2024 AIChE ANNUAL MEETING

October 27 – 31, 2024

San Diego Convention Center

Hilton San Diego Bayfront

Rational Design of Nanoscale Stabilized Oxide Catalysts for OER with OC22

Richard Tran

CHEMICAL ENGINEERING REIMAGINED

UH ENERGY TRANSITION INSTITUTE

Shell

Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

Acknowledgements

Financial funding:

Shell


Ligang Lu


Benjamin M. Comer


Sajanikumari Sadasivan


Stefan J. Raaijman


Nishant K. Sinha


Kuldeep B. Mamtani


Shibin Thundiyil


Ganesh Iyer

ENERGY TRANSITION INSTITUTE

UNIVERSITY OF HOUSTON

UH MODAL LAB


Jiefu Chen


Xuqing Wu


Yuan Zi


Liqiang Huang

The Computational Catalysis and Interface Chemistry Group

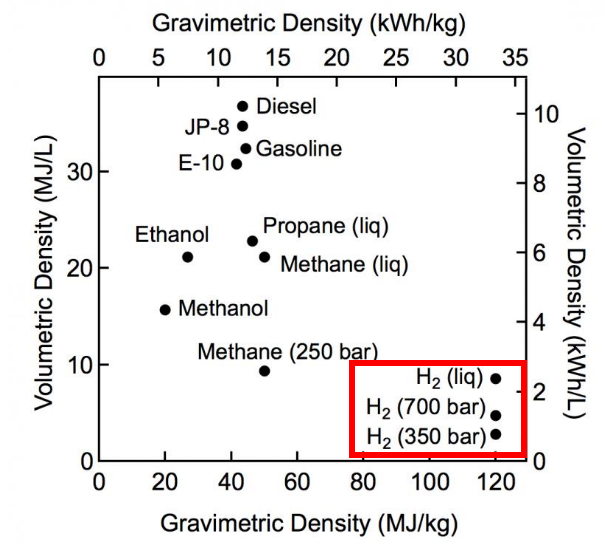

Lars Grabow

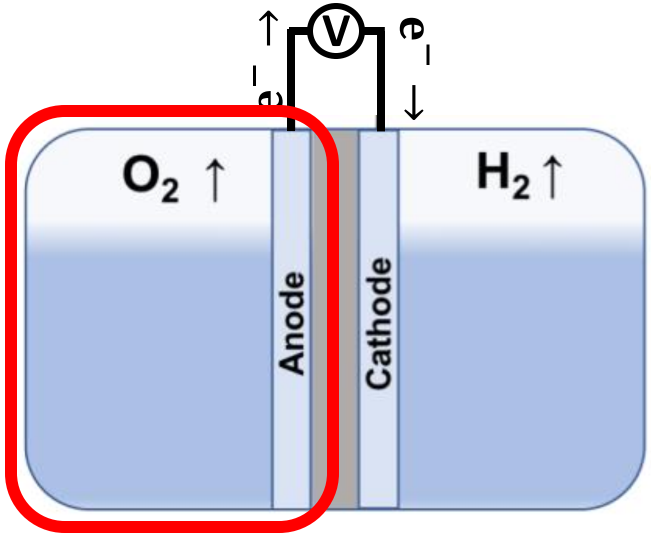

Shengguang Wang

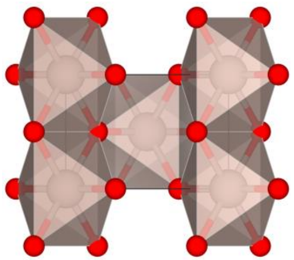
Supercomputing resources:

UNIVERSITY OF HOUSTON
Research Computing Data Core
Hewlett Packard Enterprise Data Science Institute

Oxygen evolution reaction



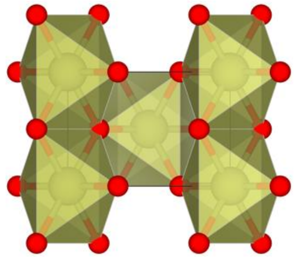




RuO_2

$18,315/kg

Ru: $24,113/kg



IrO_2

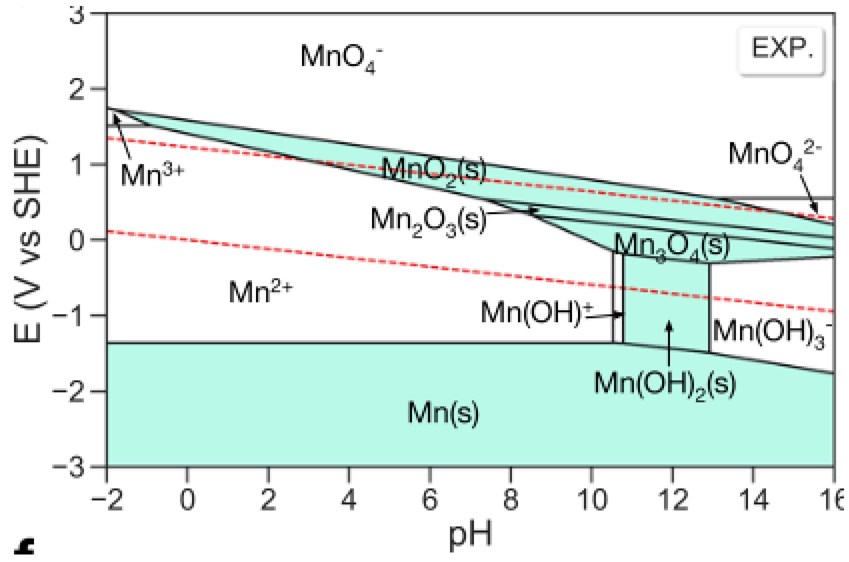
$155,727/kg

Ir: $181,651/kg

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

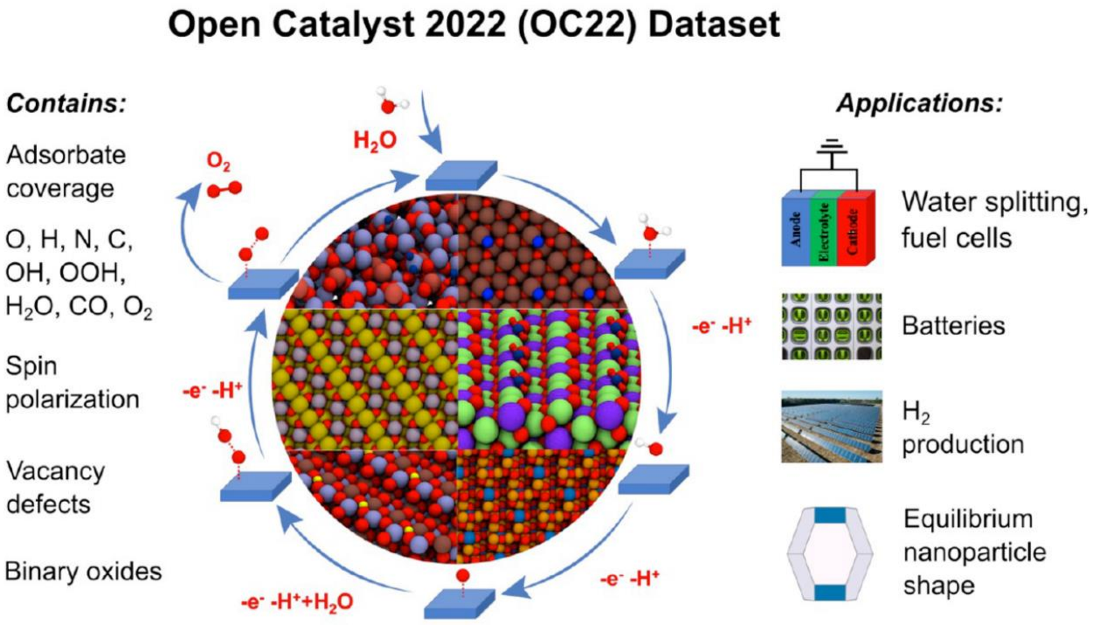
HER: $4H^+ + 4e^- \rightarrow 2H_2$

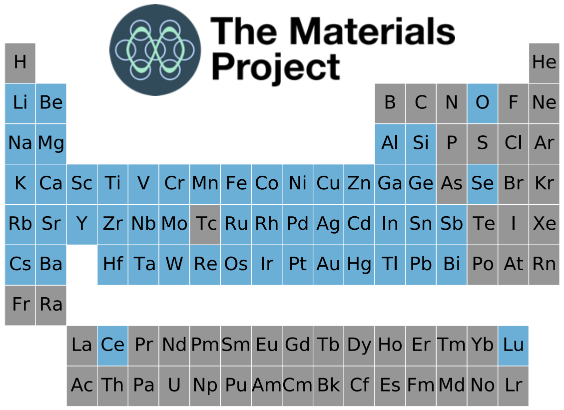
$2H_2O \rightarrow O_2 + \mathbf{2H_2}$

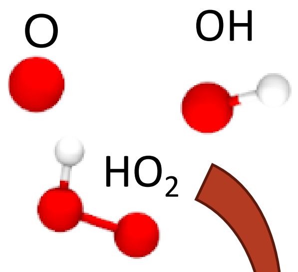


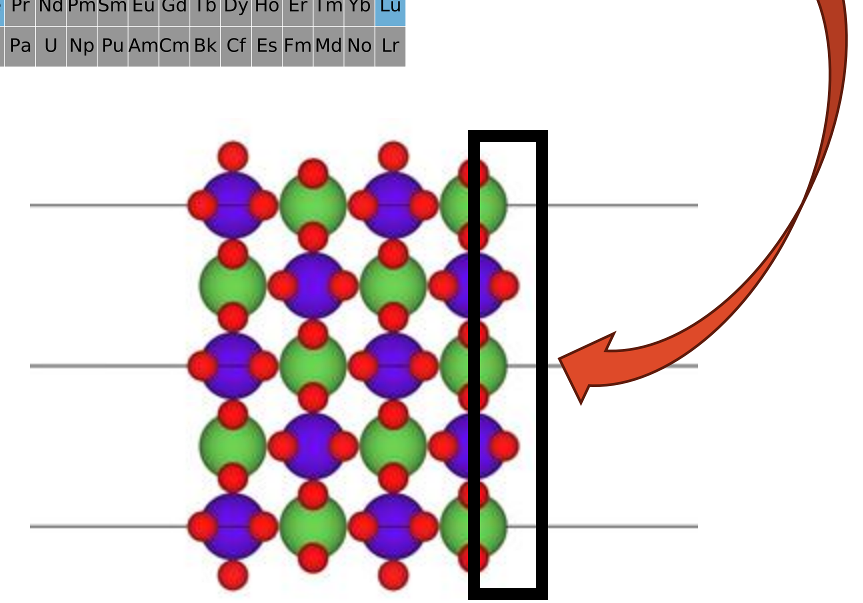
Tran, R., Lan, J., Shuaibi, M., Wood, B. M., Goyal, S., Das, A., Heras-Domingo, J., Kolluru, A., Rizvi, A., Shoghi, N., Sriram, A., Therrien, F., Abed, J., Voznyy, O., Sargent, E. H., Ulissi, Z., & Zitnick, C. L. (2022). *ACS Catalysis*, *13*, 3066–3084. https://doi.org/10.1021/acscatal.2c05426

The Open Catalyst Project 2022







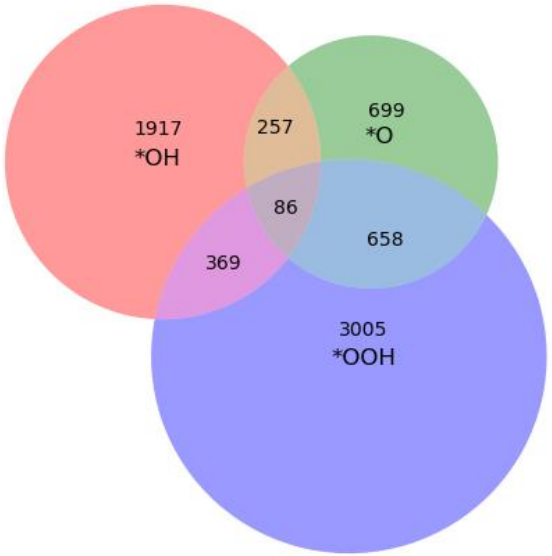


Meta AI

Fundamental AI Research (FAIR)

Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

Database scope



OC22 DFT dataset

# Predictions	6,068,572
# Materials	4,119
# Slab predictions	191,902
Ave. # slabs per material	47
# Adsorption predictions	5,876,670
Max Miller index	1

OH*	O*	OOH*
1,972,166	667,266	3,237,238

OC22 prediction dataset

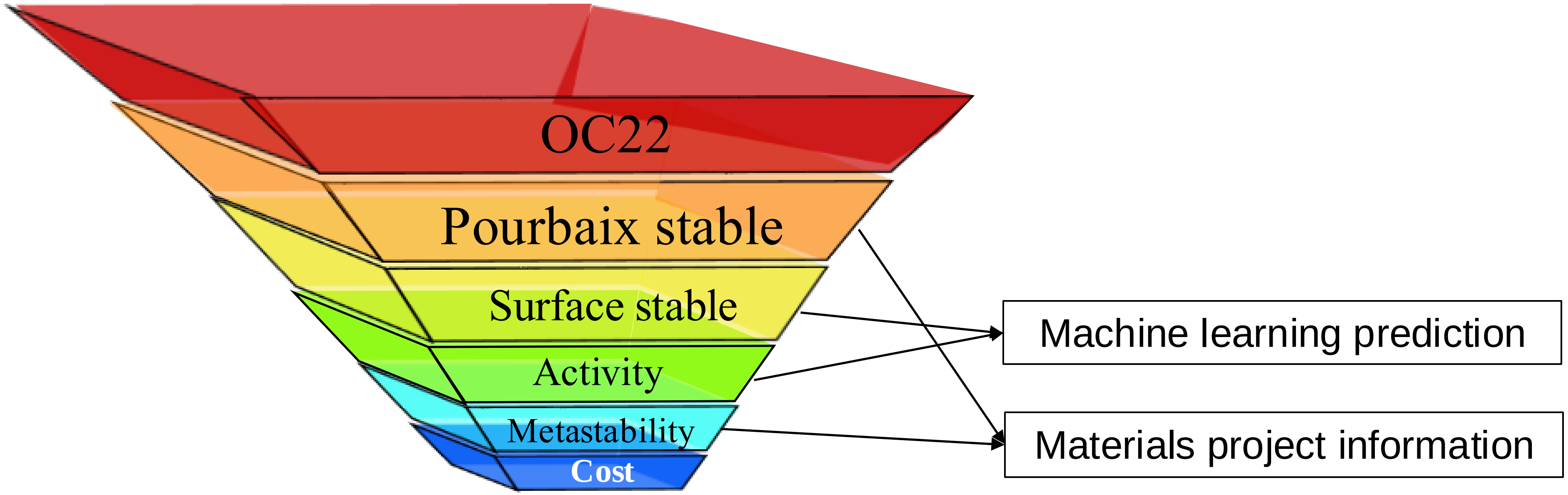
All data available at UH Dataverse Repository under:

Texas Data Repository

https://doi.org/10.18738/T8/APJFTM

Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

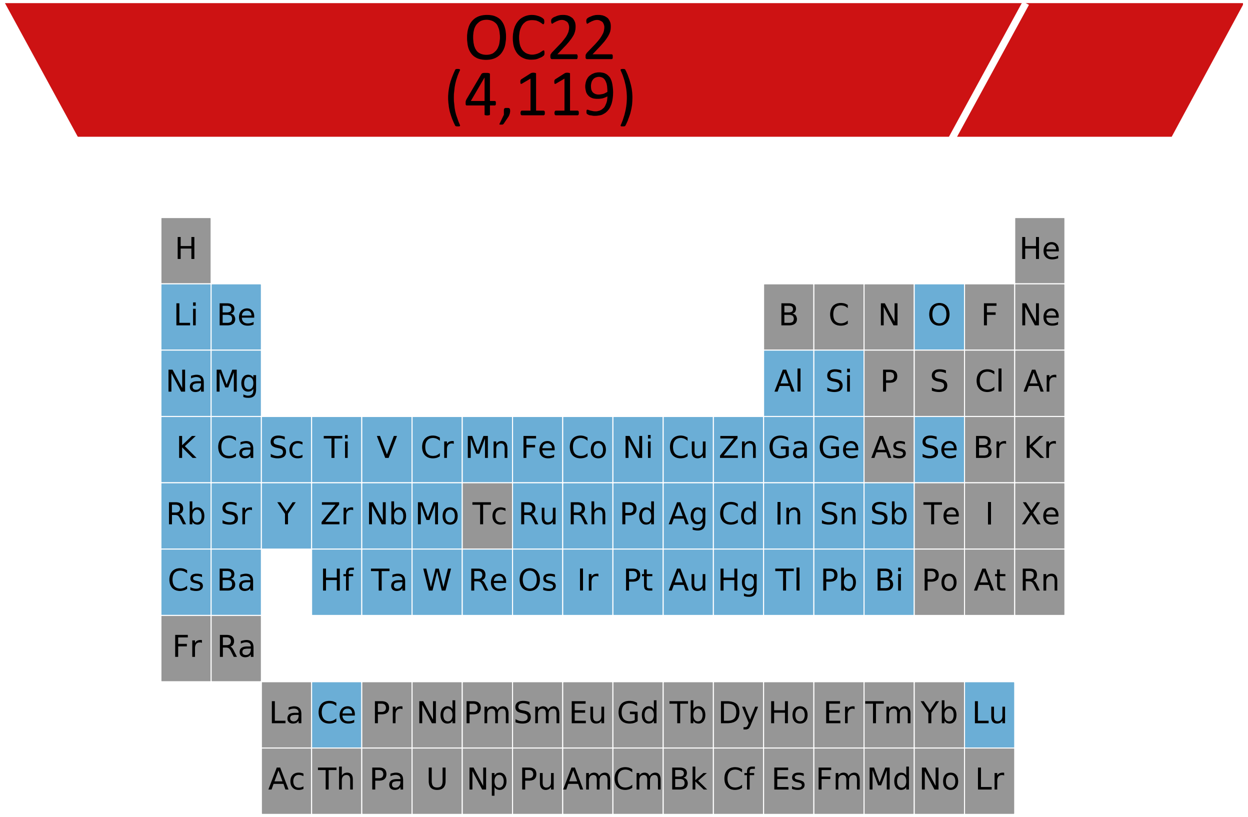
High throughput screening



2024 AIChE ANNUAL MEETING
October 27 – 31, 2024
San Diego Convention Center
Hilton San Diego Bayfront

Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

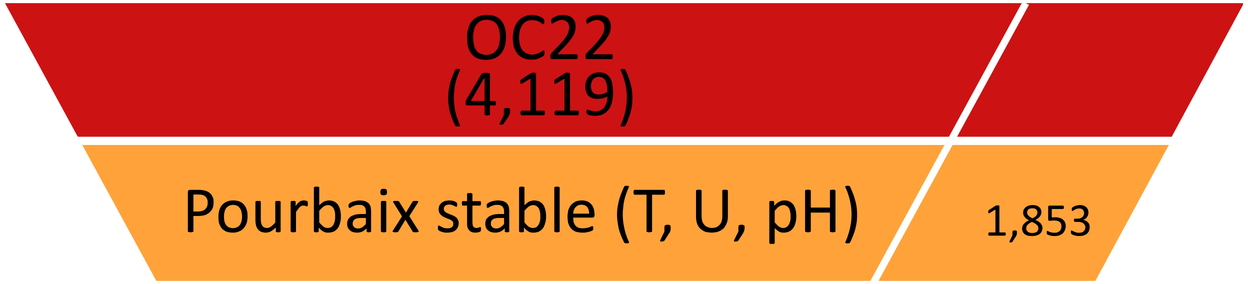
OC22 Dataset



- Total bulks in OC22: 4,732
  - Top 5 lowest E_{hull}
  - Max # of atoms in bulk: 150
  - 1720 bulks with U-values
- Total bulks in this work: 4,119
  - Omit 609 due to unconverged forces or slab exceeding 200 atoms
  - Unary bulks: 296
  - Binary bulks: 3,823

Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

Pourbaix stability



Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

Pourbaix stability

OC22
(4,119)

Pourbaix stable (T, U, pH) 1,853

$$\mathbf{\Delta G_{PBX}(pH = 1, U = 1.8\ V, T = 80^{o}C) < 0.5\ eV}$$

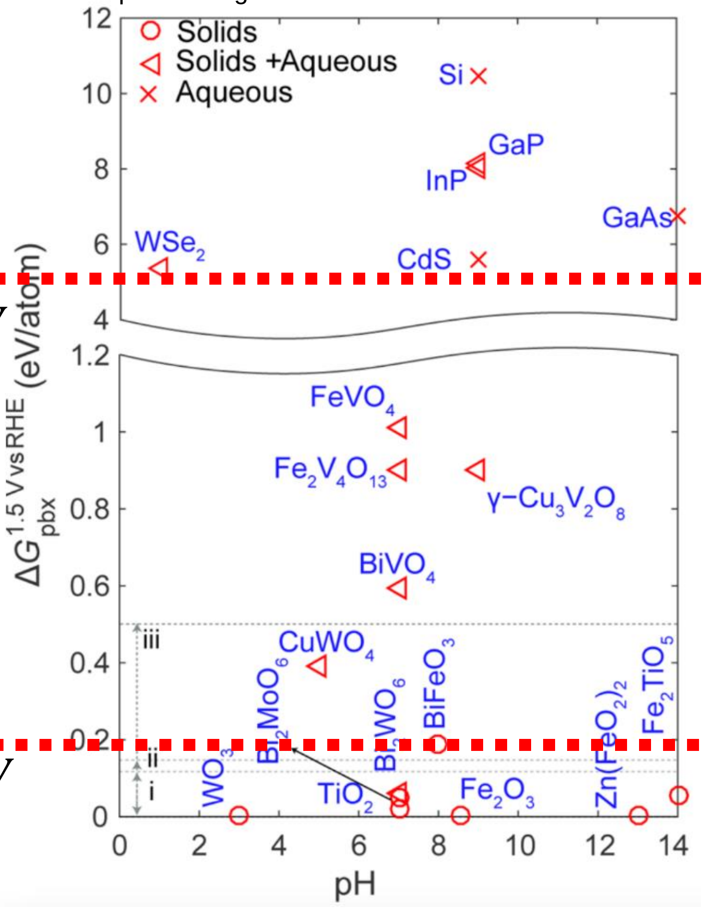
$\mathbf{\Delta G_{PBX}}$ from Materials Project:

Jain, A., Ong, S. P., Hautier, G., Chen, W., Richards, W. D., Dacek, S., Cholia, S., Gunter, D., Skinner, D., Ceder, G., & Persson, K. A. (2013). *APL Materials*, *1*(1), 011002 1. https://doi.org/10.1063/1.4812323

Singh, A. K., Zhou, L., Shinde, A., Suram, S. K., Montoya, J. H., Winston, D., Gregoire, J. M., & Persson, K. A. (2017). Electrochemical Stability of Metastable Materials. *Chemistry of Materials*, *29*(23), 10159–10167. https://doi.org/10.1021/acs.chemmater.7b03980

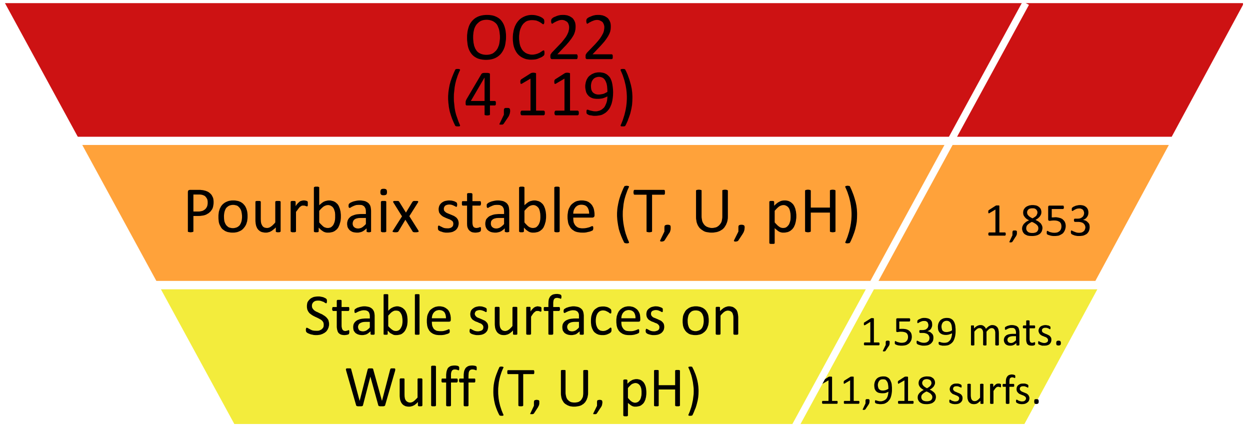
surface passivation
$\Delta G_{PBX} < 0.5\ eV$

metastability
$\Delta G_{PBX} < 0.2\ eV$



Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

Surface stability



Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

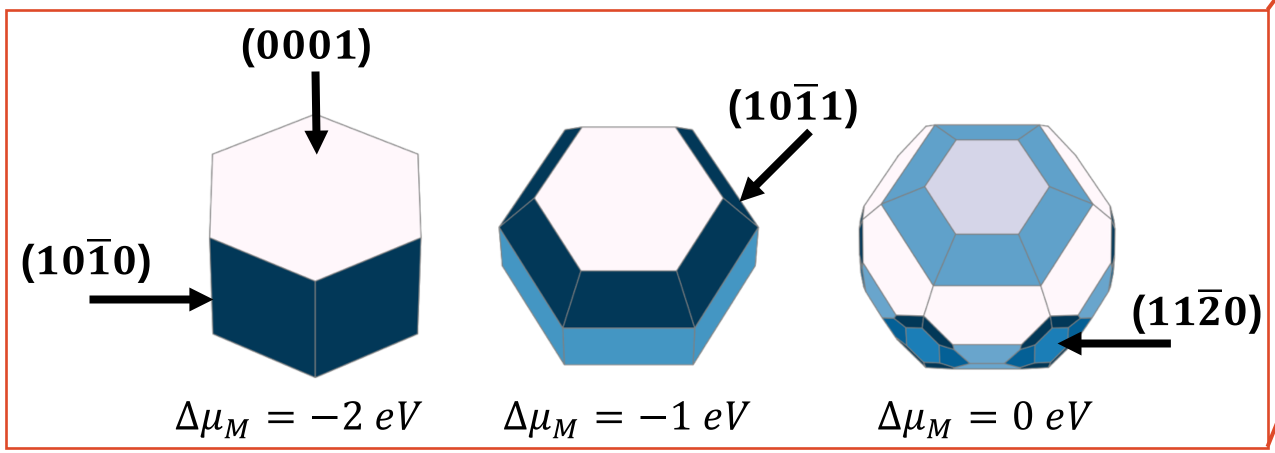
Surface stability

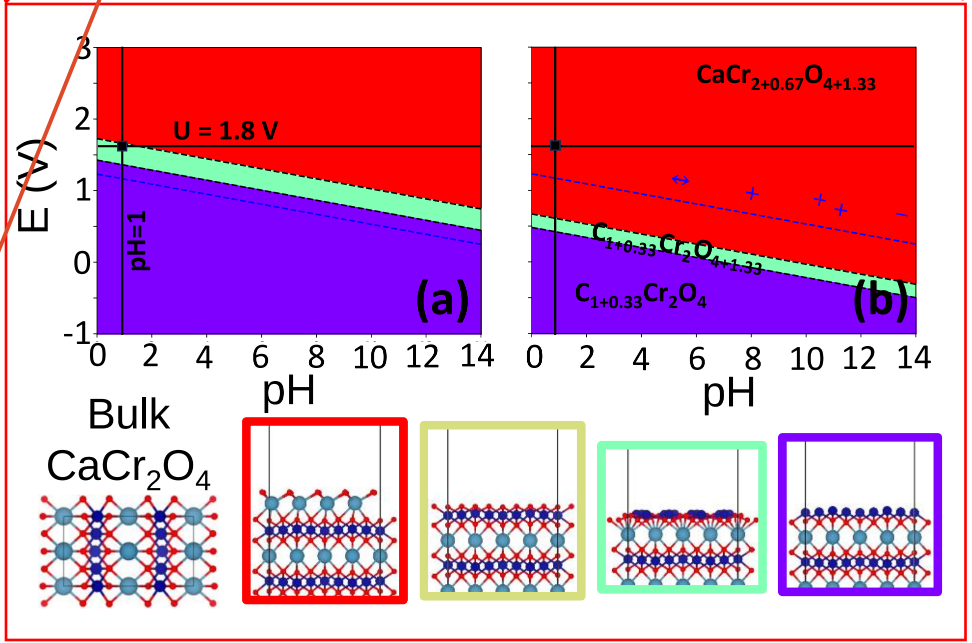
OC22 (4,119)

Pourbaix stable (T, U, pH) — 1,853

Stable surfaces on Wulff (T, U, pH) — 1,539 mats. 11,918 surfs.

$$\gamma(\mu_M, \mu_{O_2}) = \frac{E_{slab}^{A_{nx}B_{ny+k}O_{nz+j}} - nE_{bulk}^{A_xB_yO_z} + k\mu_B + j\frac{1}{2}\mu_{O_2}}{2A}$$

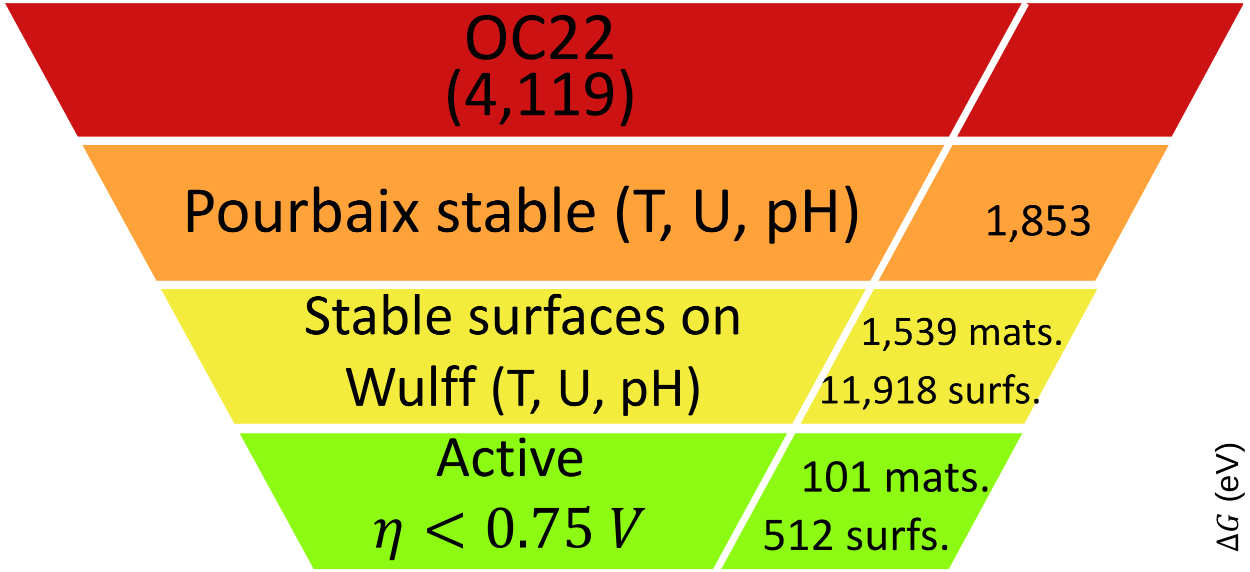


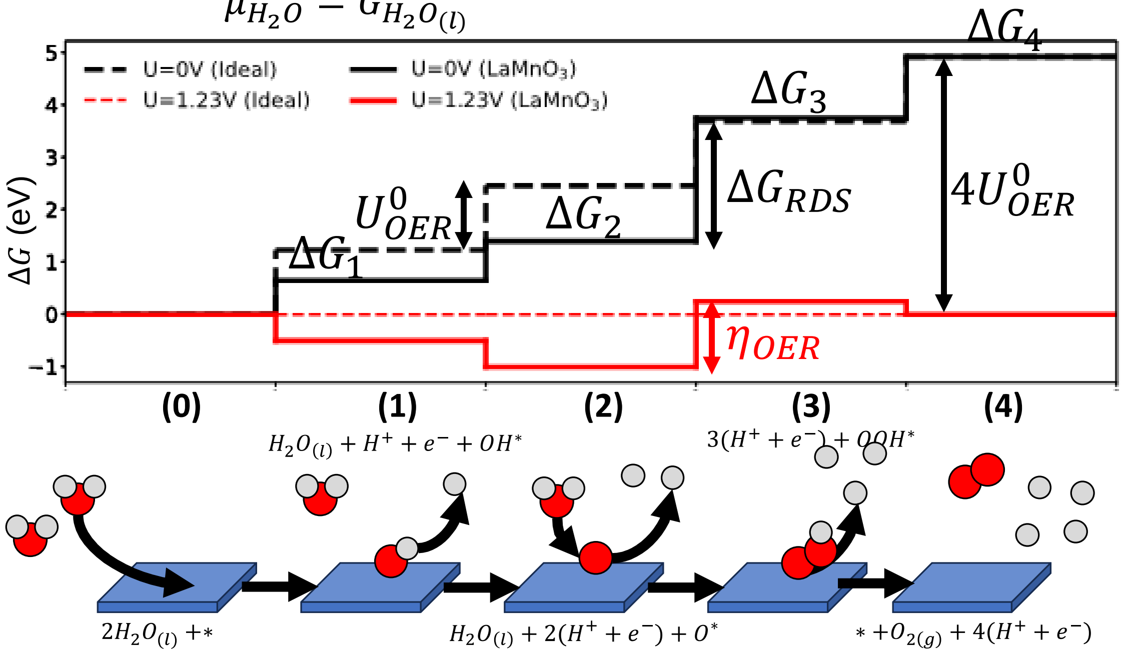


Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

OER activity (overpotential)

$$\Delta G_1 = E_{HO^*} + \frac{1}{2}\mu_{H_2} - \mu_{H_2O_{(l)}} - E^* + \Delta ZPE - T\Delta S^o$$
$$\Delta G_2 = E_{O^*} + \mu_{H_2} - \mu_{H_2O_{(l)}} - E^* + \Delta ZPE - T\Delta S^o$$
$$\Delta G_3 = E_{OOH^*} + \frac{3}{2}\mu_{H_2} - 2\mu_{H_2O_{(l)}} - E^* + \Delta ZPE - T\Delta S^o$$
$$\Delta G_4 = 2\mu_{H_2} - 2\mu_{H_2O_{(l)}}$$
$$\mu_{H_2} = \mu_{H^+} + \mu_{e^-}$$
$$\mu_{H^+} = \frac{1}{2}G_{H_{2(g)}} - k_B T pH ln(10)$$
$$\mu_{e^-} = -eU$$
$$\mu_{H_2O} = G_{H_2O_{(l)}}$$





$$\Delta G_{RDS} = \max(\Delta G_1, \Delta G_2 - \Delta G_1, \Delta G_3 - \Delta G_2, \Delta G_4 - \Delta G_3,)$$

Overpotential: $\eta_{OER} = \Delta G_{RDS} - U^0_{OER}$

$U^0_{OER} = 1.23\ V\ vs\ SHE$

Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

Metastability

OC22
(4,119)

Pourbaix stable (T, U, pH) — 1,853

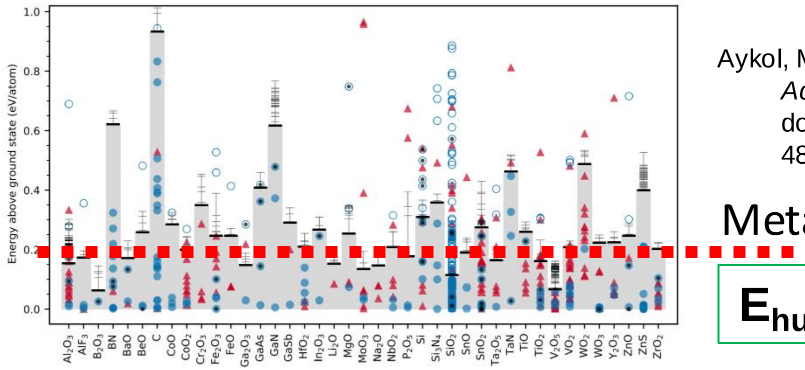
Stable surfaces on Wulff (T, U, pH) — 1,539 mats. 11,918 surfs.

Active $\eta < 0.75\ V$ — 101 mats. 512 surfs.

Metastable $E_{hull} < 0.1\ eV$ — 92

E_{hull} from Materials Project:

Jain, A., Ong, S. P., Hautier, G., Chen, W., Richards, W. D., Dacek, S., Cholia, S., Gunter, D., Skinner, D., Ceder, G., & Persson, K. A. (2013). *APL Materials*, *1*(1), 011002 1. https://doi.org/10.1063/1.4812323



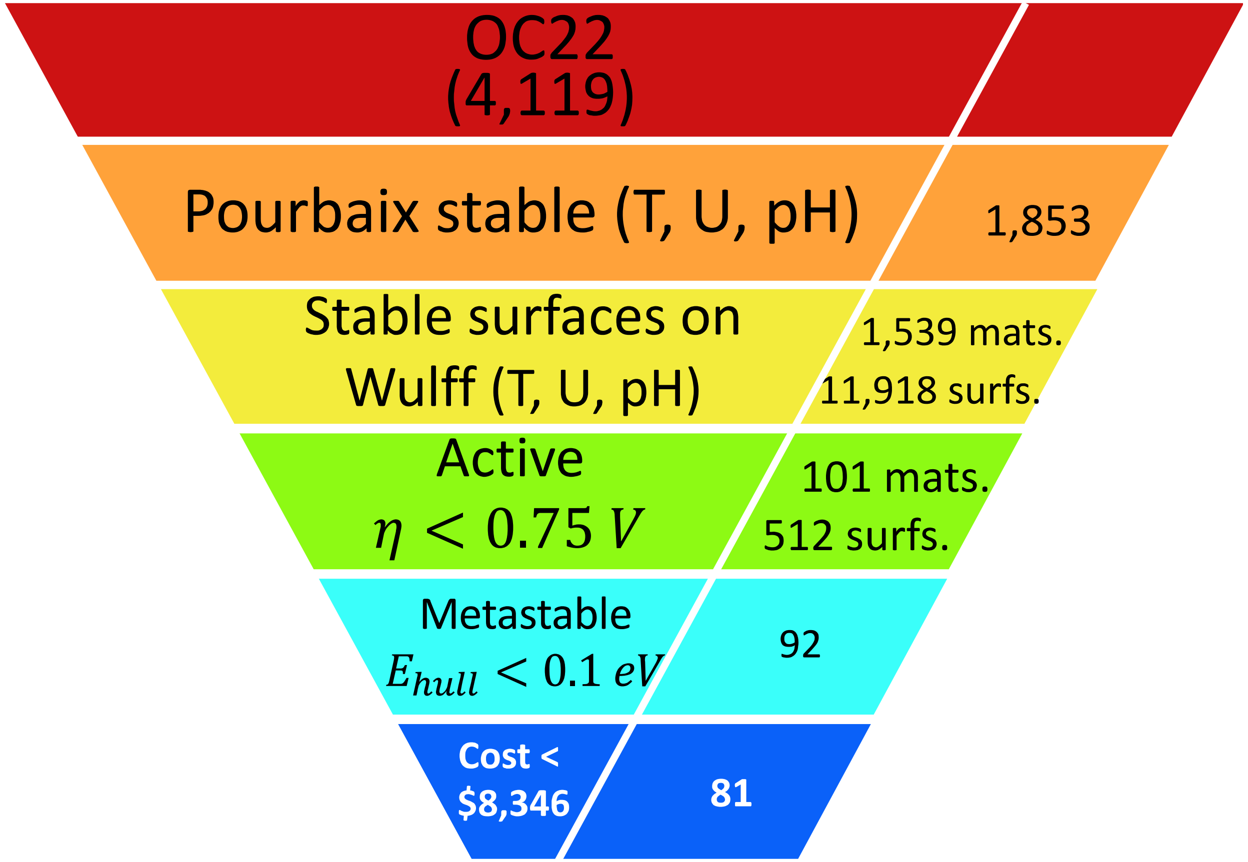
Aykol, M. *et al.* (2018). *Science Advances*, *4*(4), 1–8. doi.org/10.1126/sciadv.aaq0148

Metastability limits:

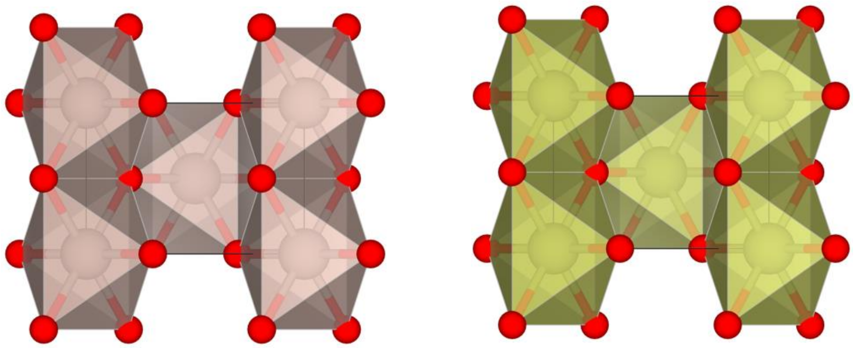
E_{hull} < 0.1 eV

Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

Material cost



Cost < $18,315/kg

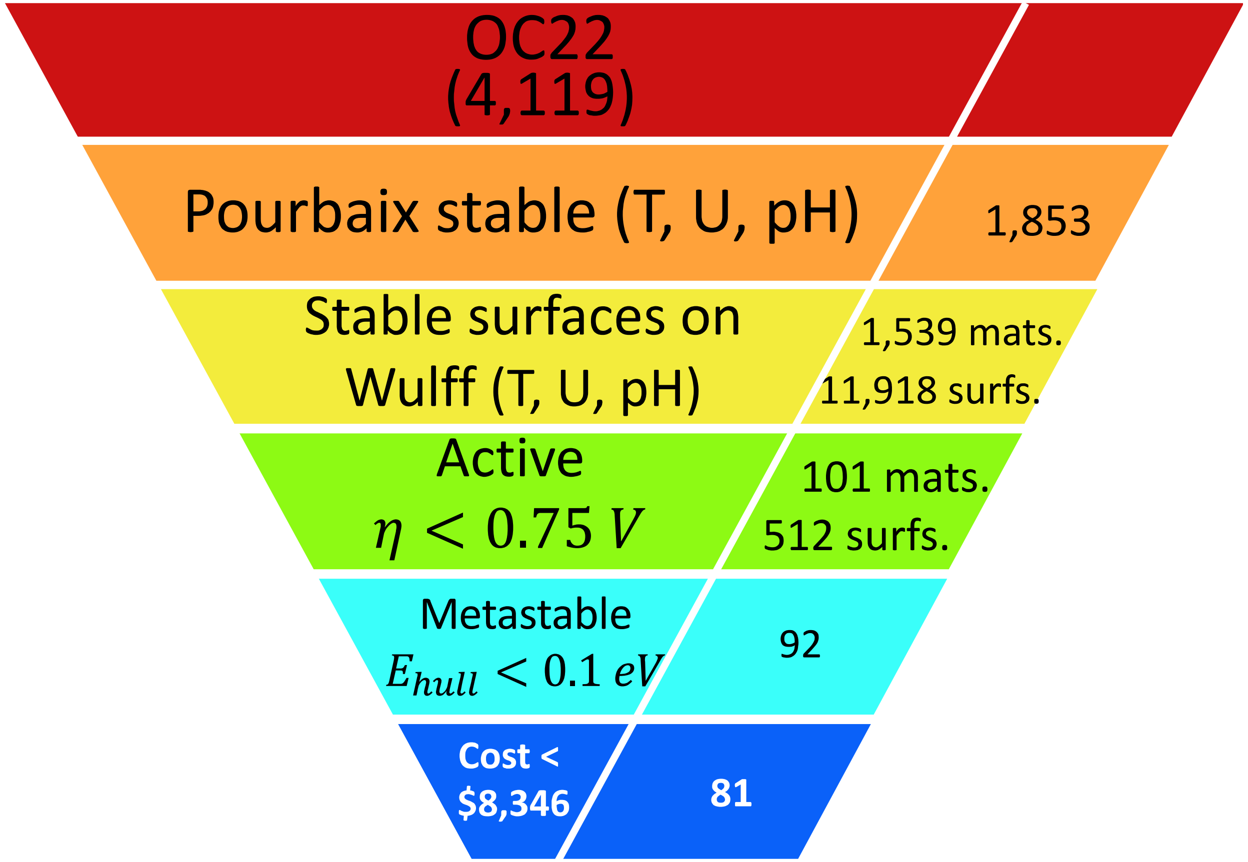


RuO_2
$18,315/kg
Ru: $24,113/kg

IrO_2
$155,727/kg
Ir: $181,651/kg

Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

Final candidates



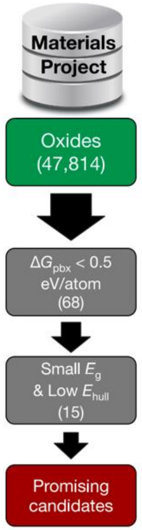
Formula	η_{OER} (V)
$MnBiO_3$	0.51
$Cu_3(SbO_3)_4$	0.37
$AgSnO_3$	0.49
$MnTlO_3$	0.2 (0.08)
$CuMoO_4$	0.46

Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

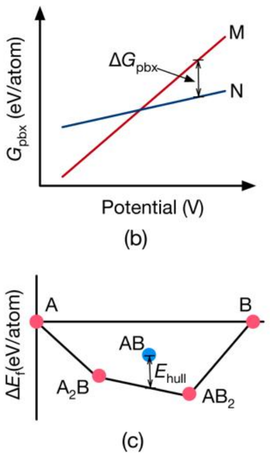
Limitations of Pourbaix stability

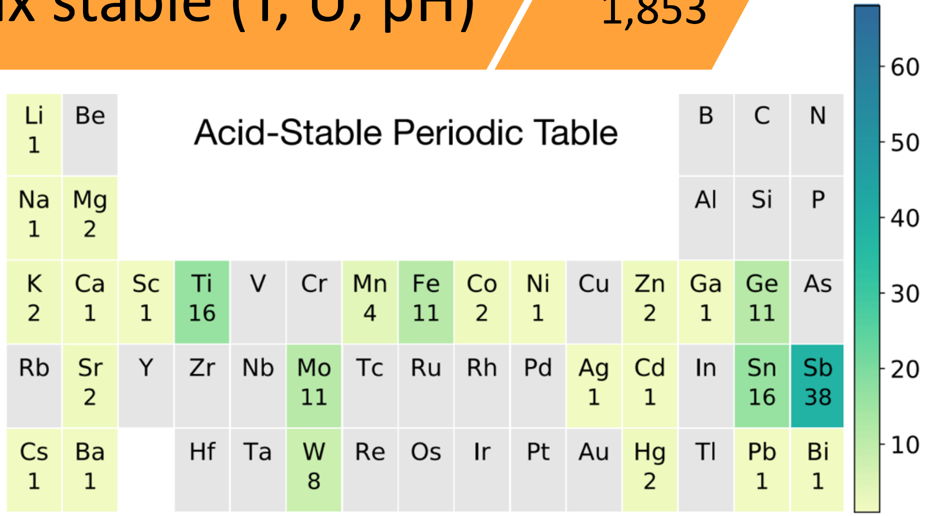
Gunasooriya, G. T. K. K., & Nørskov, J. K. (2020). Analysis of Acid-Stable and Active Oxides for the Oxygen Evolution Reaction. *ACS Energy Letters*, *5*(12), 3778–3787. https://doi.org/10.1021/acsenergylett.0c02030

Pourbaix stable (T, U, pH) 1,853



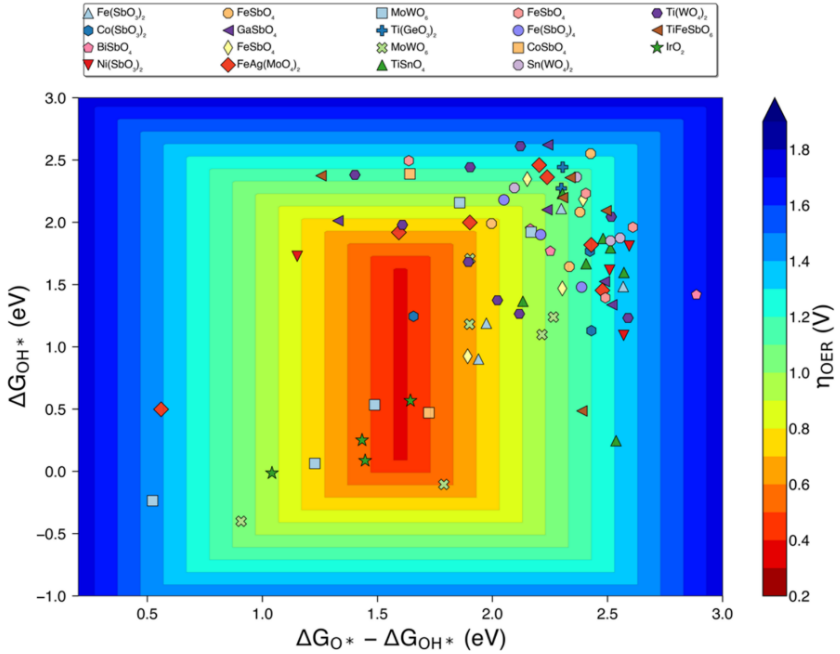
(a)





68/47,814 stable candidates!

Wang, Z., Zheng, Y. R., Chorkendorff, I., & Nørskov, J. K. (2020). Acid-Stable Oxides for Oxygen Electrocatalysis. *ACS Energy Letters*, *5*(9), 2905–2908. https://doi.org/10.1021/acsenergylett.0c01625

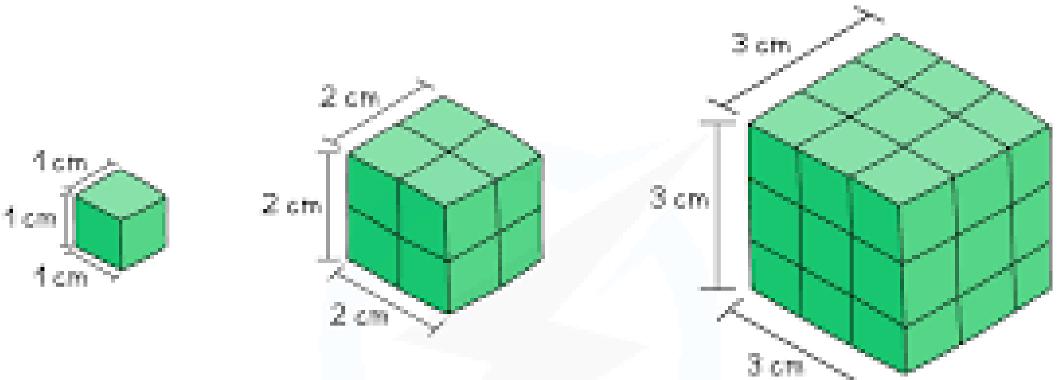


17 candidates w/ $\eta_{OER} < 0.8$ V

Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

Nanoscale stabilization

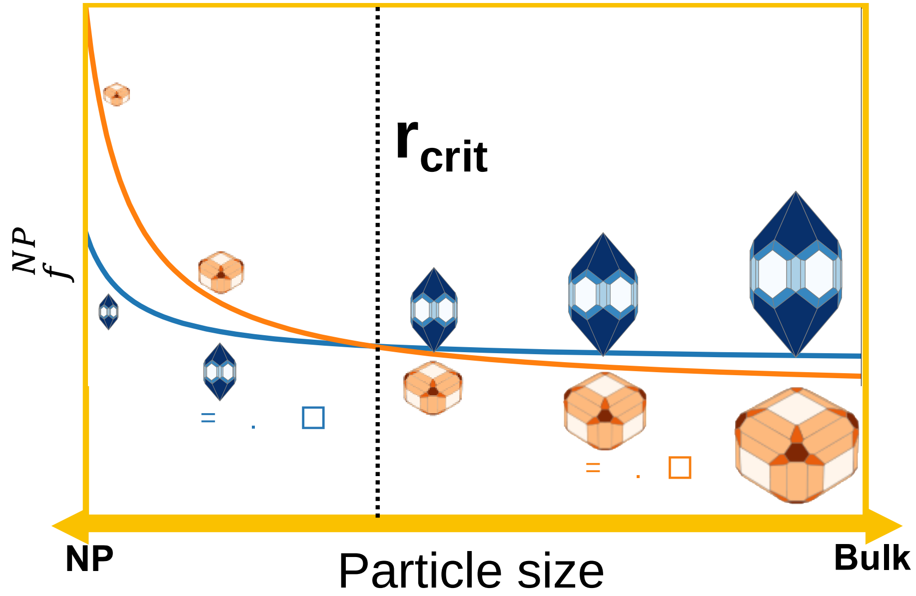
Surface area to volume ratio increases as cell size decreases→greater surface effects on material properties



Surface area	6 cm²	24 cm²	54 cm²
Volume	1 cm³	8 cm³	27 cm³
Surface area: volume	6:1	3:1	2:1

The formation energy of the nanoparticle is the sum of the surface and bulk contributions:

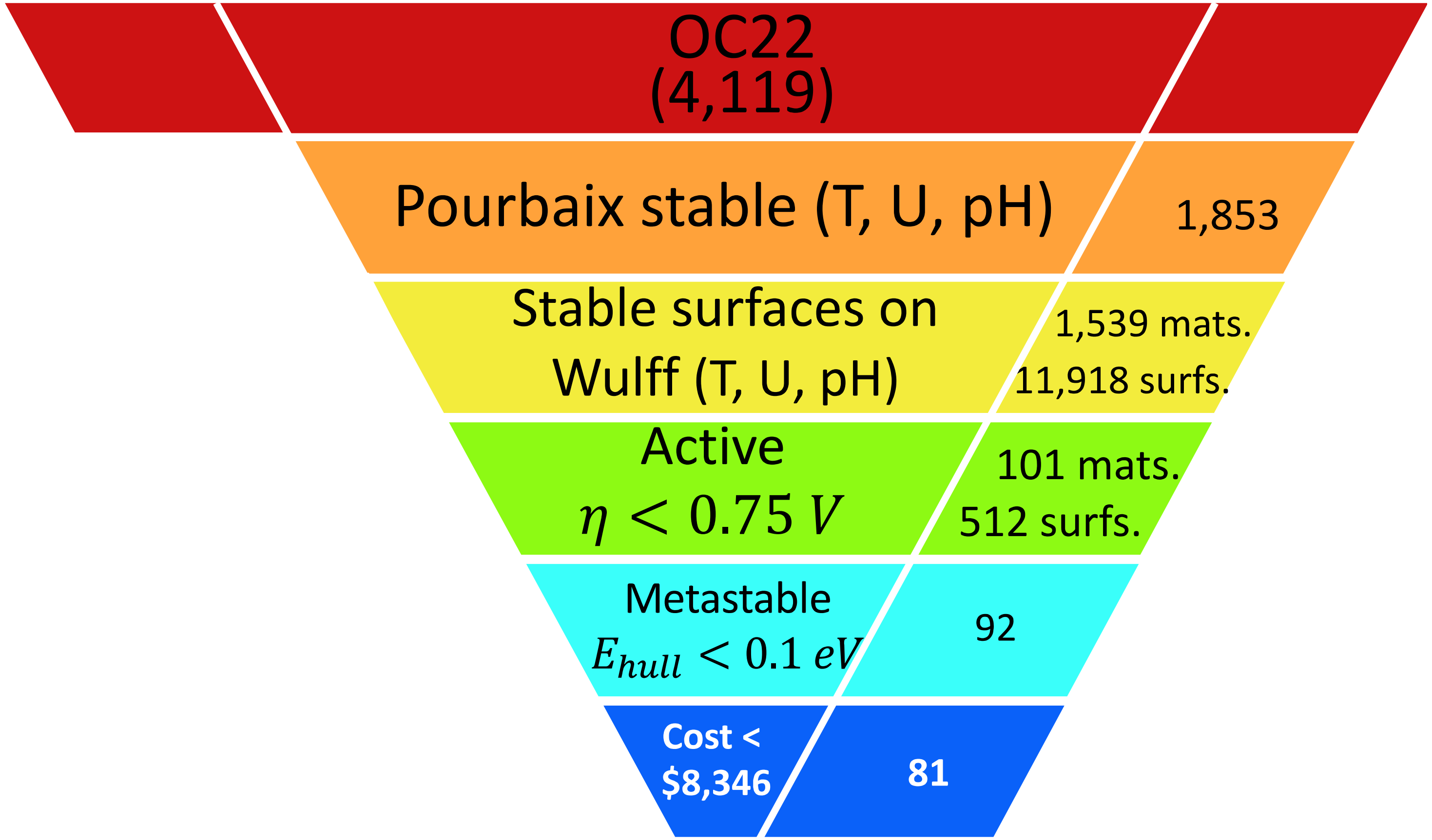
$$G_f^{NP} = E_V(\mu_{O_2}, \Delta\mu_M)\left(\frac{4}{3}\pi r^3\right) + \bar{\gamma}(\mu_{O_2}, \Delta\mu_M)(4\pi r^2)$$



- E_V bulk formation energy (eV/ Å³)
- $\bar{\gamma}$ surface energy (eV/Å²)
- r radius of particle (Å)

Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

Revised screening mechanism



Formula	η_{OER} (V)
$MnBiO_3$	0.51
$Cu_3(SbO_3)_4$	0.37
$AgSnO_3$	0.49
$MnTlO_3$	0.2 (0.08)
$CuMoO_4$	0.46
$BaMn_2O_3$	0.62
$Li(CuO)_2$	0.52
Mn_2BeO_4	0.32
$ScMn_2O_4$	0.29 (0.33)
$TiCu_3O_4$	0.38

Nanoparticles

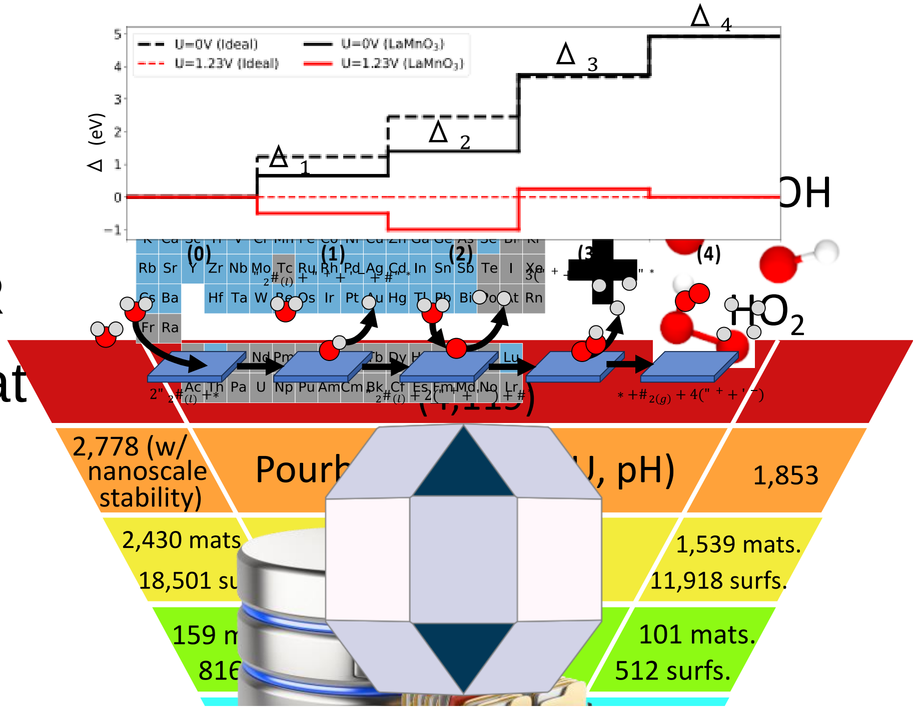
2024 AIChE ANNUAL MEETING

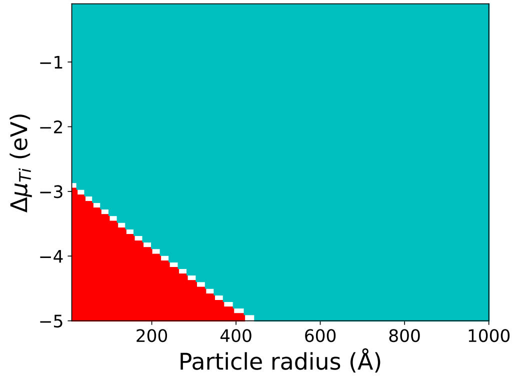
October 27 – 31, 2024
San Diego Convention Center
Hilton San Diego Bayfront

Tran, R., Huang, L., Zi, Y., Wang, S., Comer, B. M., Wu, X., Raaijman, S. J., Sinha, N. K., Sadasivan, S., Thundiyil, S., Mamtani, K. B., Iyer, G., Grabow, L. C., Lu, L., & Chen, J. (2024). Rational design of nanoscale stabilized oxide catalysts for OER with OC22. *Nanoscale*. https://doi.org/10.1039/d4nr01390e

Conclusion

- We have created a database of ML predicted **TOTAL DFT** energies for bare and adsorbed surfaces of oxides for OER
- Doing so allows us to perform complex surface analysis that typically requires enormous amounts of DFT calculations:
  - Prediction of **overpotential**
  - Prediction of **Wulff shapes**
  - Prediction of **nanoscale stability**
- The available of such analysis without the need of DFT allows us to construct complex screening frameworks for identifying oxides for OER
- **Identified 81 viable candidates for OER, with 40 additional candidates when considering nanoscale stabilization**

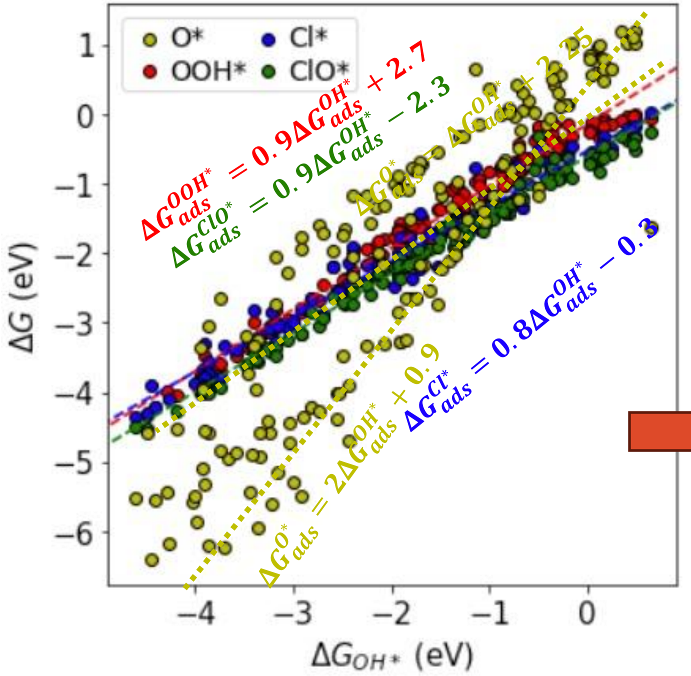


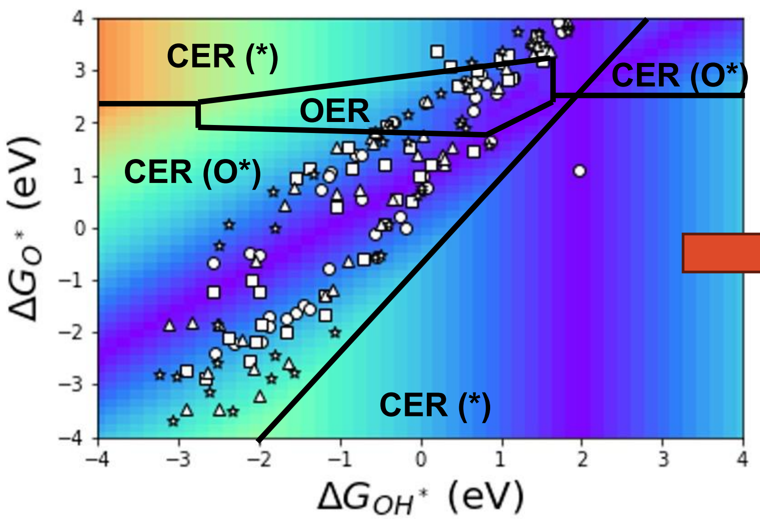


Next time: Tuning activity and selectivity between chlorine and oxygen evolution over graphene supported single atom electrocatalysts

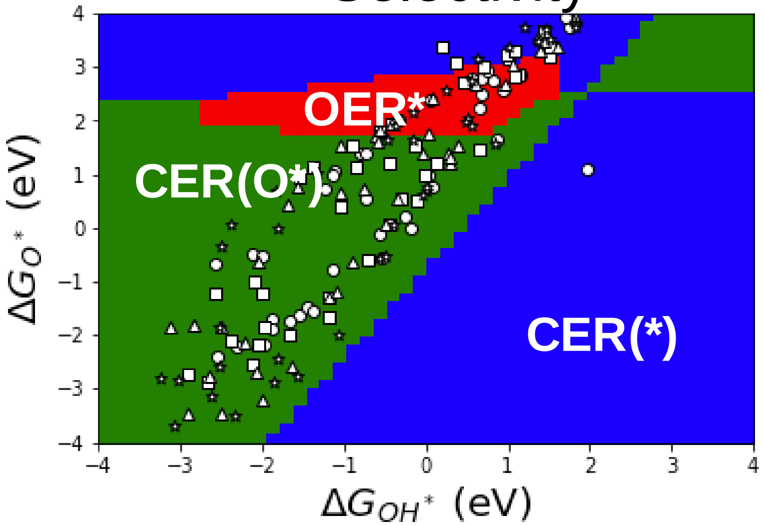
Thursday, October 31, 2024
3:30 PM PT – 3:48 PM PT
San Diego Convention Center, Room 28B

Discrepancies in scaling relationships leads to variations in selectivity





Selectivity



2024 AIChE ANNUAL MEETING

October 27 – 31, 2024

San Diego Convention Center

Hilton San Diego Bayfront

Thank you!

Questions?

CHEMICAL ENGINEERING REIMAGINED