Electrochemically-Mediated Separations for CO₂ Capture

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Carbon Capture and Mitigation

- Coal to play a major role in world’s energy future:
  - lowest-cost for base-load electricity generation
  - coal resources distributed around the world.
- Adverse environmental effects accompany its mining, transport and utilizations.
- Carbon Capture and Storage (CCS)
  - mitigate contribution of carbon-based fuel emissions to climate change,
  - capture carbon dioxide (CO₂) from point sources, e.g., power plants and other industrial facilities,
  - and store it in deep subsurface geological formations for indefinite isolation from the atmosphere.

World Primary Energy Consumption, 2005-2025

World Electricity Generation by Fuel, 2005-2030

Trillion Kilowatt-hours

Coal Combustion Capture Technology

Pre-combustion Challenges:
Low operational temperature of existing CO₂ removal technology.
More economical to combust syngas before fully shift (reducing fraction of CO₂ captured).

Post-combustion Challenges:
- Dilute CO₂ concentration in flue gas.
- Other flue gas components.
- High capital and operational costs.

Gas Separation Technology for Post-Combustion CCS

Gas/liquid contractors
Permselective membranes
High-temperature polymeric

Absorption
Alkanolamines, Blended alkanolamines
Piperazine, Amino acids
Second generation amine
Third generation sorbent,
Potassium carbonate, Chilled ammonia

Adsorption
Zeolites
Carbon
Silica
Alumina

Membrane

Biological
Algae
(photosynthesis)
Carbonic anhydrase
(enzyme-catalyzed CO₂ capture)

Reactive Solid
Metal Oxides
Sodium Bicarbonate
Sodium Hydroxide
Lithium Zirconate
Lithium Silicate

Flue Gas R&D Pathways
Exploratory Adsorption
Metal Organic Frameworks
CO₂ Hydrates
Liquid crystals
Ionic Liquids

Thermal-Swing Processes
Pressure-Swing Processes
Isothermal Processes
Electrochemical-Swing Processes
Gas Separation Technology for Post-Combustion CCS

- Increase CO₂ permeation rates
- Increase selectivity
- Improve economies of scale

- Excellent CO₂ selectivity over N₂
- Reduce capital & operational costs
- Lower energy consumed
- Minimize oxidative degradation
- Minimize SO₂ & NOₓ degradations

- Increase CO₂/N₂ selectivity
- Increase CO₂ capacity

- Required highly porous materials
- Improve long term stability
- Improve long term performance

- Challenge in economies of scale
- Long term biological activity/stability

**Flue Gas R&D Pathways**

- Absorption
- Adsorption
- Membrane
- Biological

**Flue Gas R&D Pathways**

- Thermal-Swing Processes
- Pressure-Swing Processes
- Isothermal Processes
- Electrochemical-Swing Processes

Objective of CCS R&D of DOE in The United States

- Minimum CO₂ capture = 90%
- Maximum increase in COE = 35%

**Figure 1: Goal Diagram for EPEC CCS Incremental Mills/kWh**

CCS technology requires new approaches to achieve target of 35% maximum increase in COE.
Traditional Wet-Scrubbing Process

Developed over 70 years ago as non-selective acid gas removal processes
- Today, the only real option for deploying CCS technology
- Recent solvent R&D focuses on solvent degradation and equipment corrosion
- Need significant improvement to meet 35% maximum increase in COE

Table 1. Economics of CO₂ capture by MEA scrubbing

<table>
<thead>
<tr>
<th>Year of design</th>
<th>2001</th>
<th>2006</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA (weight percent)</td>
<td>26</td>
<td>30</td>
</tr>
<tr>
<td>Power used (MWh/ton)</td>
<td>0.51</td>
<td>0.37</td>
</tr>
<tr>
<td>@5000 MWh/ton (5 ton CO₂ removed)</td>
<td>41</td>
<td>29</td>
</tr>
<tr>
<td>Capital cost ($/ton CO₂ removed per year)</td>
<td>186</td>
<td>106</td>
</tr>
<tr>
<td>@144/ton ($/ton CO₂ removed)</td>
<td>38</td>
<td>17</td>
</tr>
<tr>
<td>Operating cost and maintenance cost ($/ton CO₂ removed)</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Total cost ($/ton CO₂ removed)</td>
<td>72</td>
<td>52</td>
</tr>
<tr>
<td>Net CO₂ removal with power replaced by gas (%a)</td>
<td>72</td>
<td>74</td>
</tr>
</tbody>
</table>

The theoretical minimum work is 0.11 MWh/ton CO₂

Potential Benefit of Electrochemical-Swing Processes

- Significant decrease in total energy consumption for CCS
- Ease of integration with existing power plants
  - Decrease in indirect cost of CCS
- Applicable to other large-scale carbon emitters with no possibility for energy integration for thermal swing processes
  - Cement and chemical industries
Electrochemical Separation Processes

- Advantages of electrochemical processes in waste treatment industry:
  - Versatile
  - Energy efficient
  - Lower temperature requirements
  - Cell optimization to minimize power losses caused by overpotential and side reactions
  - Cost effective

Electrochemical-Swing Gas Separation Technologies

Electrochemical Reaction of Target Molecules

\[ \text{Ox} + \text{ne} \leftrightarrow \text{Red} \]

\[ \text{Ox} \rightarrow \text{influx} \]

\[ \text{Red} \rightarrow \text{outflux} \]

Electrochemical Reaction of Carrier Molecules

\[ \text{Ox} + \text{ne} \leftrightarrow \text{Red} \]

\[ \text{Red} \leftrightarrow \text{A + Red} \]

\[ \text{A} \rightarrow \text{influx} \]

\[ \text{A} \leftrightarrow \text{outflux} \]

Electrochemical Separation Processes

- 1970 – Electrochemical pumping of NO through thin films
  (Mode 2)

- 1974 – Molten carbonate electrochemical CO₂ concentrator
  (Mode 1)

- 1979 – Aqueous carbonate electrochemical CO₂ concentrator
  (Mode 2)

- 1981 – Flue gas desulfurization using an electrochemical SO₂ concentrator
  (Mode 1)

- 1984 – Electrochemical removal and concentration of H₂S from coal gas
  (Mode 1)

Electrochemical heterocyclic nitrogen compound separation – 1993
(Mode 2)

Electrochemically-modulated complexation: CO concentrator – 1995
(Mode 2)

(Mode 2)

Electrochemically-modulated complexation: CO₂ air capture – 2003
(Mode 2)

Separation of CO₂ from flue gas using electrochemical cells – 2010
(Mode 2)
Electrochemical Swing Gas Separation Processes

Electrochemical-Swing Gas Separation Technologies

Electrochemical Reaction of Target Molecules

Mode 1

Ox + ne ↔ Red

Ox influx outflux

Red ↔ Ox + ne

Electrochemical Reaction of Carrier Molecules

Mode 2

A influx

A outflux

Electrochemical Gas Separation of CO₂

Molten Carbonate Electrochemical Cell (1974)
- Considered for CO₂ removal in a manned spacecraft
- Electrochemical reactions:
  - Cathodic reaction: \( \text{CO}_2 + \frac{1}{2} \text{O}_2 + 2e^- = \text{CO}_3^{2-} \)
  - Anodic reaction: \( \text{CO}_3^{2-} = \text{CO}_2 + \frac{1}{2} \text{O}_2 + 2e^- \)
- High temperature operation \( \sim 700°C \)
- 60% CO₂ removal efficiency
- CO₂ removal efficiency increases with increasing current density
- Current efficiency decreases with increasing applied current density
  (still remaining challenge)

Molten Carbonate Fuel Cell (Hydrogen Mode)

Molten Carbonate CO₂ Separation Cell (Driven/Nitrogen Mode)

Winnick, J. et al., AIChE Journal 1982, 28(1):103-111
Electrochemical Gas Separation

**FGD using electrochemical SO$_2$ concentrator (1981)**  

Electrochemical reactions:

- **“Driven” mode:**
  - Cathode: $\text{SO}_2 + \text{O}_2 + 2e = \text{SO}_4^{2-}$
  - Anode: $\text{SO}_4^{2-} = \text{SO}_3 + \frac{1}{2}\text{O}_2 + 2e$

- **“Reducing-gas” mode:**
  - Cathode: $\text{SO}_2 + \text{O}_2 + 2e = \text{SO}_4^{2-}$
  - Anode: $\text{SO}_4^{2-} + 5\text{H}_2 = 4\text{H}_2\text{O} + \text{H}_2\text{S} + 2e$

Operational condition:
Concentrate SO$_2$ from 0.03% at the cathode to 10% at the anode at 600°C.

Operational energy costs:
For a 500 MWe plant burning 3.5% sulfur coal of 9000 Btu lb heating value, the total electrical energy required is about 2% of the plant power, comparing to other FGD processes requiring up to 6% of plant power.

Operating costs:
- ~ 0.05 cents/kWh in the driven mode and ~ 0.15 cents/kWh in the reducing-gas mode (wet scrubbing processes cost 0.14 to 0.20 cents/kWh).

Experimental result:
Nearly all SO$_2$ was scrubbed from the flue gas, with less than 5 ppm remained.
Electrochemical Gas Separation

Electrochemical removal of H$_2$S from coal gas (1984)

- Electrochemical reactions:
  - Cathode: H$_2$S + 2e = H$_2$ + S$^{2-}$
  - Anode: S$^{2-}$ = $\frac{1}{2}$ S$_2$ + 2e
- Feasible H$_2$S removal at high temperature
- 98% removal efficiency of H$_2$S with reasonable levels of polarization
- Favorable capital and operational costs for the H$_2$S concentrator

Removal efficiency as a function of current density

Current efficiency as a function of current density at 840°C and 65% H$_2$S cathode inlet

Electrochemical Swing Gas Separation Processes

Electrochemical-Swing Gas Separation Technologies

Electrochemical Reaction of Target Molecules

Electrochemical Reaction of Carrier Molecules

Electrochemical Facilitated Transport Processes

Electrochemical Activation

Target Capture

Target Recovery

Electrochemical Deactivation

Carrier Regeneration

Electrochemical Facilitated Transport Processes

Equilibrium Stage Processes

Step 1: Increase Carrier Affinity

Step 2: Solute Extraction

Step 3: Decrease Carrier Affinity

Step 4: Solute Stripping

Feeding Stream

Receiving Stream
**Electrochemical Gas Separation**

**Electrically Induced Carrier Transport (1970)**
( Electrochemical Facilitated Transport Processes)

- Redox carrier, ferrous chloride, facilitates electrochemical pumping of nitric oxide (NO) through thin films creating a pressure difference in the NO

Cathodic reaction:
\[
\text{Fe}^{3+} + e^{-} \leftrightarrow \text{Fe}^{2+}
\]

Anodic reaction:
\[
\text{FeNO}_2^+ \leftrightarrow \text{NO} + \text{Fe}^{3+} + e^{-}
\]


**Electrochemical Gas Separation of CO₂**

**Electrochemically-Regenerable CO₂ Absorber (1979)**
( Electrochemical Facilitated Transport Processes)

- Overall reactions: \( \text{CO}_3^{2-} + \text{H}_2\text{O} + \text{Electrical Energy} = 2\text{OH}^- + \text{CO}_2 + \text{Heat} \)

Life System, Inc. 1973, Electrochemical CO₂ Concentrator

- Pennline, H.W. *et al Fuel* 2010, 89:1307-1314

**Separation of CO₂ from flue gas using electrochemical cells (2010)**

- Electrochemical reactions:
  - Cathode reaction: \( \text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^- \)
  - Anode reaction: \( 4\text{OH}^- = \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \)
Equilibrium Staged Electrochemical Separations

- Requirements for redox active carriers:
  - Carrier soluble only in contacting phase
  - Carrier with target binding site and ability to undergo chemically reversible redox cycle in presence and absence of target molecule
  - Considerable differences in the affinity of carrier for target molecule in different oxidation states
  - Rapid kinetics of complexation reaction

- Applications:
    - Fe(II) and Fe(III) electrochemical cycling
    - Continuous electrochemically-modulated complexation separation process
    - 2,6-di-tert-butyl-1,4-benzoquinone electrochemical cycling

Electrochemical Separation Processes

- Potential-swing induces dramatic change in effective binding constant of carrier (C) toward target molecule (L)
  - Ability to control binding constant ($K_{binding}$)
  - Can approach thermodynamically-reversible separation with potential-swing processes

\[
\begin{align*}
C + ne & \leftrightarrow C^* \\
C^* + L & \leftrightarrow C^* L \\
\end{align*}
\]

\[
K_{binding} (E) = \alpha(E)K_{binding} (E^o) = \exp \left( \frac{nF}{RT} (E^o - E) \right)
\]

\[
K_{binding} (E^o) = \frac{[C^* L]}{[C^*][L]} \approx 0.1 \text{ to } 100 \text{ M}^{-1}
\]
Ideal Work for Electrochemical Separation

- Reaction during absorption process:
  \[ C + ae \leftrightarrow C^* \]
  \[ C^* + \beta CO_2 \leftrightarrow C^* (CO_2)_\beta \]

- Reaction during desorption process:
  \[ C^* (CO_2)_\beta \leftrightarrow C (CO_2)_\beta + ae \]
  \[ C (CO_2)_\beta \leftrightarrow C + \beta CO_2 \]

- Electrical energy required per mole of CO_2 separated:
  \[ W_{electrical} = \frac{\alpha}{\beta} F \langle \Delta E \rangle \]
  \[ \langle \Delta E \rangle = \langle E_{cathode} \rangle - \langle E_{anode} \rangle \]

Minimum Work of Electrochemical Separation

- Nernst Equation:
  \[ E = E^o - \frac{RT}{nF} \ln \left( \frac{[C^*]^\alpha}{[C]^\alpha} \right) = E^o - \frac{RT}{\alpha F} \ln \left( \frac{C^*}{C} \right) \]

- Equilibrium of C* with CO_2:
  \[ K_{binding} = \frac{[C^* (CO_2)_\beta]}{[C^*][CO_2]^{\beta}} \]

- Extent of reaction with respect to CO_2:
  \[ \xi = \frac{n_{CO_2,0} - n_{CO_2,t}}{n_{CO_2,0}} \]

- Electrical energy required per mole of CO_2 separated:
  \[ [C_{red}] = [C^*] + [C^* (CO_2)_\beta] \]
  \[ [C] = [C] + [C_{red}] \]
  \[ E = E^o - \frac{RT}{\alpha F} \ln \left( \frac{[C]}{[C_{red}]} \right) \left( 1 + K_{binding} [CO_2]^\beta \right) \]
  \[ \langle E_{cathode} \rangle = \frac{1}{6} E_{capture} d\xi \]
  \[ \langle E_{anode} \rangle = \frac{1}{6} E_{regeneration} d\xi \]
Minimum Work of Electrochemical Separation

**Equilibrium Stage Processes** (FOUR-STAGE PROCESSES)

1. **Step 1:** Increase Carrier Affinity
2. **Step 2:** Solute Extraction
3. **Step 3:** Decrease Carrier Affinity
4. **Step 4:** Solute Stripping

**Electrochemical Facilitated Transport Processes** (TWO-STAGE PROCESSES)

- **Feed Stream**
- **Electrode**
- **Electrochemical Activation**
- **Target Capture**
- **Electrochemical Deactivation**
- **Target Regeneration**
- **Carrier Regeneration**
- **Receiving Stream**

**Four-Stage Processes:**

\[ W_{electrical} = RT \ln \left( K_{binding} \cdot \frac{P_{CO_2, regeneration}}{V_m H_{CO_2}} \right) \]

**Two-Stage Processes:**

\[ W_{electrical} = RT \left( \ln x_{CO_2} + \frac{1-x_{CO_2}^o}{x_{CO_2}^o} \ln \left( 1-x_{CO_2}^o \right) \right) \]

Minimum Work for Electrochemical Separation

**LOG(K_{binding})**

Four Stage Process

\[ W_{electrical} = RT \ln \left( K_{binding} \cdot \frac{P_{CO_2, regeneration}}{V_m H_{CO_2}} \right) \]

Final \( CO_2 \) Partial Pressure = 1 atm

\( CO_2 \) solubility = 0.129 mol/L atm
Minimum Work for Electrochemical Separation

\[
W_{electrical} = RT \left( \ln x_{CO_2}^0 + \frac{1 - x_{CO_2}^0}{x_{CO_2}^0} \ln \left( 1 - x_{CO_2}^0 \right) \right)
\]

Two Stage Process

Two Stage Electrochemical Separation Process

CO\textsubscript{2} capture and regeneration processes mediated by simultaneous activation and deactivation of redox carriers through electrochemical processes.
**Redox Carrier for CO₂ Capture**

**Metal Organic Carrier**

- Cu(II) complexes
- Ni(II) complexes

**Organic Carriers**

- 2,6-di-tert-butyl-1,4-benzoquinone

Acid-base reaction of dianionic quinones with CO₂ - electron rich oxygens donate and share electron pairs with electrophilic carbon of CO₂ molecules to form stable carbonates.

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**Electrochemistry – Cyclic Voltammetry Technique**

Study electrochemistry of carrier by monitoring electron flowing from the electrode (reduction) and to the electrode (oxidation).

**Fermi Level**

Reduction

- Lowest Unoccupied Molecular Orbital
- Oxidized Carrier Molecular Orbital

Oxidation

- Highest Occupied Molecular Orbital
- Reduced Carrier Molecular Orbital

**Potential (V)**

**Current (A)**

---

**Electrochemistry of 2,6-dichloro-quinone (BQ-Cl2)**

- **Under Nitrogen**
  - 1st electron transfer at -0.85 V
  - 2nd electron transfer at -1.66 V

- **Under Carbon Dioxide**
  - 1st electron transfer at -0.85 V
  - 2nd electron transfer at -1.44 V

CO₂ stabilizes the dianion quinone.
Electrochemistry of 2,6-ditert-butyl-quinone (BQ-TB)

![Graph showing current (A) vs. potential (V) with 1st and 2nd electron transfer points under nitrogen and carbon dioxide]

Electrochemical Reaction with Stack Gas Components

Stack Gas
- 2,770,000 kg/hr
- 55°C, 1 atm

Vol% (# kg/hr)
- N₂: 66.6% (1,820,000)
- H₂O: 16.7% (294,000)
- CO₂: 11% (466,000)
- O₂: 4.9% (153,000)
- Ar: 0.8% (31,000)
- SO₂: 22 ppm (136)
- NO₃: 38 ppm (114)
- Hg: <1 ppb (31 kg/yr)
**Electrochemical Reaction with Stack Gas Components**

Chemical reaction between superoxide anion radical ($O_2^-$) and $CO_2$:

$$O_2 + 2CO_2 + 2e^- \rightarrow C_2O_6^{2-}$$

indicated by disappearance of oxidation peak of superoxide anion radical ($O_2^-$) in the presence of $CO_2$.

-1.3 V is the maximum cathodic potential limit for ideal redox carrier

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**Inductive Effect of Side Functional Groups**

*Inductive effect* - transmission of charge through a chain of atoms by electrostatic induction.

$$NO_2 > F > COOH > Cl > Br > I > OH > OR > C_6H_5 > H > Me_3C^- > Me_2CH^- > MeCH_2^- > CH_3$$

Electron-withdrawing

Electron-donating

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**Potential (V)**

$E^0_{\text{oxygen}} = -1.3V$

**Current (mA)**

Oxygen and Carbon Dioxide
Cyclic Voltammograms of Quinoidal Redox Carriers

- Irreversible electrochemistry
- Cathodic potential > -1.3V (NOT IDEAL CARRIER)

- Reversible electrochemistry
- Cathodic potential < -1.3V (NOT IDEAL CARRIER)

Ideal redox carrier must have “Nernstian” reversible electrochemistry in the presence and absence of CO₂

Molecularly-Optimized Redox Carrier for CO₂ Capture

- Reversible electrochemistry
- Cathodic potential > -1.3V (IDEAL CARRIER)
Concluding Remarks

- Electrochemical separations have a potential for long-term CO$_2$ scrubbing applications
- Two-stage electrochemical separator is ideal system for energy efficient CO$_2$ capture processes
- Future electrochemical CO$_2$ separations:
  - Molecular-engineered redox carrier molecule
  - Understanding of electrochemical separation
  - Advanced infrastructure materials

COE of ECMS Processes
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