Electrochemically-mediated Sorbent Regeneration in CO$_2$ Scrubbing Processes

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Project Overview

**Award Name:** Electrochemically-Mediated Sorbent Regeneration in CO₂ 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 CO₂ release in amine scrubbing processes
Amine Regeneration in CO$_2$ Capture

- **Absorber**: Temperature $T < 60^\circ C$
- **Desorber**: Temperature $T > 110^\circ C$
- **Feed gas**
- **Lean gas**
- **CO$_2$**
- **Steam**
Electrochemically Mediated Amine Regeneration

Amine Regeneration (Cathode)  CO₂ Absorption (Column)  CO₂ Desorption (Anode)

Amine-Cu Complex  CO₂  Carbamate  Cu  Cu²⁺
Electrochemically Mediated Amine Regeneration

$T < 60^\circ C$

$T = 40-80^\circ C$

$P = 1 - 10$ bar

$E \sim 0.5$ V/cell
Nernstian Description of Electrochemical Gas Separation Cycle

\[ E_{\text{cell}} = \frac{RT}{nF} \ln \left( \frac{a_{\text{Cu}_{\text{anode}}^{2+}}}{a_{\text{Cu}_{\text{cathode}}^{2+}}} \right) \]

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

\[ E = f \left( a_{\text{Cu}^{2+}}, K_1, \ldots, K_{17}, y_{CO_2\text{in}}, C_{Am} \right) \]
Nernstian Description of Electrochemical Gas Separation Cycle

\[ \ln a_{\text{Cu}^{2+}} = \frac{E_{\text{anode}} - E_{\text{cathode}}}{nF} \]

Copper loading := \[ \frac{\text{Cu}^{2+}}{2A_{\text{m}}}. \]

\[ E = f \left( a_{\text{Cu}^{2+}}, K_1, ..., K_{17}, y_{\text{CO}_2}, C_{\text{Am}} \right) \]
Prior effort: EMAR CO$_2$ capture

- CO$_2$ Loading, $\Phi$
- Copper Loading, $\eta$
- EDA
- TETA
- AEEA

- CO$_2$ Output (sccm)
- Time (hours)
- Applied Potential (Volts)

- CO$_2$ Output (sccm)
- Time (Minutes)
- Applied Current (Amps)

- Theoretical Max
- Experiment
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 ($\eta$) for cathodic reaction

$$i_0 = 2Fk_0 [EDA]^{2\alpha} [Cu(EDA)_2^{2+}]^{(1-\alpha)}$$

$$i_0 \sim \sqrt{2(1-\eta)}^{1/2} \eta^{3/4}$$

- Higher overpotential with increasing CO$_2$ content

$$\frac{i_0(EDA-CO_2)}{i_0(EDA)} \sim \left(\frac{P_o}{K_{CO_2} P_{CO_2}}\right)^\alpha \sim 0.3$$
RDE results imply asymmetrical electrode polarization

- Chronoamperometry on rotating disk electrode shows overpotential ($\eta$) for cathodic reaction

\[ i_o = 2Fk_o[EDA]^{2}\alpha [Cu(EDA)^{2+}]^{(1-\alpha)} \]
\[ i_o \sim \sqrt{2}(1-\eta)^{1/2} \eta^{3/4} \]

- Higher overpotential with increasing CO$_2$ content

\[ \frac{i_o(EDA-CO_2)}{i_o(EDA)} \sim \left( \frac{P_o}{K_{CO_2} P_{CO_2}} \right)^\alpha \sim 0.3 \]
Supporting salt affects kinetics

- Changing electrolyte can increase current density from <10 mA/cm² to >50 mA/cm²
- Addition of Cl⁻ increases current density to 100 mA/cm²
EMAR Cell Construction

Delrin end plate

Cu 101 Electrodes
(0.79mm)

Gaskets
Delrin (1.59mm)
EPDM (0.794mm)

Separator
AEM7001
(0.45mm)

Stainless steel compression plate
Continuous Bench Scale EMAR
Gas Separation and Electron Utilization: Effect of Flow Rate

Graph 1: Gas output [ml/min] vs. Time [hour]

Graph 2: Electron utilization vs. Flow rate [ml/min]
Voltage and Gas Evolution with Varying Current

![Graph showing voltage and gas evolution with varying current.](image-url)
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

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

\[ f_i = p_i \]
\[ a_i = \gamma_i c_i \]

\( \gamma_i \rightarrow \text{B-dot equation (Extended Debye Hückel)} \)


Thermodynamics modeling validation

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

$$CO₂\text{ loading} = x_C = \frac{c_C}{c_{EDA}}$$

Electrochemical Energetics

1 to 2: Oxidation
Cu(s) → Cu^{2+} + 2e^{-}

2 to 3: Reduction
Cu^{2+} + 2e^{-} → Cu(s)

\[ W = \int E \, dQ \]

\[ W_{\text{min}} = \frac{1}{F_{m,CO_2}} \left( \int_{x_{Cu}}^{1} E_{\text{ox}} \, dx_{Cu} - \int_{x_{Cu}}^{1} E_{\text{red}} \, dx_{Cu} \right) \]

Temperature: 50°C

Lean Gas

Absorber
\( T = 50°C \)

Amine

Feed Gas

CO_{2}

Desorber
\( T = 50°C \)

Amine + CO_{2}
Electrochemical Energetics

1 to 2: Oxidation
Cu(s) $\rightarrow$ Cu$^{2+} + 2e^-$

2 to 3: Reduction
Cu$^{2+} + 2e^- \rightarrow$ Cu(s)

$T = 50^\circ C$, 1m EDA + 0.5m Na$_2$SO$_4$ + 0.25m CuSO$_4$

$W_{\min} = \frac{1}{F_{m,CO_2}} \left( \int_{x_{Cu}} E_{ox} dl - \int_{x_{Cu}} E_{red} dl \right)$

$W_{\min,corrected} = \frac{1}{F_{m,CO_2}} \left( \int_{x_{Cu}} E_{ox} dl - \int_{x_{Cu}} E_{red} dl \right)$

Lean Gas

CO$_2$

Absorber
$T = 50^\circ C$

Feed Gas

Amine + CO$_2$

Desorber
$T = 50^\circ C$

Amine
Electrochemical Energetics

1 to 2: Oxidation
Cu(s) → Cu²⁺ + 2e⁻

2 to 3: Reduction
Cu²⁺ + 2e⁻ → Cu(s)

\[
W_{min} = \frac{1}{F_{m, CO_2}} \left( \int_{x_{Cu}}^{1} E_{ox} \, dx - \int_{x_{Cu}}^{1} E_{red} \, dx \right)
\]

\[
W_{min, corrected} = \frac{1}{F_{m, CO_2}} \left( \int_{x_{Cu}}^{1} E_{ox} \, dx - \int_{x_{Cu}}^{1} E_{red} \, dx \right)
\]

\[
W_{EMAR} = \frac{1}{F_{m, CO_2}} \left( \int_{x_{Cu}}^{1} E_{ox} \, dx - \int_{x_{Cu}}^{1} E_{red} \, dx \right)
\]
Minimum EMAR Work: Co-Current Operation

\[ T = 50^\circ C, \text{1m EDA} + 0.5\text{m Na}_2\text{SO}_4 + 0.25\text{m CuSO}_4 \]

Ionic current via \( \text{SO}_4^{2-} \) migration

Potential vs SHE [V]

Copper loading [—]

Specific Capacity [C/kgw] + 1000

anode

cathode

0 \[ \text{—} \] \( x \) \[ \text{—} \] 1
Minimum EMAR Work: Co-Current Operation

$T = 50^\circ\text{C}, 1\text{m EDA} + 0.5\text{m Na}_2\text{SO}_4 + 0.25\text{m CuSO}_4$

Ionic current via SO$_4^{2-}$ migration

![Graph showing potential vs. SHE (V) and copper loading (mass%)]

- Potential vs SHE (V)
- Copper loading (mass%)
- Specific Capacity (C/kgw) - (C/kgw) + 1000

1. Anode
2. Cathode
3. Oxidation
4. Reduction

0, 19.3, 38.6, 57.9, 77.2, 96.5

26.
$T = 50^\circ\text{C}, 1\text{ m EDA} + 0.5\text{ m Na}_2\text{SO}_4 + 0.25\text{ m CuSO}_4$

Ionic current via $\text{SO}_4^{2-}$ migration

Minimum EMAR Work: Co-Current Operation

Potential vs SHE [V]

Norm. position along the cell $x [-]\]

Copper loading on anode [\text{[-]}]

Copper loading on cathode [\text{[-]}]
Minimum EMAR Work: Co-Current Operation

\[ T = 50^\circ C, 1 \text{m EDA} + 0.5 \text{m Na}_2\text{SO}_4 + 0.25 \text{m CuSO}_4 \]

Ionic current via \( \text{SO}_4^{2-} \) migration

**Diagram:**
- **Potential vs SHE [V]:**
  - \( E_{\text{ox}} \)
  - \( E_{\text{red}} \)
- **Norm. position along the cell \( x \) [\( - \)]:**
  - 0
  - 0.2
  - 0.4
  - 0.6
  - 0.8
- **Copper loading on anode [\( - \)]:**
  - 0.8
  - 0.6
  - 0.4
  - 0.2
- **Copper loading on cathode [\( - \)]:**
  - 0.8
  - 0.6
  - 0.4
  - 0.2

**Notes:**
- **NOT A LINEAR SCALE!**
Minimum EMAR Work: Co-Current Operation

\[ T = 50^\circ C, 1m \text{EDA} + 0.5m \text{Na}_2\text{SO}_4 + 0.25m \text{CuSO}_4 \]

Ionic current via \( \text{SO}_4^{2-} \) migration

\[ \Delta V \]

\[ \text{Potential vs SHE [V]} \]

\[ E_{\text{ox}} \]

\[ E_{\text{red}} \]

Norm. position along the cell \( x \) [—]

Copper loading on anode [—]

Copper loading on cathode [—]
Finite Electrode Overpotential: Segmented Electrodes

\[ T = 50^\circ C, 1\text{m EDA} + 0.5\text{m Na}_2\text{SO}_4 + 0.25\text{m CuSO}_4 \]

Ionic current via SO\(_4^{2-}\) migration

![Diagram showing segmented electrodes and current flow](image)
EMAR Work with Segmented Electrodes

![Diagram showing anode and cathode with EMAR work graph showing EMAR work vs. number of electrode segments for co-current and counter-current flow.]
**Effect of Operating Parameters on Overall Energetics**

**Base case**

$T_{\text{abs}} = 50^\circ\text{C}$,  
$T_{\text{des}} = 50^\circ\text{C}$  
Cu Shift $= 60\%$  
$P_{\text{des}} = 1$ bar,  
overpotential $= 0.1\text{V}$
Process Energetics comparison

[1] Econamine process, Case10, Rev.2a, NETL (2013)
Cost of Electricity and CO$_2$ Avoided

Purchased equipment component cost breakdown

- Absorber: 48%
- Pumps: 4%
- E-cell: 11%
- Reboiler: 24%
- Flash Tank: 3%
- Compressor: 2%
- Blower: 1%

Cost of electricity [kWh]:
- No CC: 6
- EMAR: 7
- 7m MEA: 8
- MDEA, piperazine: 9

CO$_2$ avoided cost [$/tonne]

Shift in copper loading [%]

Desorption pressure [bar]

1 [$/m^2$]
- 5
- 10
- 25
- 50

CO$_2$ avoided cost [$/tonne]
Conclusion

EMAR is an alternative CO₂ desorption at low temperature (less amine degradation) and with electricity (easier retrofit)

A high electron utilization of 0.8mol CO₂ per mol e⁻.

Effective and stable approach for flue gas CO₂ capture
## Project Risks and Mitigation Strategies

<table>
<thead>
<tr>
<th>Technical Risks</th>
<th>Probability</th>
<th>Impact</th>
<th>Risk Mitigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ sorbents and metal ion systems unsuccessful</td>
<td>Medium</td>
<td>Low</td>
<td>Wide range of candidate sorbents available. Initial results are promising</td>
</tr>
<tr>
<td>Electrochemical cell models low in fidelity and do not permit optimization</td>
<td>Moderate</td>
<td>Low</td>
<td>Complexity of underlying mechanisms in electrochemical cell presents risk for modeling. Parametric experiments will generate sufficient data for empirical optimization.</td>
</tr>
<tr>
<td>Process found to be too sensitive for long-term operations and disturbances</td>
<td>Moderate</td>
<td>Moderate</td>
<td>Preliminary testing is encouraging. Degradation of electrodes or sorbents possible, but can be mitigated through design of electrode configurations</td>
</tr>
</tbody>
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## Resource and Management Risks

<table>
<thead>
<tr>
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<tbody>
<tr>
<td><strong>Cost of bench-scale system after optimization more expensive than planned</strong></td>
</tr>
<tr>
<td><strong>Probability</strong></td>
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<tr>
<td>Low</td>
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<tr>
<th>Management Risks</th>
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<tbody>
<tr>
<td><strong>Process performance reaches a plateau that does not satisfy DOE research goals</strong></td>
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<tr>
<td><strong>Probability</strong></td>
</tr>
<tr>
<td>Moderate</td>
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