Integrating CO_2-Selective Polymer Layers and Electrocatalytic Conversion (FWP-1022482)

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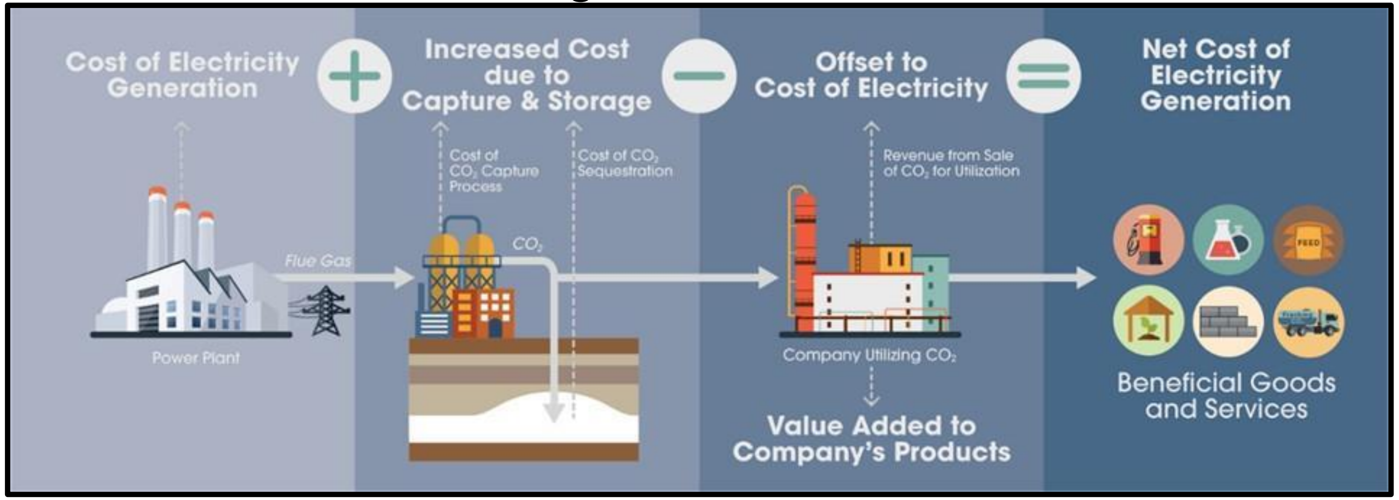
Motivation

Traditional carbon capture, separation, compression, and sorbent regeneration incur energy penalties and increase cost.

- Combining these separate steps into an "all-in-one" process would reduce the energy requirements, complexity, and cost of CO_2 utilization strategies.

Energy Generation | **CO_2 Capture & Storage** | **CO_2 Utilization** | **Reduced carbon footprint & cost**



Objective

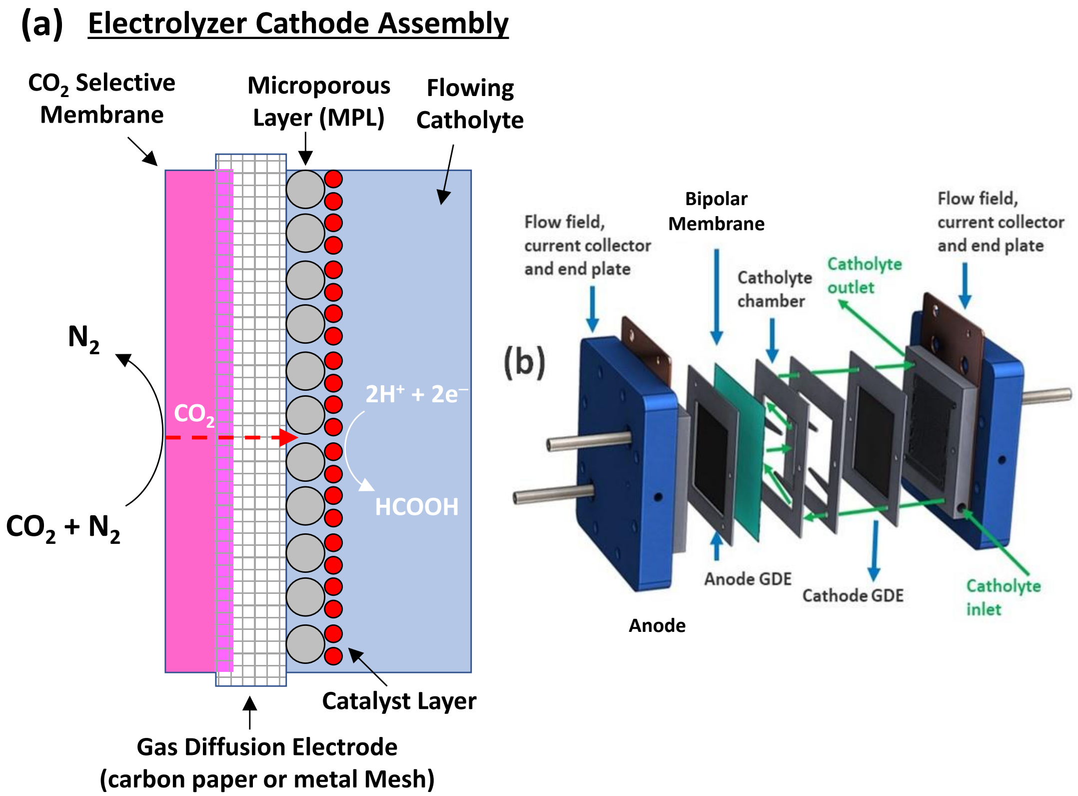
Integrate CO_2 selective membranes into electrolyzer device to capture and convert dilute CO_2 into formic acid (formate).

Team Expertise:

- Electrochemical conversion of CO_2 into formate at industrially-relevant current density.
- CO_2-selective membranes for separation from dilute streams.
- LCA and TEA.

Challenges :

- Incorporating CO_2-selective polymers into electrode architectures and optimizing the interfaces.
- Improving bipolar membrane (BPM) fabrication and lamination strategies to improve performance/durability.
- Developing accelerated degradation and variable load testing protocols.



Task Structure and PIs

Task 2: LCA/TEA and process optimization.

- Timothy.Skone@netl.doe.gov (LCA) & Gregory.Hackett@netl.doe.gov (TEA).

Task 3: Membrane synthesis and evaluation.

- David.Hopkinson@netl.doe.gov (contributions from INL and Univ. Pitt.)

Task 4: Membrane/electrode interfacing.

- David.Hopkinson@netl.doe.gov & Douglas.Kauffman@netl.doe.gov

Task 5: Cathode optimization.

- Douglas.Kauffman@netl.doe.gov

Task 6: Electrochemical evaluation.

- Douglas.Kauffman@netl.doe.gov

Task 7: 25cm^2 scale electrolyzer validation, component-level diagnostics, and BPM.

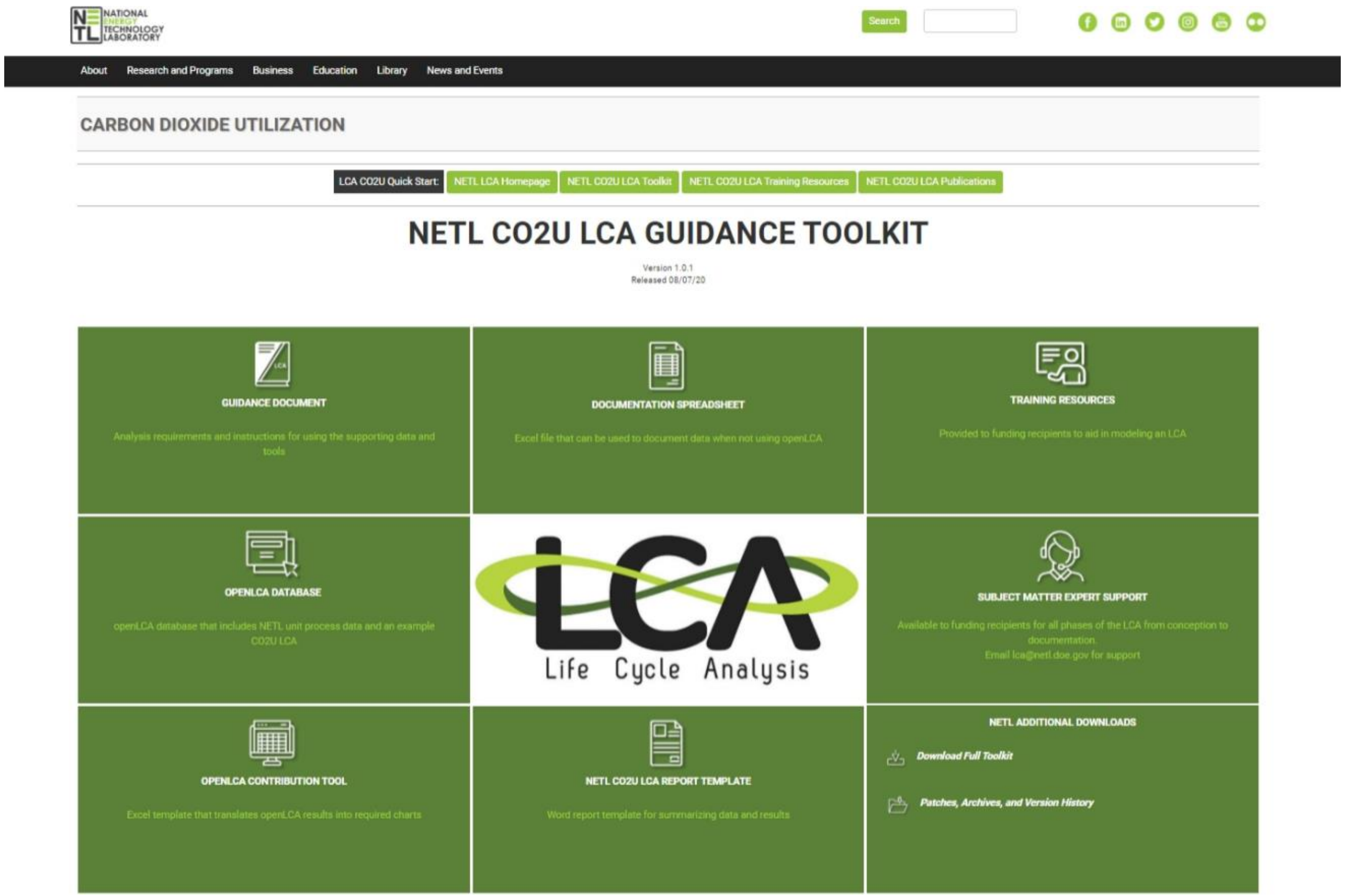
- Kenneth.Neyerlin@nrel.gov & Brian.Pivovar@nrel.gov

Key Milestones

- **BP1.**
  - Milestone M2.1 (BP1): Complete initial LCA/TEA screening studies (on track).
  - Milestone M3 (BP1): Down select at least one formulation for incorporation into GDE (completed).
  - Milestone M4.1 (Go/No-Go; BP1): Demonstrate membrane/GDE assembly with CO_2/N_2 selectivity ≥ 10 and a CO_2 flux ≥ 5 x 10^{-4} mol/hr/cm^2 (completed).
- **BP2.**
  - Milestone M2.2 (BP2): Complete process-level system optimization study.
  - Milestone M4.2 (BP2): Increase membrane CO_2 flux to ≥ 0.005 mol_{CO2}/hr/cm^2 with CO_2/N_2 selectivity ≥ 10.
  - Milestone M6 (Go/No-Go; BP2): Demonstrate 5-cm^2 electrolyzer performance of polymer-incorporated GDE that operates with > 50% FE and > 100 mA/cm^2 at < 20% CO_2 concentration.
- **BP3.**
  - Milestone M4.3 (BP3): Complete final LCA/TEA using optimized systems design and experimental input.
  - Milestone M4.3 (BP3): Increase membrane CO_2 flux to ≥ 0.01 mol_{CO2}/hr/cm^2 with CO_2/N_2 selectivity ≥ 10.
  - Milestone M7 (Go/No-Go; BP3): Demonstrate 25-cm^2 electrolyzer performance of polymer-incorporated GDE with ≥ 250 mA/cm^2 and ≥ 70% formate FE over 24-hr operation with ≤ 20% CO_2 inlet streams.

Background: LCA, TEA, and Systems Opt.

Design, Process, and Cost Engineering at NETL

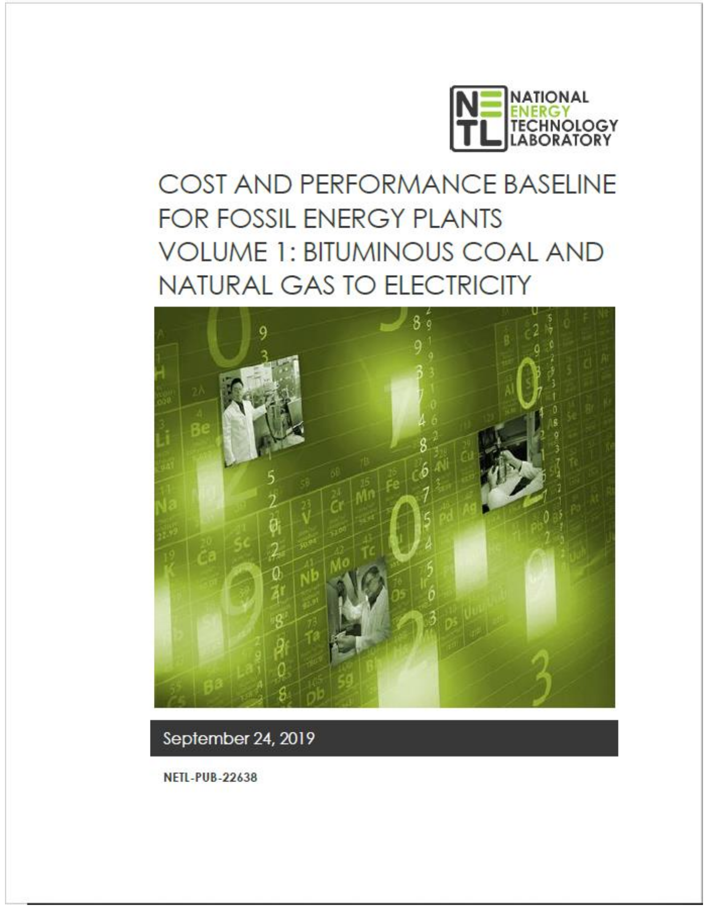


Background: LCA, TEA, and Systems Opt.

Cost and Performance Baseline and Other TEA Examples

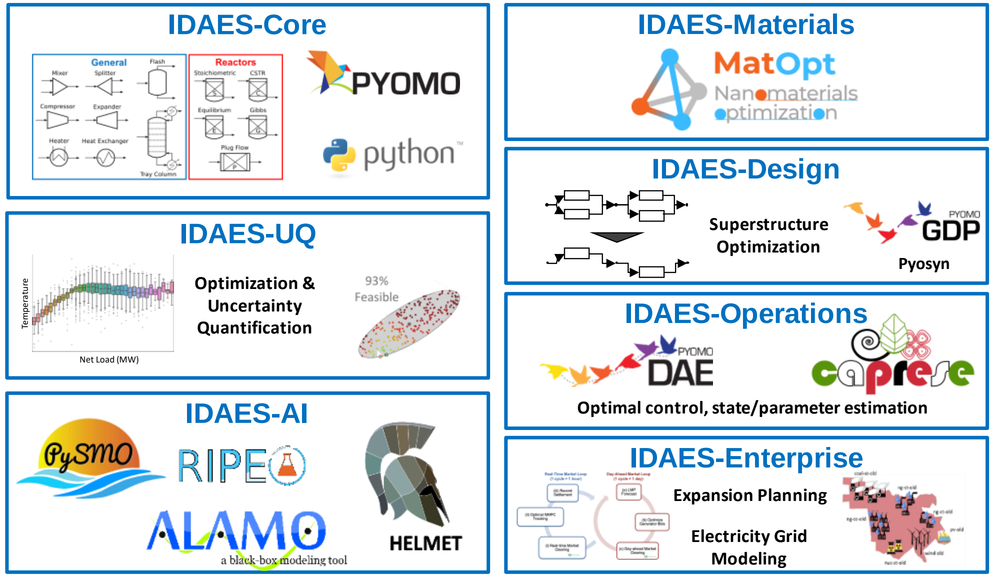
- **NETL has conducted a wide variety of TEA of power generating systems in addition to carbon utilization technologies to draw comparison from, including the following:**
- **Technology Expertise:**
  - Combustion Systems (natural gas, biomass, and coal)
  - Gasification Systems (dry and slurry feed, coal and biomass)
  - Oxy-combustion Systems (atmospheric and elevated pressure)
  - Chemical Looping
  - Solid Oxide Fuel Cells/Solid Oxide Electrolysis Cells
  - Fuels and Chemicals(e.g., H_2, NH_3, methanol, etc.) Production from Fossil Fuels
  - Supercritical CO_2 Power Cycles (direct and indirect)
  - Process Water Treatment/ Zero Liquid Discharge Systems
  - Bulk Energy Storage
  - CO_2 Capture Systems (solvent, sorbent, membrane, cryogenic)
  - Direct Air Capture
  - CO_2 Purification and Compression
  - Air Separation Units (cryogenic, ion transport membrane)
  - Hydrogen Recovery (membranes, sorbents)
  - Combustion Turbines
  - Steam Turbines (subcritical through adv. Ultra-supercritical steam conditions)
  - CO_2 Utilization Technologies (EOR, Cements, Algal, EC, Microwave)
  - Direct Power Extraction/ Magnetohydrodynamics

NETL Energy Analysis Library Link



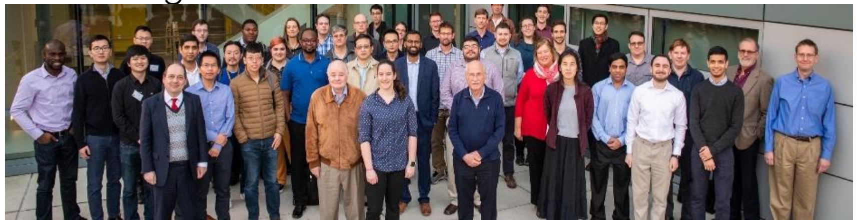
NETL Bituminous Baseline Report Link

Background: IDAES Integrated Platform



Open Source: https://github.com/IDAES/idaes-pse

Lee, et al., **The IDAES Process Modeling Framework and Model Library – Flexibility for Process Simulation and Optimization**, 2021, *Journal of Advanced Manufacturing and Processing*



2020 R&D 100 WINNER

Rigorous modeling capabilities that enable design and optimization of complex, interacting technologies and systems

Core capabilities

- Libraries of customizable unit models enabling rapid construction of optimizable process flowsheets
- Simultaneous optimization of process design and operation
- Advanced machine learning/surrogate modeling
- Rigorous uncertainty quantification/propagation enabling robust optimization with performance guarantees
- Multi-scale modeling from materials to energy market scales

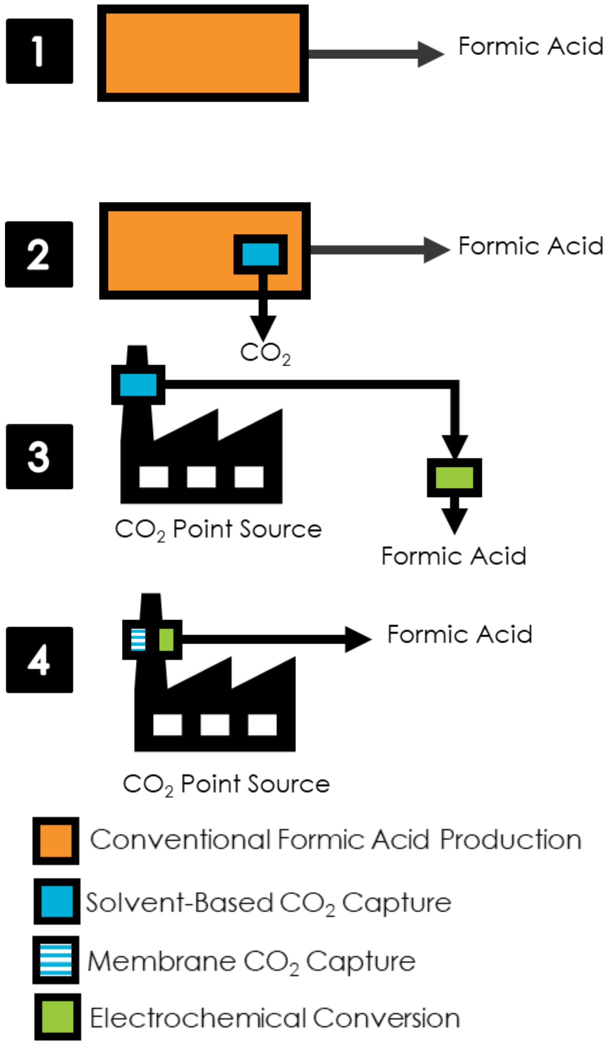
Enabling several ongoing collaborative projects

- ARPA-E DIFFERENTIATE (natural gas solid oxide fuel cell systems)
- National Alliance for Water Association (NAWI)
- Tri-LAB/GMI-DISPATCHES (hybrid, multi-input, multi-output energy systems)
- ARPA-E FLECCS (flexible carbon capture)
- EMRE CRADA (direct air capture)

Task 2: TEA/LCA

Approach

- Compare performance, cost, and environmental impact of integrated capture/electrochemical-conversion system against three base cases
  - 1) "business as usual" production with unabated carbon emissions
  - 2) "business as usual" production with solvent capture and storage
  - 3) separate CO_2 capture and electrochemical CO_2 conversion



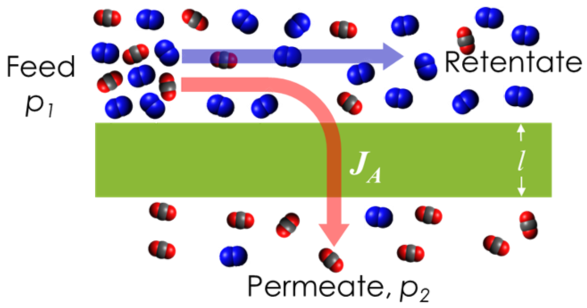
Sensitivity Analysis for Levelized Cost of Production (LCOP)

- Membrane CO_2 Flux
- CO_2 Electrolyzer Faradaic Efficiency, Current Density, Voltage, Single-Pass Conversion

Progress

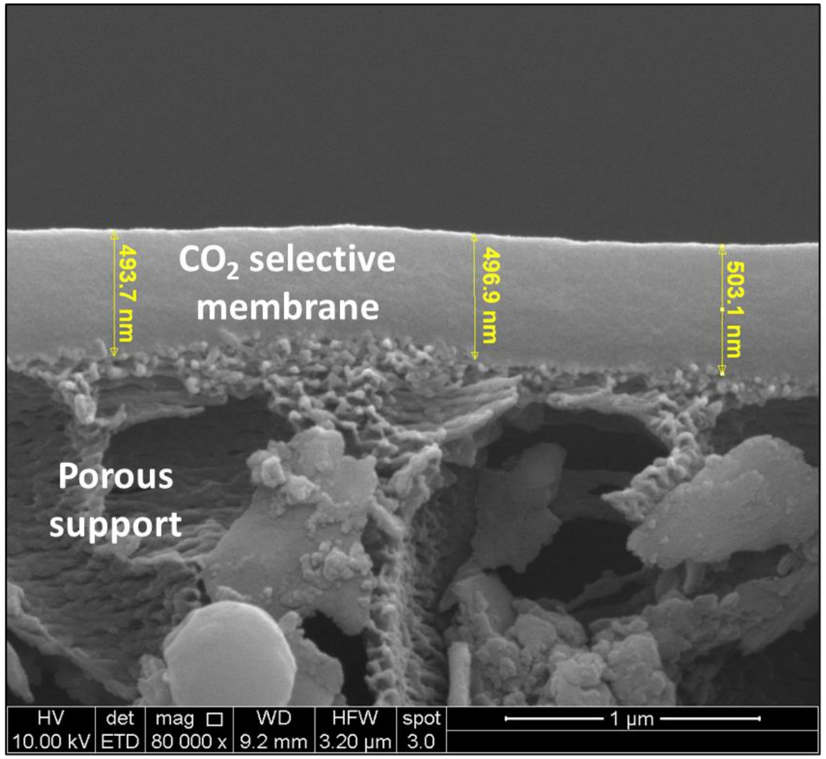
- Design Basis / Analysis Plan development completed.
- Milestone M2.1 (09/30/2022; on track): Complete initial LCA/TEA screening.

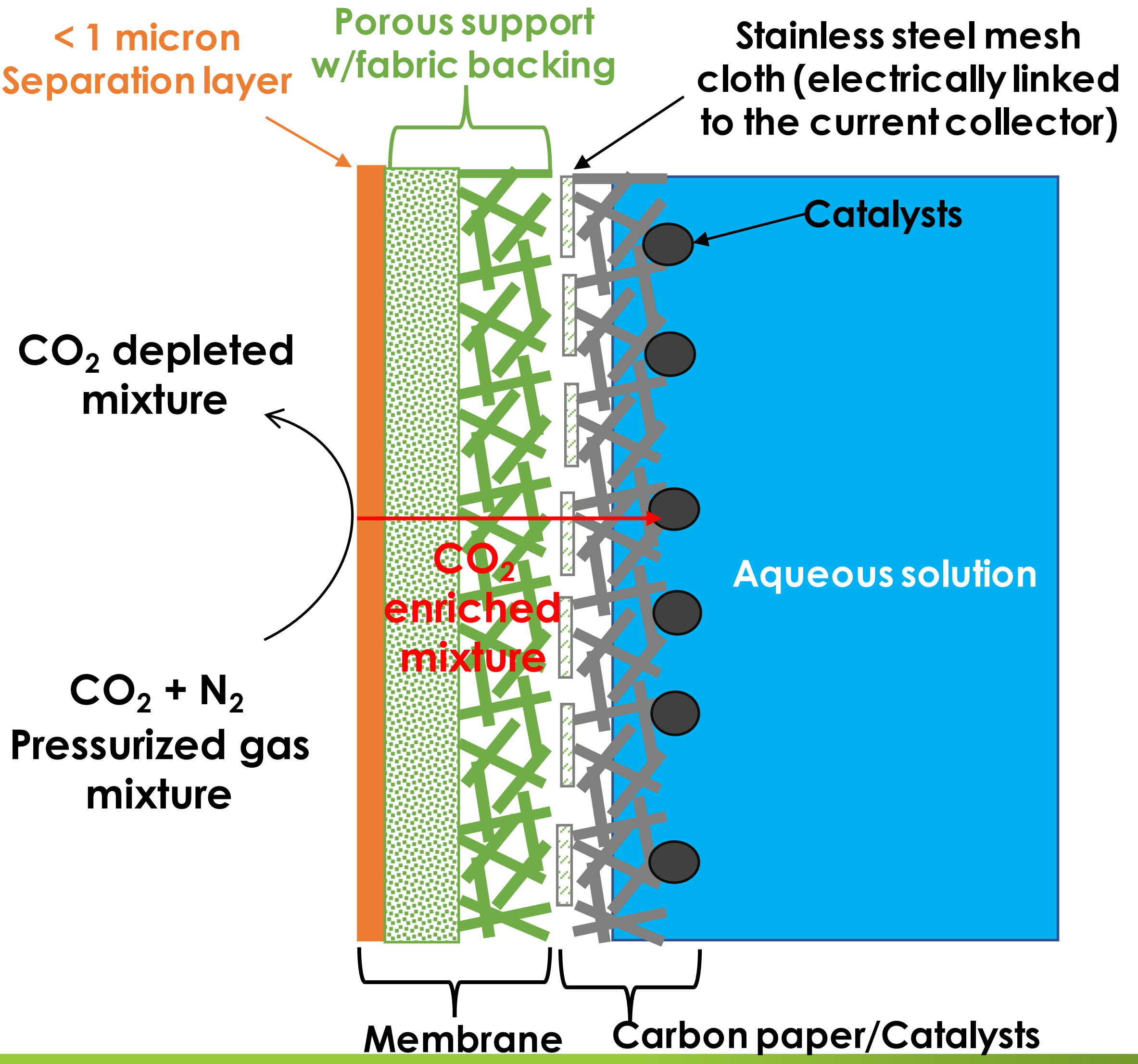
Tasks 3 & 4: Membrane/Electrode Interfacing



flux: $J_A = \frac{P_A}{l}(p_1 - p_2)$

gas permeance





Tasks 3 & 4: Gas permeation of membrane/GDE assemblies

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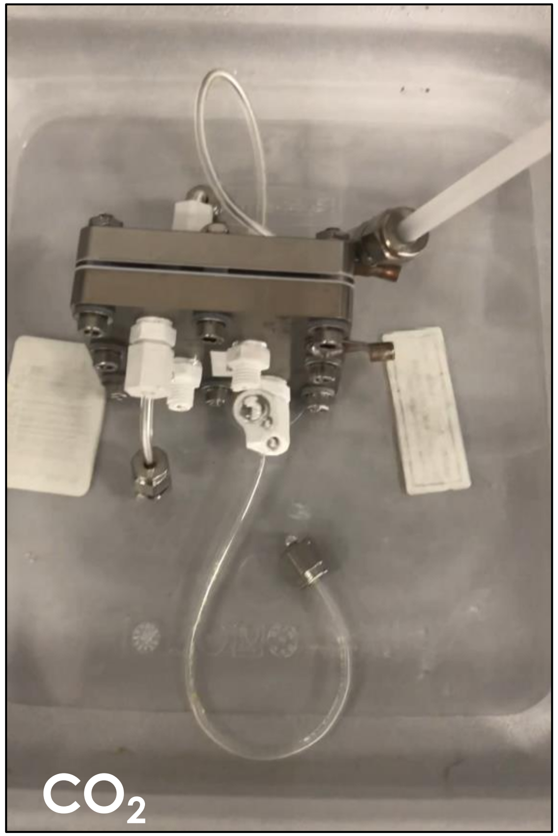
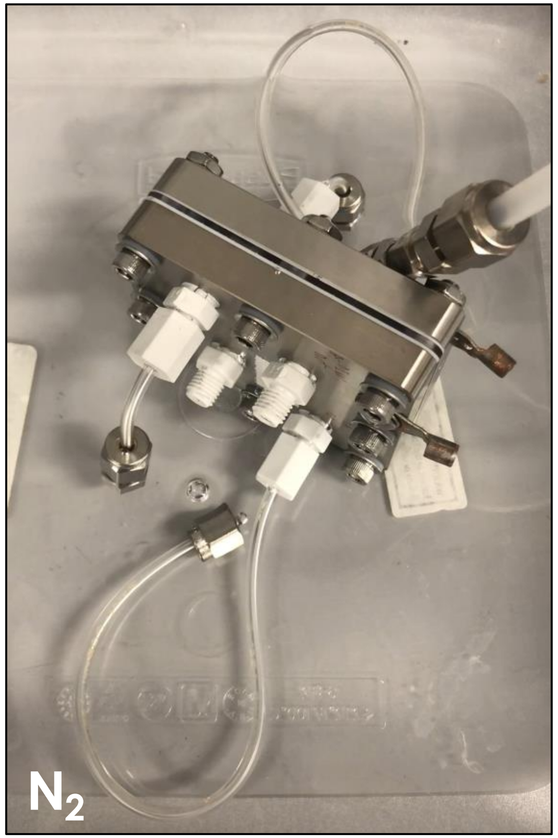
Pure-gas permeation through membrane and GDE





Pressure drop across the membrane (2022#4) are 8 psi in both cases.

CO_2-selective membranes	CO_2 flux @ 0.5 bar pressure drop (mol/hour/cm^2)	CO_2/N_2 selectivity
2022#04	0.019	>12
2022#08	0.025	13
2022#12	0.024	12

Milestone M2.1 and M3 (09/30/2022): ***Completed***
Demonstrated polymer/GDE assembly with CO_2/N_2 selectivity ≥ 10 and a CO_2 flux ≥ 5 x 10^{-4} mol/hour/cm^2.

**** CO_2 flux sufficient for ~350 mA/cm^2**

Task 5: Gas Diffusion Electrode Optimization

- **Optimize catalyst ink on GDE**
  - NETL-developed, doped-SnO_2 cathode catalyst.
  - Evaluate ratio of catalyst, carbon, Nafion binder, and influence of hydrophobic MPL.

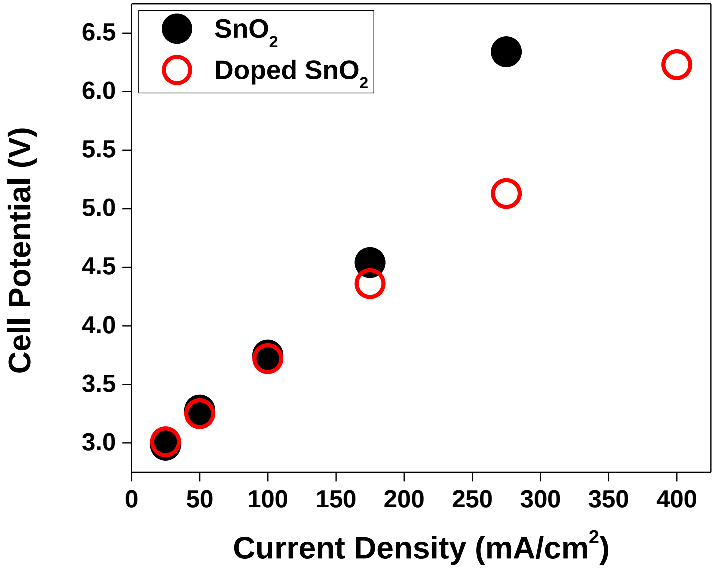
- **<u>Milestone M5 completed</u>.** Optimize cathode catalyst and MPL layer for formate production.

GDE Optimization

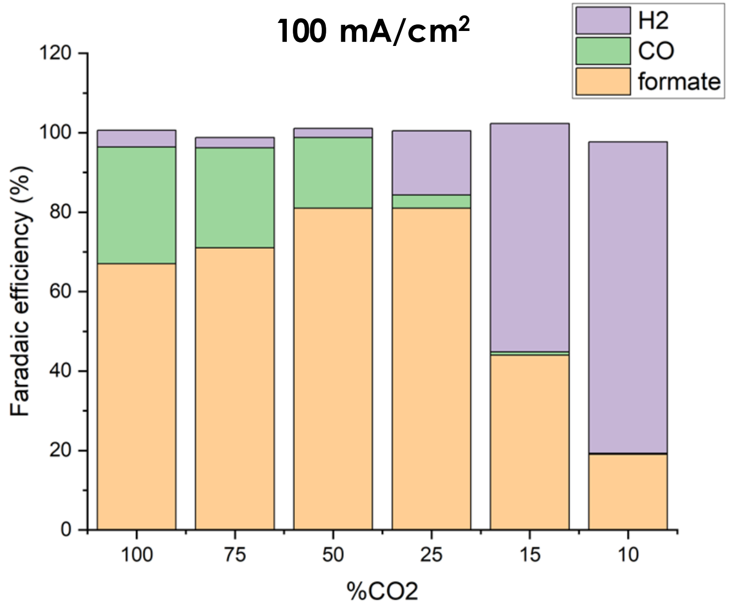
- Optimized loading, Toray PTFE content, incorporation of MPL, and catalyst ink to maximize performance.
- Catalyst performance in dilute CO_2 (no separation membrane)
- Initial tests with interfaced GDE/CO_2 membrane

Catalyst Performance

(pure CO_2)



FE vs. CO_2 Concentration



Unpublished results; provisional patent application submitted & manuscript in preparation.

Task 6: Electrochemical Evaluation

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- **This task will evaluate the electrochemical performance of electrodes containing CO2-selective polymer layers in 5 cm^2 electrolyzers.**
  - Scheduled to begin in BP2 (Oct. 2022).
  - Milestone M6 (Go/No-Go; BP2): Demonstrate 5cm^2 electrolyzer performance of polymer-incorporated GDE that operates with > 50% FE and > 100 mA/cm^2 at < 20% CO_2 concentration.
  - **Current results *without* CO_2-selective membrane**:
    - ~80% FE at 100 mA/cm^2 in 25% CO_2
    - ~43% FE at 100 mA/cm^2 in 15% CO_2
  - Inclusion of CO_2 selective membranes will allow operation at higher current density and lower CO_2 concentrations!

Task 7: Scaling and BPM Development

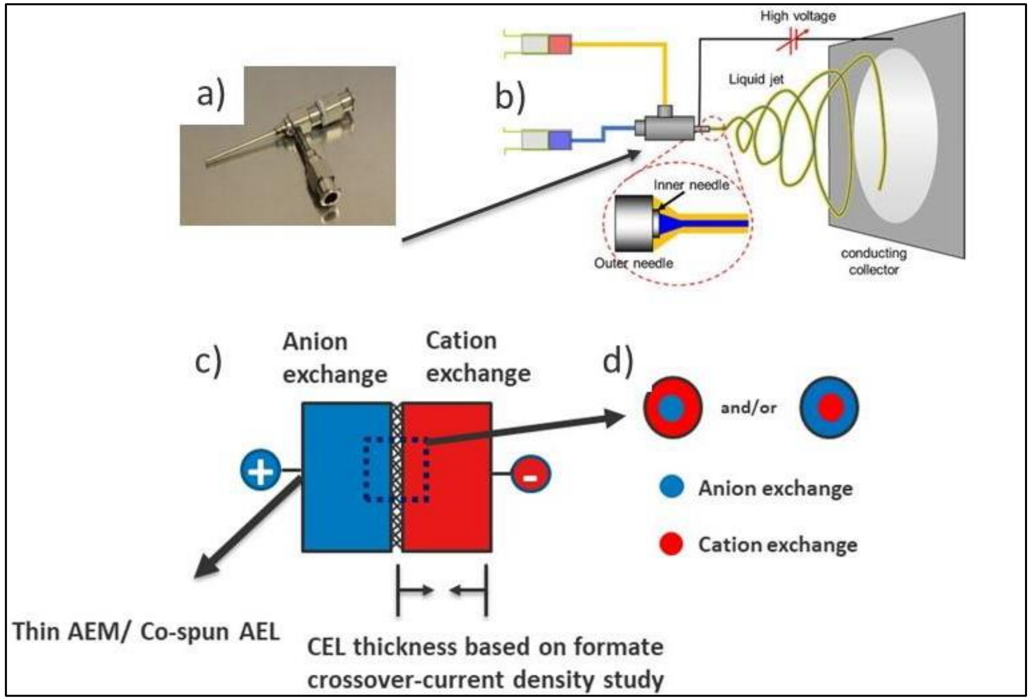
NREL had developed 25cm^2 electrolyzer device hardware that can sustain 500 mA/cm^2 and high faradaic efficiency.

- Substantial reductions in operating voltage are possible by optimizing the bipolar membrane that separates the cathode and anode, as well as specific component design (*e.g.* gas/catholyte flow-field design, gasketing, etc.).

Efforts to improve Bipolar membranes.

- Coaxial spun BPMs are advantageous over typical 2D BPM interfaces with a higher surface area for transport and an interpenetrating junction architecture to overcome delamination.

- Initial progress in tailoring the BMP synthetic conditions has reduced charge transfer resistance (R_{ct}) and should lower operating voltages.



Summarized Progress and path forward.

Budget Period 1.

- Successfully integrated a CO_2-selective polymer membrane onto a gas diffusion electrode (GDE).
- Optimized catalyst layer and GDE construction.
- Finishing initial /LCA to estimate cost savings and carbon footprint reductions.

Next Steps (Budget period 2).

- Demonstrate electrochemical performance of integrated membrane/GDE in dilute CO_2 streams.
  - > 50% FE and > 100 mA/cm^2 at < 20% CO_2 concentration.
- Optimize BPM synthesis.
- Continue to improve CO_2 flux through membrane.
- Process optimization efforts for final LCA/TEA.

Final Deliverables (BP3).

- Demonstrate 24-hour electrochemical performance in 25cm^2 electrolyzer at ≥250 mA/cm^2 and ≥70% formate FE with ≤20% CO_2 inlet streams
- Final comprehensive LCA/TEA report with experimental data and optimized system design.

Questions or Comments?

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Thank you for your attention!

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Synthesis of Value-Added Organic Products

Technology Performance Data

Electrochemical reduction of CO_2 into formate / formic acid

	Units	Measured/Current Performance	Projected/Target Performance
Synthesis Pathway Steps[1]			
Step 1 (based on CO_2)	mol^{-1}	$CO_2 + 2e^- + 2H^+ \rightarrow HCOOH$	
Step 2	mol^{-1}	Balanced chemical equation	
Step n	mol^{-1}	Balanced chemical equation	
Source of external intermediate 1		Renewable energy (electrons)	
Source of external intermediate 2		(e.g., natural gas, oil, renewable energy, etc)	
Source of external intermediate n		(e.g., natural gas, oil, renewable energy, etc)	
Reaction Thermodynamics[2,3]			
Reaction[4]		Electrochemical; formal potential E0 = -0.12 V *vs.* RHE)	
ΔH^o_{Rxn}	KJ/mol	378.6 (from: 10.1021/acs.chemrev.8b00705)	
ΔG^o_{Rxn}	KJ/mol	350.9 (from: 10.1021/acs.chemrev.8b00705)	
Conditions		(range)	(range)
CO_2 Source[5]		25-100%	<25%
Catalyst[6]		Doped SnO_2	Doped SnO_2
Pressure	bar	1	1
CO_2 Partial Pressure	bar	0.25-1	<0.25
Temperature	^oC	20	20
Performance		(range)	(minimum)
Nominal Residence Time[7]	sec	seconds	TBD
Selectivity to Desired Product[8]	%	60-90	>90
Product Composition[9]		(range)	(optimal)
Desired Product	mol%	30% single-pass conversion	TBD; must optimize single-pass conversion and flow rates to sustain selective CO_2 conversion without HER.
Desirable Co-Products	mol%		
" "	mol%		
Unwanted By-Products	mol%	<10	0
" "	mol%		
Grand Total	**mol%**	**40%**	**TBD**