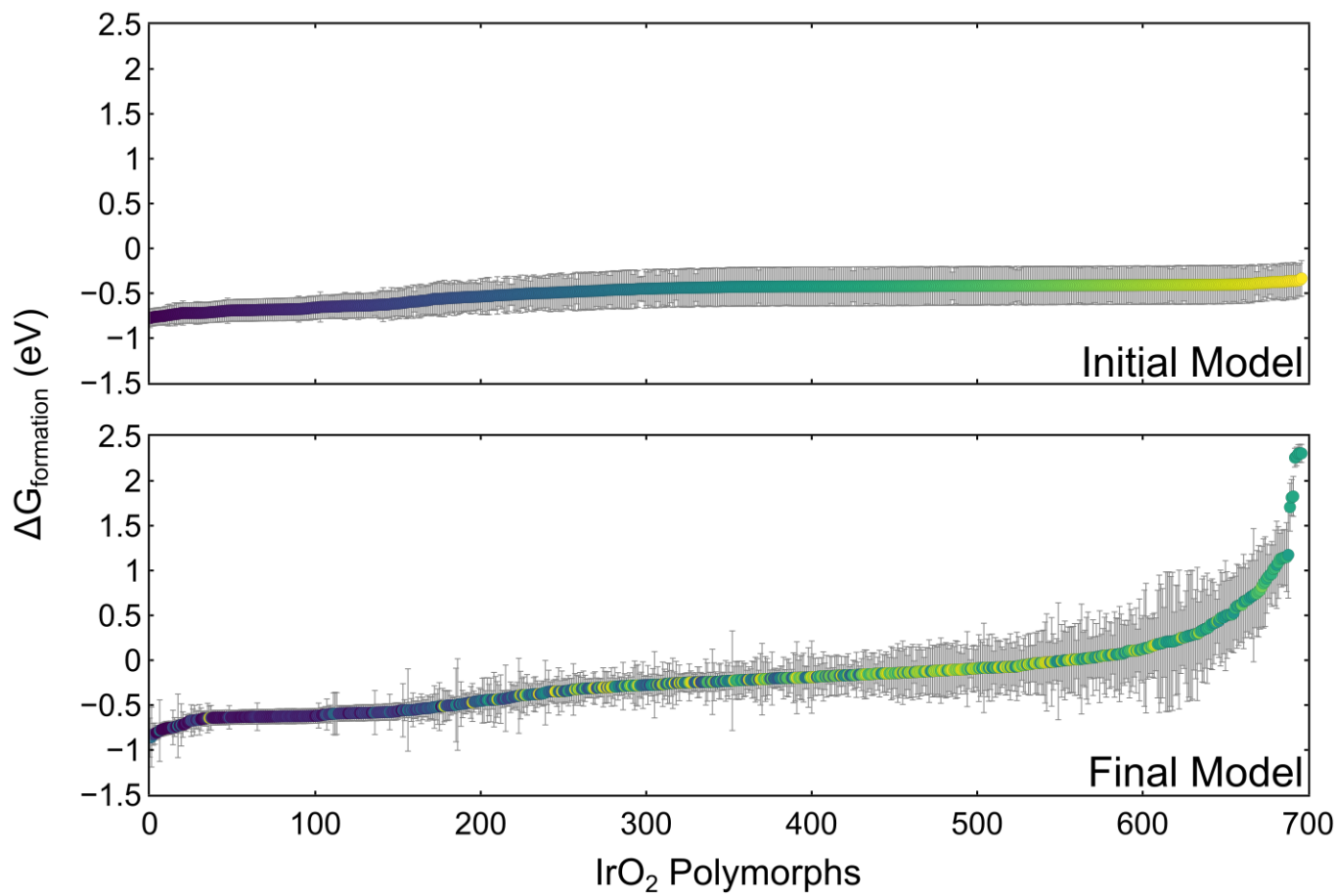


Figure 1: TMP.

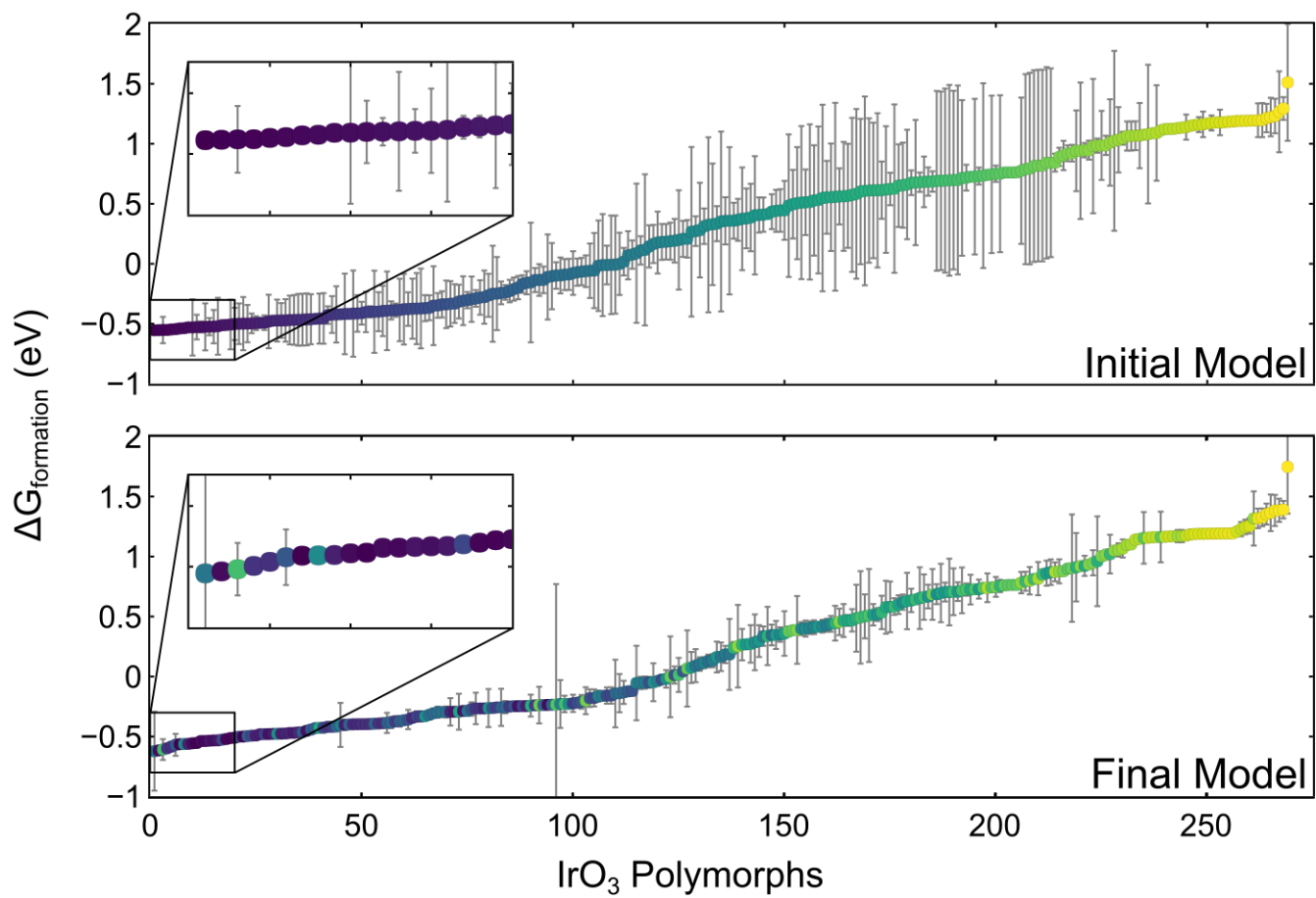


Figure 2: TMP.

### III. Electrochemical OER Application

In the following section we will demonstrate the merit of our bulk crystal searching method by investigating the 4 most stable structures for the oxygen evolution reaction, an important electrochemical reaction with application in energy storage technologies.

#### Bulk Pourbaix

The electrochemical stability phase diagram (E vs. pH) was constructed from all bulk crystals of Ir, IrO<sub>2</sub>, IrO<sub>3</sub>, and aqueous dissolved IrO<sub>4</sub>[4-]. Only the most stable structure for each stoichiometry is visible on the Pourbaix diagram which correspond to TEMP and are shown in Fig. 3

Under acidic condition (i pH 7) and in the bias region of of interest for the OER, there exists a region of stability for the novel  $\alpha$ -AlF<sub>3</sub> IrO<sub>3</sub> structure found herein.

At a pH=0 the bound of stability for  $\alpha$ -AlF<sub>3</sub> IrO<sub>3</sub> spans TEMP

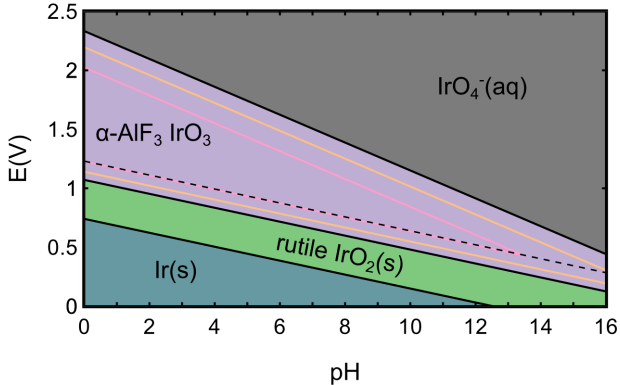


Figure 3: Electrochemical bulk phase stability diagram (Pourbaix) of the Ir-O-H chemical space.

#### b. OER Activities and Surfaces

The OER activity (expressed in over-potential) for surfaces cut from the IrO<sub>2</sub>, and the 3 most stable polymorphs of IrO<sub>3</sub> are shown in Fig. 4. The specific facets were chosen from

the highest intensity x-ray diffraction peaks from powder-diffraction spectra simulated in VESTA.

To determine the most likely experimentally abundant surface facets and surface coverages, a surface energy Pourbaix diagram was constructed (TEMP). See (SI for surface energy/Pourbaix part) for the method used to calculate surface energies.

### **c. OER Intermediate Scaling**

Write stuff

## **Conclusion**

And in conclusion we presented work here...

## **Acknowledgement**

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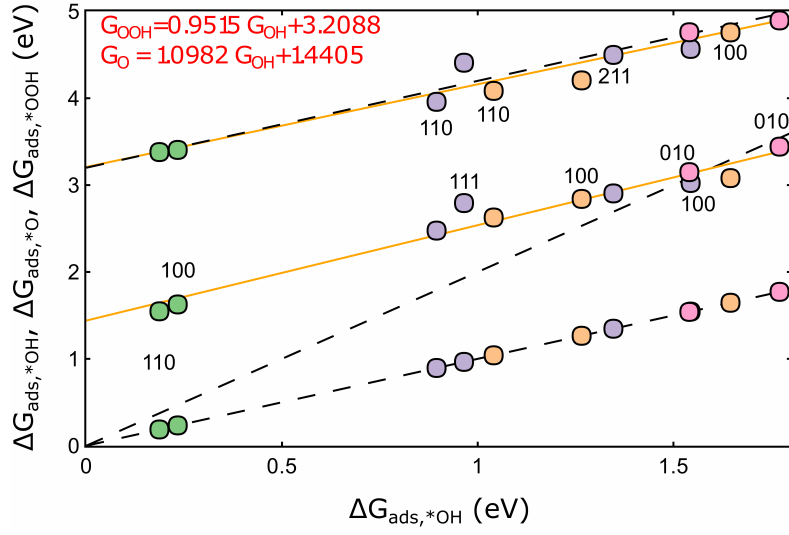


Figure 5: Scaling relationship between DG of adsorption of the intermediate species of the OER using  $\Delta G_{ads,*OH}$  as a descriptor.  $\Delta G_{ads,*OOH}$ ,  $\Delta G_{ads,*O}$ , and  $\Delta G_{ads,*OH}$  are plotted on the y-axis.

# Supporting Information Available

## Machine Learning Algorithm Methods

Relevant details about the ML Gaussian process here

## 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 Monkshort-packing 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

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

- \* Stable stoicheometric 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 V RHE)

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

## References

- (1) Smith, A.; Smith, J. TEMP title. **9999**, *1*.

## Graphical TOC Entry

