Electrochemically-Driven Carbon Dioxide Separation

DE-FE0031955

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U.S. Department of Energy

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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

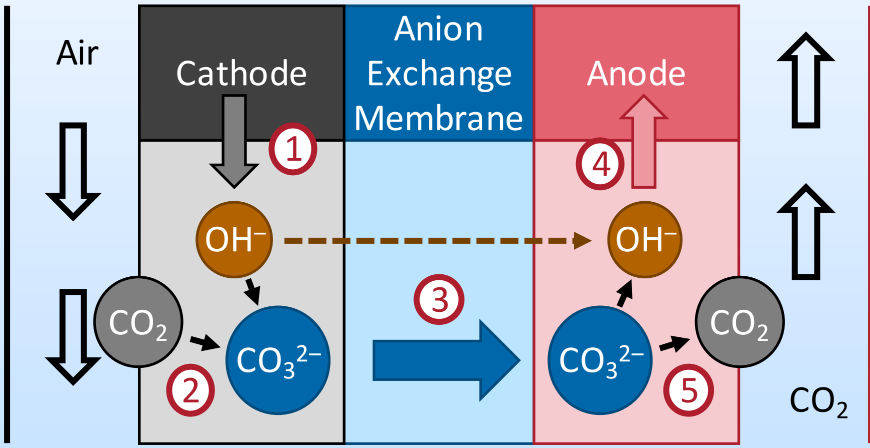
Project Objectives:

- Develop electrochemically-driven CO_2 separator with 0.4 mol/m^2-hr air capture at <235 kJ/mol$_{CO2}$ (1.5 MWh/t)
- Characterize poly(aryl piperidinium) (PAP) properties to support future development

Technology Background

Symmetrical electrodes are used to charge and discharge:
Nickel(II) hydroxide **anode**/ Nickel(III) oxy-hydroxide **cathode**

OH^- is produced to convert CO_2 in air to CO_3^{-2}/HCO_3^{-1} and shuttle across the membrane where it is concentrated for release as high purity CO_2 product.



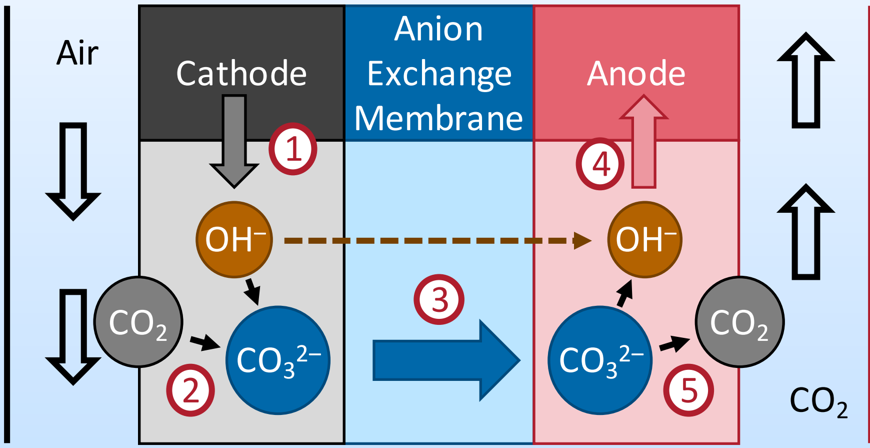
Technology Background

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.

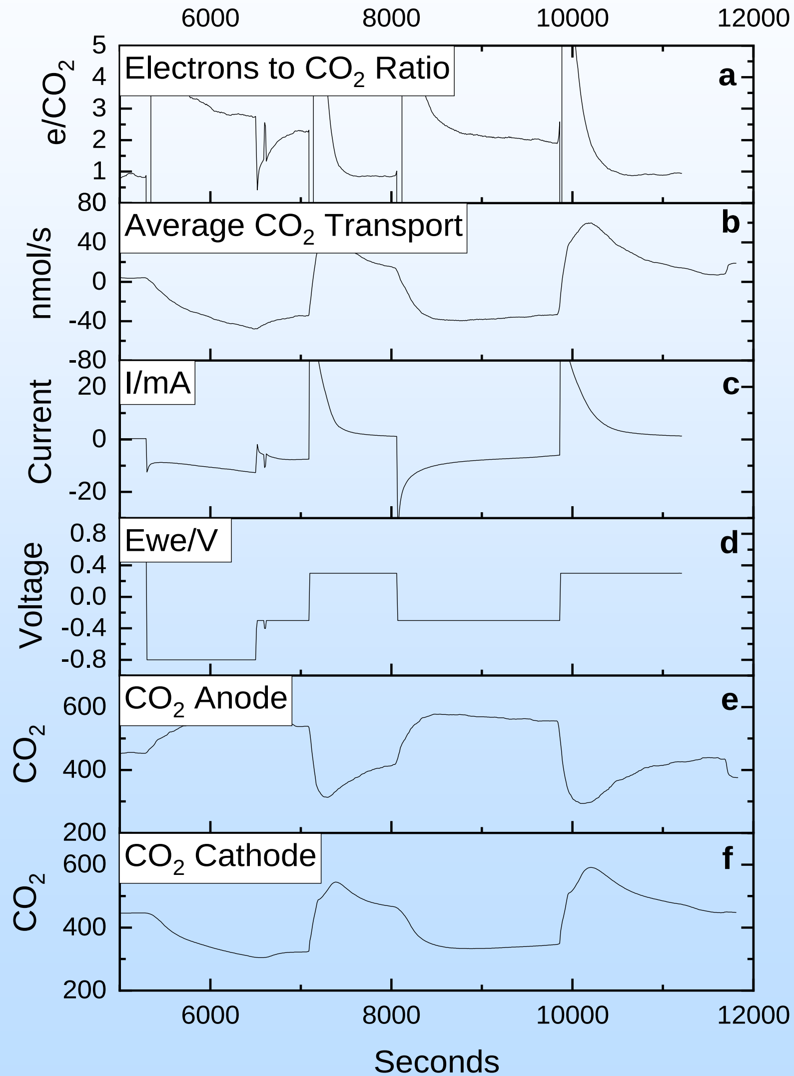
Continuous operation.



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

Task 4: Membrane Electrode Assembly Testing	Determine best method of electrode production. 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

Task 4: Membrane Electrode Assembly Testing	June 2021- Improved electro-precipitation of $Ni(OH)_2$ onto Nickel foam electrodes. Aug. 2021-Finalizing cell test station.
Task 3: Polymer/Membrane Characterization	July 2021 - Conductivity tests underway highlighting strong relationship to humidity. Aug. 2021- In situ pH monitoring being developed.
Task 2: Membrane Fabrication	Work to be started.

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

Task 4.1 Electrode Fabrication

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.

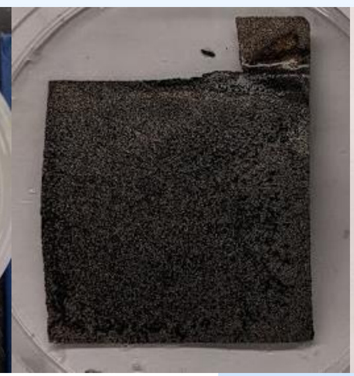
Task 4.1 Electrode Fabrication Improvement

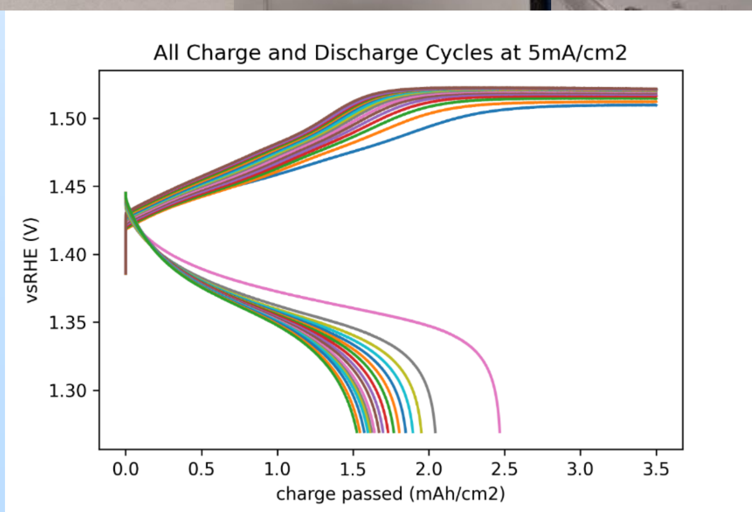
Sample produced at 20 mA cm^{-2} and an initially cycled at 5 mA cm^{-2} showed significant physical degradation

<u>Deposition</u>

<u>Capacity Cell</u>

<u>Post Test</u>

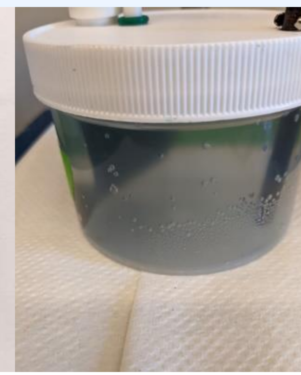




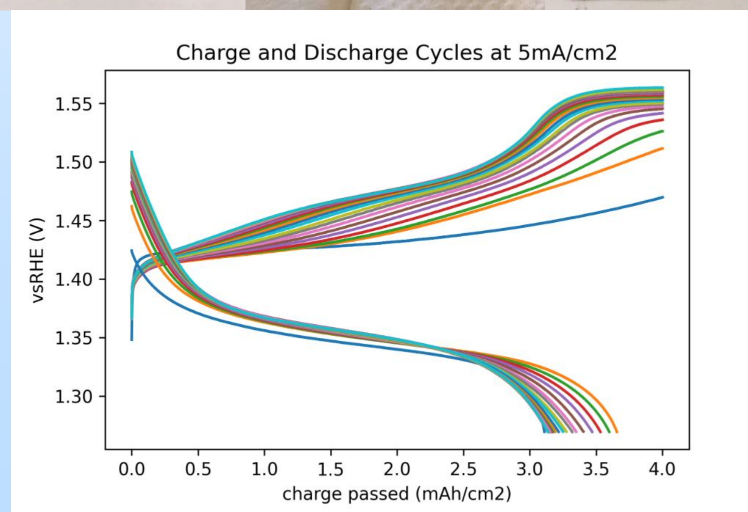
Sample produced at 10 mA cm^{-2} an initially cycled at 5 mA cm^{-2} showed improved stability and significantly improved performance.

<u>Deposition</u>

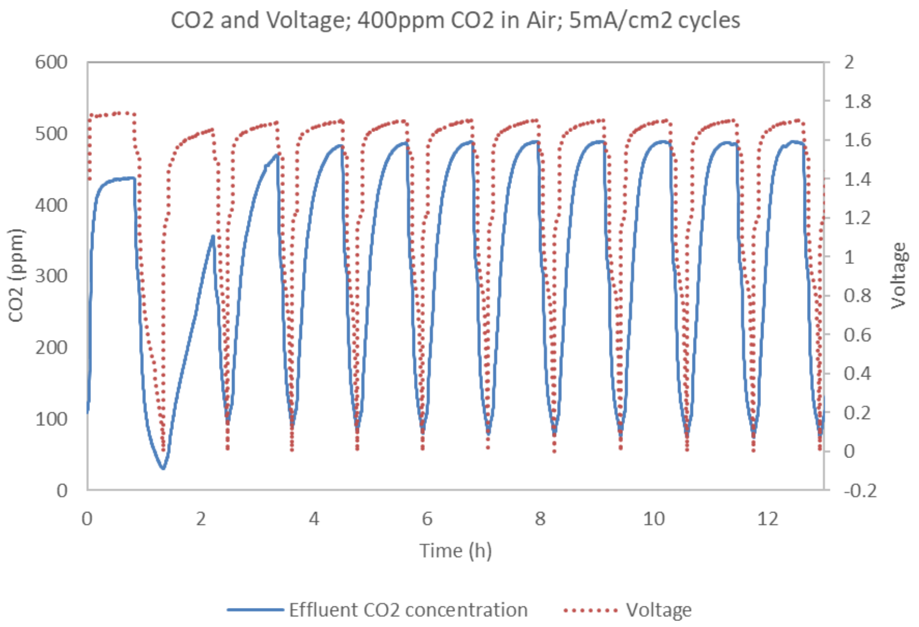
<u>Capacity Cell</u>

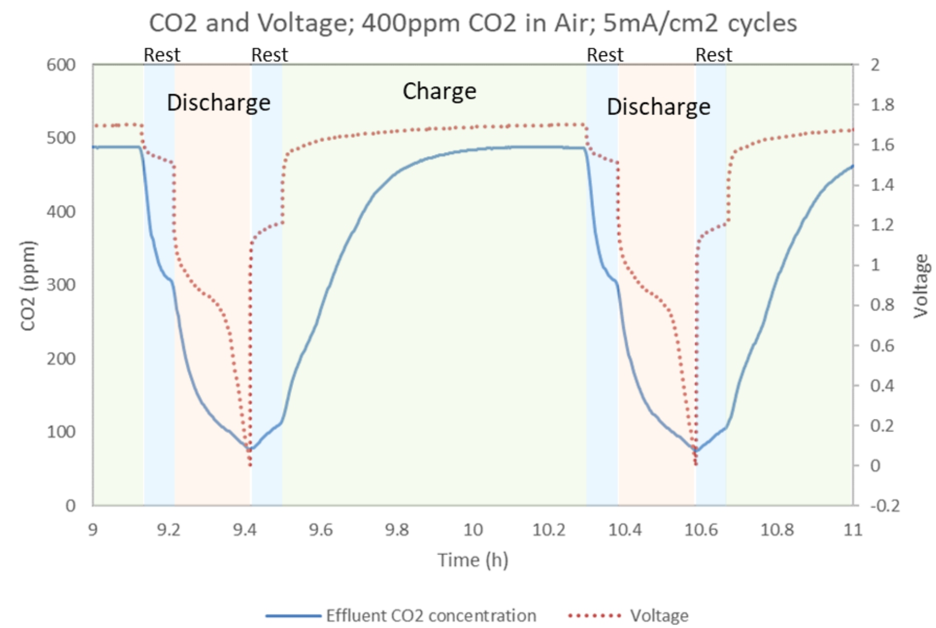


<u>Post Test</u>



Task 4.3 EDCS Testing-Half Cell





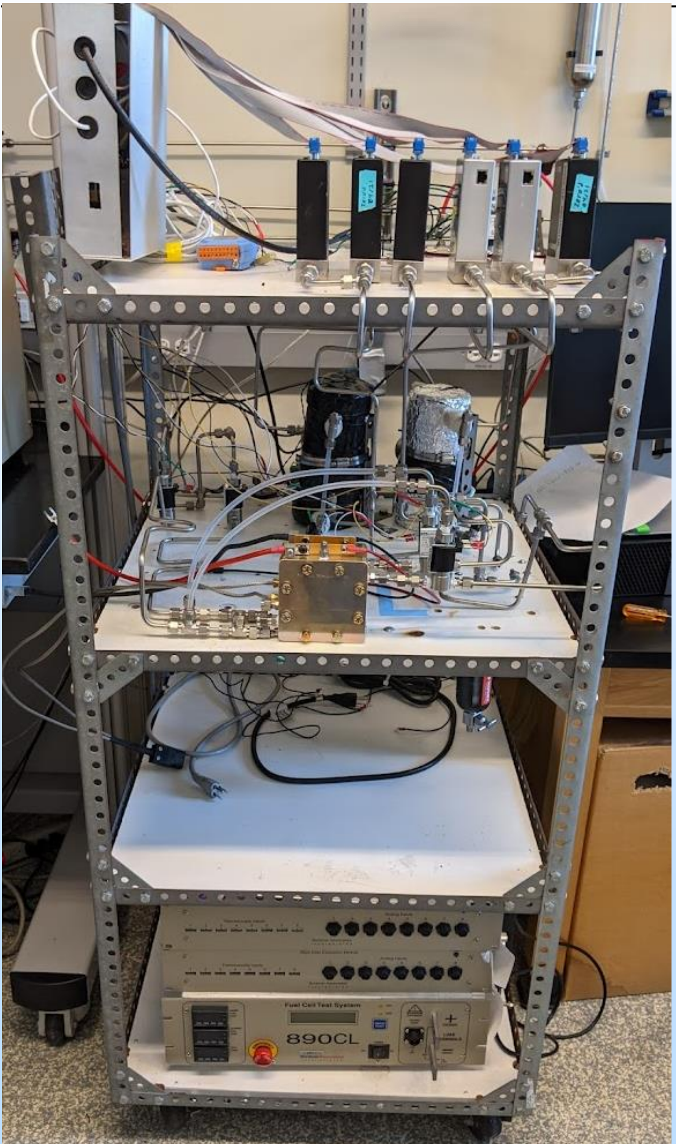
Preliminary Transfer of CO_2 across PAP membrane with a $Ni(OH)_2$ and Pt/H_2 half cells.

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.

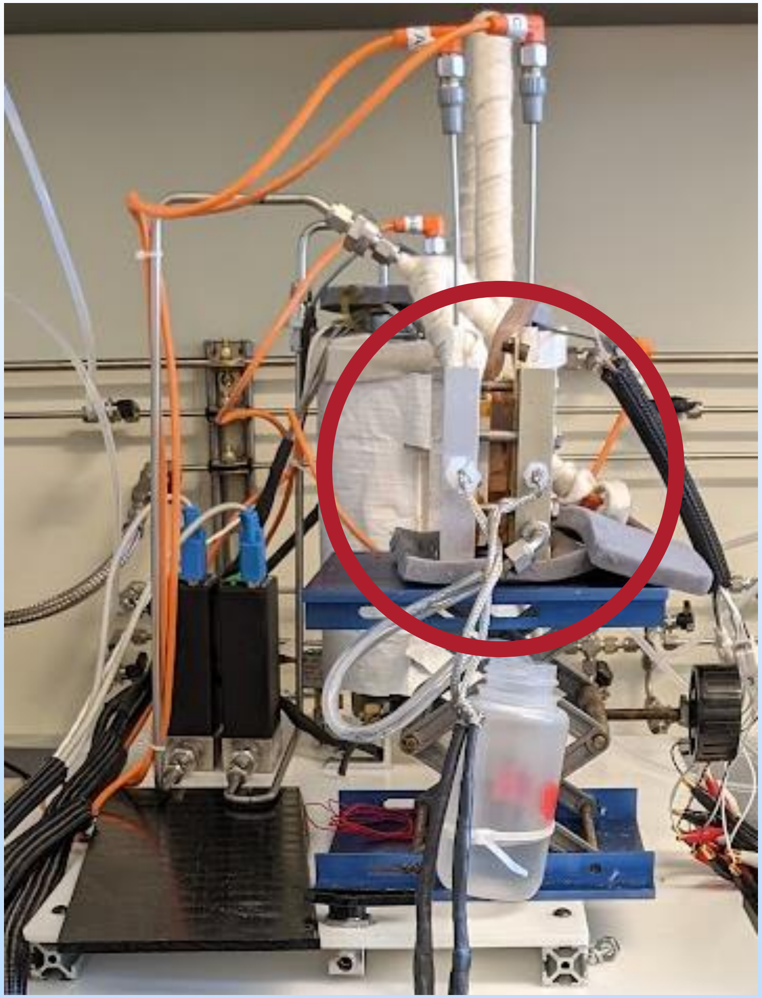
Top Layer - Flow Control

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

Third Layer - Condensate Control

Bottom Layer – Central Control Interface

Task 3 Membrane Test Fixture

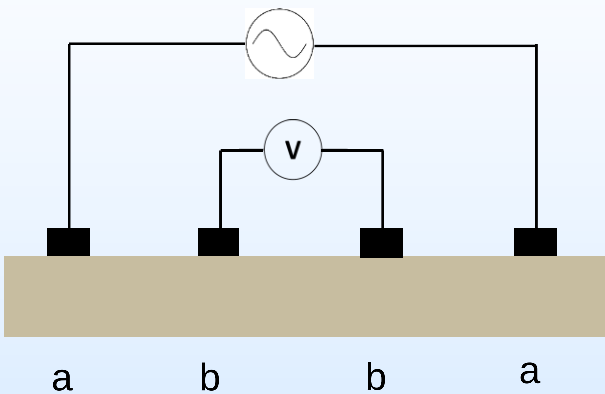


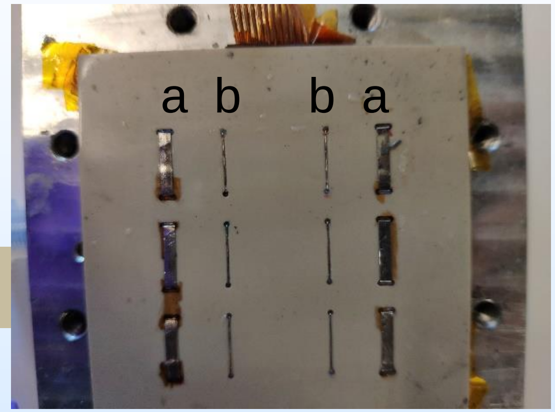
Conductivity is a key characterization parameter. It affects the feasibility and power consumption of the device.

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.

Task 3 Membrane Test Fixture

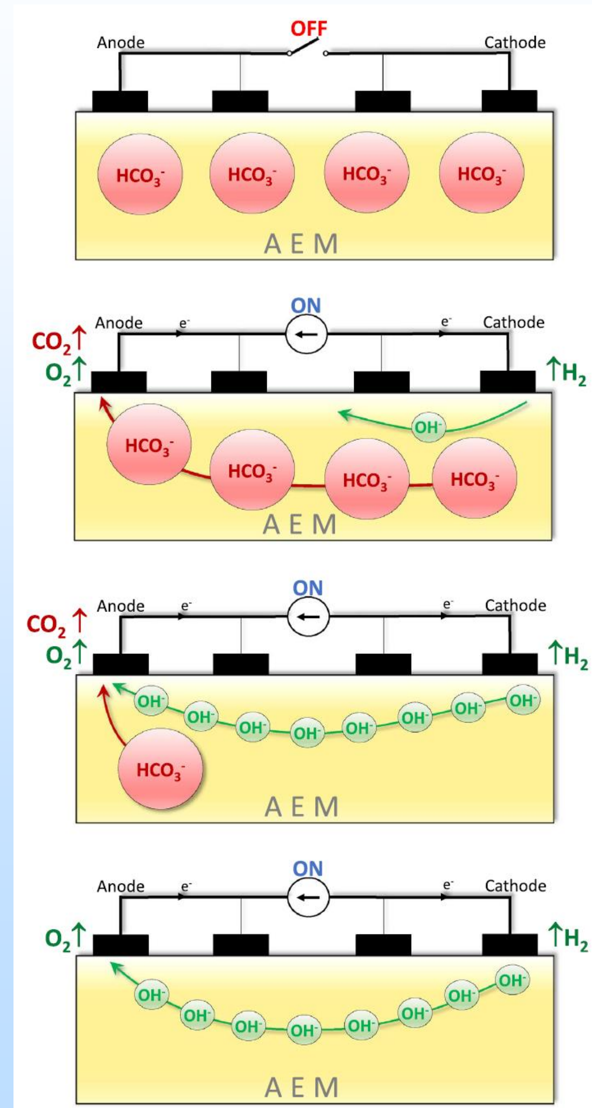




4-electrode measurement eliminates effect from electrode polarization to give true ionic conductivity

$$\kappa = \frac{l_{\mathrm{b}}}{Rw\delta}$$

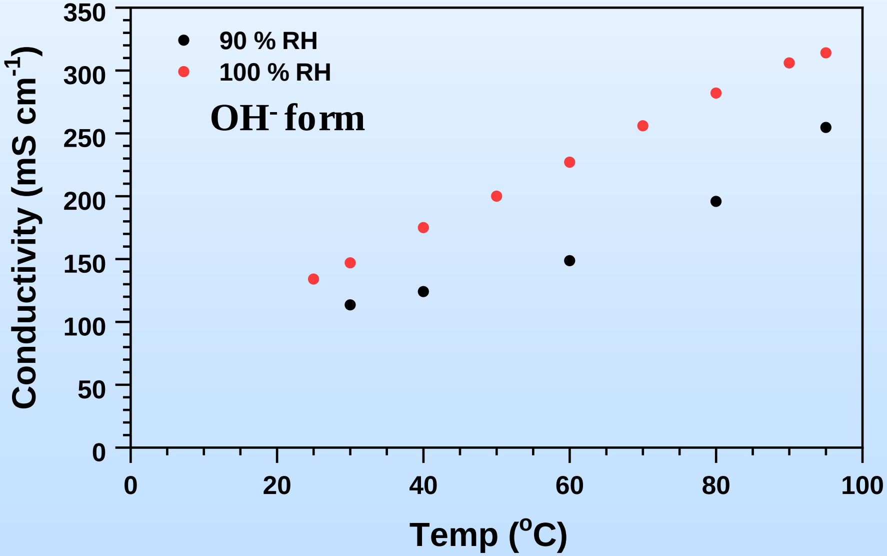
R	resistance
w	width of membrane
δ	thickness of membrane
l_{b}	distance of inner electrodes



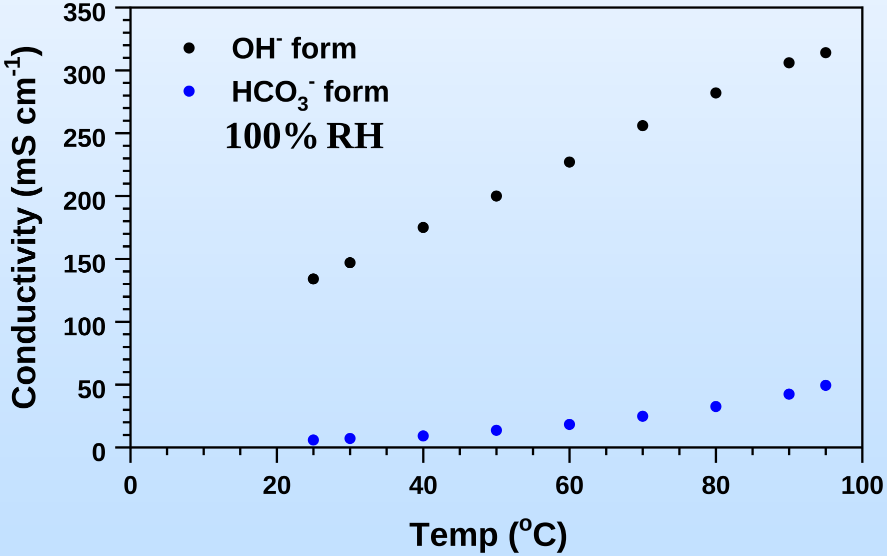
H. Schwan, *Rev. Sci. Instrum.*, 1968, 39, 481
N. Ziv, D. Dekel, *Electrochem. Commun.*, 2018, 88, 109

Task 3.1 Membrane Conductivity

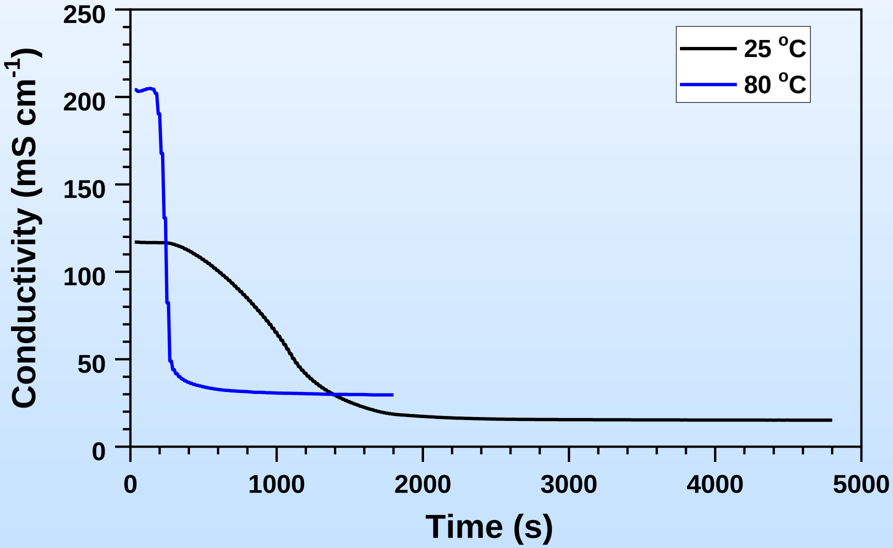
Conductivity shown to be strongly dependent on %RH.



Known difference in conductivity between HCO_3^- and OH^-.



Task 3.2 Carbonation Process



Monitored membrane carbonation from OH^- to HCO_3^- at two different temperatures in CO_2 enriched stream.

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

Plans for future

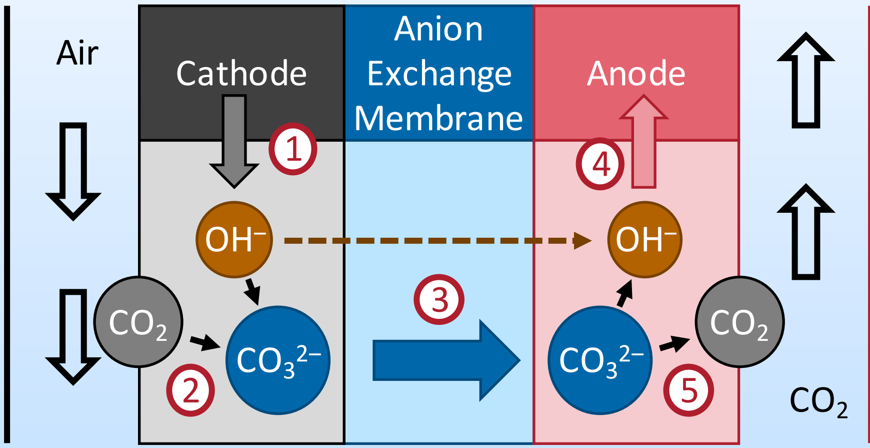
Current Project	After this project
Task 4.3 Full Cell Testing	Optimize Cell Performance
Task 2.3 Structured Membrane Production	Scale up study with stack system
Task 5 Energy evaluation	Capital cost study for commercialization

Summary Slide

Core electrochemical methodology works.

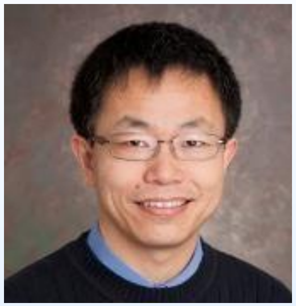
Provides an alternative path to prevailing amine-based systems that require temperature and/or pressure swings.

Potential for both direct air capture and point source.



Appendix

Team



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UNIVERSITY OF DELAWARE

Thank you to our many colleagues whose foundational work made this project possible:

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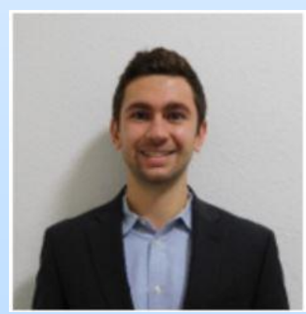
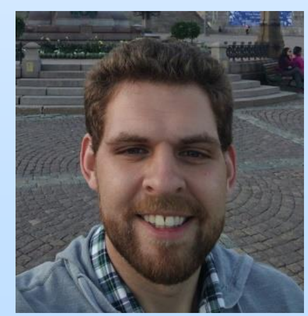
Rohan Razdan
Catherine Weiss
Lin Shi
Junwu Xiao

Thank you to Versogen for supplying PAP the anion exchange membrane and ionomer used for developing this project.



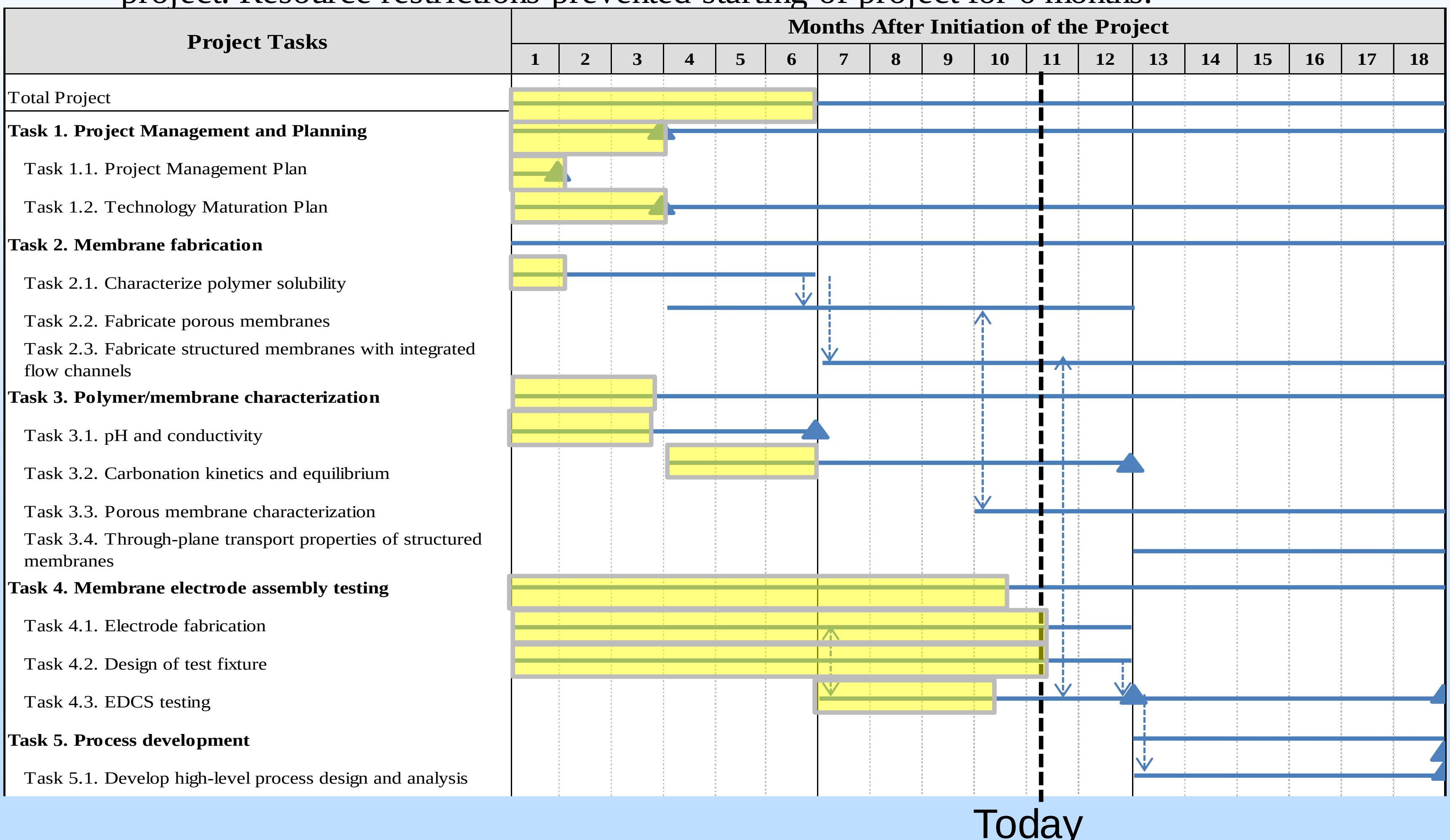
Nick Oliveira



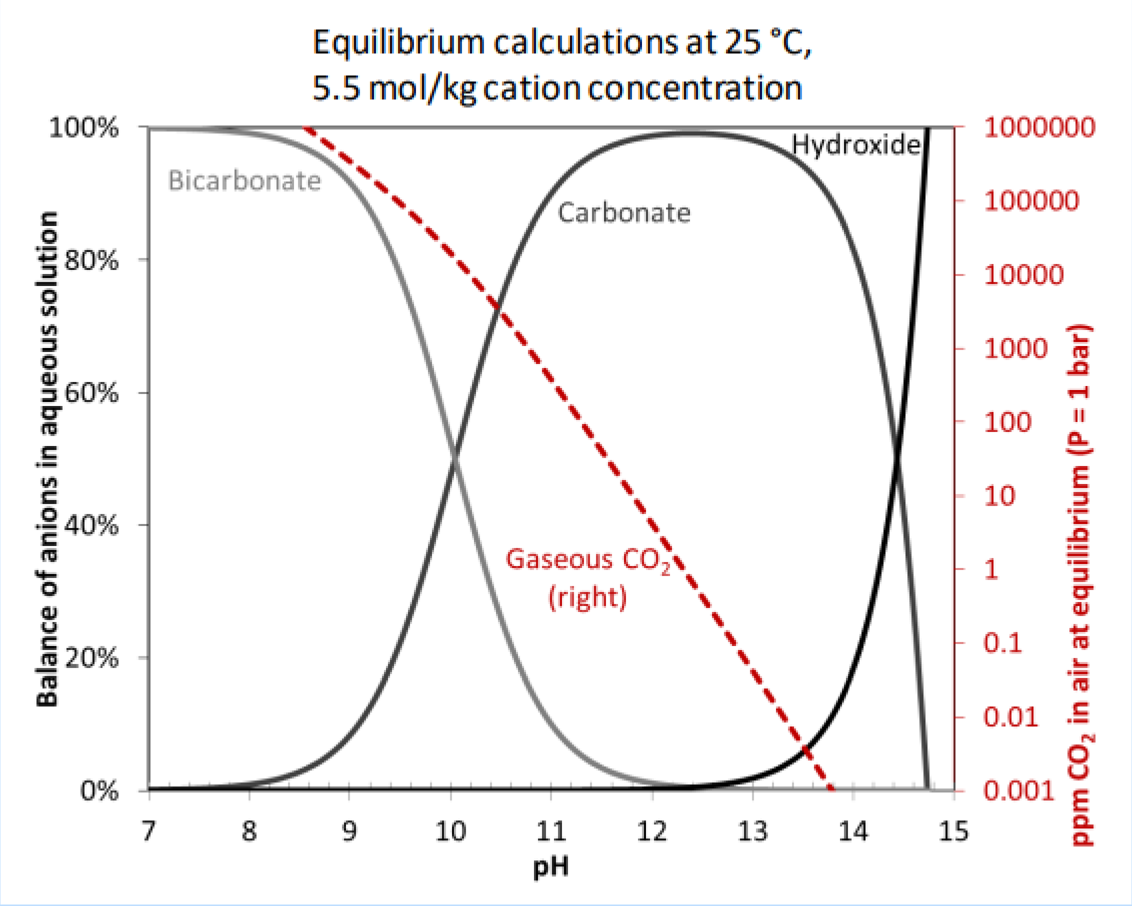
James Buchen

Gantt Chart

- 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.



CO_2 Alkaline Equilibrium



Acid-base equilibria:

$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-}$

$H_2CO_3 + OH^- \rightleftharpoons H_2O + HCO_3^-$

Carbon dioxide hydration:

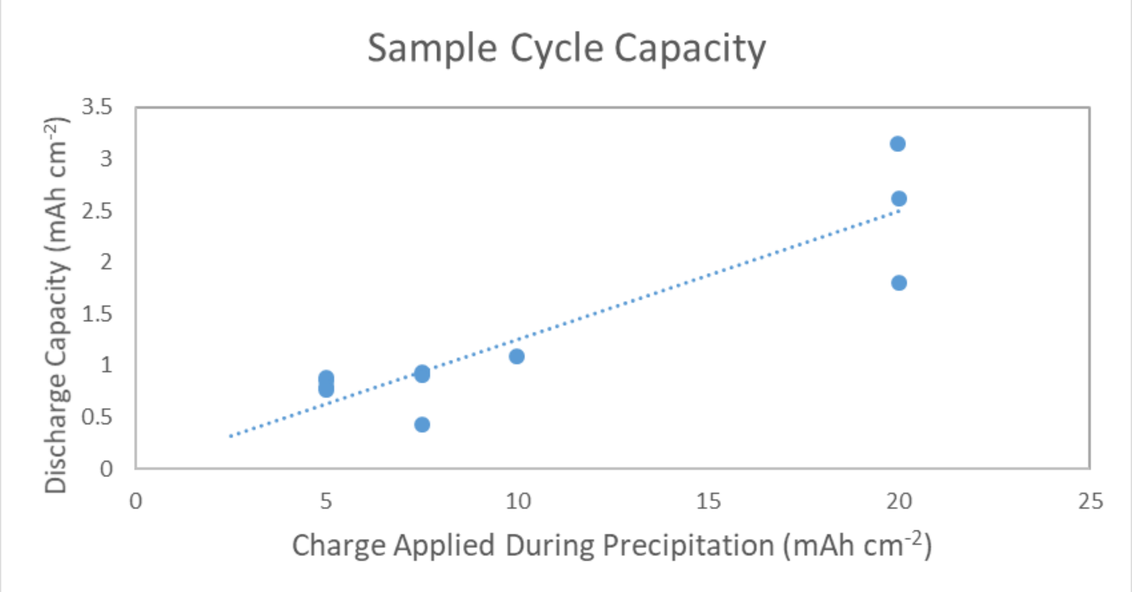
$CO_{2\,(g)} \rightleftharpoons CO_{2\,(aq)}$

$CO_{2\,(aq)} + H_2O \rightleftharpoons H_2CO_3$

$CO_{2\,(aq)} + OH^- \rightleftharpoons HCO_3^-$

Electrode Production Setup

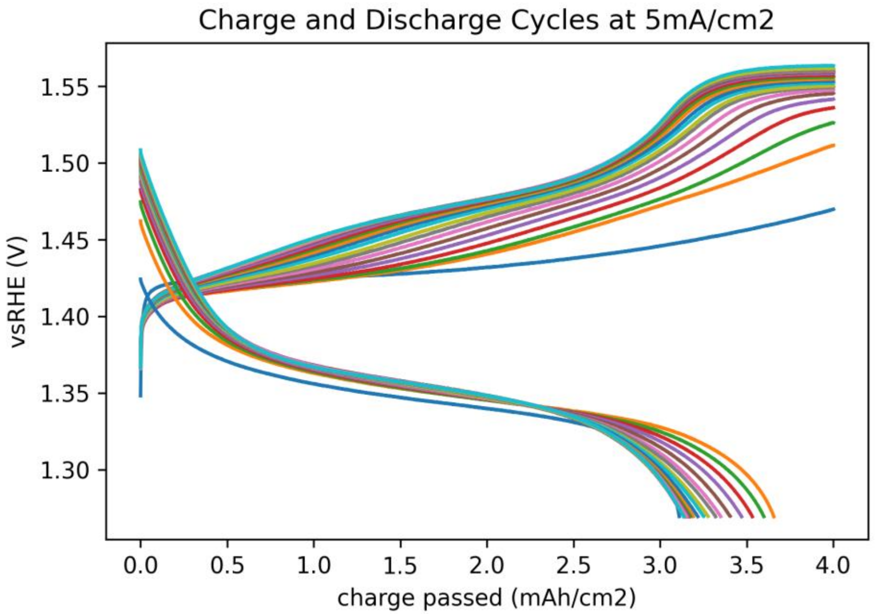
Lower current densities produced more physically stable electrodes. *(Right- Case of lost active material on high current density sample 20mA cm^{-2}. This is not appreciably observed at lower current densities <10mA cm^{-2})*

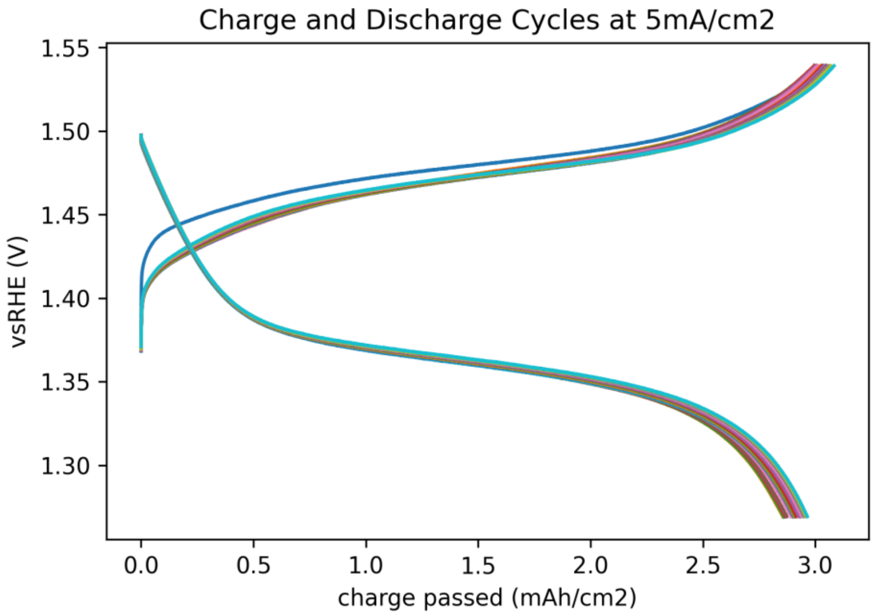


Higher total current applied to electrodes produced higher capacity electrodes.

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