Electrochemically-Driven Carbon Dioxide Separation

DE-FE0031955

Yushan Yan
University of Delaware

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Project Overview

Funding: $800,000 federal + $200,000 cost share

Period of Performance: 10/1/2020 – 3/31/2022

Participants: University of Delaware

Project Objectives:
– Develop electrochemically-driven CO$_2$ separator with 0.4 mol/m$^2$-hr air capture at <235 kJ/mol$_{CO_2}$ (1.5 MWh/t)
– Characterize poly(aryl piperidinium) (PAP) properties to support future development
Symmetrical electrodes are used to charge and discharge: Nickel(II) hydroxide \textbf{anode}/Nickel(III) oxy-hydroxide \textbf{cathode}

$\text{OH}^-$ is produced to convert $\text{CO}_2$ in air to $\text{CO}_3^{2-}/\text{HCO}_3^{-1}$ and shuttle across the membrane where it is concentrated for release as high purity $\text{CO}_2$ product.
Air is fed at ambient conditions.

Electrodes are run at constant current until the NiOOH cathode is consumed and no more OH\(^{-}\) is produced.

Voltage supplied needs to overcome ohmic resistance, pH differential, and cell voltage.

Continuous operation.
Technology Background

Previous work showed efficacy of this concept.

Proof of concept accumulation of CO$_2$ at the Anode and removal of CO$_2$ from the cathode prompting development of this project.
# Technology Background

## Advantages

- Hydroxide needed for CO$_2$ capture is generated in-situ.
- Powered by renewable energy instead of fossil fuel sources.
- No expensive thermal or pressure swings required to separate out CO$_2$.

## Disadvantages

- Moisture management in the cell may be needed to maintain carbonate conductivity and could be difficult in some locations.
- Capital cost of electrochemical system.
# Technical Approach - 3 core tasks

|                                            | Create a test station and perform full cell experiments. |
| Task 3: Polymer/Membrane Characterization   | Measure fundamental kinetics and transport under different %RH and pH conditions.  
|                                            | Enables modeling and full cell optimization that can be constructed in future studies. |
| Task 2: Membrane Fabrication               | Design process for building a membrane with high in-plane, air-flow properties. |
## Technical Approach-3 core tasks

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Task 3: Polymer/Membrane Characterization</td>
<td>July 2021 - Conductivity tests underway highlighting strong relationship to humidity. Aug. 2021 - In situ pH monitoring being developed.</td>
</tr>
<tr>
<td>Task 2: Membrane Fabrication</td>
<td>Work to be started.</td>
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</tbody>
</table>
# Progress and Current Status

| Task 4: Membrane Electrode Assembly Testing | Task 4.1 Electrode Fabrication  
Task 4.2 Design of Test Fixture  
Task 4.3 EDCS Testing |
|------------------------------------------|---------------------------------|
| Task 3: Polymer/Membrane Characterization | Task 3 Membrane Test Bench  
Task 3.1 Conductivity  
Task 3.2 Carbonation Kinetics and Equilibrium |
There are several ways to make Ni(OH)$_2$.

Chose an electro-precipitation method in a 3-electrode cell to control the amount and structure of Ni(OH)$_2$ applied to a nickel foam substrate.

Total current during precipitation determines amount deposited, the structure is affected by the current density during precipitation.
Sample produced at 20 mA cm\(^{-2}\) and initially cycled at 5 mA cm\(^{-2}\) showed significant physical degradation. Sample produced at 10 mA cm\(^{-2}\) and initially cycled at 5 mA cm\(^{-2}\) showed improved stability and significantly improved performance.
Task 4.3 EDCS Testing-Half Cell

Preliminary Transfer of CO$_2$ across PAP membrane with a Ni(OH)$_2$ and Pt/H$_2$ half cells.

CO$_2$ is measured at the outlet of the Ni(OH)$_2$ electrode half of the cell

Representative charge and discharge Cycle. Future work to optimize charge duration and prevention of oxygen evolution.

Starting point for moving to full cell work.
Task 4.2 Design of Test Fixture

DAC test station with capabilities of switching types of gas and polarity in conjunction with electrode charge and discharge cycles.

Top Layer - Flow Control

Second Layer - RH% Control, Gas Mixing, DAC Cell

Third Layer - Condensate Control

Bottom Layer – Central Control Interface
Task 3 Membrane Test Fixture

Conductivity is a key characterization parameter. It affects the feasibility and power consumption of the device.

This 4-electrode setup allows for characterization of conductivity.

Circled in red is the cell with the 4-electrode setup, surrounded by controls for humidity, temperature, CO$_2$ concentration, and flow rates.
4-electrode measurement eliminates effect from electrode polarization to give true ionic conductivity

\[ \kappa = \frac{l_b}{Rw\delta} \]

- \( \kappa \): resistance
- \( l_b \): width of membrane
- \( w \): thickness of membrane
- \( \delta \): distance of inner electrodes

**Task 3.1 Membrane Conductivity**

Conductivity shown to be strongly dependent on %RH.

Known difference in conductivity between HCO$_3^-$ and OH$^-$. 

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**Graphs:**

- **Left Graph:**
  - Conductivity (mS cm$^{-1}$) vs. Temp (°C)
  - 90% RH
  - 100% RH
  - OH$^-$ form

- **Right Graph:**
  - Conductivity (mS cm$^{-1}$) vs. Temp (°C)
  - OH$^-$ form
  - HCO$_3^-$ form
  - 100% RH
Monitored membrane carbonation from \( \text{OH}^- \) to \( \text{HCO}_3^- \) at two different temperatures in \( \text{CO}_2 \) enriched stream.

Intend to extract kinetic and transport parameters from this methodology to be used in future modeling work.
## Plans for future

<table>
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<th>Current Project</th>
<th>After this project</th>
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<td>Task 4.3 Full Cell Testing</td>
<td>Optimize Cell Performance</td>
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<td>Task 2.3 Structured Membrane Production</td>
<td>Scale up study with stack system</td>
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<tr>
<td>Task 5 Energy evaluation</td>
<td>Capital cost study for commercialization</td>
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</table>
Core electrochemical methodology works.

Provides an alternative path to prevailing amine-based systems that require temperature and/or pressure swings.

Potential for both direct air capture and point source.
Thank you to our many colleagues whose foundational work made this project possible:

- Junhua Wang
- Yun Zhao
- Stevi Matz
- David Yan
- Santiago Rojas-Carbonell
- Rohan Razdan
- Catherine Weiss
- Lin Shi
- Junwu Xiao

Thank you to Versogen for supplying PAP the anion exchange membrane and ionomer used for developing this project.
• Highlighted sections is actual completion to date. Number of months are shown since start of project. Resource restrictions prevented starting of project for 6 months.

<table>
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<tr>
<th>Project Tasks</th>
<th>Months After Initiation of the Project</th>
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<tr>
<td>Total Project</td>
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<tr>
<td>Task 1. Project Management and Planning</td>
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<td>Task 1.1. Project Management Plan</td>
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<td>Task 1.2. Technology Maturation Plan</td>
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<td>Task 2. Membrane fabrication</td>
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<tr>
<td>Task 2.1. Characterize polymer solubility</td>
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<td>Task 2.2. Fabricate porous membranes</td>
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<td>Task 2.3. Fabricate structured membranes with integrated flow channels</td>
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<td>Task 3. Polymer/membrane characterization</td>
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<td>Task 3.1. pH and conductivity</td>
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<td>Task 3.2. Carbonation kinetics and equilibrium</td>
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<td>Task 3.3. Porous membrane characterization</td>
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<td>Task 3.4. Through-plane transport properties of structured membranes</td>
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<tr>
<td>Task 4. Membrane electrode assembly testing</td>
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<td>Task 4.2. Design of test fixture</td>
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<td>Task 5. Process development</td>
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<tr>
<td>Task 5.1. Develop high-level process design and analysis</td>
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Today
CO$_2$ Alkaline Equilibrium

Acid-base equilibria:

HCO$_3^-$ + OH$^- \rightleftharpoons$ CO$_3^{2-}$

H$_2$CO$_3$ + OH$^- \rightleftharpoons$ H$_2$O + HCO$_3^-$

Carbon dioxide hydration:

CO$_2$(g) $\rightleftharpoons$ CO$_2$(aq)

CO$_2$(aq) + H$_2$O $\rightleftharpoons$ H$_2$CO$_3$

CO$_2$(aq) + OH$^- \rightleftharpoons$ HCO$_3^-$
Electrode Production Setup

Lower current densities produced more physically stable electrodes. *(Right- Case of lost active material on high current density sample 20mA cm$^{-2}$. This is not appreciably observed at lower current densities <10mA cm$^{-2}$)*

Higher total current applied to electrodes produced higher capacity electrodes.

The highest capacity sample produced thus far was with 10mA cm$^{-2}$ over 2 hours.
Electrode cycling in 1 M KOH

Charge and Discharge curves of best charge capacity Ni(OH)$_2$ Electrode

Cut off electrode charge before oxygen evolution plateau.

Produced stable discharge capacities with 95.8±0.5% columbic efficiency.

Only a modest 6% drop in capacity of compared with the hold in Oxygen evolution state.
Equipment PFD