2024 AIChE ANNUAL MEETING

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

Tuning Chlorine vs Oxygen Evolution on Graphene Supported Single Atom Electrocatalysts

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CHEMICAL ENGINEERING REIMAGINED

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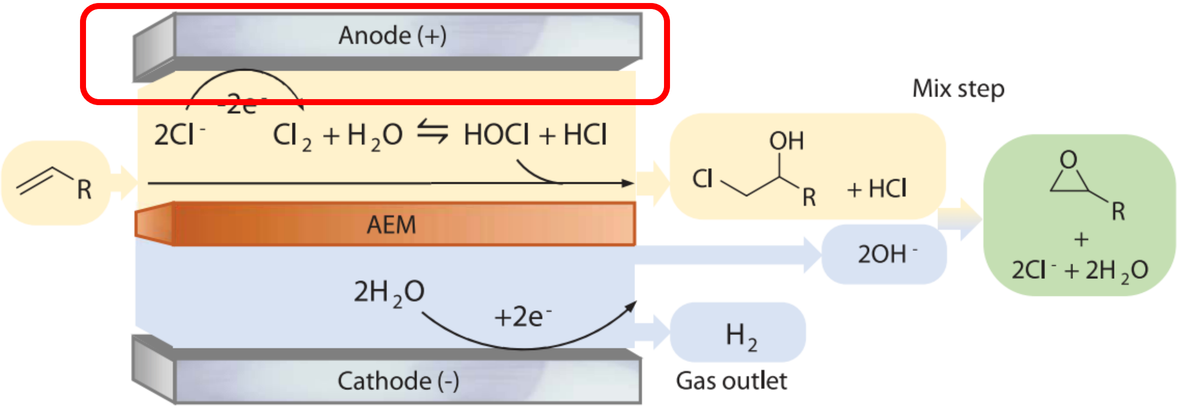
Decoupling CER from OER



Ethylene/propylene oxide and H_2 production from CER

Leow, W. R. *et. al.* (2020). *Science*, *368*(6496), 1228–1233. https://doi.org/10.1126/science.aaz8459

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

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

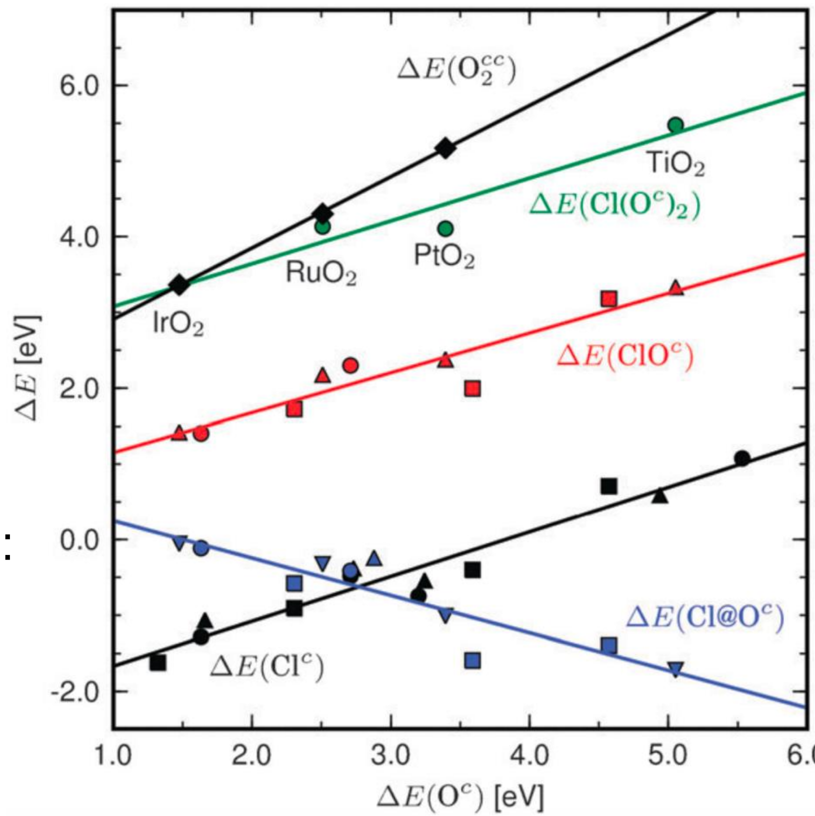
CER: $2Cl^- \leftrightarrow Cl_2 + 2e^-$

$$U^0_{CER} = 1.36 \text{ V vs SHE}$$

Typical electrocatalysts, dimensionally stable anodes (DSA):

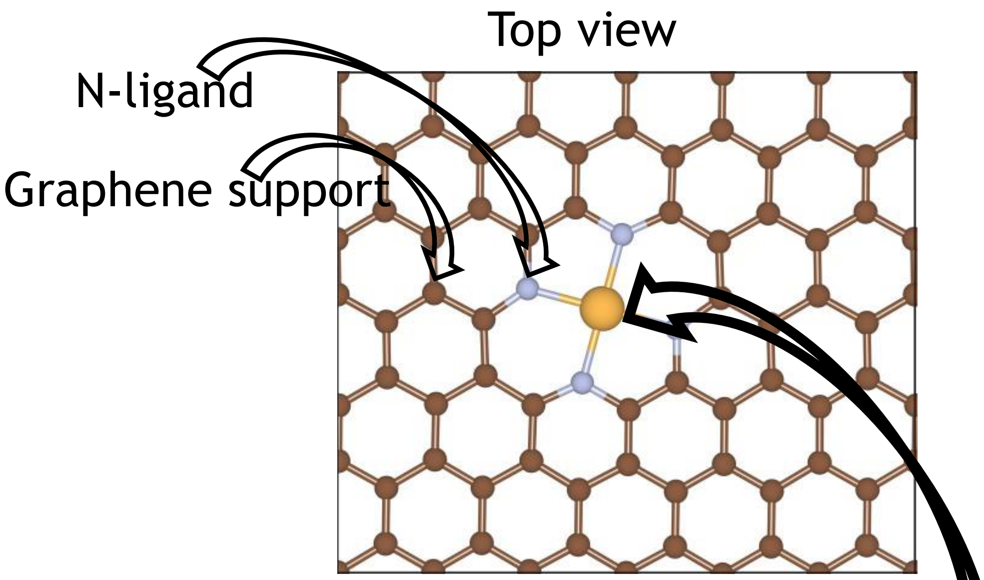
	η_{OER} (V)	η_{CER} (V)
RuO_2	0.2-0.4	0.0-0.1
IrO_2	0.4-0.6	0.2-0.4

Hansen, H. A., *et al.* (2010). *Physical Chemistry Chemical Physics*, *12*(1), 283–290. https://doi.org/10.1039/b917459a

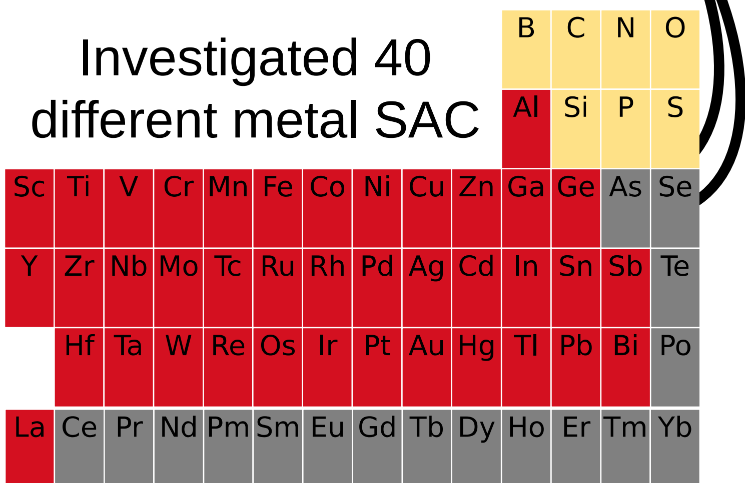


OER and CER are coupled on oxide catalysts
→prevents independent tuning/selectivity

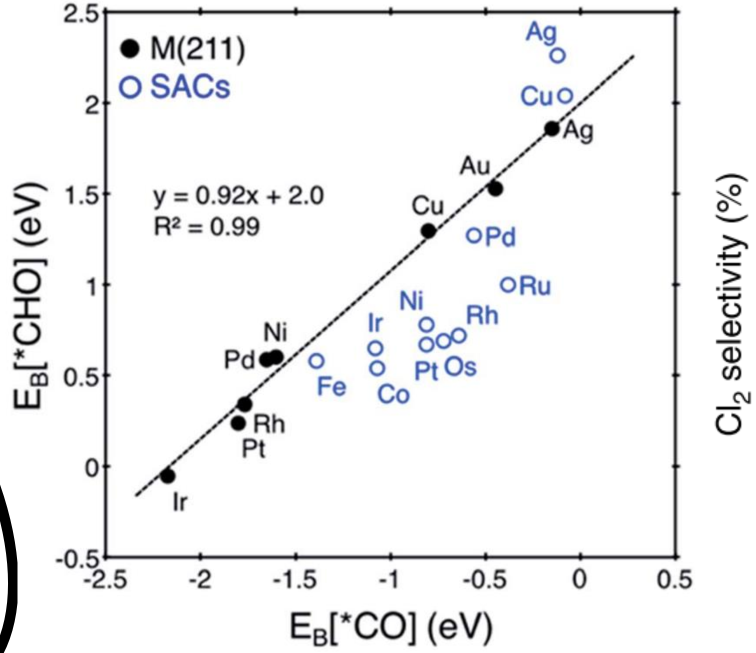
Graphene supported SACs



Investigated 40 different metal SAC

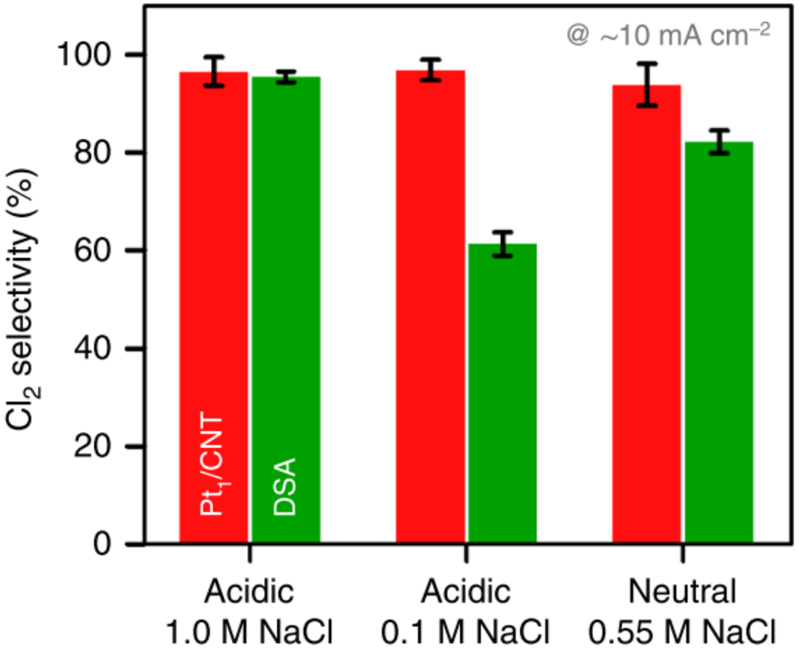


Back, S. *et al.* (2017). *Chemical Science*, *8*(2), 1090–1096.



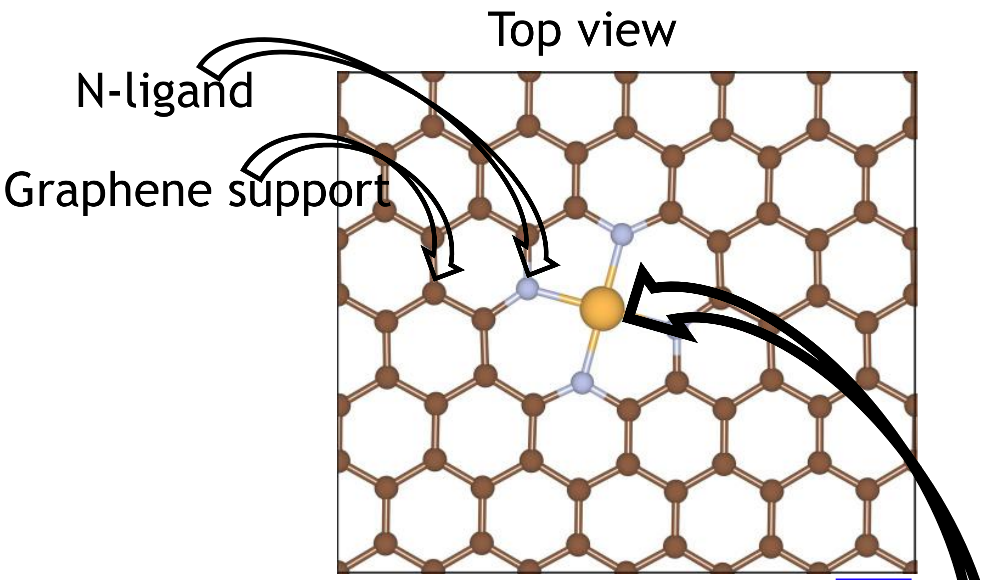
SACs demonstrate different scaling relationships when compared to metal surfaces and oxides for different reactions

Lim, T. *et al.* (2020). *Nature Communications*, *11*(1).

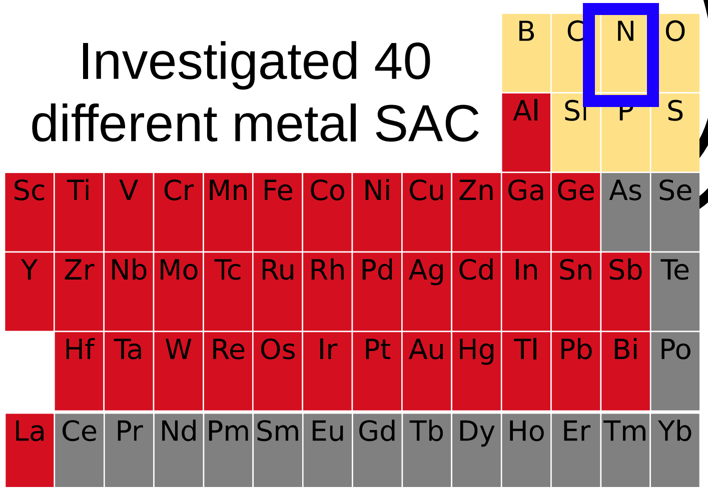


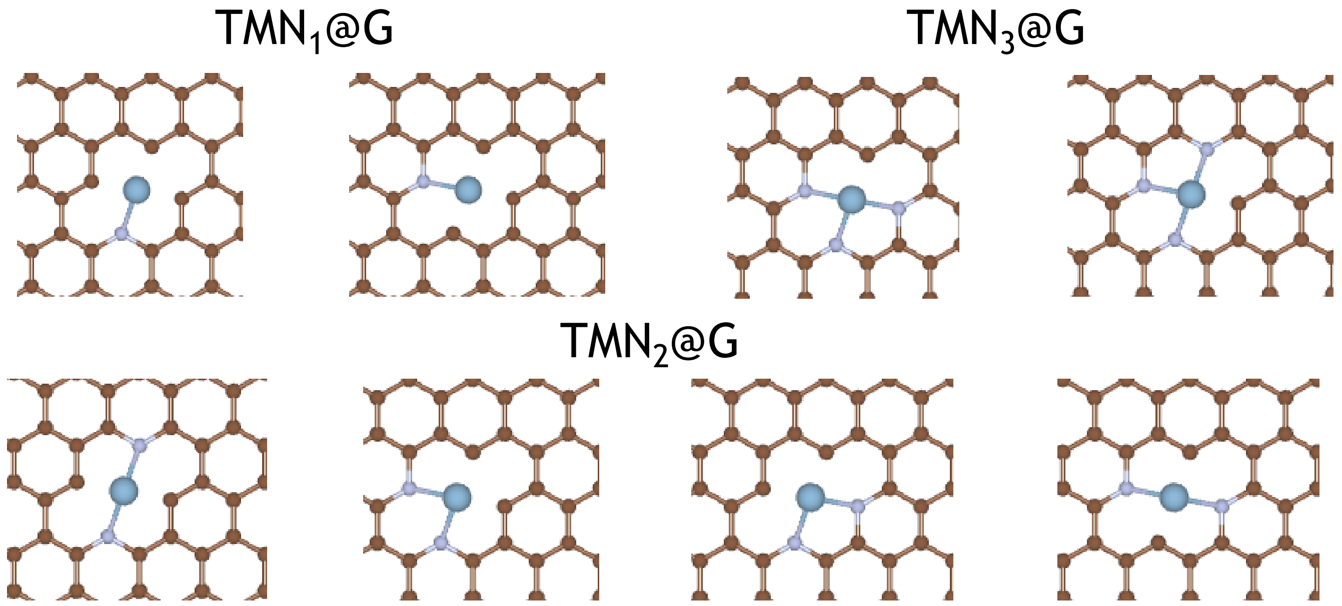
Pt SACs improve selectivity relative to DSAs across different pH conditions

DFT simulations

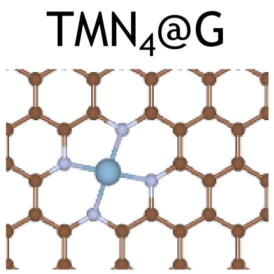


Investigated 40 different metal SAC





Only investigate the most stable configuration for each TMN_X → 160 catalysts to be evaluated for OER/CER



- 14.8 Å x 12.8 Å sheet
- GGA PBE w/ BEEF-vdW
- K-points: 6 x 6 x 1

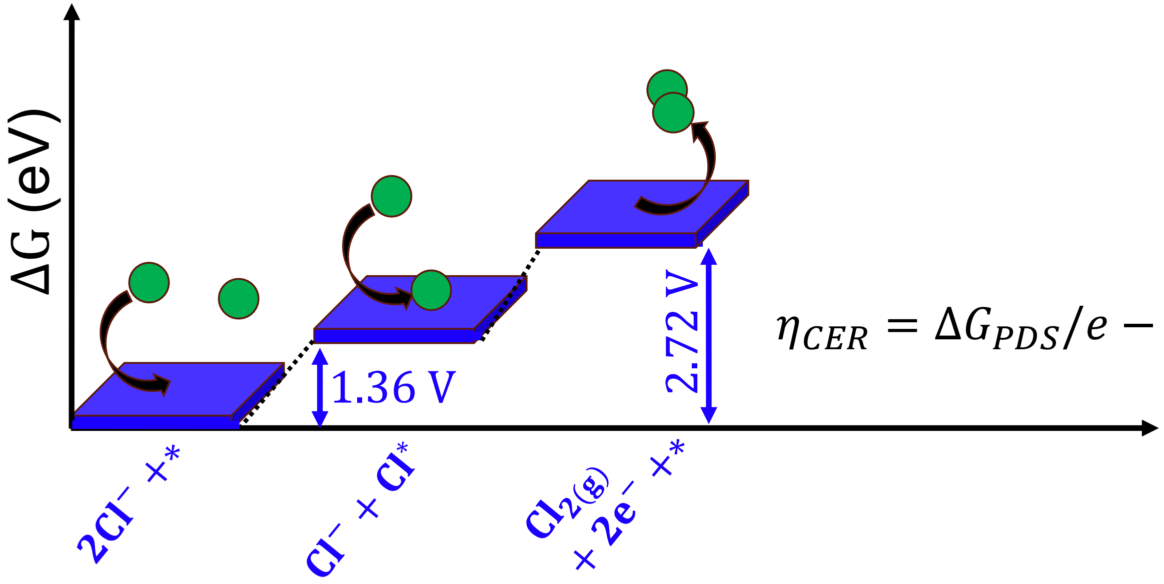
CER/OER intermediates

$$U_{CER}^{0} = 1.36\ V\ vs\ SHE,$$
$$2U_{CER}^{0} = 2.72\ V$$
$$G_{corr} = \Delta ZPE - T\Delta S^{o}$$

$$\Delta G_1 = E_{Cl^*} - \mu_{Cl} - E^* + G_{corr}$$
$$\Delta G_2 = \mu_{Cl_2} + 2\mu_{e^-} - 2\mu_{Cl}$$
$$\Delta G_{PDS} = \max(\Delta G_1, \Delta G_2 - \Delta G_1)$$

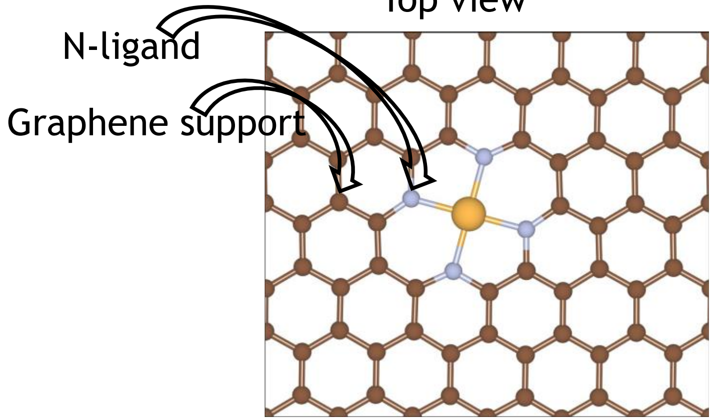
$$\mu_{Cl} = \frac{1}{2} G_{Cl_{2(g)}} + \ln(a_{Cl^-}) k_B T) - eU + 1.36$$

The Volmer-Heyrovsky mechanism



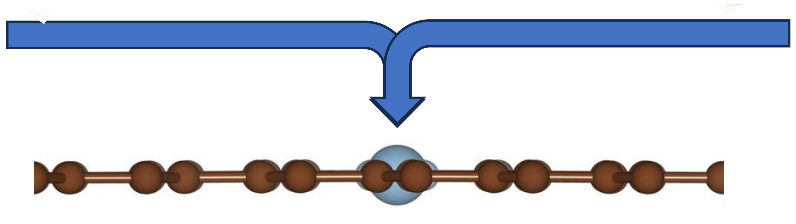
$$\eta_{CER} = \Delta G_{PDS}/e - 1.36$$

Top view



Calculated 5 adsorbates

Cl*



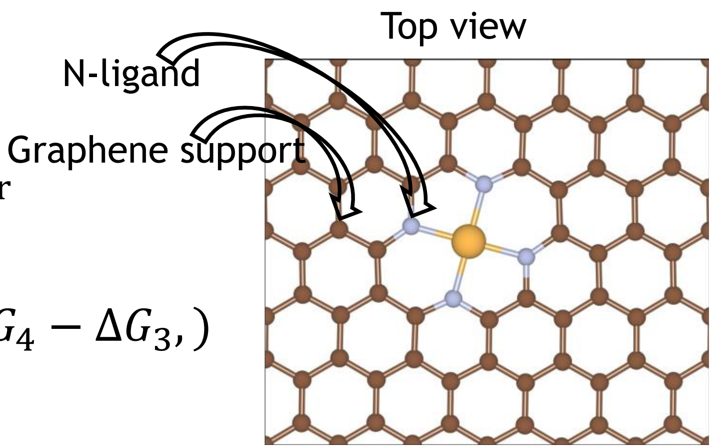
Side view

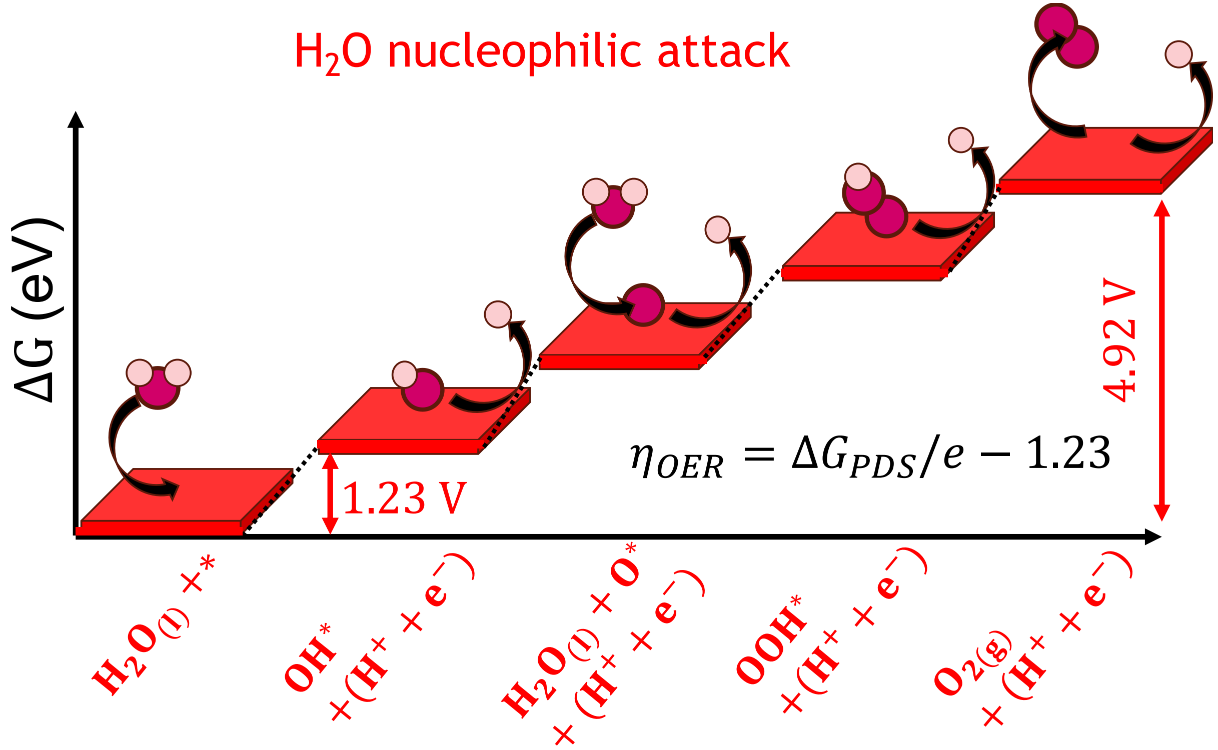
CER/OER intermediates

$$U^0_{OER} = 1.23\ V\ vs\ SHE,$$
$$4U^0_{OER} = 4.92\ V$$
$$\mathrm{G_{corr}} = \Delta ZPE - T\Delta S^o$$

$$\mu_{H_2} = G_{H_{2(g)}} - 2(k_B T pH ln(10) - eU)$$

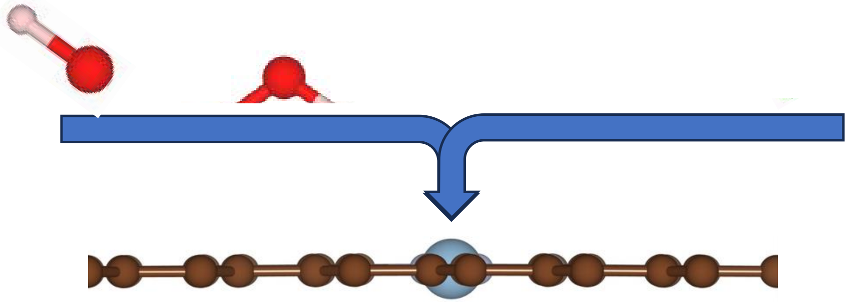
$$\Delta G_1 = E_{HO^*} + \frac{1}{2}\mu_{H_2} - \mu_{H_2O_{(l)}} - E^* + \mathrm{G_{corr}}$$
$$\Delta G_2 = E_{O^*} + \mu_{H_2} - \mu_{H_2O_{(l)}} - E^* + \mathrm{G_{corr}}$$
$$\Delta G_3 = E_{OOH^*} + \frac{3}{2}\mu_{H_2} - 2\mu_{H_2O_{(l)}} - E^* + \mathrm{G_{corr}}$$
$$\Delta G_4 = 2\mu_{H_2} - 2\mu_{H_2O_{(l)}}$$
$$\Delta G_{PDS} = \max(\Delta G_1, \Delta G_2 - \Delta G_1, \Delta G_3 - \Delta G_2, \Delta G_4 - \Delta G_3,)$$





Calculated 5 adsorbates

OH*   OOH*   O*   Cl*



Side view

CER/OER intermediates

$U^0_{CER} = 1.36\ V\ vs\ SHE,$
$2U^0_{CER} = 2.72\ V$

$G_{corr} = \Delta ZPE - T\Delta S^o$

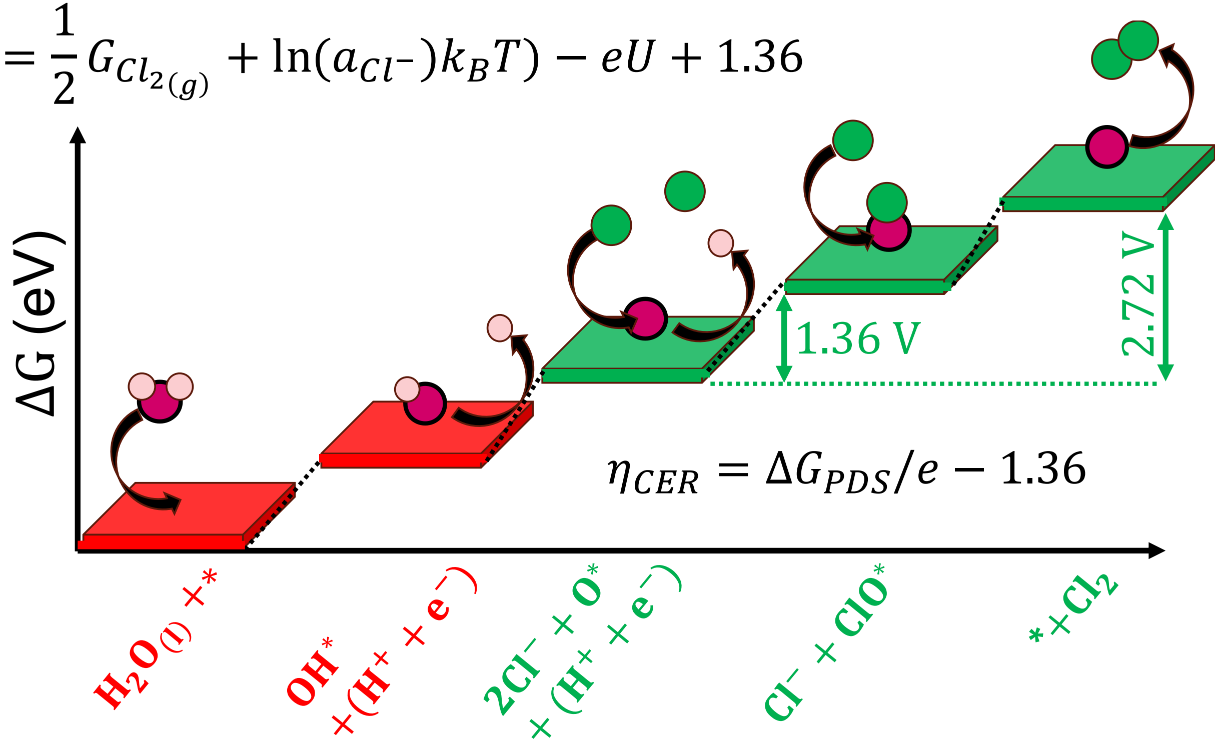
$$\Delta G_1 = E_{O^*} + \mu_{H_2} - \mu_{H_2O_{(l)}} - E^* + G_{corr}$$

$$\Delta G_2 = E_{ClO^*} - \mu_{H_2} - \mu_{H_2O_{(l)}} - \mu_{Cl} - E^* + G_{corr}$$

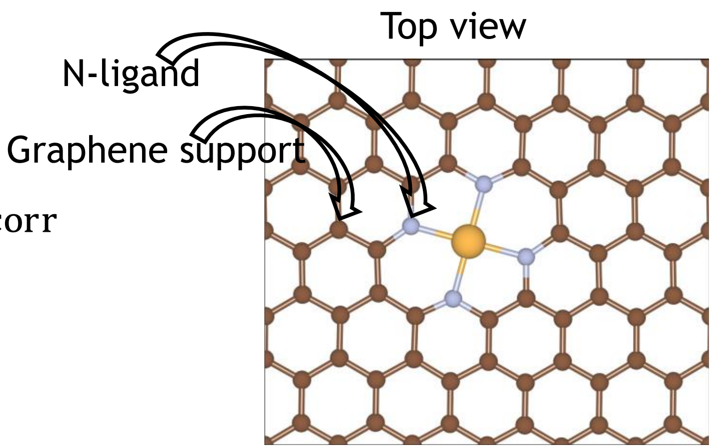
$$\Delta G_3 = E_{O^*} + \mu_{Cl_2} + \mu_{H_2} - \mu_{H_2O_{(l)}} - E^* - 2\mu_{Cl} + G_{corr}$$

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

$$\mu_{Cl} = \frac{1}{2}G_{Cl_{2(g)}} + \ln(a_{Cl^-})k_BT) - eU + 1.36$$

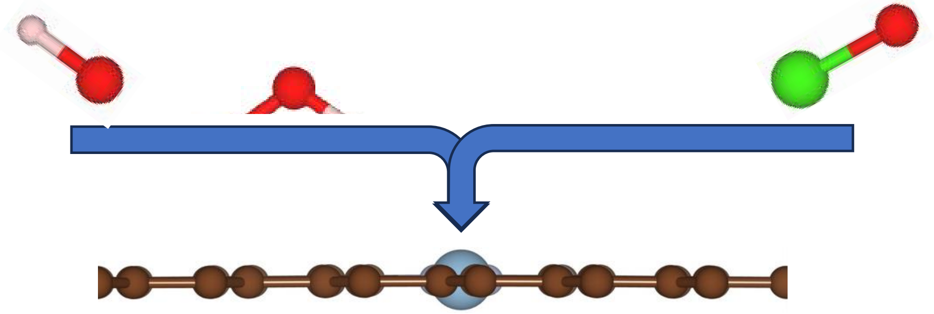


$$\eta_{CER} = \Delta G_{PDS}/e - 1.36$$



Calculated 5 adsorbates

OH* OOH* O* Cl* ClO*



Side view

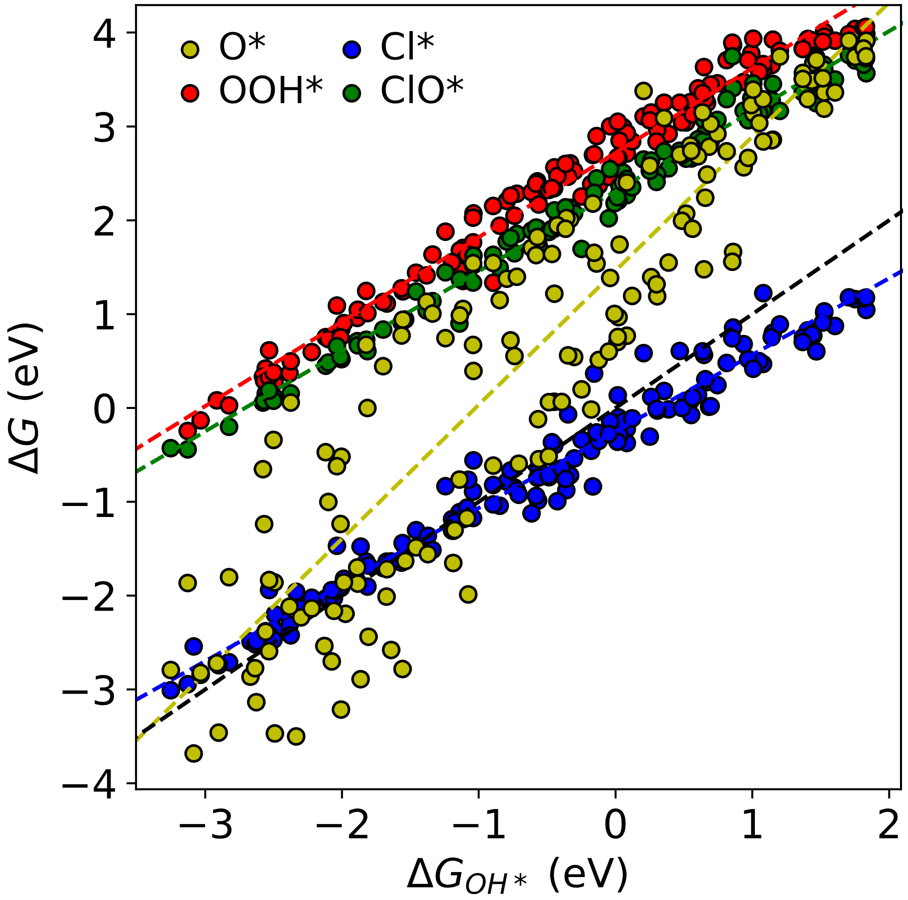
Scaling relationships

$\Delta G_{O^*} = 1.4\Delta G_{OH^*} + 1.5$

$\Delta G_{OOH^*} = 0.9\Delta G_{OH^*} + 2.7$

$\Delta G_{ClO^*} = 0.9\Delta G_{OH^*} + 2.3$

$\Delta G_{Cl^*} = 0.8\Delta G_{OH^*} - 0.2$



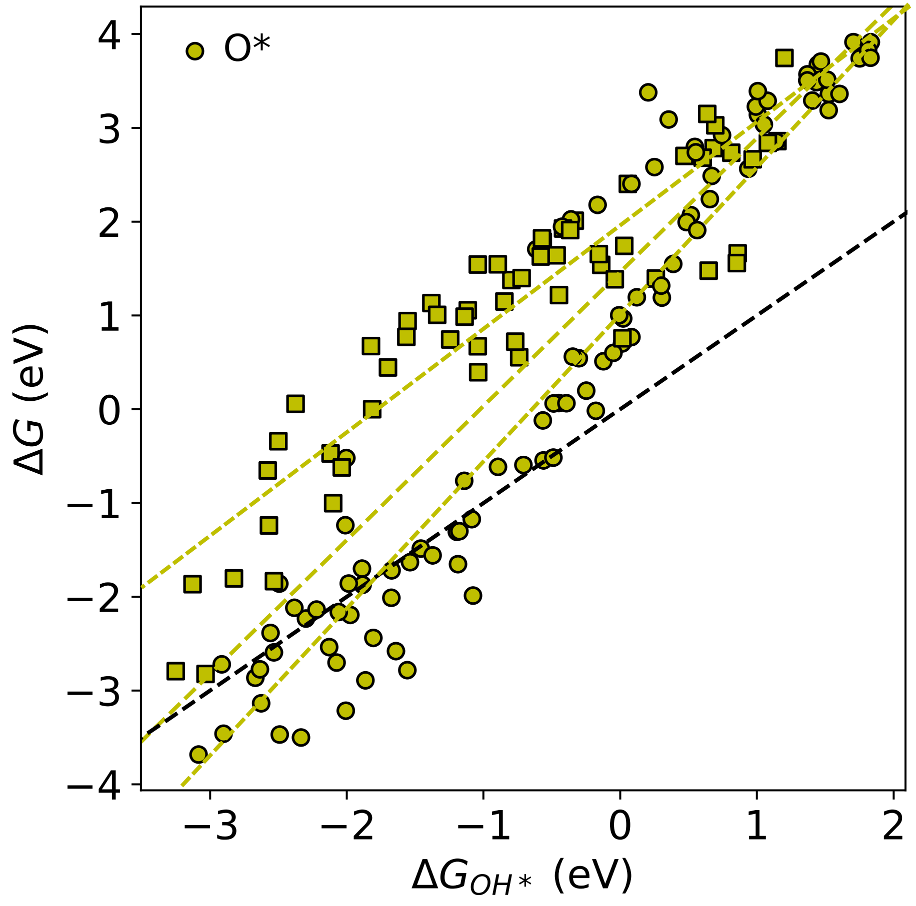
Scaling relationships

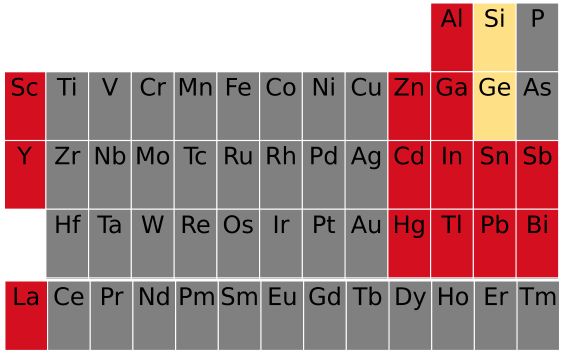
$\Delta G_{O^*} = 1.4\Delta G_{OH^*} + 1.5$

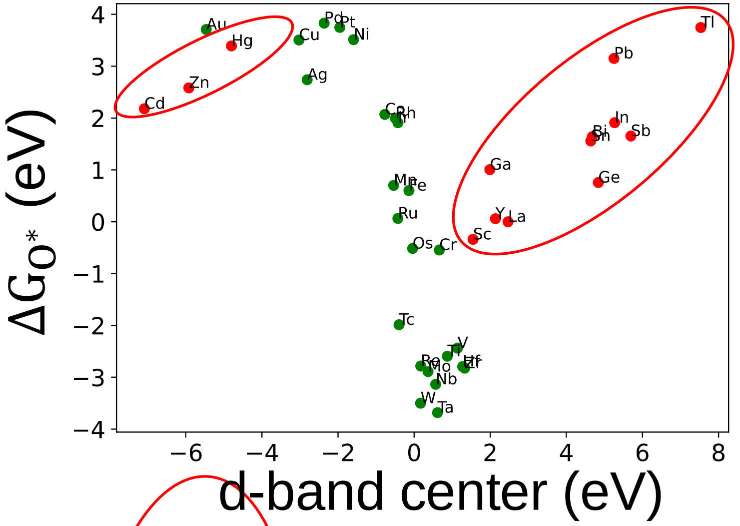
■ $\Delta G_{O^*} = 1.1\Delta G_{OH^*} + 1.9$

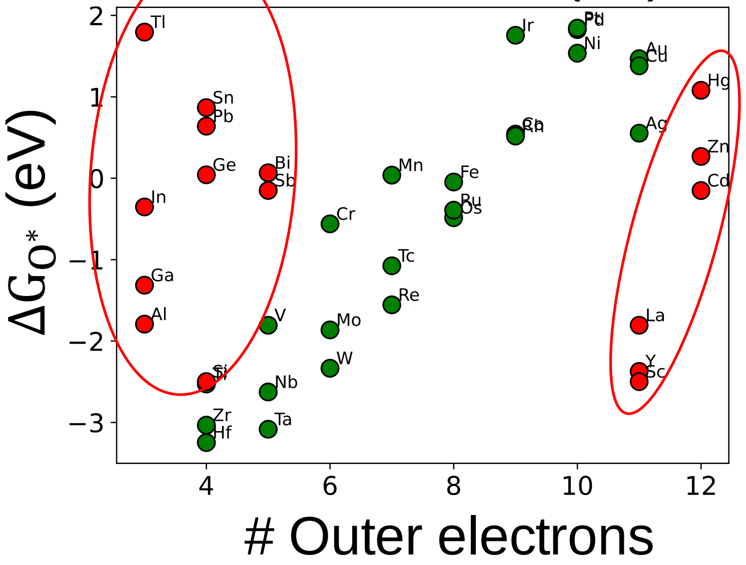
● $\Delta G_{O^*} = 1.6\Delta G_{OH^*} + 1.2$

H. Xin, S. Linic, J. Chem. Phys. 132 (2010) 221101



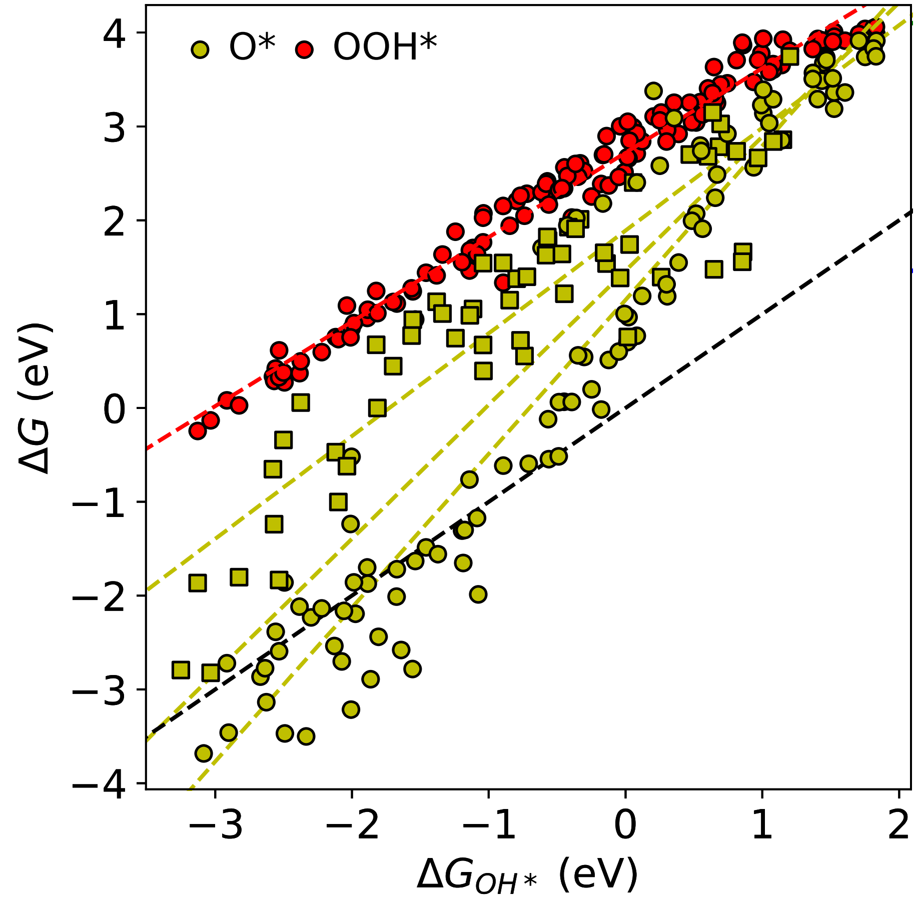






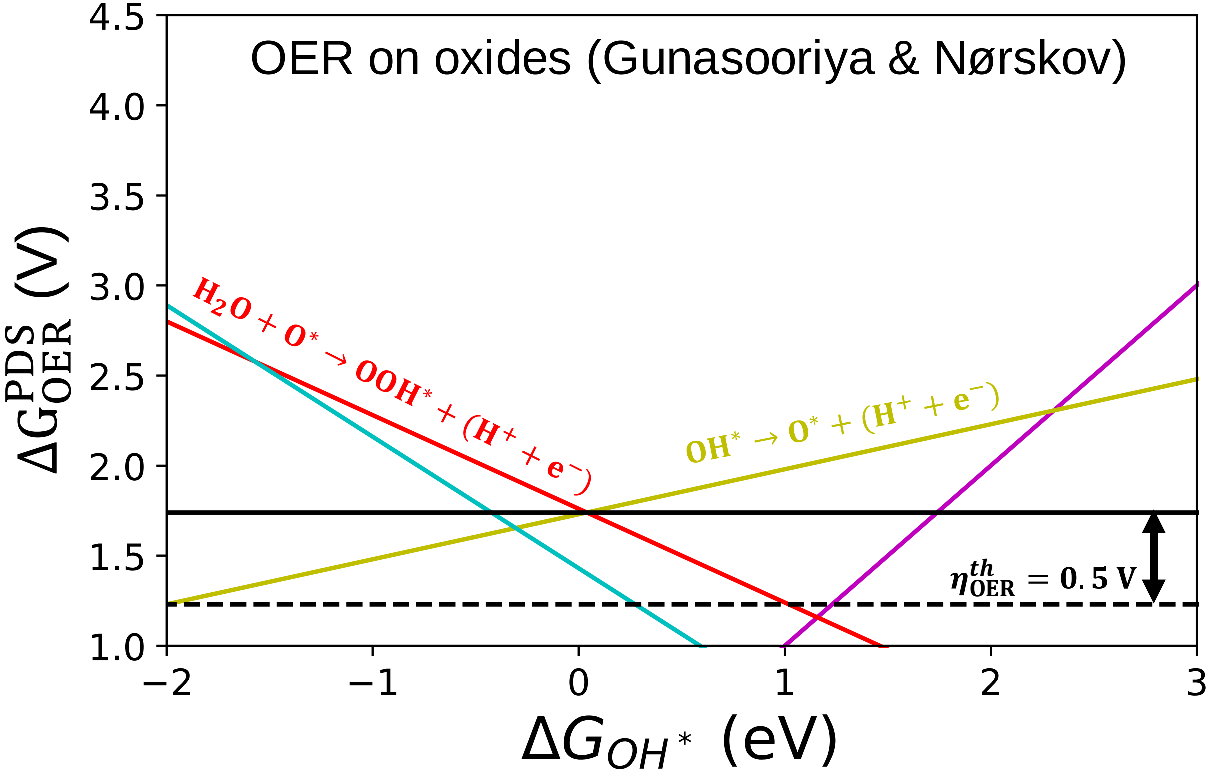
Sabatier principle

Gunasooriya, G. T. K. K., & Nørskov, J. K. (2020). *ACS Energy Letters*, *5*(12), 3778–3787. https://doi.org/10.1021/acsenergylett.0c02030



$\Delta G_{OOH^*} = 0.73G_{OH^*} + 3.49$ $\quad \Delta G_{OOH^*} - G_{O^*} = -0.52G_{OH^*} + 1.76$

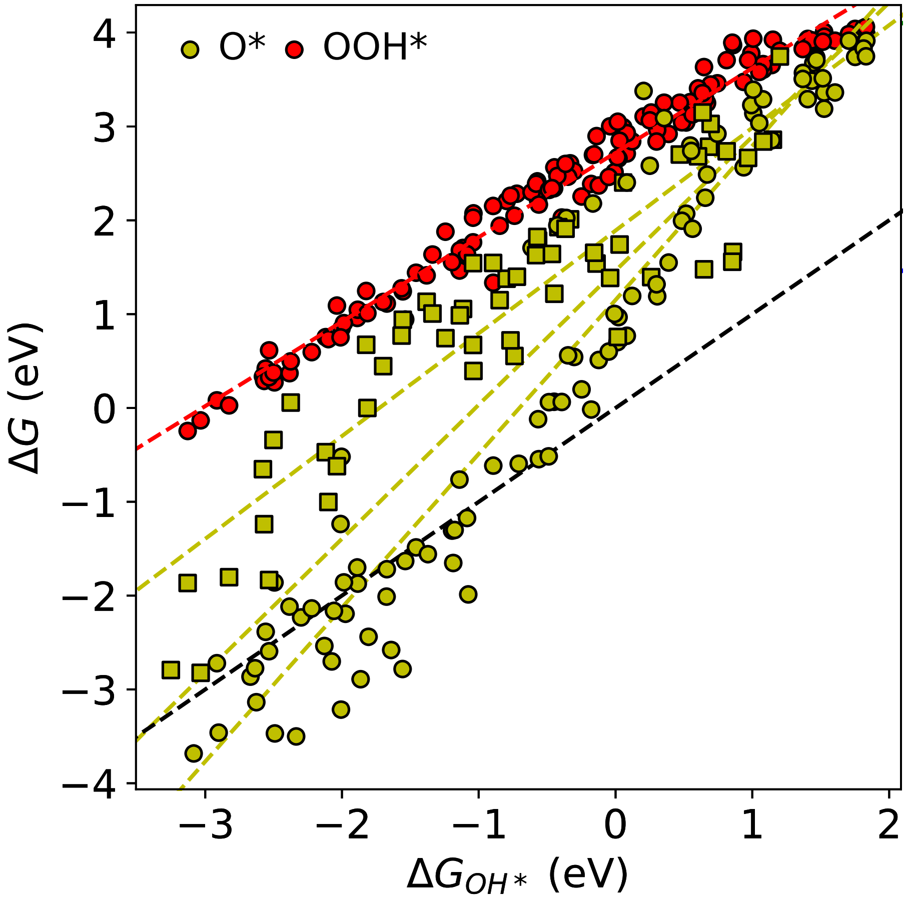
$\Delta G_{O^*} = 1.25G_{OH^*} + 1.73$ $\quad \Delta G_{O^*} - G_{OH^*} = 0.25G_{OH^*} + 1.73$



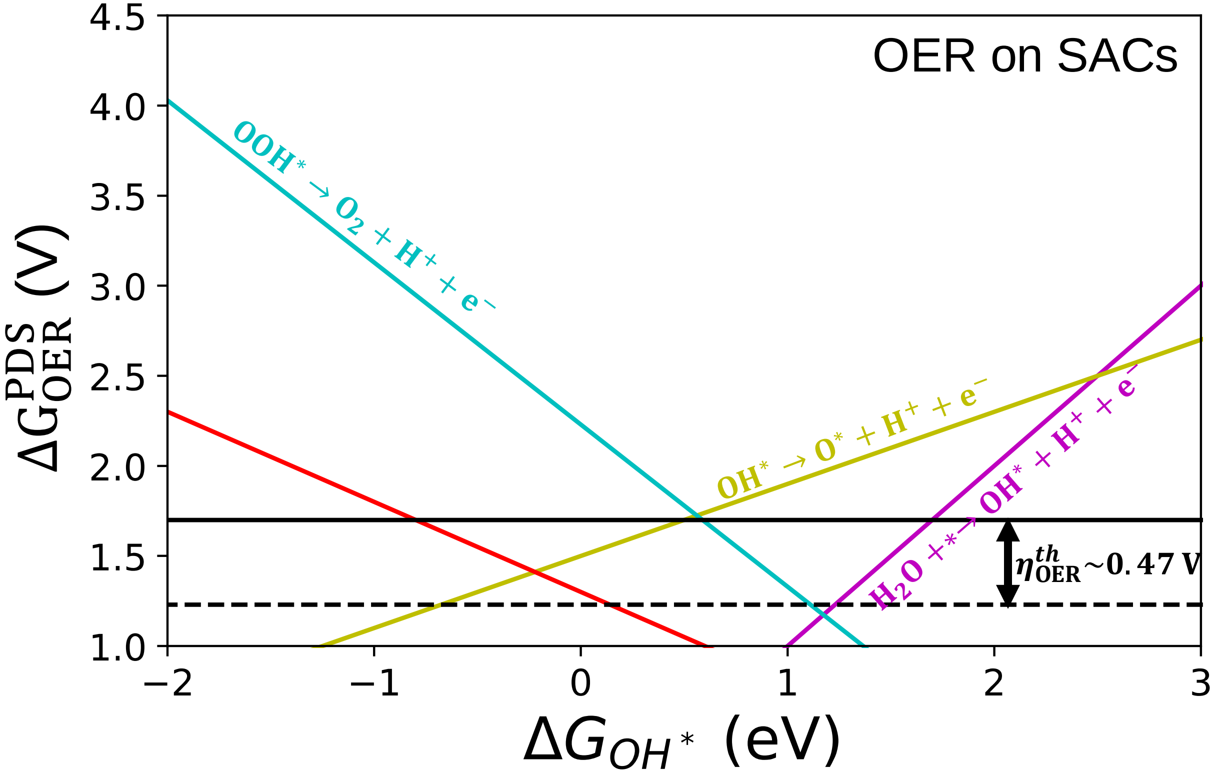
Sabatier principle

$\Delta G_{O^*} = 1.4\Delta G_{OH^*} + 1.5$

$\Delta G_{OOH^*} = 0.9\Delta G_{OH^*} + 2.7$



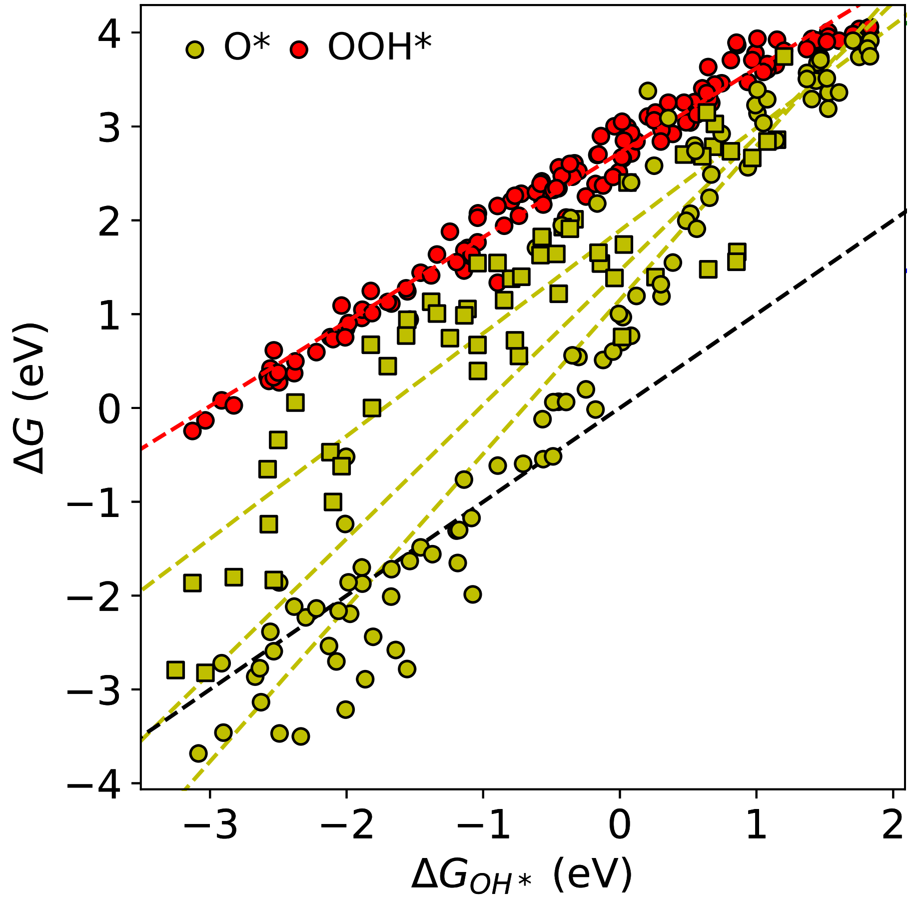
$\Delta G_{O^*} - \Delta G_{OH^*} = 0.4 G_{OH^*} + 1.4$



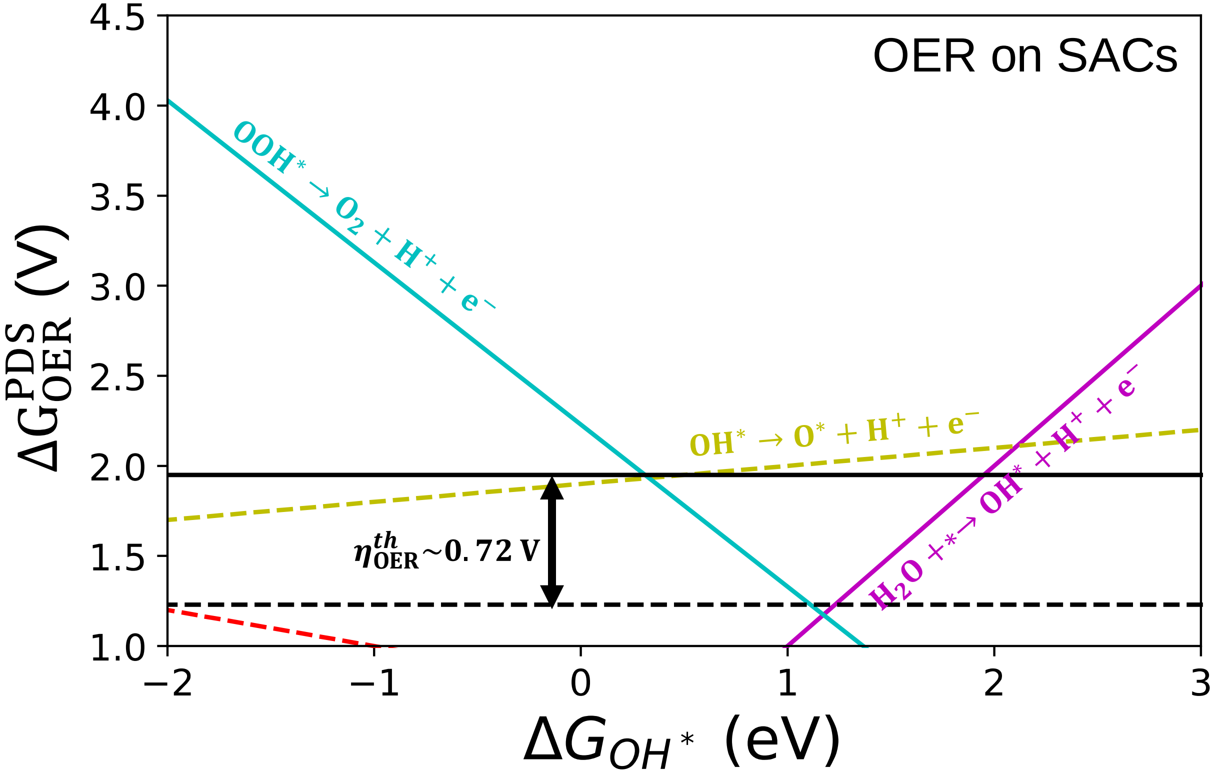
Sabatier principle

$\Delta G_{OOH^*} = 0.9\Delta G_{OH^*} + 2.7$

$\Delta G_{O^*} = 1.1\Delta G_{OH^*} + 1.9$



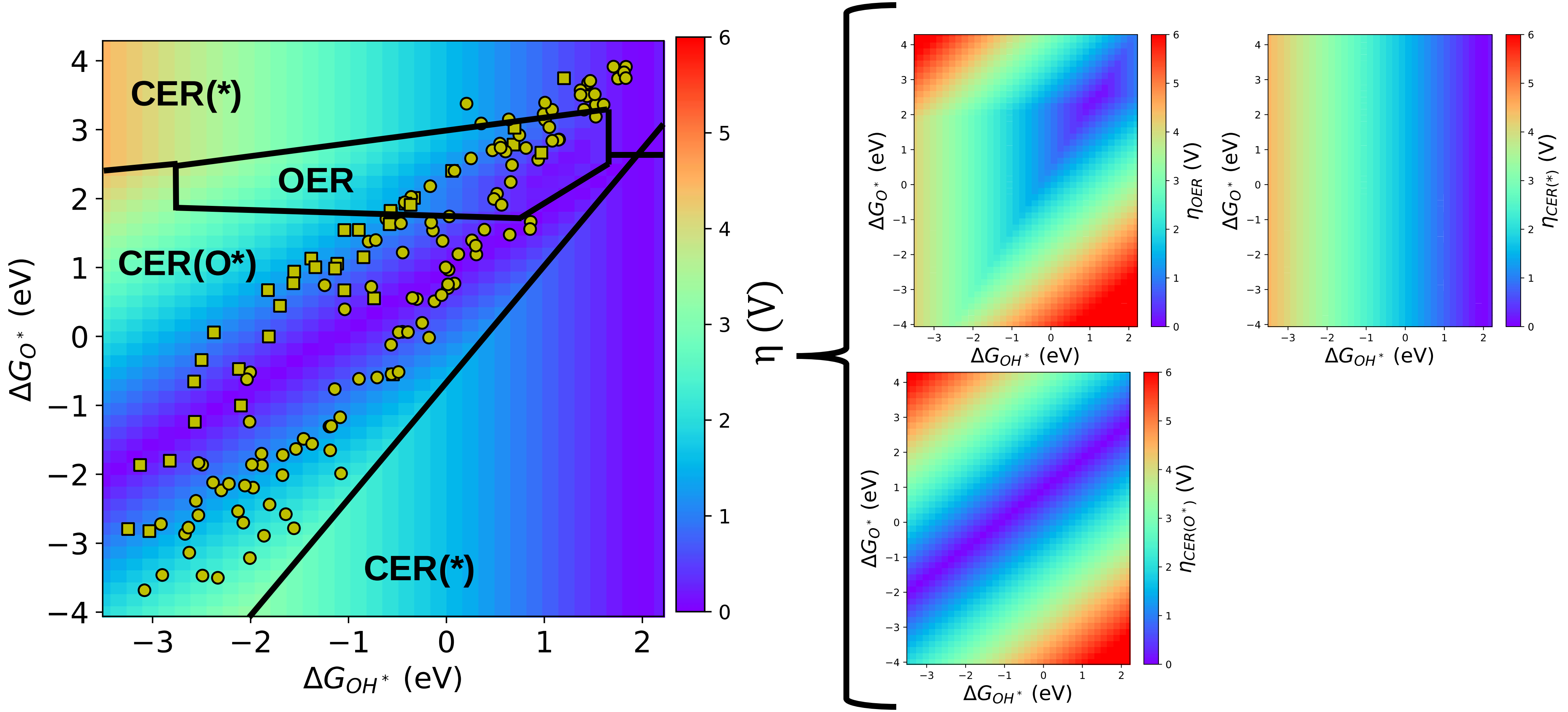
$\Delta G_{O^*} - \Delta G_{OH^*} = 0.1G_{OH^*} + 1.9$



Selectivity and activity

$$sel = (U^{o}_{OER} + \eta_{TD(OER)}) - (U^{o}_{CER} + \eta_{TD(CER)})$$

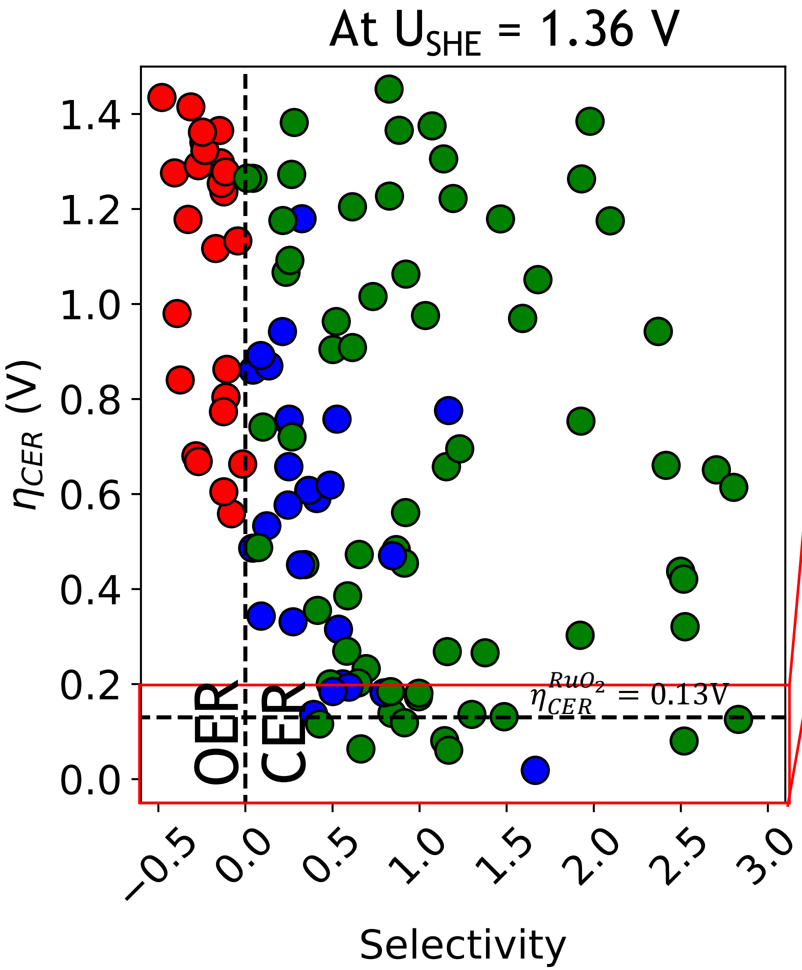
$sel > 0$ → CER, $selectivtiy < 0$ → OER

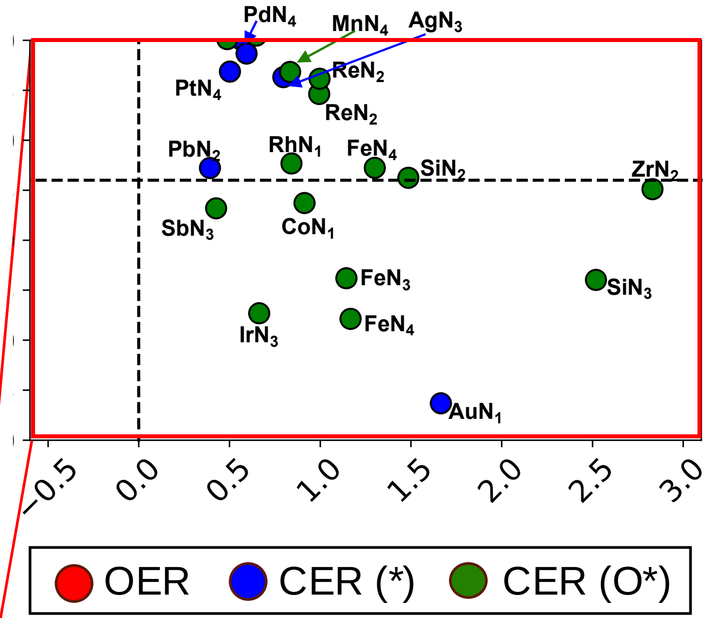


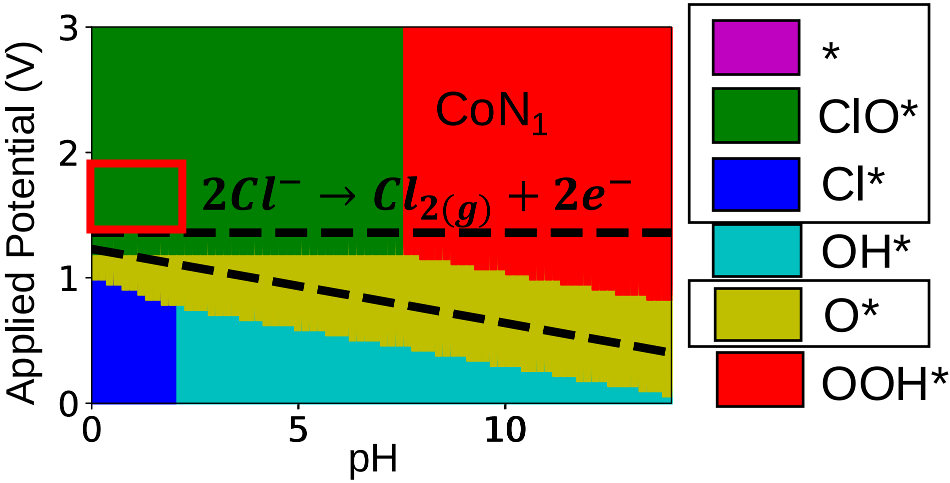
Candidate catalysts CER

$sel = (U^{o}_{OER} + \eta_{TD(OER)}) - (U^{o}_{CER} + \eta_{TD(CER)})$

$sel > 0$ → CER, $selectivtiy < 0$ → OER



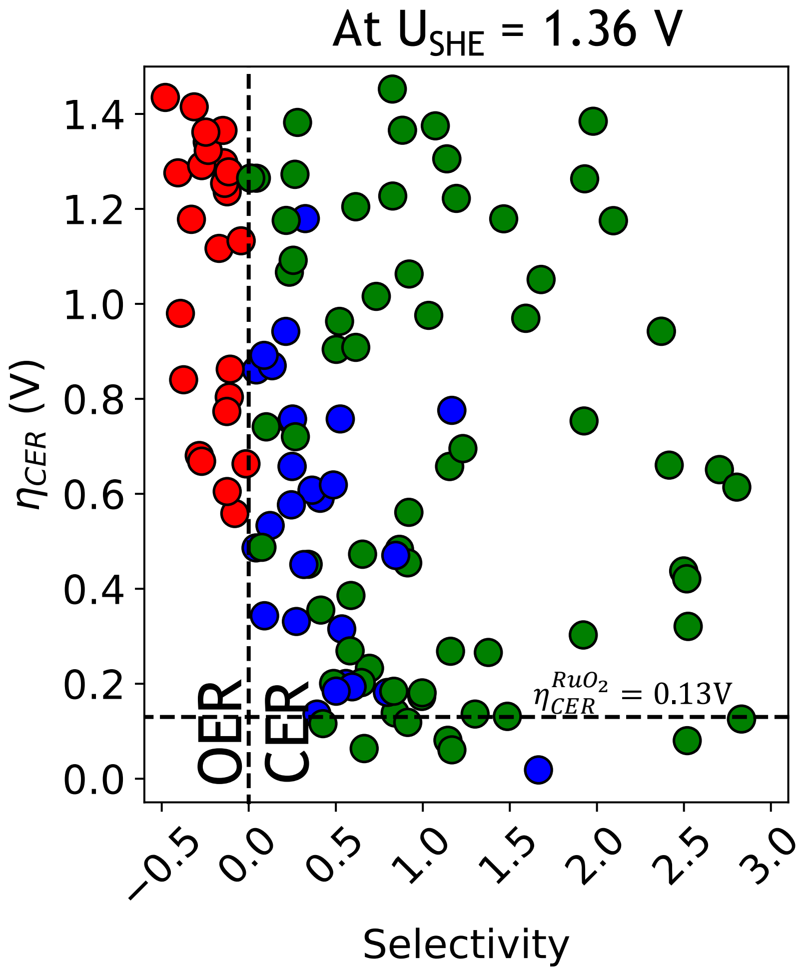




Candidate catalysts CER

$$sel = (U^{o}_{OER} + \eta_{TD(OER)}) - (U^{o}_{CER} + \eta_{TD(CER)})$$

$sel > 0$ → CER, $selectivtiy < 0$ → OER

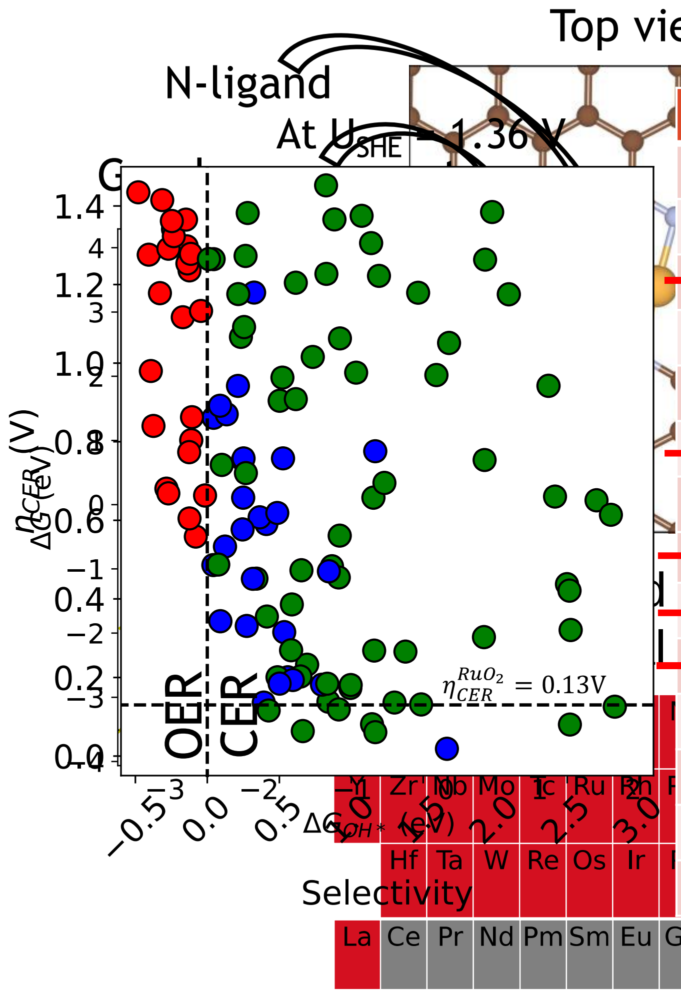


	Selectivity	η_{CER} (V)
CoN_1	0.91	0.12
FeN_1	1.30	0.14
FeN_2	0.99	0.17
FeN_3	1.14	0.08
FeN_4	1.17	0.06
HfN_2	3.36	0.05
HfN_3	3.87	0.06

	Selectivity	η_{CER} (V)
IrN_3	0.66	0.06
MnN_4	0.83	0.18
RhN_1	0.84	0.14
RhN_2	1.00	0.18
SiN_3	2.52	0.13
SbN_3	0.43	0.12
ZrN_2	2.83	0.13

Conclusion

- Evaluated CER vs OER for 160 SACs (MN_X@G, M=40 dopants, X=1,2,3,4)
- We found a split in scaling relationship between ΔG_{O^*} vs ΔG_{OH^*}.
  - Dopants with a slope of 1 do not obey the d-band center model for adsorption
  - Results in a shift in theoretical η_{OER}^{Th} and change in selectivity
- Si, Fe, Zr, Rh, Mn, Ir, and Hf are ideal for CER via the ClO* precursor.



	Selectivity	η_{CER} (V)
IrN_3	0.66	0.06
MnN_4	0.83	0.18
~~RhN_1~~	~~0.84~~	~~0.14~~
RhN_2	1.00	0.18
SiN_3	2.52	0.13
~~SbN_3~~	~~0.43~~	~~0.12~~
ZrN_2	2.83	0.13
~~CoN_1~~	~~0.91~~	~~0.12~~
~~FeN_1~~	~~1.30~~	~~0.14~~
~~FeN_2~~	~~0.99~~	~~0.17~~
FeN_3	1.14	0.08
FeN_4	1.17	0.06
HfN_2	3.36	0.05
HfN_3	3.87	0.06

Acknowledgements

Funding and Support

Texas Center for Superconductivity
UNIVERSITY OF HOUSTON

TcSUH

Supercomputing resources

UNIVERSITY OF HOUSTON

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Lars Grabow

Najmeh Honari

Hong Zhong

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Thank you!

Questions?

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