ChemCatBio

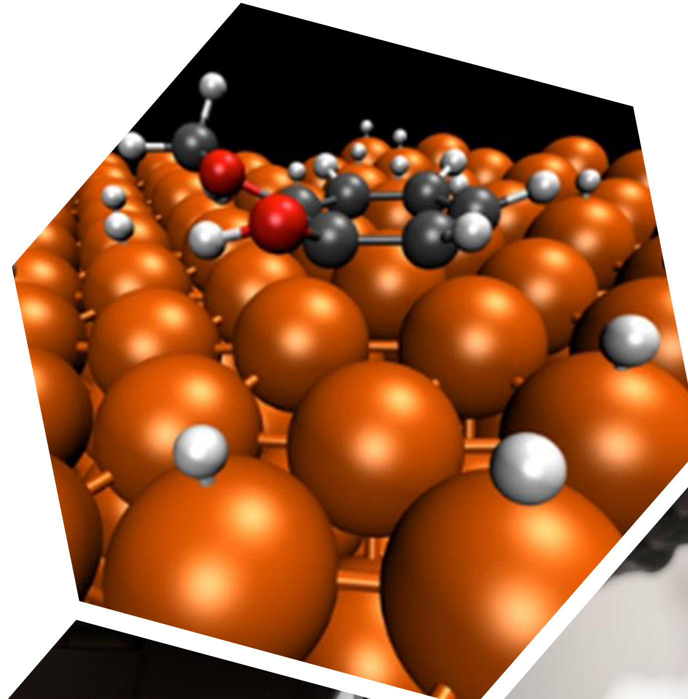
Chemical Catalysis for Bioenergy

DOE BETO 2019 Project Peer Review: CO_2

CO_2 Utilization: Thermo- and Electro-catalytic Routes to Fuels and Chemicals

Jack Ferrell, NREL

March 7th, 2019



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BIOENERGY TECHNOLOGIES OFFICE

ChemCatBio Foundation

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

- **Catalytic Upgrading of Biochemical Intermediates** (NREL, PNNL, ORNL, LANL, NREL*)
- **Catalytic Upgrading of Indirect Liquefaction Intermediates** (NREL, PNNL, ORNL)
- **Catalytic Fast Pyrolysis** (NREL, PNNL)
- **Electrocatalytic and Thermocatalytic CO_2 Utilization** (NREL, ORNL*)

*FY19 Seed Project

Enabling Capabilities

- **Advanced Catalyst Synthesis and Characterization** (NREL, ANL, ORNL, SNL)
- **Catalyst Cost Model Development** (NREL, PNNL)
- **Consortium for Computational Physics and Chemistry** (ORNL, NREL, PNNL, ANL, NETL)
- **Catalyst Deactivation Mitigation for Biomass Conversion** (PNNL)

Industry Partnerships (Directed Funding)

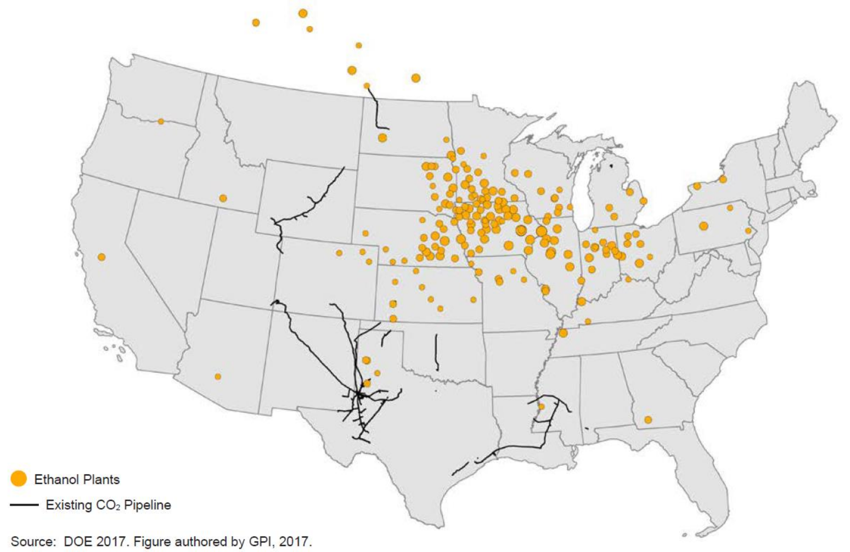
- **Gevo** (NREL)
- **ALD Nano/JM** (NREL)
- **Vertimass** (ORNL)
- **Opus12**(NREL)
- **Visolis** (PNNL)
- **Lanzatech** (PNNL) - Fuel
- **Gevo** (LANL)
- **Lanzatech** (PNNL) - TPA
- **Sironix** (LANL)

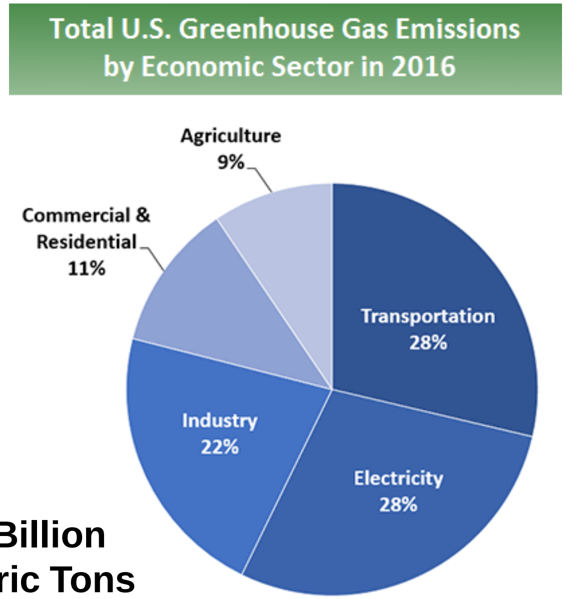
Cross-Cutting Support

- **ChemCatBio Lead Team Support** (NREL)
- **ChemCatBio DataHUB** (NREL)

Problem Statement

- Ethanol biorefineries largest supplier of CO_2 to US merchant gas markets[1]
  - 200M gal/year ethanol plant releases 72 tons CO_2/hr
- Inexpensive, intermittent electricity available & increasing
- ***Opportunity to increase economic viability of biorefineries***
  - Drive down cost (MFSP) of primary product (ethanol)
  - Improve biorefinery carbon utilization
- First CO_2 Utilization technologies will use pure CO_2 waste streams
- Opportunity to develop technologies that will ultimately reach a *much larger market*





6.5 Billion Metric Tons

US EPA, 2018

[1]http://ethanolproducer.com/articles/14122/ethanol

Goal Statement

Goal: *Advance the state-of-the-art (SOA) for both electrochemical and thermochemical conversion of CO_2 via catalyst and electrolyzer development. Provide an assessment of the potential of each route to enhance biorefinery profitability.*

Objectives:

- Identify & rank most desired CO_2 conversion products
  - In collaboration with the Feasibility Study (Schaidle PI)
- Establish experimental baseline based on published results
- Develop catalysts & electrolyzer configurations that outperform baseline (**Target**: 20% reduction in overpotential for C_{2+} products)

Outcome

- Facilitate economic processing of large biorefinery waste stream

Quad Chart Overview

Timeline

- Start: 10/1/2017
- End: 9/30/2020
- 47% Complete

Budget

	Total Costs Pre FY17	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded			354k	1500k

Collaboration within BETO

- *Feasibility Study of Utilizing Electricity to Produce Intermediates from CO_2 and Biomass. 2.1.0.304 (Josh Schaidle PI)*
- *CO_2 Valorization via Rewiring Metabolic Network. 2.3.2.106 (Pin-Ching Maness PI)*
- *Advanced Catalyst Synthesis and Characterization (ACSC). 2.5.4.304 (Susan Habas PI)*

BETO Barriers Addressed

- Ct-E: Improving Catalyst Lifetime
- Ct-F: Increasing the Yield from Catalytic Processes
- Ct-G: Decreasing the Time and Cost to Developing Novel Industrially-Relevant Catalysts

Objective:

- Develop catalysts & electrolyzer configurations that outperform established baseline

End of Project Goal:

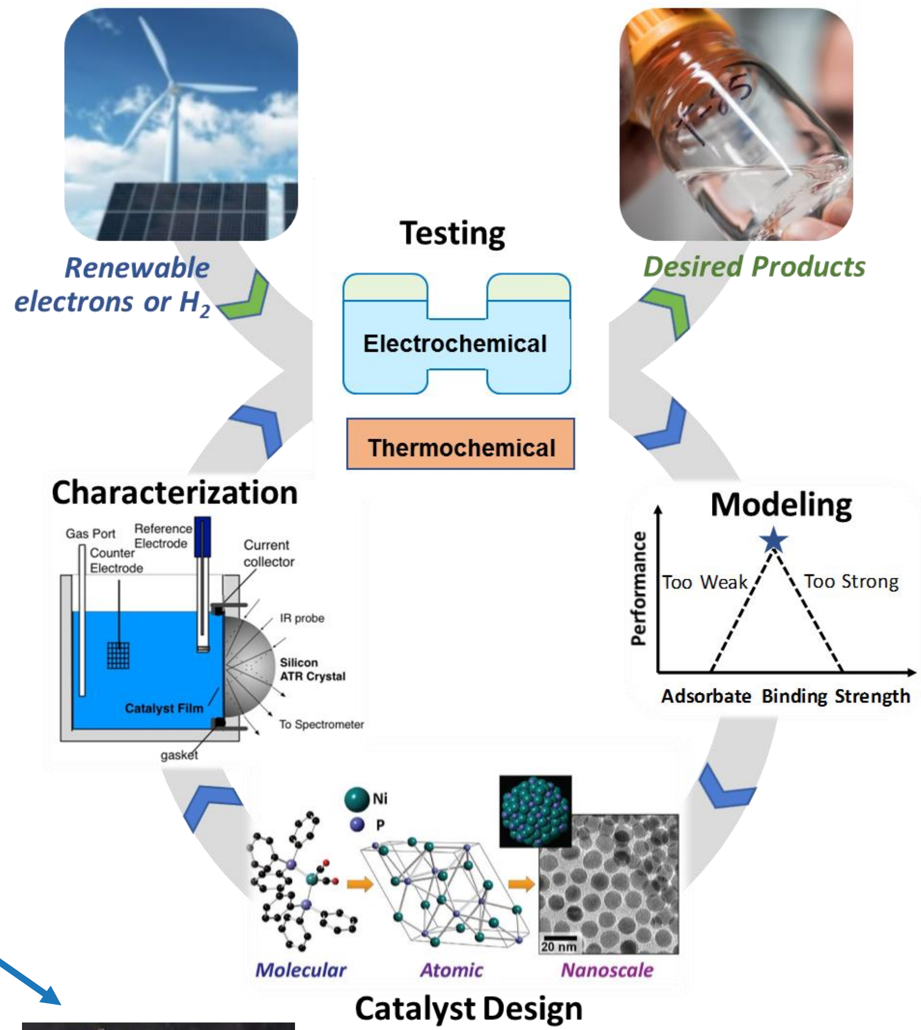
- Demonstrate Enhanced Biorefinery Profitability: For the most promising pathway studied, show how a biorefinery could increase profits from a CO_2 waste stream.

Cross Office Collaboration

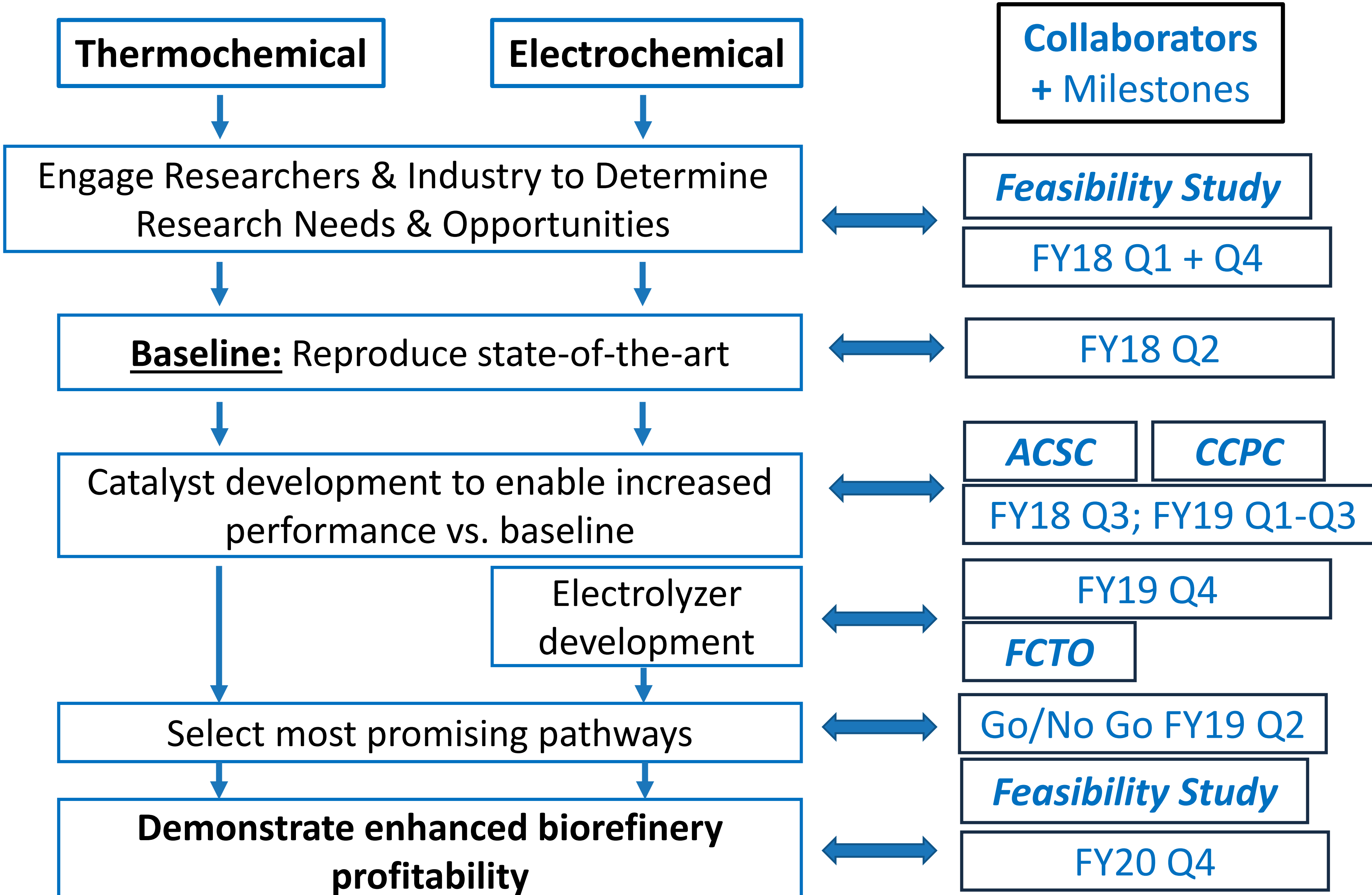
- *Industrially scalable waste CO_2 reduction to useful chemicals and fuels.* **FCTO** (Todd Deutsch PI)

Project Overview

- Catalyst development for two routes
  - <u>Thermochemical</u>
    - Water electrolysis to produce renewable hydrogen
  - <u>Electrochemical</u> (low-temp)
    - Direct use of renewable electricity to drive CO_2 conversion
- Leverage advanced capabilities within ChemCatBio
  - ***Identify, synthesize, characterize, and test new catalysts for CO_2 conversion to desired C_{2+} products***
- Electrolyzer development – existing options insufficient
  - Order of magnitude difference in performance between aqueous cell and electrolyzer with gas-phase CO_2
- Creation of *standard methods for electrocatalyst evaluation* in relevant environment



Management Approach



Technical Approach: Tunable Materials

Top Technical Barriers Identified by Feasibility Study

Electrochemical

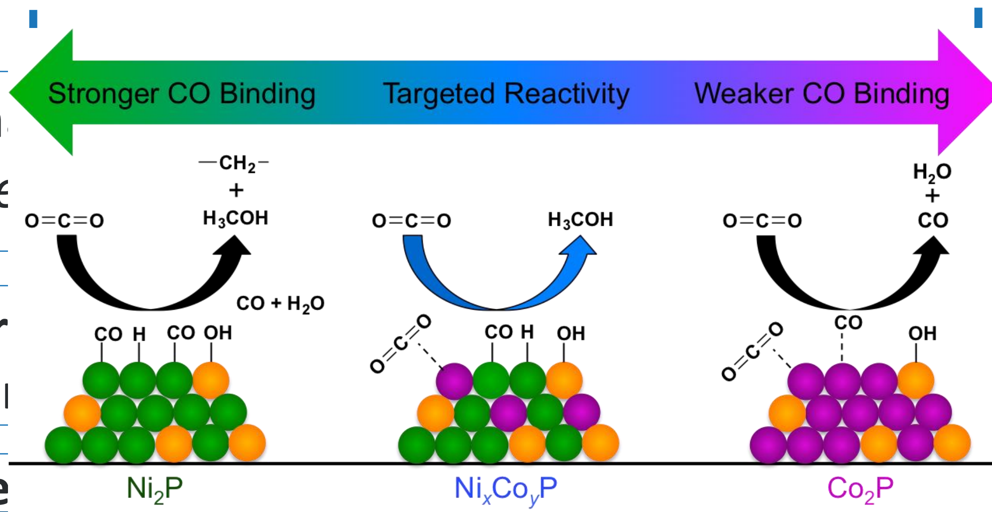
- High overpotential, low energy efficiency
- Poor selectivity to individual C_{2+} products
- Low single-pass CO_2 conversion

Thermochemical

- Process Intensification & Scale-down
- Developing multi-functional water and CO_2 tolerant catalysts

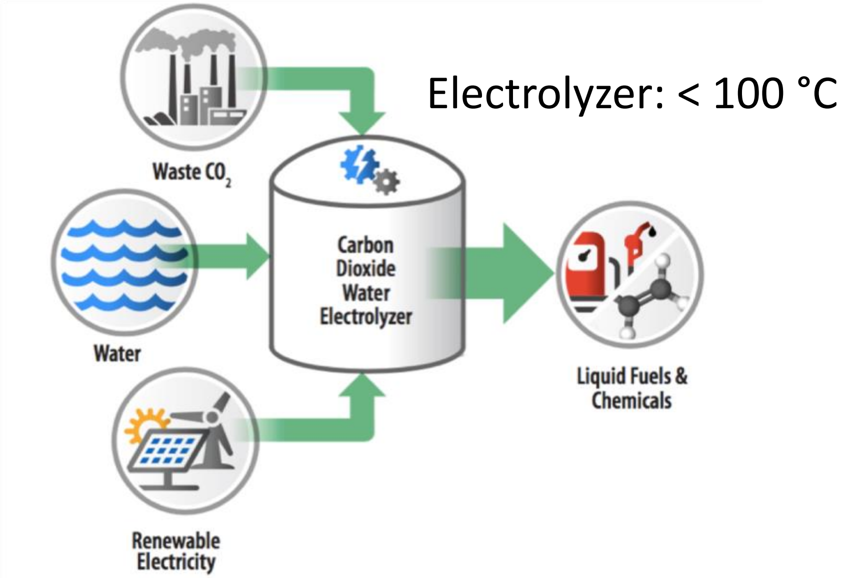
<u>*Hypothesis*</u>: Tun *or stabilization of key reaction inte* ance catalysts

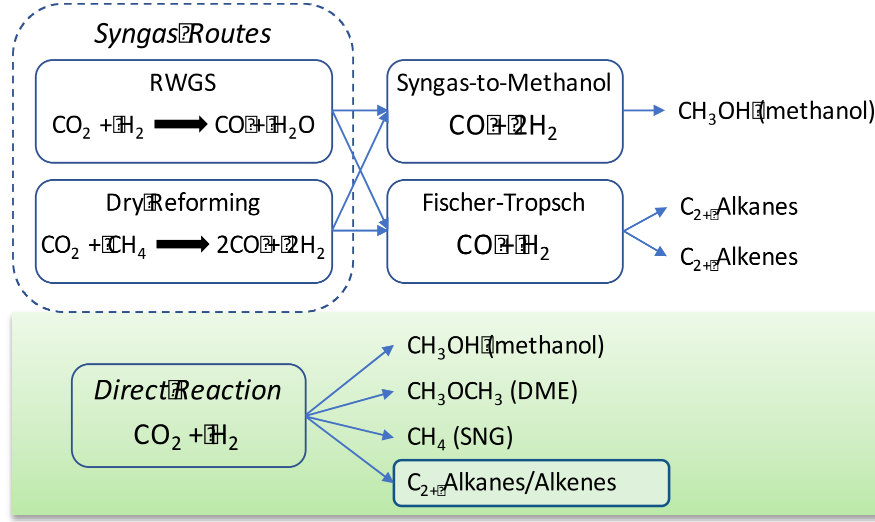
- **Identify pr** nal Physics & Chemistr
- **Synthesize** d Synthesis



Success Factor: Develop catalysts that advance state-of-the-art by addressing identified technical barriers

Technical Approach





Electrochemical

- Targeting formation of C_{2+} products with high efficiency & selectivity

Thermochemical

- Targeting direct formation of C_{2+} products via multi-functional catalysts

Success Factors

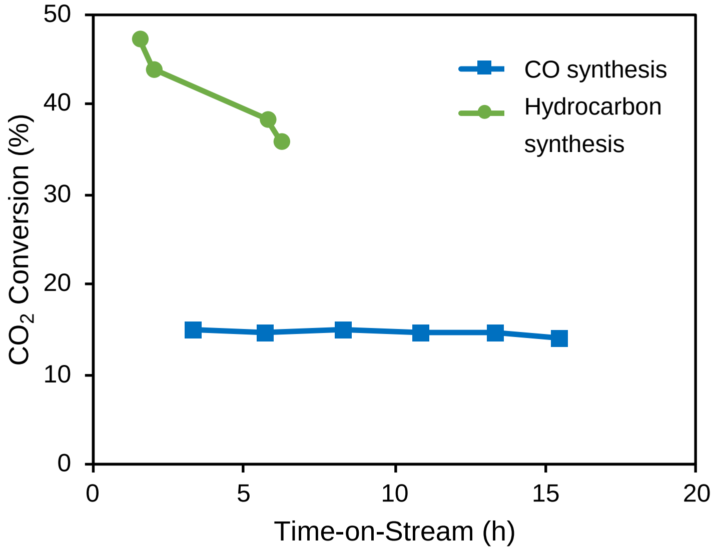
- ***Electrochemical***: Develop catalysts & electrolyzers that enable long-term and efficient operation at high currents
- ***Thermochemical***: Develop catalysts that enable process intensification & scale-down

Progress: Thermochemical

- Bulk MoC is state-of-the-art for thermochemical CO_2 conversion
- ***Reproduced literature values*** with NREL catalysts @ two conditions

Temp. (°C)	Press. (MPa)	WHSV (h^{-1})	H_2:CO_2 ratio	Conv. (%)	Selectivity (mol%) CO	CH_4	C_2H_6	C_3H_8	Ref.
CO synthesis									
300	0.1	23.6	2	14.8	93.3	4.8	1.5	0.3	
300	0.1	23.6	2	8.7	93.5	6.5	–	–	1
Hydrocarbon synthesis									
300	2	3.9	5	36.0	6.4	68.9	17.5	5.1	
300	2	3.9	5	24	28	45	13	9	2

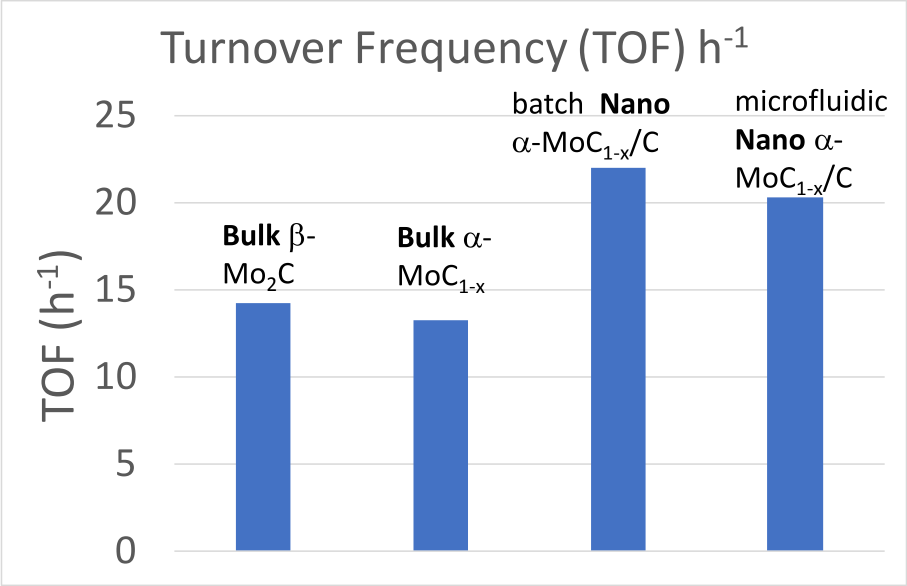
- Despite good RWGS activity, *MoC binds CO_2 too strongly*
  - Cokes during C-C coupling
- CH_4 main hydrocarbon product
  - Undesirable terminal product

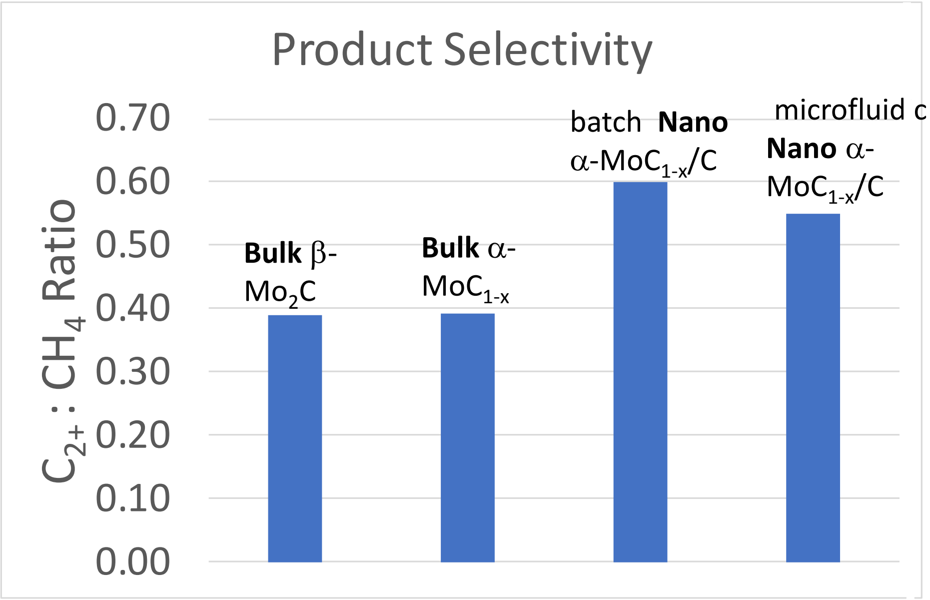


[1] Porosoff, et al., *Angew. Chem. Int. Ed.*, 2014, 53, 6705 [2] Xu, et al., *Catal. Lett.*, 2015, 145, 1365

Progress: Thermochemical - Nanoscale Carbides

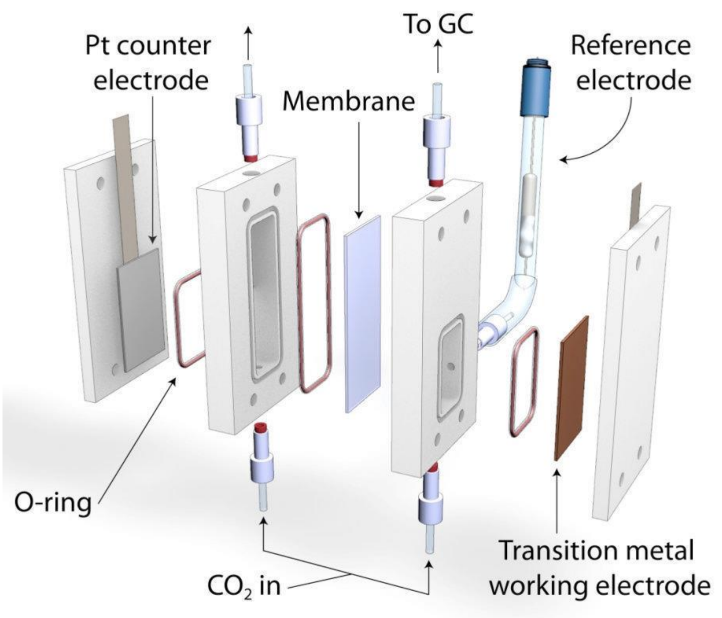
- **Nanoscale carbides promising: more active, more selective**
- Bulk carbides show slight deactivation
- Nanoscale MoC shows increase in conversion with TOS
- *Nanoscale MoC more active per Mo site*
- Bulk β-Mo_2C favors complete hydrogenation to CH_4
- *Nanoscale catalysts enhance selectivity to C_{2+} products relative to CH_4*



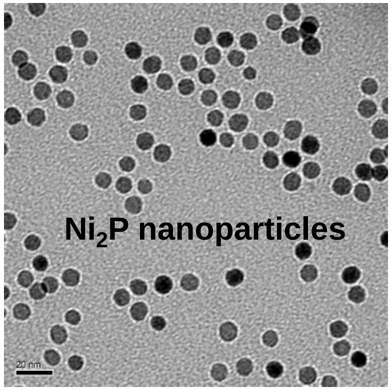


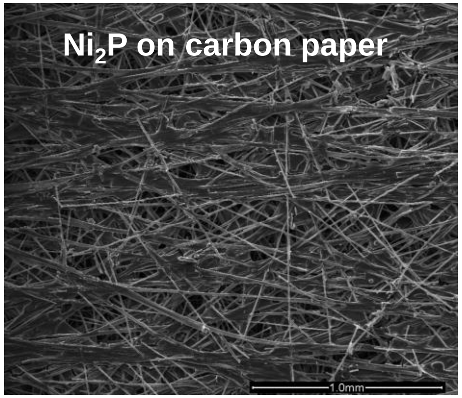
Progress: Electrochemical - Metal Phosphides

- **Successfully reproduced SOA results with Cu[1]**
  - 10 mA/cm^2 total current @ 1.1 V (vs. RHE)
    - *Low current typical of aqueous systems*
  - Built electrochemical cell to match SOA
    - Small electrolyte volume, large electrodes – aid in product detection



- Recent results with phosphides promising – C_3-C_4 products[2]
- **Ni_2P** electrochemical testing
  - Supported on carbon paper
  - $KHCO_3$ electrolyte
    - 0.1 M and 0.5 M

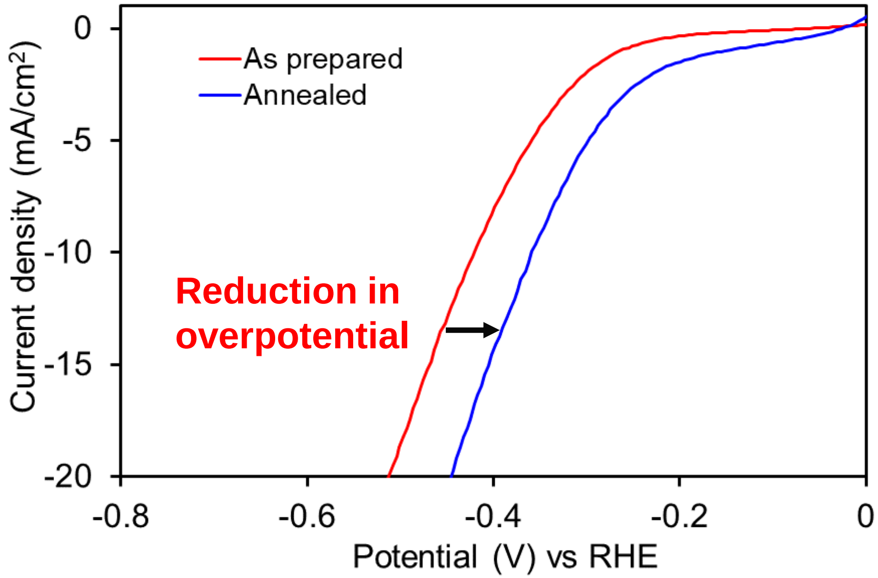




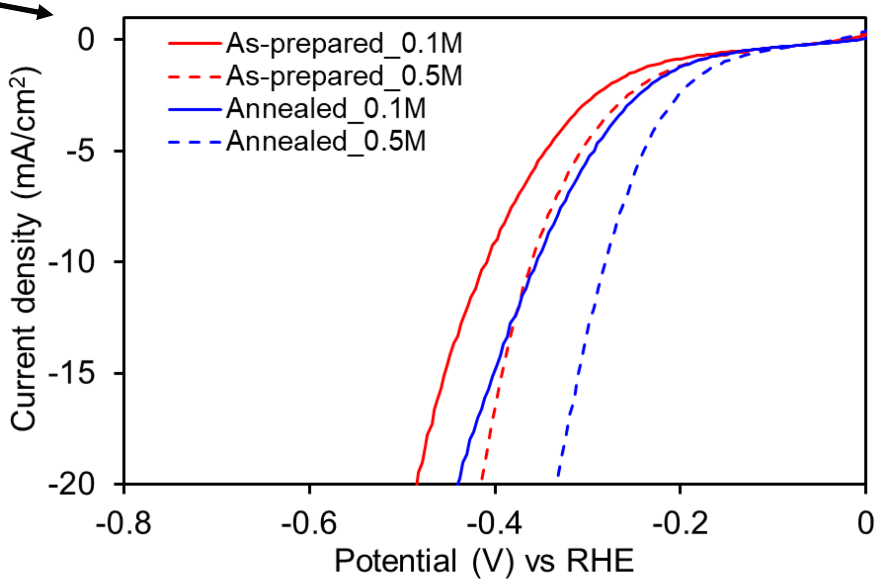
[1]Jaramillo et. al., *Energy Env. Sci.*, 2012, 5, 7050 [2]Dismukes et. al., *Energy Env. Sci.*, 2018, 11, 2550

Progress: Electrochemical - Nickel Phosphide

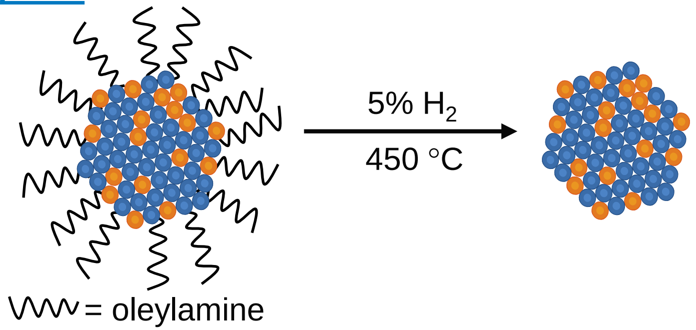
- Ni_2P supported on carbon paper is electrochemically active
- **Annealing** (removal of ligands) has positive effects on electrochemical activity
  - *Reduction in overpotential*
  - *Increase in electrochemically-active surface area*
  - *Reduction in charge transfer resistance*



- Effect of **$KHCO_3$ concentration**
  - *Reduction in overpotential* for both Ni_2P catalysts in more concentrated electrolyte

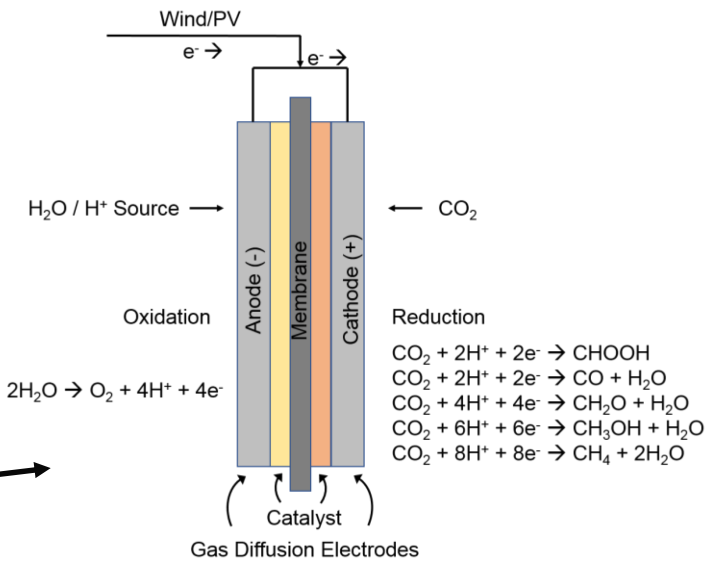


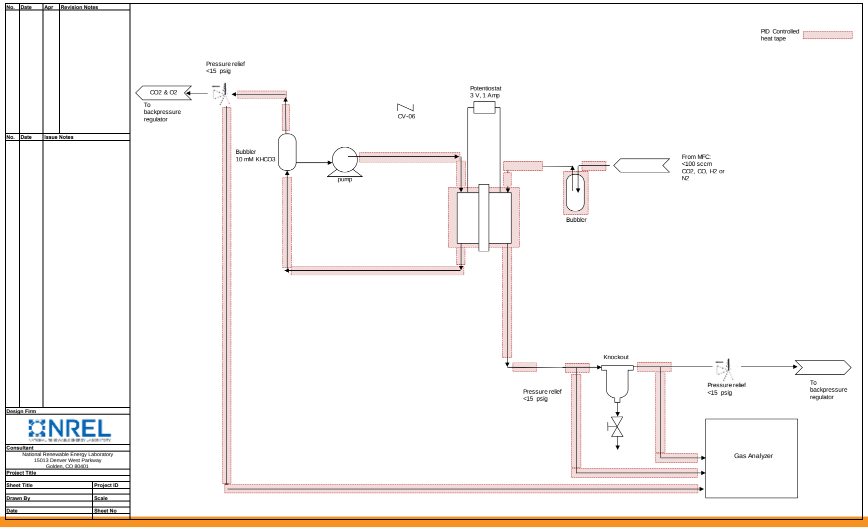
Ni$_2$P annealed to remove insulating organic surface ligands



Progress: Electrolyzer Development

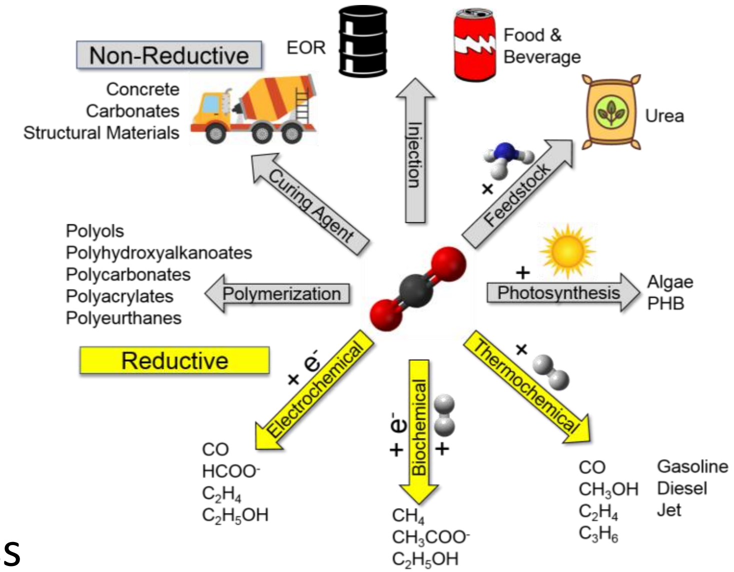
- Widely-accepted that any scalable electrolyzer *must operate on gas-phase CO_2*
  - Aqueous systems mass transfer limited (~20 mA/cm^2)
  - *Aqueous results may not translate to electrolyzer*
- **Focusing on membrane-electrode-assemblies (MEAs)**
  - Polymer membrane + catalysts
  - Stacked together for scaleup
- **Design/Retrofit/Build electrolyzer**
  - Experiment in ventilated enclosure
  - Interface analytical
  - Liquid circulation





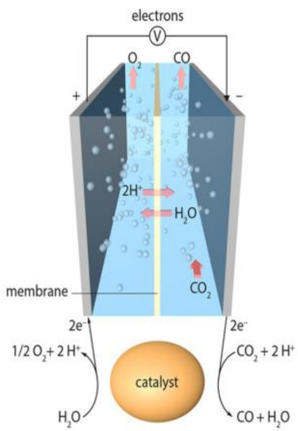
Relevance

- ***Expanding BETO feedstock slate***
  - BETO actively investigating strategies for adding value to waste streams such as CO_2
- ***Addressing top technical barriers*** identified by Feasibility Study for C_{2+} products
  - Electrochemical: New catalysts to reduce overpotential & increase selectivity, new electrolyzer architectures
  - Thermochemical: New catalysts to enable process intensification & scale-down
- Will assess impact of new catalysts on MFSP
- *Tunable multi-functional materials* to advance state-of-the-art
  - Thermochemical: carbides to enable process intensification
  - Electrochemical: phosphides + electrolyzer development

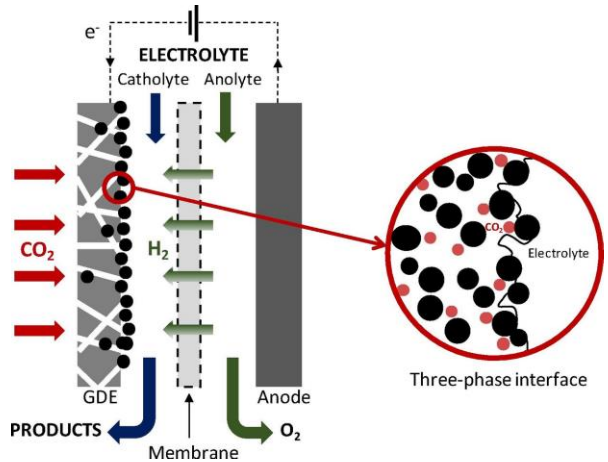


Relevance

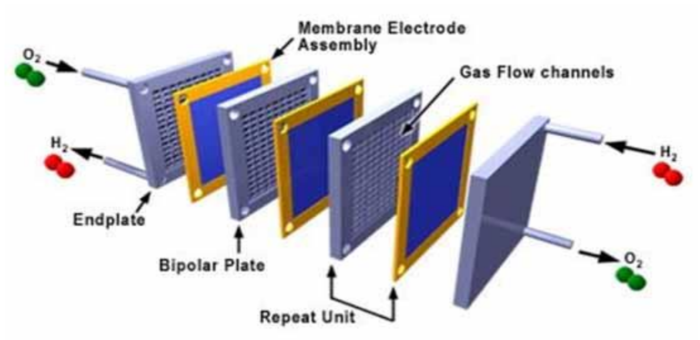
Aqueous

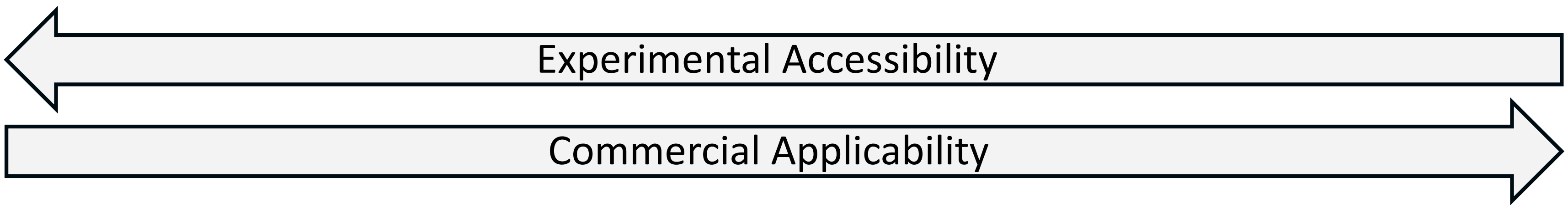


Gas Diffusion Electrode (GDE)



Membrane Electrode Assembly (MEA)





- $[CO_2]$ ~ 35mM in aqueous solution
- Currents to ~1-20 mA/cm^2
- *Bulk of catalyst development performed in aqueous systems*

- GDE with flowing liquid electrolytes
- Currents to 100's mA/cm^2
- *Scalable with flowing electrolytes? Long-term operation?*

- Gas-phase operation
- Currents to 100's mA/cm^2
- Easily scalable into a stack configuration
- ***No consensus on CO_2 MEA***
  - Alkaline, proton exchange, or bipolar membrane
  - Buffer layers to control pH

https://science.energy.gov/bes/highlights/2012/bes-2012-12-b/
https://ars.els-cdn.com/content/image/1-s2.0-S0021951715003
http://liliumco.com/images/product_b.jpg784-gr1_lrg.jpg

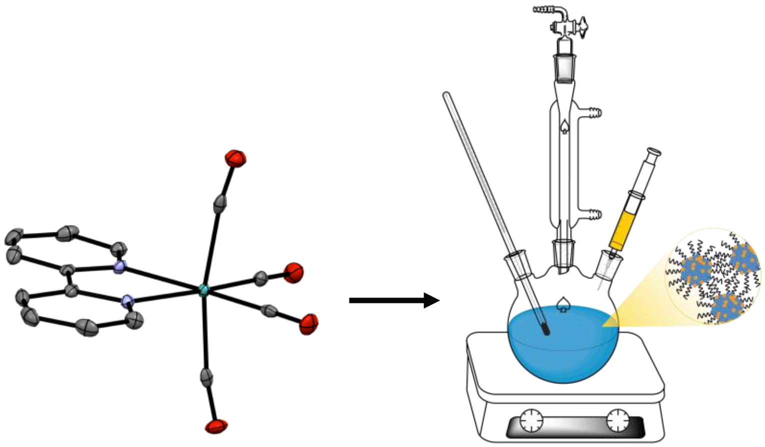
Nature Catalysis 1 (2018) 32-39

https://dioxidematerials.com/technology/co2-electrolysis/

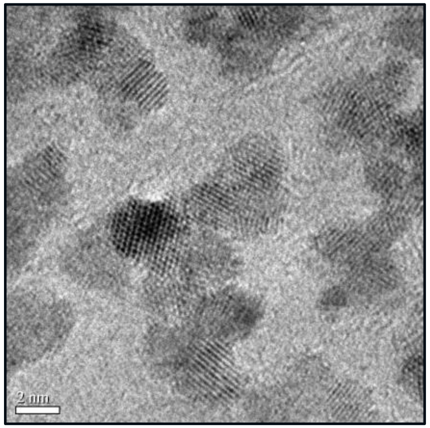
Future Work: Thermochemical

- ***Inform next-generation of catalysts for CO_2 conversion***
- Catalyst development for direct C_{2+} hydrocarbons & olefins
  - Tunable nanoscale carbides
    - Control size, shape, composition
    - Tunable hydrogenation & acidic sites
    - Alloying & Metal modification
    - High surface area supports (C, SiO_2, TiO_2, Al_2O_3)
- Investigate catalyst under working conditions
  - *In-situ* or post-reaction characterization to monitor catalyst changes during CO_2 conversion
  - Correlate catalyst features with performance
  - *FY19 Q3 Milestone*

Leverage ACSC Capabilities

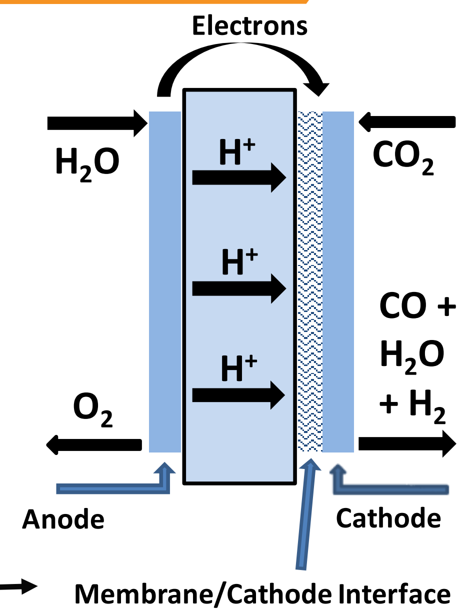


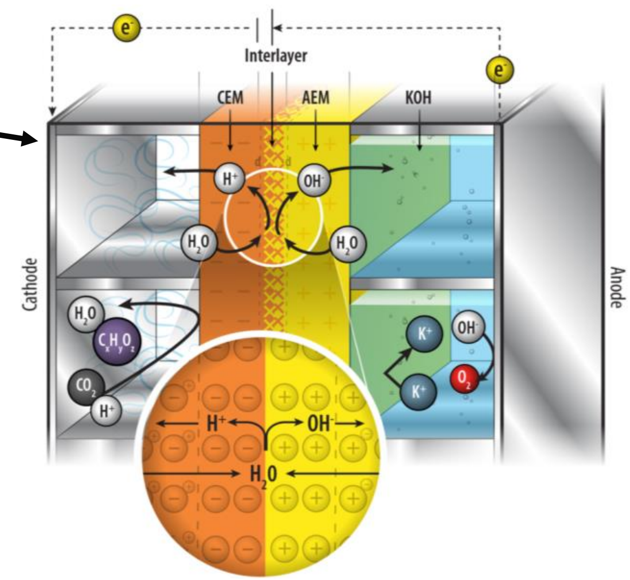
Nanoscale α-MoC_{1-x}



Future Work: Electrochemical

- <u>Electrocatalyst development</u>
  - Metal phosphides & mixed metal phosphides (*FY19 Q2 Milestone*)
  - Incorporation of promising catalysts into MEAs
- <u>Electrolyzer development</u>
  - Test alkaline and proton exchange membrane MEAs (*FY19 Q4 Milestone*)
    - Effect of different buffer layers
  - Compare with bipolar membrane MEAs
    - In collaboration with FCTO (Deutsch PI)
  - Explore economic tradeoffs in collaboration with the Feasibility Study (2.1.0.304, Schaidle PI)
  - *Testbed: reproducible system for catalyst evaluation in realistic environment*
    - *Standard methods for electrocatalyst testing*





Summary

Approach: CO_2 Utilization has potential to increase biorefinery profitability

- Both ***electrochemical*** and ***thermochemical*** routes under investigation
  - Catalyst development required to advance both
  - Leveraging capabilities within ChemCatBio & NREL

Progress: Reproduced state-of-the-art results

- Thermochemical: nanoscale carbides have advanced state-of-the-art
- Electrochemical: actively researching novel phosphides & new electrolyzer architectures

Relevance: Engaged CO_2 community to determine research needs

- Executing research to address needs and ***advance state-of-the-art***
- *Opportunity for biorefineries to be first players in growing field*

Future Work: Continue catalyst & reactor development

- Economic projections (with Feasibility Study) to remain relevant

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CCPC

www.cpcbiomass.org

ChemCatBio
Chemical Catalysis for Bioenergy

Energy Materials Network
U.S. Department of Energy

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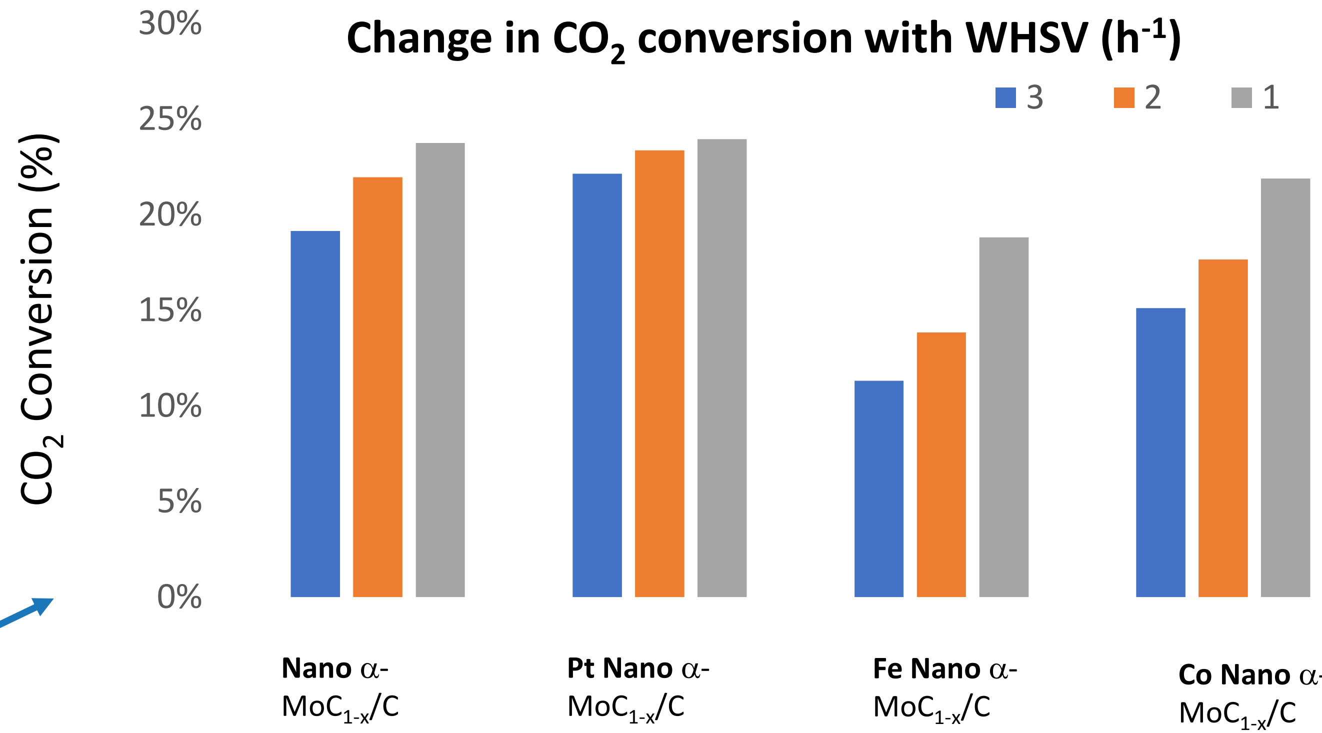
Questions?

ChemCatBio
Chemical Catalysis for Bioenergy

Progress: Thermochemical - Metal-Modified Nanoscale Carbides

- **Pt, Fe & Co** metal-modifiers
- Metal-modified catalysts *reach stable performance more quickly*



- <u>Activity</u>: Pt/MoC > MoC > Co/MoC > Fe/MoC
- Pt/MoC & MoC operate near RWGS equilibrium (~23% conversion)
- Consistent selectivity change with CO_2 conversion – *sequential reaction path*
  - CO_2 → CO → Hydrocarbons