Green Methanol via an Integrated Direct Air Capture, CO_2 Electrolyzer, and Hydrogenation Reactor

Project Number: FE0032415

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THE UNIVERSITY OF
TENNESSEE
KNOXVILLE

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Project Overview

- Funding: DOE ($399,999); Cost-share ($100,002)
- Project Performance Dates: 12/20/2023 – 9/19/2024
- Overall Project Objectives: Advance the TRL through experimental and modeling to enhance the efficiencies while assessing the TEA/LCA of an integrated reactor for simultaneous capture and conversion of CO_2 to methanol.

Project Participants

THE UNIVERSITY OF TENNESSEE KNOXVILLE

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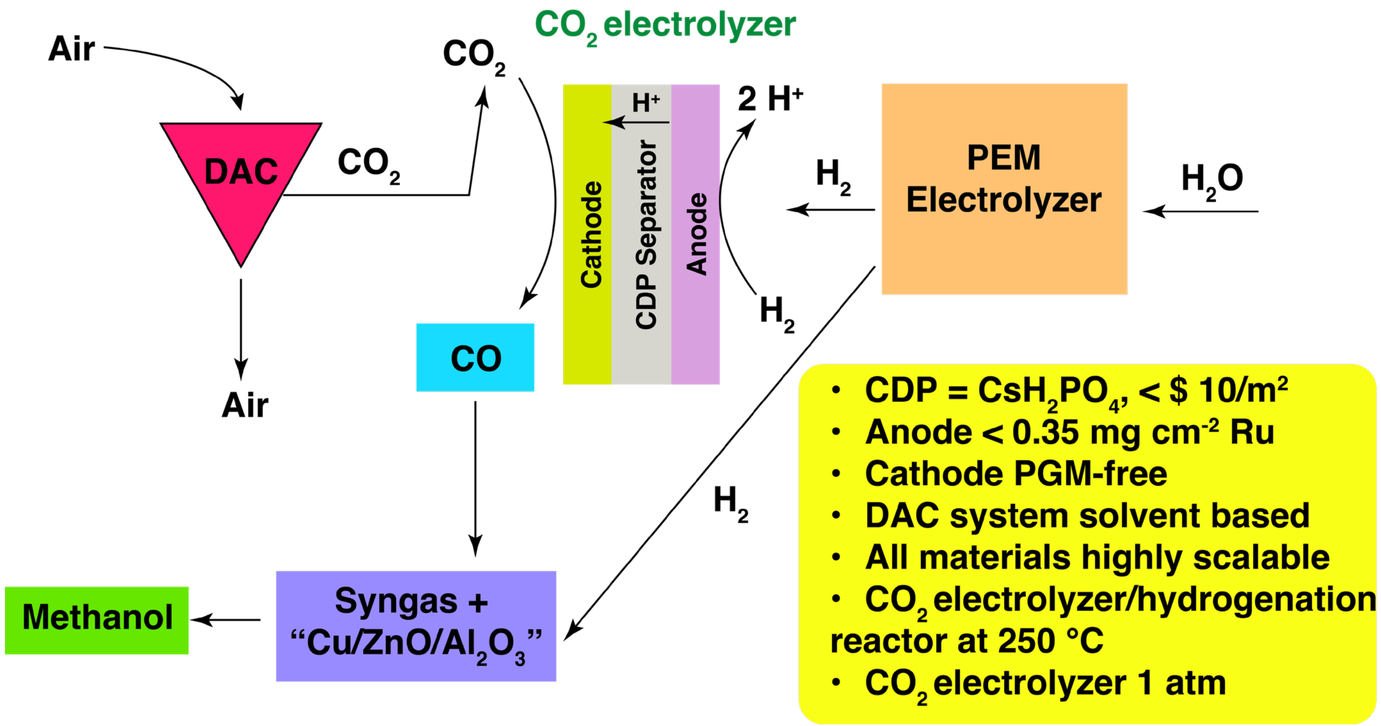
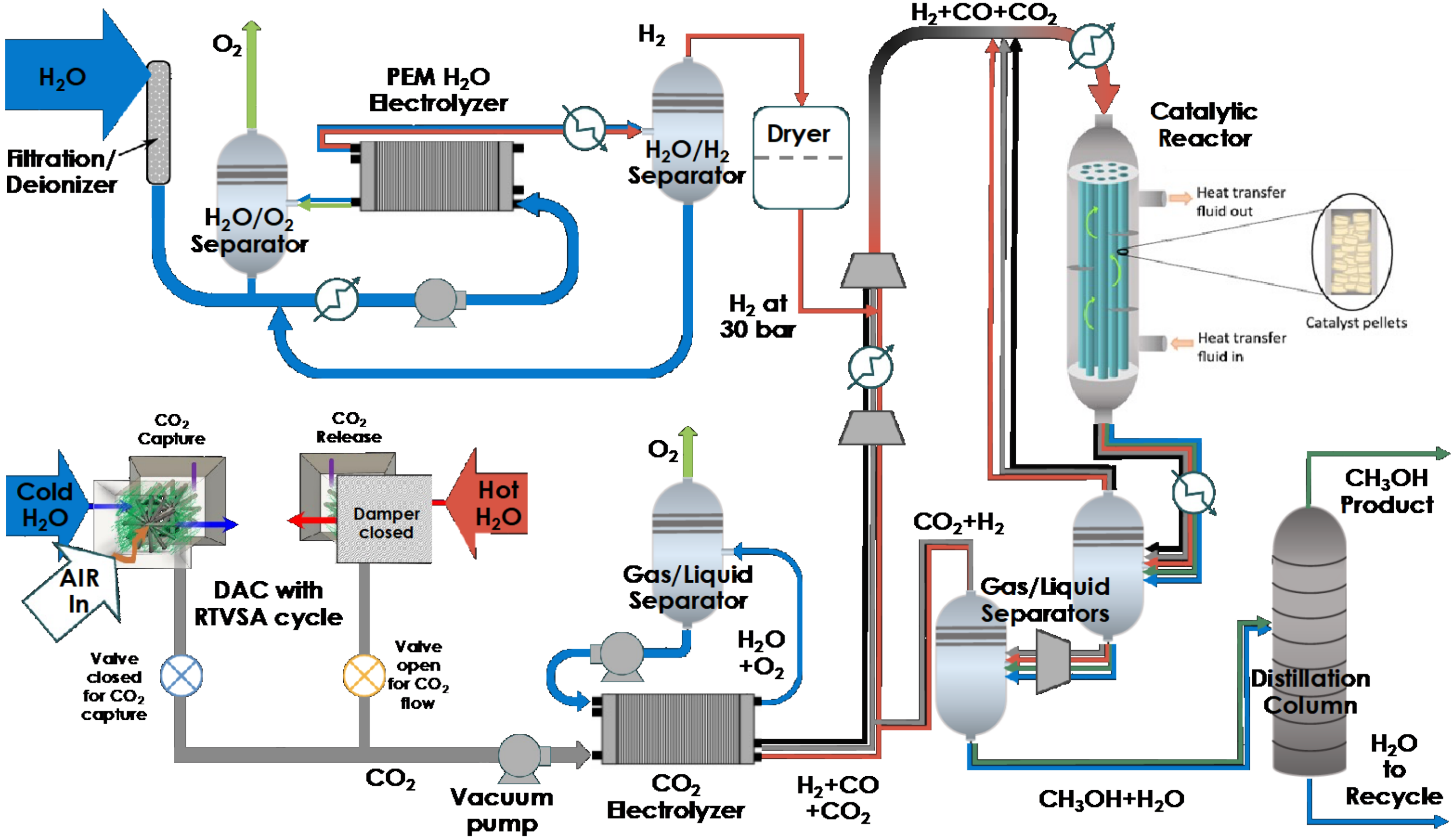
Technology Background



- **CDP = CsH_2PO_4, < $ 10/m^2**
- **Anode < 0.35 mg cm^{-2} Ru**
- **Cathode PGM-free**
- **DAC system solvent based**
- **All materials highly scalable**
- **CO_2 electrolyzer/hydrogenation reactor at 250 °C**
- **CO_2 electrolyzer 1 atm**

- Key innovation: CO_2 electrolyzer
  - Low overpotential w/ large current densities, high efficiency, and selectivity
  - Overcomes challenges with competing CO_2 electrolyzers such as **water management and membrane durability**
- Other components of integrated reactor use "off-the-shelf" mature technologies – derisks approach
  - DAC based on ORNL/Holocene
  - PEM electrolyzer for H_2 source
  - Hydrogenation catalyst well understood

System Overview



- Targets for 1000 tons of MeOH per year
  - Controlled CO_2 feed from DAC with RH ~ 3%
  - CO_2 electrolyzer < 50 m^2 and 600 mA/cm^2
  - Methanol synthesis @ 50 bar with gains in yield from counter-current stripping with wet H_2

Advantages and Challenges

- CO_2 fed into GDE: **No solubility limits**
- CDP provides a > 10x cost savings over competing polymer membranes
- Cathode catalyst is simple and inexpensive mixed metal oxide
- HOR more compatible with the cathodic CO_2RR: more balanced and integrated electrolysis process
- Lower energy consumption: Using separate electrolyzer for H_2 generation reduces h’s (HER vs OER)
- Eliminates need to manage and control the complex and often harsh conditions required for OER, simplifying the reaction setup and maintenance

- Cathode catalyst durability: corrosion resistant supports will need further investigation
- Scale-up of MEAs: Some work has been done to try roll-to-roll processing of CDP-based materials previously, but R&D efforts are needed
- Integrated reactor thermodynamics and efficiencies need to be demonstrated

Technical Approach

- Selection of DAC system: Thermodynamics and cost considerations of DAC and integration and sizing into reactor is critical
  - Modeling of competing systems using ASPEN
- Optimization of CO_2 electrolyzer
  - Electrode structure and catalyst dispersion greatly impacts performance
  - Multi-physics modeling of scaled-up electrolyzer
- Evaluation of CO-to-methanol reactor
  - Modeling using ASPEN
- Culminating in System Model

Project Scope and Milestones

- Risk mitigation
  - Initial DAC system was identified but kept agnostic to allow for evaluation of competing technologies
  - Catalyst support and fabrication had adequate parameter space to allow for systematic investigation and optimization
- Scope: Limited experimental investigations with modeling driving design of integrated reactor
- Milestones
  - Electrolyzer Q2 performance target met
  - DAC Q3 performance target met
  - Working towards integrated reactor design and DEI/CB Q4 targets

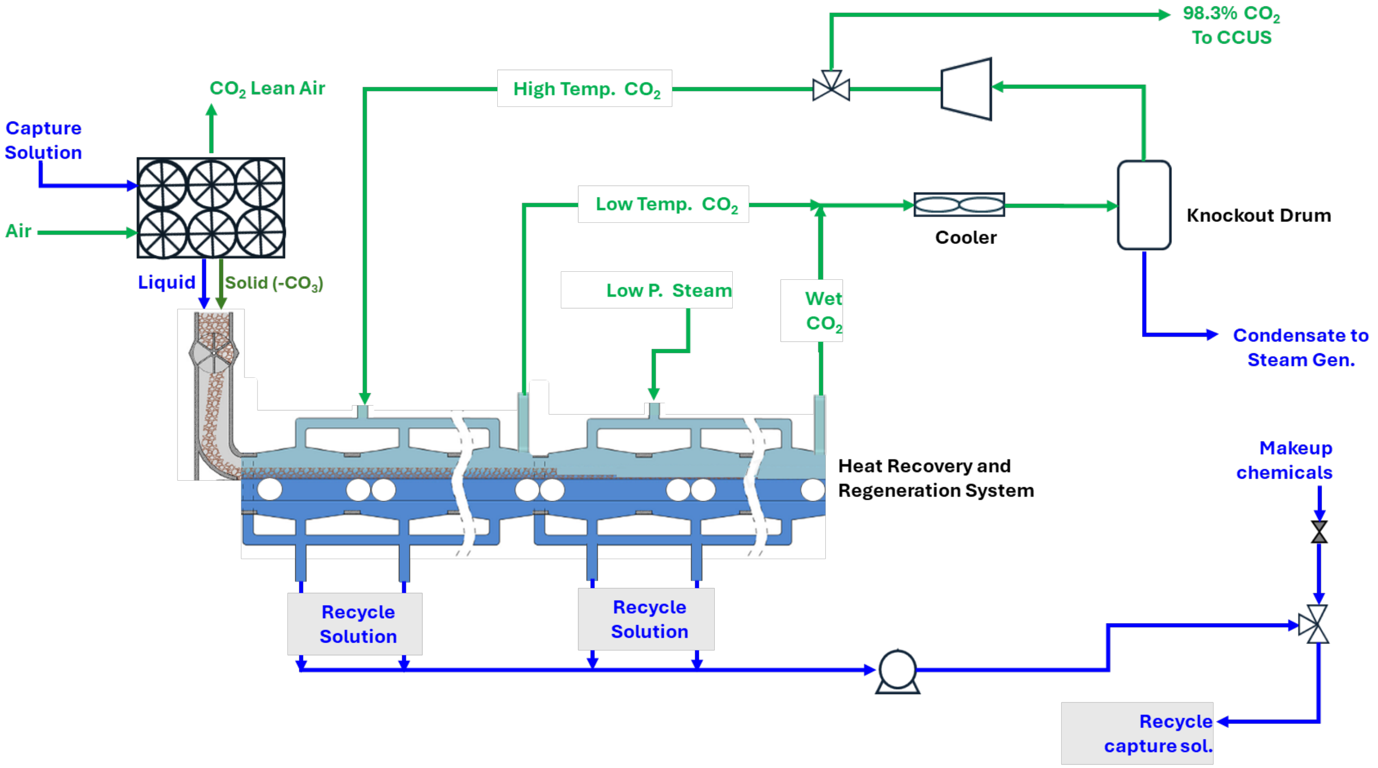
DAC Evaluation

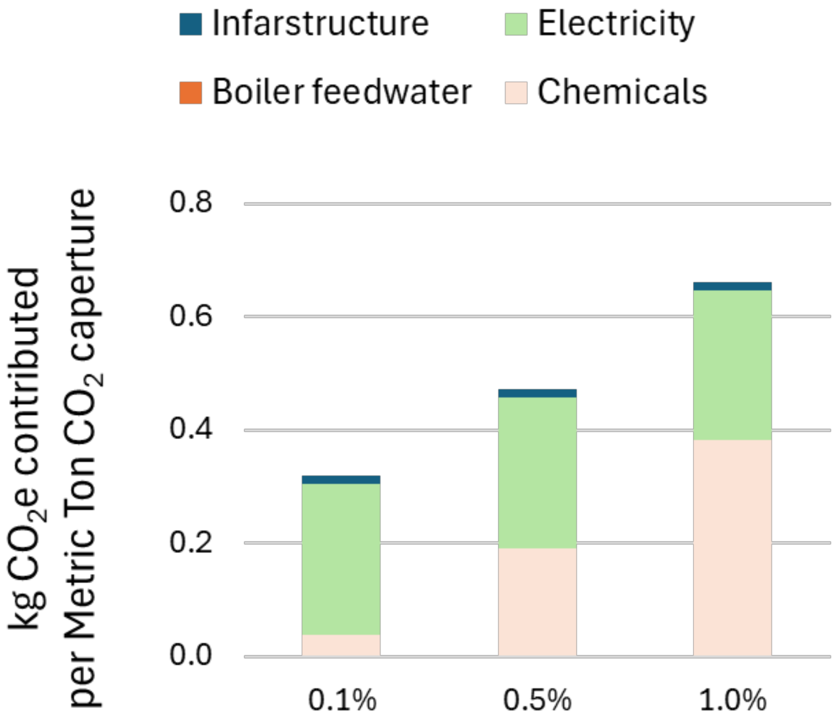
Energy for the catalyst regeneration is one of the cost and GHG emissions drivers

Material	Regeneration Temperature [°C]	Notes
Aqueous hydroxides (e.g. KOH)	900	High temperature requires NG – adding to carbon footprint
Solid sorbent (e.g. CA/SiO_2/PEI)	90-200	High pressure drop and mass transport limitations at air contactor
Amino acid solvent (ORNL)	100-120	Practical for commercial air contactor design. Low temperature catalyst regeneration allows using electrification options.

- The amino acid solvent system is being scaled up at ORNL (up to 3 kg CO_2 per day and scaled up to 10 metric tons CO_2 per year by Holocene.

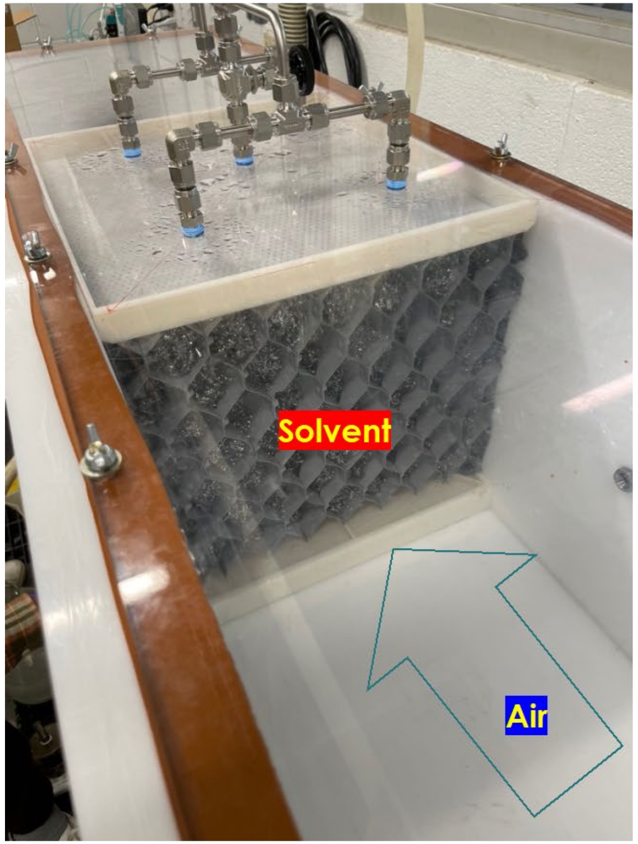
DAC System – Conceptual Model & Simulation

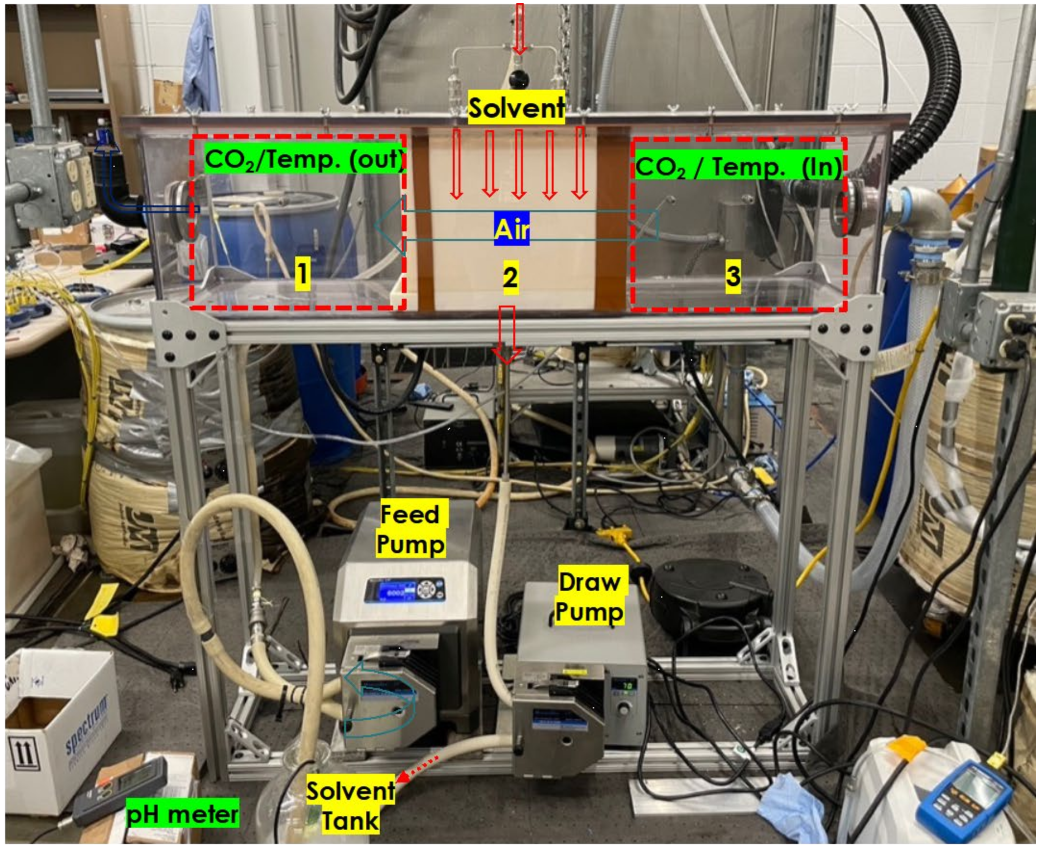




- Solvent deactivation rate (replacement rate) significantly impacts emissions
- Possible net-negative emissions when deactivation rate < 1%.

DAC Pilot Scale at ORNL



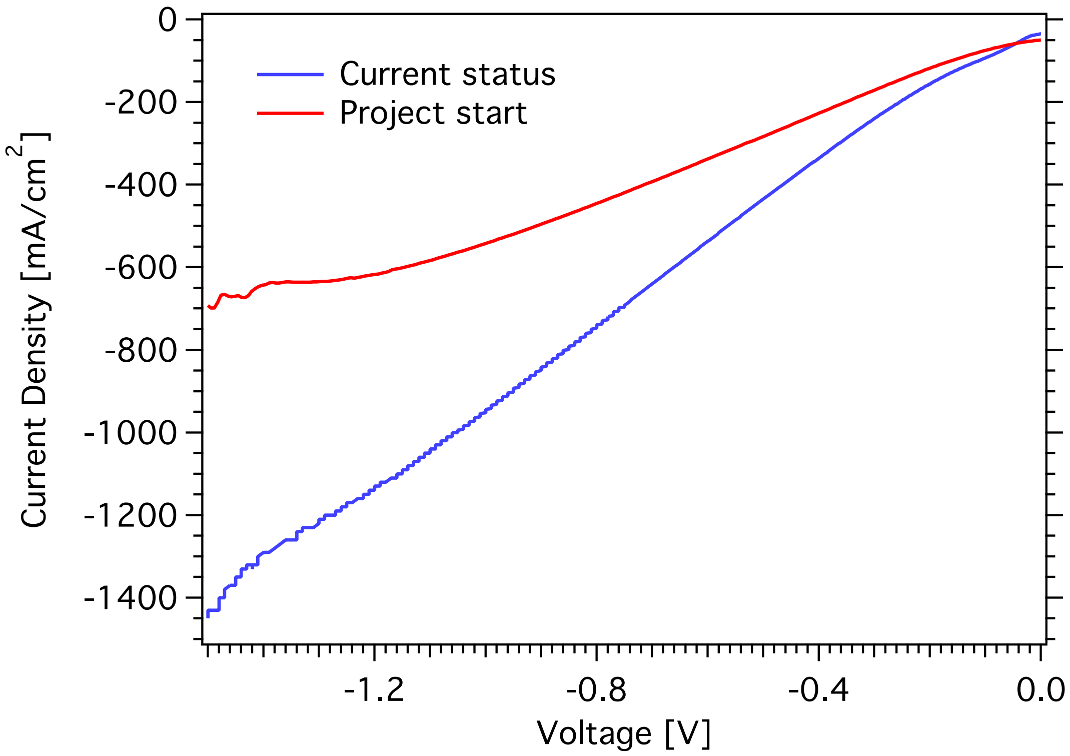


- 1 ft^3 wind tunnel prototype
- Cross-flow operation:
  - Solvent – top-to-bottom
  - Air – Left-to-right
- Updated version has 3 packing elements
  - Stacked to give 3 ft^3

Innovations in CO_2 Electrolysis

- Current commercial CO_2 electrolyzers (Twelve, Dioxide Materials) use Ag-based catalysts and typically generate CO at 300-600 mA/cm^2
  - **Our electrolyzer can produce CO with FE > 98% at over 750 mA/cm^2**
  - **Our cathode catalyst uses inexpensive metal oxides**
- Current commercial CO_2 electrolyzers use either PEM or AEM polymer membranes which are expensive and require sophisticated water management, risks of electrode flooding, and chemical instability is an issue
  - **At scale, we believe our CDP “membrane” can be > 100x less expensive**
  - **Humidification of our electrolyzer is operationally simple and requires ~ 3% RH**
  - **TEA suggests that CapEx and OpEx costs can be lowered by 4-6x and ~ 2x over competing technologies**

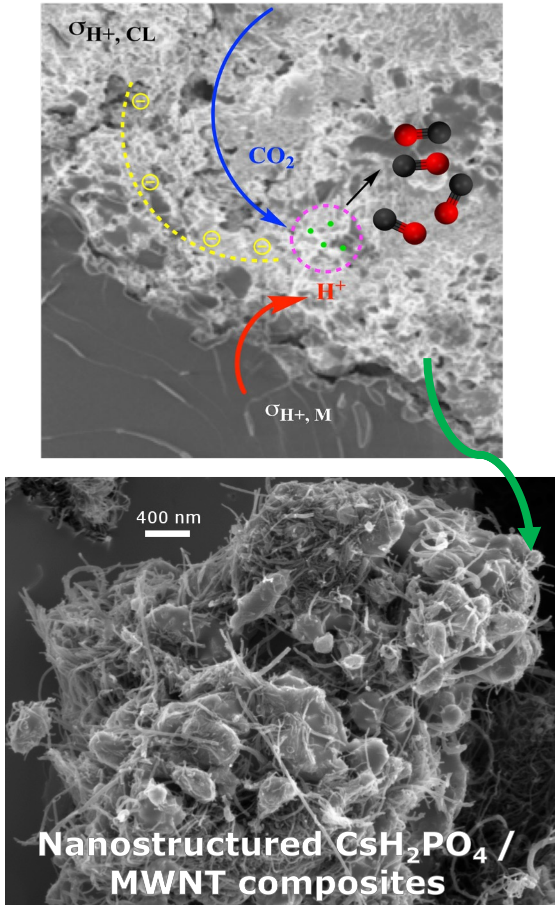
Improved CO_2 Electrolyzer: Nanocomposite Cathodes



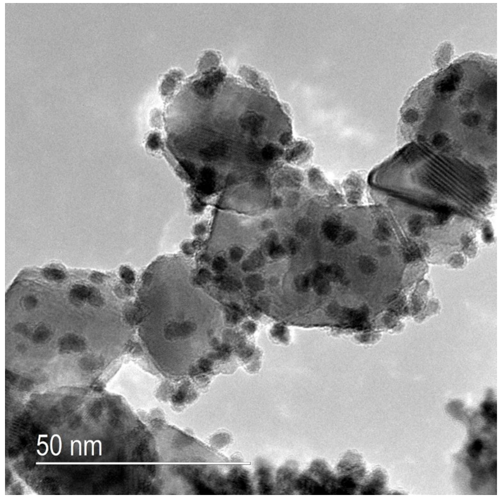
Cell potential [V]	j [mA/cm^2]	FE_{CO} [%]	FE_{H2} [%]
0.3	240	99.5	< 0.5
0.4	338	99.4	< 0.6
0.5	435	99.4	< 0.6
0.6	553	99.2	0.8
0.7	640	98.6	1.4
0.8	750	98.2	1.8
1.0	948	86.7	13.3

- Experimental efforts addressed electrode porosity, catalyst dispersion, and nano-templating of CDP electrolyte

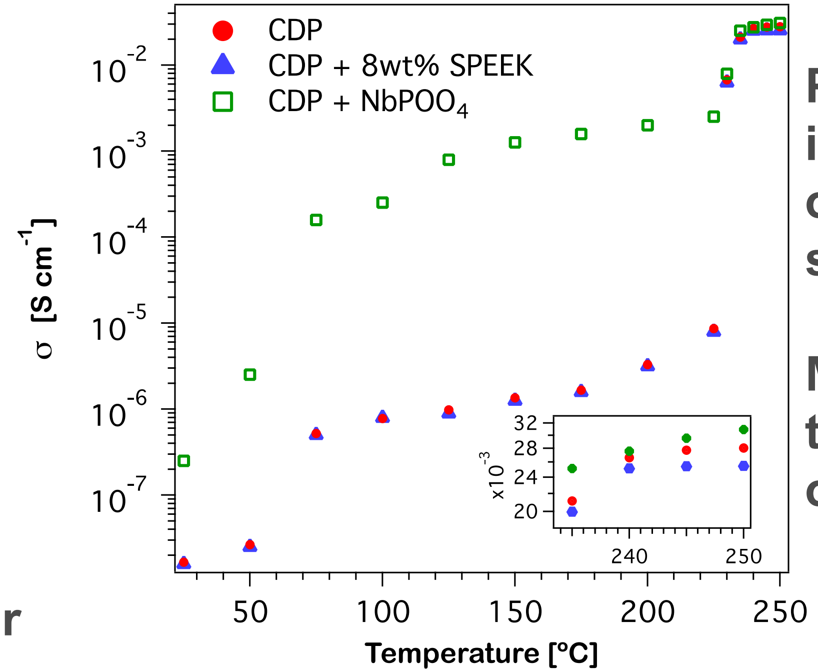
Methods to Increase Performance



Improved electrode structure

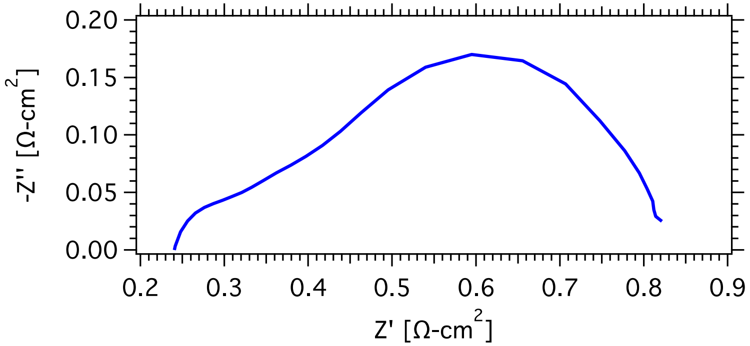


NP co-catalysts may suppress HER at higher potentials



Polymers may allow improved processibility of membrane w/o sacrificing conductivity

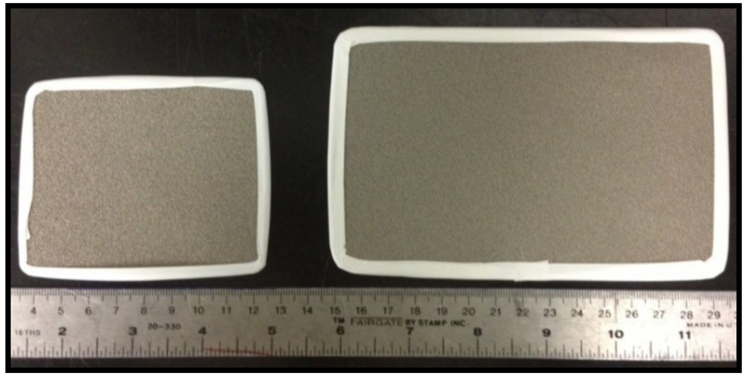
May also reduce thickness to lower ohmic losses

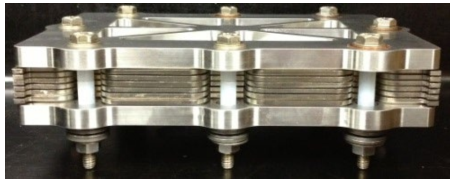


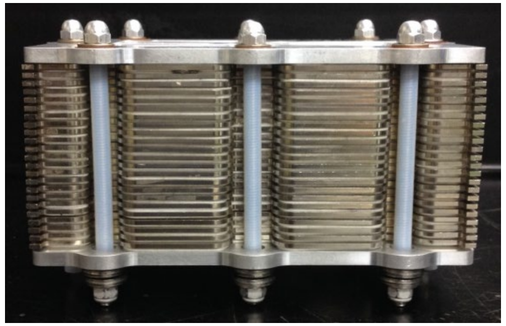
- Reduced R_{CT} – better kinetics!
- DRT analysis underway

Scale-Up of CO_2 Electrolyzer

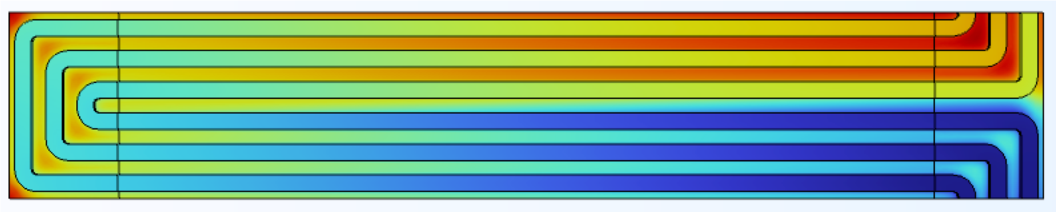
- Materials evaluation at 1.5 cm^2 scaled to 15 cm^2
- Future: Stacks w/ 50 or 125 cm^2 – Flow field design
- **Aluminum and stainless steel hardware and polymer seals**



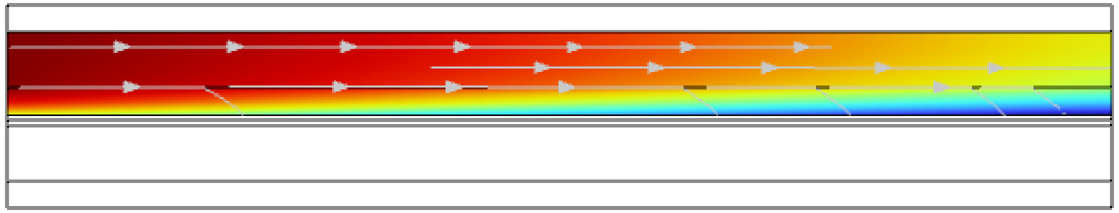




COMSOL Modeling of Electrolyzer

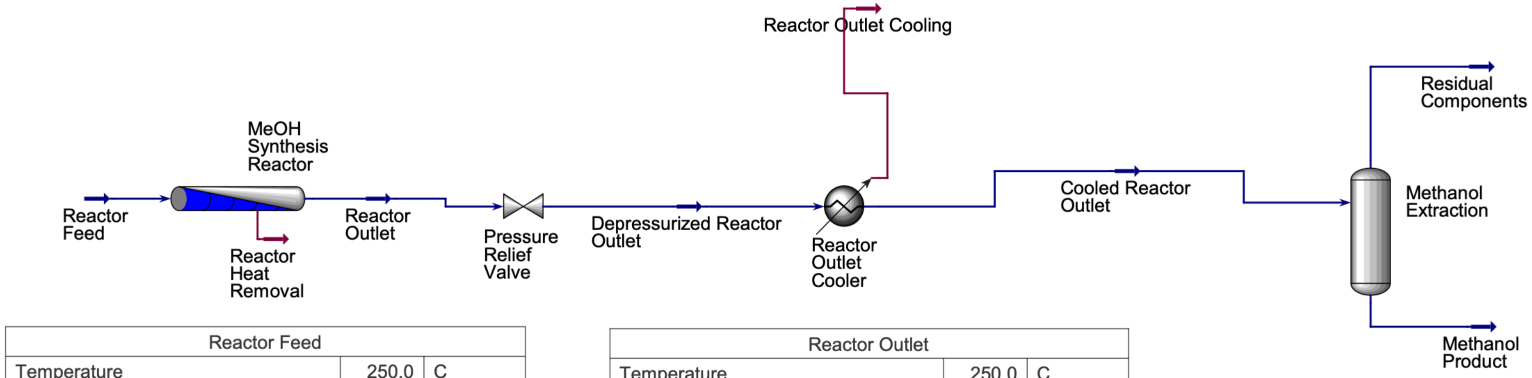


- Lab-scale model used “dead-end” flow fields
- Serpentine flow fields necessary for scaled up reactor
- At low-flow rates, HER competition increases – sets balance of per-pass CO_2 conversion efficiency, utilization, and FE
- Other flow fields and 3D models are being constructed



- Addressing issues related to mass-transport efficiencies and homogeneous reactivity across electrode structure

ASPEN/HYSYS Model of Hydrogenation



Reactor Feed		
Temperature	250.0	C
Pressure	7500	kPa
Molar Flow	28.44	kgmole/h
Master Comp Mole Frac (CO)	0.3125	
Master Comp Mole Frac (CO2)	0.0625	
Master Comp Mole Frac (Hydrogen)	0.6250	
Master Comp Mole Frac (Methanol)	0.0000	
Mass Flow	363.0	kg/h
Master Comp Mass Flow (CO)	248.9	kg/h
Master Comp Mass Flow (CO2)	78.2	kg/h
Master Comp Mass Flow (H2O)	0.0	kg/h
Master Comp Mass Flow (Hydrogen)	35.8	kg/h
Master Comp Mass Flow (Methanol)	0.0	kg/h

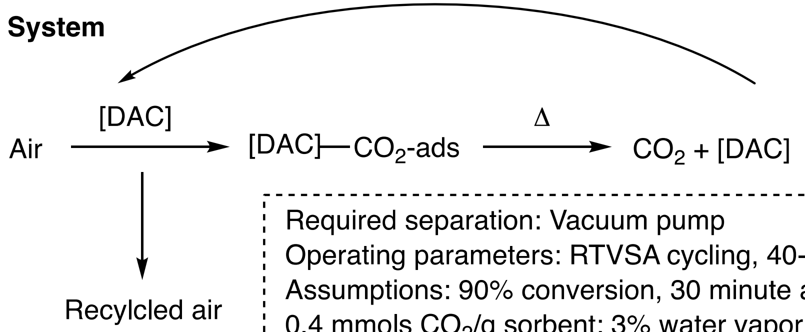
Reactor Outlet		
Temperature	250.0	C
Pressure	7497	kPa
Molar Flow	16.87	kgmole/h
Master Comp Mole Frac (CO)	0.1846	
Master Comp Mole Frac (CO2)	0.1047	
Master Comp Mole Frac (Hydrogen)	0.3672	
Master Comp Mole Frac (Methanol)	0.3428	
Mass Flow	363.0	kg/h
Master Comp Mass Flow (CO)	87.2	kg/h
Master Comp Mass Flow (CO2)	77.7	kg/h
Master Comp Mass Flow (H2O)	0.2	kg/h
Master Comp Mass Flow (Hydrogen)	12.5	kg/h
Master Comp Mass Flow (Methanol)	185.3	kg/h

Methanol Product		
Temperature	25.00	C
Pressure	101.3	kPa
Master Comp Mole Frac (Methanol)	0.9963	
Master Comp Mass Frac (Methanol)	0.9968	
Master Comp Mass Flow (Methanol)	130.0981	kg/h

- Model accounts for CO production from electrolyzer

Summary of Carbon Negative MeOH Production

DAC System

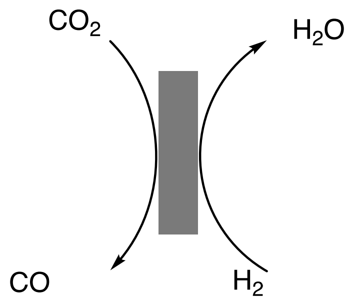


$\text{Air} \xrightarrow{[DAC]} [DAC]\text{—}CO_2\text{-ads} \xrightarrow{\Delta} CO_2 + [DAC]$

Recylcled air

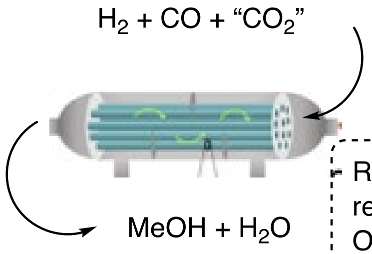
Required separation: Vacuum pump
Operating parameters: RTVSA cycling, 40-70 °C
Assumptions: 90% conversion, 30 minute adsroption/regeneration cycle; 0.4 mmols CO_2/g sorbent; 3% water vapor
Flow: 1852 s-L CO_2/min; 9259 m^3 air/min; 1909 s-L/min vacuum pump flow
36 L/h Air/g sorbent
Thermodyanmic requirements: 1.4 x 10^2 MWh for 1000 tonnes of MeOH

CO_2 electrolyzer



Required separation: Gas/liquid separator for water removal
Operating temperature: 250 °C
Assumptions: 50% per pass CO_2 conversion
Thermal requirements: 9.7 x 10^2 MWh for 1000 tonnes of MeOH
Electricity requirments: 4.3 x 10^3 MWh for 1000 tonnes of MeOH
Kinetics: 500 mA/cm^2 -> 118 kg/h CO produced

Methanol Reactor



Required separation: Gas/liquid separator for water removal; distillation
Operating temperature: 250 °C
Pressure: 10-20 bar
Assumptions: 90% per pass CO conversion
Thermal requirements: 4.9 x 10^2 MWh for 1000 tonnes of MeOH
Electricity requirments: 3.7 x 10^2 MWh for 1000 tonnes of MeOH
Kinetics: ~120 kg/h methanol produced

Technical Lessons Learned

- Initial solid-state DAC was not the most suitable system for our needs
  - Integrated reactor will adopt amino acid system
- As CO_2 utilization increases, FE tends to decrease due to mass transport limitations and incomplete CO_2 consumption
  - Spatial variations in FE due to differences in CO_2 availability across the catalyst
  - Varying inlet CO_2 flow rates showed that higher flow rates maintain high FE but lower CO_2 utilization, whereas lower flow rates increase CO_2 utilization but decrease faradaic efficiency due to the formation of H_2 instead of CO
  - Flow field can mitigate mass transport limitations and improve performance
- Electrode morphology is critical

Community Benefits Plan (CBP) Overview

Overarching intention of the CBP: in this CBP, we present an integrated approach to assessing the impacts of the technology on jobs, environment and community perceptions by:

(i) Engaging university-based communities (including an HBCU and an MSI) in dialogue about a proposed plant.

(ii) Identifying potentially impacted localities and populations and the specific impacts expected.

(iii) Engaging representatives of underserved universities in the scientific work of the project.

(iv) Engaging a regional electricity provider in these discussions.

- Overview of SMART (Specific, Measurable, Achievable, Relevant, and Timely) Goals or “Commitments” stated in the CBP.

Community Benefits Plan (CBP) Overview

SMART (Specific, Measurable, Achievable, Relevant, and Timely) Goals or "Commitments" stated in the CBP.

(i) Hiring of summer interns from HBCU/MSI pools.

(ii) Engagement of HBCU partner community re: siting of Phase 2 prototype demonstration activity.

(iii) Plan for increasing diversity of the applicant pool.

(iv) Using process including UTK societal team participants along with industry-facing partner, identify one community of interest and engage to begin assessing environmental impacts of proposed Phase 2 deliverable.

CBP Timeline / Implementation Roadmap

Planning to Make a Plan

Timeline:

- Q1/Q2: multiple CBP milestones, mostly oriented to preliminary team formation and charging the teams. Completed.
- Q2: Identification of interns to participate in the work of the project. Given the short project length, focused in internal; proposal written for more (‘100K Innovation Fund).
- Q3: ‘Town hall’ discussions of (preliminary) design, engaging TSU and UPR as well as other stakeholders; completion of geographic surveys to identify likely communities affected and possible effects. Underway.
- Q4: Reporting of full plan for each element of CBP, including update J40 and community engagement plans.

Plans for Near Future Testing, Development, and Commercialization

- DAC
  - Continue scaling up system in partnership with ORNL and Holocene
  - Demonstrate captured CO_2 delivery into electrolyzer at optimized flow rates and humidification levels to corroborate benchtop scale studies
- CO_2 electrolyzer
  - Catalyst durability studies and ASTs
  - Fabricate and test flow fields
  - 3D multiphysics modeling and DRT analysis to identify other loss mechanisms
- Integrated reactor
  - Build and demonstrate lab-scale integrated demonstration reactor
- Spin-out to partner

Summary

- CDP-based solid acid electrolyzer offers a unique technology platform with potentially transformative operating efficiencies and thermal integration with methanol production
- ORNL/Holocene DAC system is the best-case for systems integration
- TEA/LCA high level calculations suggest that over 1.5 kg of CO_2 may be mitigated per tonne of methanol produced at a cost of $697-748 per tonne

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