Electrochemically-mediated Sorbent Regeneration in CO_2 Scrubbing Processes

NETL Pittsburgh, PA | August 26, 2019

Principal Investigator

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Submitted to

U.S. Department of Energy

Office of Fossil Energy

National Energy Technology Laboratory

Project Overview

Award Name: Electrochemically-Mediated Sorbent Regeneration in CO_2 Scrubbing Processes (FE0026489**)**

Funding:

DOE	$1,202,052
Cost Share	$ 310,601
Total	$1,512,653

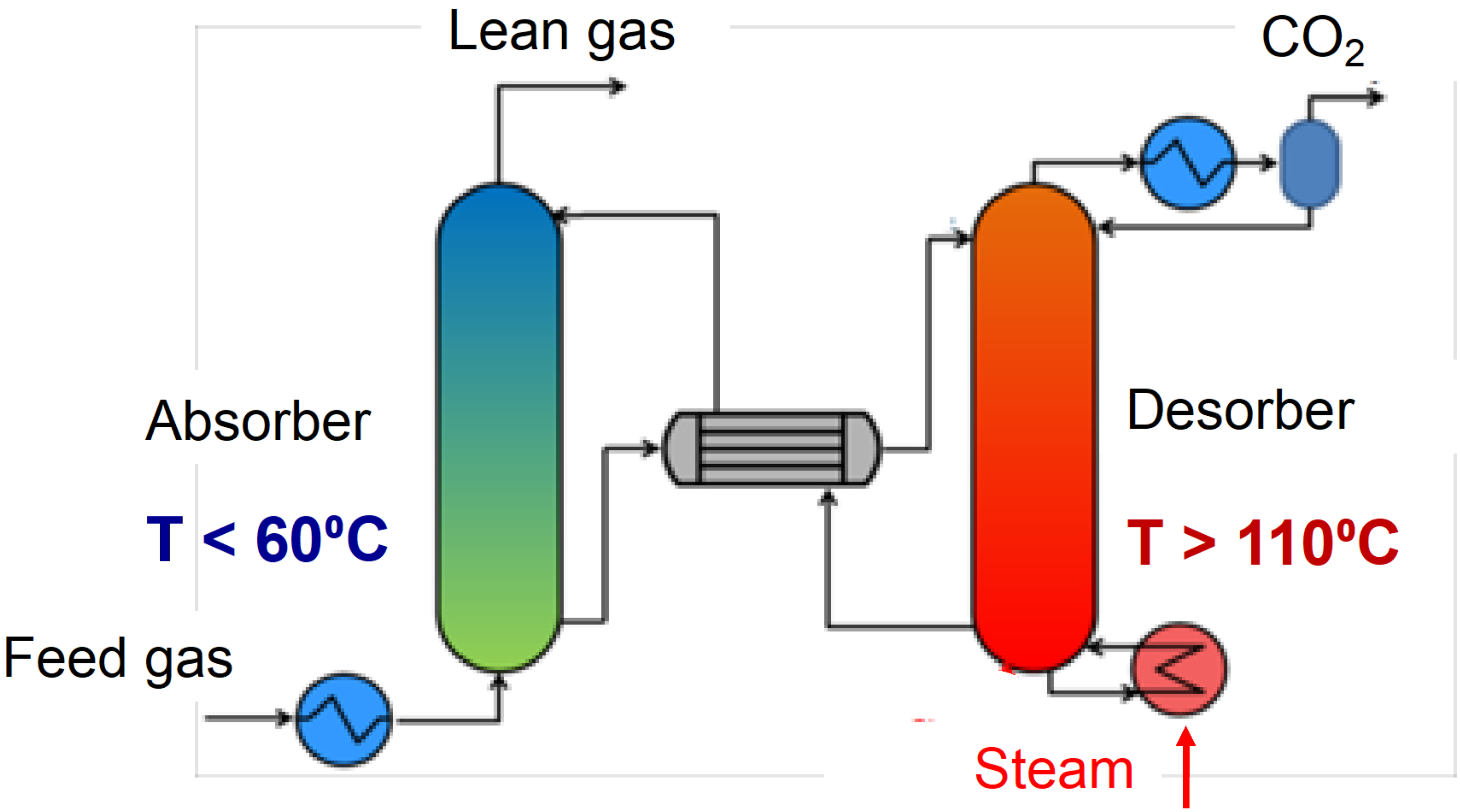
Project Period: August 1, 2017 – December 31, 2020

Project PIs: T. Alan Hatton, Howard Herzog

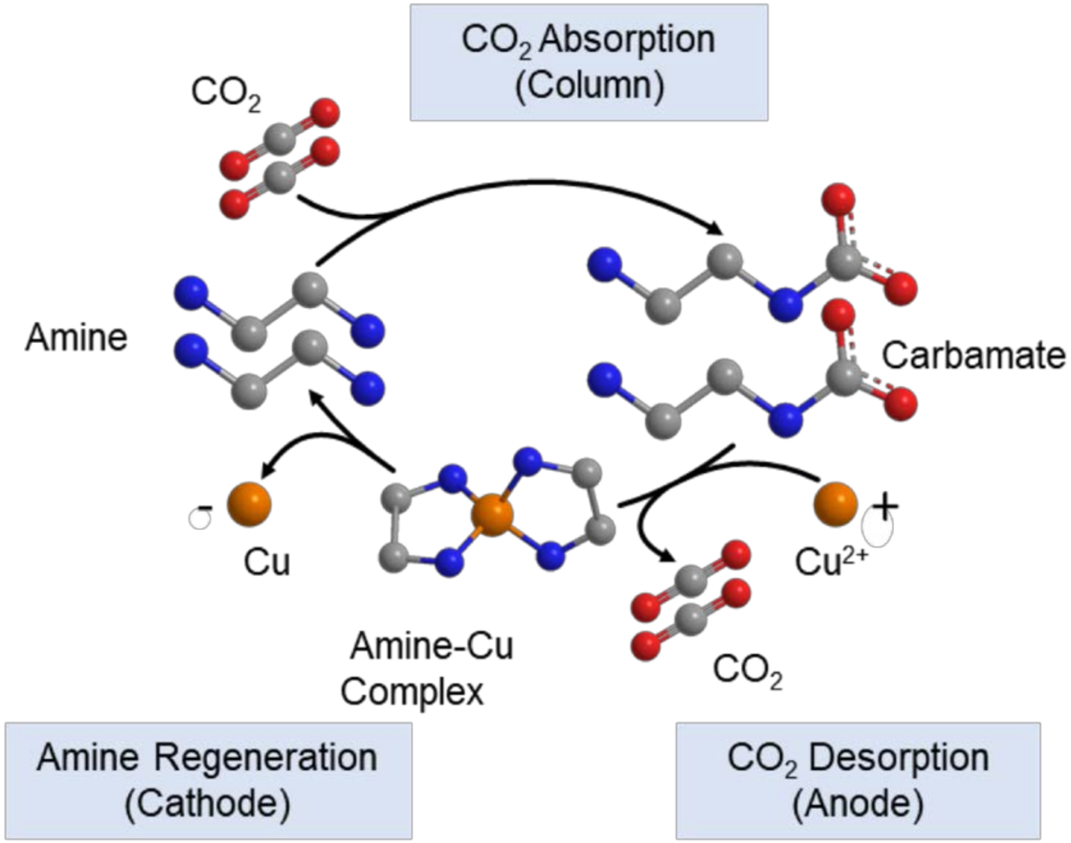
DOE Project Manager: Ted McMahon, Bruce Lani, David Lang

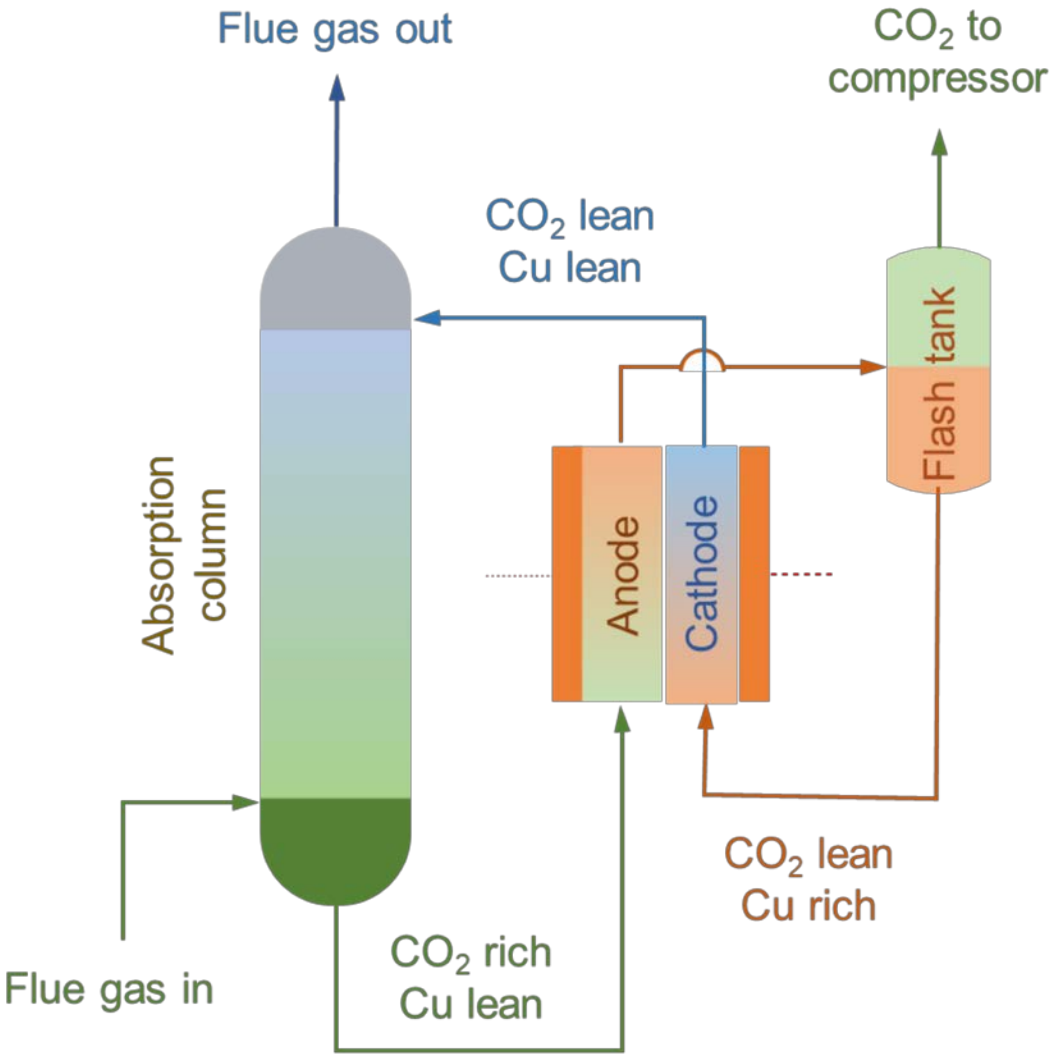
Overall Project Objectives: Develop, characterize and implement electrochemically mediated sorbent regeneration and CO_2 release in amine scrubbing processes

Amine Regeneration in CO_2 Capture

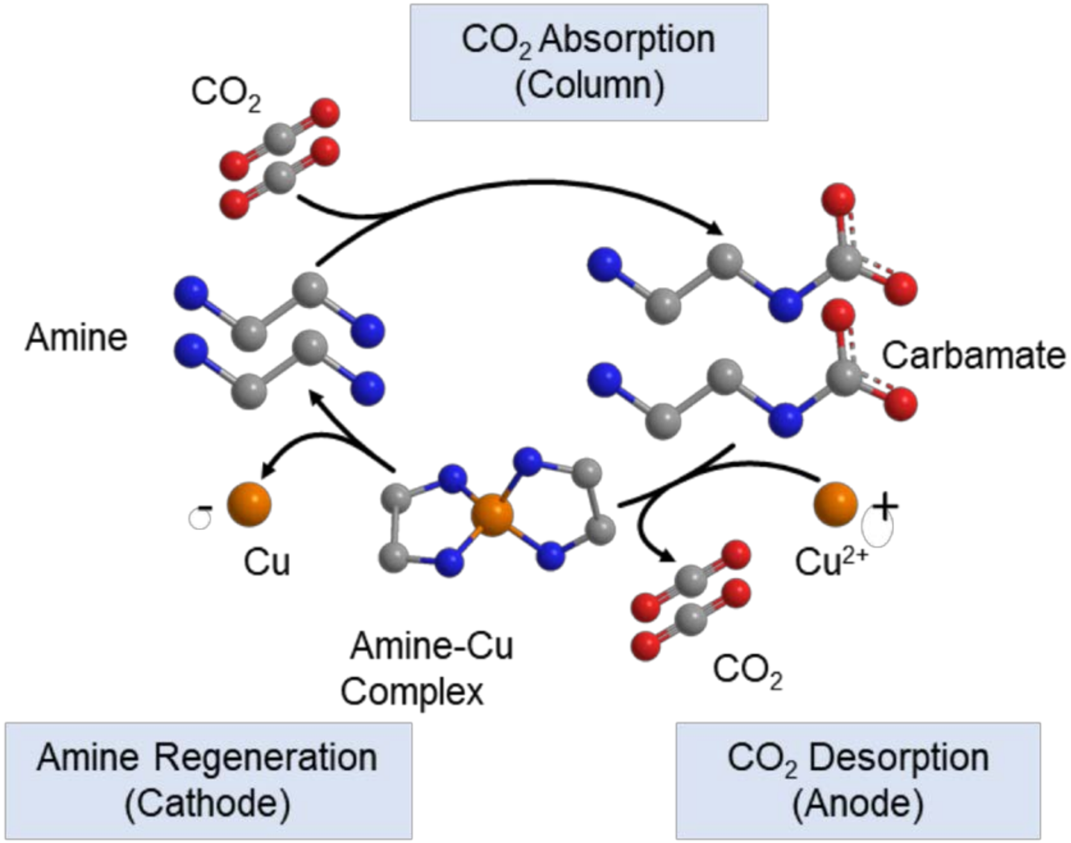


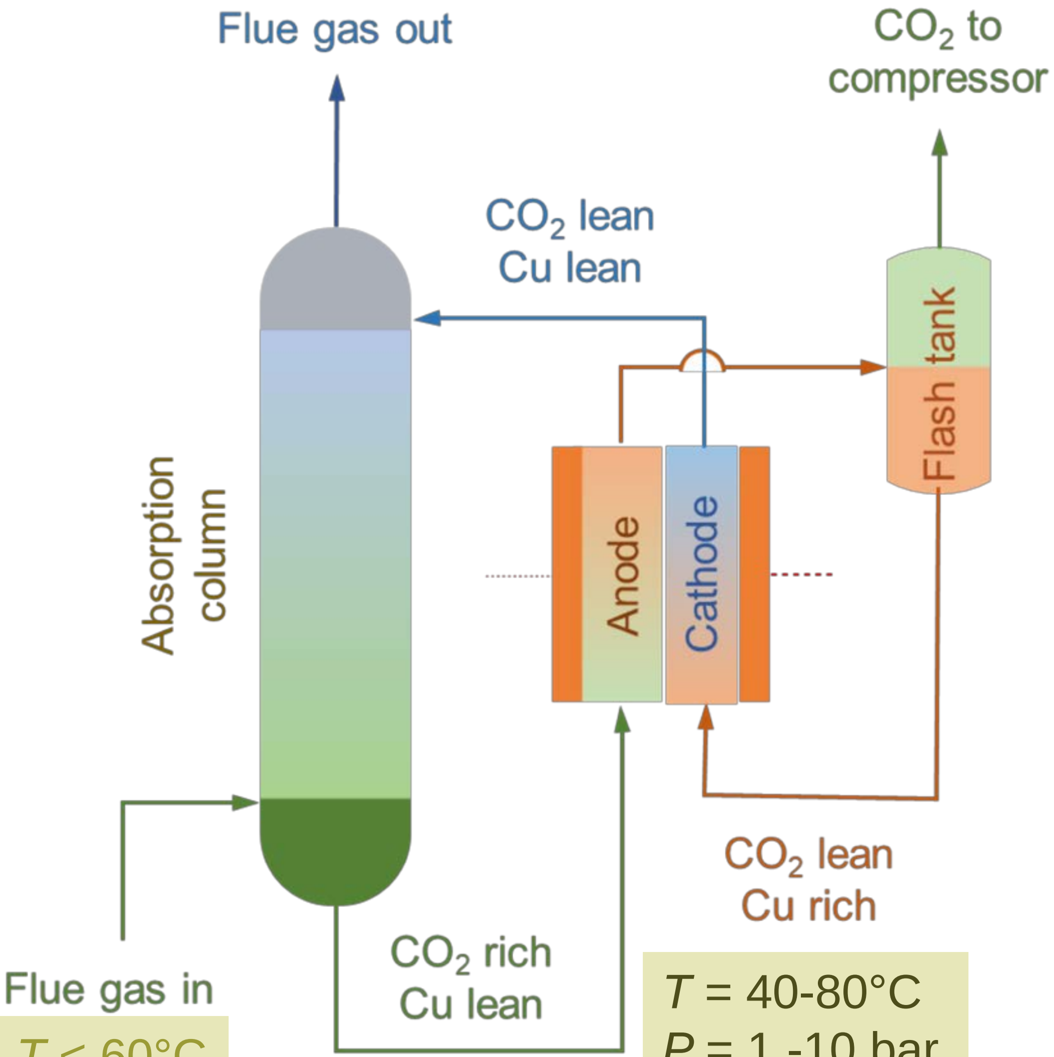
Electrochemically Mediated Amine Regeneration





Electrochemically Mediated Amine Regeneration

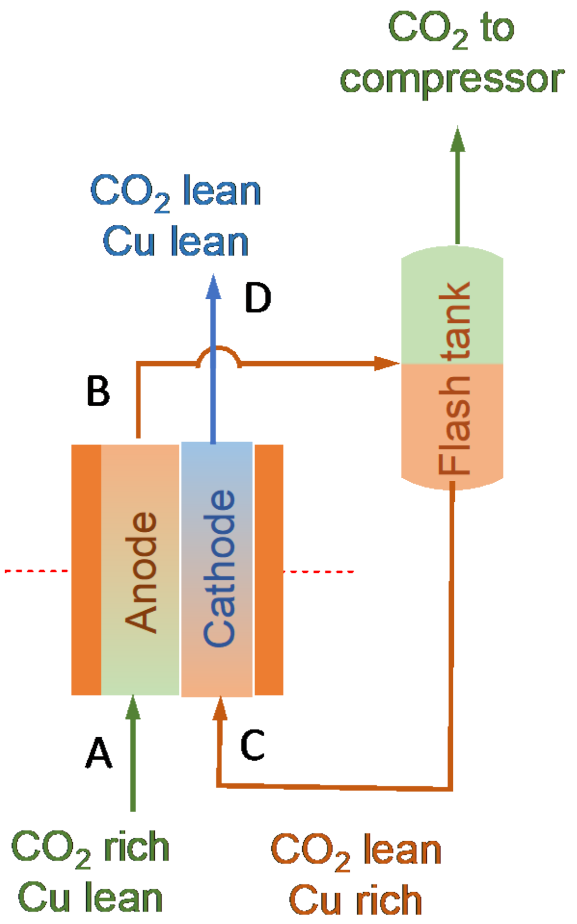


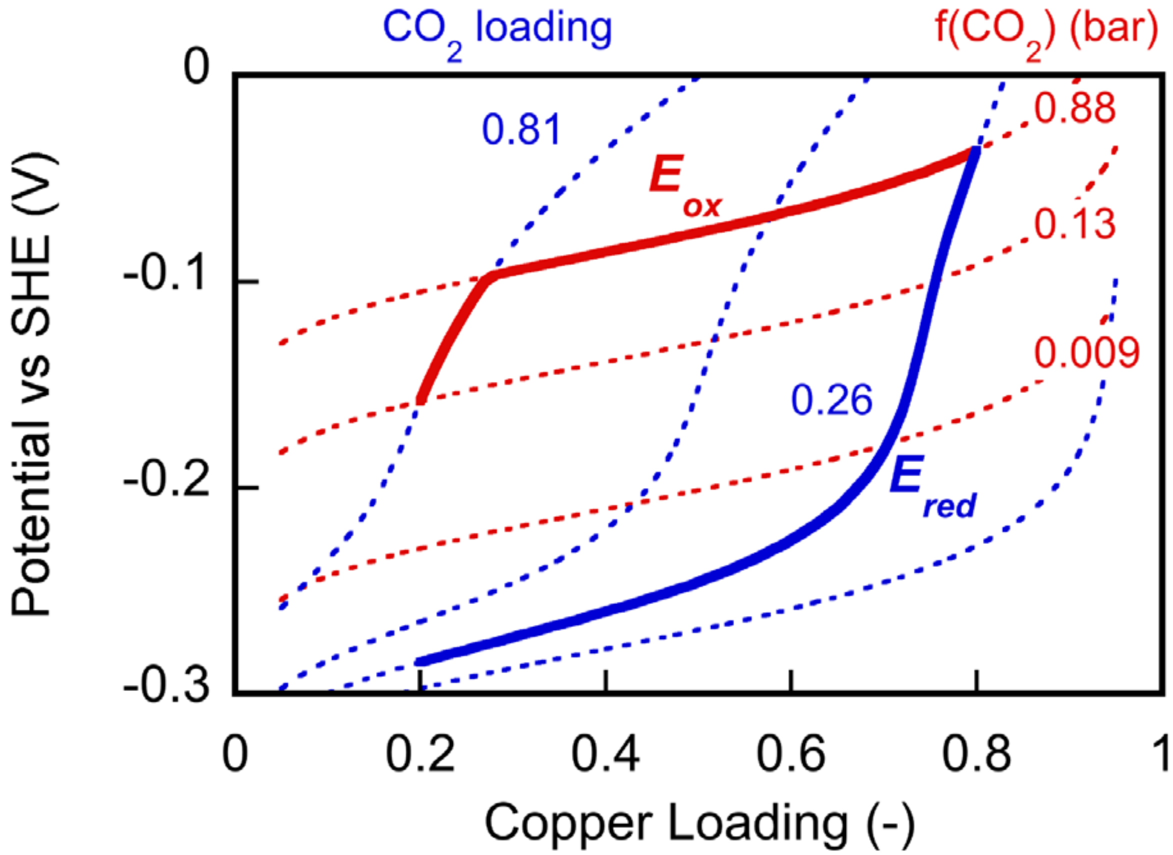


T < 60°C

T = 40-80°C
P = 1 -10 bar
E ~ 0.5 V/cell

Nernstian Description of Electrochemical Gas Separation Cycle





$$E_{cell} = \frac{RT}{nF} \ln\left(\frac{a_{Cu_{anode}^{2+}}}{a_{Cu_{cathode}^{2+}}} \right)$$

$$copper\ loading := \frac{Cu^{2+}}{2Am_o}$$

$$E = f\left(a_{Cu_o^{2+}}, K_1, \ldots, K_{17}, y_{CO_2 in}, C_{Am}\right)$$

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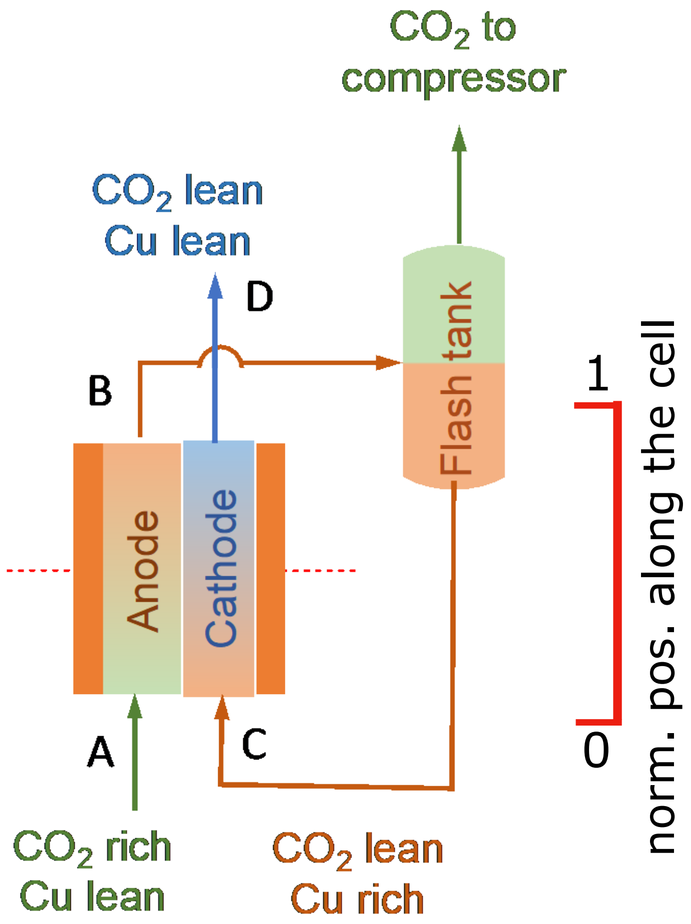

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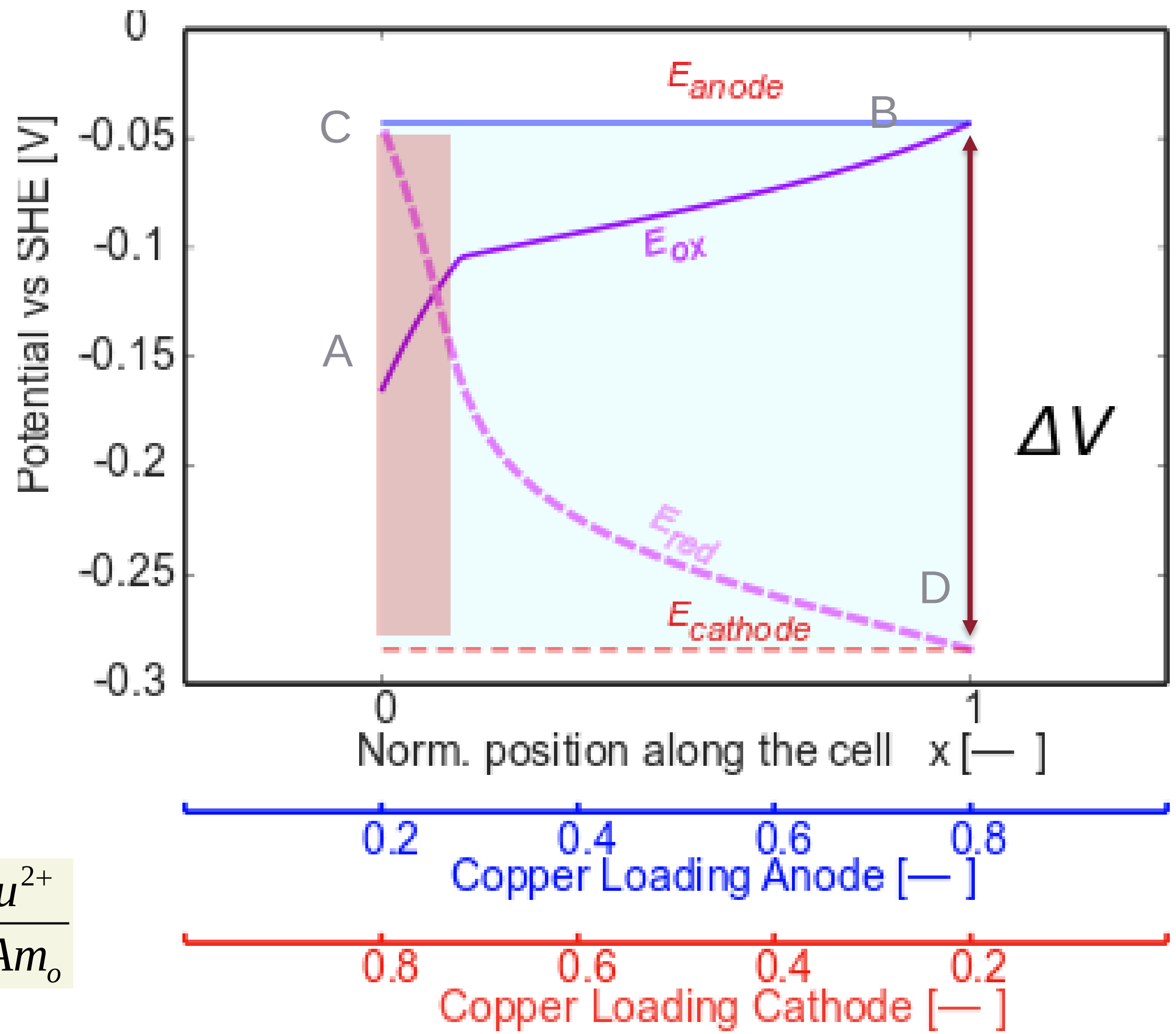

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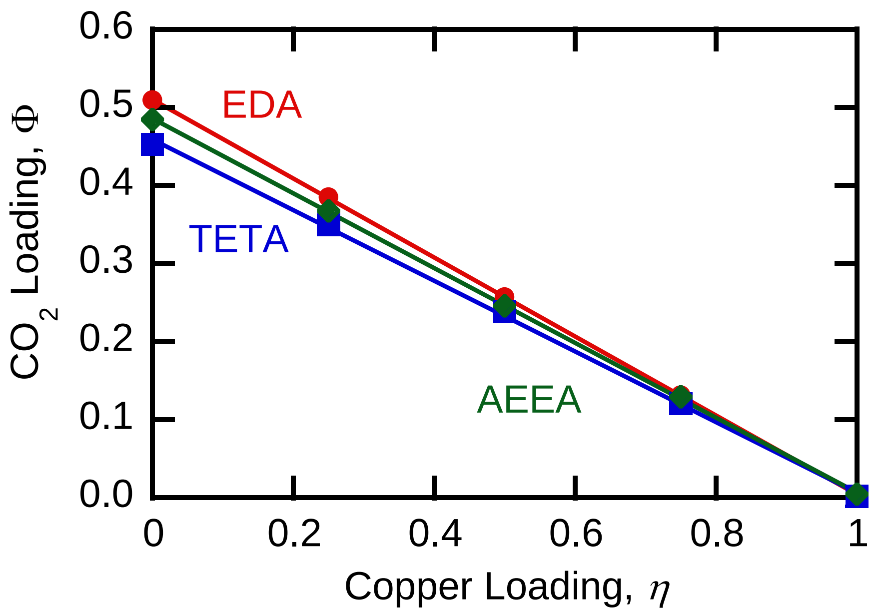
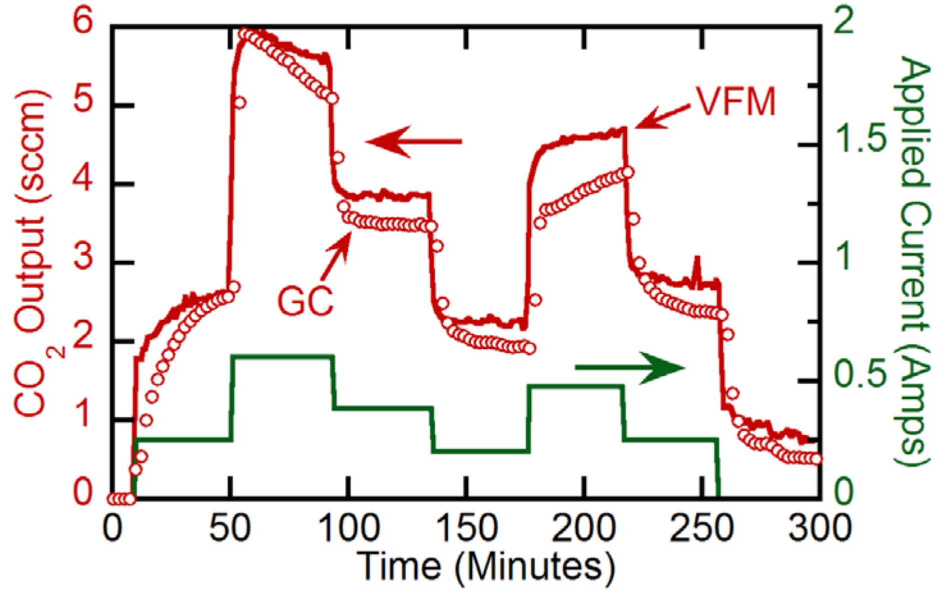
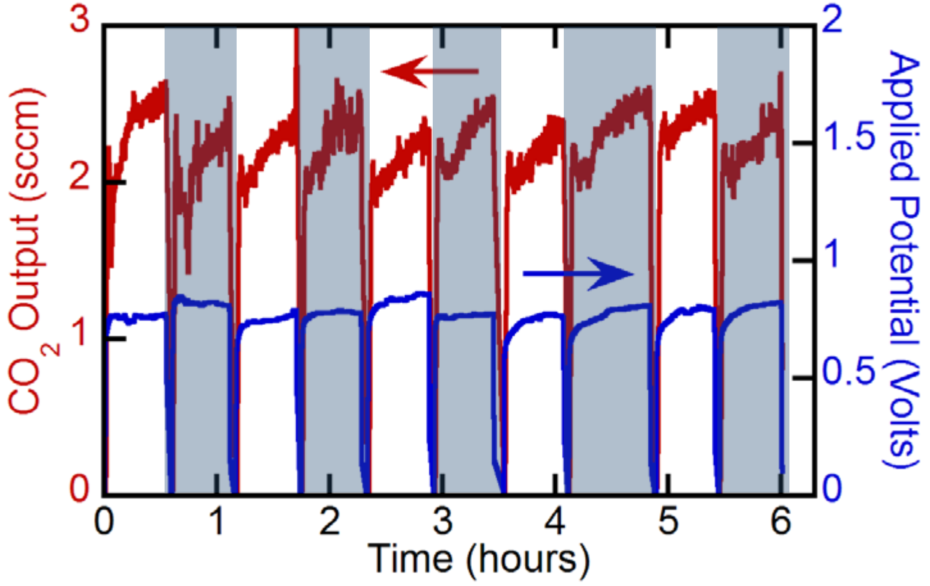
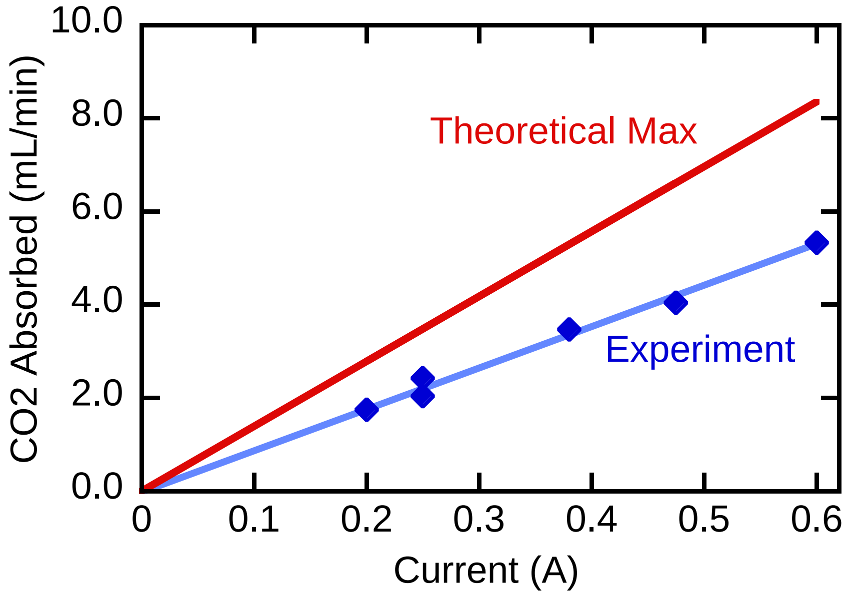
Prior effort: EMAR CO_2 capture

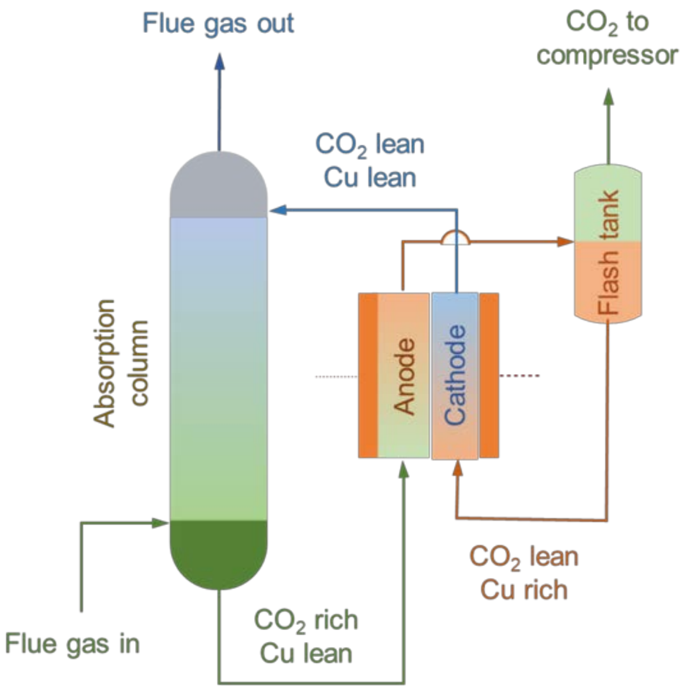


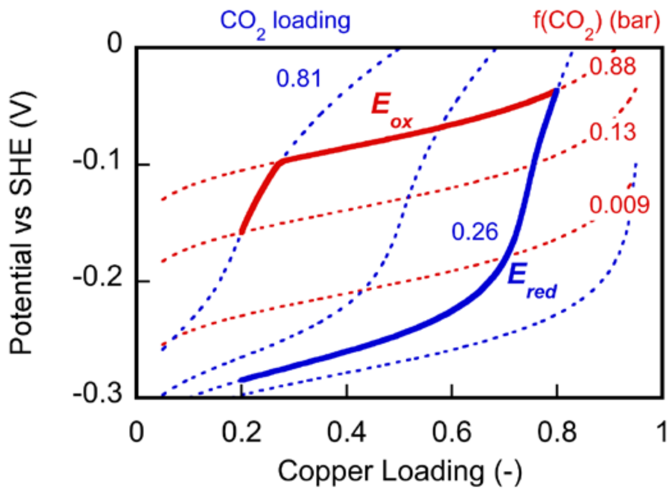


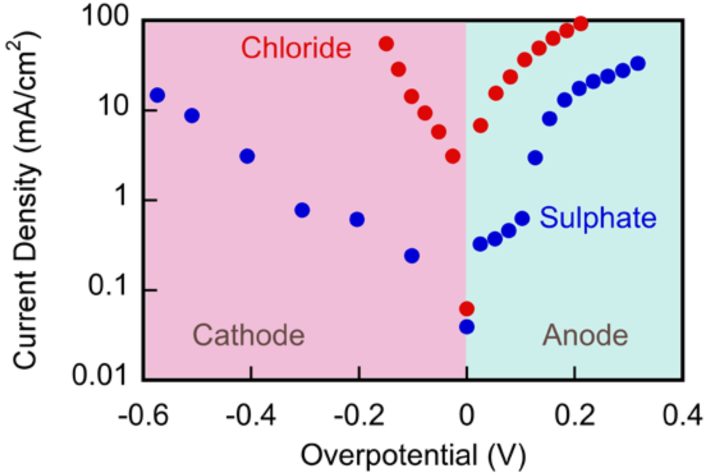




EMAR Advantages and Challenges







Advantages:

- Does not need steam and extensive retrofitting
- Lower operation temperature
- Can desorb at pressure
- Can utilize low grade waste heat to improve efficiency

Challenges:

- Overpotentials intrinsic to electrochemical systems
- Efficiency losses due to ion migration
- Stable cyclic operation

Technical Approach

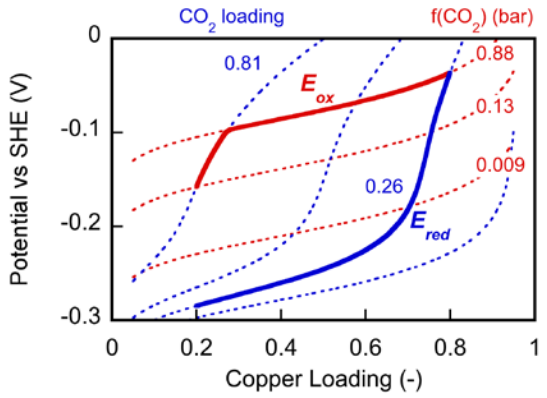
Evaluation of amine-metal pairs
- Thermodynamics
- Kinetics

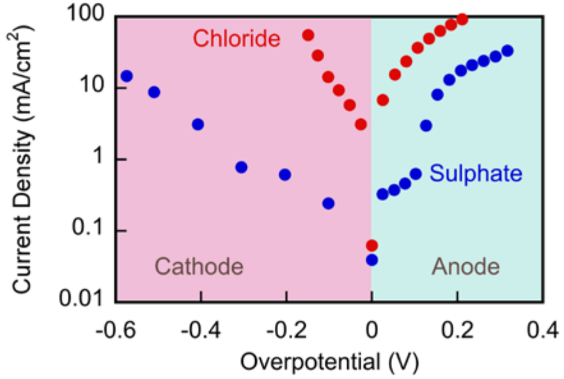
Electrochemical characterization
- Evaluate supporting electrolyte
- Overpotentials required

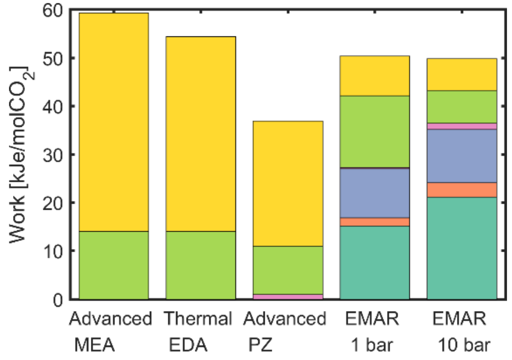
Electrochemical cell modeling

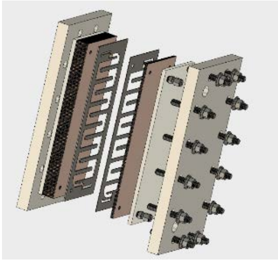
Process modeling
- Energetics
- Techno-economic analysis

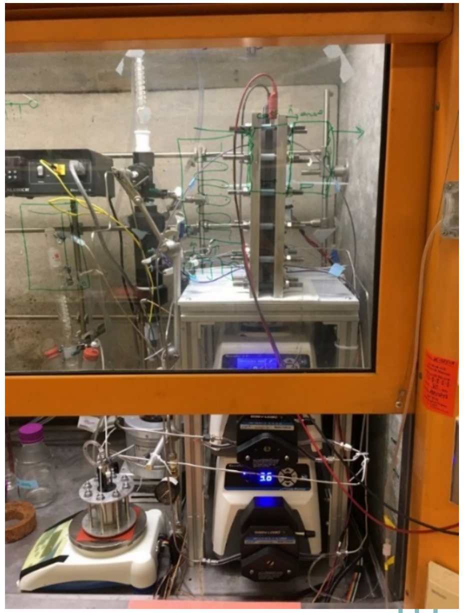
Bench scale demonstration



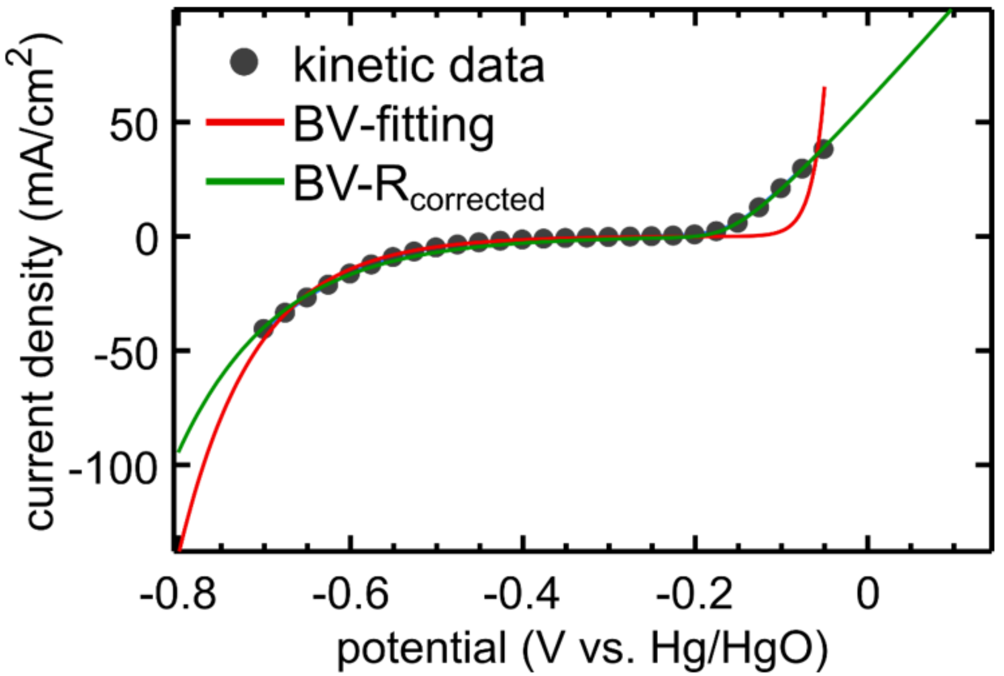


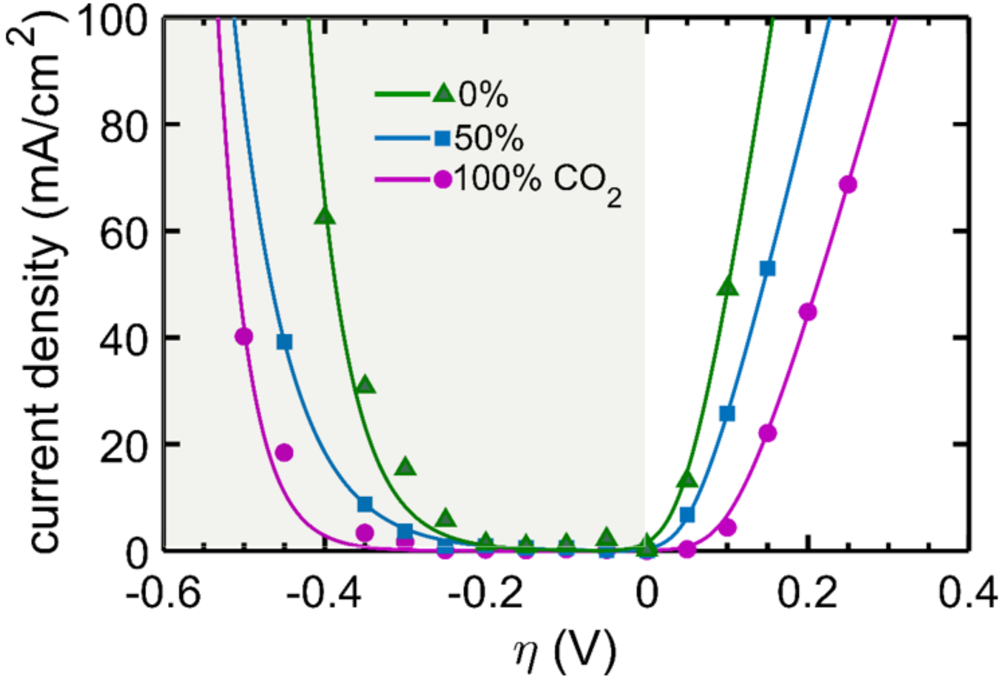






RDE results imply asymmetrical electrode polarization





- Chronoamperometry on rotating disk electrode shows overpotential (η) for cathodic reaction

$$i_o = 2Fk_o[EDA]^{2\alpha}[Cu(EDA)_2^{(2+)}]^{(1-\alpha)}$$

$$i_o \sim \sqrt{2}(1-\eta)^{1/2}\eta^{3/4}$$

- Higher overpotential with increasing CO_2 content

$$\frac{i_o(EDA-CO_2)}{i_o(EDA)} \sim \left(\frac{P_o}{K_{CO_2}P_{CO_2}}\right)^{\alpha} \sim 0.3$$

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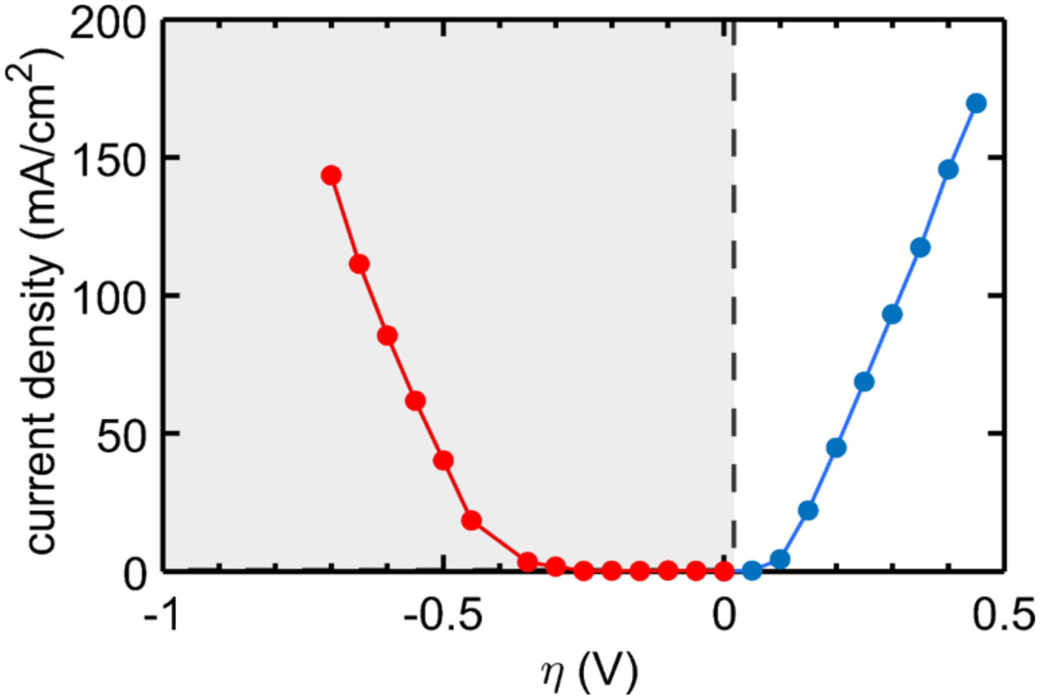

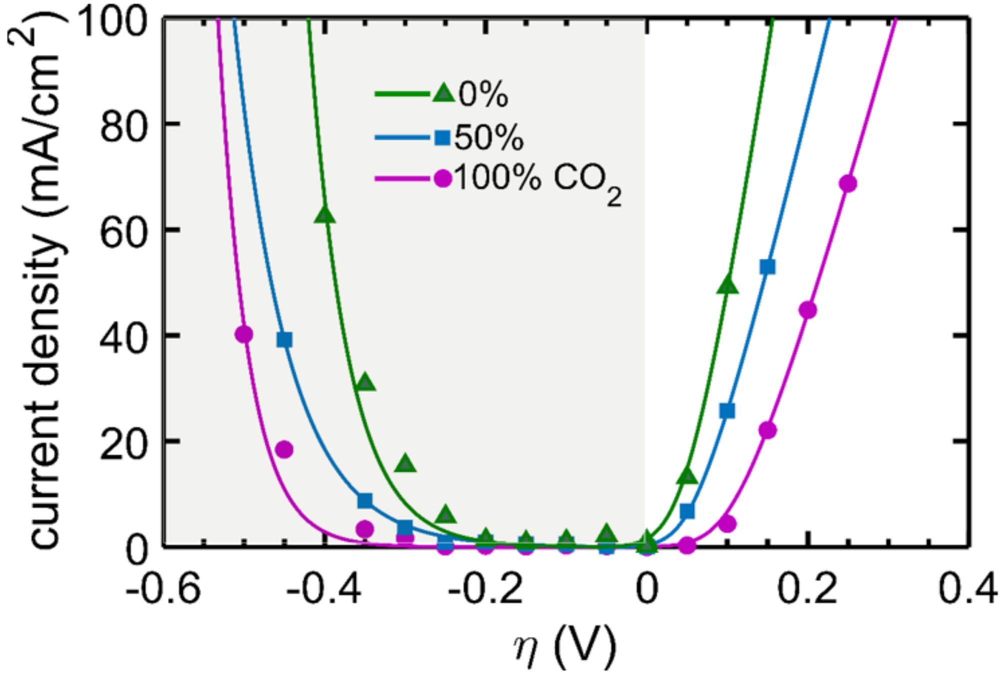

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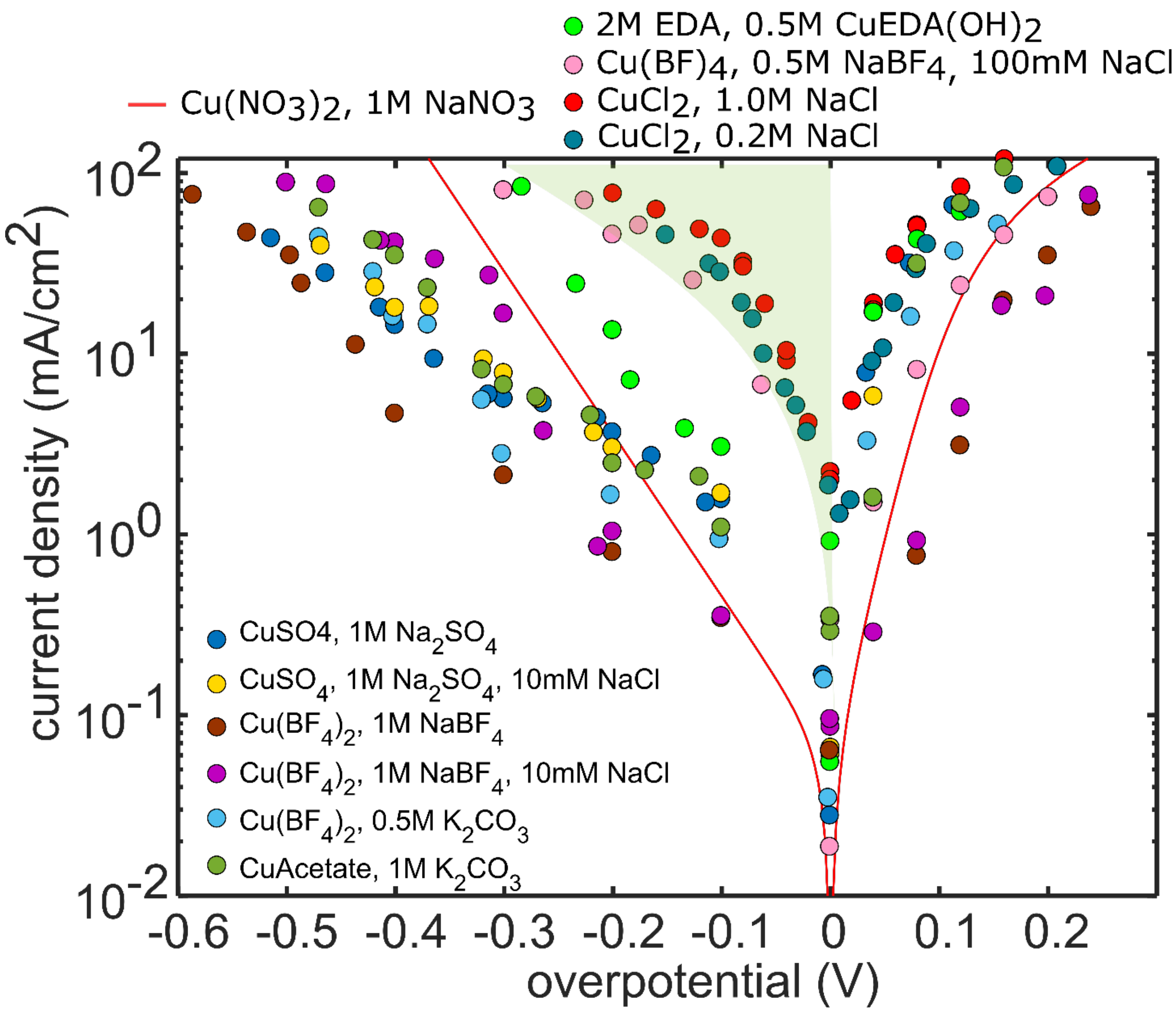
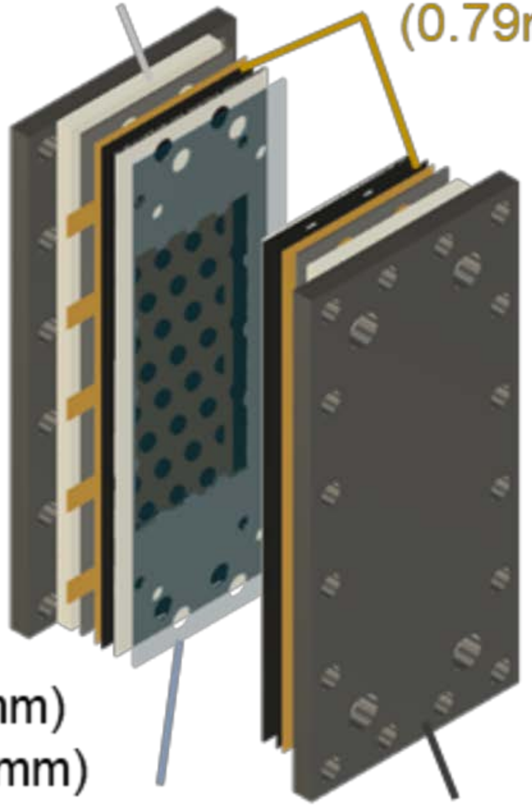
Supporting salt affects kinetics

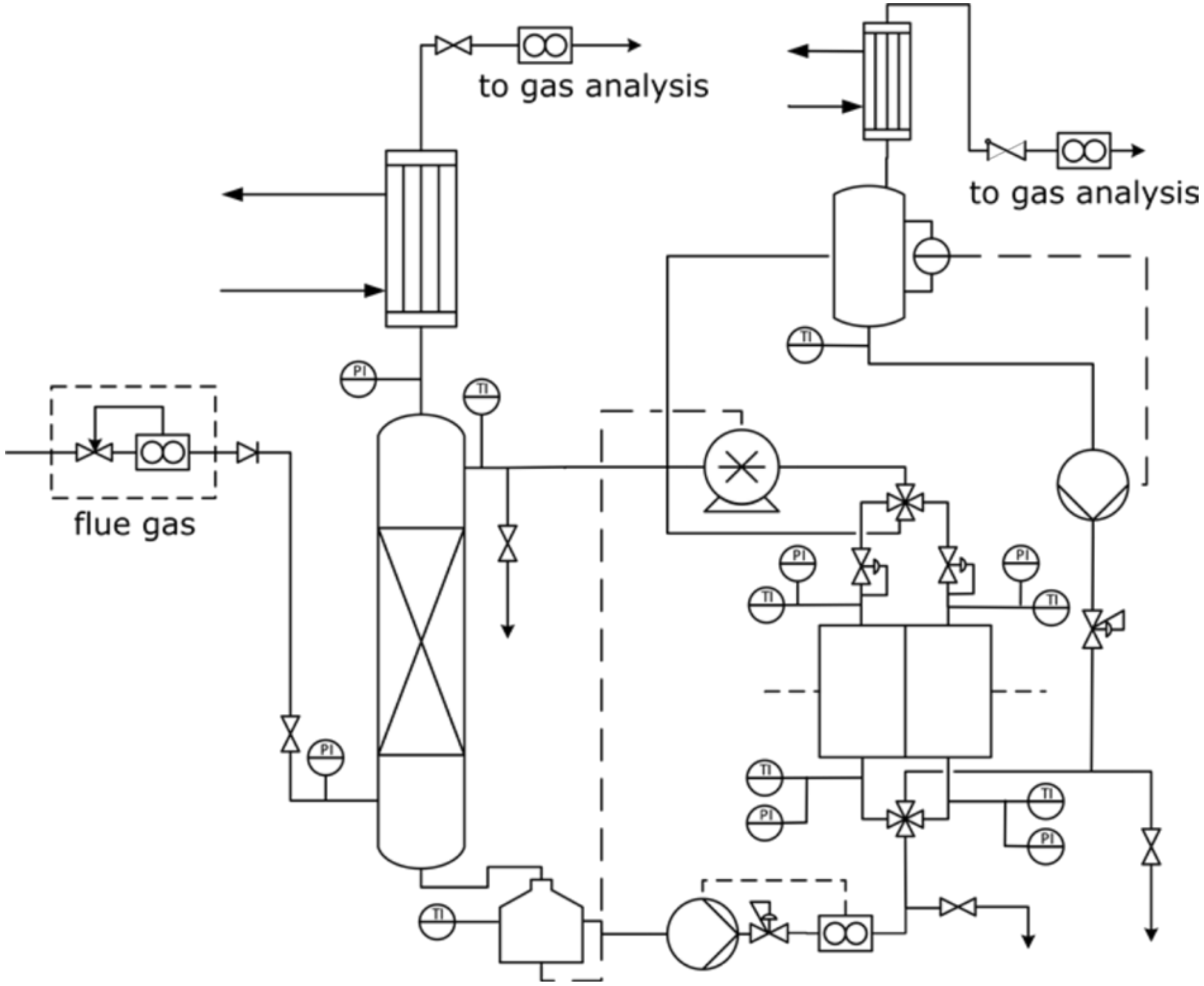


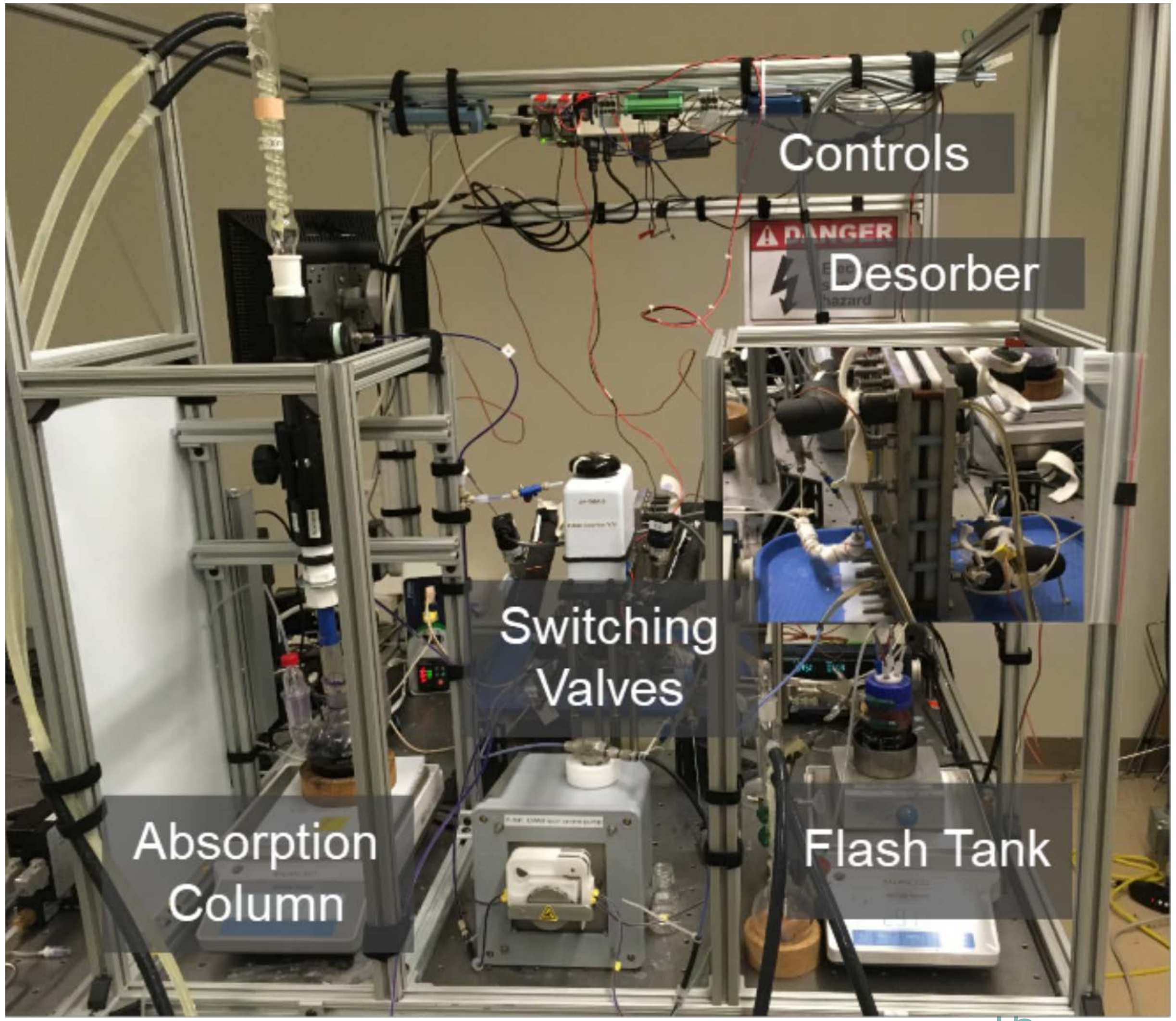
- Changing electrolyte can increase current density from <10 mA/cm^2 to >50mA/cm^2
- Addition of Cl$^-$ increases current density to 100 mA/cm^2

EMAR Cell Construction

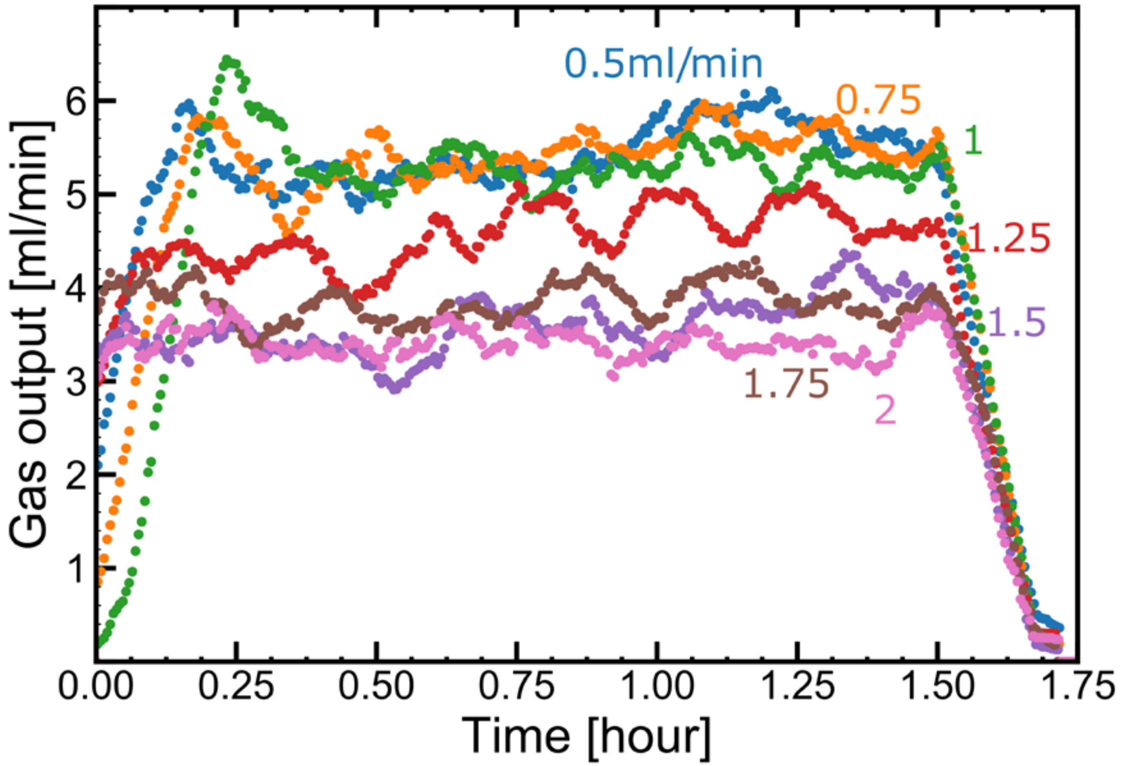


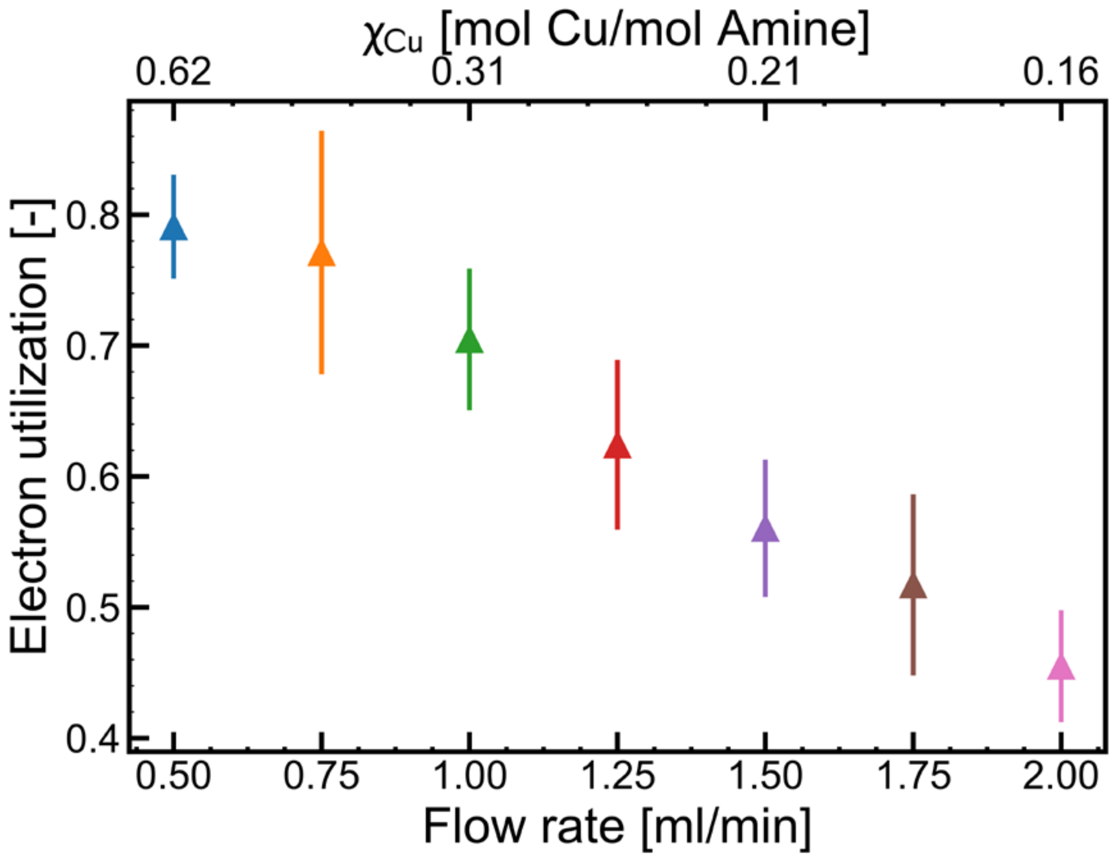
Continuous Bench Scale EMAR



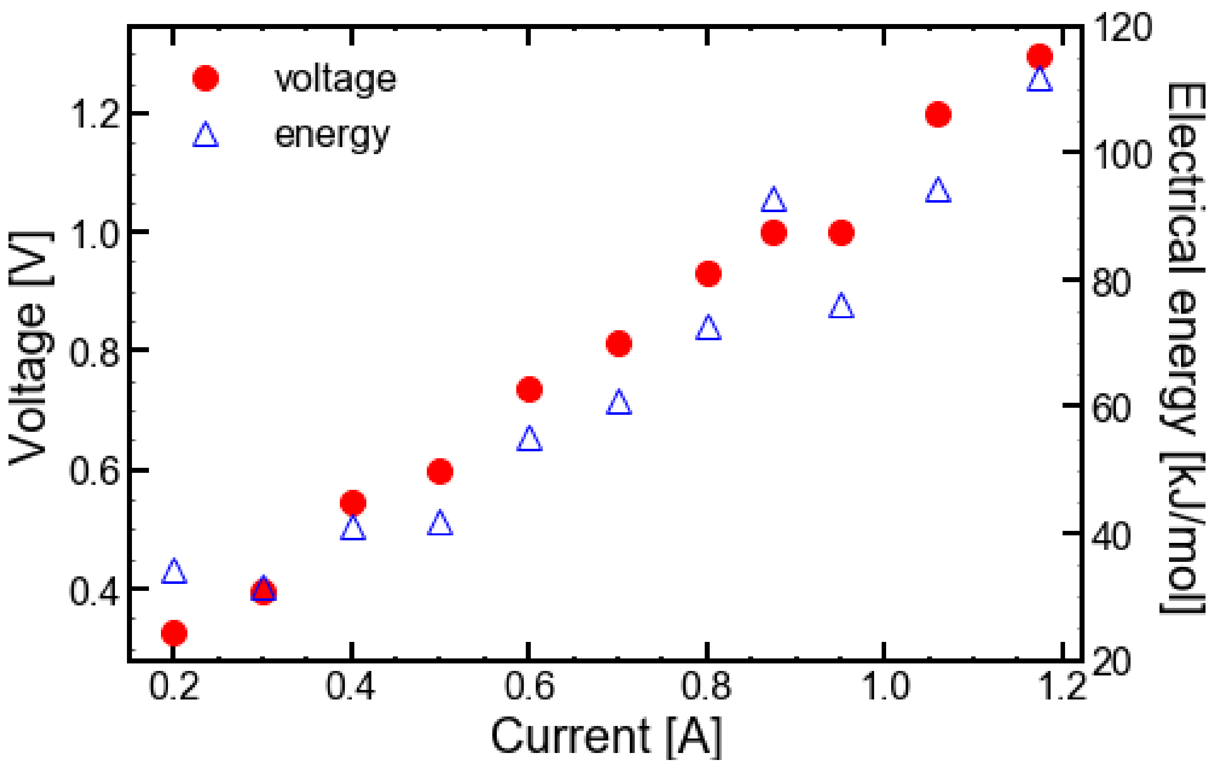


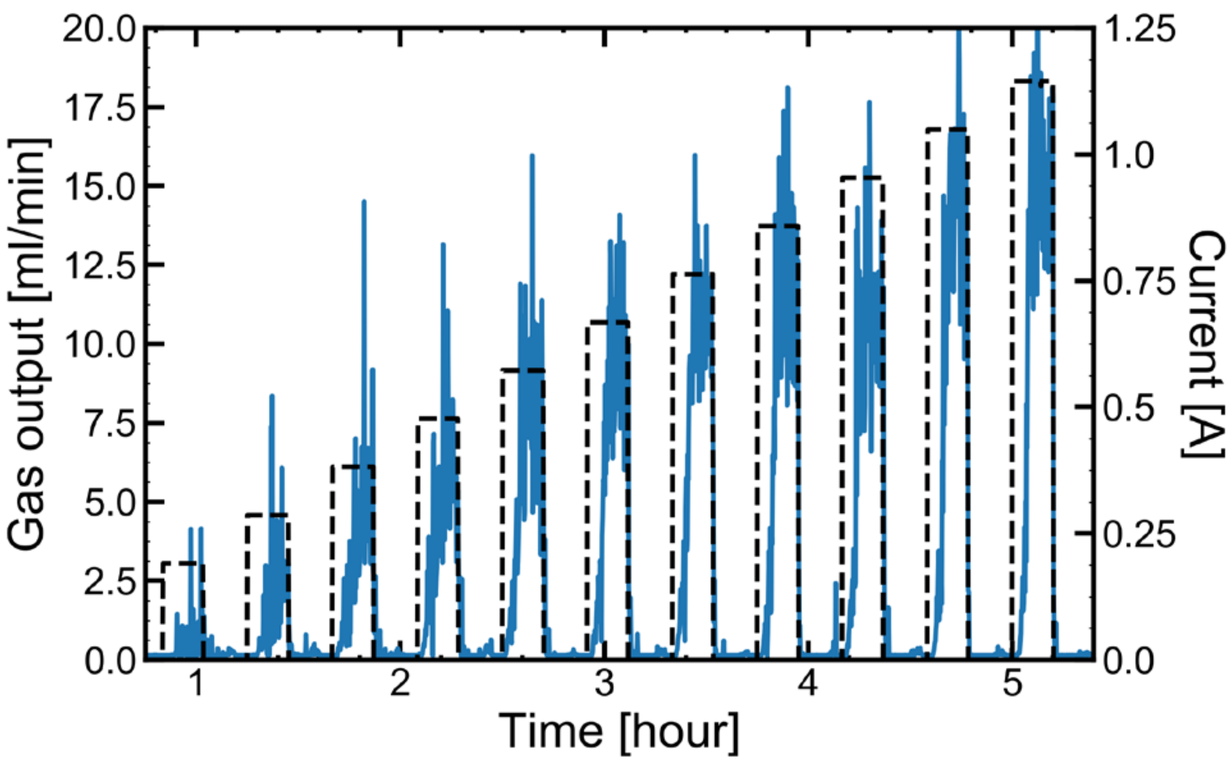
Gas Separation and Electron Utilization: Effect of Flow Rate



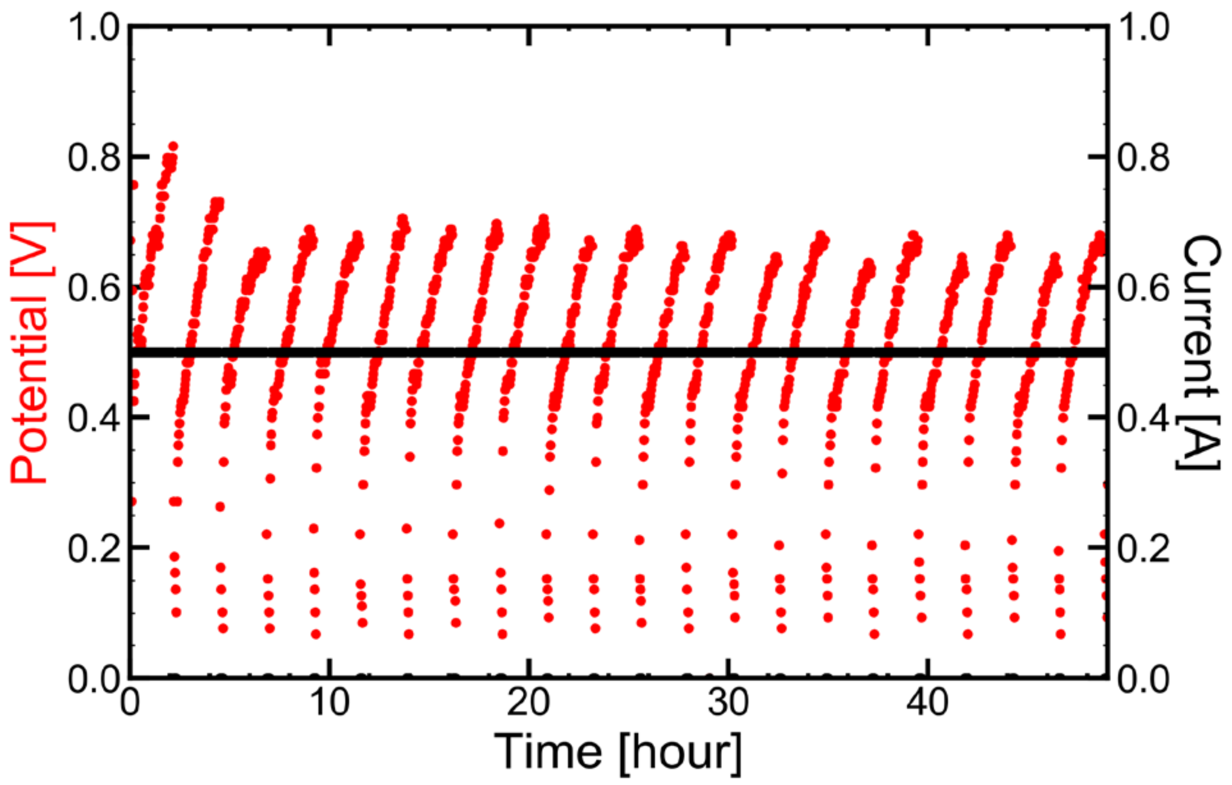


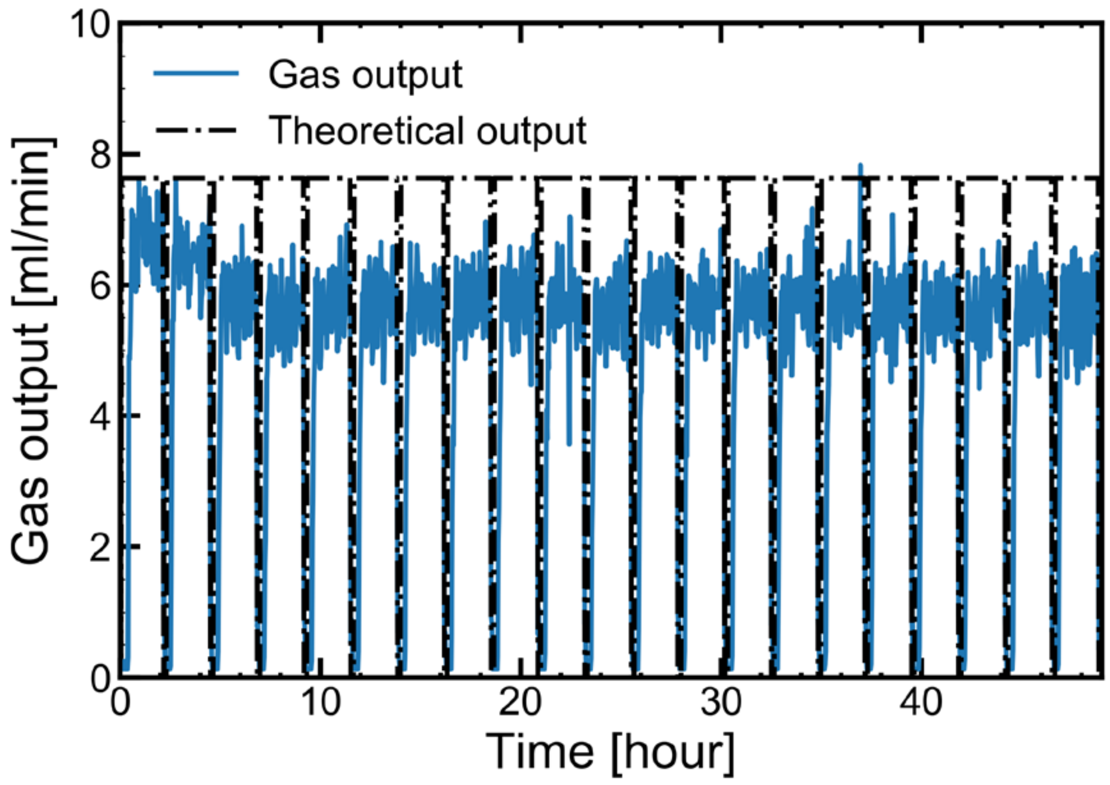
Voltage and Gas Evolution with Varying Current





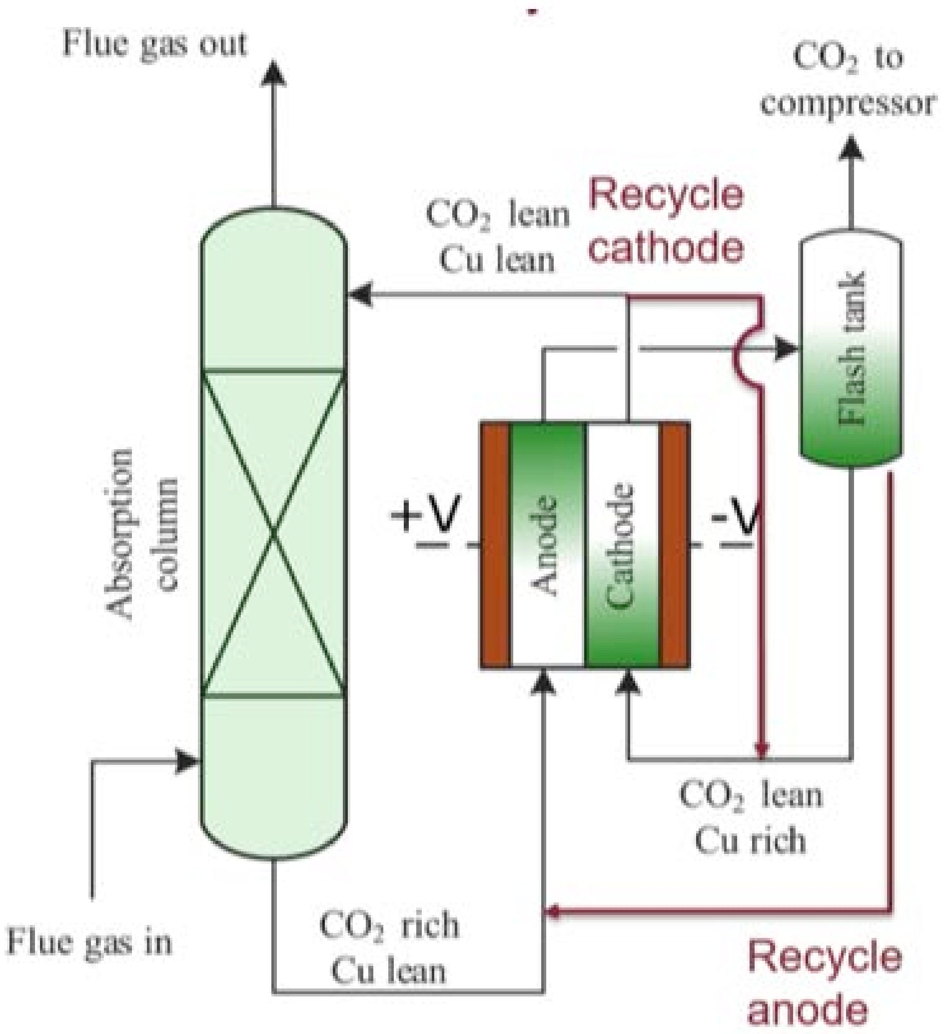
Continuous Operation under Constant Current





Enhanced Electrode Stability with Recycle

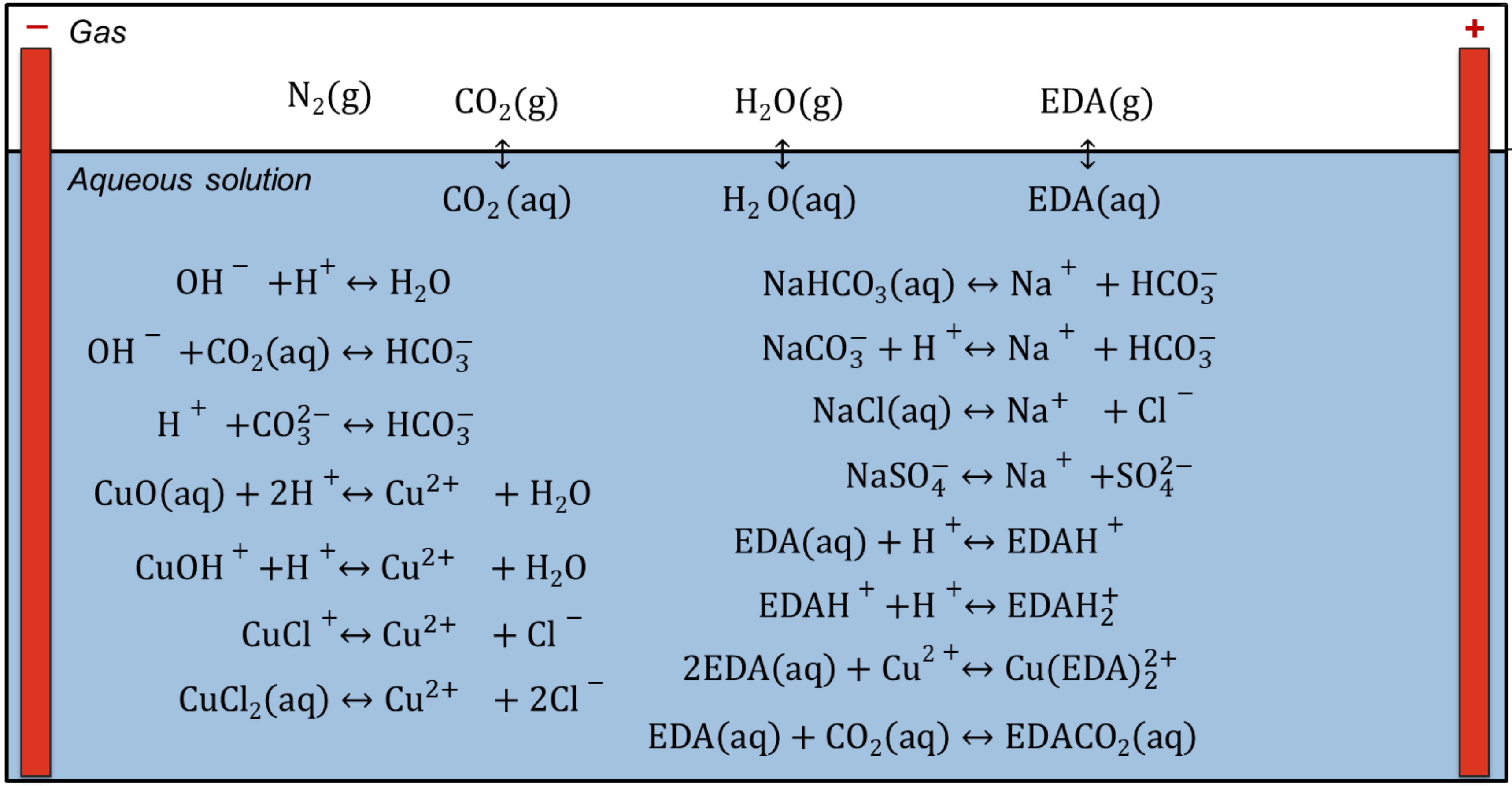
40 hr with no recycle



200 hr with recycle

EMAR thermodynamics modeling

EMAR electrolyte speciation with copper electrodes and EDA as the amine



$f_i = p_i$

$a_i = \gamma_i c_i$

$\gamma_i \rightarrow$ B-dot equation (Extended Debye Hückel)

To calculate:

- Electrochemical Energetics
- Process energetics (compressor, pump, hot water utilities, etc.)

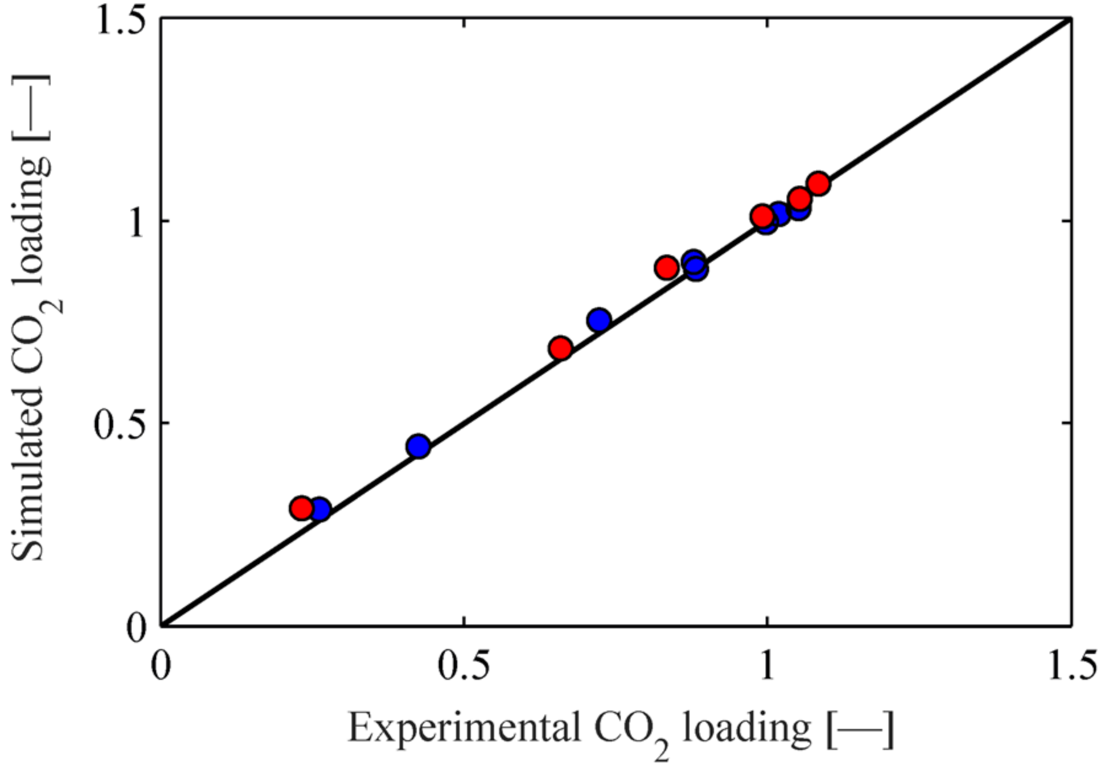
Wolery, (2002); Paoletti, *Pure Appl Chem*, 56, (1984): 491-522; Stern, *PhD Thesis,* (2013)

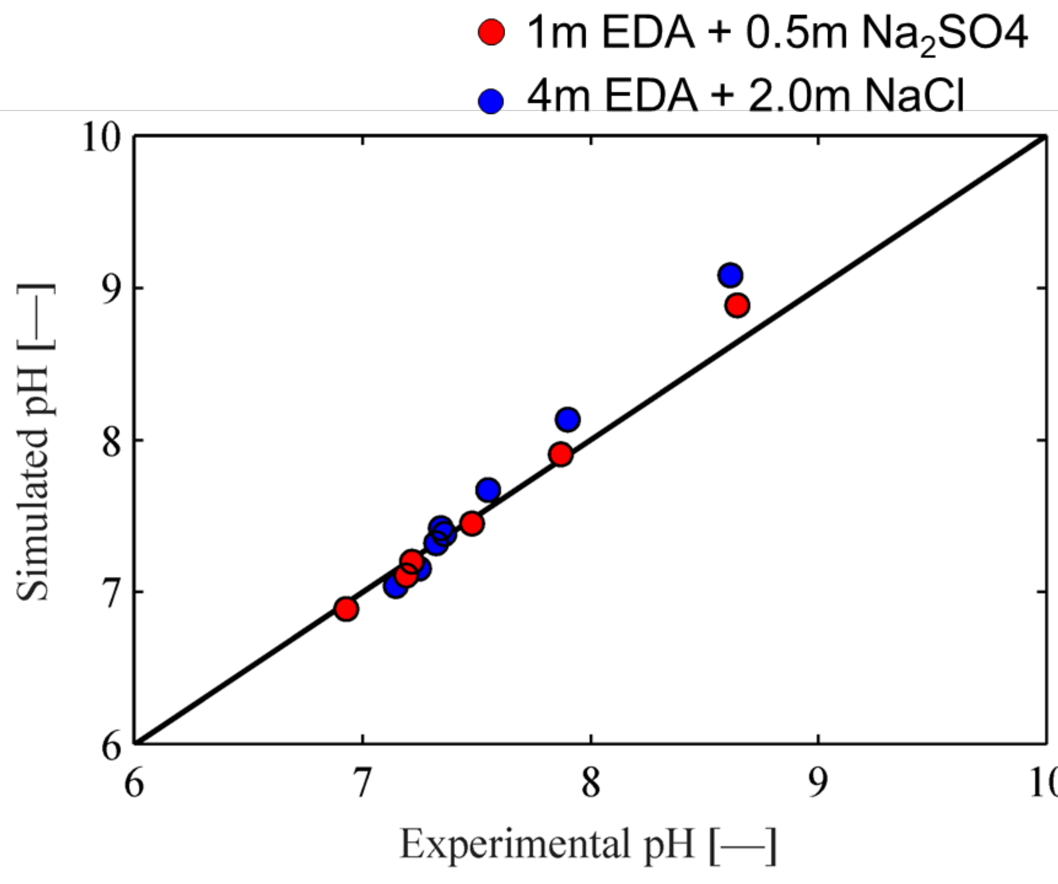
Hatton Group, *Int. J. Greenhouse Gas Control.* 2019, *82*, 48-58.

Thermodynamics modeling validation

CO_2 capacity/loading measurements at 50°C under different f_{CO2} and c_{Cu}

$$CO_2 \text{ loading} = x_C = \frac{c_C}{c_{EDA}}$$





Hatton Group, *Int. J. Greenhouse Gas Control.* 2019, *82*, 48-58.

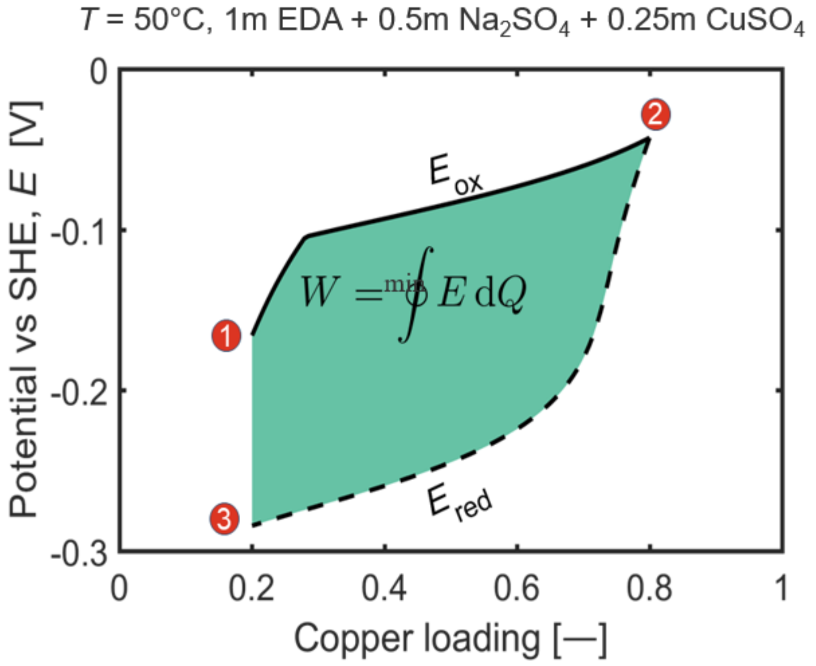
Electrochemical Energetics

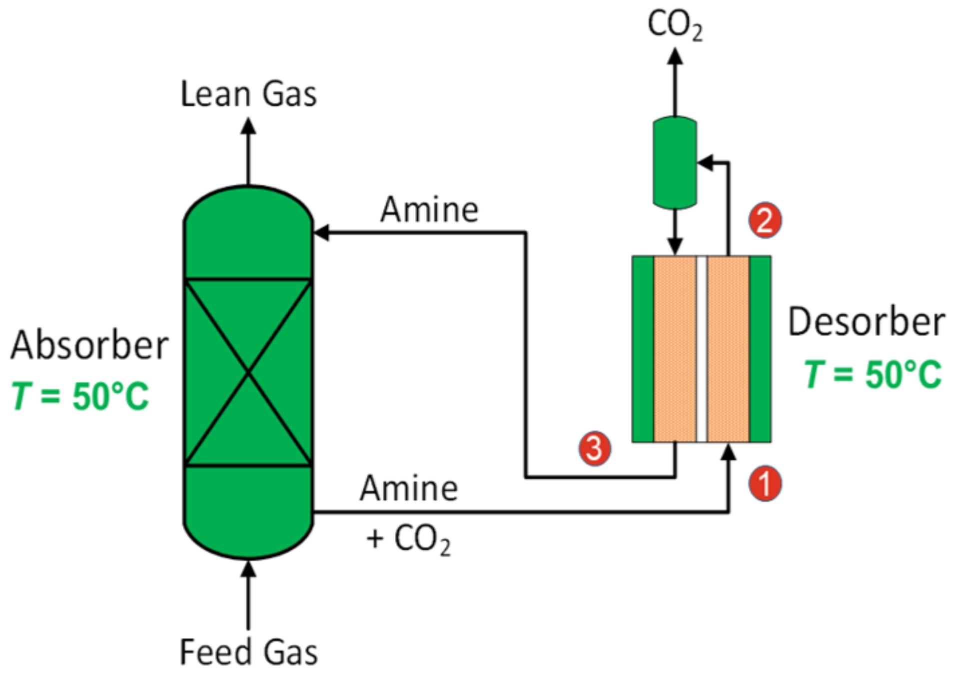
1 to 2: Oxidation

$Cu(s) \rightarrow Cu^{2+} + 2e^-$

2 to 3: Reduction

$Cu^{2+} + 2e^- \rightarrow Cu(s)$





$$W_{\min} = \frac{1}{F_{m,CO2}}\left(\int_{x_{Cu}} E_{ox} dI - \int_{x_{Cu}} E_{red} dI\right)$$

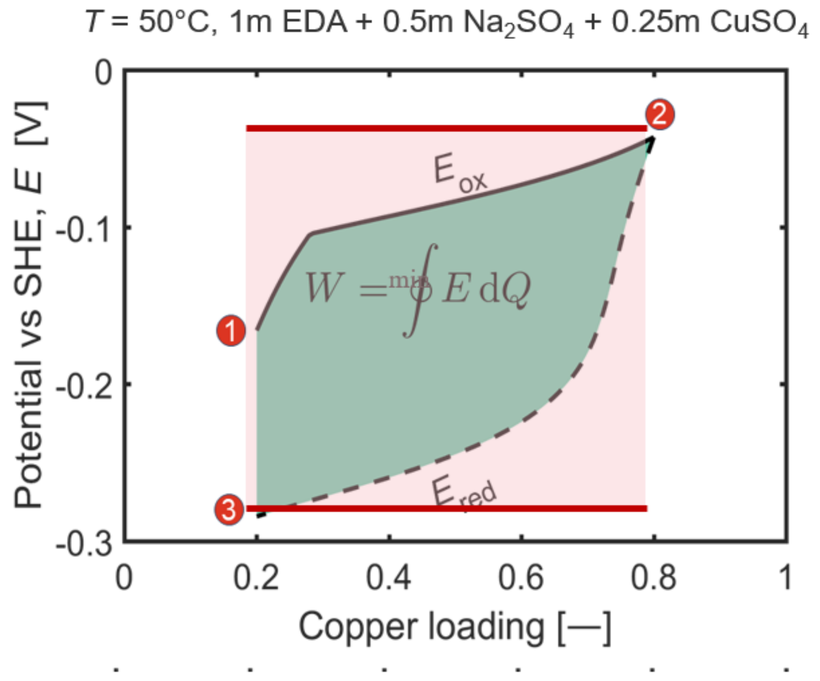
Electrochemical Energetics

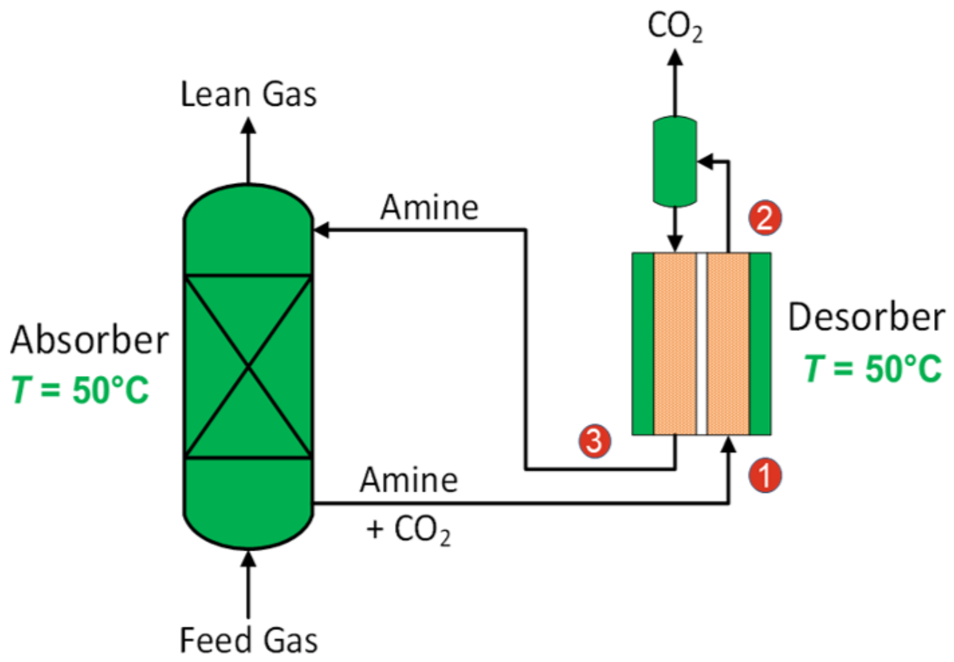
① to ②: Oxidation

$Cu(s) \rightarrow Cu^{2+} + 2e^-$

② to ③: Reduction

$Cu^{2+} + 2e^- \rightarrow Cu(s)$





$$W_{\min} = \frac{1}{F_{m,CO2}}\left(\int_{x_{Cu}} E_{ox}\,dI - \int_{x_{Cu}} E_{red}\,dI\right)$$

$$W_{\min,corrected} = \frac{1}{F_{m,CO2}}\left(\int_{x_{Cu}} E_{ox}\,dI - \int_{x_{Cu}} E_{red}\,dI\right)$$

Electrochemical Energetics

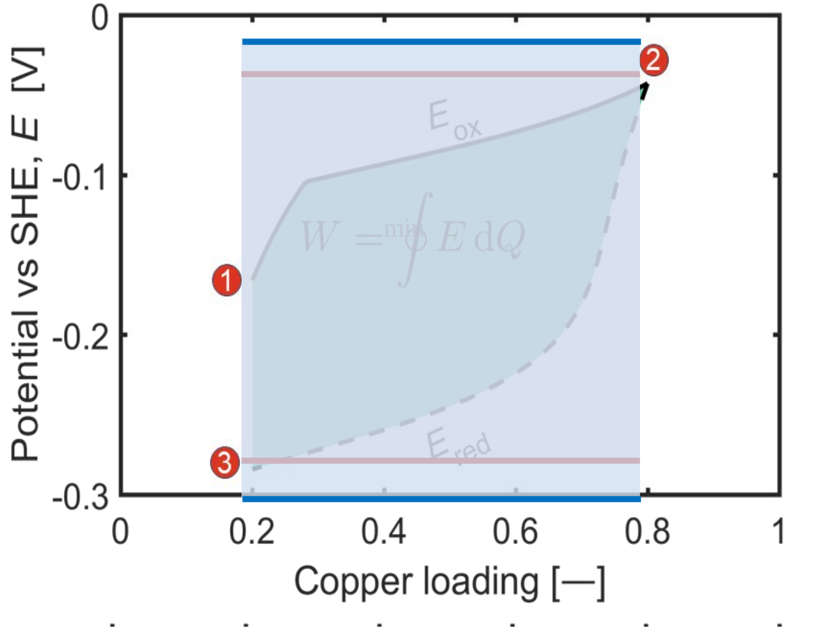
❶ to ❷: Oxidation

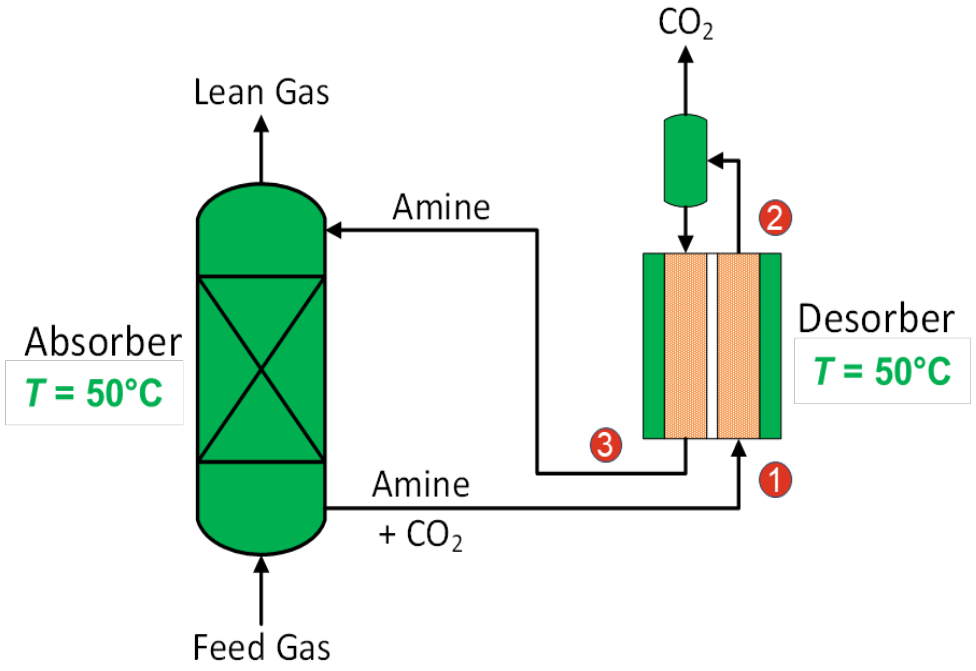
Cu(s) → Cu^{2+} + $2e^-$

❷ to ❸: Reduction

Cu^{2+} + $2e^-$ → Cu(s)

T = 50°C, 1m EDA + 0.5m Na_2SO_4 + 0.25m $CuSO_4$



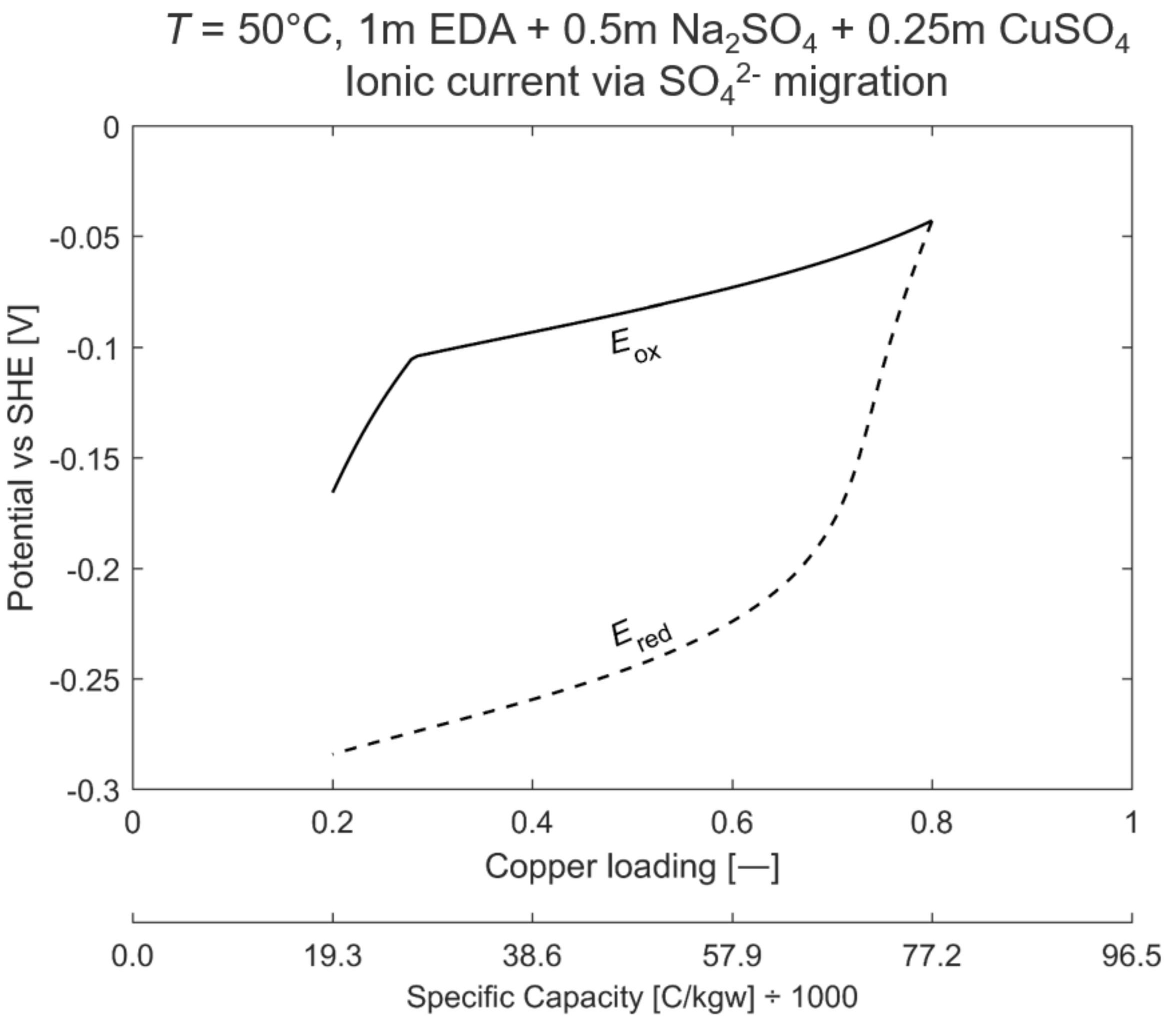


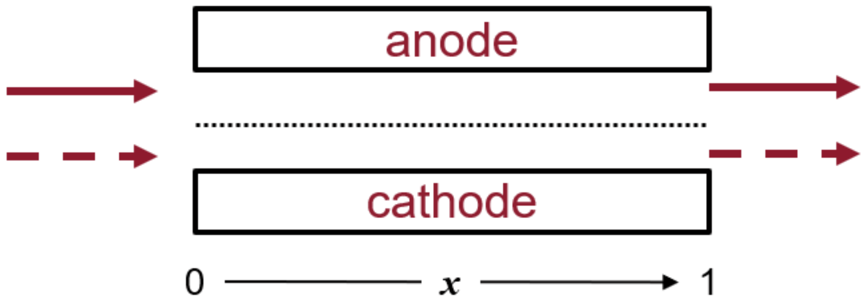
$$W_{\text{min}} = \frac{1}{F_{\text{m,CO2}}}\left(\int_{x_{\text{Cu}}} E_{\text{ox}}\text{d}I - \int_{x_{\text{Cu}}} E_{\text{red}}\text{d}I\right)$$

$$W_{\text{min,corrected}} = \frac{1}{F_{\text{m,CO2}}}\left(\int_{x_{\text{Cu}}} E_{\text{ox}}\text{d}I - \int_{x_{\text{Cu}}} E_{\text{red}}\text{d}I\right)$$

$$W_{\text{EMAR}} = \frac{1}{F_{\text{m,CO2}}}\left(\int_{x_{\text{Cu}}} E_{\text{ox}}\text{d}I - \int_{x_{\text{Cu}}} E_{\text{red}}\text{d}I\right)$$

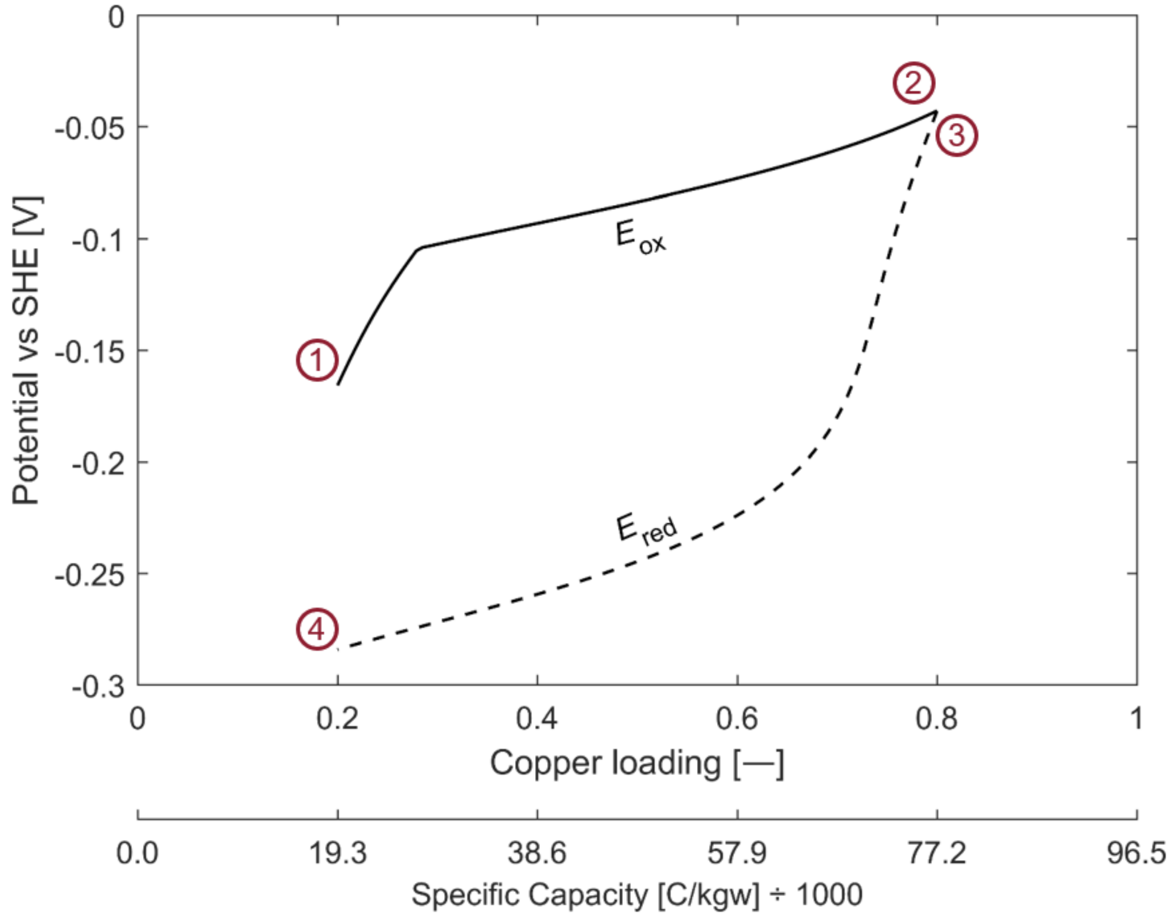
Minimum EMAR Work: Co-Current Operation

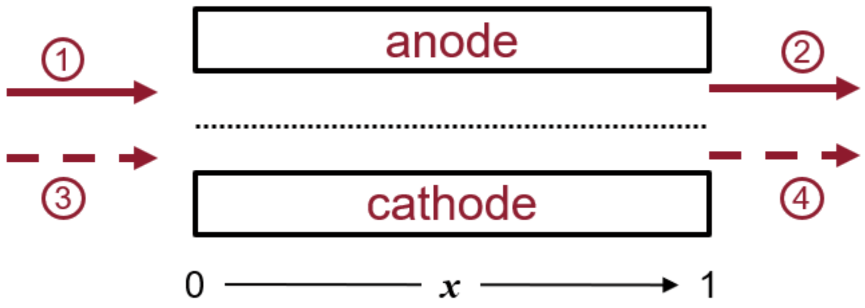




Minimum EMAR Work: Co-Current Operation

T = 50°C, 1m EDA + 0.5m Na_2SO_4 + 0.25m $CuSO_4$
Ionic current via SO_4^{2-} migration





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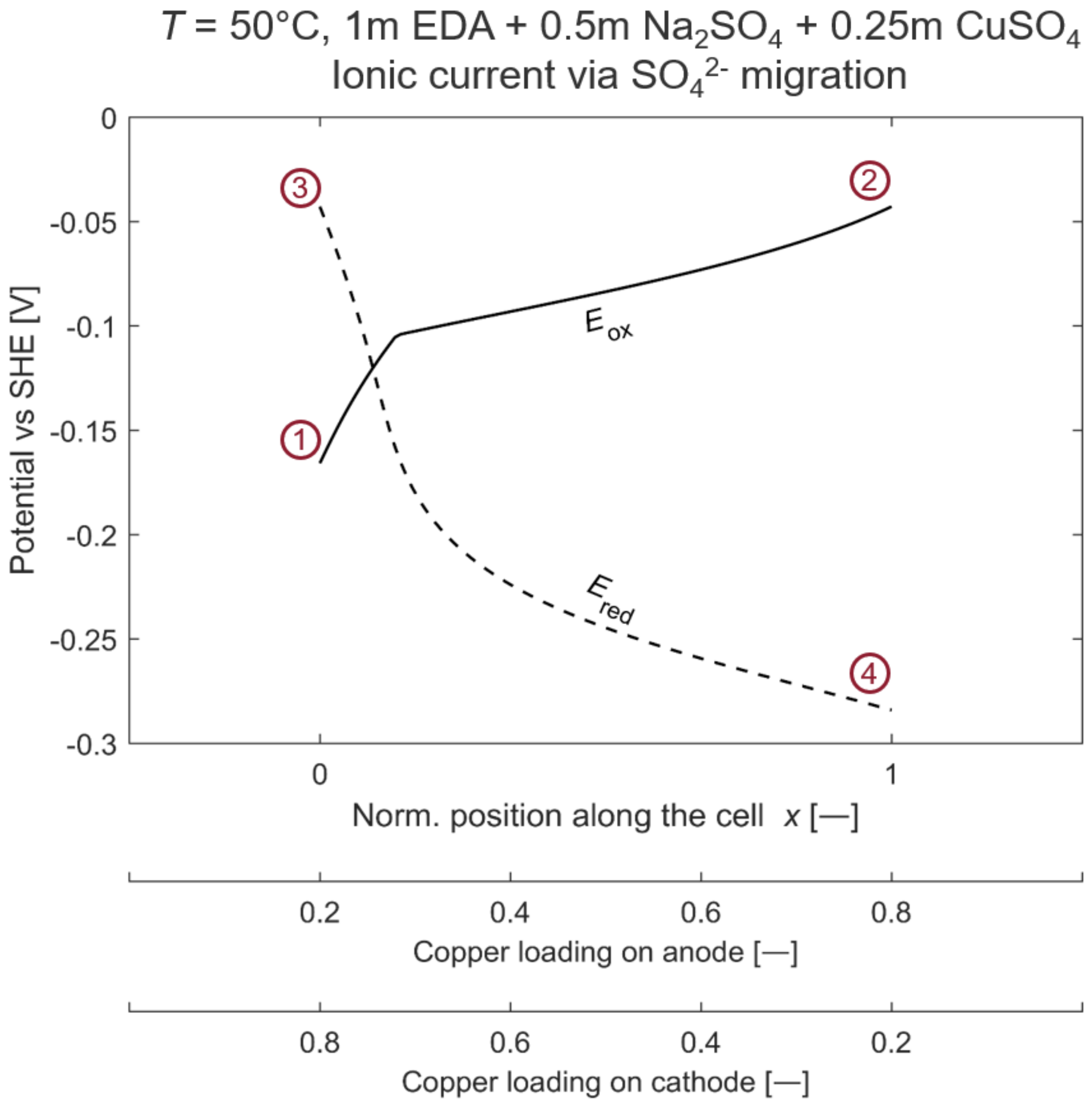

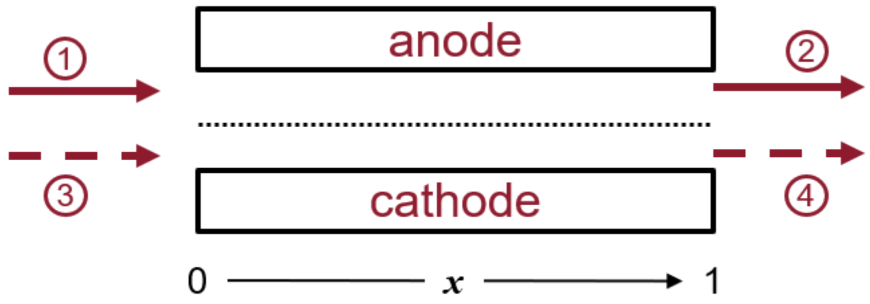

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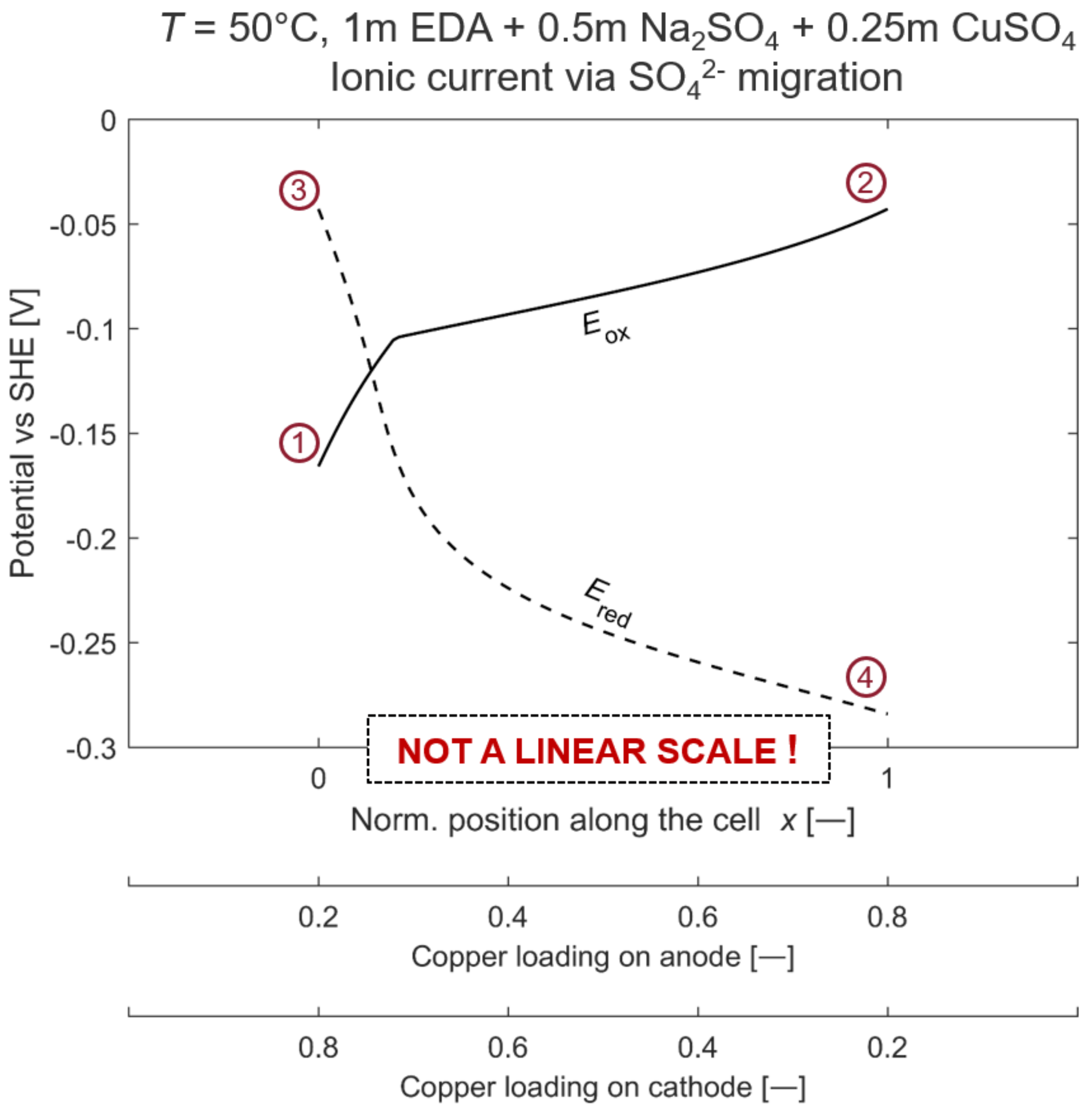

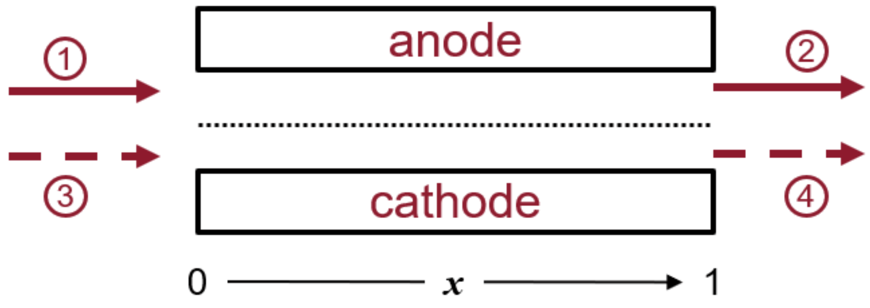

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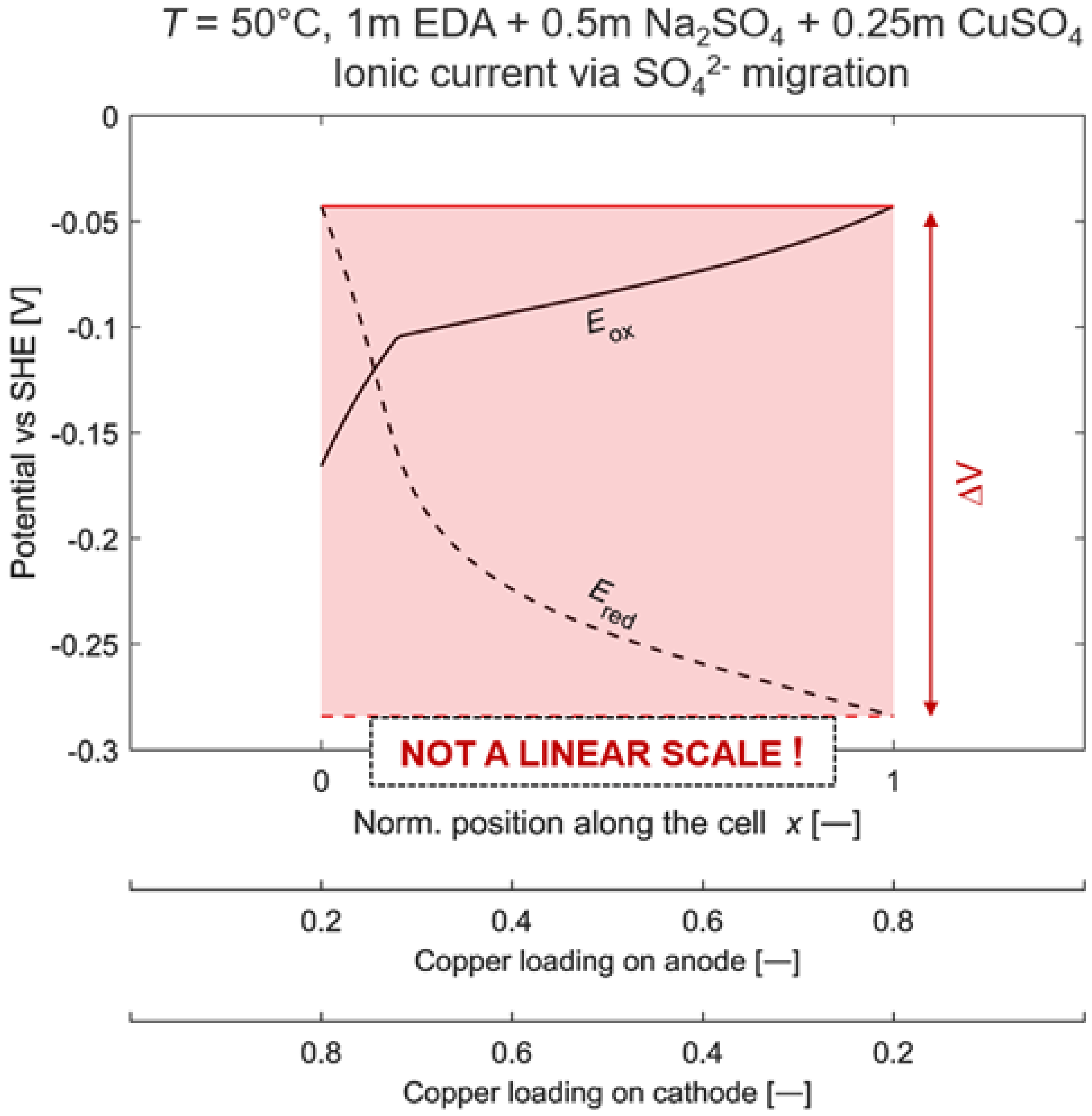
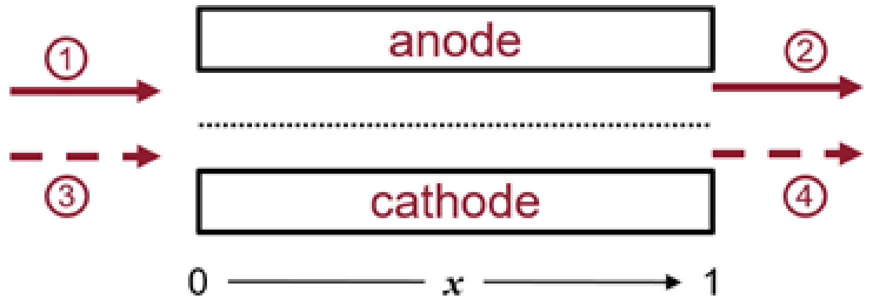
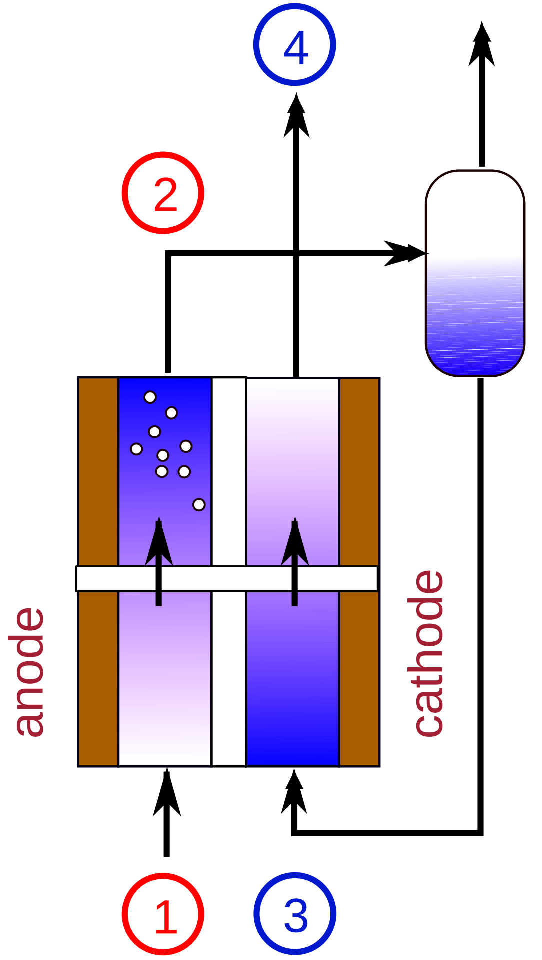
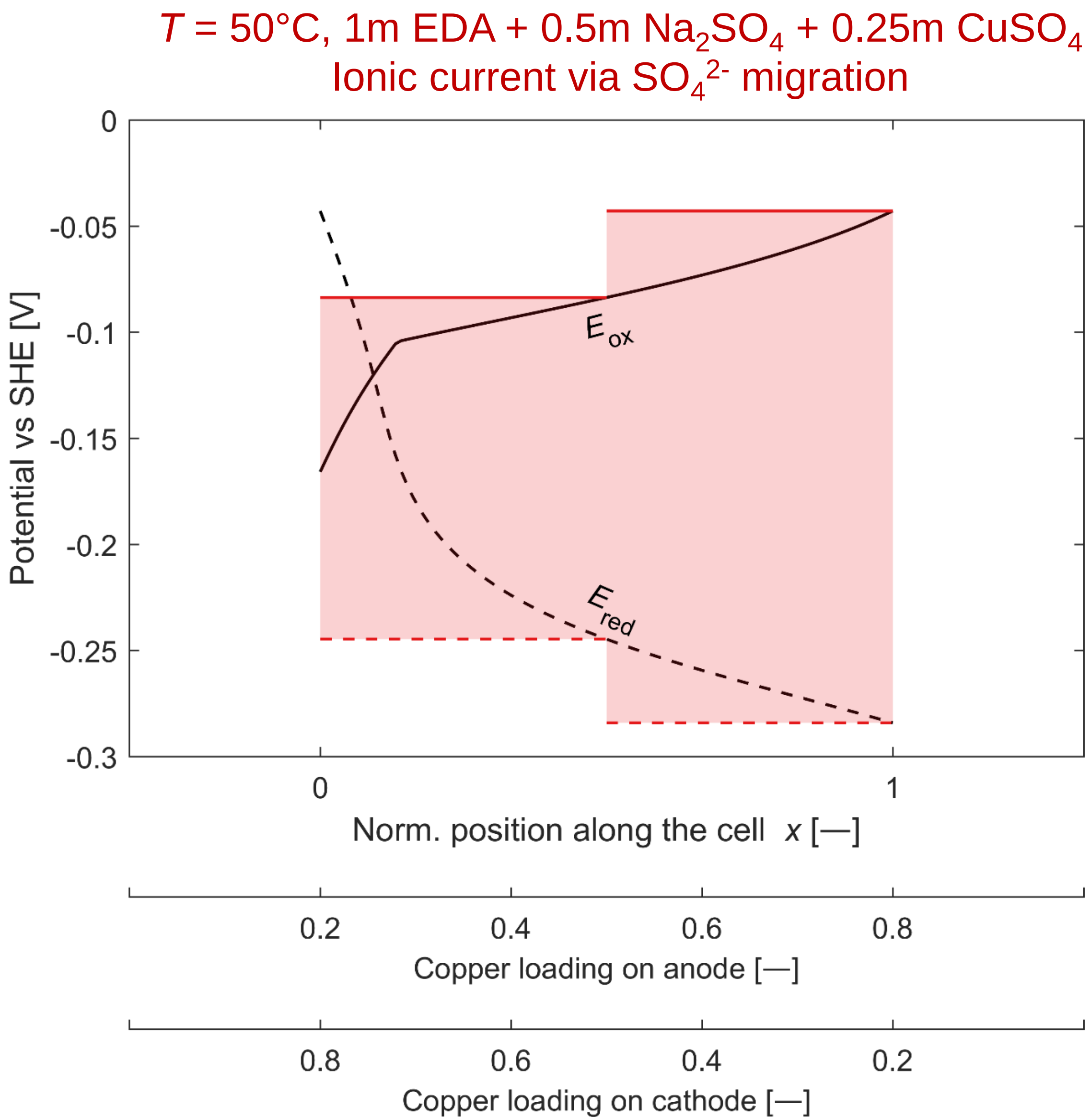


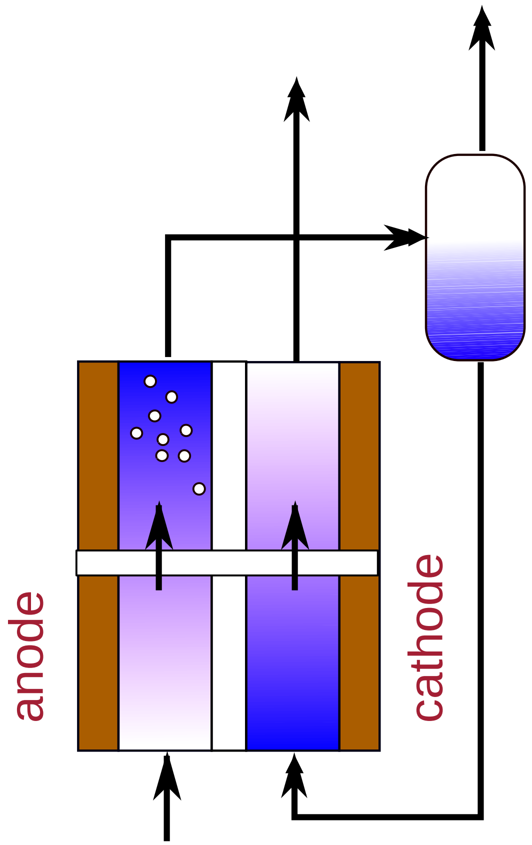


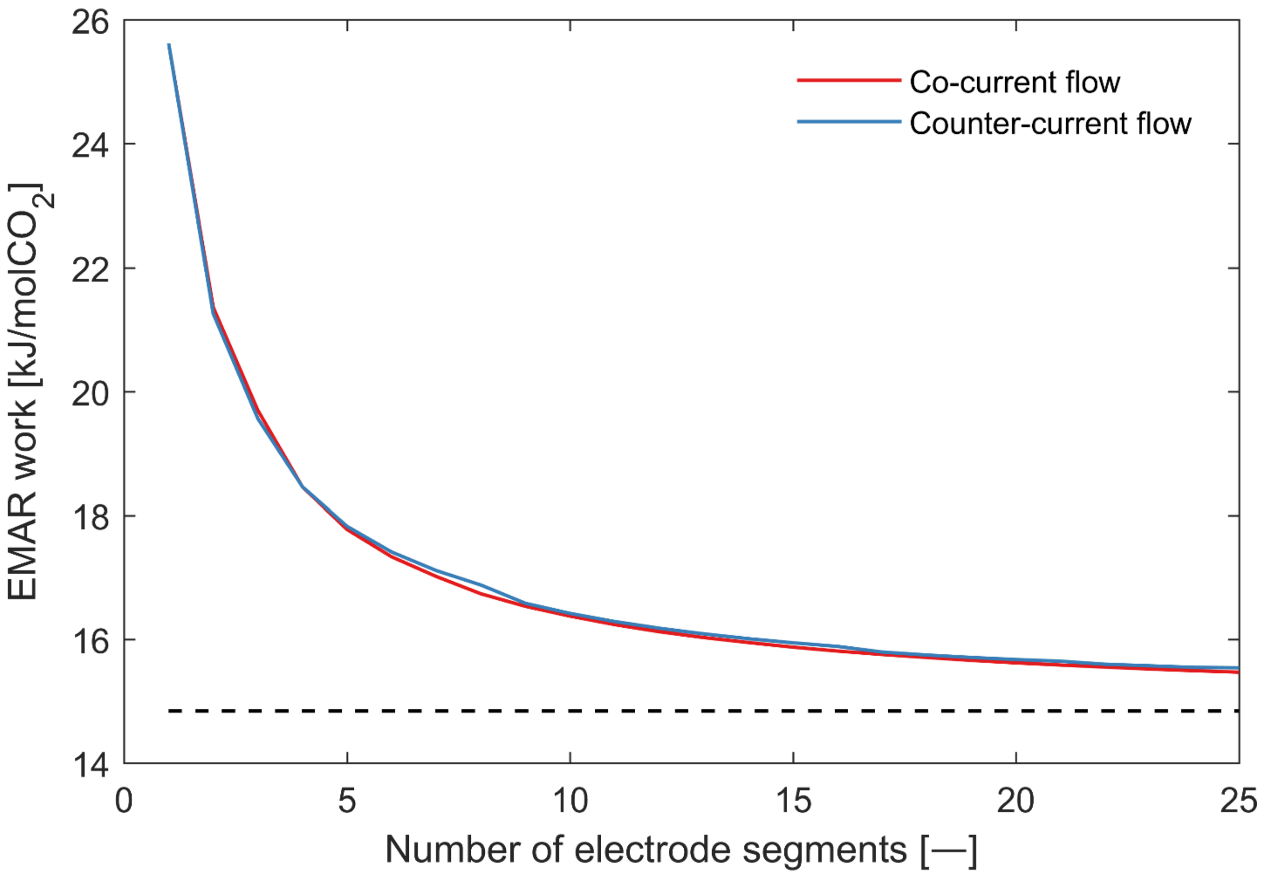
Finite Electrode Overpotential: Segmented Electrodes





EMAR Work with Segmented Electrodes

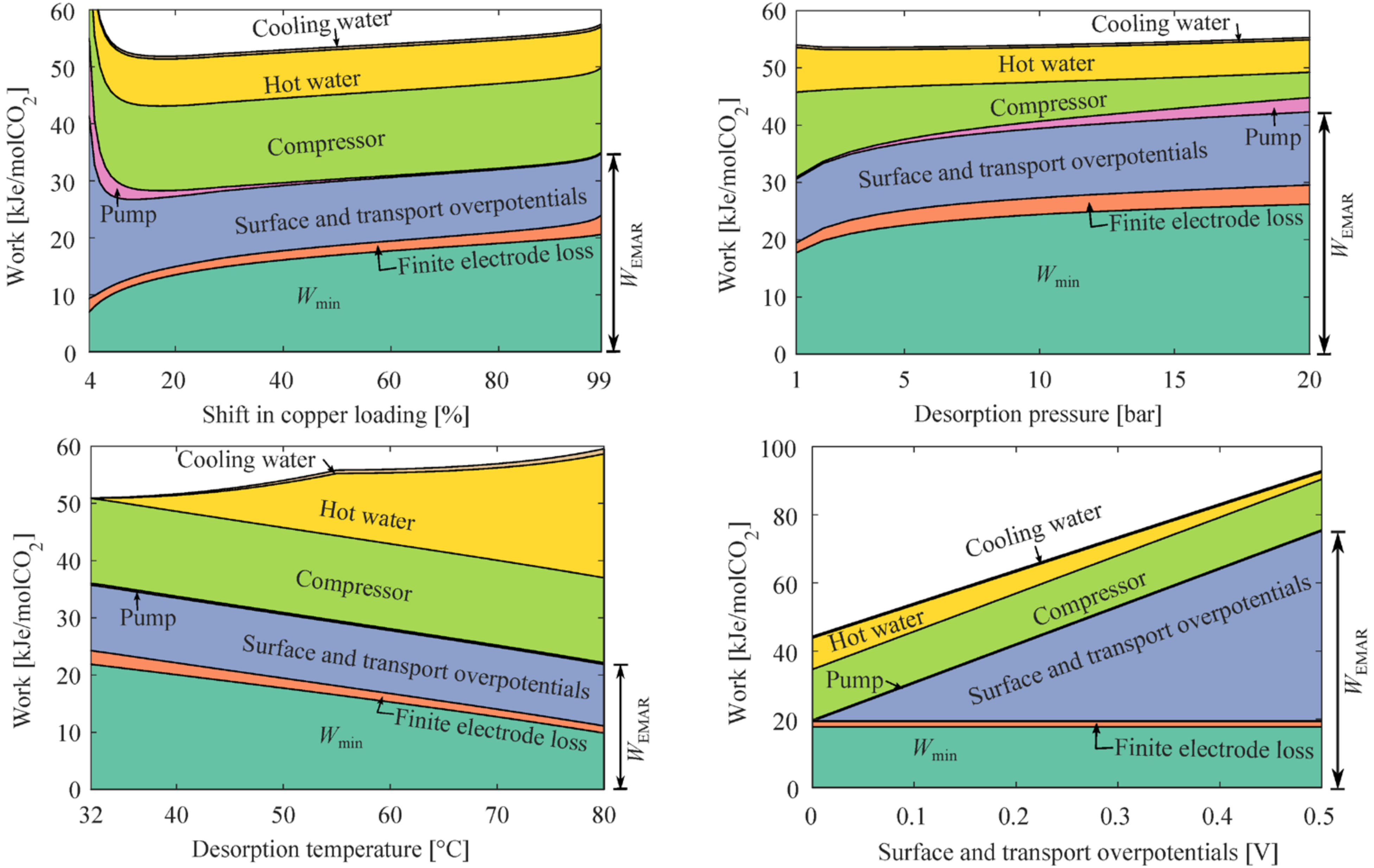




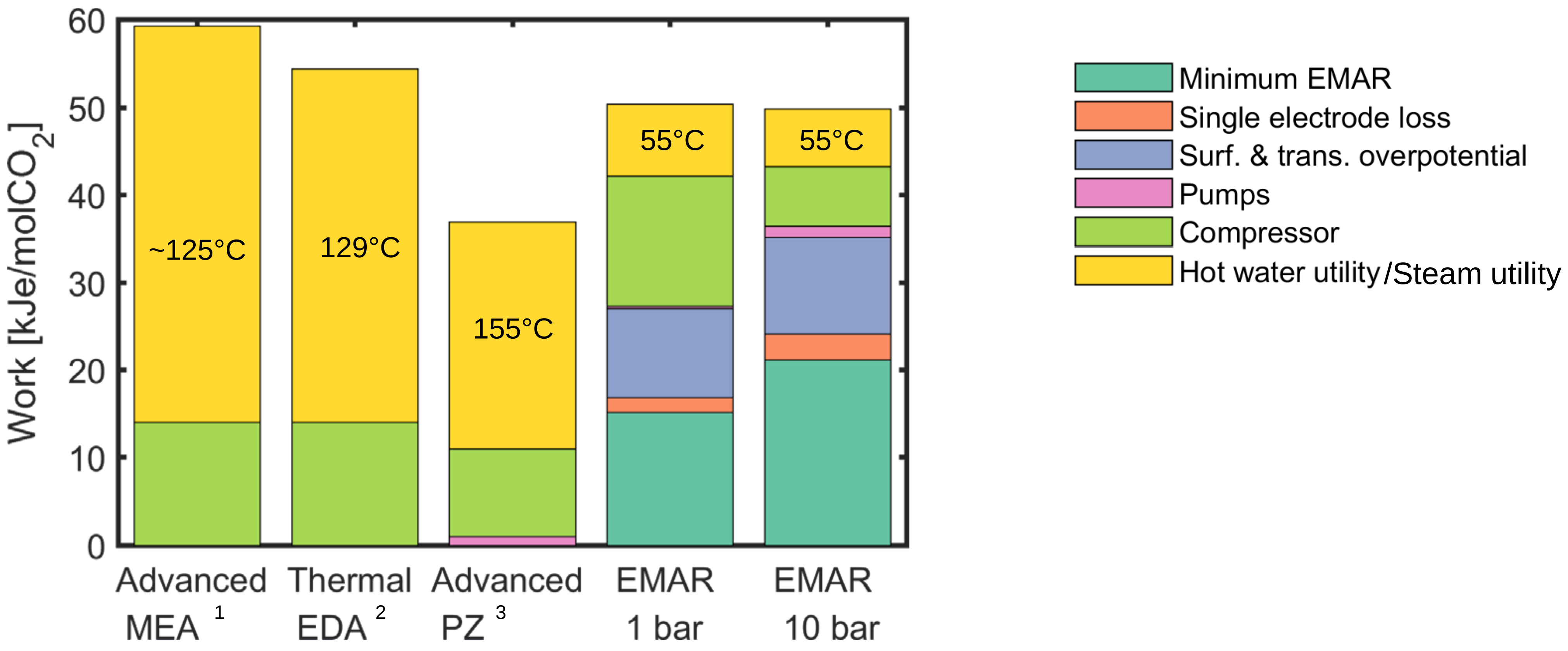
Effect of Operating Parameters on Overall Energetics

Base case

T_{abs} = 50°C,
T_{des} = 50°C
Cu Shift = 60%
P_{des} = 1 bar,
overpotential = 0.1V

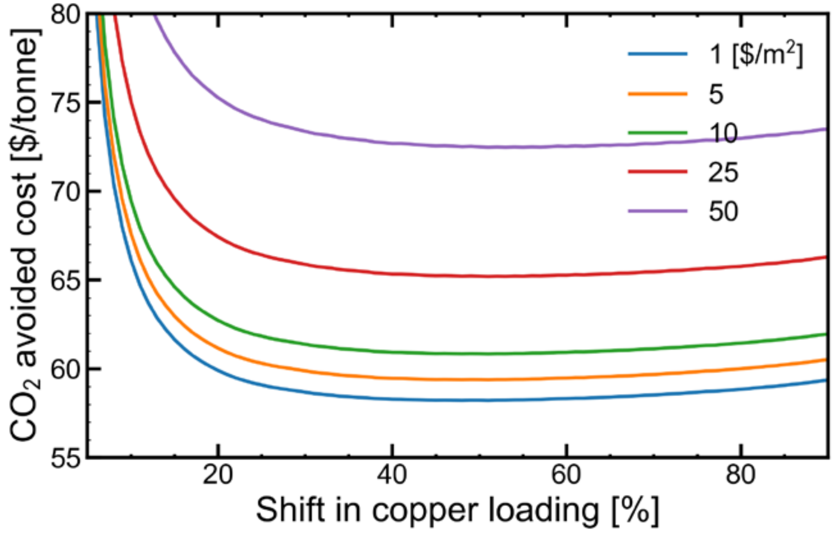


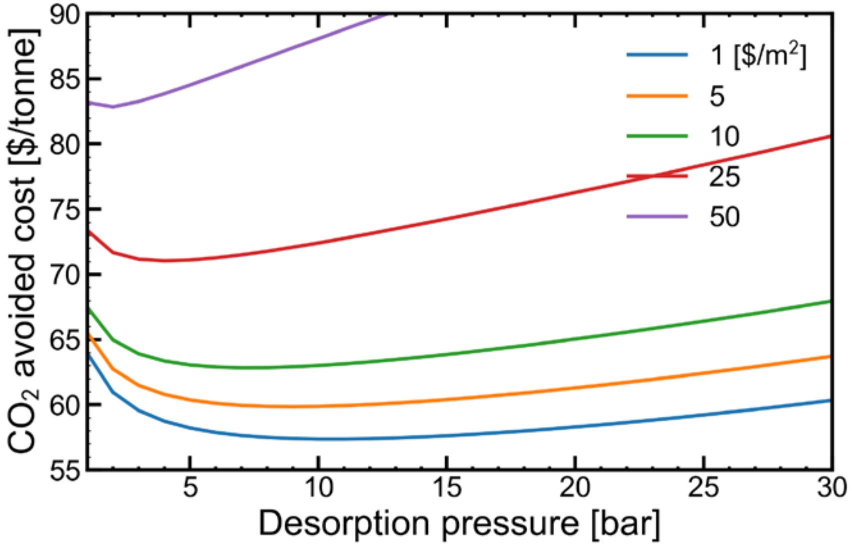
Process Energetics comparison

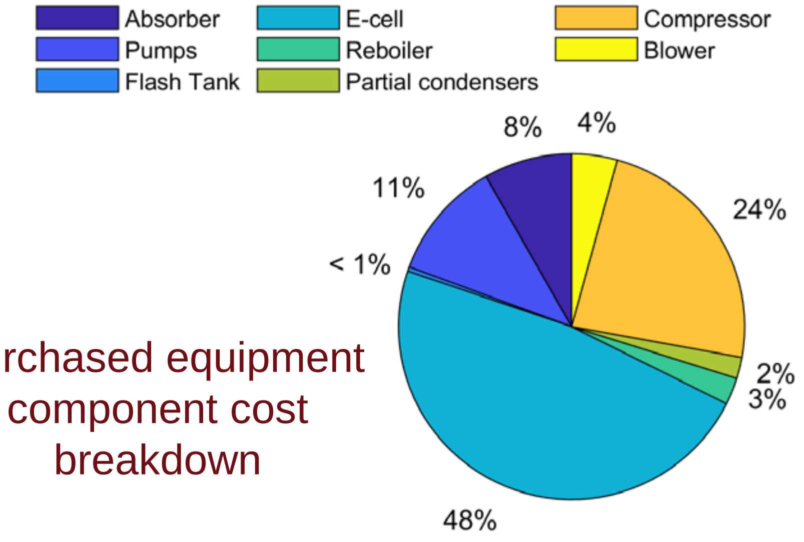


[1] Econamine process, Case10, Rev.2a, NETL (2013)
[2] Rabensteiner et al., *Int J Greenh Gas Con*, 27 (2014), 1-14
[3] Lin and Rochelle, *Chem Eng J*, 283, (2016): 1033-1043

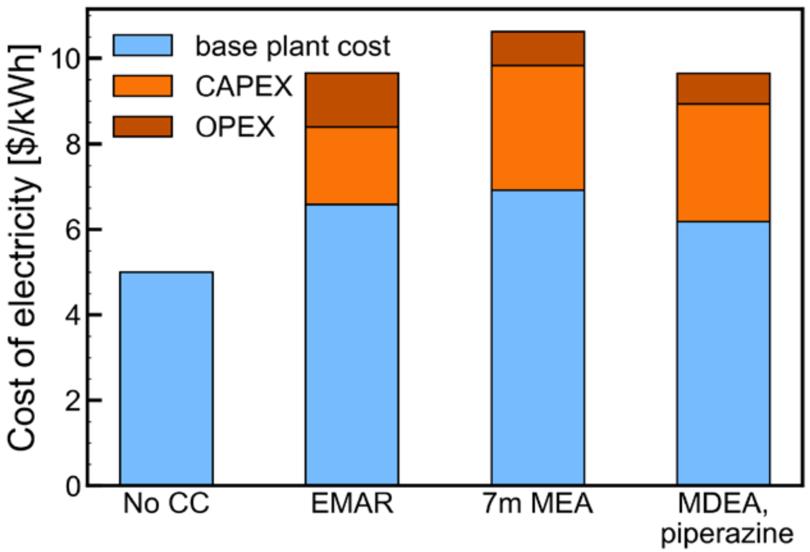
Cost of Electricity and CO_2 Avoided



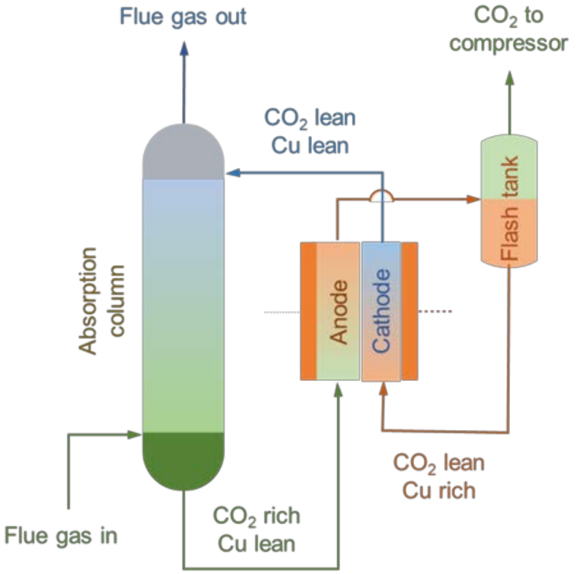


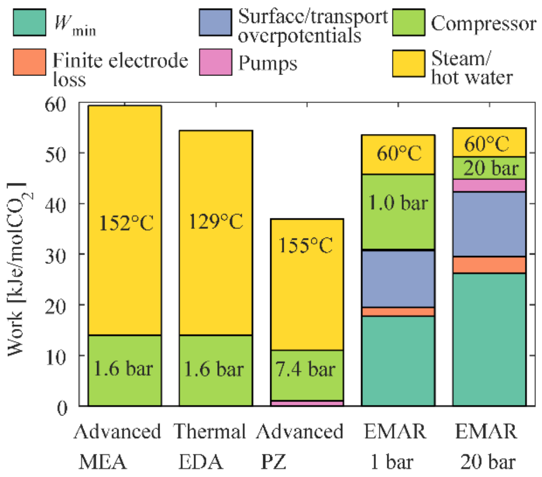


Purchased equipment component cost breakdown



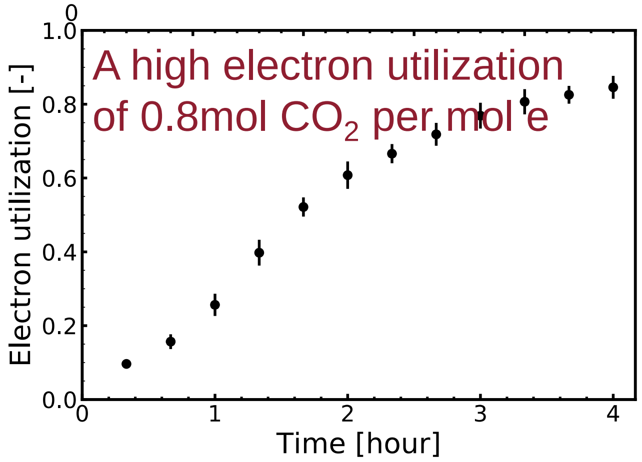
Conclusion



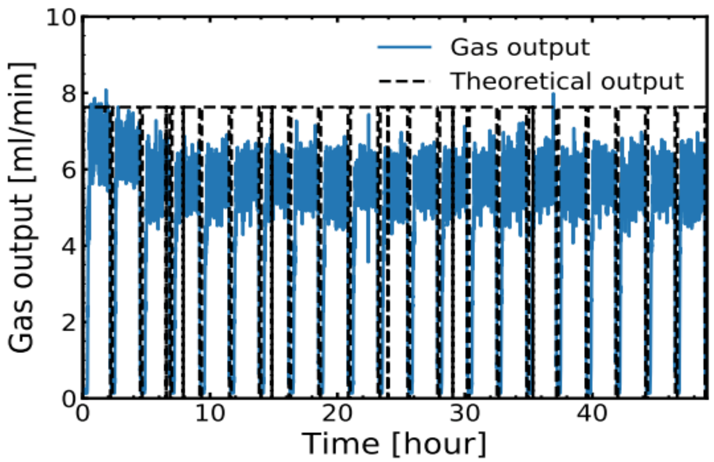


Favorable energetics and costs relative to conventional thermal amine processes

EMAR is an alternative CO_2 desorption at low temperature (less amine degradation) and with electricity (easier retrofit)



A high electron utilization of 0.8mol CO_2 per mol e



Effective and stable approach for flue gas CO_2 capture

Project Risks and Mitigation Strategies

Technical Risks	Probability	Impact	Risk Mitigation
CO_2 sorbents and metal ion systems unsuccessful	Medium	Low	Wide range of candidate sorbents available. Initial results are promising
Electrochemical cell models low in fidelity and do not permit optimization	Moderate	Low	Complexity of underlying mechanisms in electrochemical cell presents risk for modeling. Parametric experiments will generate sufficient data for empirical optimization.
Process found to be too sensitive for long-term operations and disturbances	Moderate	Moderate	Preliminary testing is encouraging. Degradation of electrodes or sorbents possible, but can be mitigated through design of electrode configurations

Resource and Management Risks

Resource Risks	Probability	Impact	Risk Mitigation
Cost of bench-scale system after optimization more expensive than planned	Low	Low	Most of the components of the system have been procured and operated in previous work, but the optimized system might involve more expensive equipment, especially for automation.

Management Risks	Probability	Impact	Risk Mitigation
Process performance reaches a plateau that does not satisfy DOE research goals	Moderate	High	The progress reports will allow the project team to evaluate the performance of the process and determine whether it is possible to explore new dimensions for performance improvements.

Acknowledgement

Mike Stern

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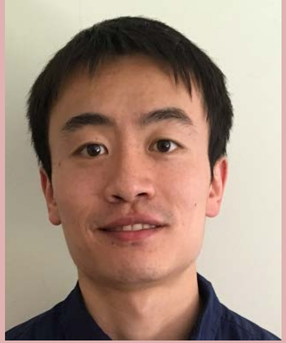
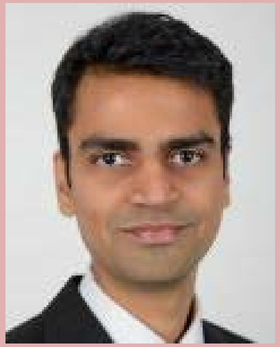
Ryan Shaw



Miao Wang



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