Electrochemically driven carbon dioxide separation

DE-FE0031955

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U.S. Department of Energy

National Energy Technology Laboratory

Carbon Management Project Review Meeting

August 15 - 19, 2022

Project Overview

Funding: $1,050,000 federal + $262,500 cost share

Period of Performance: 10/1/2020 – 3/31/2023

Participants: University of Delaware

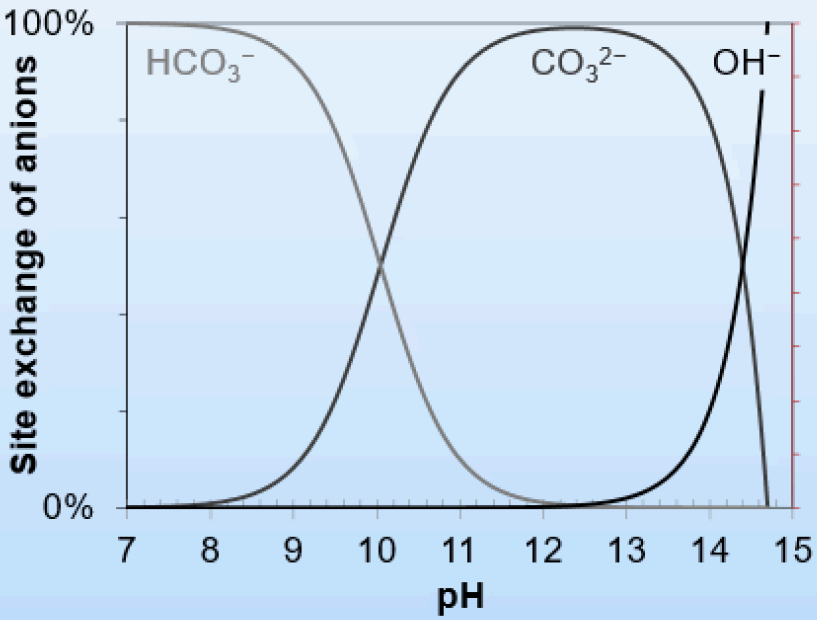
Project Objectives:

- Develop electrochemically-driven CO_2 separator (EDCS) with 155 kg/m^{2}yr air capture at <5.4 GJ/t (1.5 MWh/t)
- Characterize PAP ionomer properties to support future development
- Demonstrate EDCS module with 200 g/day removal and >0.4 CO_2 captured per electron

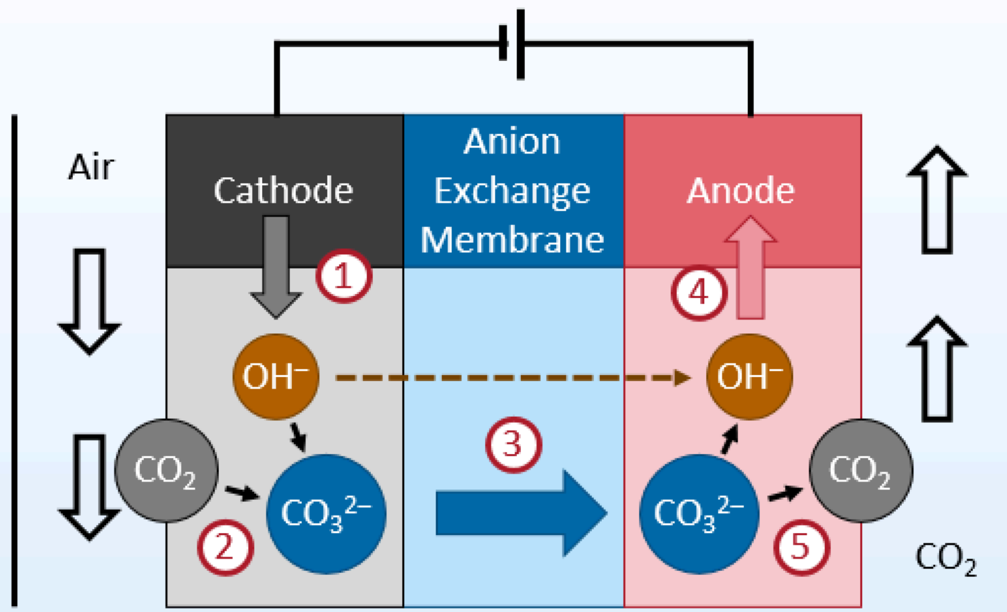
Technology Background

Principles of operation

1. Generate OH^-
2. Scrub CO_2 as CO_3^{2-}
3. Transport CO_3^{2-}
4. Consume OH^-
5. Release CO_2



Electrochemically driven CO_2 separator (EDCS)



Conditions: 0-40 °C, 70-96% RH, 1 atm

Electrochemical OH^- gen./cons.

$$NiOOH + H_2O + e^- \rightleftharpoons Ni(OH)_2 + OH^-$$

Chemical CO_2 capture/release

$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$

$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O$$

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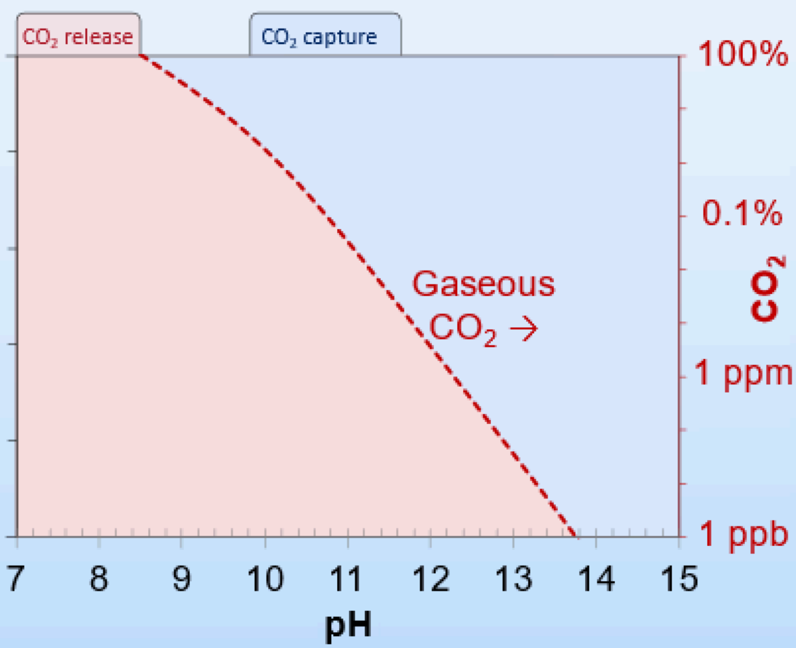
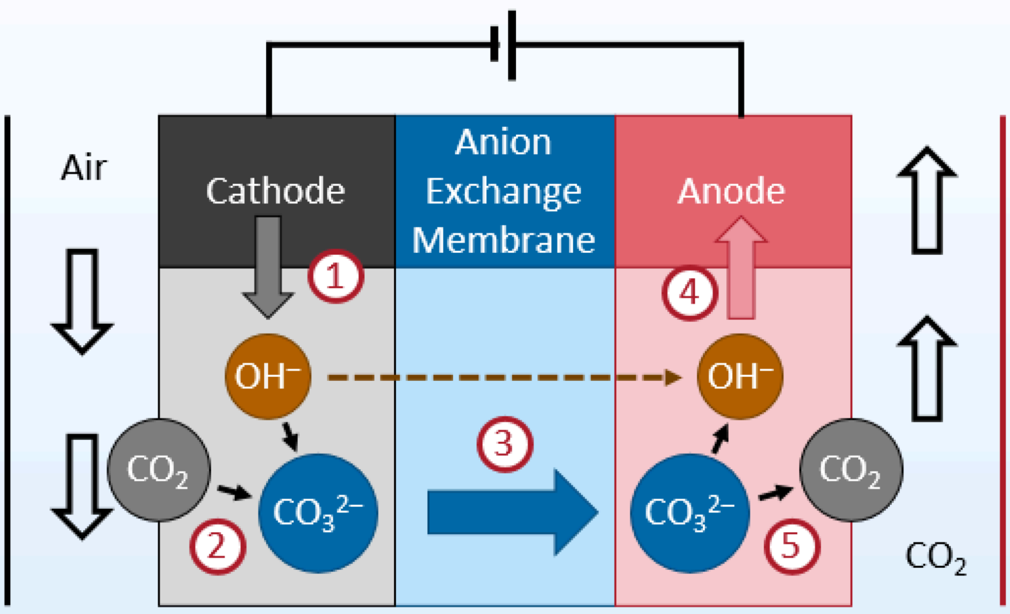


Electrochemically driven CO_2 separator (EDCS)



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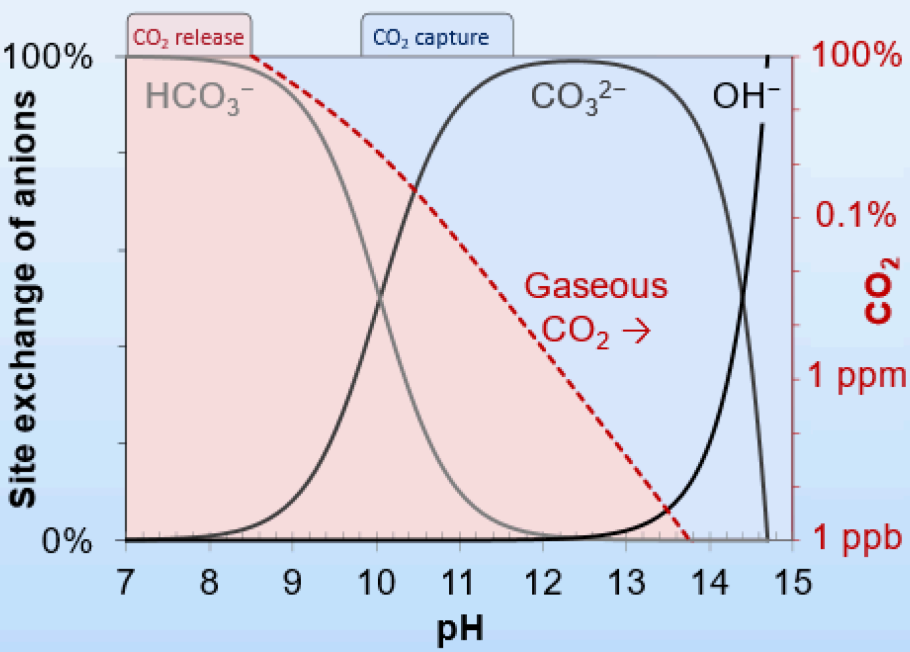
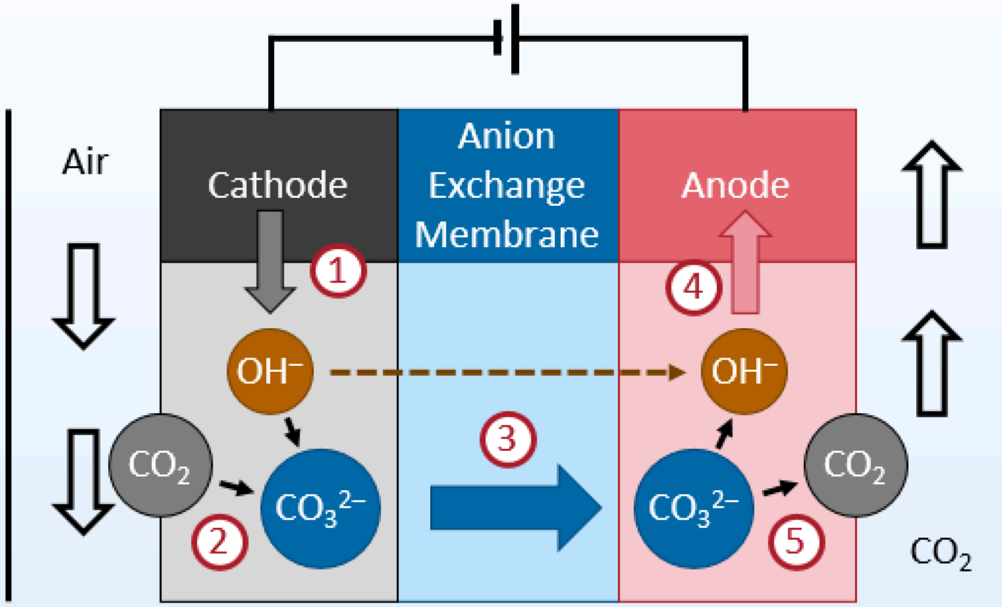


Electrochemically driven CO_2 separator (EDCS)



Conditions: 0-40 °C, 70-96% RH, 1 atm

Electrochemical OH^- gen./cons.

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Chemical CO_2 capture/release

$$\mathrm{CO_2 + OH^- \rightleftharpoons HCO_3^-}$$

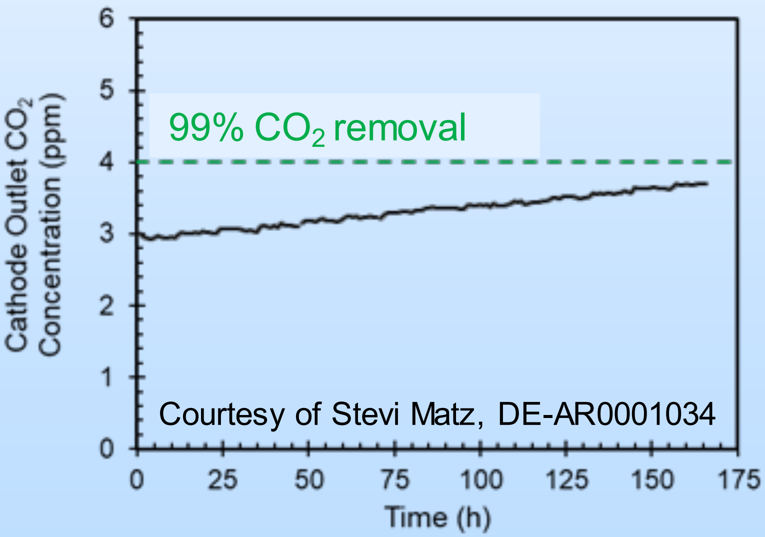
$$\mathrm{HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O}$$

Technology Background

Development prior to project

H_2-EDCS – fuel cell chemistry

400 ppm CO_2 in, 60 °C
500 kg/m^2-yr, 99% removal
35 GJ/t H_2 consumption
(Not optimized for DAC)



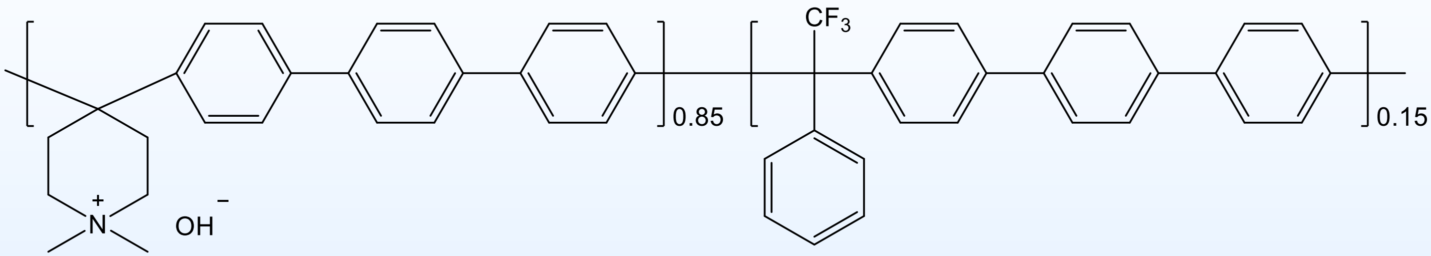
Technoeconomic advantages

- Low energy consumption
  - Target: 5.4 GJ/t
  - Achieved: 3-4 GJ/t
- Continuous operation
- High volumetric productivity (10-100 t/m^3yr)
- Electrically powered

Technoeconomic challenges

- Electrode cycling
- Side reaction (O_2 evolution)
  - O_2 contamination
  - Electrode unbalancing
- Unknown capital cost

Technology Background



Poly(aryl piperidinium) (PAP)

- Anion exchange membrane and ionomer
- Good conductivity for OH^-, CO_3^{2-}, and HCO_3^-
- High water content and water permeability
- Chemically and mechanically robust
- Originally developed for fuel cells and electrolyzers

Wang, J.; Yan, Y. et al. *Nat. Energy* **2019**, *4* (5), 392–398. https://doi.org/10.1038/s41560-019-0372-8.

Technical Approach/Project Scope

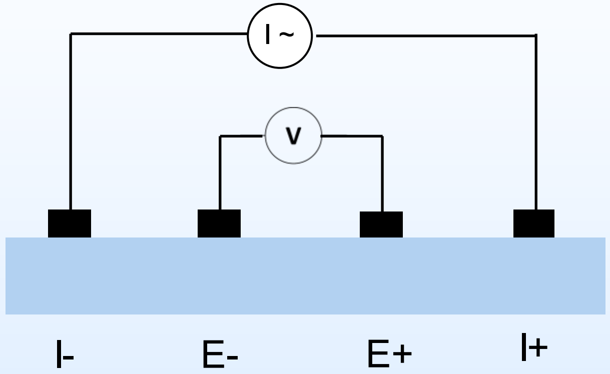
1. **Project management and planning**
2. **Membrane fabrication –** Make flow-through PAP porous absorbers
3. **Polymer/membrane characterization –** Characterize PAP polymer properties
4. **Membrane electrode assembly testing –** Test EDCS performance in cells & stacks
5. **Process development –** High-level process design and analysis

Mile-stone	Sub-task	Milestone Description	Planned Completion	Status
4	3.1	**Membrane anion transport:** Establish operating window where conductivity is ≥ 5 mS/cm.	3/31/2021	Complete
5	3.2	**Membrane CO_2 capture and release:** Establish operating window where first-order rate constant is ≥1000 s^{-1} and where thick-film mass transfer coefficient is ≥1 mm/s.	9/30/2022	In progress
6	4.3	**Initial cell testing and performance:** Demonstrate basic level of performance: ≤7.2 GJ/t (2 MWh/t_{CO2}), 40 kg/m^2yr CO_2 production (25 cm^2)	9/30/2021	Complete
7	4.3	**Final cell performance:** Characterize wide range of operating parameters. Final targets: ≤5.4 GJ/t (1.5 MWh/t_{CO2}), 155 kg/m^2yr CO_2 production (25 cm^2)	12/31/2022	In progress
8	4.3	**Initial EDCS stack performance:** Demonstrate an EDCS module with 100 g/day CO_2 capture from air at 420 ppm CO_2 with hydrogen consumption of <1.5 H_2 per CO_2 (9.8 GJ/t) at ≥50% capture fraction and 30 °C maximum temperature. Maintain performance for 50 hr.	6/30/2022	In progress
9	4.3	**Final EDCS stack performance:** Demonstrate an EDCS module with 200 g/day CO_2 capture from air at 420 ppm CO_2 with hydrogen consumption of <1.25 H_2 per CO_2 (8.1 GJ/t) at ≥60% capture fraction and 30 °C maximum temperature. Maintain performance for 200 hr.	12/31/2022	Future
10	5.1	**Process flowsheet:** Complete flowsheet showing high-level process design and calculate mass and energy flows	3/31/2023	Future

Success criteria:
- Characterize PAP properties to enable modeling and analysis
- Demonstrate technical feasibility at moderate performance level

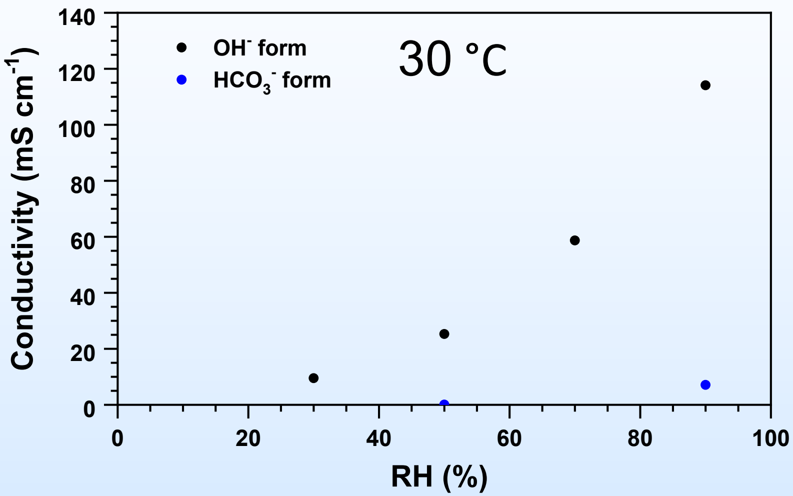
Progress and Current Status of Project

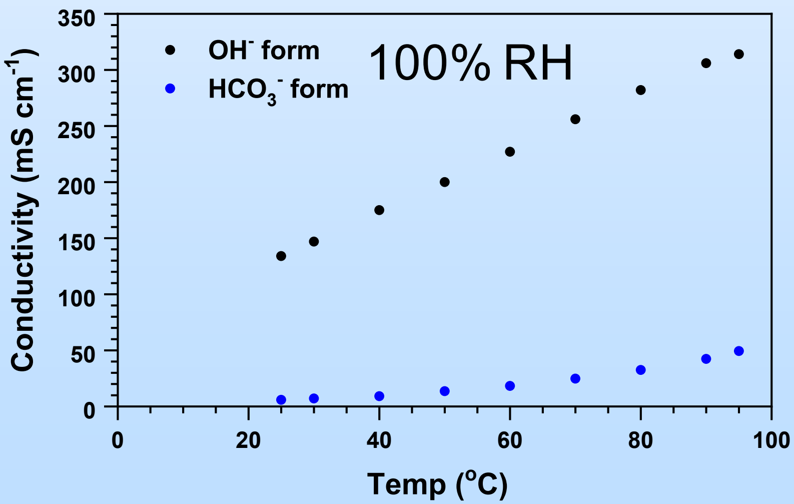
PAP Anion Conductivity



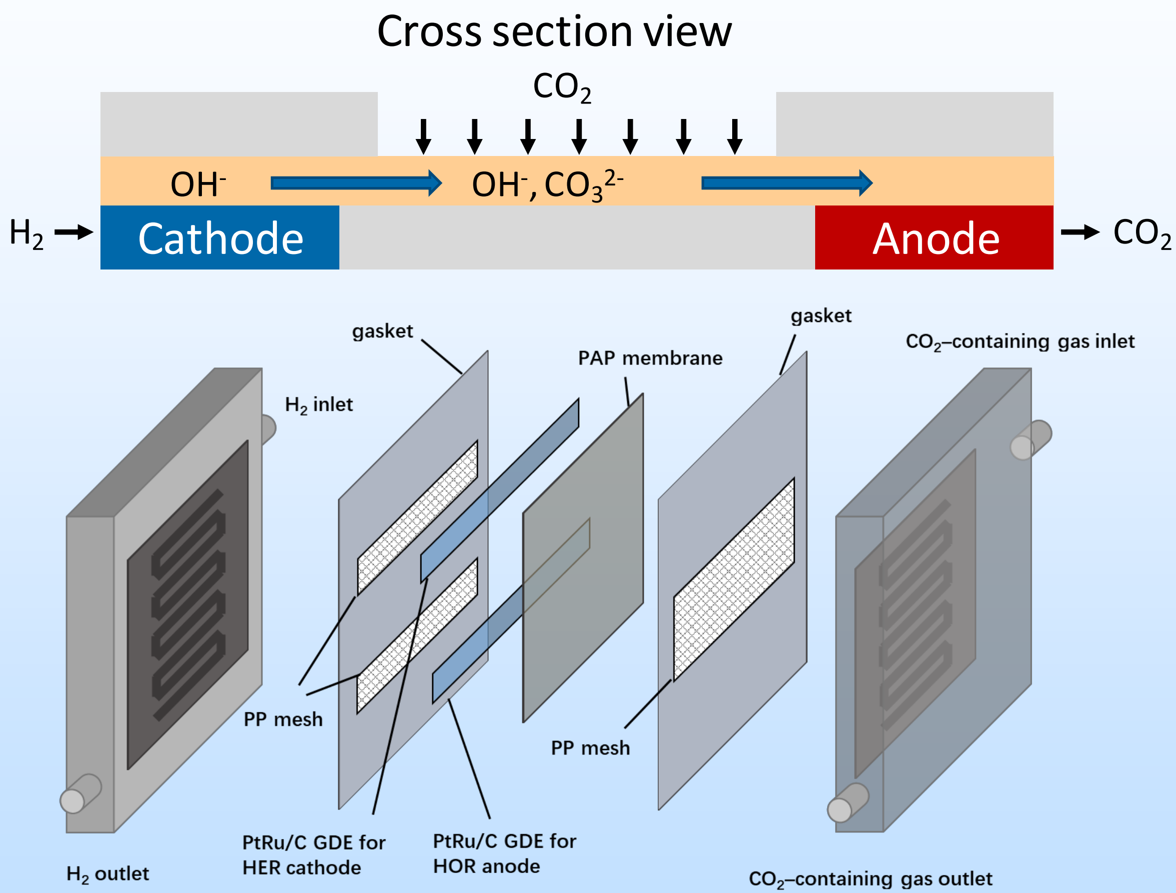
4-electrode in-plane conductivity measurement

- Control T, RH
- Electrochemically generate OH^- with DC current
- Chemically convert to HCO_3^- with 10% CO_2



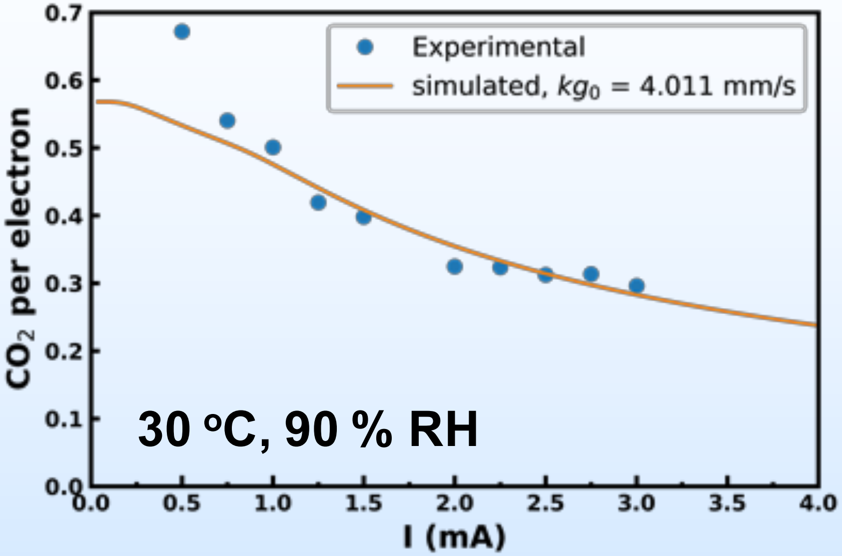


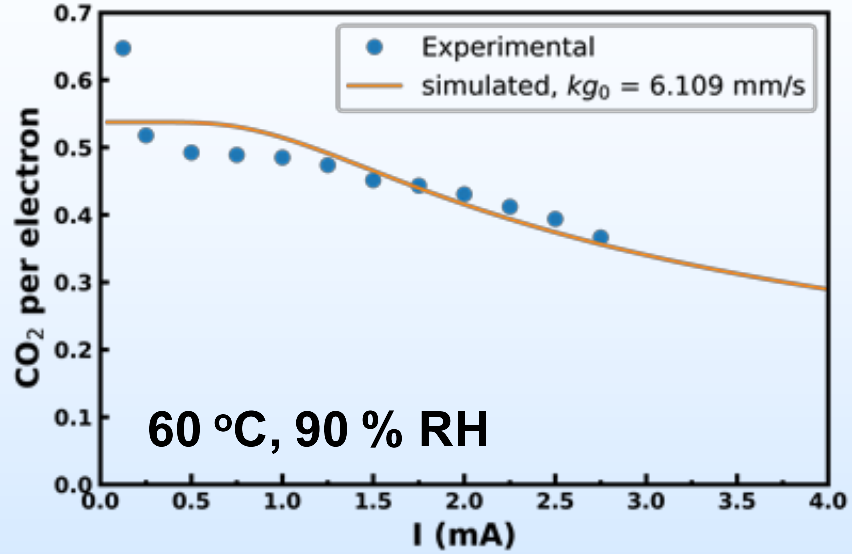
PAP Carbonation Kinetics

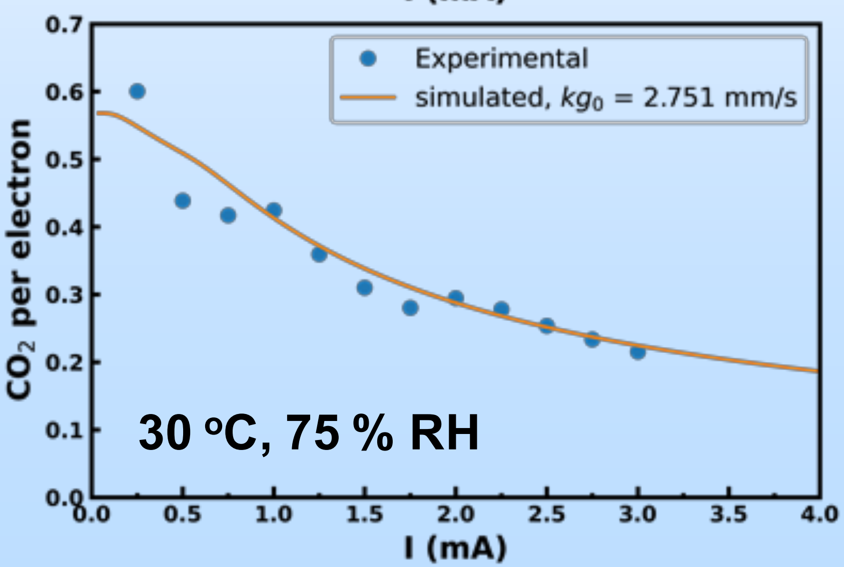


Control: T, RH, p_{CO2}, OH^- generation rate (current)
Measure: CO_2 released at anode (equal to CO_2 captured)
Analyze: 1-D model with thick-film reaction-diffusion with constant k_{g0} (mm/s)

PAP Carbonation Kinetics





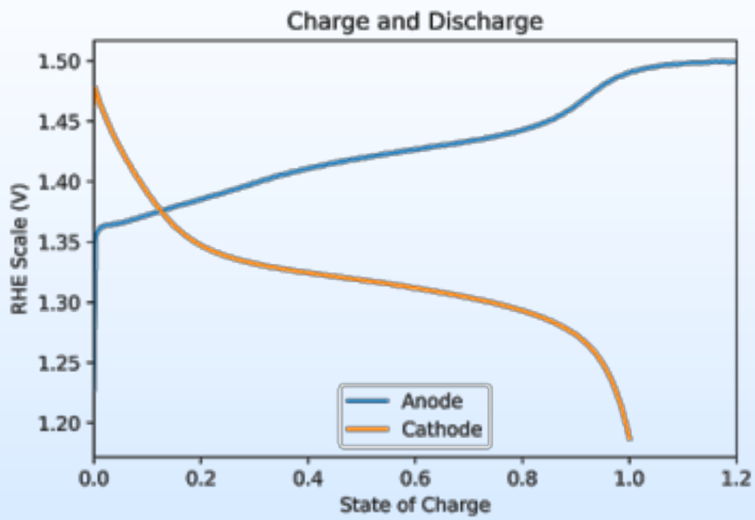


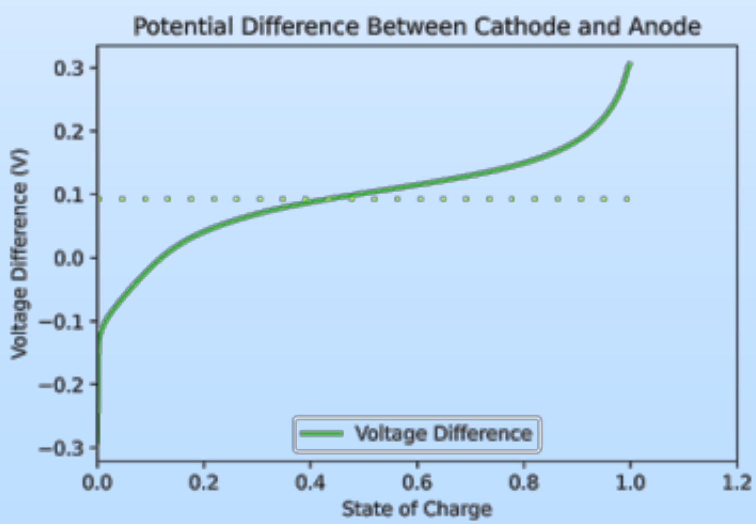
T (°C)	RH%	k_{g0} (mm s^{-1})
30	75	2.75
30	90	4.01
45	90	4.93
60	90	6.11

$$k_{g0} = H_S^{cc}\sqrt{k_2 c_0 D_{CO_2}}$$

H_S^{cc}: Henry's law solubility constant
k_2: Rate constant for $CO_2 + OH^-$
c_0: Membrane cation concentration
D_{CO_2}: Diffusion coefficient of dissolved CO_2

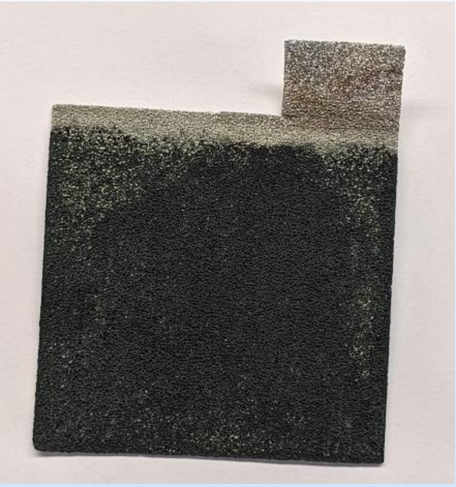
$Ni(OH)_2$ Electrodes





Electrodeposition

Nickel foam → $Ni(OH)_2$ electrode

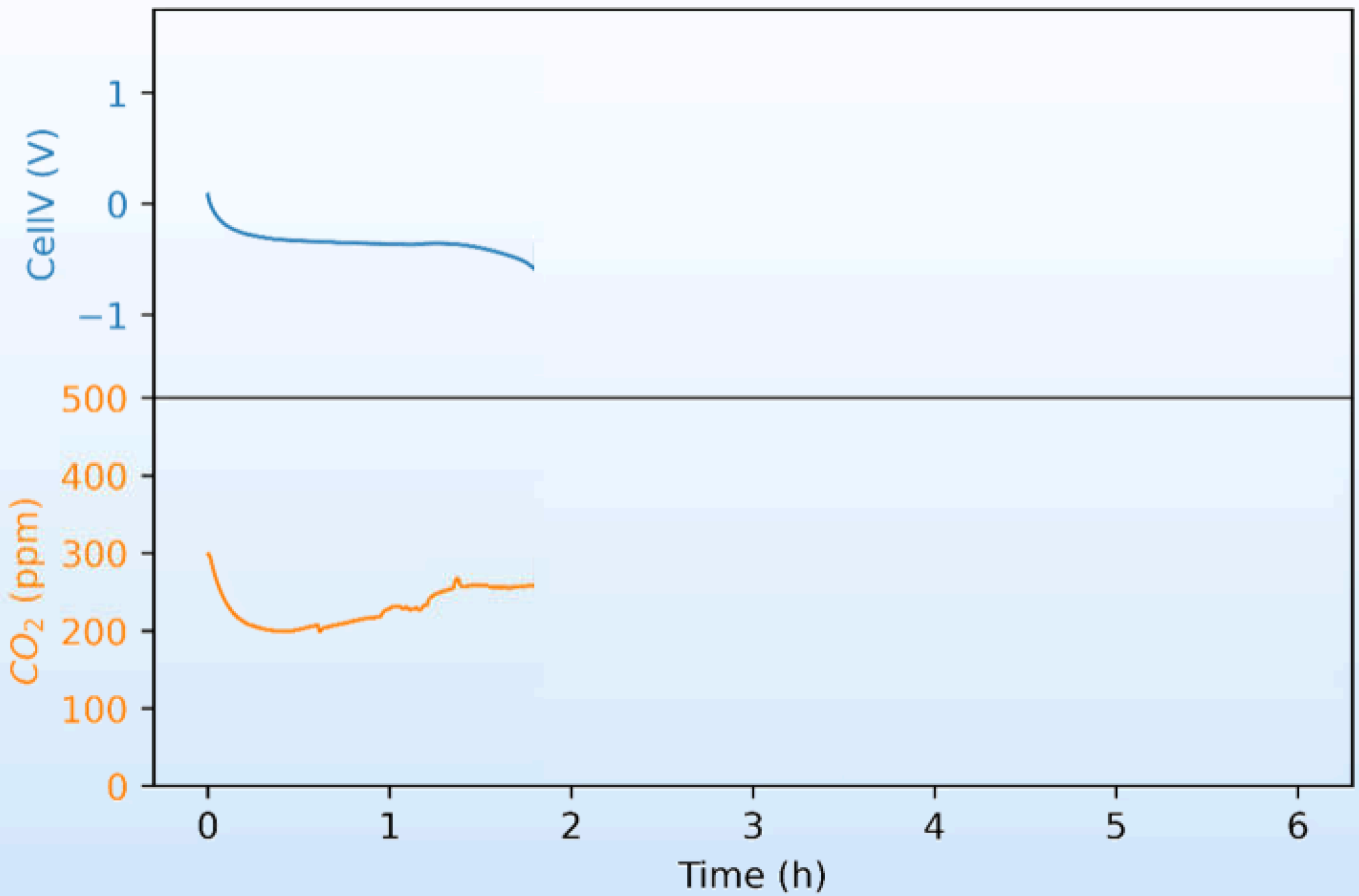


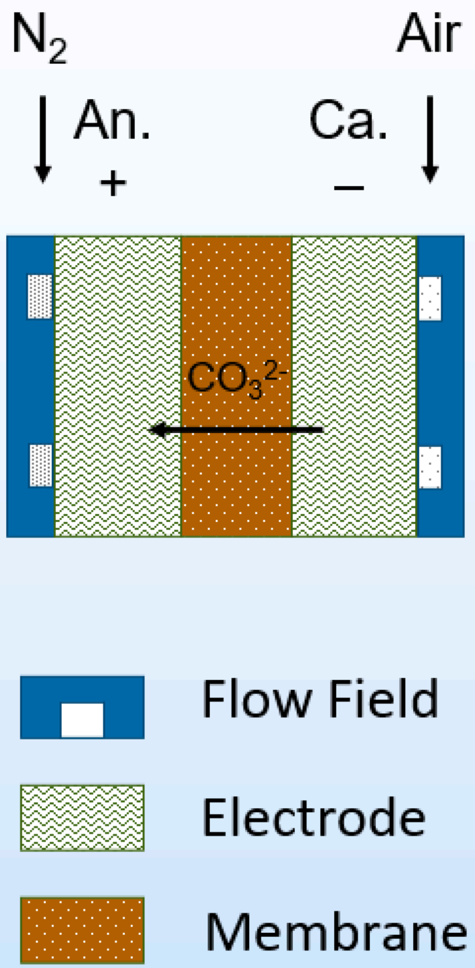
Pre-cycling results show 0.09 V average voltage from electrodes

$Ni(OH)_2$: 0.09 V at 2 e^-:CO_2 = 0.4 GJ/t
H_2-O_2: ~0.40 V at 2 e^-:CO_2 = 1.8 GJ/t

EDCS voltage = Electrode voltage + Ohmic loss + pH gradient voltage

Typical EDCS cell behavior





2 mA/cm², 25 cm² cell, 30 °C, 96% RH
Cathode: 1 SLPM air (400 ppm CO_2)
Anode: 1 SLPM N_2 (sweep gas)

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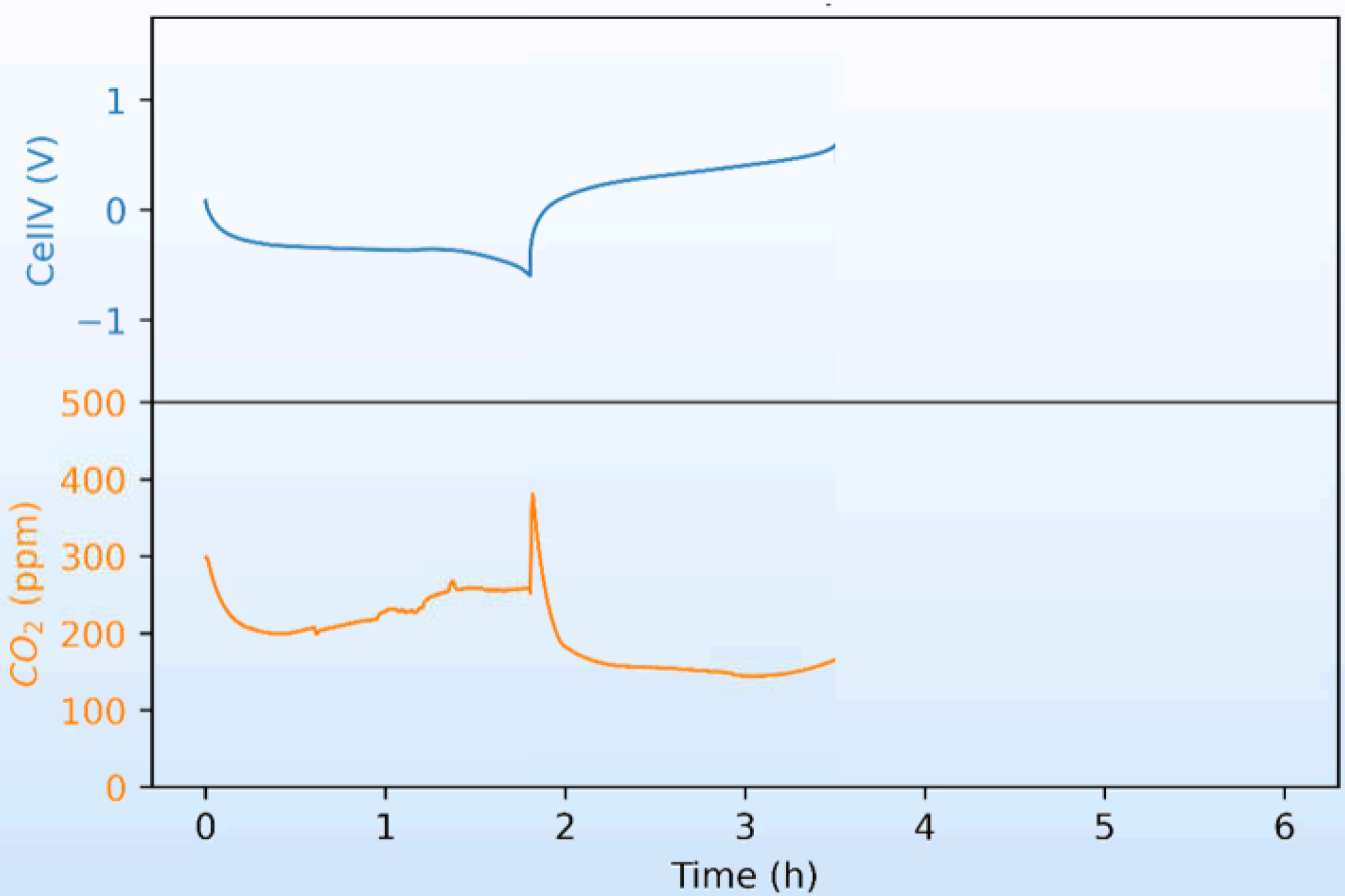

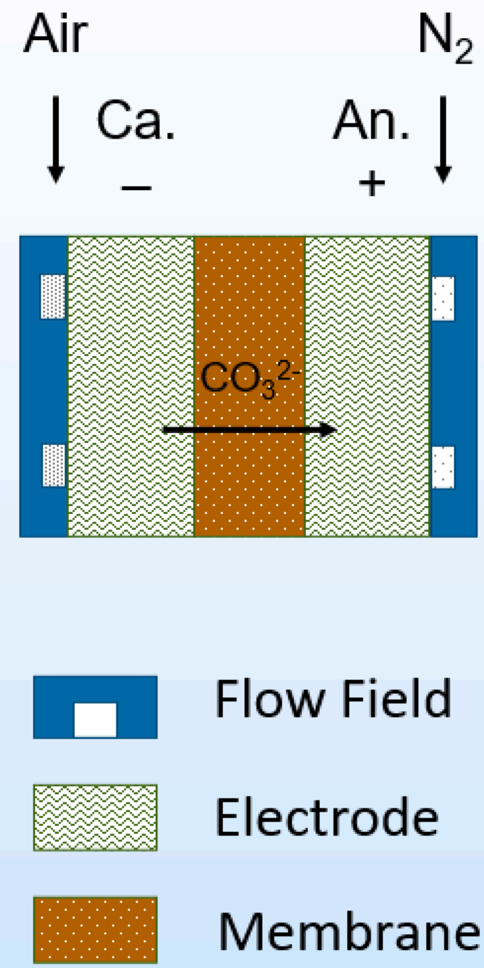

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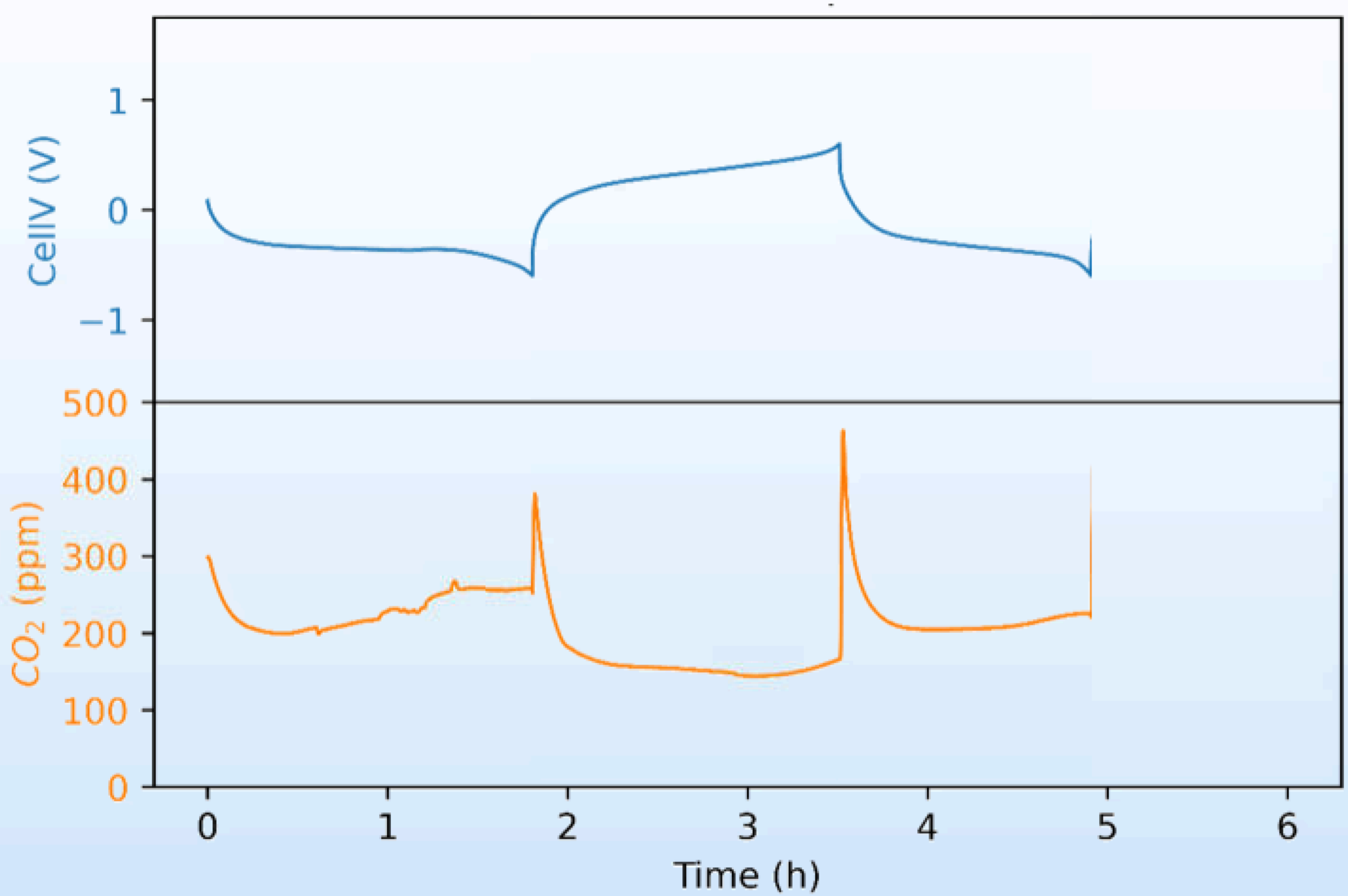

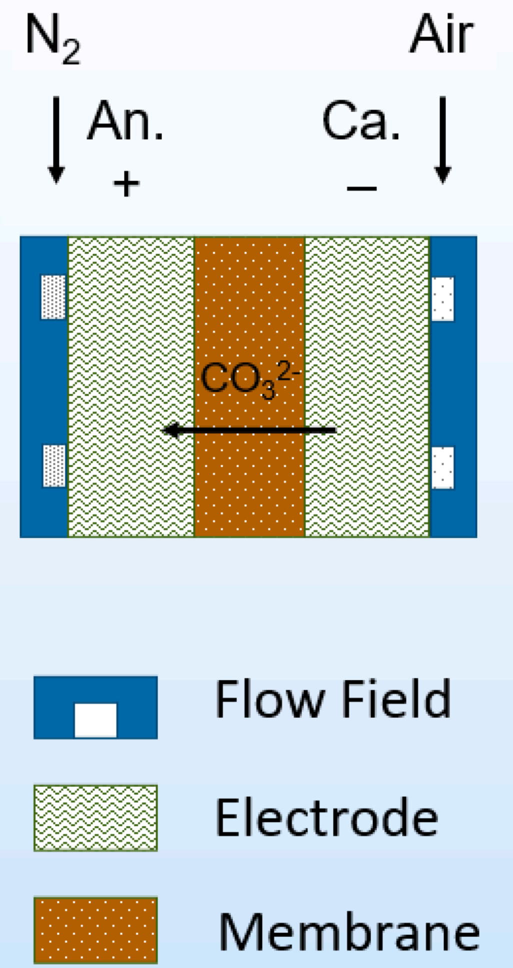

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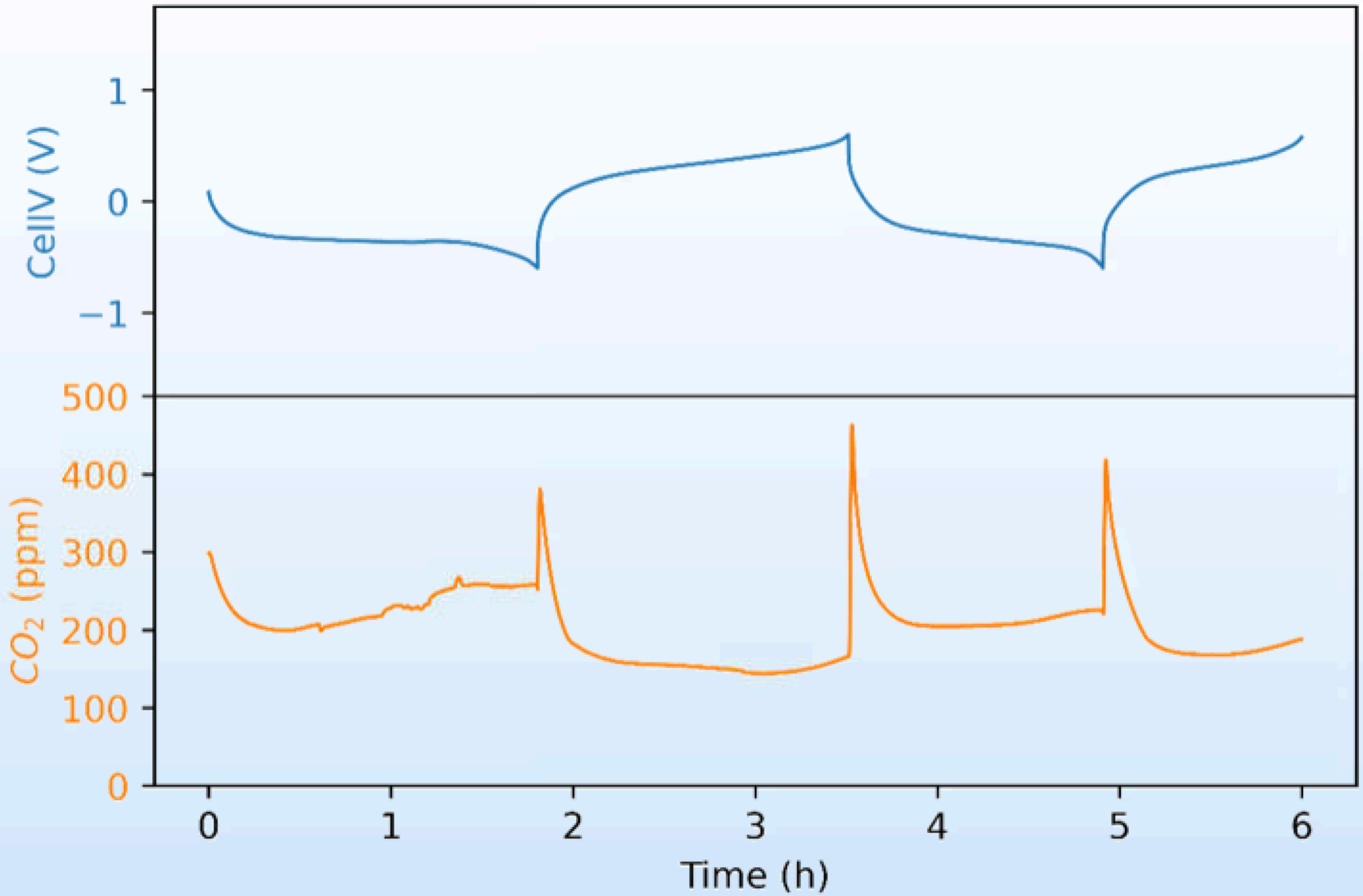

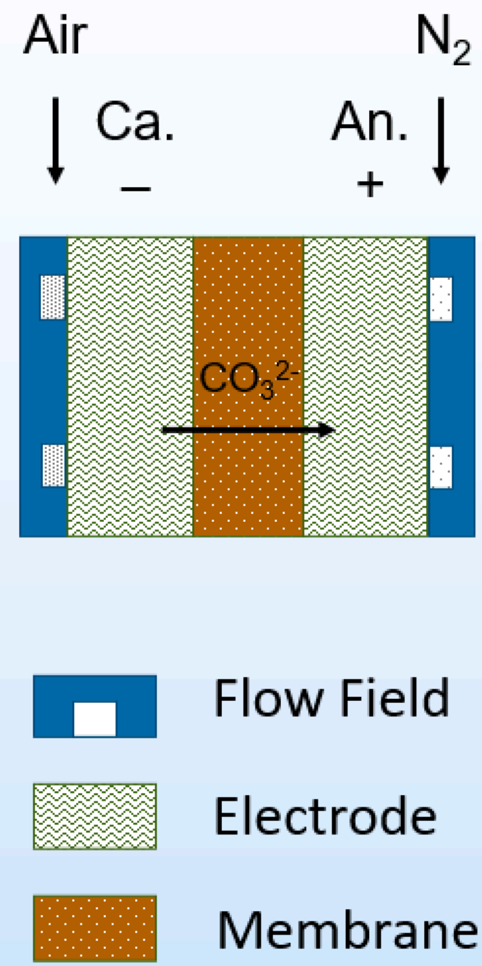

2 mA/cm^2, 25 cm^2 cell, 30 °C, 96% RH
Cathode: 1 SLPM air (400 ppm CO_2)
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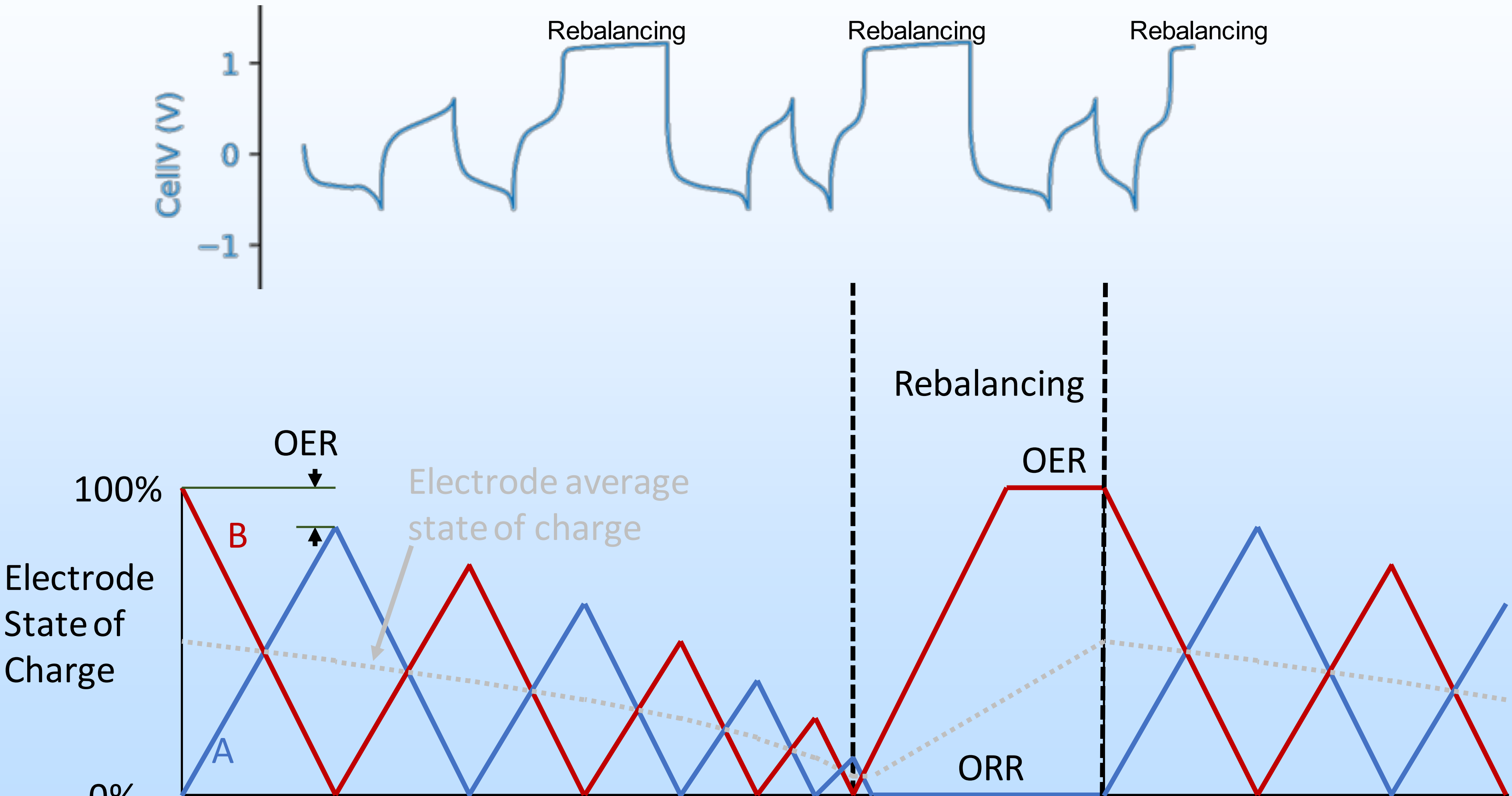
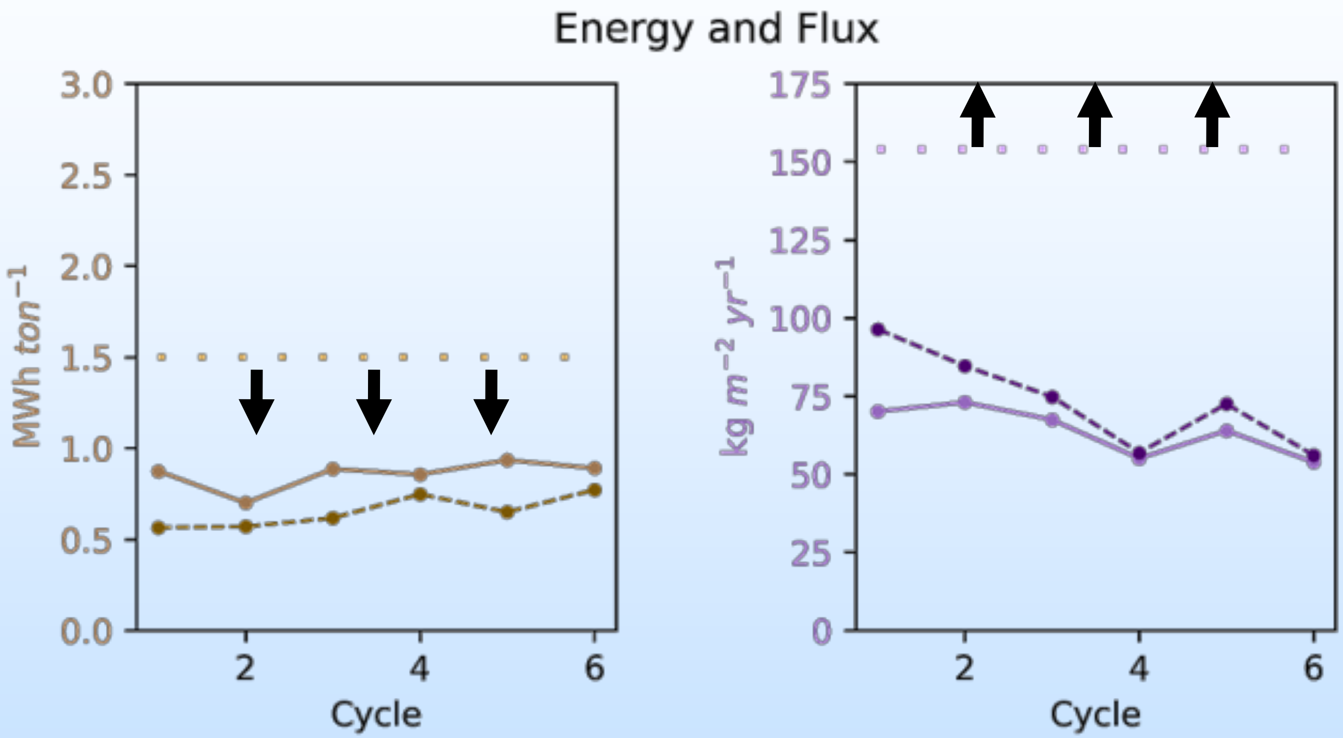
Electrode rebalancing



OER: Oxygen evolution reaction   ORR: Oxygen reduction reaction

EDCS Cell Performance



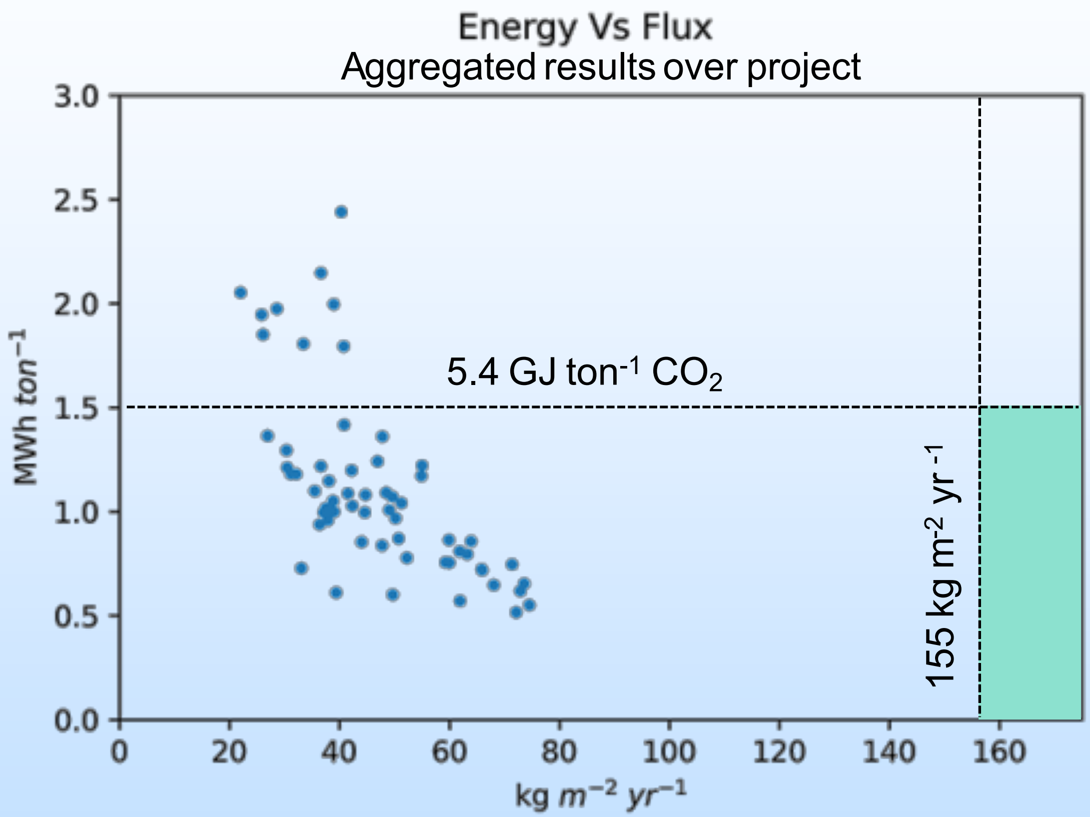
Target below 1.5 MWh · ton^{-1}
(Operating Expenditures)
Exceeding Goals

Target above 155 kg · m^{-2} · yr^{-1}
(Capital Expenditures)
Need to Improve

$$CycleEnergy\left[\frac{MWh}{ton_{co_2}}\right] = \frac{I\left|\int V(t)dt\right|}{\int j(t)dt}$$

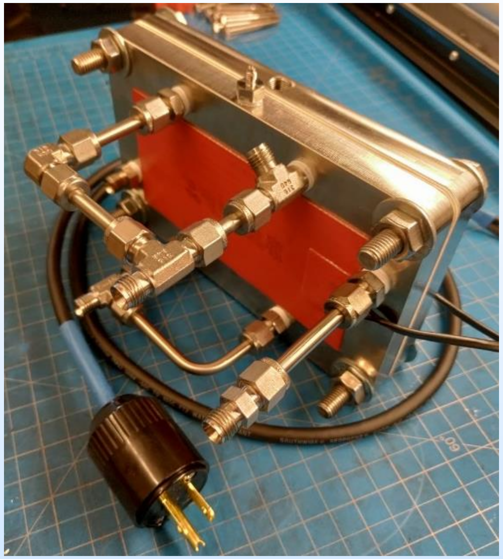
$$Flux\left[\frac{kg}{m^2yr}\right] = j = \frac{\Delta c_{CO_2}Q}{A}$$

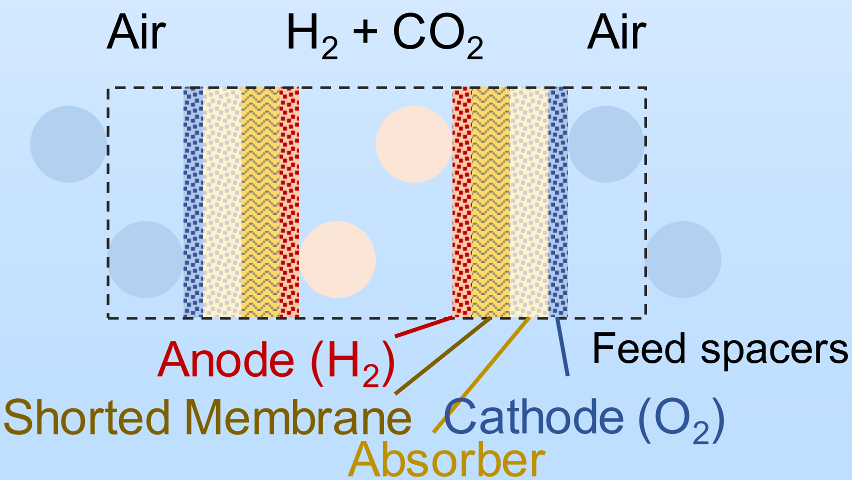
EDCS Cell Performance



Need to improve CO_2 flux

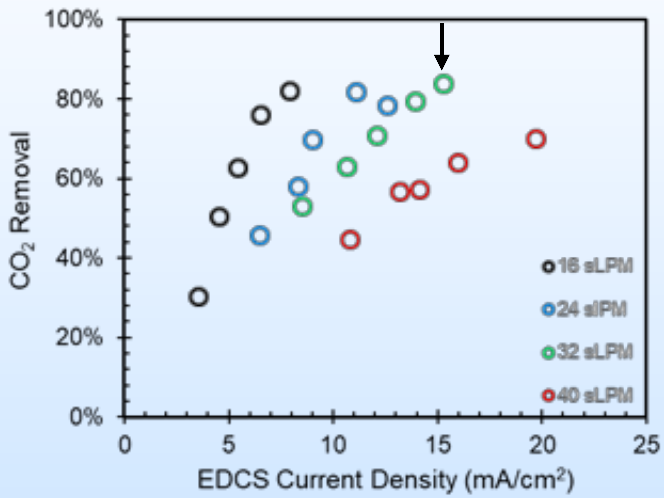
EDCS Module (H_2 powered)

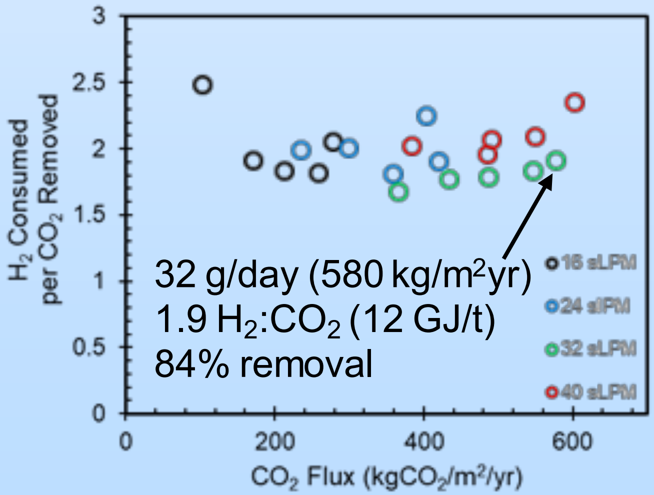




(In coordination with award DE-AR0001034)

2 cell stack, 200 cm^2 total, 30 °C





Plans for future testing

- Improve $Ni(OH)_2$ EDCS flux
  - Add absorber interlayer (already demonstrated in H_2-EDCS)
  - Increase ionomer-gas contact area (smaller pores)
  - Tune membrane ionic resistance
- Optimize H_2-EDCS module performance
  - Tune membrane ionic resistance
  - Add hydrogen diffusion barrier to improve control of current density
  - Scale up to 16 cells
- Continue to characterize key properties of PAP
  - Make thin-film kinetic measurements (separate kinetics from diffusion)
  - Characterize thermodynamic equilibrium
  - Evaluate kinetics of CO_3^{2-} conversion to HCO_3^- (reduce energy use)

Plans for future development/commercialization

- New EDCS stack, optimized for DAC
  - Lower air pressure drop
  - Cheaper construction

- Bench-scale integrated system demonstration
  - Evaluate balance of plant
  - Gather data for technoeconomic analysis

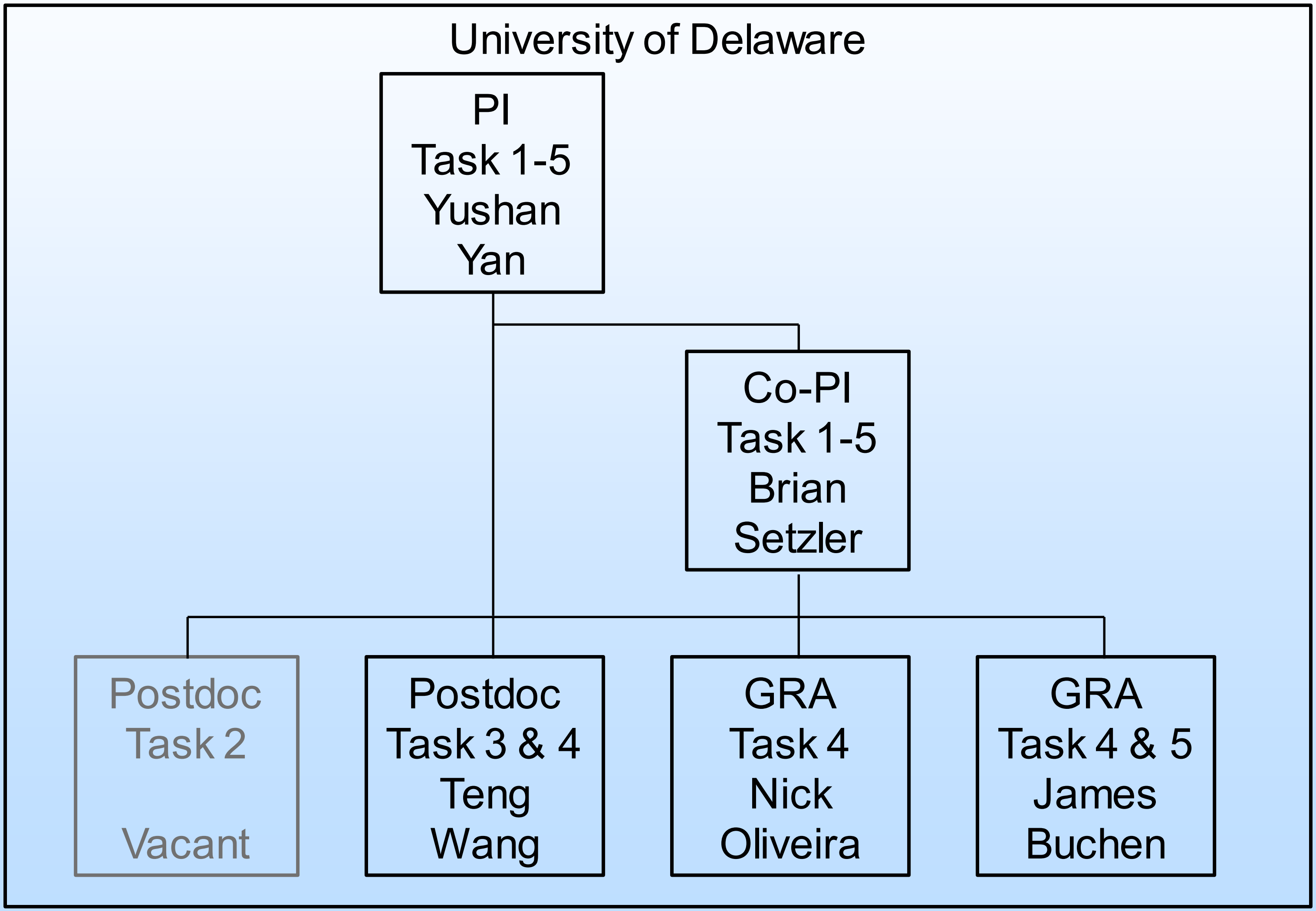
- Commercialization
  - $Ni(OH)_2$-EDCS is already licensed
  - Evaluating appropriate strategy for H_2-EDCS

Summary Slide

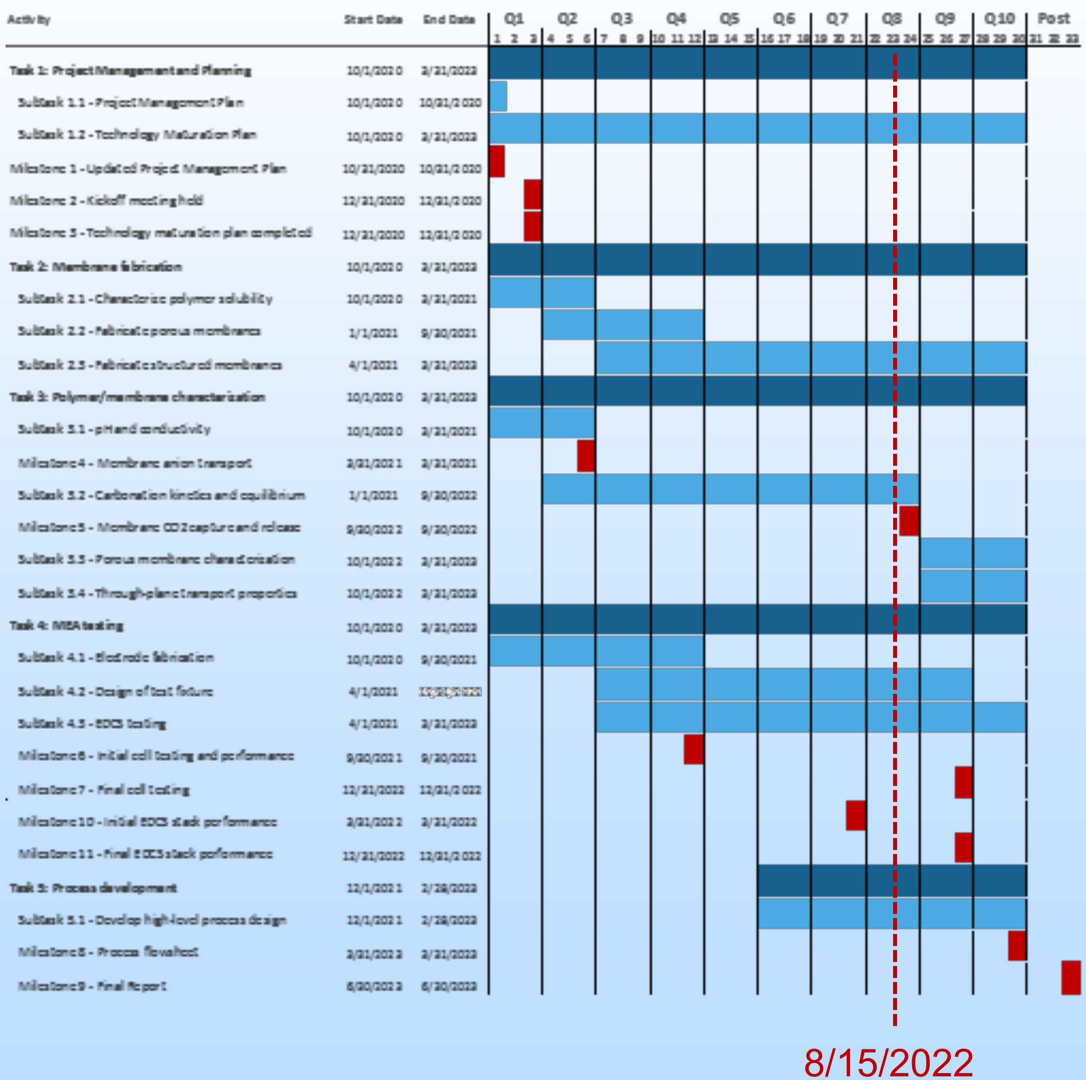
- PAP polymer characterization
  - Conductivity, thick-film reaction-diffusion
  - To do: thin-film kinetics, thermodynamics
- $Ni(OH)_2$ EDCS cell
  - Energy: 3 GJ/t, exceeds target
  - Flux: 75 kg/m^2yr, needs 2x improvement
  - Electrode rebalancing needs optimization
- EDCS module
  - Energy: 12 GJ/t, needs improvement
  - Flux: 580 kg/m^2yr, exceeds target

Appendix

Organization Chart



Gantt Chart

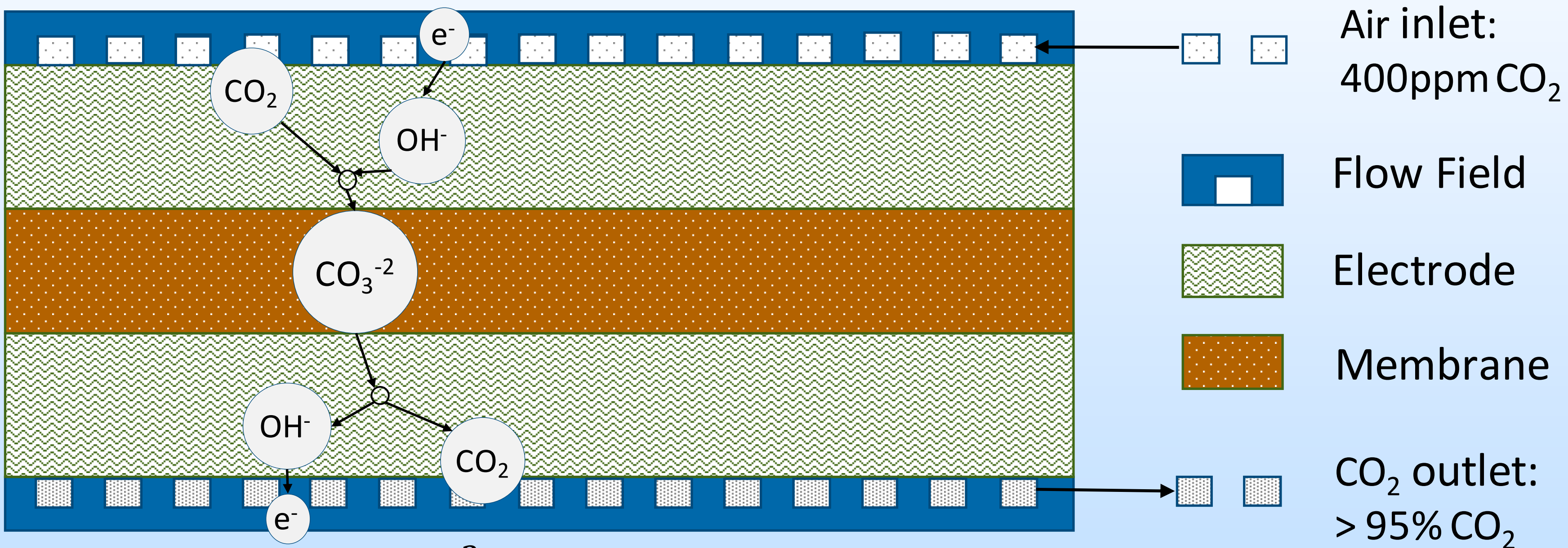


Activity
Start Date
End Date
Q1 Q2 Q3 Q4 Q5 Q6 Q7 Q8 Q9 Q10 Post
Task 1: Project Management and Planning 10/1/2020 3/31/2023
Subtask 1.1 - Project Management Plan 10/1/2020 10/31/2020
Subtask 1.2 - Technology Maturation Plan 10/1/2020 3/31/2023
Milestone 1 - Updated Project Management Plan 10/31/2020 10/31/2020
Milestone 2 - Kickoff meeting held 12/31/2020 12/31/2020
Milestone 3 - Technology maturation plan completed 12/31/2020 12/31/2020
Task 2: Membrane fabrication 10/1/2020 3/31/2023
Subtask 2.1 - Characterize polymer solubility 10/1/2020 3/31/2021
Subtask 2.2 - Fabricate porous membranes 1/1/2021 9/30/2021
Subtask 2.3 - Fabricate structured membranes 4/1/2021 3/31/2023
Task 3: Polymer/membrane characterization 10/1/2020 3/31/2023
Subtask 3.1 - pH and conductivity 10/1/2020 3/31/2021
Milestone 4 - Membrane anion transport 3/31/2021 3/31/2021
Subtask 3.2 - Carbonation kinetics and equilibrium 1/1/2021 9/30/2022
Milestone 5 - Membrane CO2 capture and release 9/30/2022 9/30/2022
Subtask 3.3 - Porous membrane characterization 10/1/2022 3/31/2023
Subtask 3.4 - Through-plane transport properties 10/1/2022 3/31/2023
Task 4: MEA testing 10/1/2020 3/31/2023
Subtask 4.1 - Electrode fabrication 10/1/2020 9/30/2021
Subtask 4.2 - Design of test fixture 4/1/2021
Subtask 4.3 - EDCS testing 4/1/2021 3/31/2023
Milestone 6 - Initial cell testing and performance 9/30/2021 9/30/2021
Milestone 7 - Final cell testing 12/31/2022 12/31/2022
Milestone 10 - Initial EDCS stack performance 3/31/2022 3/31/2022
Milestone 11 - Final EDCS stack performance 12/31/2022 12/31/2022
Task 5: Process development 12/1/2021 2/28/2023
Subtask 5.1 - Develop high-level process design 12/1/2021 2/28/2023
Milestone 8 - Process flowsheet 3/31/2023 3/31/2023
Milestone 9 - Final Report 6/30/2023 6/30/2023
8/15/2022

Technology overview

$Cathode$: $NiO(OH) + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$

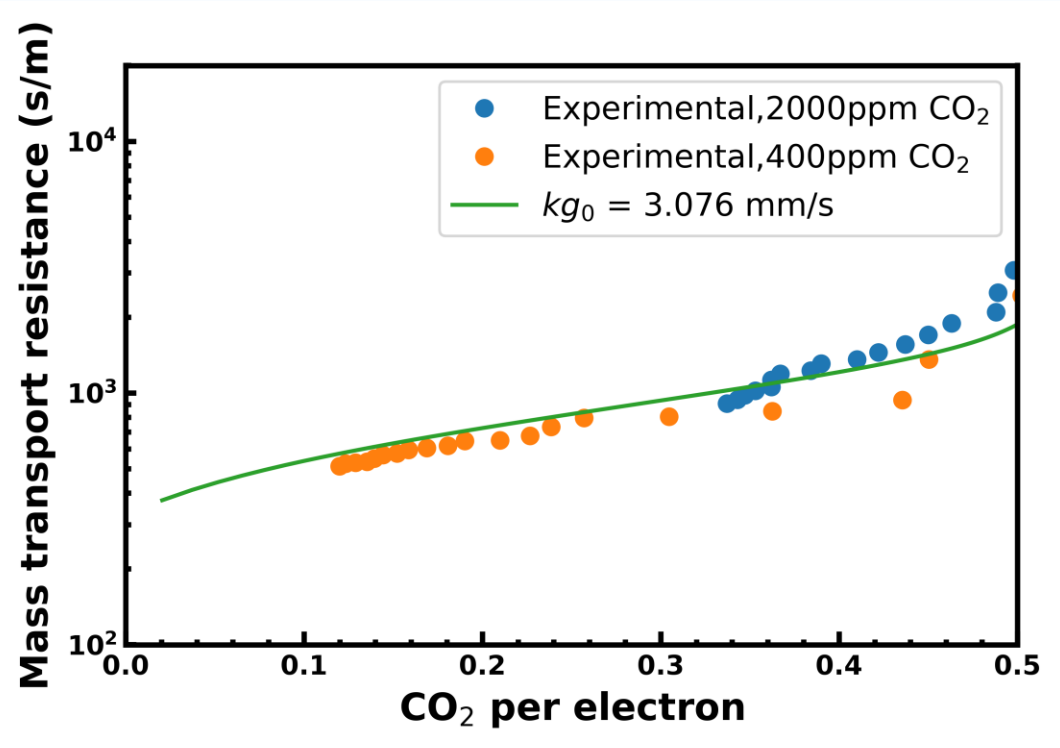
$Ionomer$: $CO_2 + 2OH^- \rightarrow CO_3^{2-} + H_2O$



$Ionomer$: $CO_3^{2-} + H_2O \rightarrow CO_2 + 2OH^-$

$Anode$: $Ni(OH)_2 + OH^- \rightarrow NiO(OH) + H_2O + e^-$

Carbonation kinetics model



R_{MT}	Cell mass transport resistance (s/m)
p_{CO_2}	Partial pressure of CO_2 (Pa)
R	Ideal gas constant (8.3145 J/molK)
T	Temperature (K)
$\langle N_{CO_2} \rangle$	Average CO_2 flux into membrane (mol/m^{2}s)
k_g	Local mass transfer coefficient into membrane, dependent on hydroxide concentration (m/s)
k_{g0}	Mass transfer coefficient into membrane at 100% hydroxide concentration (m/s)
y_h	Site exchange of hydroxide (%)
L	Length of CO_2 exposure window (m)
x	In-plane spatial coordinate (m)
H_S^{cc}	Henry's law solubility constant of CO_2 in membrane, (concentration ratio, membrane / gas)
k_2	2nd order rate constant between CO_2 and OH^- (m^3/mol s)
c_0	Cation concentration in membrane (mol/m^3)
D_{CO_2}	Diffusion coefficient of CO_2 in membrane (m^2/s)

30 °C, 90% RH, 400 or 2000 ppm CO_2

Experiment: $R_{MT} = \frac{p_{CO_2}}{RT\langle N_{CO_2} \rangle}$

Model: $R_{MT} = \langle k_g \rangle^{-1} = \left(\int_0^L k_{g0}\sqrt{y_h}\,dx \right)^{-1} = \left(\int_0^L H_S^{cc}\sqrt{k_2 c_0 y_h D_{CO_2}}\,dx \right)^{-1}$

EDCS Stack Capital Cost

EDCS stack capital costs ($/($t_{CO2}$/yr))								
Stack $/m² / CO_2 kg/m²yr	20	30	40	50	60	80	100	150
100	200	300	400	500	600	800	1000	1500
200	100	150	200	250	300	400	500	750
300	67	100	133	167	200	267	333	500
400	50	75	100	125	150	200	250	375
500	40	60	80	100	120	160	200	300
600	33	50	67	83	100	133	167	250
700	29	43	57	71	86	114	143	214
800	25	38	50	63	75	100	125	188
900	22	33	44	56	67	89	111	167
1000	20	30	40	50	60	80	100	150