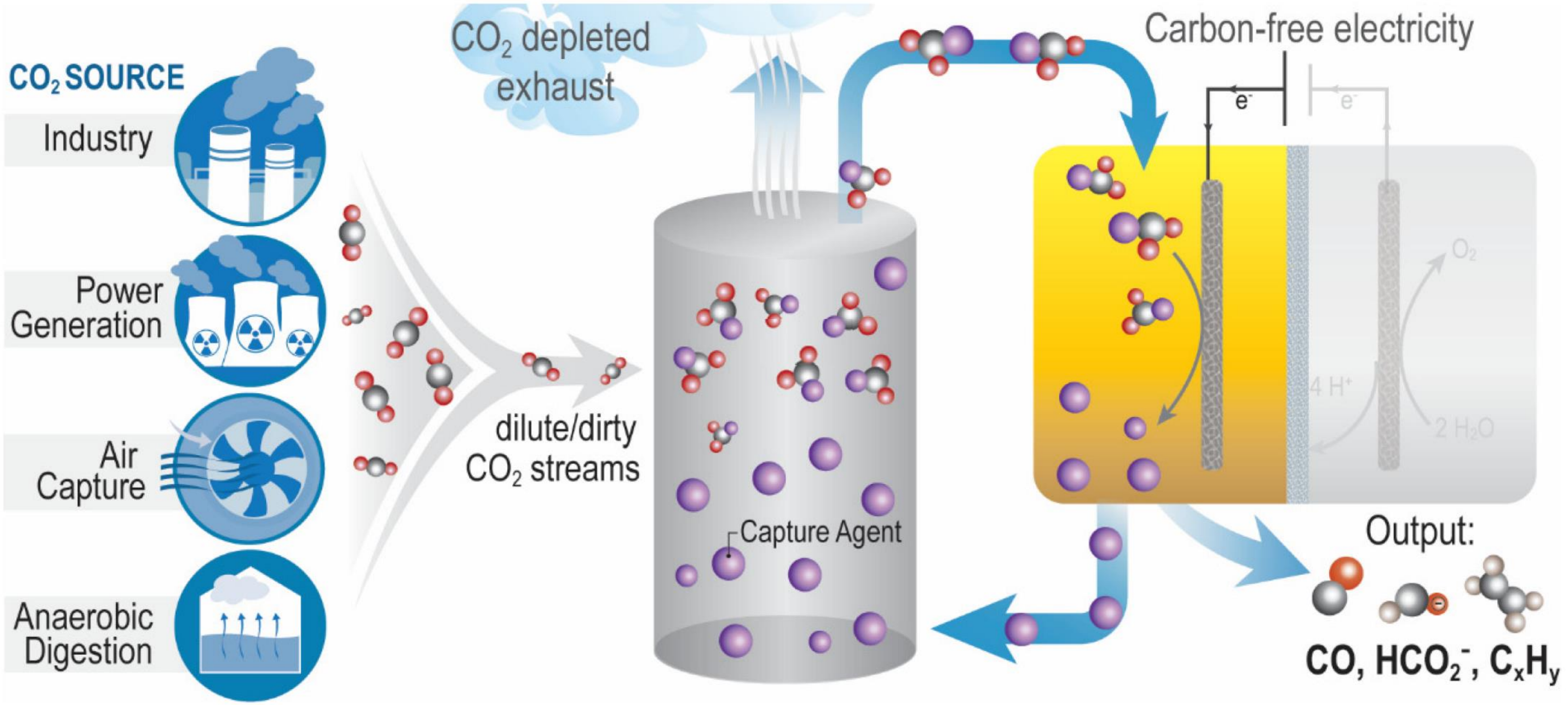
Center for Closing the Carbon Cycle (4C)

Energy Frontier Research Center (EFRC)

Jenny Yang, Director

Integrating CO_2 Capture and Conversion: *Center for Closing the Carbon Cycle (4C)*

MISSION: To advance synergistic capture and conversion of carbon dioxide (CO_2) from dilute streams into useful products through the convergent study of sorbents and catalysts.



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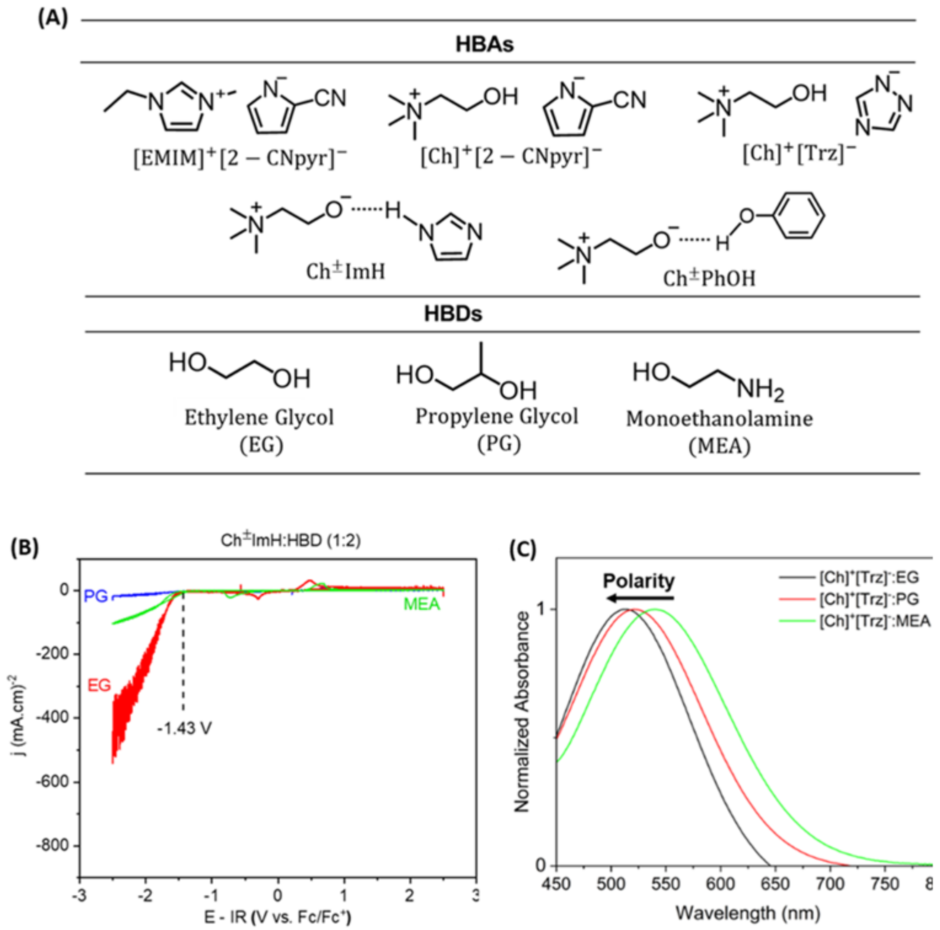
New Sorbent Discovery

High CO_2 Capacity Ionic Liquids



Parameters

- Electrochemical stability

Solvatochromic methods used to determine:

- Kamlet-Taft parameters ET(30)
- HBD acidity (α)
- HBD basicity (β)
- polarizability (π*)

Work will also:

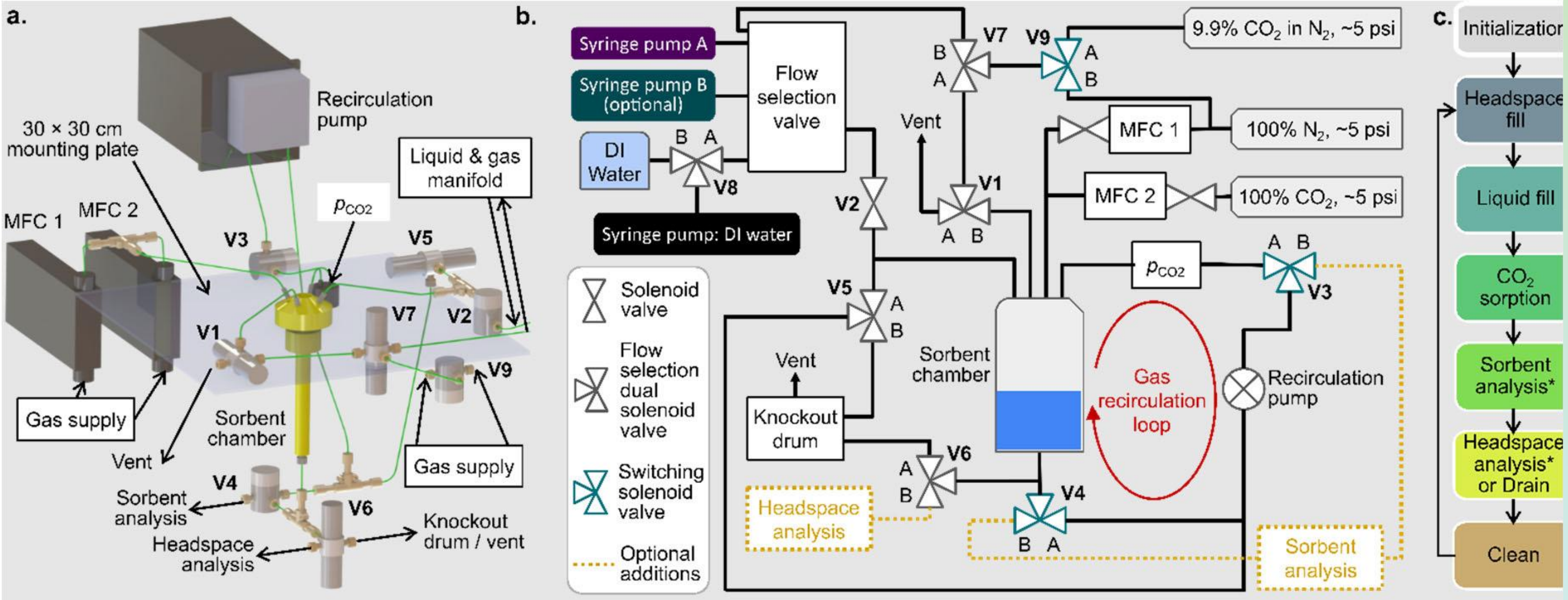
- assess solvent viscosity changes due to CO_2 complexation
- implications of IL dilution

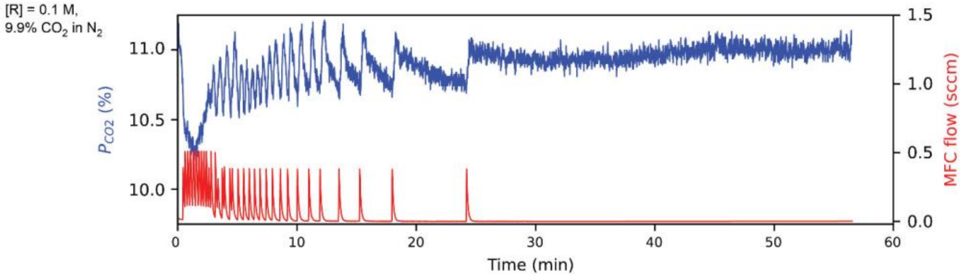
Gurkan (CWRU)
"From high-purity synthesis to key experimental considerations for evaluating functionalized ionic liquids for combined capture and electrochemical conversion of CO_2", in review

High-throughput Evaluation of New Sorbents

The **Carbon Capture Screening Instrument (CCSI)** is designed to:

1. prepare sorbent media, including solvent and supporting electrolyte identity and concentration
2. measure kinetics and thermodynamics of CO_2 sorption at a chosen p_{CO2}
3. transfer the electrolyte containing the CO_2 adduct to an electrochemical cell to measure the electrochemical voltage window and/or the reduction potential with a chosen catalyst





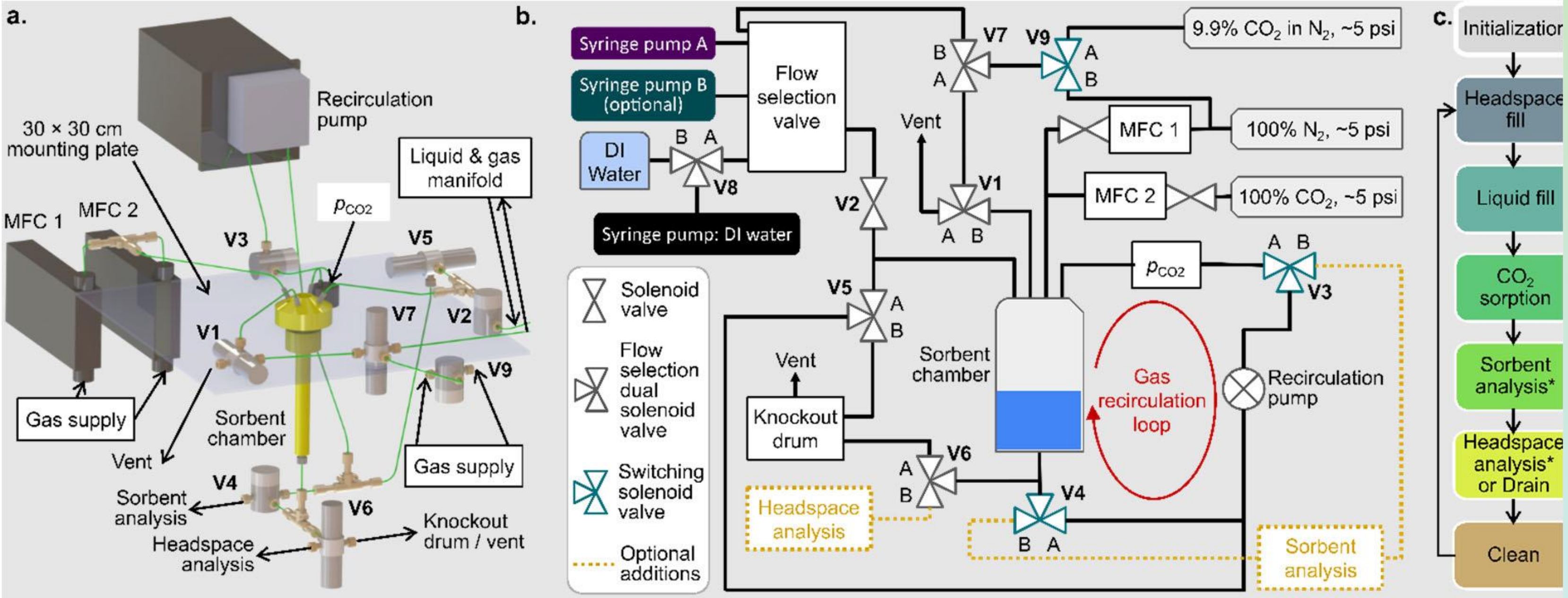
CCSI data for the sorption of CO_2 from a 9.9% atmosphere by an aqueous 0.1 M tetramethylammonium pentafluorophenoxide sorbent.

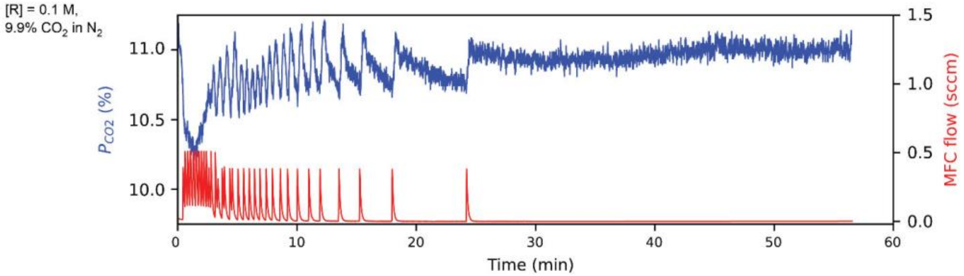
Gregoire (Caltech)
“Accelerated screening of carbon dioxide capture by liquid sorbents”, in revision

High-throughput Evaluation of New Sorbents

Future opportunities:

- electrochemical voltage window
- tolerance to liquid or gas impurities
- product distribution from electroreduction with select heterogeneous catalysts
- stability (corrosion) of select heterogeneous catalysts
- solvatochromic determination of Kamlet-Taft parameters to establish descriptors for sorption
- rheology, for example viscosity changes with CO_2 sorption
- ionic conductivity





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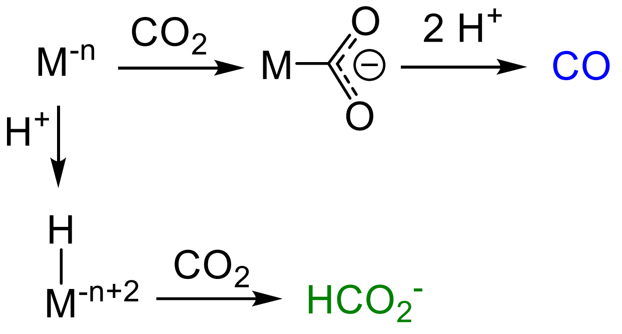
New Sorbents for Catalysis

How can we translate knowledge from CO_2 reduction to captured-CO_2 reduction?

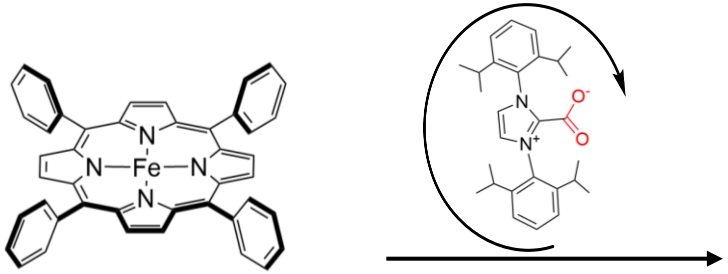
In CO_2 reduction, CO & HCO_2^- are the most common products & have distinct mechanisms

CO_2 first pathway

Protonation first pathway

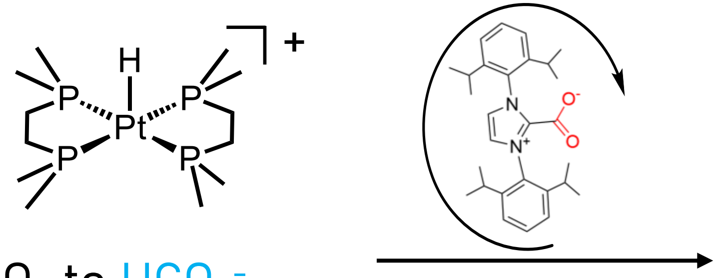


Carbene-CO_2 adducts were identified computationally



90% CH_4
6% H_2

CO_2 to CO catalyst

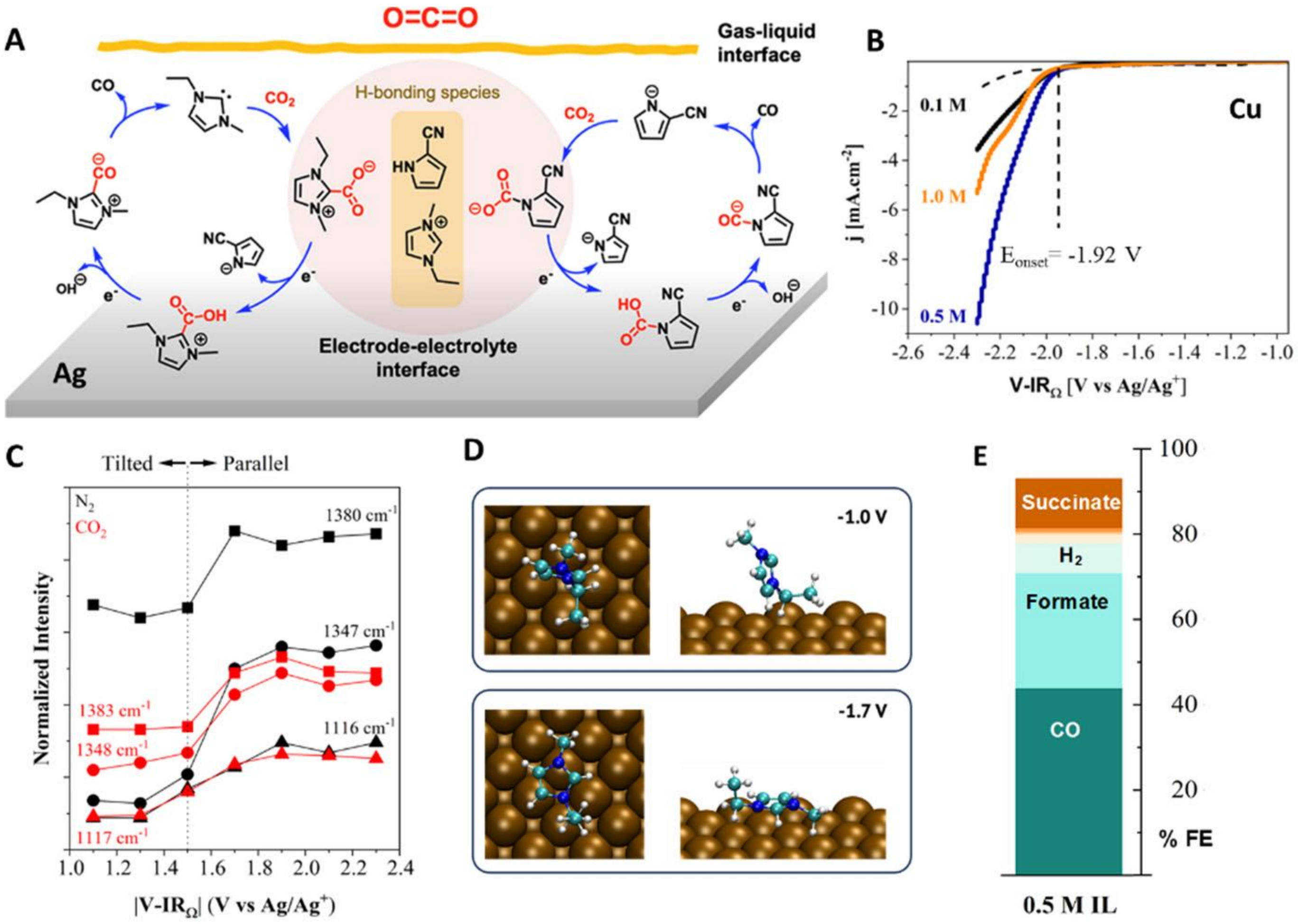


96% HCO_2^-
2% H_2

CO_2 to HCO_2^- catalyst

Yang (UCI)

CO_2 Reduction in Ionic Liquids



- Succinate was observed as a product with Cu
- Advanced electrochemical techniques and *in situ* spectroscopy were used to characterize the interfacial structure
- H-bond donation and cation/anion assembly at electrode is important for selectivity

Gurkan (CWRU), Sacci (ORNL)
Spurgeon (Louisville), Kumar (ECSU), Velazquez (UC Davis)

Tailoring Electrochemical CO2 Reduction on Copper by Reactive Ionic Liquid and Native Hydrogen Bond Donors, ACIE, **2023**, e202312163.

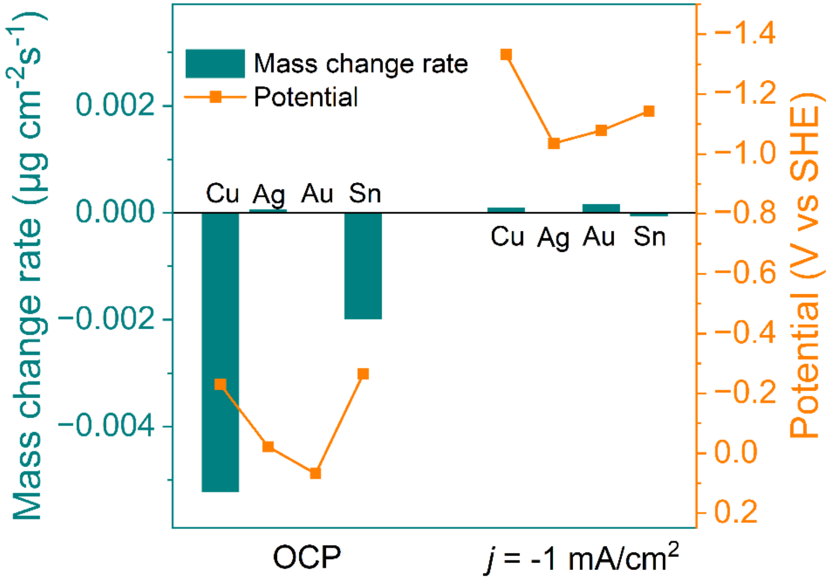
Activity Descriptors for RCC – Amine Sorbents

$2RNH_2 + CO_2 \rightleftharpoons RNHCOO^- + RNH_3^+$

$RNHCOO^- + ne^- + nH^+ \rightarrow RNH_2 + \text{products}$

Cu before and after RCC experiments

We discovered corrosion is an emergent phenomenon that needs to be addressed



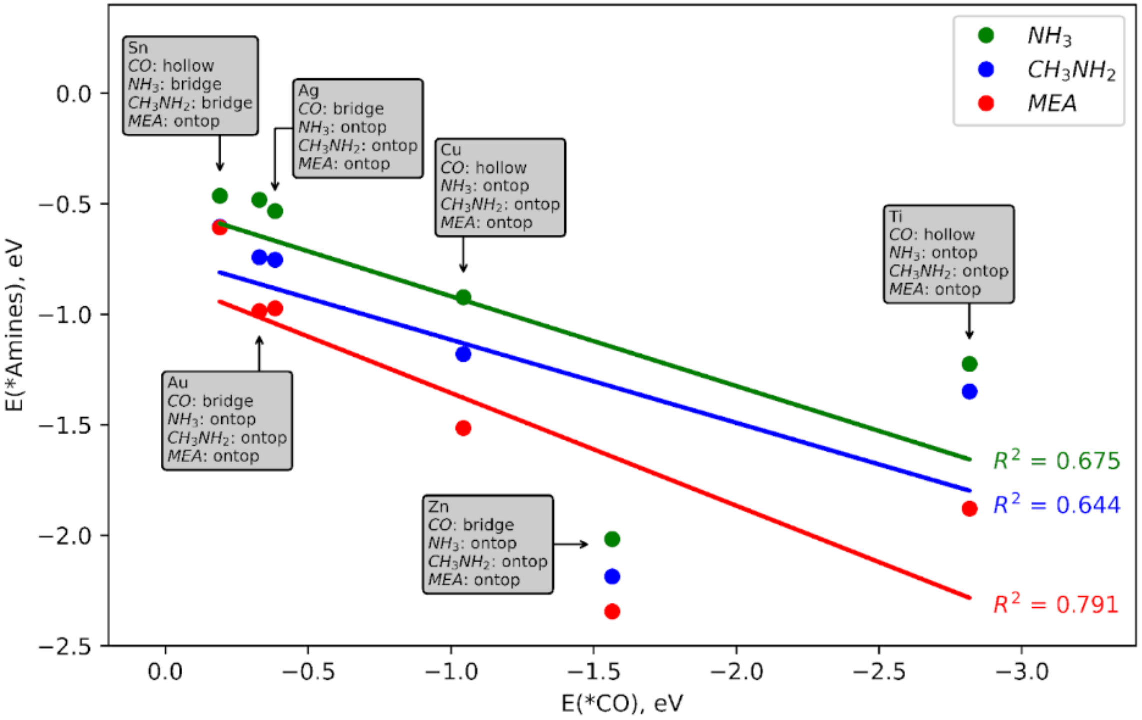
Corrosion rate and potential

Morales Guio (UCLA), Stieber (CPP), Alexandrova (UCLA)

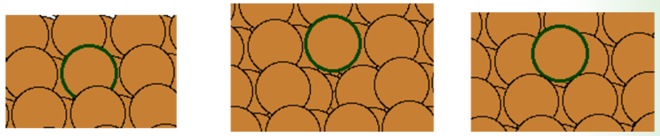
"Finding Activity and Stability Descriptors beyond those for CO2 Reduction", submitted

Addressing Corrosion

Calculated binding energies of CO and amines on transition metals



Comparison of amines and phenoxides on Cu



	Cu	Cu_vacancy	Cu_adatom
Methylamine	0.00	-0.01	0.46
Ethylamine	0.20	0.01	0.50
dimethylamine	0.32	0.31	0.61
phenoxide	0.94	0.73	1.22
2,6-dimethylphenoxide	1.13	1.08	1.21

Scientific Achievement: Predicted that branched amines and alkoxides have a lower affinity for Cu, suggesting steric hindrance will slow down corrosion rates.

Morales Guio (UCLA), Stieber (CPP), Alexandrova (UCLA)

“Finding Activity and Stability Descriptors beyond those for CO2 Reduction”, submitted

4-Year Goals

Sorbent Discovery

- Expand the CO_2 sorbent space to develop CO_2 source and RCC application based libraries
- Understand descriptors to tailor properties (CO_2 binding, tolerance to impurities, etc)
- Develop descriptors for reduction or functionalization

Catalysis Development

- Understand translational aspects of CO_2R and RCC
- Establish new descriptors for RCC that include durability

RCC

- Understand C-speciation at reactive surfaces/catalysts
- Develop new RCC via sorbent-catalyst co-design for selective and high-efficiency transformations

Acknowledgements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U Michigan, Molecular Catalysis Lead


Josh Spurgeon
U Louisville, Heterogeneous Catalysis Lead


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UC Irvine


Robert Nielsen
UC Irvine


Chantal Stieber
Cal Poly Pomona


Burcu Gurkan
CWRU


Bijandra Kumar
ECSU


Robert Sacci
ORNL


Gabriel Veith
ORNL


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PNNL


Jesus Velazquez
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UCLA


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UCLA


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CU


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UC Davis

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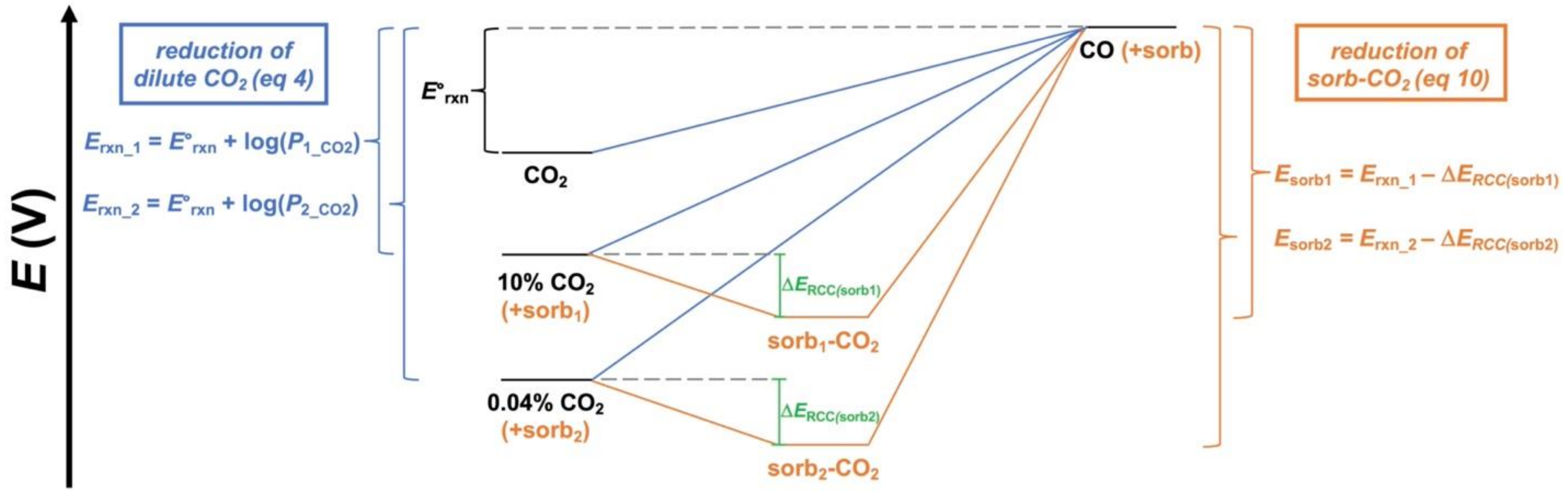
Standards for Electrochemical Efficiency



Appel (PNNL), Yang (UCI)

"Maximum and Comparative Efficiency Calculations for Integrated Capture and Conversion CO_2", ACS Energy Lett., accepted