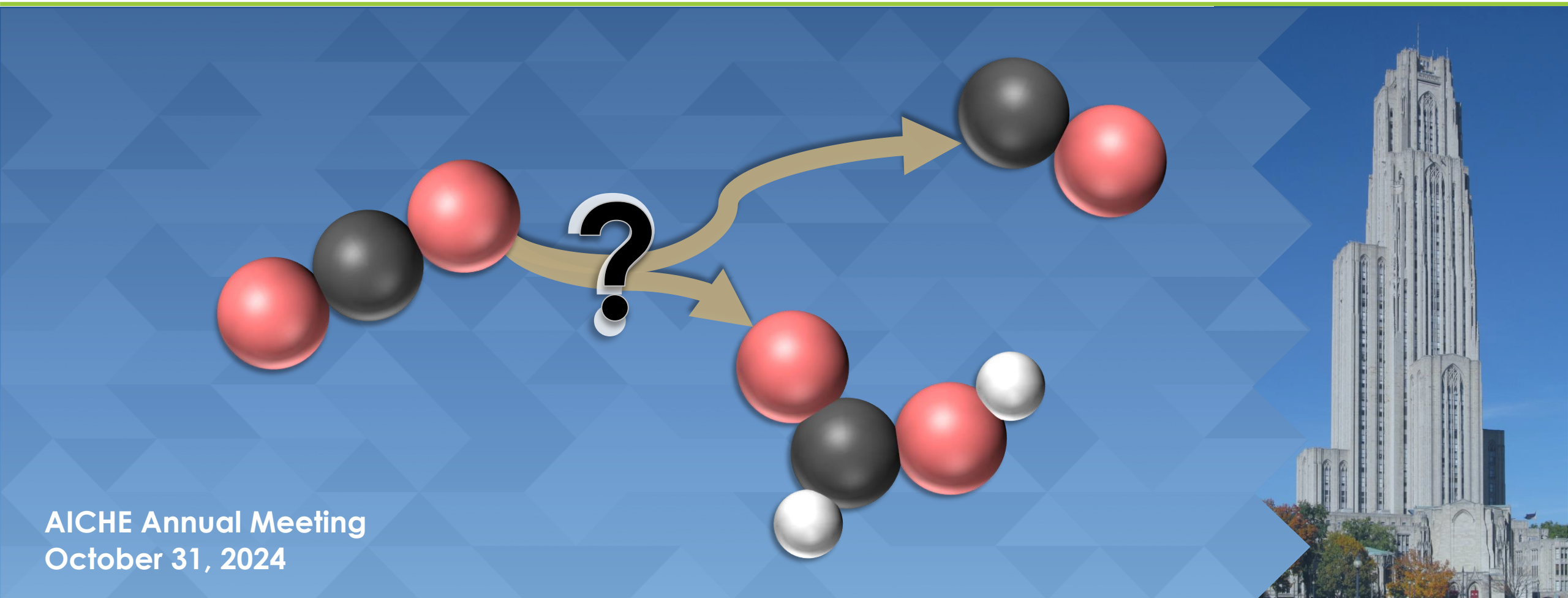
Understanding Selectivity Control in the Electrocatalytic Reduction of CO_2 to Liquid Products in Gas-Fed Electrolyzers

NATIONAL ENERGY TECHNOLOGY LABORATORY

John El Berch
Department of Chemical & Petroleum Engineering
University of Pittsburgh



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Disclaimer

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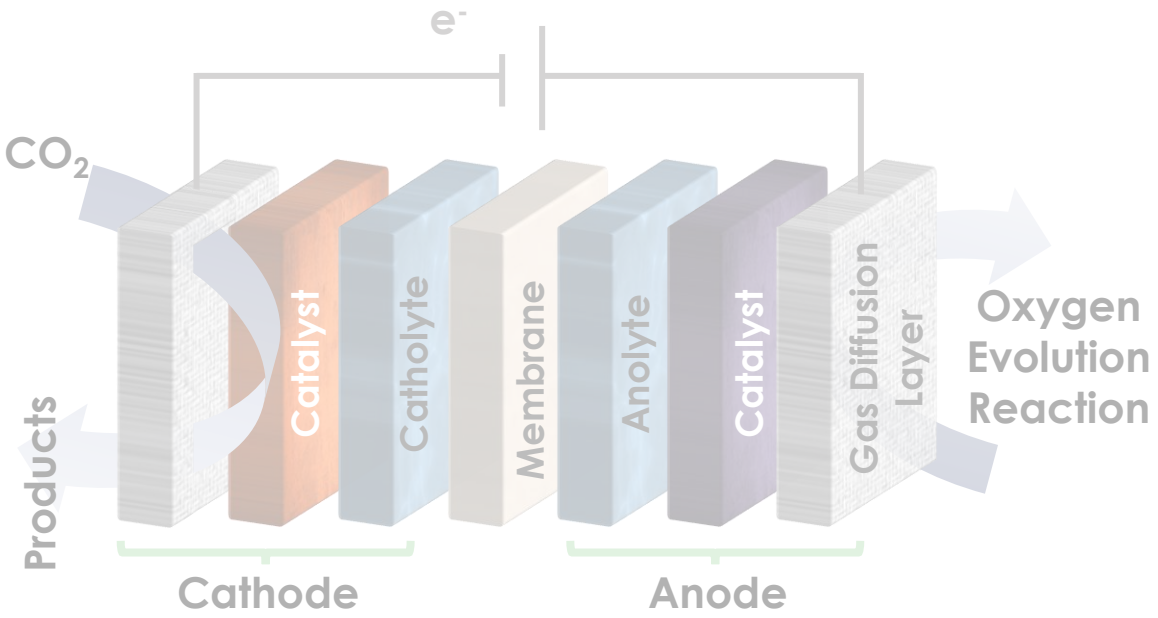
Authors

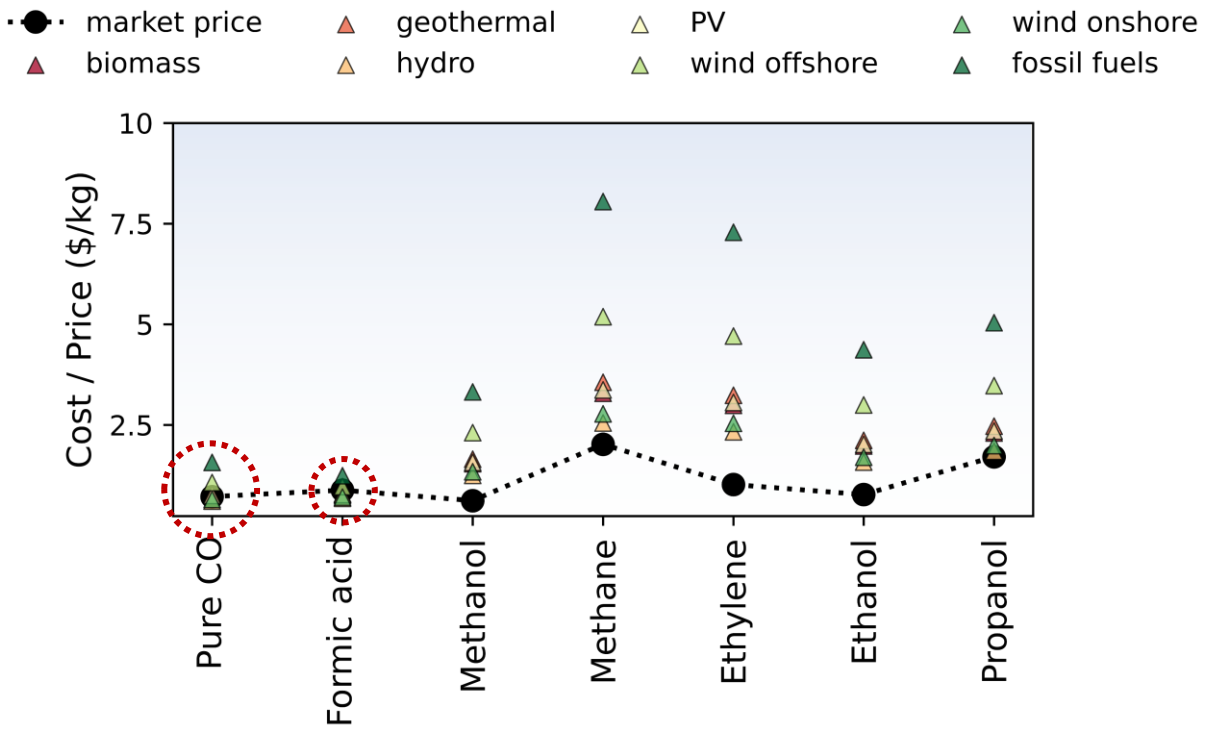
John El Berch[1,2,3], James Ellis[1,2], Douglas Kauffman[1,2], Giannis Mpourmpakis[1,2,3]

1. National Energy Technology Laboratory, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA.
2. NETL Support Contractor, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA.
3. Department of Chemical & Petroleum Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA.

CO_2 electroreduction commercialization progress



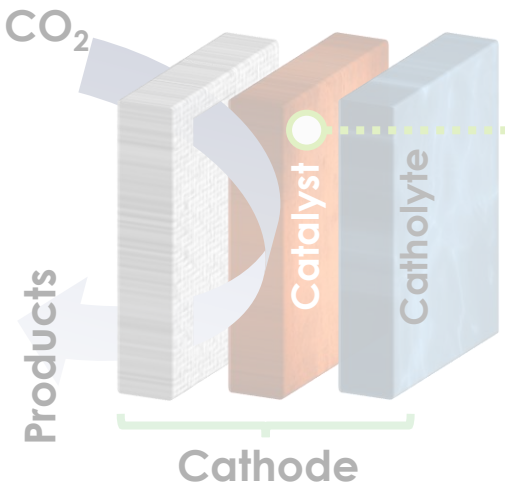
Gas-fed flow electrolyzers show promise for large-scale applications[1]



CO_2 electroreduction (CO_2RR) to CO and HCOOH is closer to commercialization[2]

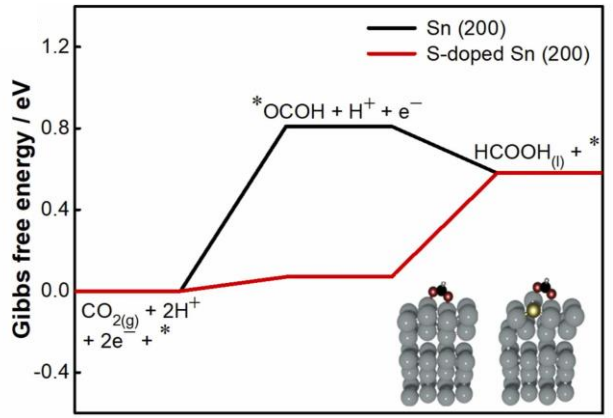
1. Fan *et al.* *Science Advances*, **6**, eaay3111.
2. Leonzio *et al.* (2024), *Chemical Engineering Research and Design*, **208**, 934-955.

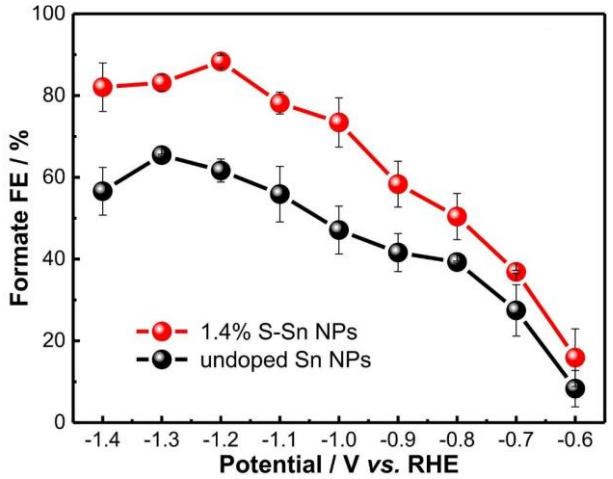
Cathode composition and CO_2RR selectivity



28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As
46 Pd	47 Ag	48 Cd	49 In	50 **Sn**	51 Sb
78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi

H_2 | $HCOO^-$ | CO | C_{2+}

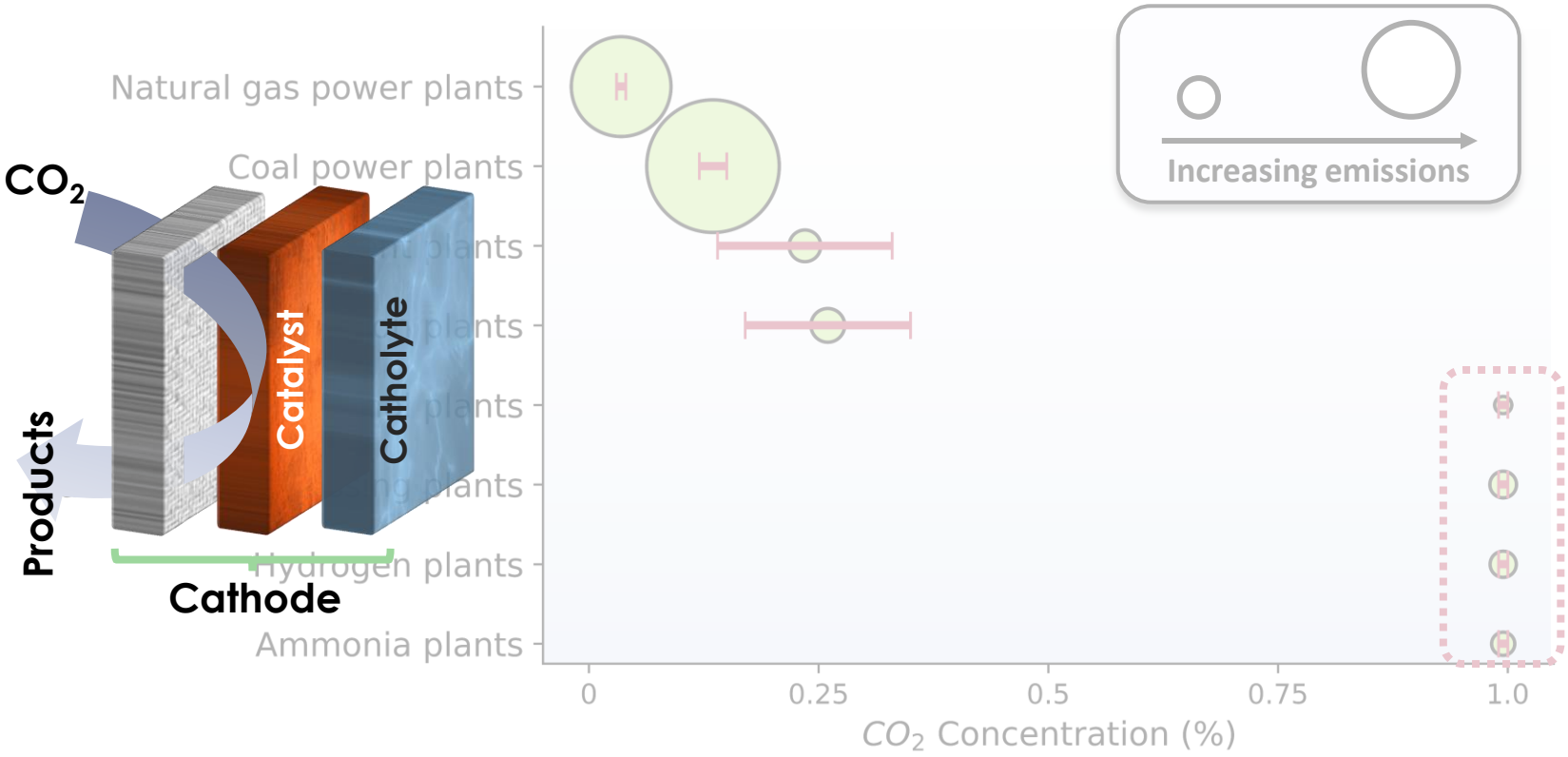




Selectivity primarily defined by electrode material[1,2] and fine-tuned via doping[3]

1. Hori (2008), "Electrochemical CO_2 Reduction on Metal Electrodes". In *Modern Aspects of Electrochemistry*. Eds C. G. Vayenas *et al.* Springer New York. pp 89-189
2. Wang *et al.* (2024), *Angewandte Chemie International Edition*, **63**, e202401821.
3. Nguyen-Phan, T., Ellis, J., Nagarajan, A., Howard, B., Mpourmpakis, G., and Kauffman, D. (2024), *Applied Catalysis B: Environmental*, **340**, 123250.

Variations on CO_2 inlet concentrations



Highly concentrated CO_2 streams are just 2.6% of net supply[1]

Understand the interplay between CO_2 inlet concentration and surface oxidation on product selectivity

1. Badgett *et al.* (2022), *iScience*, **25**, 104270.
2. Von Der Assen *et al.* (2016), *Environmental Science & Technology*, **50**, 1093-1101.
3. Van Daele *et al.* (2022), *Journal of CO2 Utilization*, **65**, 102210

Preliminary CO_2RR results on a SnO_2 cathode

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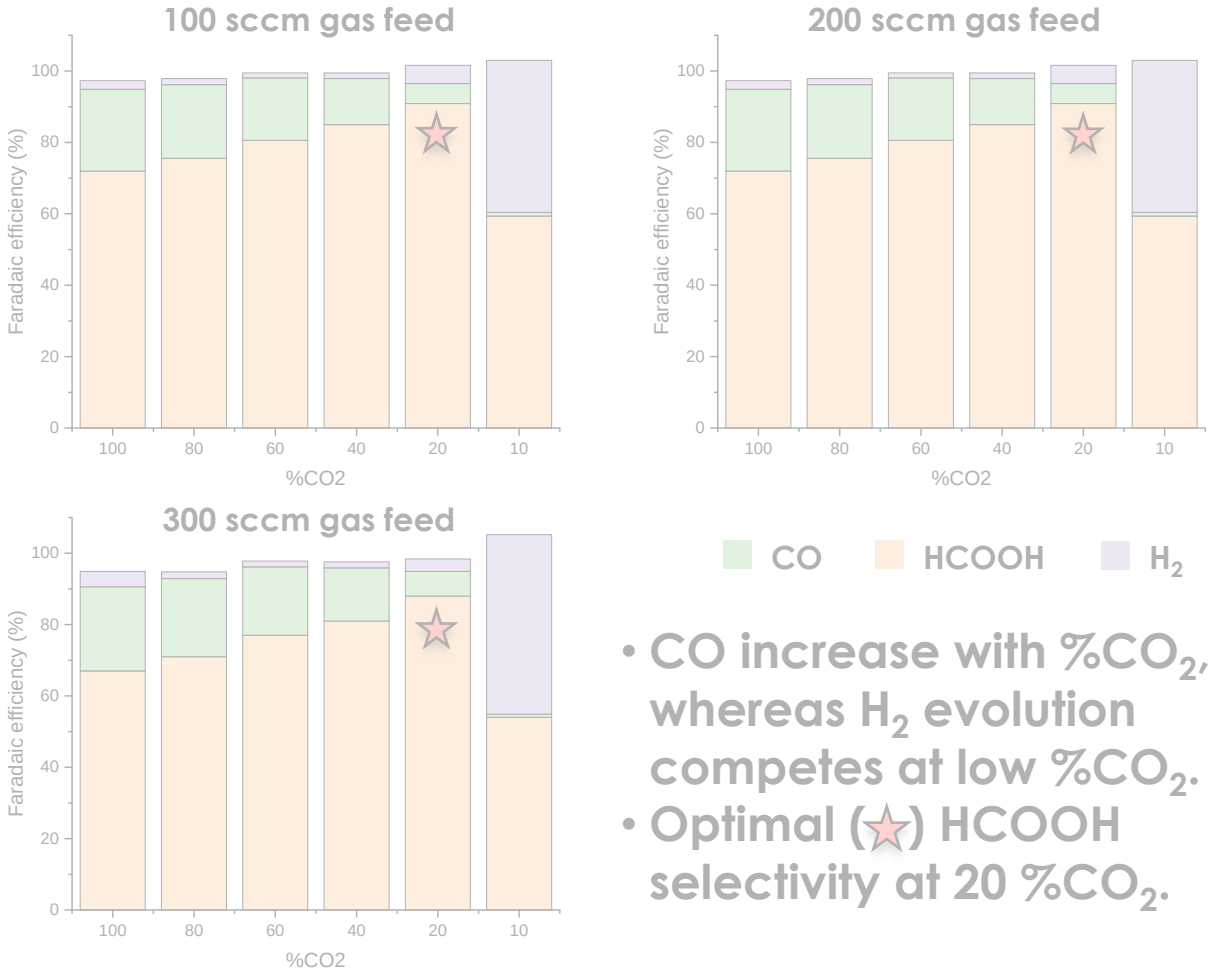
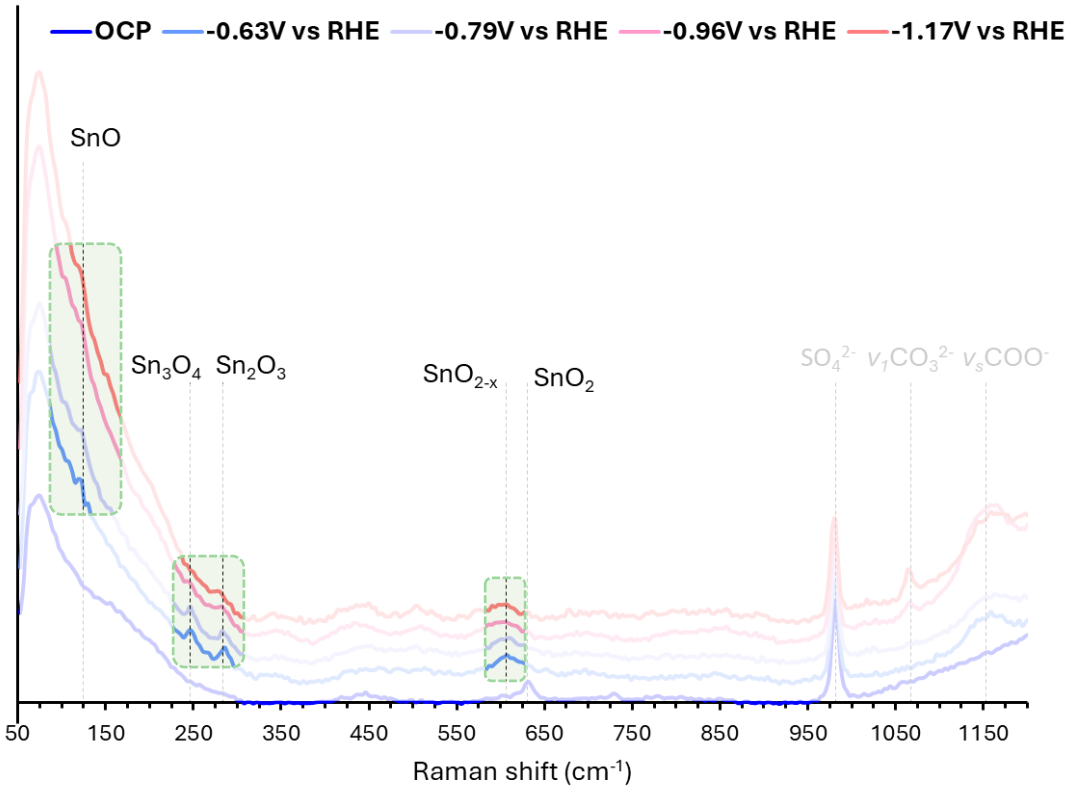
Constant current density 100 mA/cm²



- CO increase with $\%CO_2$, whereas H_2 evolution competes at low $\%CO_2$.
- Optimal (☆) HCOOH selectivity at 20 $\%CO_2$.

Half-cell *in situ* Raman experiments



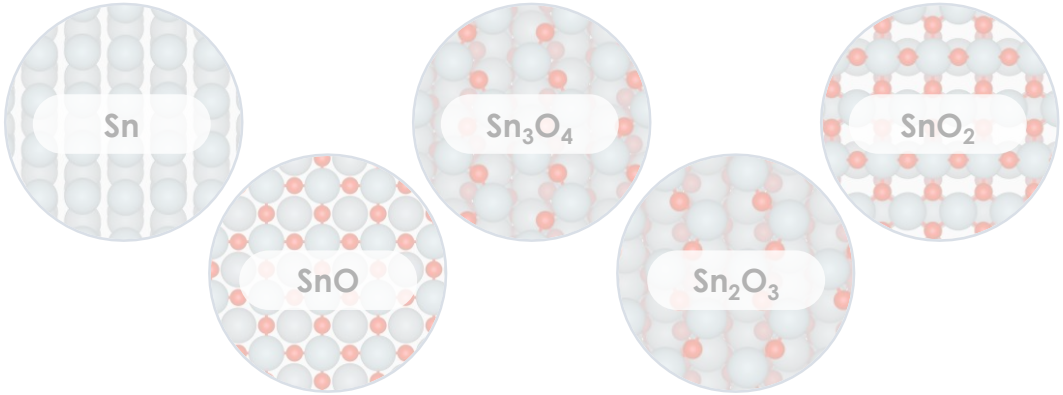
Partially reduced Sn peaks remain at increasing cathode potentials

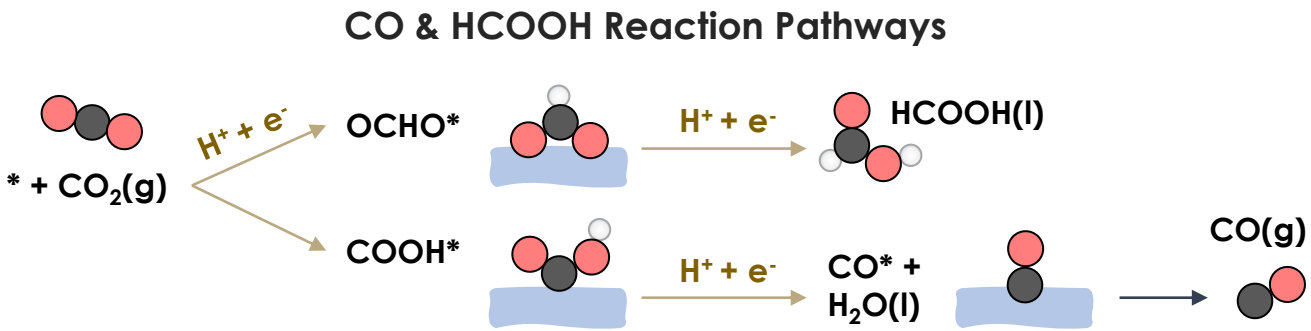
Ellis, J., El Berch, J., Mpourmpakis, G., Kauffman, D. *In preparation*.

Computational methods

Periodic DFT calculations using the CP2K software package:

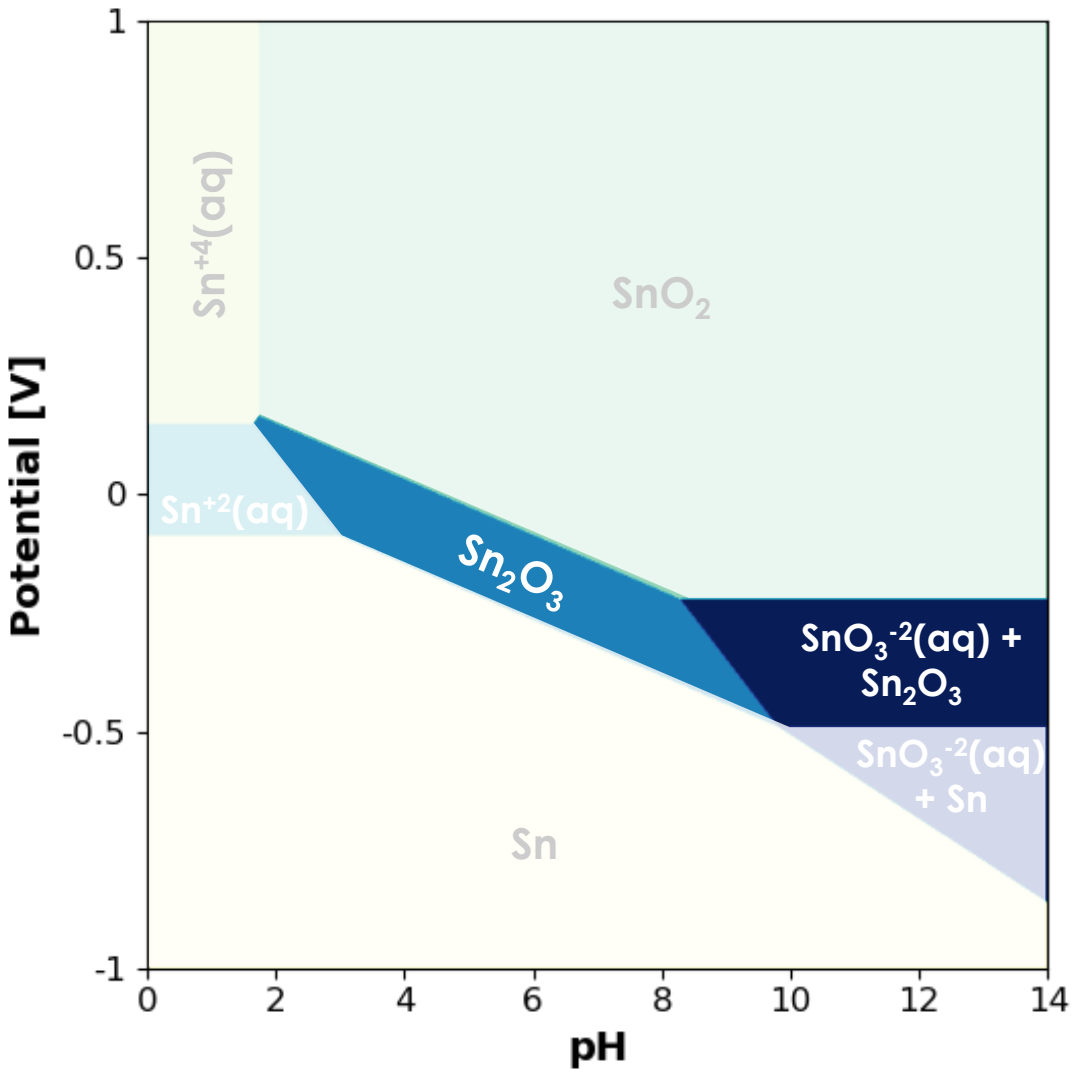
- PBE exchange-correlation functional[1].
- Grimme's D3 dispersion corrections[2].
- MOLOPT basis sets[3] with an auxiliary planewave basis set's cutoff of 500 Ry.
- Goedecker, Teter, and Hutter pseudopotentials[4].
- Energy of proton-electron pairs accounted for with the computational hydrogen electrode approximation[5].



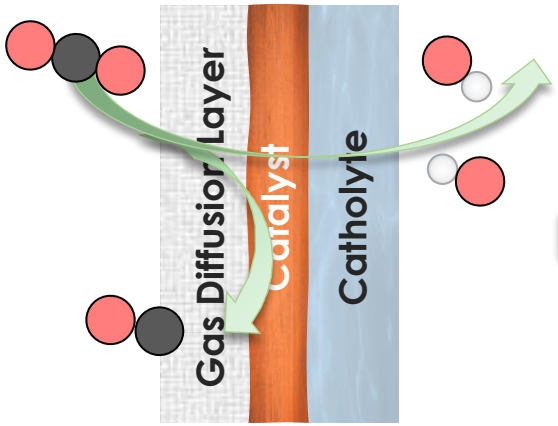


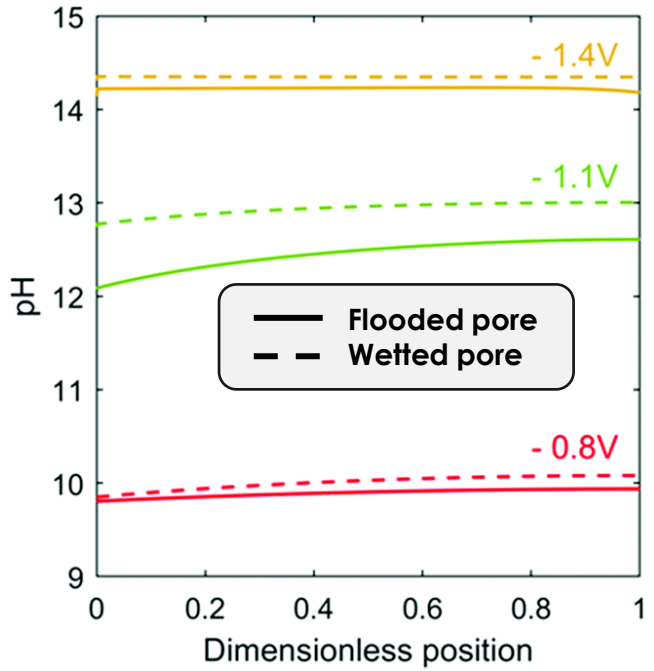
1. Perdew *et al.* (1996), *Physical Review Letters*, **77**, 3865-3868
2. Grimme *et al.* (2010), *The Journal of Chemical Physics*, **132**, 154104.
3. Vandevondele & Hutter (2007), *The Journal of Chemical Physics*, **127**, 114105
4. Goedecker *et al.* (1996), *Physical Review B*, **54**, 1703-1710
5. Nørskov *et al.* (2004), *The Journal of Physical Chemistry B*, **108**, 17886-17892.

Predicted phase stability of Sn (Pourbaix diagram)



Partially oxidized Sn_2O_3 stable at low cathodic potentials and basic environments

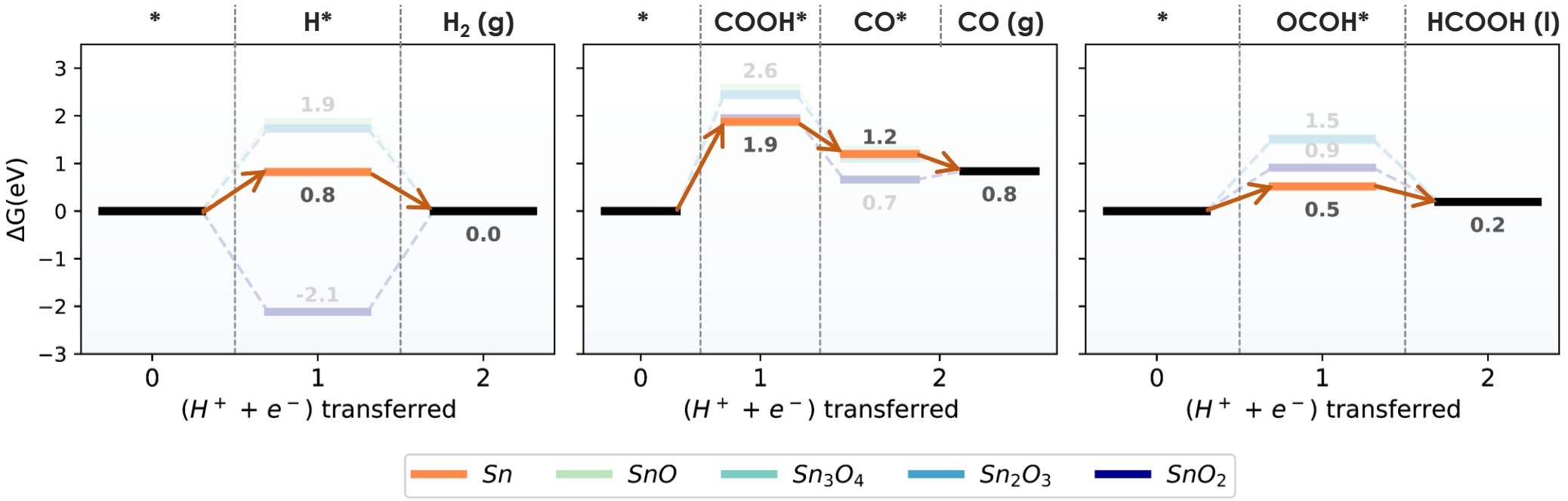




Local basic environment expected due to OH production[2,3]

1. Ellis, J., El Berch, J., Mpourmpakis, G., Kauffman, D. *In preparation*.
2. Van Daele *et al.* (2022), *Journal of CO2 Utilization*, **65**, 102210
3. Weng *et al.* (2018), *Physical Chemistry Chemical Physics*, **20**, 16973-16984.

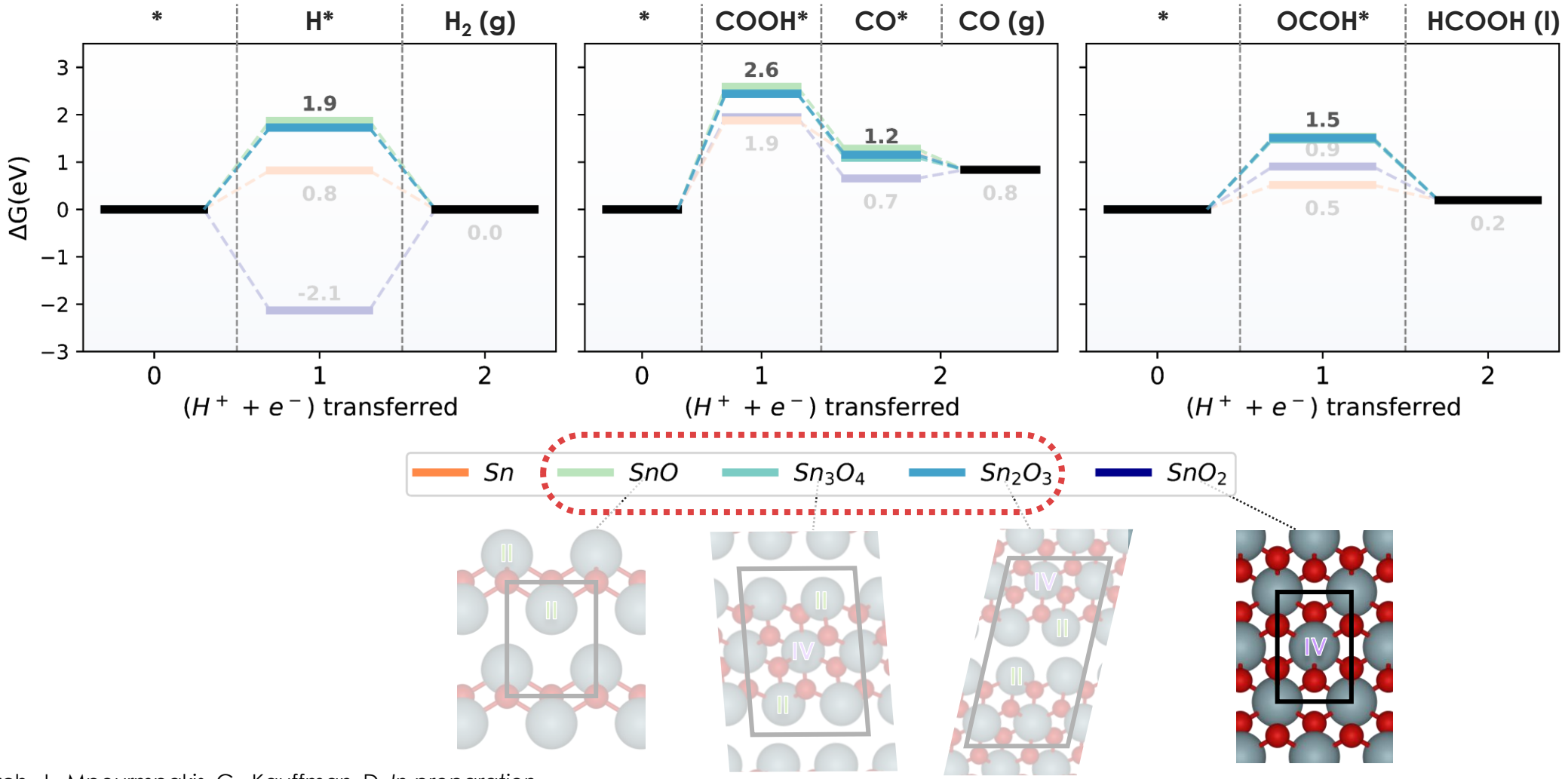
CO_2RR pathways on Sn_xO_y surfaces



- **HCOOH is the thermodynamically favored product.**
- **Lower thermodynamic barriers on metallic Sn.**

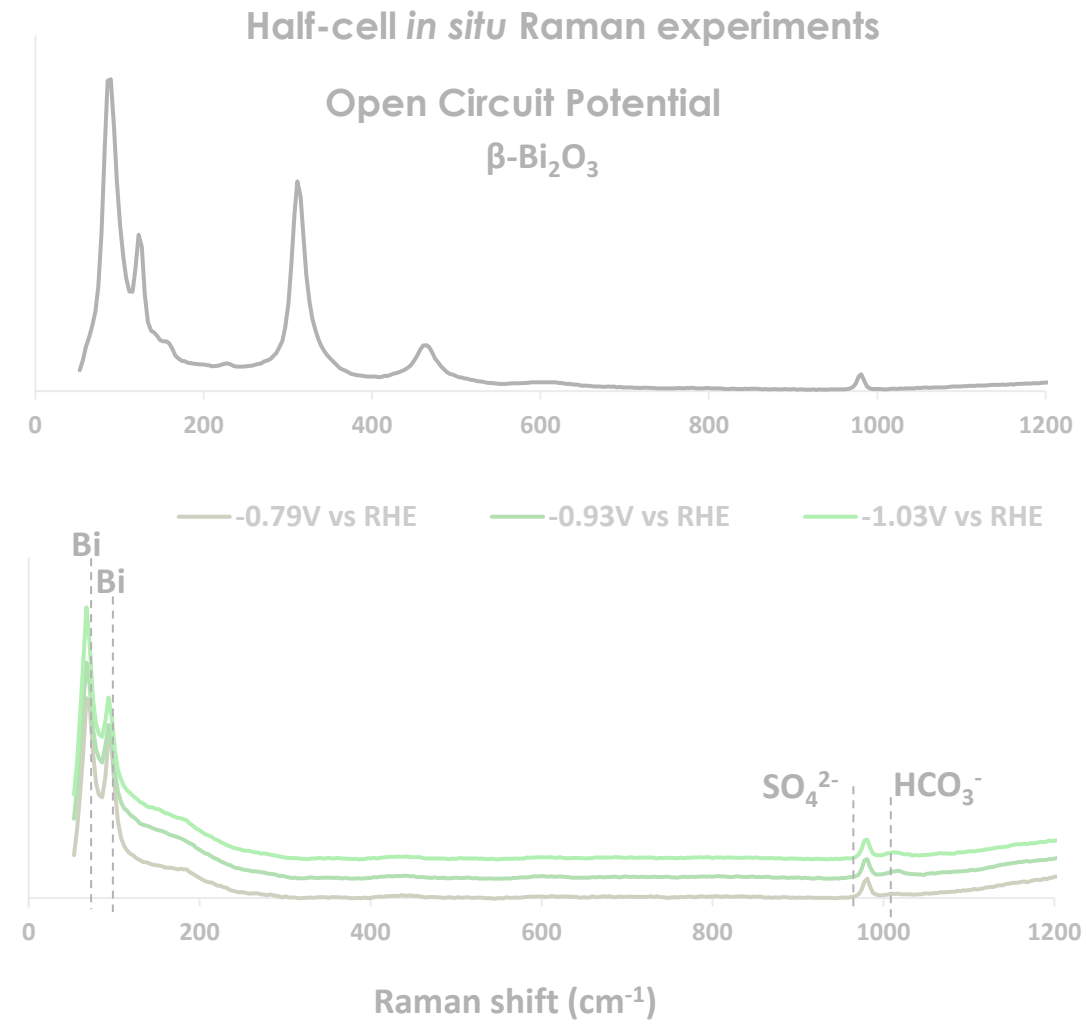
Ellis, J., El Berch, J., Mpourmpakis, G., Kauffman, D. *In preparation*.

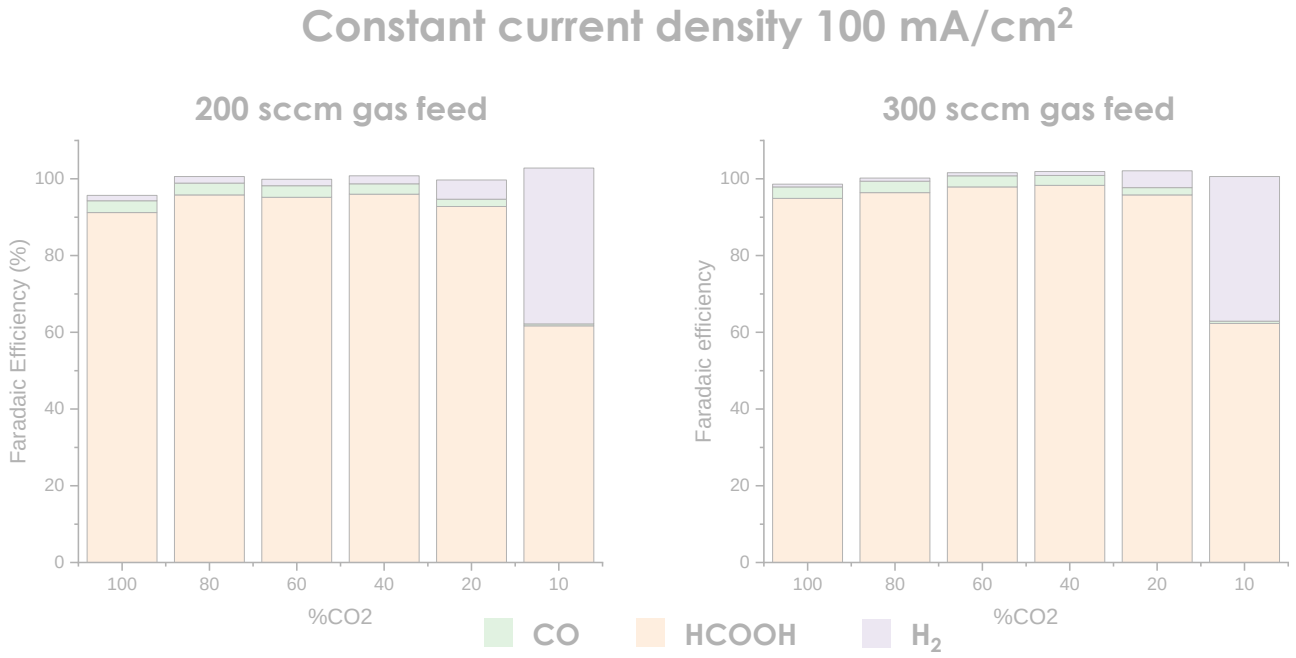
CO_2RR pathways on Sn_xO_y surfaces

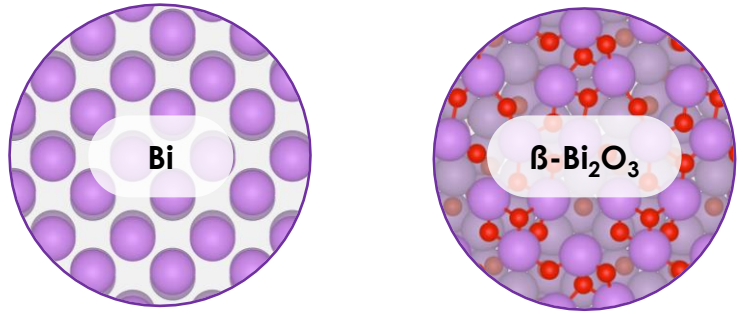


Ellis, J., El Berch, J., Mpourmpakis, G., Kauffman, D. *In preparation*.

Preliminary CO_2RR results on a Bi_2O_3 cathode

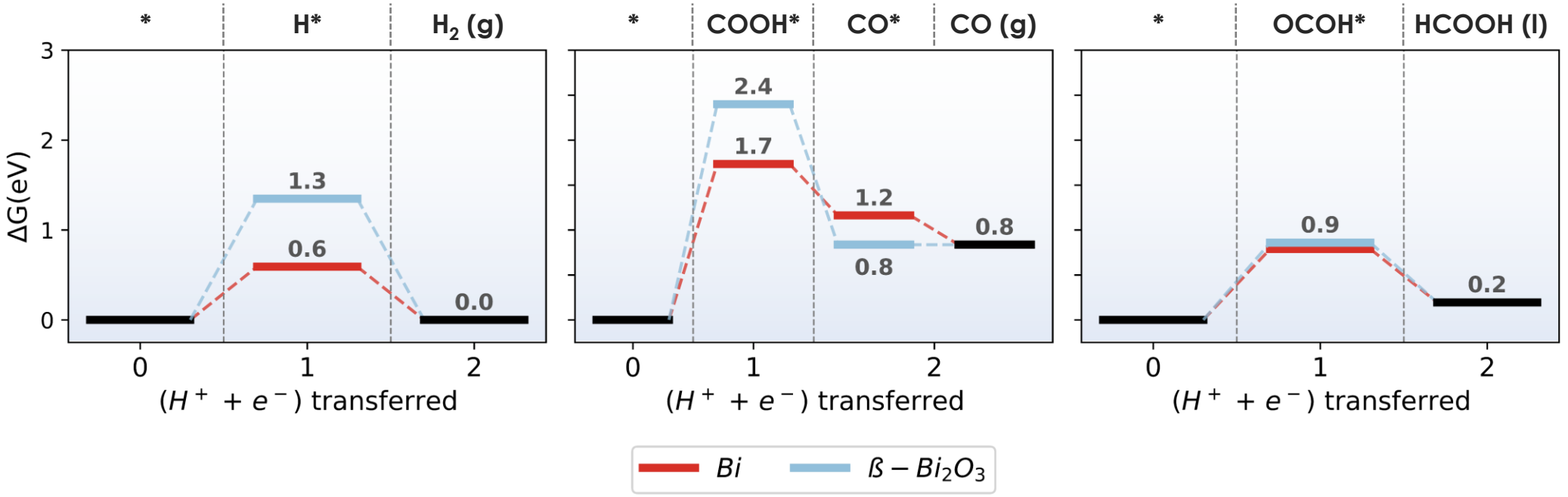






Ellis, J., El Berch, J., Mpourmpakis, G., Kauffman, D. *In preparation*.

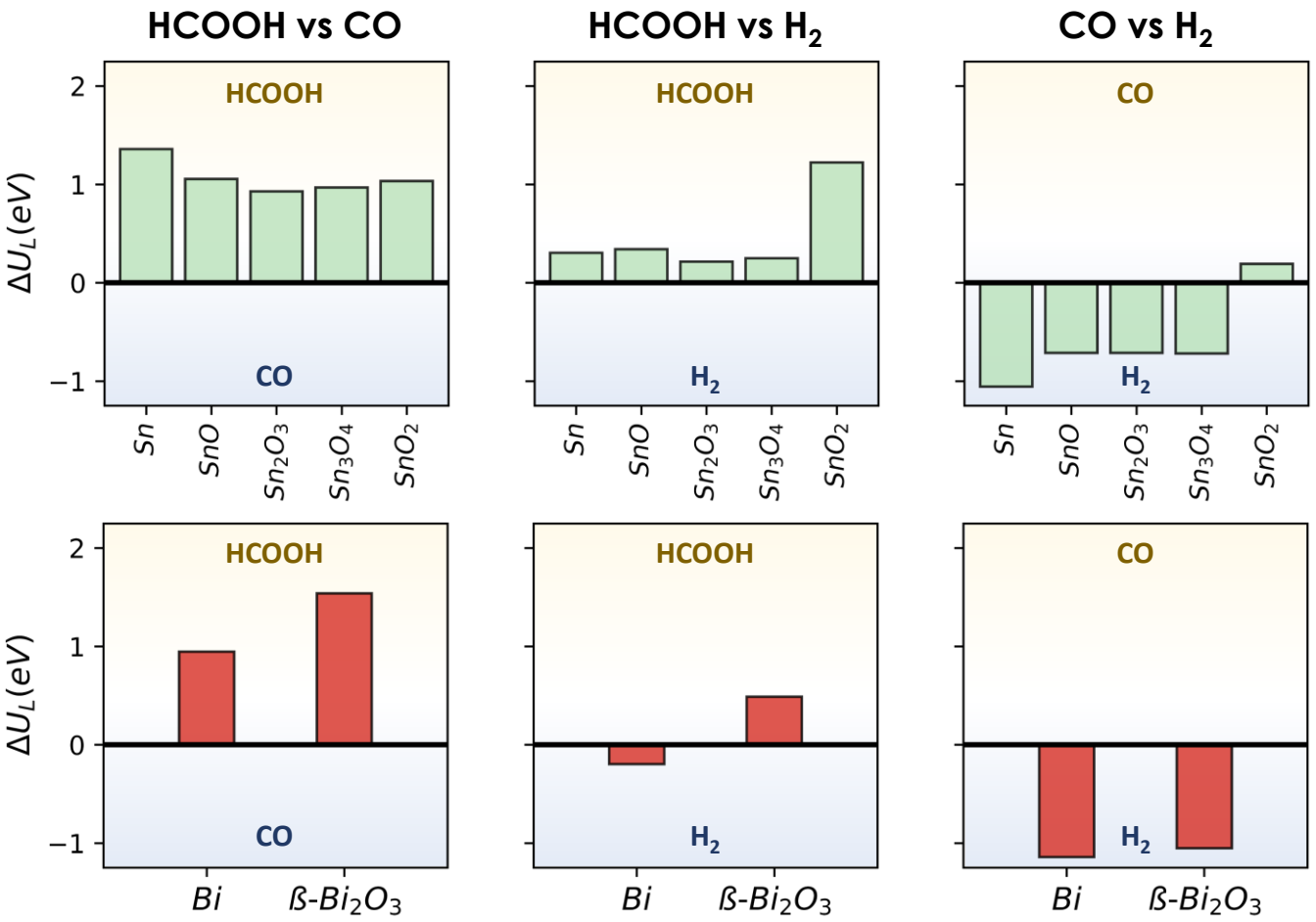
CO_2RR pathways on ß-Bi_2O_3 and Bi surfaces

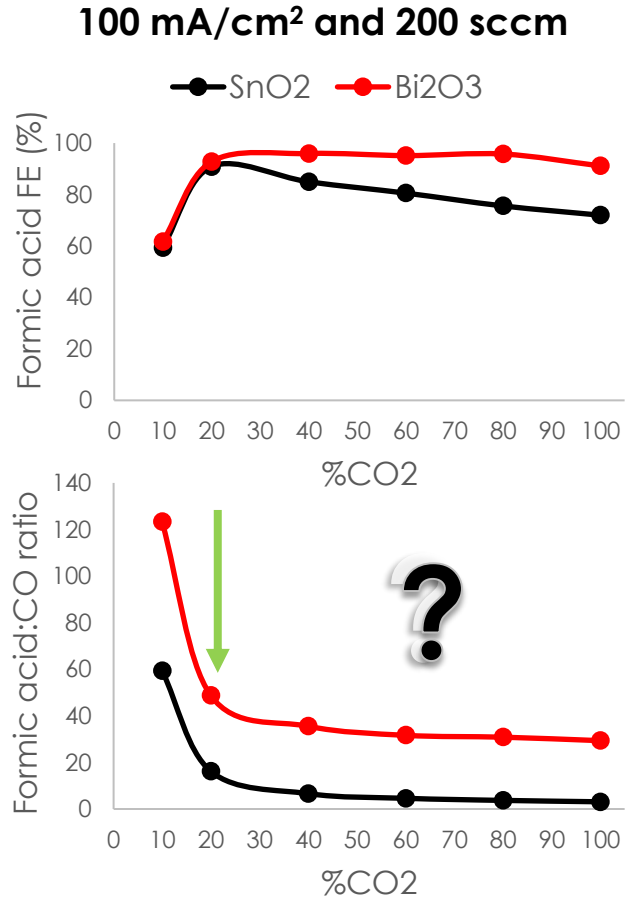


- **Lower thermodynamic barriers on metallic Bi.**
- **H_2 slightly favored thermodynamically over reduced Bi.**

Ellis, J., El Berch, J., Mpourmpakis, G., Kauffman, D. *In preparation*.

Combined selectivity trends of Bi and Sn

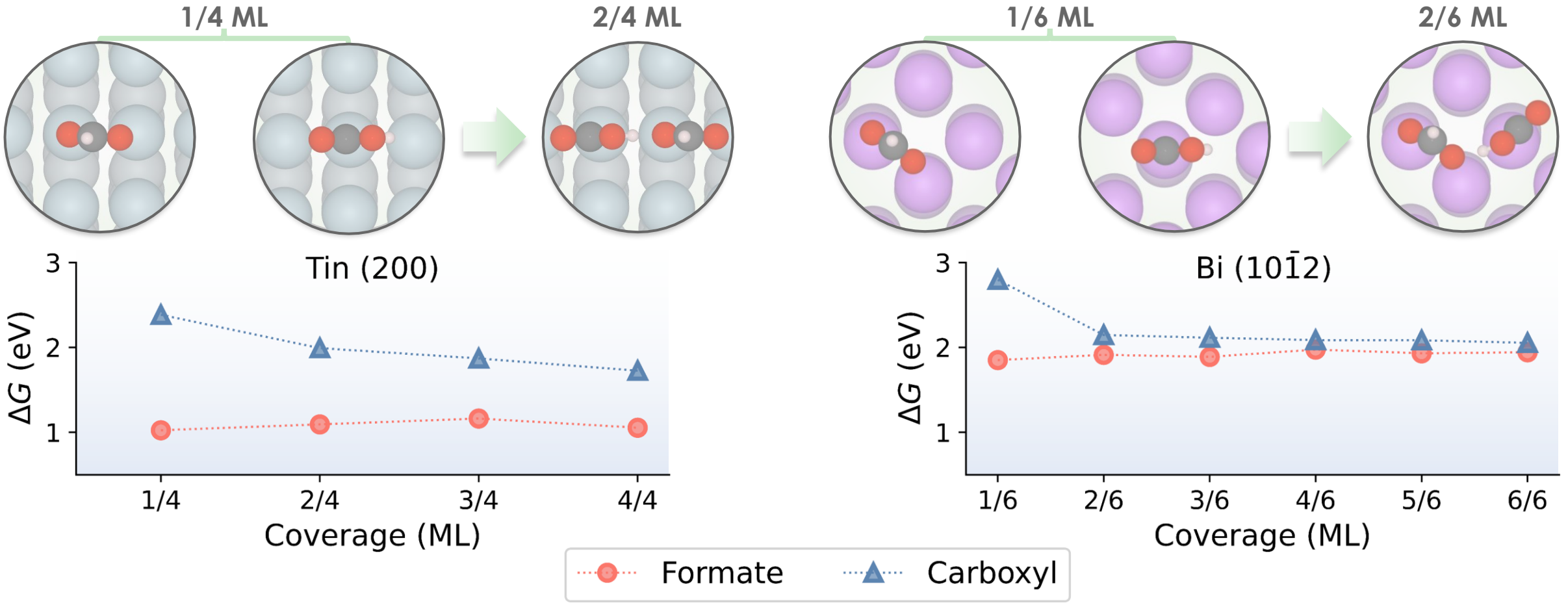




- H_2 evolution competing at lower $\%CO_2$.
- Sn partial oxides might decrease CO_2 selectivity.

Ellis, J., El Berch, J., Mpourmpakis, G., Kauffman, D. *In preparation*.

Lateral interactions and carboxyl stability



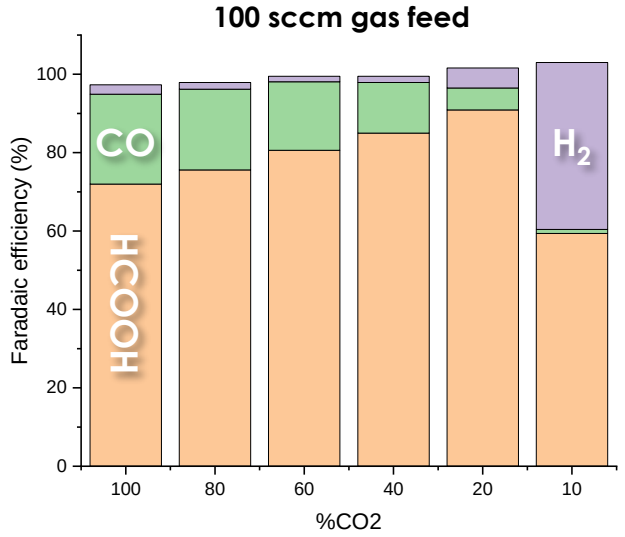
Lateral interactions stabilize the carboxyl intermediate (favoring CO production)

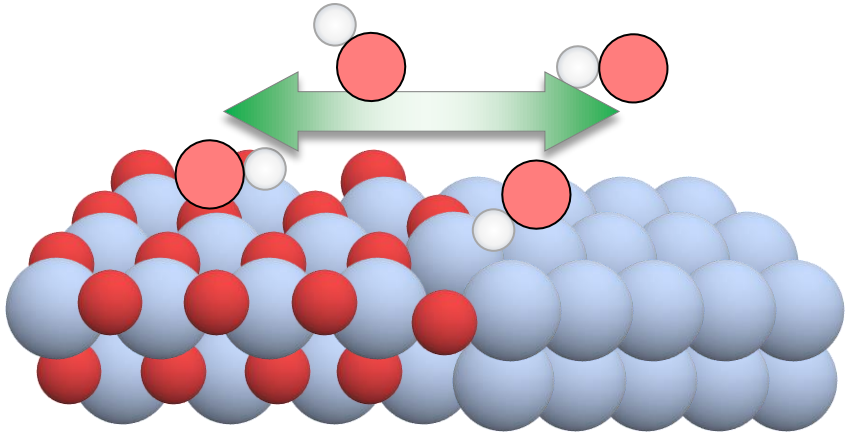
1. Ellis, J., El Berch, J., Mpourmpakis, G., Kauffman, D. *In preparation*.
2. Chen *et al.* (2021), *ACS Catalysis*, **11**, 4349-4361.

Summary

1

Mixed oxide/reduced Sn phase, resulting in shifts in CO:HCOOH ratio

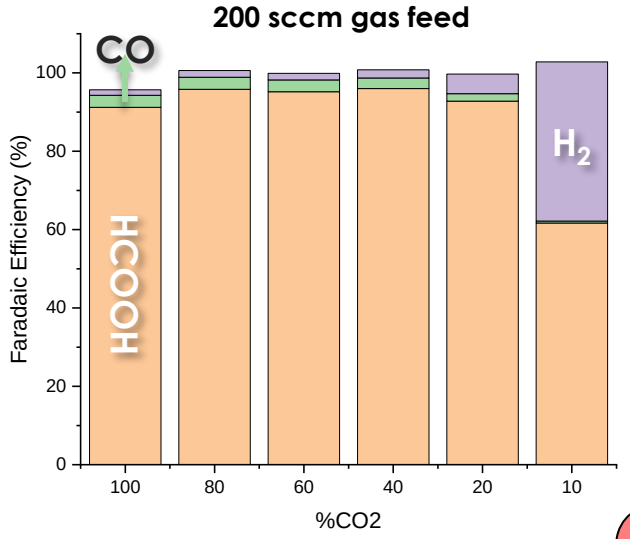


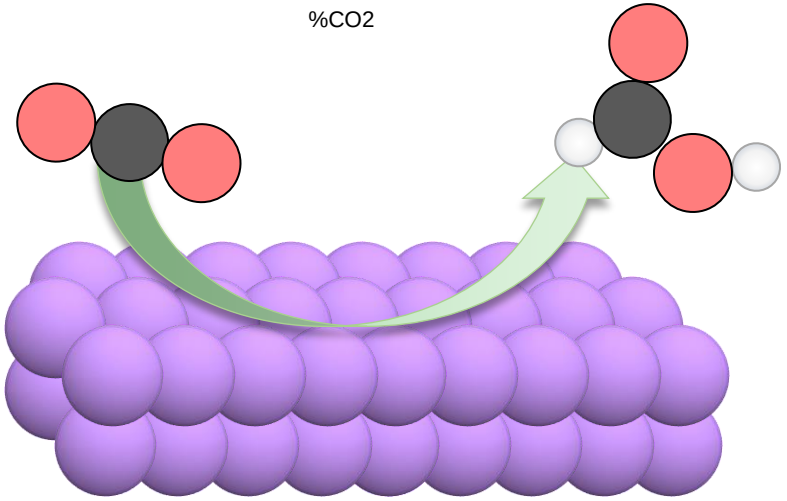


Summary

1. Mixed oxide/reduced Sn phase, resulting in shifts in CO:HCOOH ratio

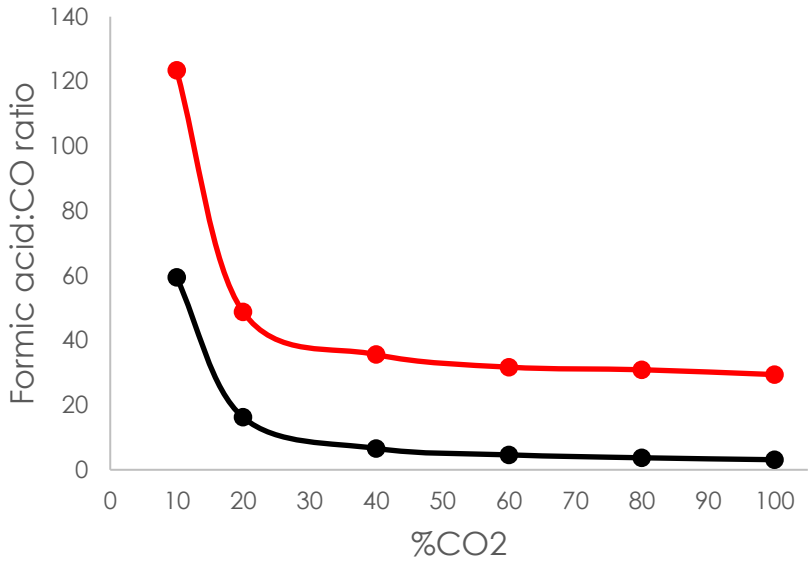
2. **Reduced Bi phase, resulting in higher HCOOH selectivity**

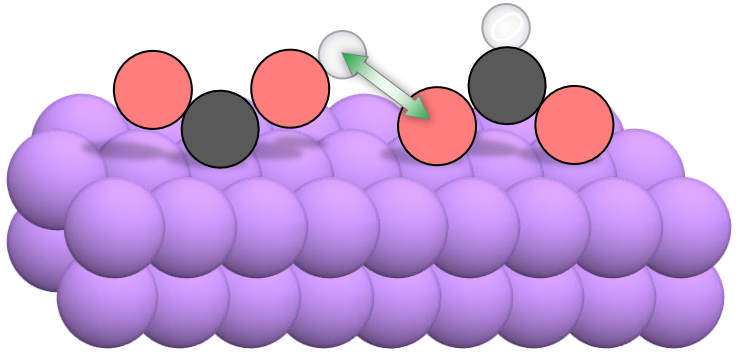




Summary

1. Mixed oxide/reduced Sn phase, resulting in shifts in CO:HCOOH ratio
2. Reduced Bi phase, resulting in higher HCOOH selectivity
3. **Lateral interactions stabilize the carboxyl intermediate (CO pathway)**





Acknowledgements

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- Prof. Giannis Mpourmpakis
- My lab-mates at the Computer Aided Nano and Energy Lab (CANELa)
- Dr. James Ellis and Dr. Douglas Kauffman (NETL)

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Fossil Energy and Carbon Management

NATIONAL ENERGY TECHNOLOGY LABORATORY

CENTER for RESEARCH COMPUTING

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Supporting Information

Outline

1. Computational methods
2. Computational results
3. Experimental results
4. Additional background

Building the Pourbaix diagram (Persson *et al* framework)

The framework[1] proposes a way to compute the formation energies of ions combining DFT and experimental data

Solid and liquid (other than water) materials

$$\mu^0 = E^{DFT} - Ts^{DFT} - \Sigma(E_i^{DFT} - Ts_i^{DFT})$$

State of interest (e.g., Li_2O)

Reference states (e.g., 2xLi and O)

Ion species

$$\mu^0 = \mu^{0,EXP} + \mu_S^{0,\ DFT\ -\ exp}$$

Experimental potential of aq species (e.g., Li^+)

DFT error computed on a solid material (e.g., Li_2O)

Use these potentials in conjunction with Nernst equation to obtain most stable phases

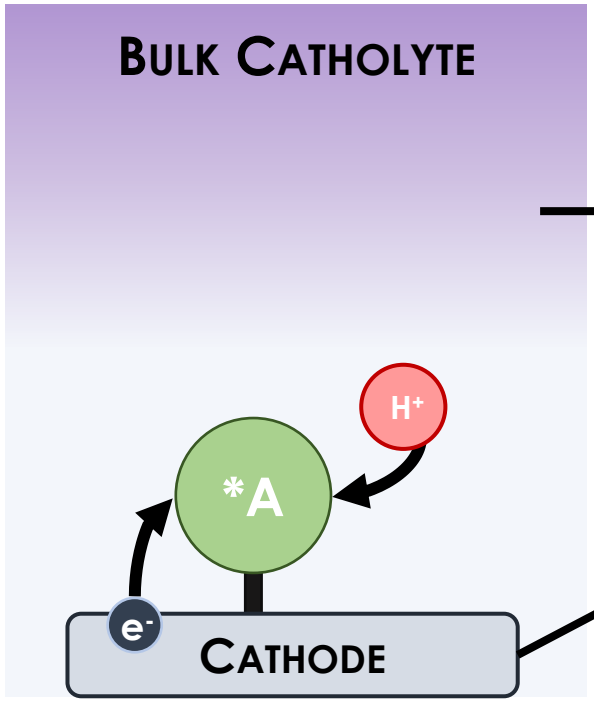
$$[Reactants] + H_2O \longleftrightarrow [Products] + mH^+ + ne^-$$

$$-nFE = \Delta G^0_{Rxn} + 2.303*RT*\log(a_{reactant}/a_{product}) - 2.303*RT*m*pH$$

In this work: used the atomic simulation environment (ASE) Pourbaix function (assume all dissolved species have a concentration of 10^{-6} M) with computed μ^0 values.

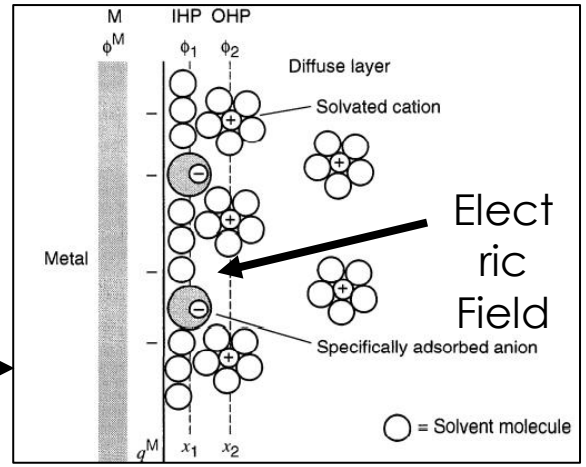
1. Persson *et al.* (2012). *Physical Review B.* **85.** 235438

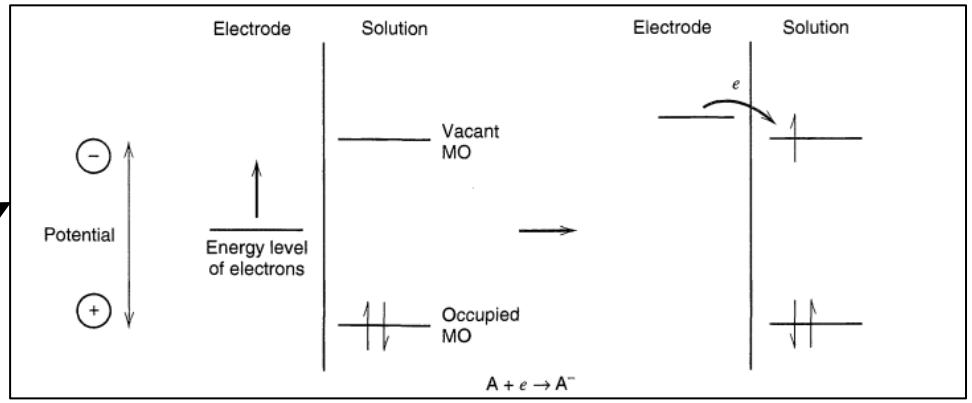
Complexities in obtaining transition states



Electron transfer (non-equilibrium)

Solvated ions, and the electric field in the double layer are difficult to simulate[1]

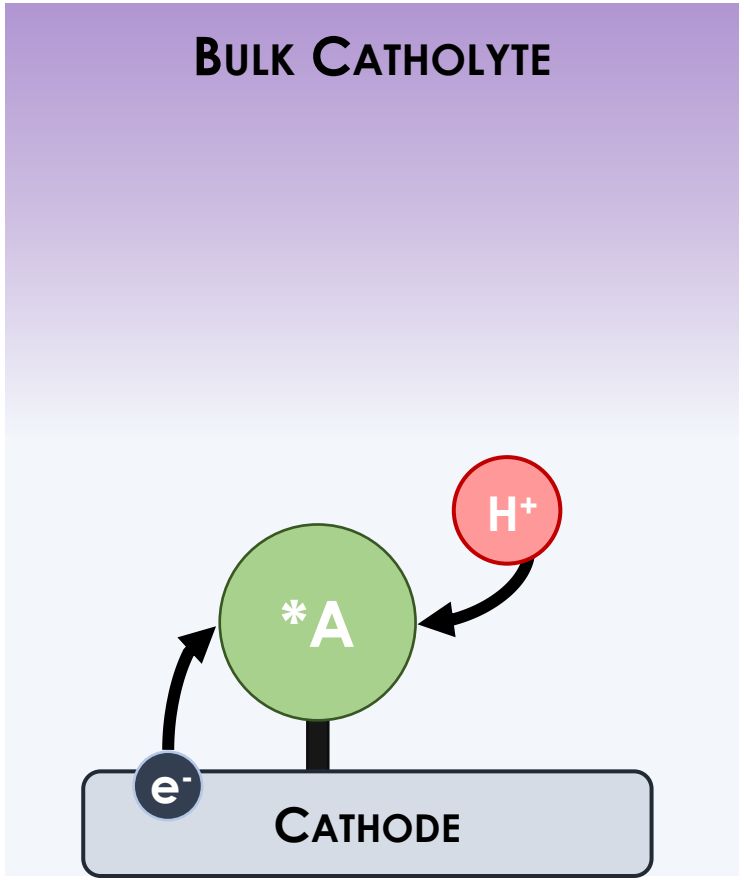




Applied potential shifts the Fermi level (average energy of available electrons @ 0K) of the electrode[2]

1. Akhade, Sneha A., et al. ***Catalysis Today*** 288 (2017): 63-73.
2. Bard, Allen J., Larry R. Faulkner, and Henry S. White. *Electrochemical methods: fundamentals and applications*. John Wiley & Sons, 2022.

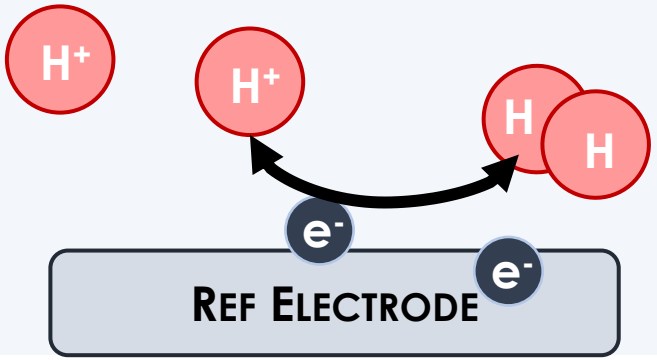
Computational Hydrogen Electrode (CHE)



$$G_{IS} = G_{A^*} + \mu_{H+} + \mu_{e-}$$

We use the Computational Hydrogen Electrode (CHE) Approach[3]

This reaction is in equilibrium (analogous to the Reversible Hydrogen Electrode)

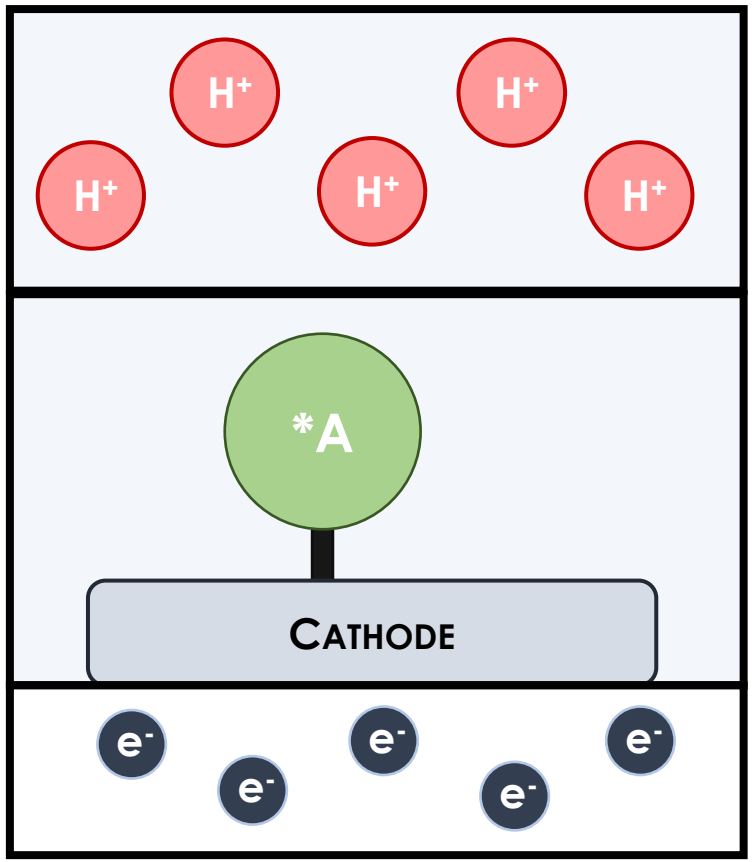


$$\tfrac{1}{2} G_{H2} = \mu_{H+} + \mu_{e-}$$

1. Akhade, Sneha A., et al. ***Catalysis Today*** 288 (2017): 63-73.
2. Bard, Allen J., Larry R. Faulkner, and Henry S. White. *Electrochemical methods: fundamentals and applications*. John Wiley & Sons, 2022.
3. Nørskov, Jens Kehlet, et al. ***The Journal of Physical Chemistry B*** 108.46 (2004): 17886-17892.

CHE helps just with reaction energies

Rethink the initial state



Reservoir

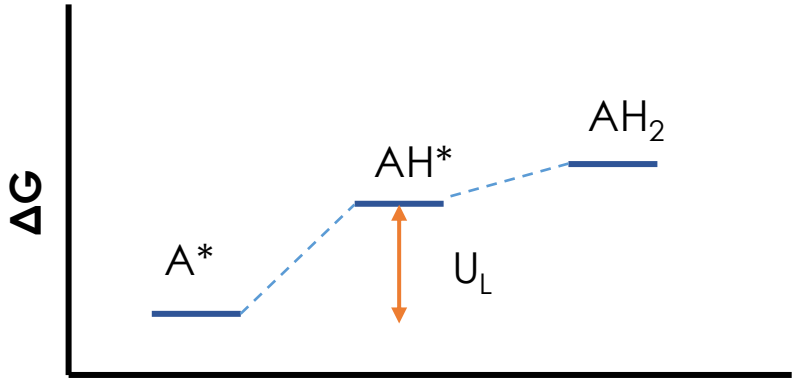
Simulate this

Reservoir

We simulate a series of Proton-Coupled Electron Transfer (PCET) steps

$$\Delta G = G_{AH^*} - G_{A^*} + \mu_{H+} + \mu_{e-} + neU$$

FINAL STATE — INITIAL STATE — APPLIED POTENTIAL BIAS

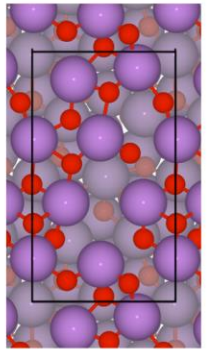


The Limiting Potential (U_L) is equal to ΔG_{max} /e … the min potential one must supply for the reaction to be thermodynamically favored

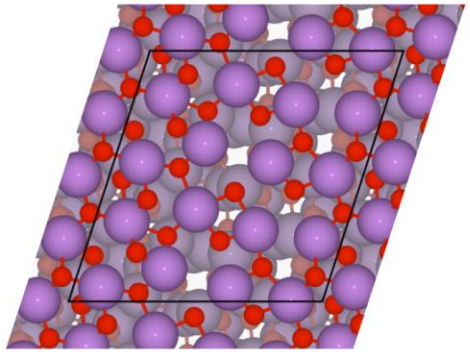
1. Nørskov, Jens Kehlet, et al. ***The Journal of Physical Chemistry B*** 108.46 (2004): 17886-17892.
2. Oberhofer, H., **(2018)**, "Electrocatalysis Beyond the Computational Hydrogen Electrode", In: Andreoni, W., Yip, S. (eds) "Handbook of Materials Modeling". *Springera*

Slab models

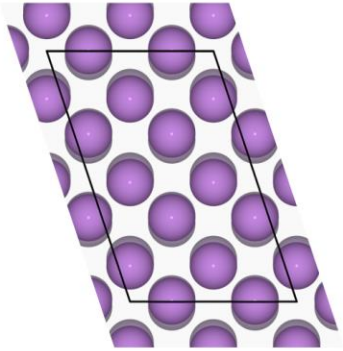
a) ß-Bi_2O_3 (201)



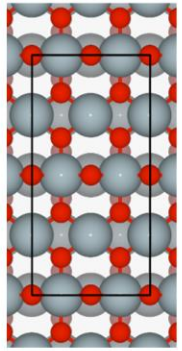
b) α-Bi_2O_3 (120)



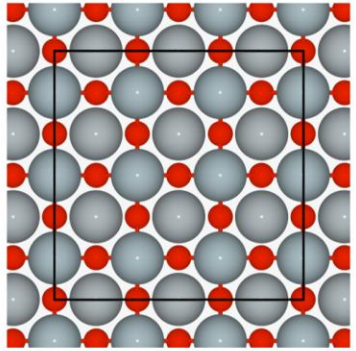
c) Bi ($10\bar{1}2$)



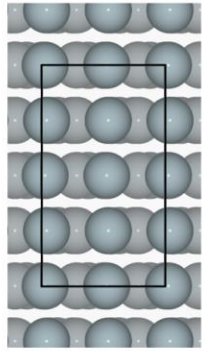
d) SnO_2 (110)



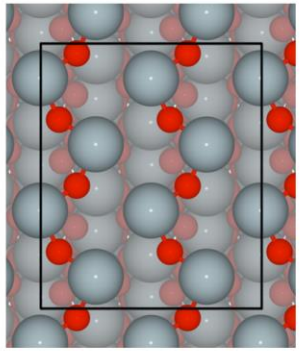
e) SnO (001)



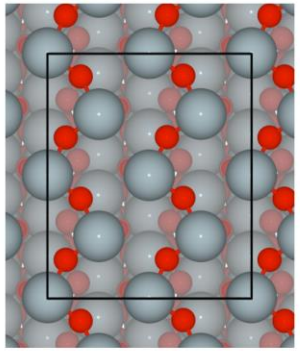
f) Sn (200)



a) Sn_2O_3 (100)



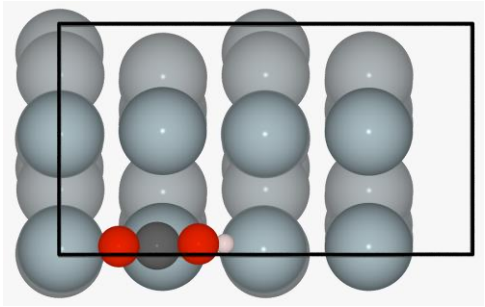
b) Sn_3O_4 (100)



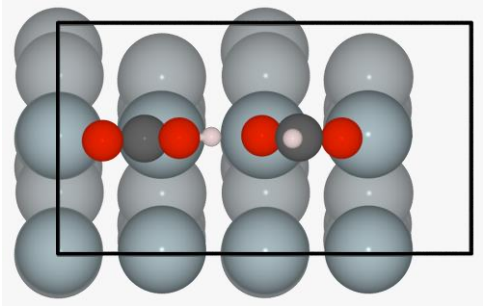
Coverage on Sn

Carboxyl

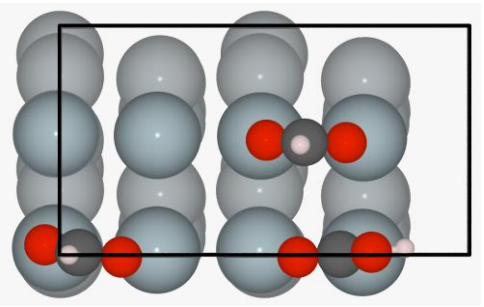
1/4 ML



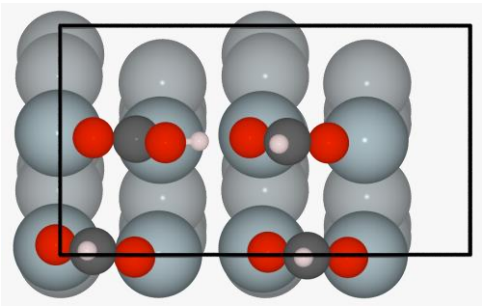
2/4 ML



3/4 ML

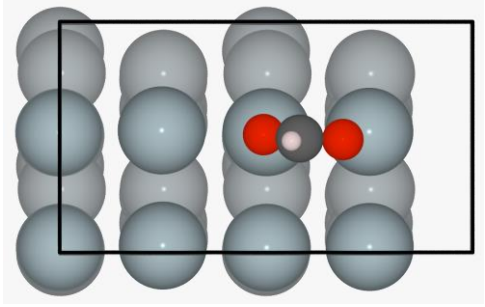


4/4 ML

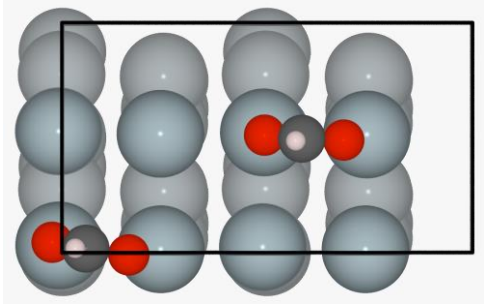


Formate

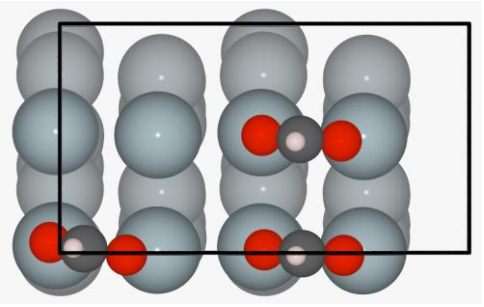
1/4 ML



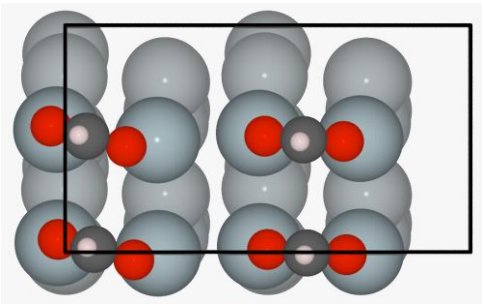
2/4 ML



3/4 ML



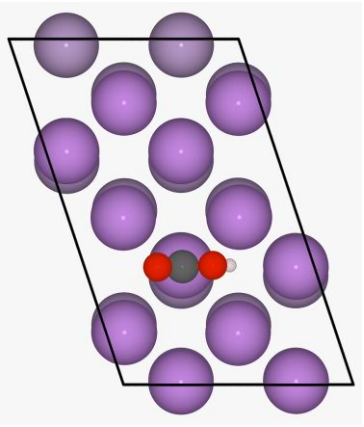
4/4 ML



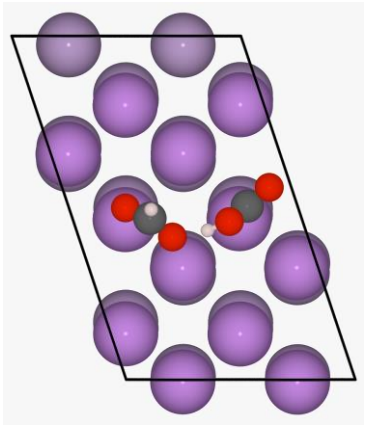
Coverage on Bi

Carboxyl

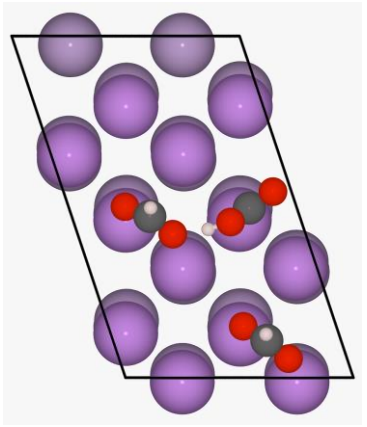
1/6 ML



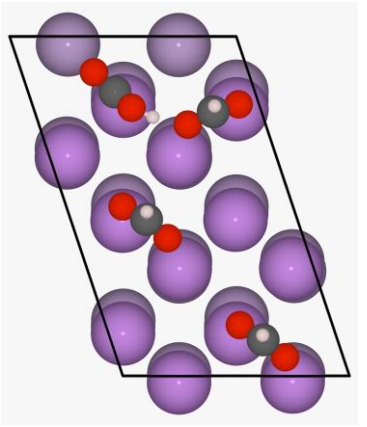
2/6 ML



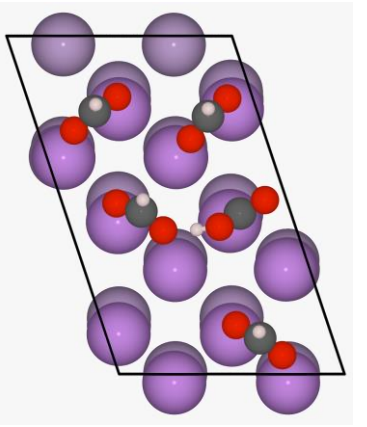
3/6 ML



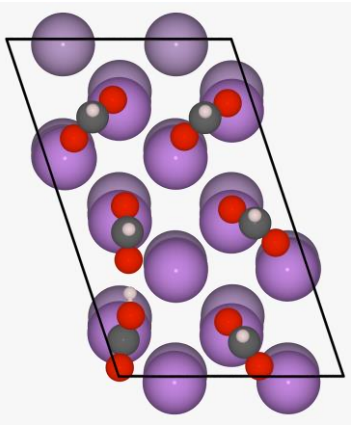
4/6 ML



5/6 ML

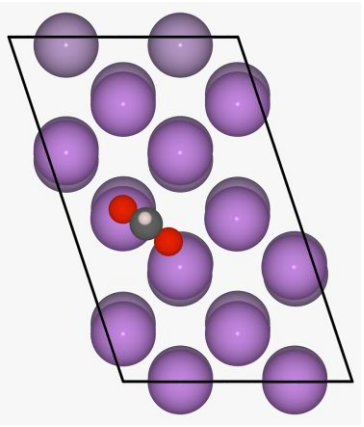


6/6 ML

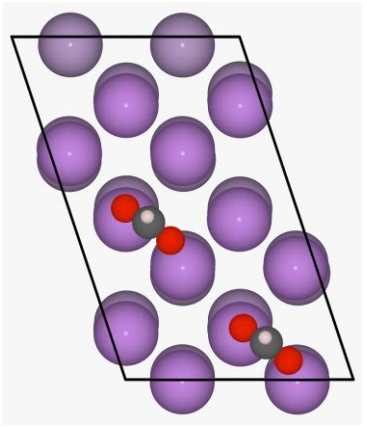


Formate

1/6 ML



2/6 ML



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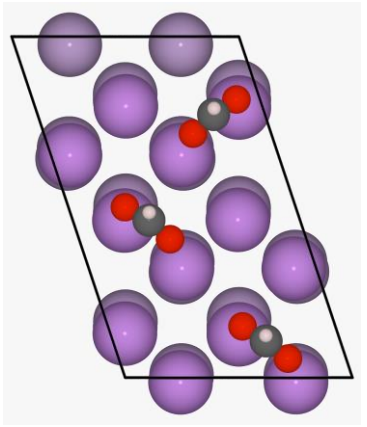
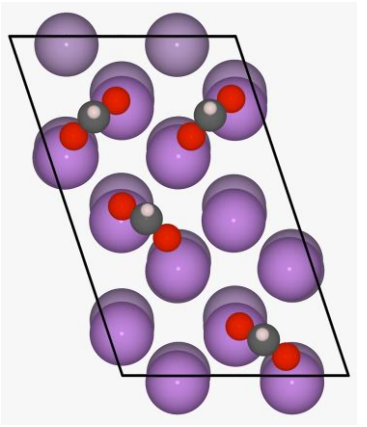
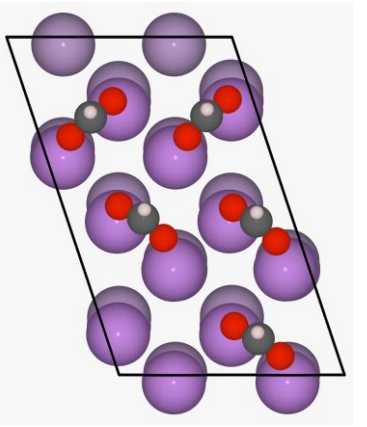


4/6 ML



5/6 ML



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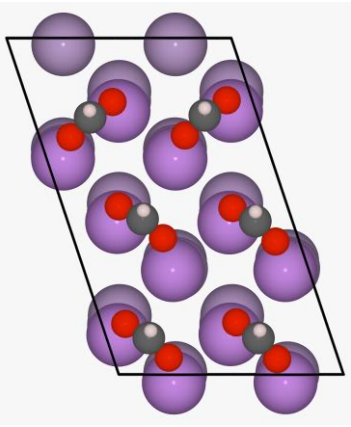
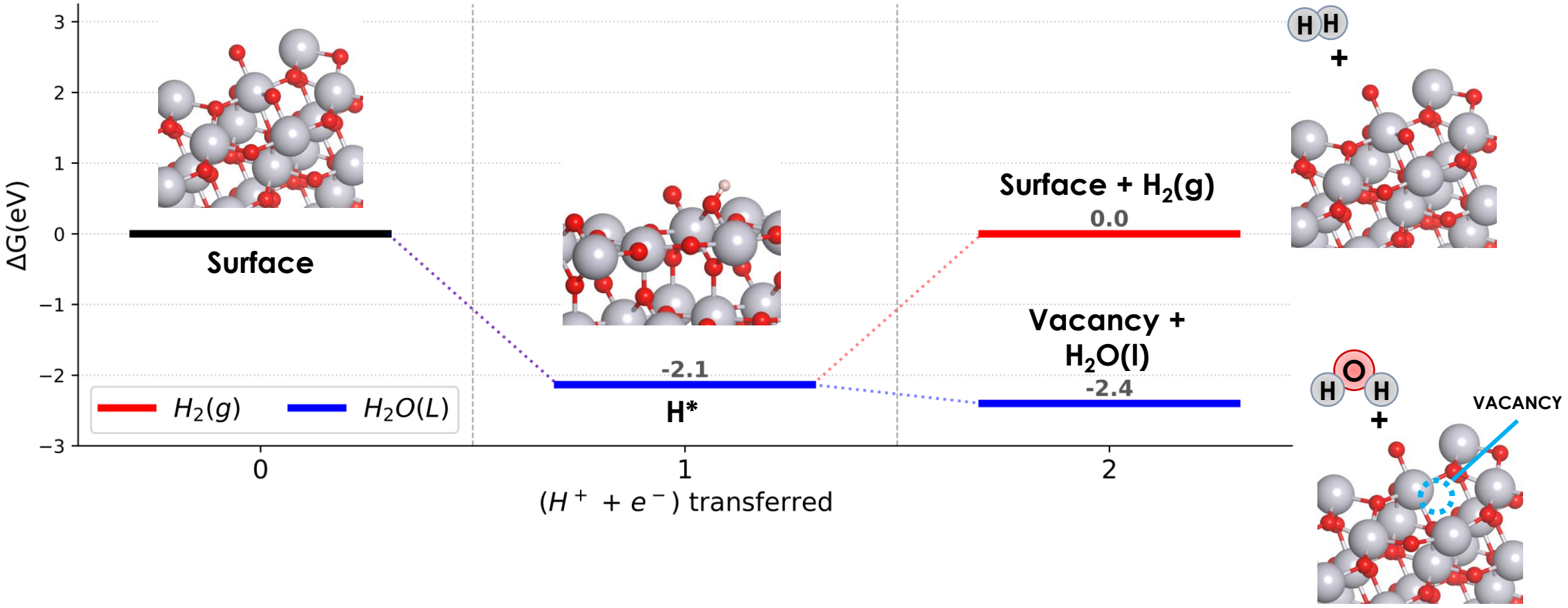


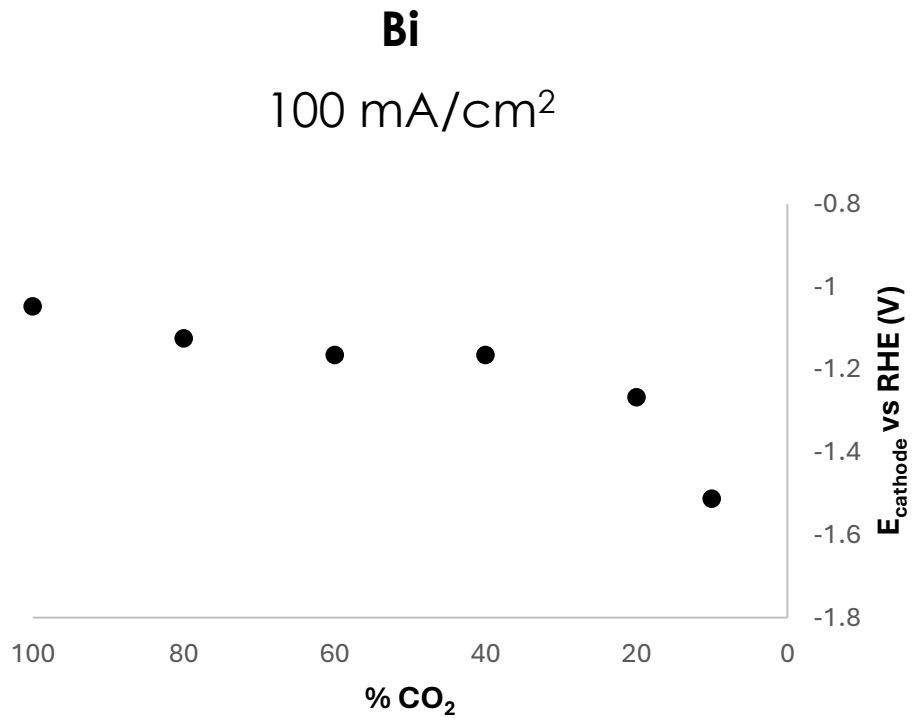
SnO_2 strong H binding: generating a vacancy

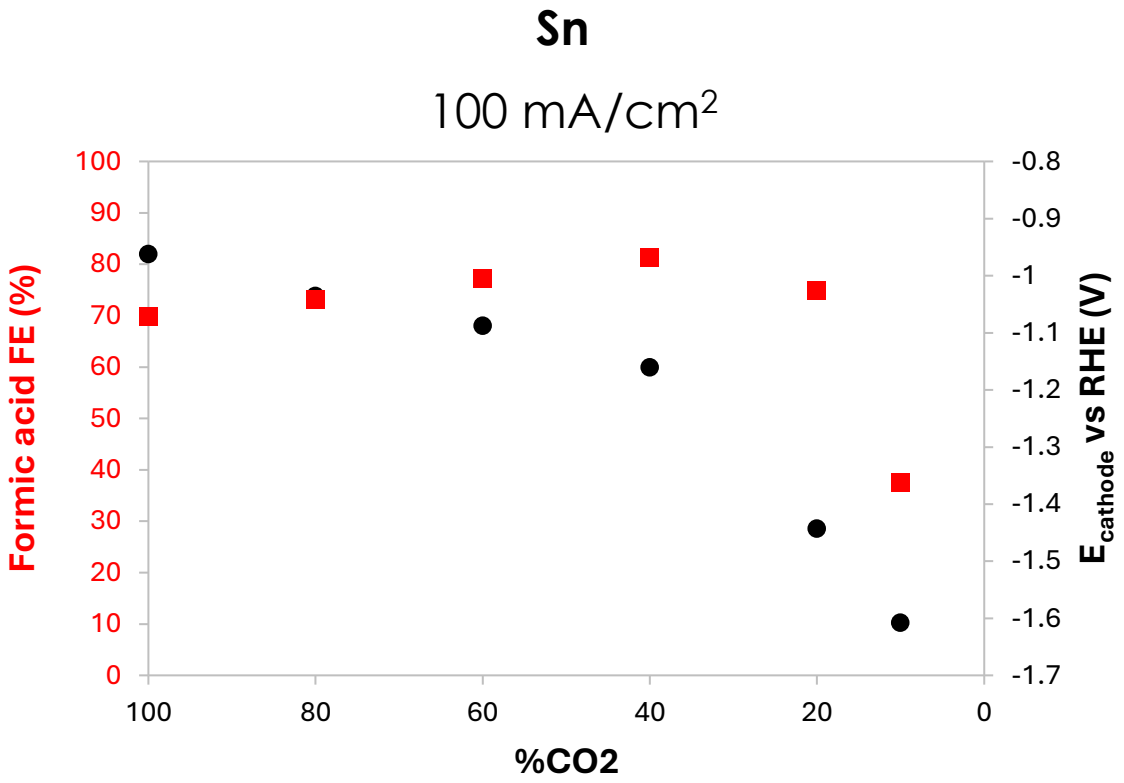
NATIONAL ENERGY TECHNOLOGY LABORATORY

SnO_2 is readily reduced to form H_2O



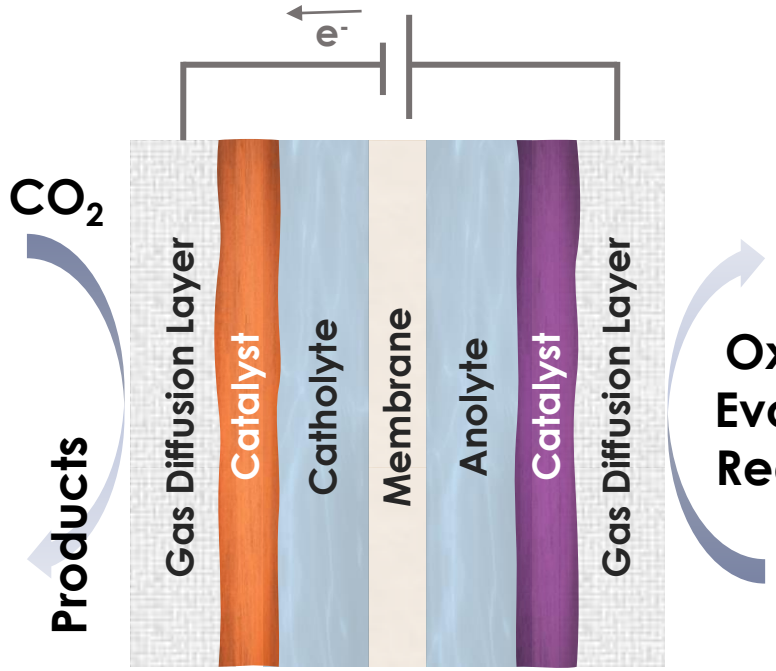
Half cell reactor studies





CO_2 electroreduction

Gas-fed flow electrolyzers can convert CO_2 at ambient conditions



$CO_2 + 2(H^+ + e^-) \rightarrow CO + H_2O$
$CO_2 + 2(H^+ + e^-) \rightarrow HCOOH$

Closer to commercialization[1]

$CO_2 + 8(H^+ + e^-) \rightarrow CH_4 + 2H_2O$
$2CO_2 + 12(H^+ + e^-) \rightarrow C_2H_4 + 4H_2O$
$2CO_2 + 14(H^+ + e^-) \rightarrow C_2H_6 + 4H_2O$
$3CO_2 + 18(H^+ + e^-) \rightarrow C_3H_7OH + 5H_2O$

More electron transfer steps

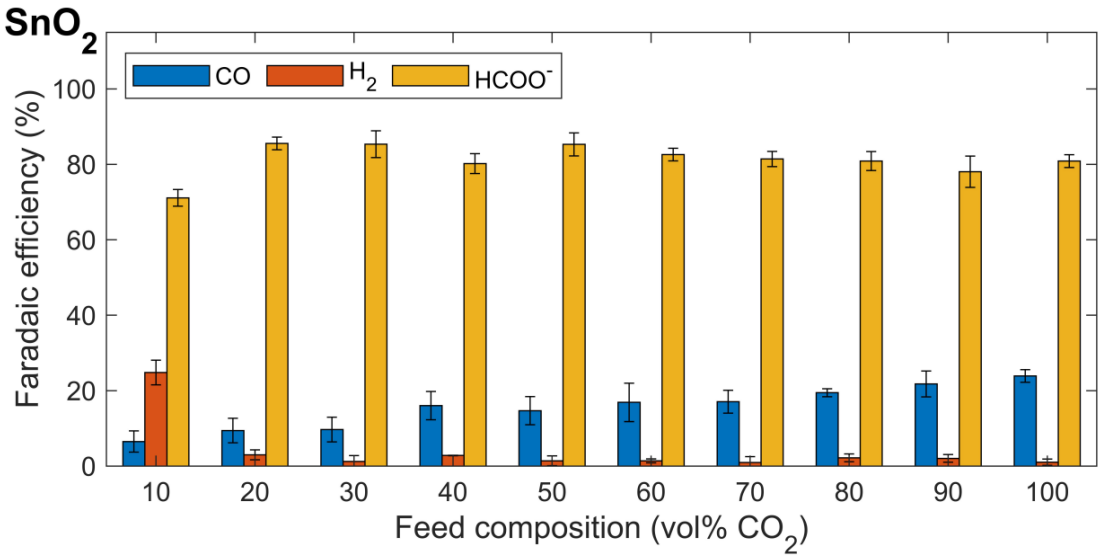
Only Cu-based catalysts[2]

1. Shin *et al.* (2021), *Nature Sustainability*, **4**, 911-919
2. Nitopi *et al.* (2019), *Chemical Reviews*, **119**, 7610-7672

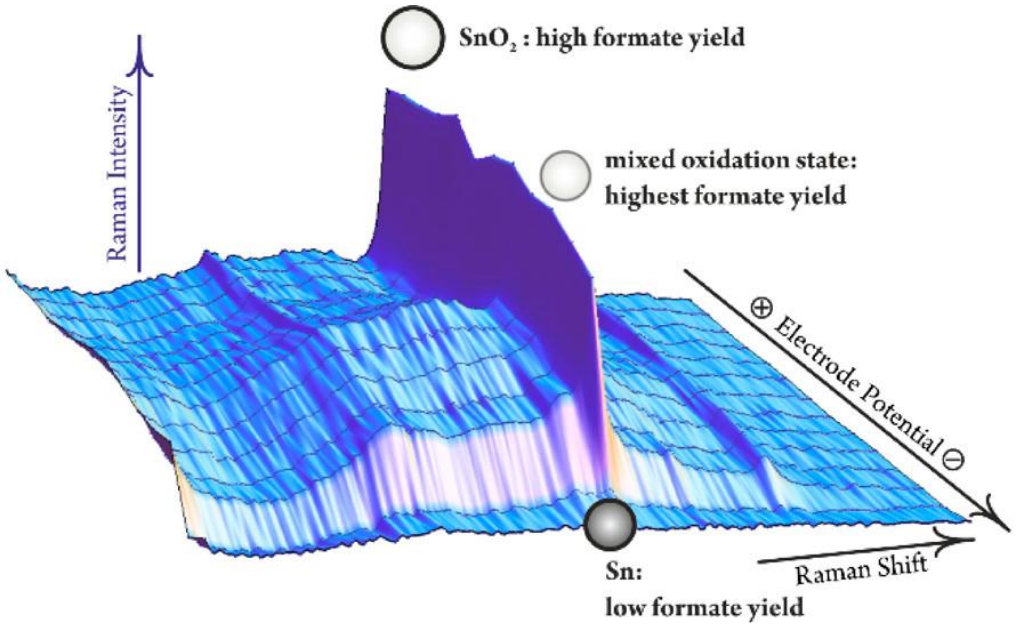
Effects of feed concentration on CO_2RR selectivity

Gas-fed flow electrolyzer: CO_2RR experiments[1]

CO_2 diluted in N_2 | fixed current density at 100 mA/cm^2



CO_2 inlet concentrations impact product selectivity in gas-fed flow electrolyzers



Partially oxidized Sn reported as the most selective phase[2]

1. Van Daele *et al.* (2022), *Journal of CO2 Utilization*, **65**, 102210
2. Dutta *et al.* (2015), *ACS Catalysis*, **5**, 7498-7502