About me:

High-throughput screening with the Open Catalyst Project

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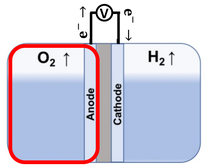
Motivation

1. High-throughput (HT) screening of catalysts using density functional theory (DFT) is expensive.
2. Machine learning potentials can speed up HT screening by predicting DFT-like quantities.
3. Allows construction of customizable screening frameworks for identifying viable catalysts
4. **Will focus on screening catalysts for H_2O splitting**



OER: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

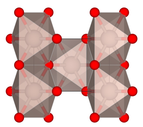
HER: $4H^+ + 4e^- \rightarrow 2H_2$

$2H_2O \rightarrow O_2 + 2H_2$

OER for electrolysis is **slow**

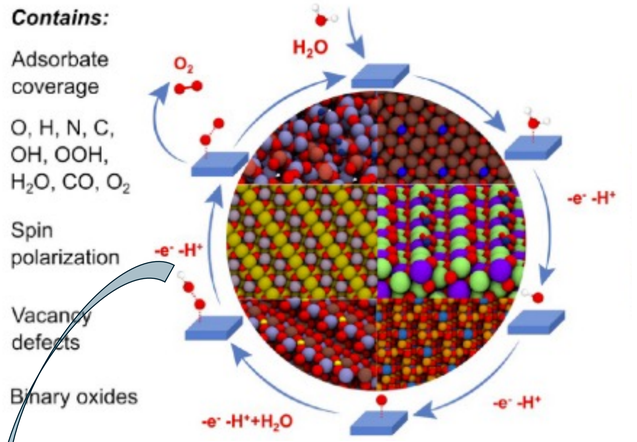
Oxides are promising OER catalysts but...

pH Activity Stability

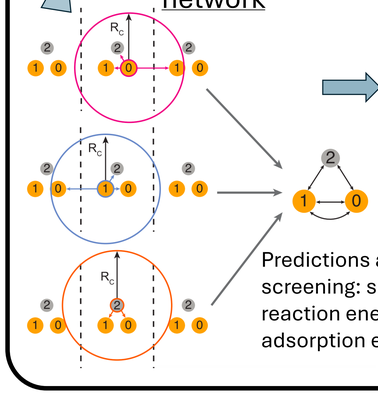


RuO_2 has good activity, but super expensive ($18,315/kg), also unstable. Need to find oxides that are **(1) active, (2) cheap, (3) stable**

Interpolated OC22 dataset



Graph neural network



Scope of database

# predictions: 6 mil		
# materials: 4,119		
Ave. # slabs per material: 47		
# slab predictions: 191,902		
# adslab predictions: 2.5 mil		
OH*	O*	OOH*
2 mil	667,266	> 3 mil

Predictions allows for variety of analysis in screening: surface energy (γ →Wulff shapes), reaction energies (ΔG_{rxn} →overpotentials η), adsorption energies (E_{ads} →TOF/selectivity)

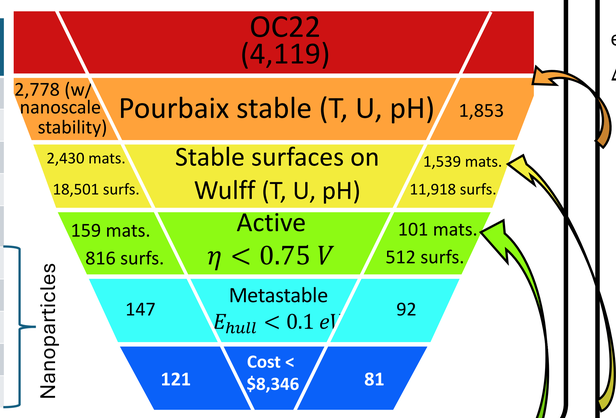
High-throughput screening

Candidates identified through screening frameworks considered with varying reaction conditions and criteria for Pourbaix stability.

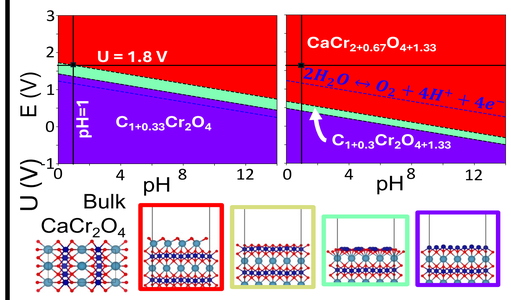
T (℃)	60	60	80	80
U (V)	1.8	1.2-2	1.8	1.2-2
Bulk	122[a]	99[e]	120[i]	99[m]
Bulk/Wulff	83[b]	62[f]	81[j]	62[n]
Bulk/Wulff/Nano	111[c]	83[g]	121[k]	84[o]

Electrochemical stability significantly reduces candidates due to the required acidic conditions (pH~1). Nanoscale stability offers a means to better stabilize oxides under these conditions. We also introduce surface stability in addition to bulk stability. Only facets that are Pourbaix stable on the Wulff construction are considered as catalytic surfaces when analyzing the overpotential/activity.

Formula	η_{OER} (V)	Rxn conditions
$MnBiO_3$	0.51	a,b,c,i,j,k
$Cu_3(SbO_3)_4$	0.37	a,e,i,m
$AgSnO_3$	0.49	a,e,i,m
$MnTlO_3$	0.2 (**0.08**)	a,b,c,i,j,k
$CuMoO_4$	0.46	a,b,c,e,f,g, i,j,k,m,n,o
$BaMn_2O_3$	0.62	k
$Li(CuO)_2$	0.52	k
Mn_2BeO_4	0.32	c,g,k,o
$ScMn_2O_4$	0.29 (**0.33**)	k
$TiCu_3O_4$	0.38	g,o

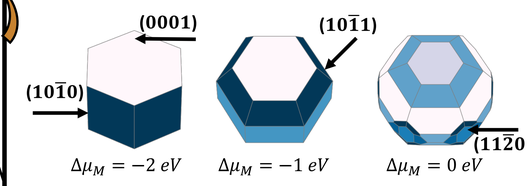


Electrochemical and nanoscale stability



Pourbaix diagrams can be used to determine bulk/surface electrochemical stability by plotting the formation energy of the bulk (ΔG_{PBX}) or surface energy (γ) as a function of pH and applied potential (U). Formation energies are referenced to the chemical potential of oxygen given by:

$$\Delta\mu_{O_2} = \mu_{O_2} - \mu^o_{O_2} = 4.92 + 2\mu^\circ_{H_2O} - 4\left(\frac{1}{2}\mu^\circ_{H_2} - eU - k_BTpHln10\right) + \Delta G^{O^*}_{corr}$$

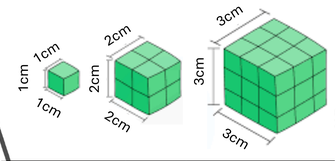


From γ of facets (hkl), we can construct the Wulff shape which indicates which surfaces are most likely to appear on the equilibrium crystal of a material.

Surface energy:

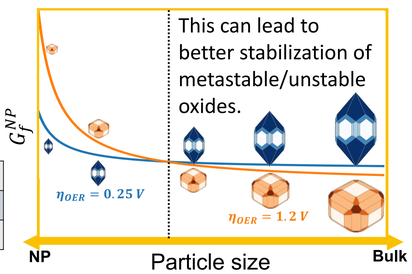
$$\gamma(\mu_M, \mu_{O_2}) = \frac{E^{A_{nx}M_{ny+k}O_{nz+j}}_{slab} - nE^{A_xM_yO_z}_{bulk} + k\mu_M + j\frac{1}{2}(\mu_{O_2})}{2A}$$

We can define nanoparticle formation energy (G^{NP}_f) as the sum of surface and bulk formation energy: $G^{NP}_f(\mu_{O_2}, \mu_M) = \Delta G^V_{PBX}\left(\frac{4}{3}\pi r^3\right) + \bar{\gamma}(4\pi r^2)$



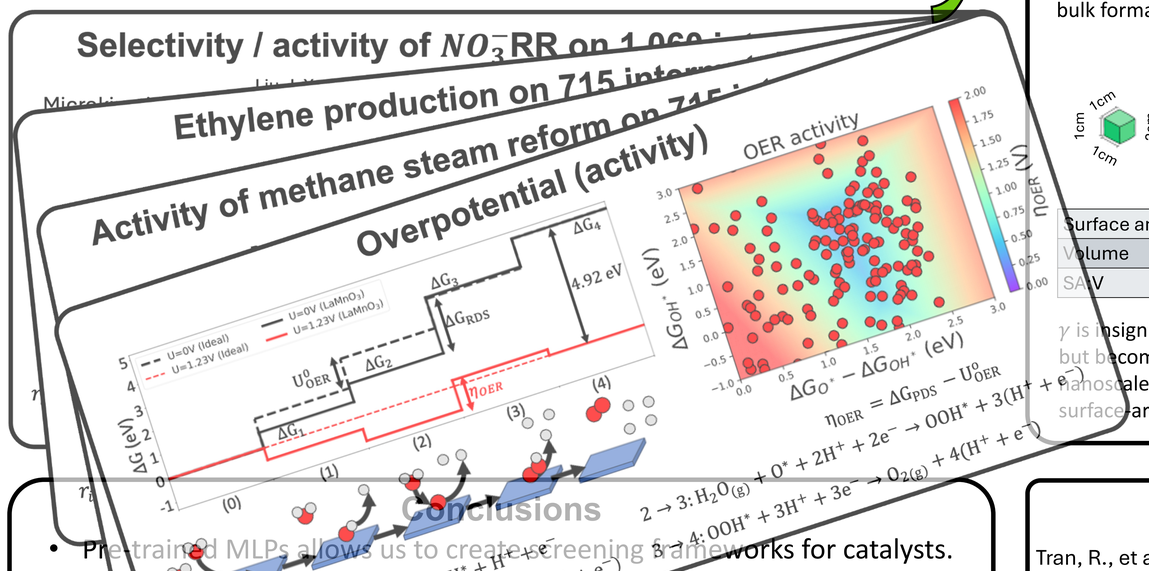
Surface area	6 cm^2	24 cm^2	54 cm^2
Volume	1 cm^3	8 cm^3	27 cm^3
SA:V	6:1	3:1	2:1

γ is insignificant at the macroscale, but becomes relevant to at the nanoscale due to the increase in surface-are-to-volume ratio.



This can lead to better stabilization of metastable/unstable oxides.

We use the volume, surface area, and surface energy of the Wulff shape to describe G^{NP}_f.



Conclusions

- Pre-trained MLPs allows us to create screening frameworks for catalysts.
- Do so by combining surface property predictions (E_{ads}, ΔG_{rxn}, etc.) w/ electrochemistry, MKM, BEP, etc. to estimate TOF / selectivity /η_{OER}
- Example of such a framework identifies oxide electrocatalysts for OER.
- Predicting total DFT energy of slabs allows for thermodynamic analysis: Wulff shapes, G^{NP}_f, and η_{OER} to help identify acid stable catalysts.
- We developed such a framework to identify 122 (68) bulk (nano) stable oxide catalysts for OER.

Citations

Tran, R., et al. (2022). *ACS Catalysis*. https://doi.org/10.1021/acscatal.2c05426
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