Electrochemical Conversion of Carbon Dioxide to Alcohols

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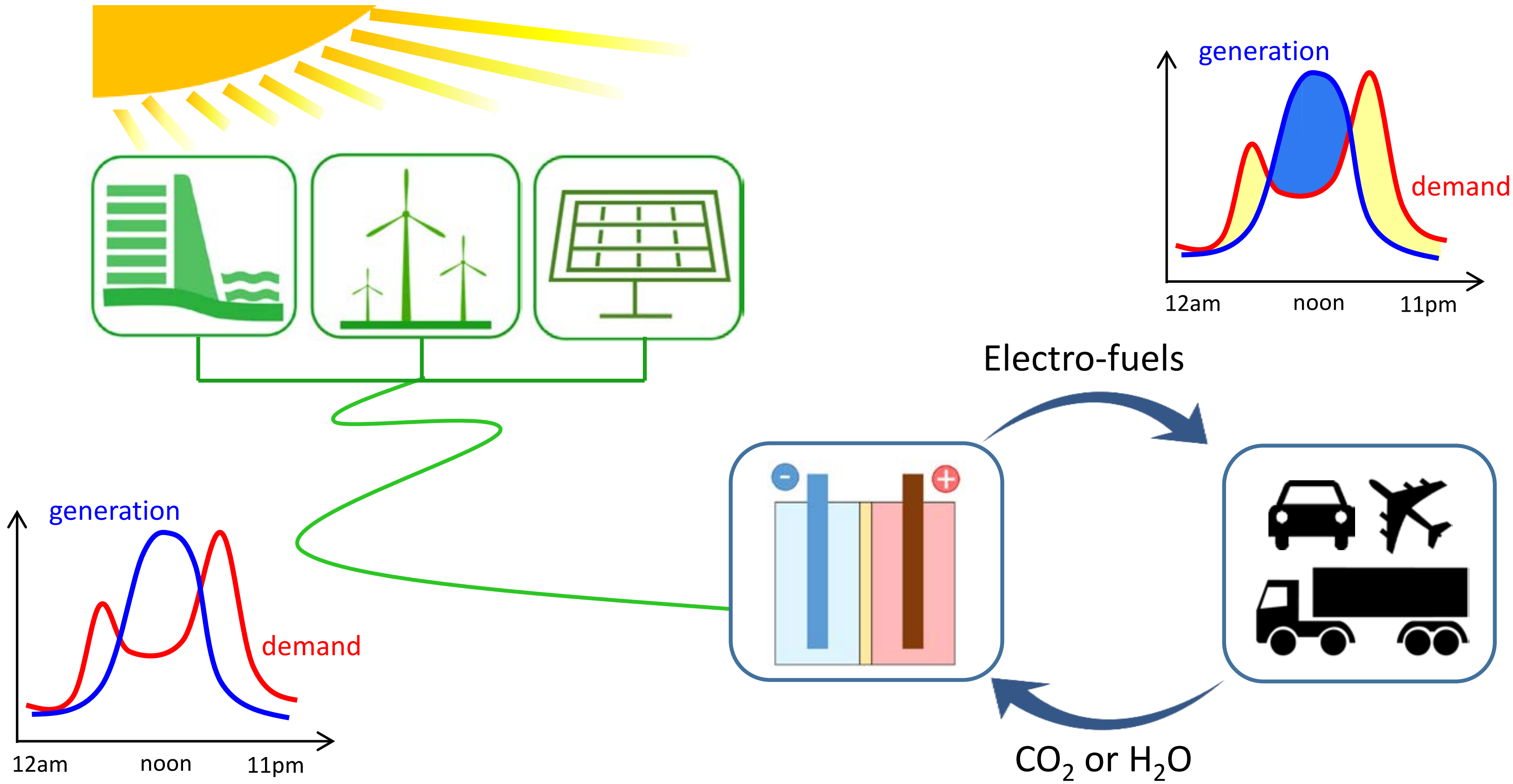
University of Delaware, Newark, DE (USA)

DOE/NETL Project Kick-Off Meeting, Morgantown, WV

July 10, 2017

My research



Representative publications:

JACS 139, 3774-3783 (**2017**); JACS 139, 1885-1893 (**2017**); Nano Energy 29, 439-456 (**2016**); ACS Catal. 5, 4586-4591 (**2015**); ACS Catal. 5, 4293-4299 (**2015**); Nat. Commun. 6:6567 (**2015**); Nat. Commun. 5:3242 (**2014**).

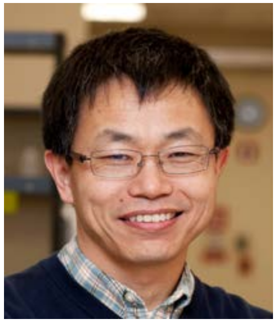
Faculty at UD (CO_2 related)

Feng Jiao
Associate Professor
Chemical & Biomolecular Engineering

Expertise:
Electrocatalysis, CO_2 Utilization, Nanomaterials, Batteries.

Raul Lobo
Claire D. LeClaire Professor
Chemical & Biomolecular Engineering

Expertise:
Heterogeneous Catalysis, CO_2 Capture, Zeolites, Biomass.



Yushan Yan
Distinguished Engineering Professor
Chemical & Biomolecular Engineering

Expertise:
Electrocatalysis, Polymer Electrolyte Membranes, Flow Batteries, Zeolites.

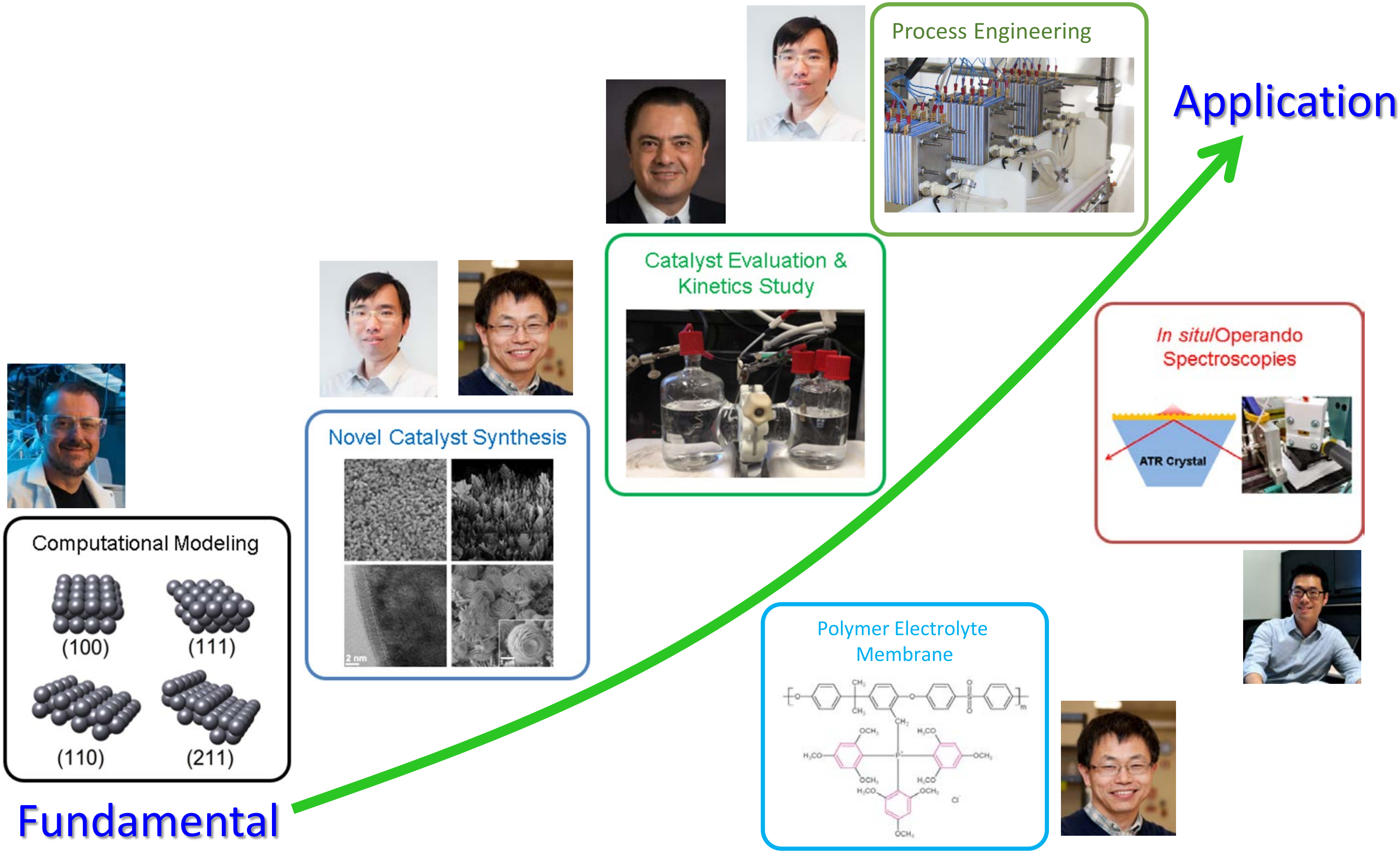
Dionisios G. Vlachos
Allan and Myra Ferguson Professor
Chemical & Biomolecular Engineering

Expertise:
Heterogeneous Catalysis, Computational Modeling, Biomass.

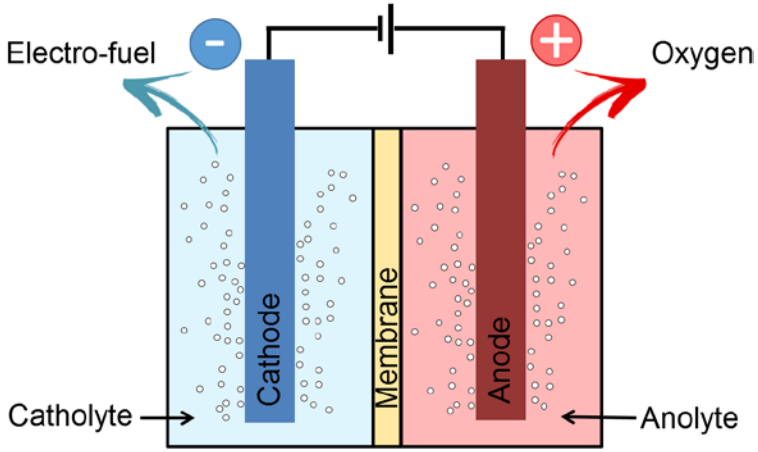
Bingjun Xu
Assistant Professor
Chemical & Biomolecular Engineering

Expertise:
Electrocatalysis, Spectroscopies, Thermochemical Cycles.

Key capabilities: CO_2 capture and utilization



Introduction to CO_2 Electrolysis



Reaction	E (V) vs. SHE
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	-0.61
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	-0.53
$CO_2 + 4H^+ + 4e^- \rightarrow C + 2H_2O$	-0.20
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$	-0.48
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	-0.38
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0.24

Technical Challenges:

❖ **Selectivity**
– multiple pathways with similar potentials

❖ **Overpotential** (energy penalty)
– additional energy cost

Key half reactions:

Oxidation: $2H_2O \longrightarrow 4H^+ + 4e^- + O_2$

Reduction: $\boxed{CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O}$

or $2H^+ + 2e^- \longrightarrow H_2$

Carbon monoxide:

✓ 2-electron process
– low electricity consumption

✓ Gas at ambient conditions
– easy to separate from liquid

✓ Important feedstock for existing chemical processes

✓ High selectivity (>90%, Ag) can be achieved.

Other products:

❖ Formate/formic acid (80%, Sn)

❖ Ethanol (15-20%, Cu)

❖ Propanol (15-20%, Cu)

❖ Acetaldehyde (20-30%, Cu)

1) Hori, in Modern Aspects of Electrochemistry. (Springer, New York, 2008), vol. 42, pp. 89-189.
2) Jiao *et al*. Nano Energy, 2016.

Electrocatalysts: CO_2 to Ethanol

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad E^0 = -0.10\ V$$

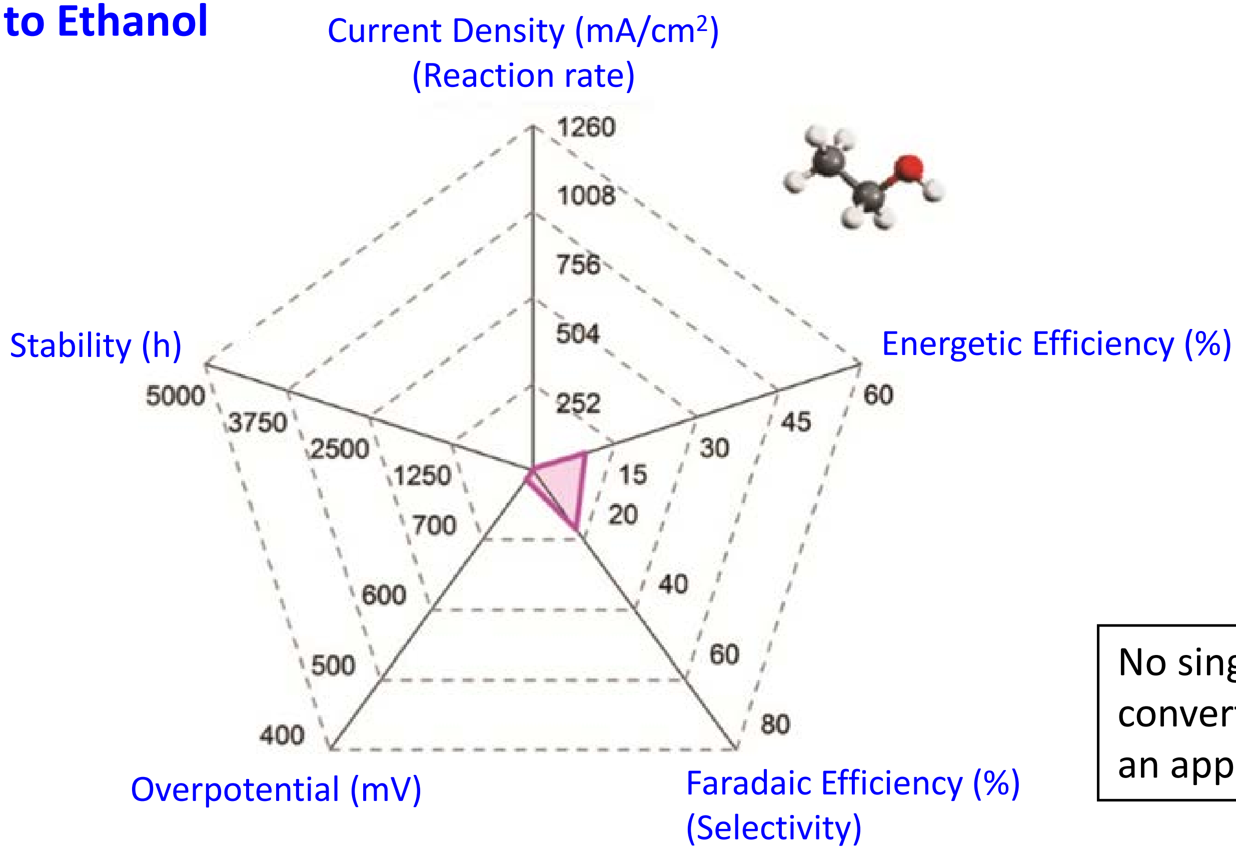
$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad E^0 = 0.17\ V$$

$$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O \qquad E^0 = 0.09\ V$$

Liquid products (alcohols) are ideal:

- High volumetric energy density, portability
- Valuable, easily incorporated in current infrastructure

CO_2 to Ethanol



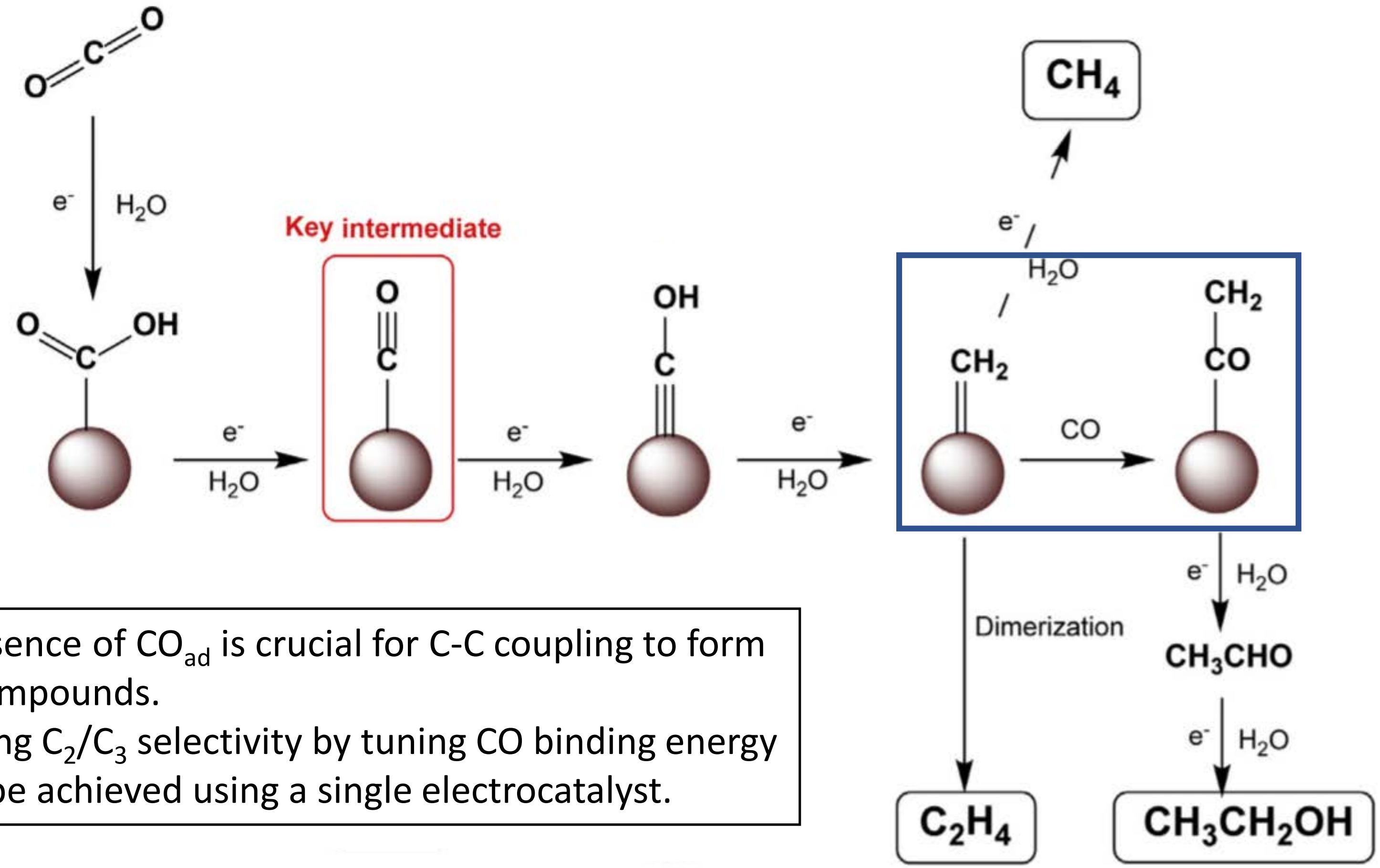
No single electrocatalyst can convert CO_2 into ethanol with an appreciable performance.

Javier Perez-Ramirez et al. *Green Chemistry.* 2015. pp 5114-5130

CO_2 to Alcohols

Copper is the only monometal that catalyzes CO_2 reduction to hydrocarbons in aqueous.

Proposed mechanism:



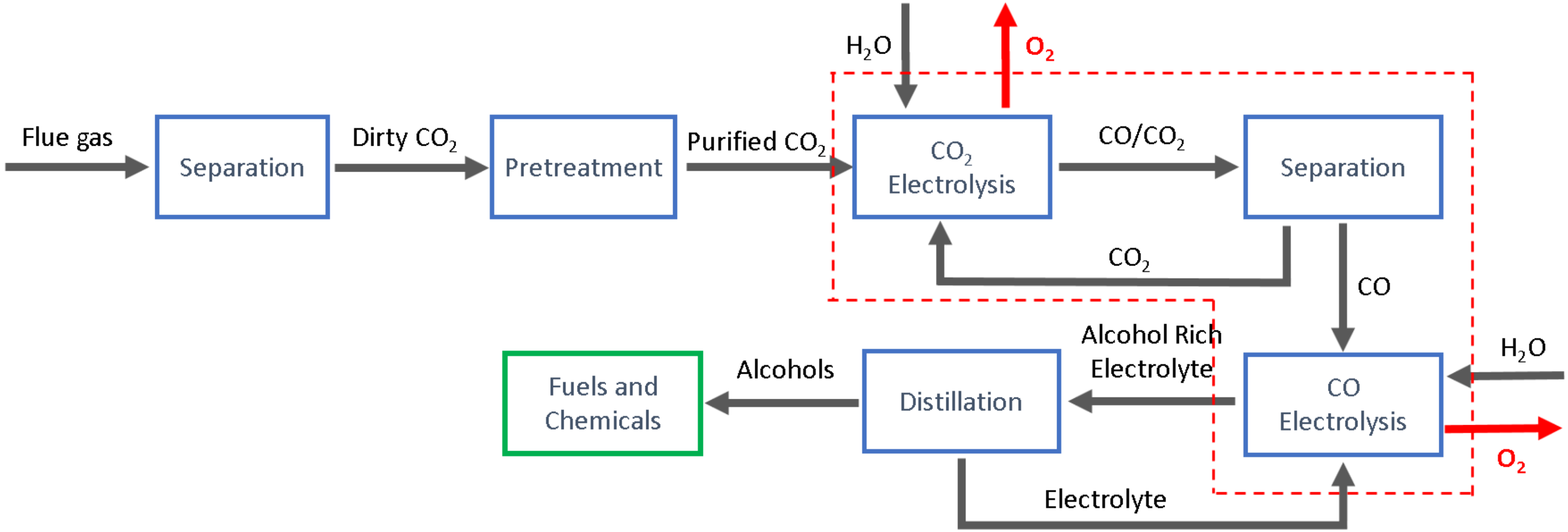
- The presence of CO_{ad} is crucial for C-C coupling to form C_2/C_3 compounds.
- Enhancing C_2/C_3 selectivity by tuning CO binding energy cannot be achieved using a single electrocatalyst.

Sichao Ma et al. *Journal of Power Sources,* pp. 219-228, 2016.

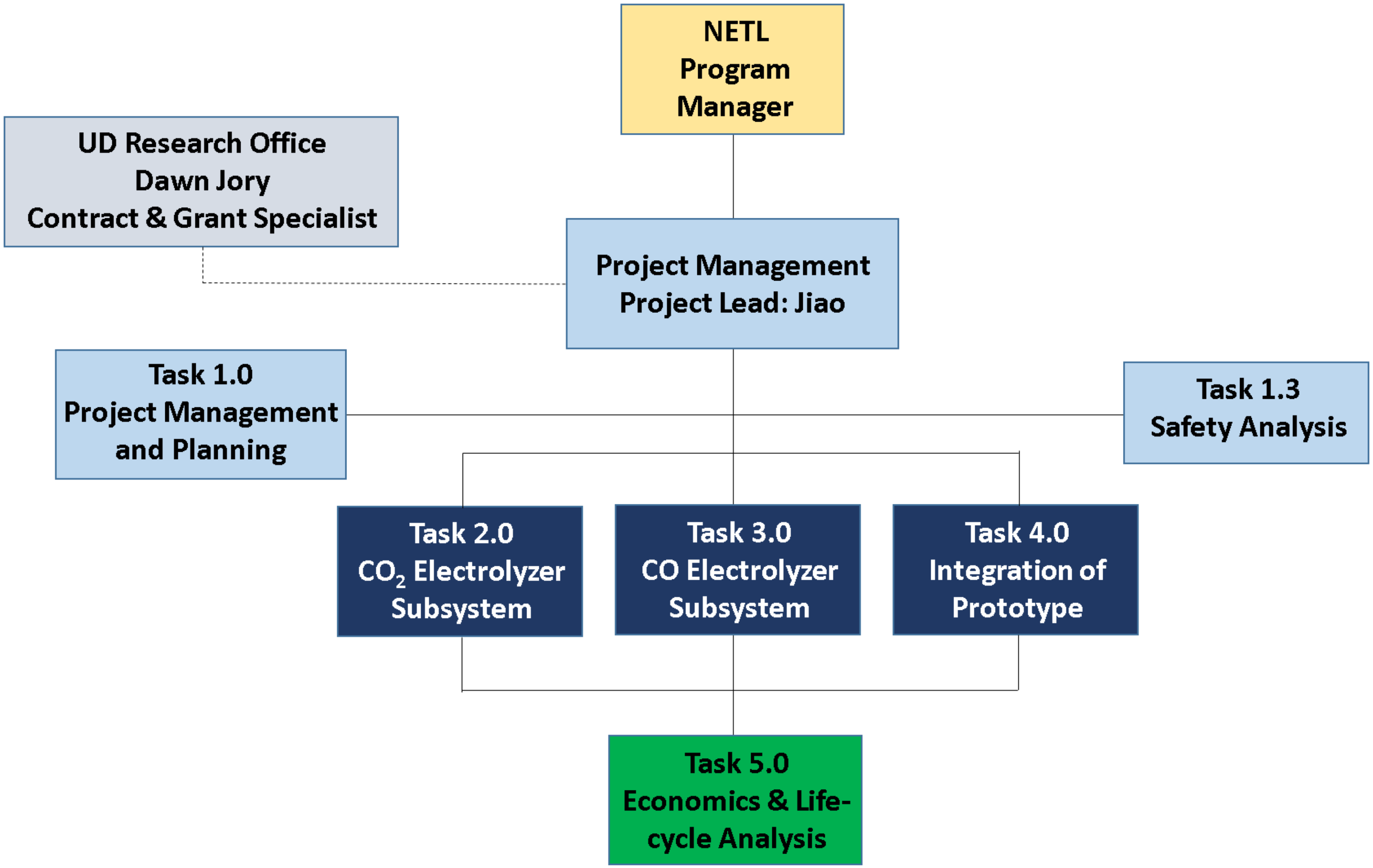
Project Objectives and Approach

1) Development of critical components for an electrochemical system that is able to convert CO_2 into C_2/C_3 alcohols
2) Demonstration of key functions of an integrated electrochemical system for CO_2 conversion using flue gas from coal-fired power plants
3) Full analysis of economics and life-cycle of the CO_2 electrolysis technology for CO_2 emissions mitigation from coal-fired power plants

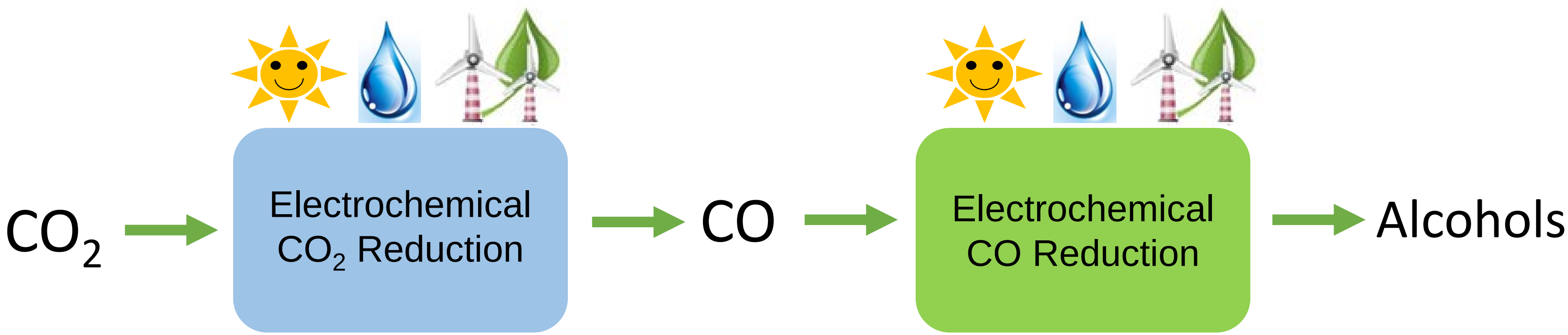
Our Approach:

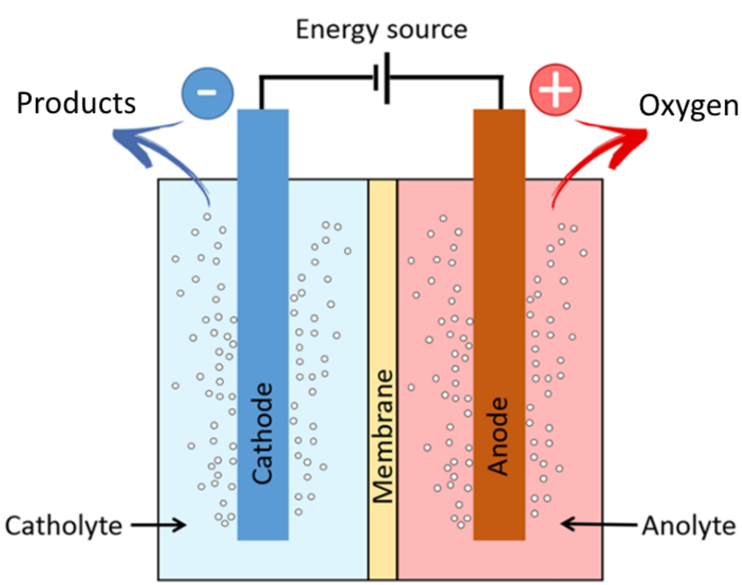


Project Management



Proposed Two-stage Process and its Chemistry





Subsystem: CO_2 electrolyzer

Cathode reaction: $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$

Anode reaction: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

Overall reaction: $2CO_2 \rightarrow 2CO + O_2$

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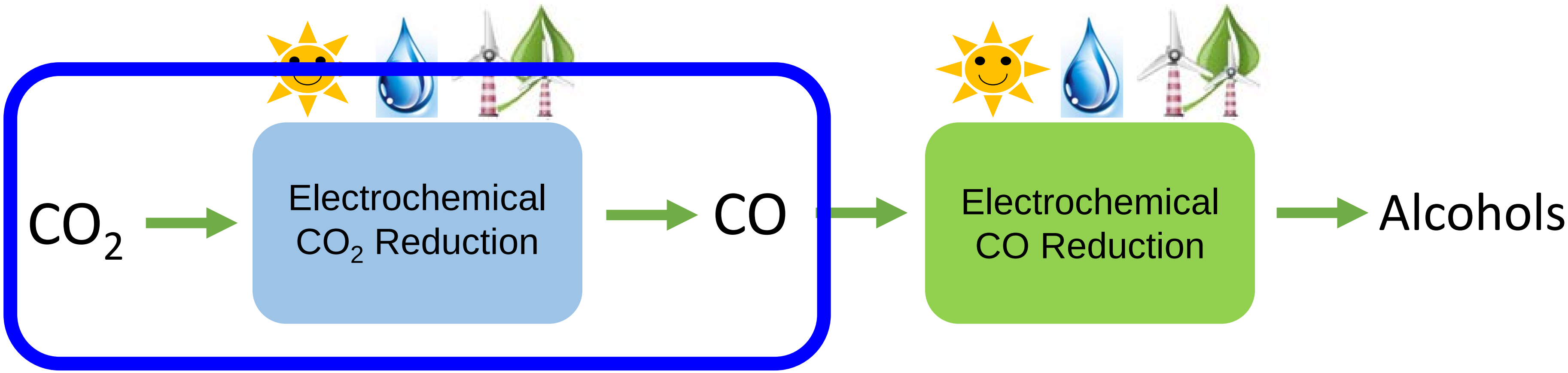

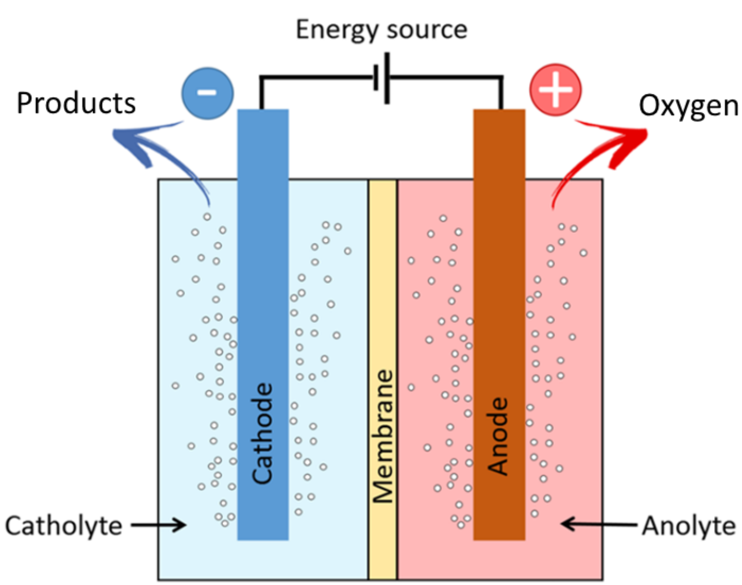

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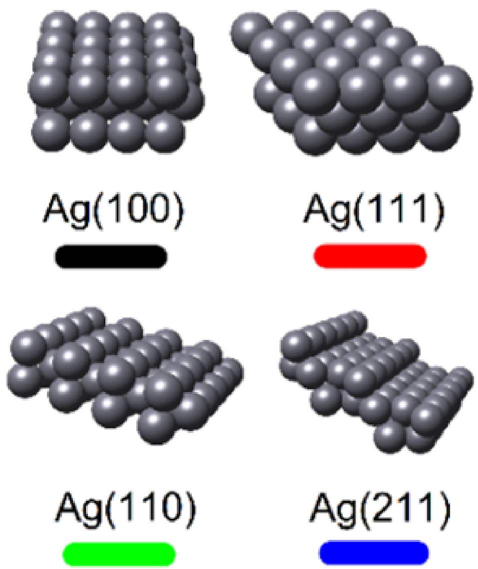
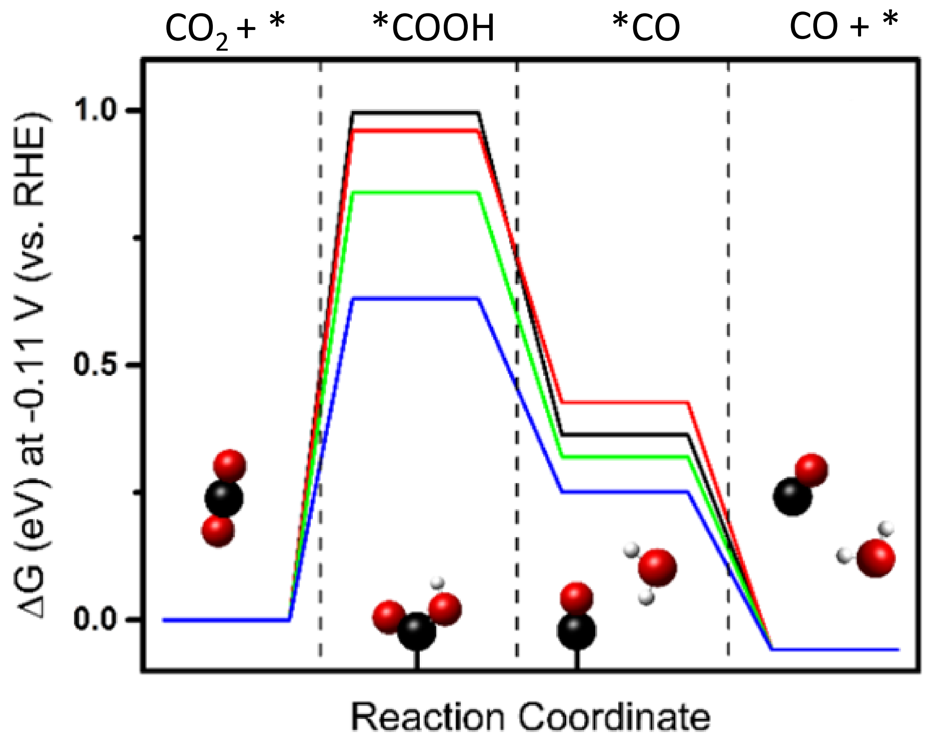
Silver electrocatalyst for CO_2 reduction

- Highly selective for CO_2 to CO conversion
- Ag ($15/oz.) is cheaper than Au ($1162/oz.)
- Stable in aqueous electrolytes

CO:
Ag, Au, Zn

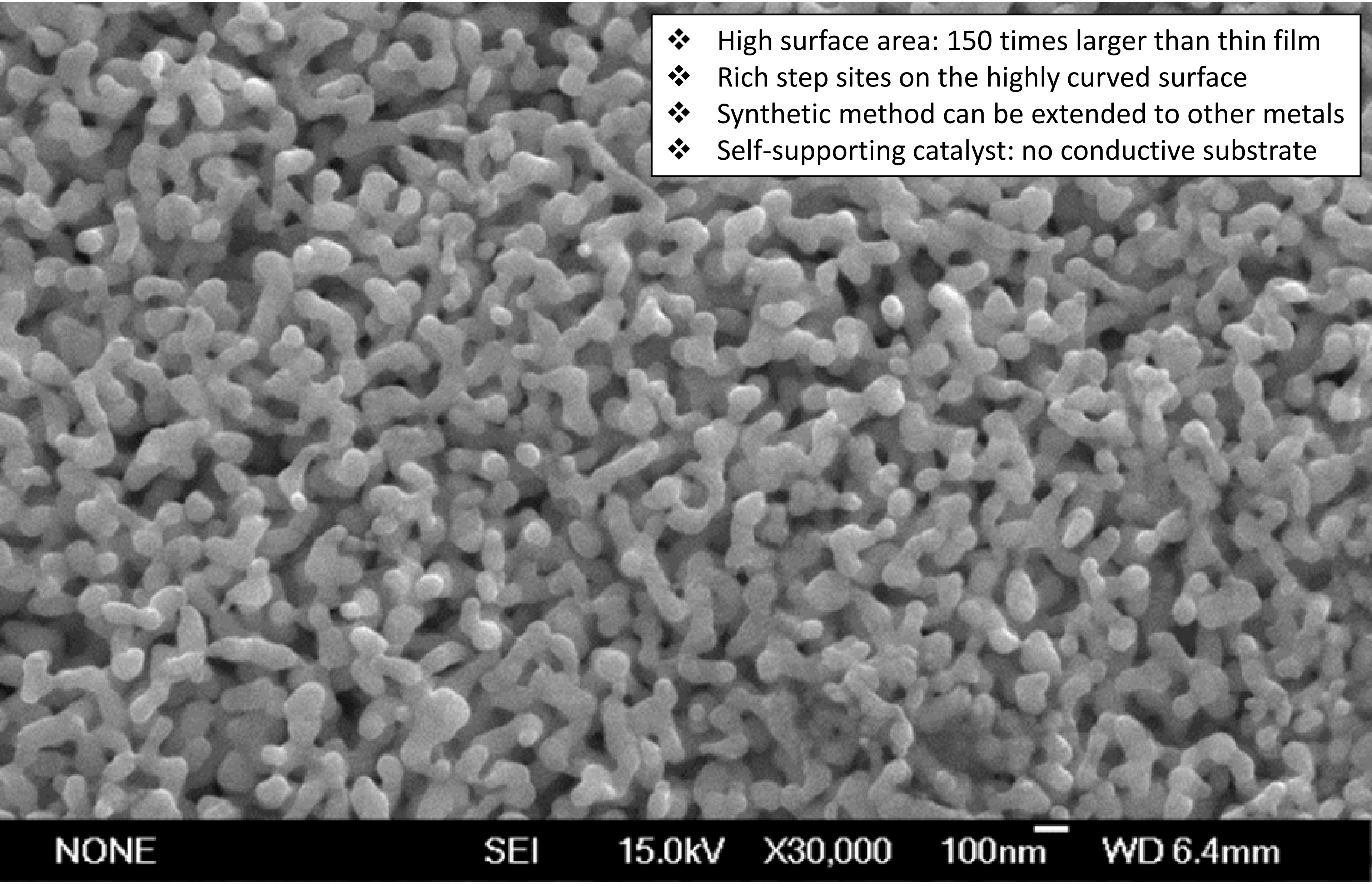




A step surface of Ag is more favorable for electrochemical CO_2 reduction.

Rosen, Hutchings, Lu, Rivera, Zhou, Vlachos, & Jiao* *ACS Catalysis* 5, 4293 (**2015**).

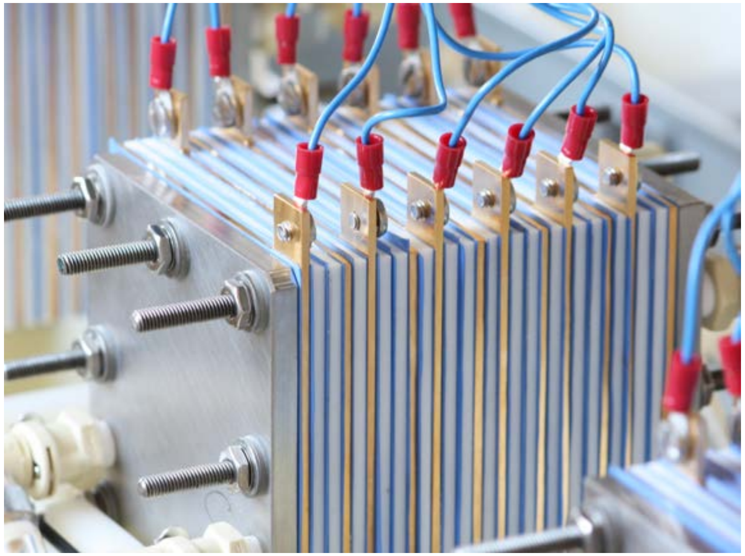
- High surface area: 150 times larger than thin film
- Rich step sites on the highly curved surface
- Synthetic method can be extended to other metals
- Self-supporting catalyst: no conductive substrate

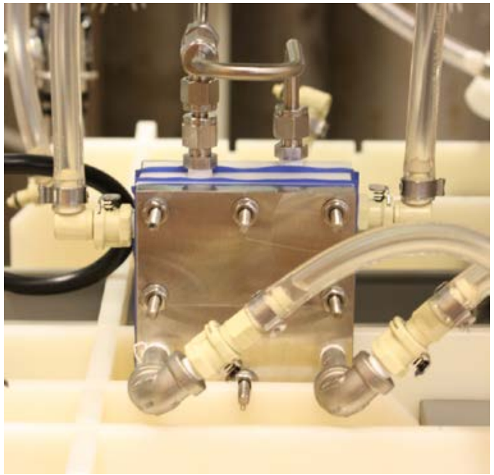


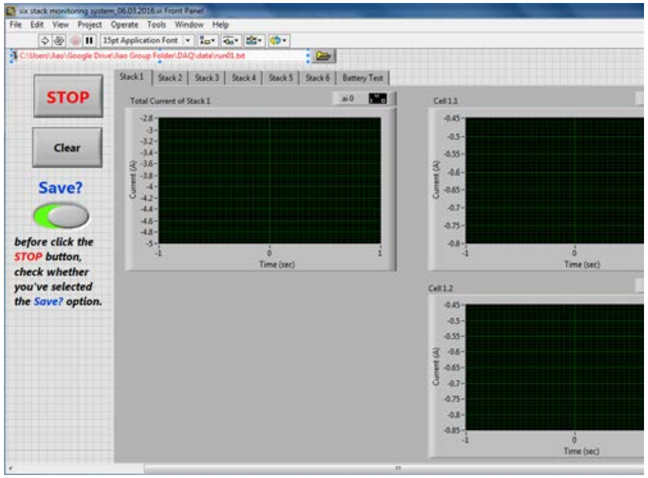
CO_2 electrolyzer prototype

- Funded by NASA
- Built in June 2016
- 36 electrochemical cells arranged in 6 stacks
- 2 membrane separator
- Engineering safety controls
- Customized software for data acquisition

CO_2 Electrolyzer Prototype







- CO_2 Process Rate:
  450 grams/day
- Power Consumption:
  50 watts (per stack)

Task 2.0: CO_2 Electrolyzer Subsystem Development

Subtask 2.1: Conceptual Design of CO_2 Electrolyzer Subsystem

- Process control & optimization

Subtask 2.2: Development of Nanostructured Ag Cathode

- High current density (production rate) & low overpotential (energy penalty)
- High selectivity towards CO
- Robust & stable

Subtask 2.3: Development of Non-Precious Metal-based Anode

- High current density & low overpotential
- Robust & stable

Subtask 2.4: Development of Gas/Liquid Contactor and Gas/Liquid Separator

- CO_2 delivery to catalyst (active site)
- Product separation

Subtask 2.5: Fabrication of CO_2 Electrolyzer Subsystem

- Scale up
- Integration

Subtask 2.6: Evaluation of CO_2 Electrolyzer Subsystem Performance

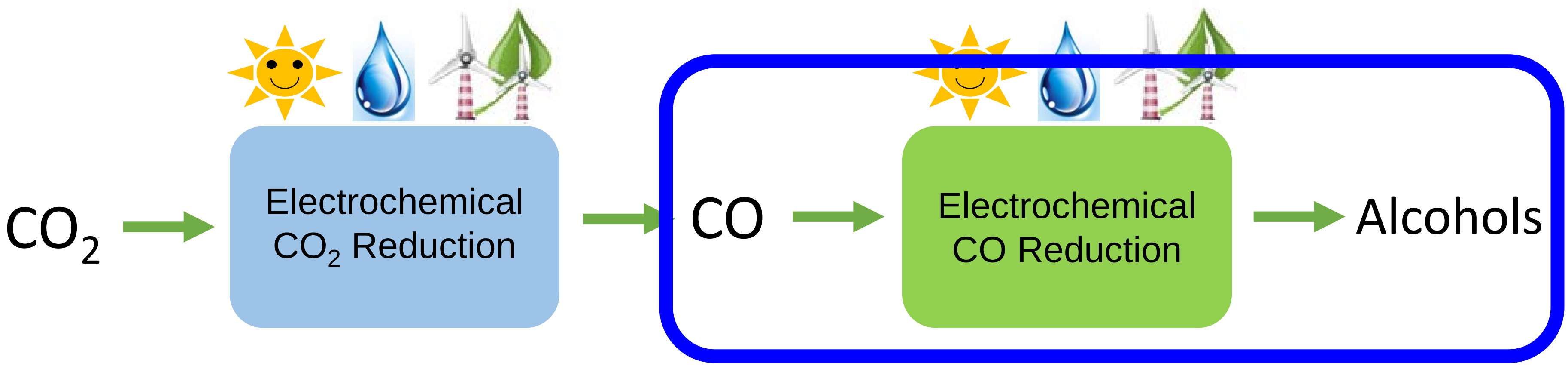
Subtask 2.7: Alternative CO_2 Electrolyzer Design for Performance Enhancement

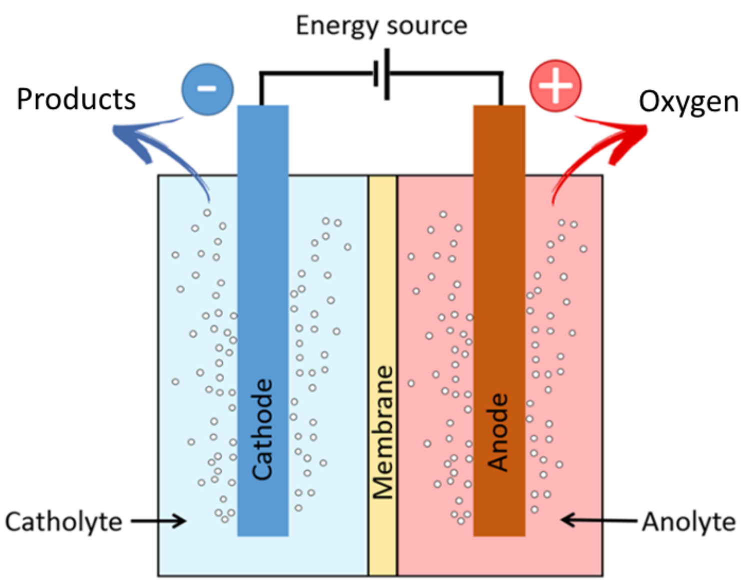
- Boost performance using alternative designs

The Key Performance Parameters for the proposed CO_2 electrolyzer subsystem are:

- CO Faradaic efficiency higher than **70%** at the subsystem level
- Cell voltage less than **3.0 V** with a total current of **5 A**
- Continuous operation for more than **3 hours** with less than **20%** performance loss

Proposed Two-stage Process and its Chemistry





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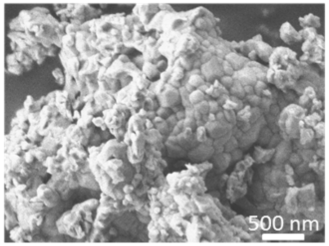
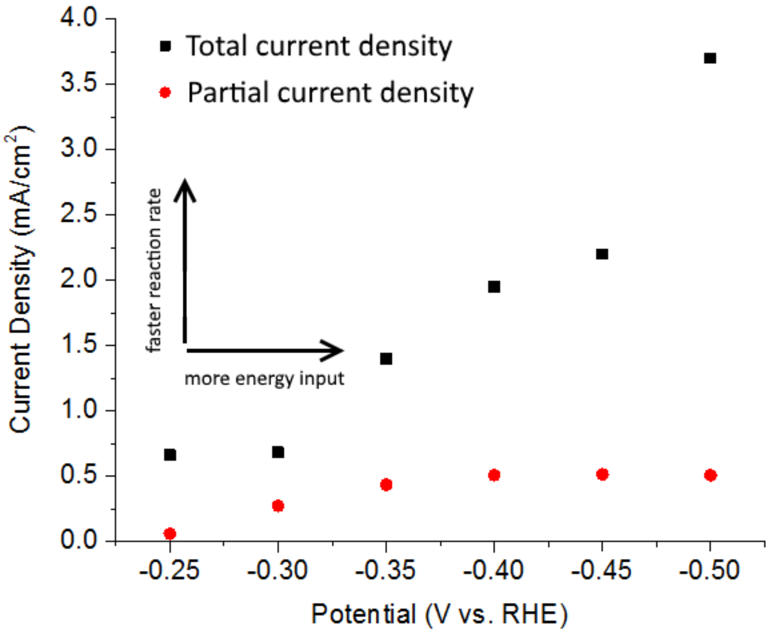
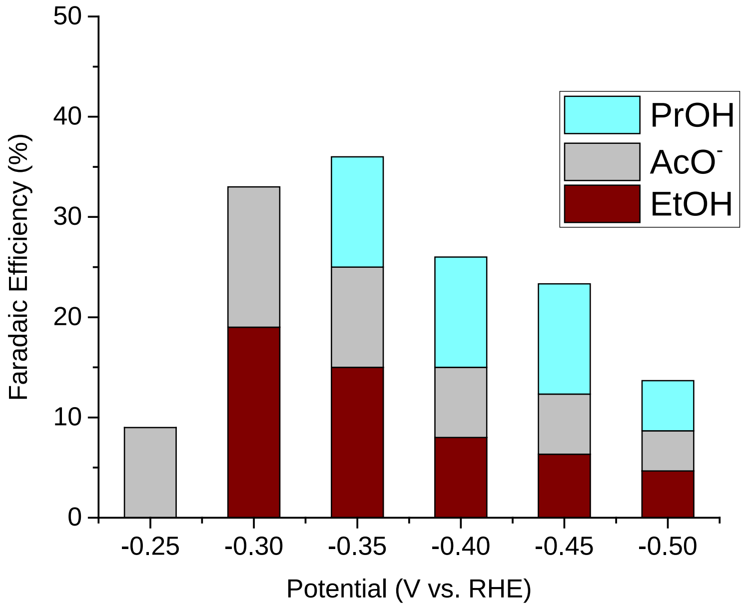
Overall reaction: $2CO + 3H_2O \rightarrow C_2H_6O + 2O_2$

Annealed Cu Particles for CO Reduction

Cu particles (≈ 1 µm) were annealed at 500 °C for 6 hrs and deposited on carbon paper GDL (1 mg/cm^2).





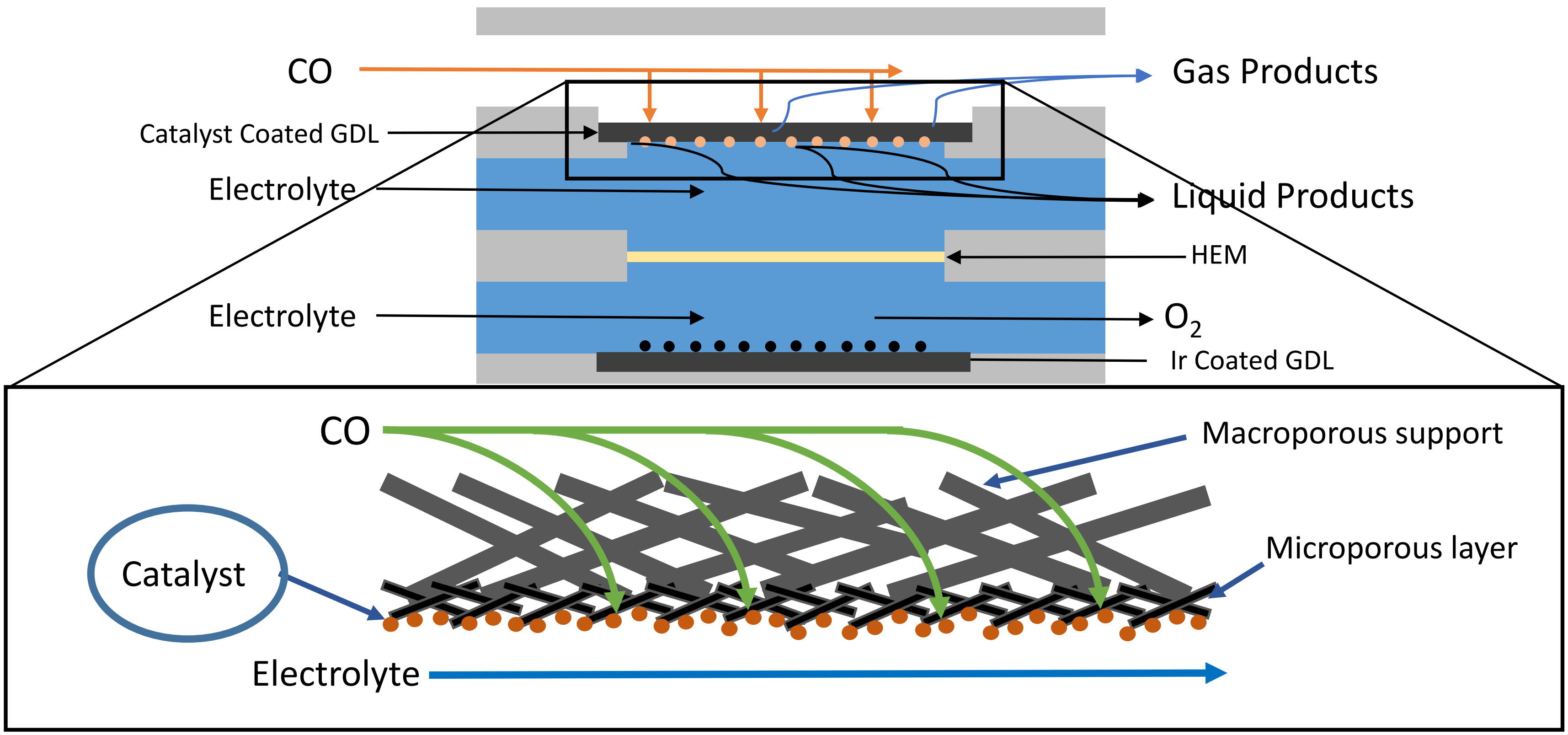


- Selective towards alcohols at moderate overpotentials
- Max. current density: 0.5 mA/cm^2 with n-PrOH selectivity of 10%
- Low current density is due to the low solubility of CO in the aqueous electrolyte

Flow cell design for CO to alcohols

The low solubility of CO in aqueous electrolyte motivates a direct gas feed.

Flow cell schematic:



A gas diffusion layer allows CO to be fed directly to the catalyst/electrolyte interface.

Task 3.0: Development of CO Electrolyzer Subsystem

Subtask 3.1: Conceptual Design of CO Electrolyzer Subsystem
- Process control & optimization

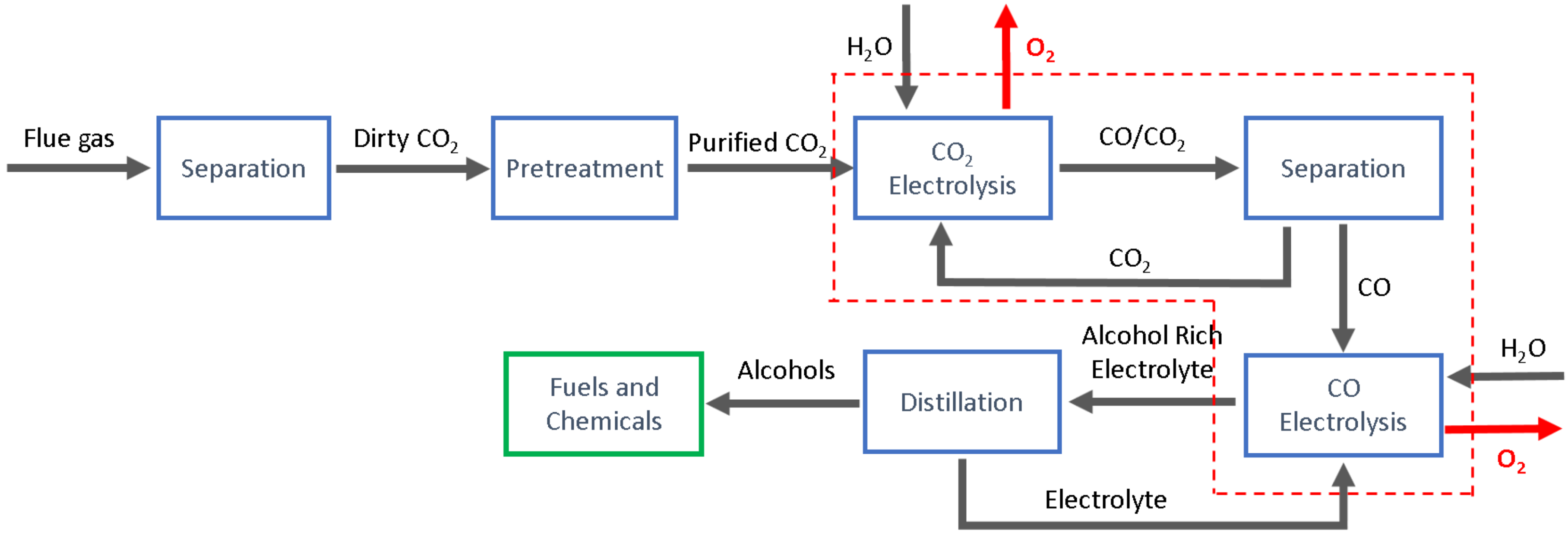
Subtask 3.2: Development of Nanostructured Cu Cathode
- High current density (production rate)
- High selectivity towards alcohols
- Robust & stable

Subtask 3.3: Development of CO Electrolysis Flow Cell and Multi-cell Stack
- Electrode/electrolyte interface

Subtask 3.4: Fabrication and Evaluation of CO Electrolyzer Subsystem
- Scale up
- Integration

The Key Performance Parameters for the proposed CO electrolyzer subsystem are:
- Alcohol Faradaic efficiency higher than **40%** at the subsystem level
- Cell voltage less than **3.0 V** with a total current of **10 A**
- Continuous operation for more than **3 hours** with less than **20%** performance loss

System Integration and Evaluation



Subsystem integration efforts:

- CO/CO_2 separation strategy
- Pressures and flow rates between subsystems
- Production rates of subsystems
- Process control & safety
- System compatibility with flue gases

Task 4.0: Integration and Evaluation of the Complete Electrolyzer System

Subtask 4.1: Conceptual Design of Integrated Electrolyzer System for C_2/C_3 Alcohol Production

- Process control & optimization

Subtask 4.2: Fabrication and Integration of CO_2 Electrolyzer and CO Electrolyzer Subsystems

- Scale up (matches of production rates)
- Integration (balance of pressure, flow rate, and heat)

Subtask 4.3: Evaluation of the Performance of the Complete Electrolyzer System

Subtask 4.4: Optimize the Performance of the Complete Electrolyzer System

Subtask 4.5: Investigation of Flue Gas Compatibility

- SO_x, NO_x, N_2, O_2, H_2 contamination effects

The Key Performance Parameters for the integrated electrolyzer system are as follows:

- Overall energy efficiency higher than **28%** at the system level
- Continuous operation for more than **3 hours** with less than **30%** performance loss

Task 5.0: Economics and Life-cycle Analysis

Subtask 5.1: Technical Scalability and Economic Feasibility Study
Subtask 5.2: Life-cycle Analysis
Subtask 5.3: Technology Gap Analysis

The team will conduct a process scalability assessment, an economic feasibility study, lifecycle analysis and technology gap analysis based on the data collected from the R&D project. The compiled results from these studies will be delivered at the conclusion of the task.

Project Schedule and Milestones

				Budget Period 1						Budget Period 2					
				06/01/2017-11/30/2018						12/01/2018-05/31/2020					
	Start Date	End Date	Cost	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 1.0 - **Project Management and Planning**	6/1/2017	5/31/2020	$50,000												
Subtask 1.1 - Project Management and Planning	6/1/2017	5/31/2020													
Subtask 1.2 - Briefings and Reports	6/1/2017	5/31/2020													
Subtask 1.3 – Safety and Environmental Analysis	6/1/2017	5/31/2020													
Milestones															
Milestone 1.a - Updated Project Management and Planning				X											
Milestone 1.b - Complete Kick-off Meeting				X											
Milestone 1.c - Complete Review Meetings						X			X		X		X		
Milestone 1.d - Complete Midterm Report										X					
Milestone 1.e - Complete Final Review Meeting															X
Milestone 1.f - Complete Final Report															X
Milestone 1.g - Complete Safety and Environmental Analysis						X			X			X			
Task 2.0 - **Development of CO_2 Electrolyzer Subsystem**	6/1/2017	11/30/2018	$250,000												
Subtask 2.1 - Conceptual Design of CO_2 Electrolyzer Subsystem	6/1/2017	8/31/2017													
Subtask 2.2 - Development of Nanostructured Ag Cathode	6/1/2017	11/31/2017													
Subtask 2.3 - Development of Non-precious Metal-based Anode	6/1/2017	11/31/2017													
Subtask 2.4 - Development of Gas/Liquid Contactor and Gas/Liquid Separator	12/1/2017	2/28/2018													
Subtask 2.5 - Fabrication of CO_2 Electrolyzer Subsystem	3/1/2017	5/31/2018													
Subtask 2.6 - Evaluation of CO_2 Electrolyzer Subsystem Performance	6/1/2018	8/31/2018													
Subtask 2.7 - Alternative CO_2 Electrolyzer Design for Performance Enhancement	9/1/2018	11/30/2018													
Milestones															
Milestone 2.a - Complete the Conceptual Design of CO_2 Electrolyzer				X											
Milestone 2.b - Complete the Development of Electrocatalysts					X										
Milestone 2.c - Complete the Development of Contactor and Separator						X									
Milestone 2.d - Complete the Fabrication of CO_2 Electrolyzer Subsystem							X								
Milestone 2.e - Complete the Evaluation of CO_2 Electrolyzer Subsystem								X							
Milestone 2.f - Complete the Evaluation of Alternative CO_2 Electrolyzer Design									X						

Project Schedule and Milestones

Task 3.0 - Development of CO Electrolyzer Subsystem	6/1/2017	11/30/2018	$200,000												
Subtask 3.1 - Conceptual Design of CO Electrolyzer Subsystem	6/1/2017	8/31/2017													
Subtask 3.2 - Development of Nanostructured Cu Cathode	9/1/2017	2/28/2018													
Subtask 3.3 - Development of CO Electrolysis Flow Cell and Multi-cell Stack	3/1/2018	5/31/2018													
Subtask 3.4 - Fabrication and Evaluation of CO Electrolyzer Subsystem	6/1/2018	11/30/2018													
Milestones															
Milestone 3.a - Complete the Conceptual Design of CO Electrolyzer				X											
Milestone 3.b - Complete the Fabrication of CO Electrolyzer Subsystem								X							
Milestone 3.c - Complete the Evaluation of CO Electrolyzer Subsystem									X						
Task 4.0 - Integration and Evaluation of the Complete Electrolyzer System	12/1/2018	5/31/2020	$400,000												
Subtask 4.1 - Conceptual Design of Integrated Electrolyzer System for C2/C3 Alcohol Production	12/1/2018	2/28/2019													
Subtask 4.2 - Fabrication and Integration of CO_2 Electrolyzer and CO Electrolyzer Subsystems	12/1/2018	8/31/2019													
Subtask 4.3 - Evaluation of the Performance of the Complete Electrolyzer System	9/1/2019	2/29/2020													
Subtask 4.4 - Optimize the Performance of the Complete Electrolyzer System	3/1/2020	5/31/2020													
Subtask 4.5 - Investigation of Flue Gas Compatibility	3/1/2020	5/31/2020													
Milestones															
Milestone 4.a - Complete the Conceptual Design of the Integrated Electrolyzer System										X					
Milestone 4.b - Complete the Fabrication of the Integrated Electrolyzer System												X			
Milestone 4.c - Complete the Evaluation of the Integrated Electrolyzer System														X	
Milestone 4.d - Complete the Optimization of the Integrated Electrolyzer System															X
Milestone 4.e - Complete the Flue Gas Compatibility Investigations															X
Task 5.0 - Economics and Life-cycle Analysis	6/1/2019	5/31/2020	$100,000												
Subtask 5.1 - Refinement of the Cost Analysis Using the Experimental Data	6/1/2019	11/30/2019													
Subtask 5.2 - Re-evaluation of the Performance Metrics Using the Experimental Data	9/1/2019	2/29/2020													
Subtask 5.3 - Revisit the Life-cycle Analysis	3/1/2020	5/31/2020													
Milestones															
Milestone 5.a - Complete the Cost Analysis													X		
Milestone 5.b - Updated Performance Metrics														X	
Milestone 5.c - Complete the Life-cycle Analysis															X

Key Decision Points

Decision Point	Date	Success Criteria
Go/no-go Decision Point #1	11/30/2018	[1] Completion of subsystem fabrication and evaluation. [2] CO_2 electrolyzer subsystem meets all the Key Performance Parameters: CO Faradaic efficiency higher than 70% at the subsystem level, cell voltage less than 3.0 V with a total current of 5 A, continuous operation for more than 3 hours with less than 20% performance loss. [3] CO electrolyzer subsystem meets all the Key Performance Parameters: alcohol Faradaic efficiency higher than 40% at the subsystem level, cell voltage less than 3.0 V with a total current of 10 A, continuous operation for more than 3 hours with less than 20% performance loss.
Go/no-go Decision Point #2	5/31/2020	[1] Completion of system fabrication, integration, and evaluation. [2] Demonstration of the performance of integrated electrolyzer system meeting all the Key Performance Parameters: overall energy efficiency higher than 20% at the system level, continuous operation for more than 3 hours with less than 30% performance loss.

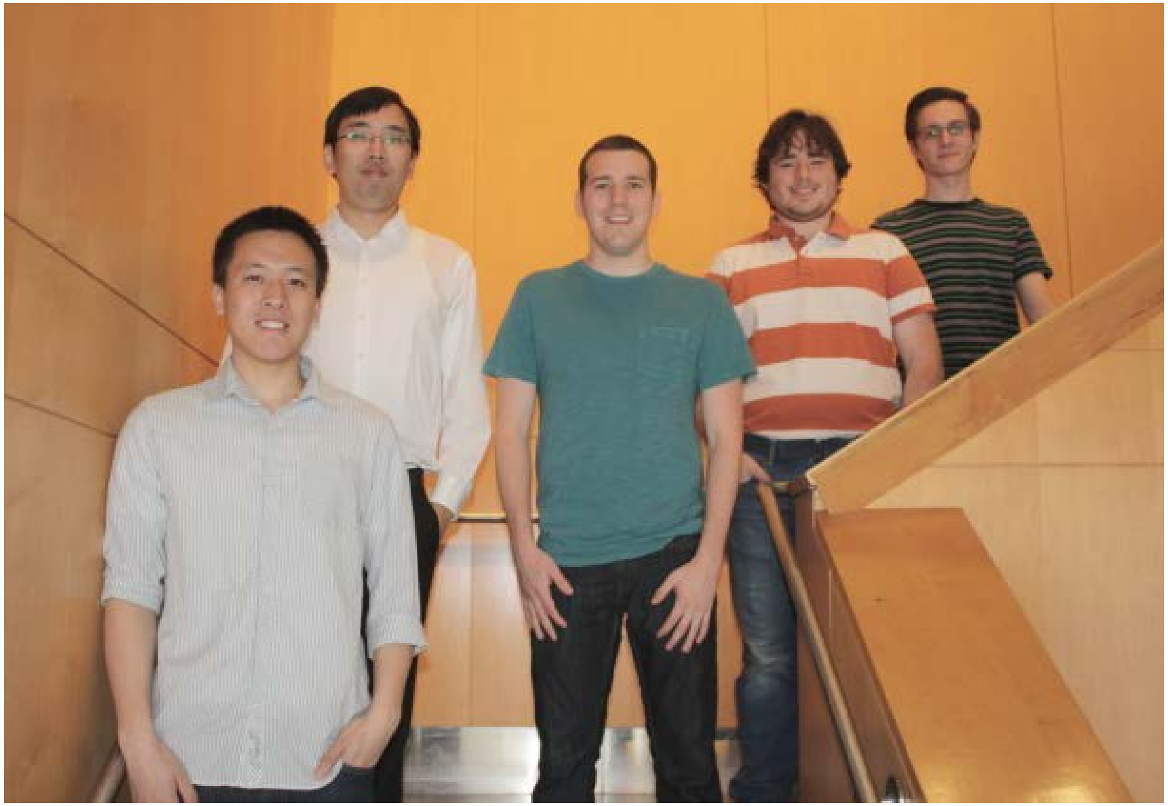
Project Funding Profile

	Budget Period 1 06/01/2017 - 11/30/2018		Budget Period 2 12/01/2018 - 05/31/2020		Total Project	
	Government Share	Cost Share	Government Share	Cost Share	Government Share	Cost Share
Applicant	$421,099	$105,275	$378,901	$94,725	$800,000	$200,000
Total	$421,099	$105,275	$378,901	$94,725	$800,000	$200,000
Cost Share	80%	20%	80%	20%	80%	20%

Anticipated Outcomes

- The feasibility of the proposed approach for reduction of CO_2 emission will be demonstrated.
- Two subsystems, i.e., CO_2 electrolyzer and CO electrolyzer, will be designed, fabricated, and evaluated. The key functions will be demonstrated for the integrated system in the laboratory environment.
- Economic and life-cycle models will be established and assessed using experimental data.
- A Technology Readiness Level 4 (TRL 4) will be reached at the end of project.

Acknowledgements



UDRF, UDRF-SI
UDEI, EPSCoR

CAREER, STTR

NDI, ND

Game Changing
Program, EPSCoR

DOE/NETL

Collaborators:
Dion Vlachos, Yushan Yan, Bingjun Xu, John Xiao, Robert Birkmire, University of Delaware
Jingguang Chen, Columbia University
Ken Burke, NASA Glenn Research Center

Thank you