Electrochemical Conversion of Carbon Dioxide to Alcohols (FE0029868)

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University of Delaware, Newark, DE (USA)

2017 NETL CO_2 Capture Technology Project Review Meeting

August 23, 2017

UNIVERSITY OF DELAWARE

Project Funding: $1,000,000 ($800,000 DOE share; $200,00 UD Share)

Budget Period 1: 06/01/2017-11/30/2018

Budget Period 2: 12/01/2018-05/31/2020

	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%

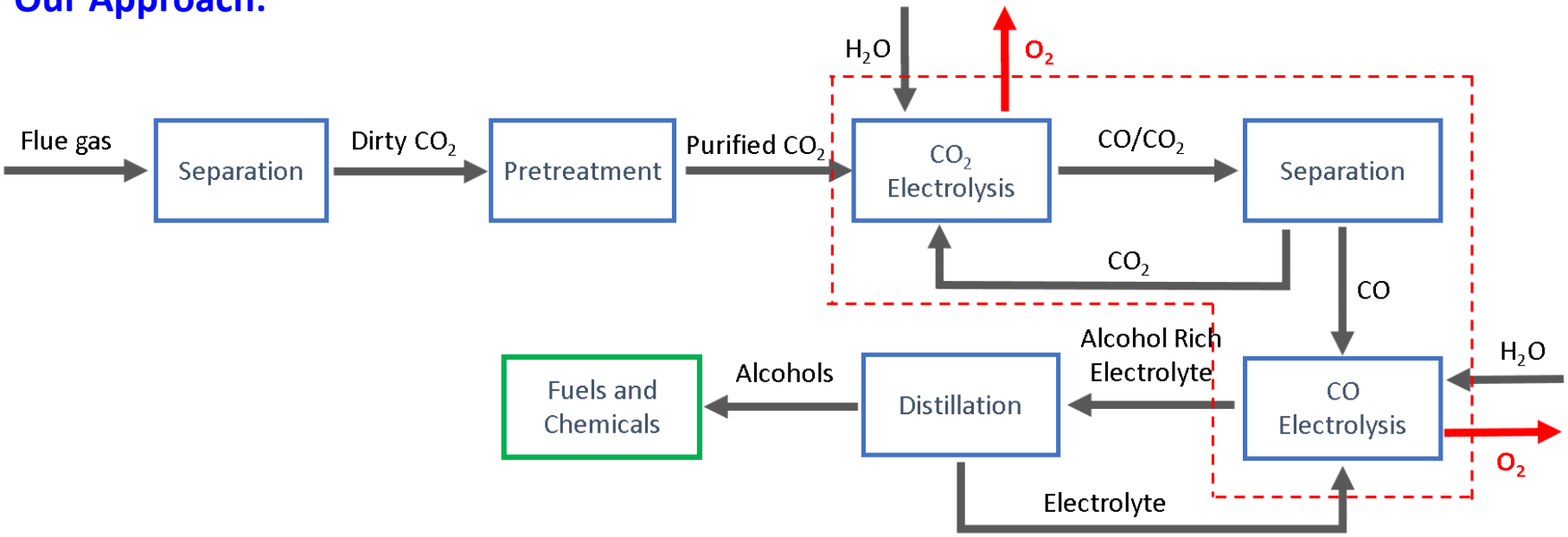
Project was officially launched on June 1st, 2017.

Kick-off meeting was held on July 10th, 2017.

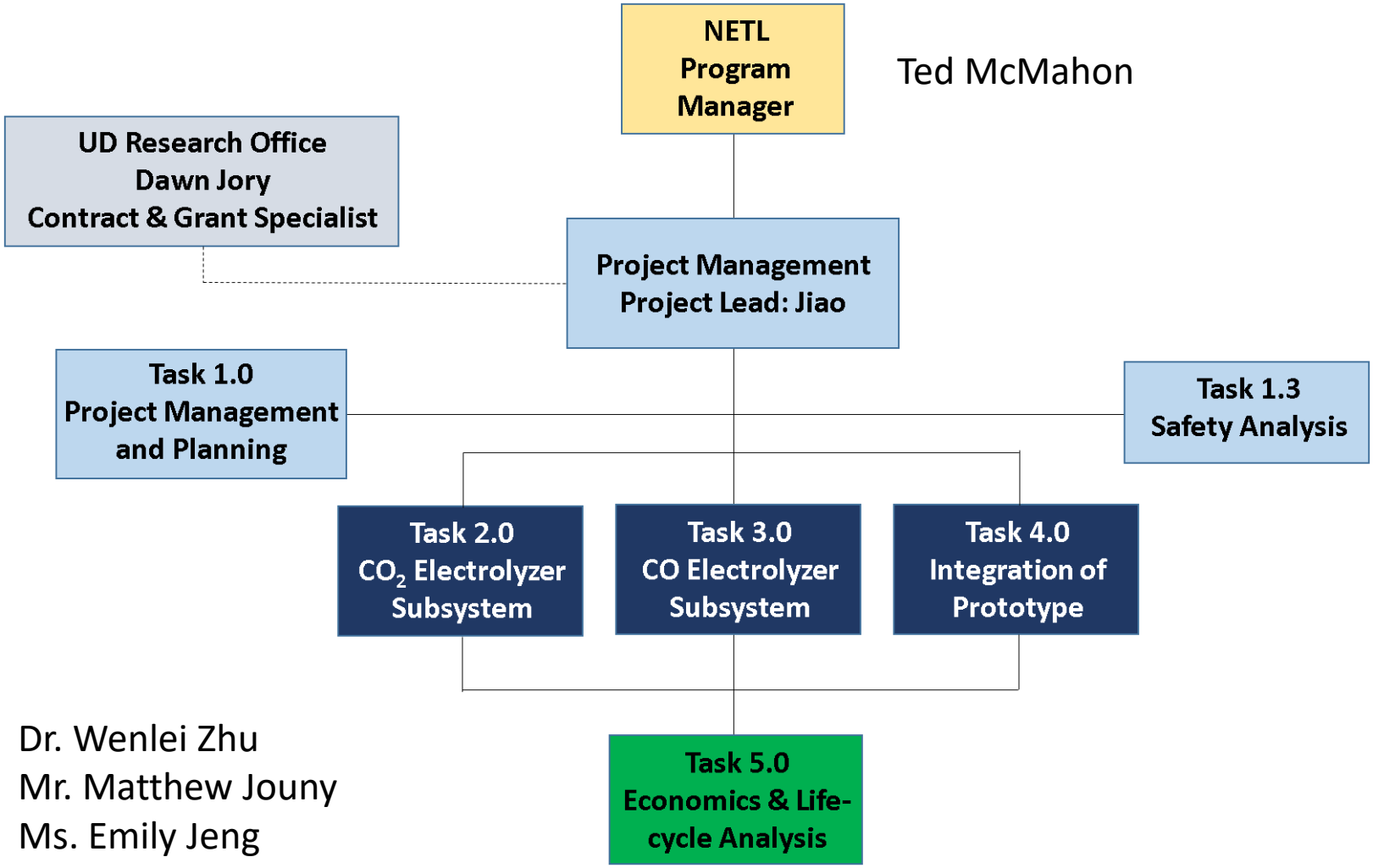
Project Objectives and Approach

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:

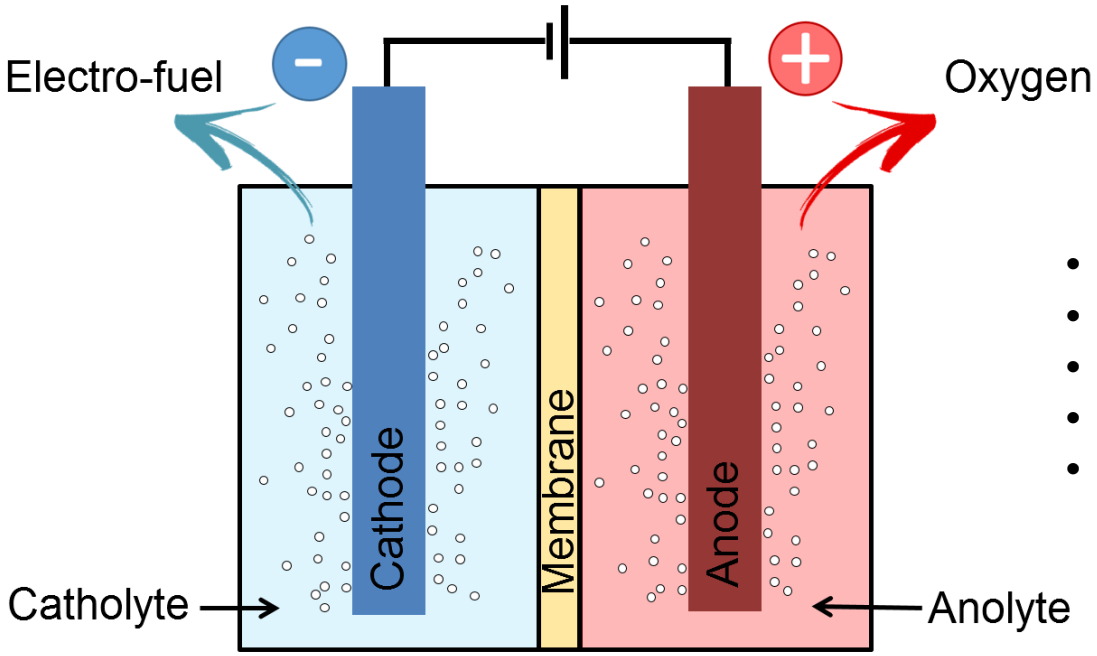


Project Management



Dr. Wenlei Zhu
Mr. Matthew Jouny
Ms. Emily Jeng

CO_2 Utilization via Electrolysis



- Near ambient operating conditions
- Quick response time (easy on/off)
- Scale-out technology
- Ideal for distributed CO_2 sources
- Easy to couple with renewables

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) was achieved.

Other products:

❖ Formate/formic acid (80%, Sn)

❖ Ethanol (15-20%, Cu)

❖ Propanol (15%, Cu)

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

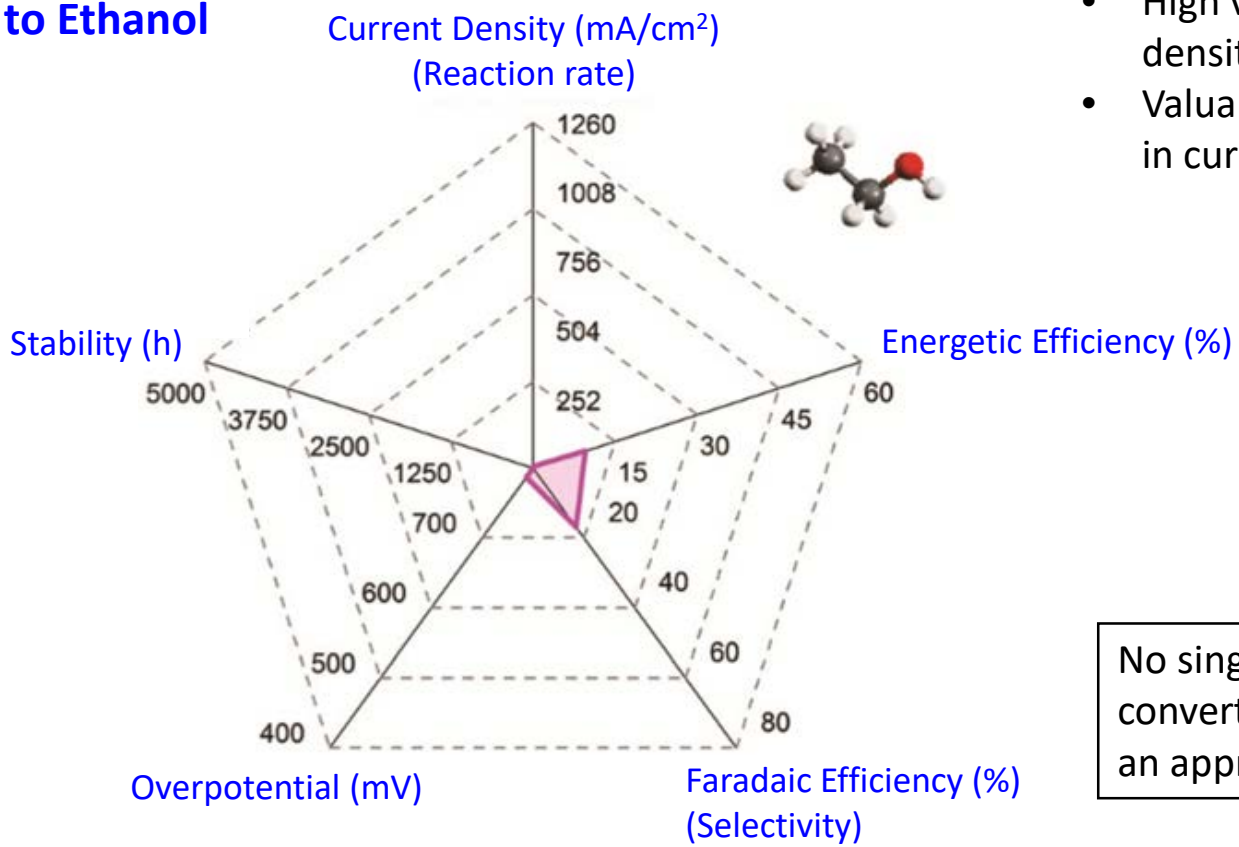
Electrocatalysts: CO_2 to Ethanol

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

Liquid products (alcohols) are ideal:

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

CO_2 to Ethanol



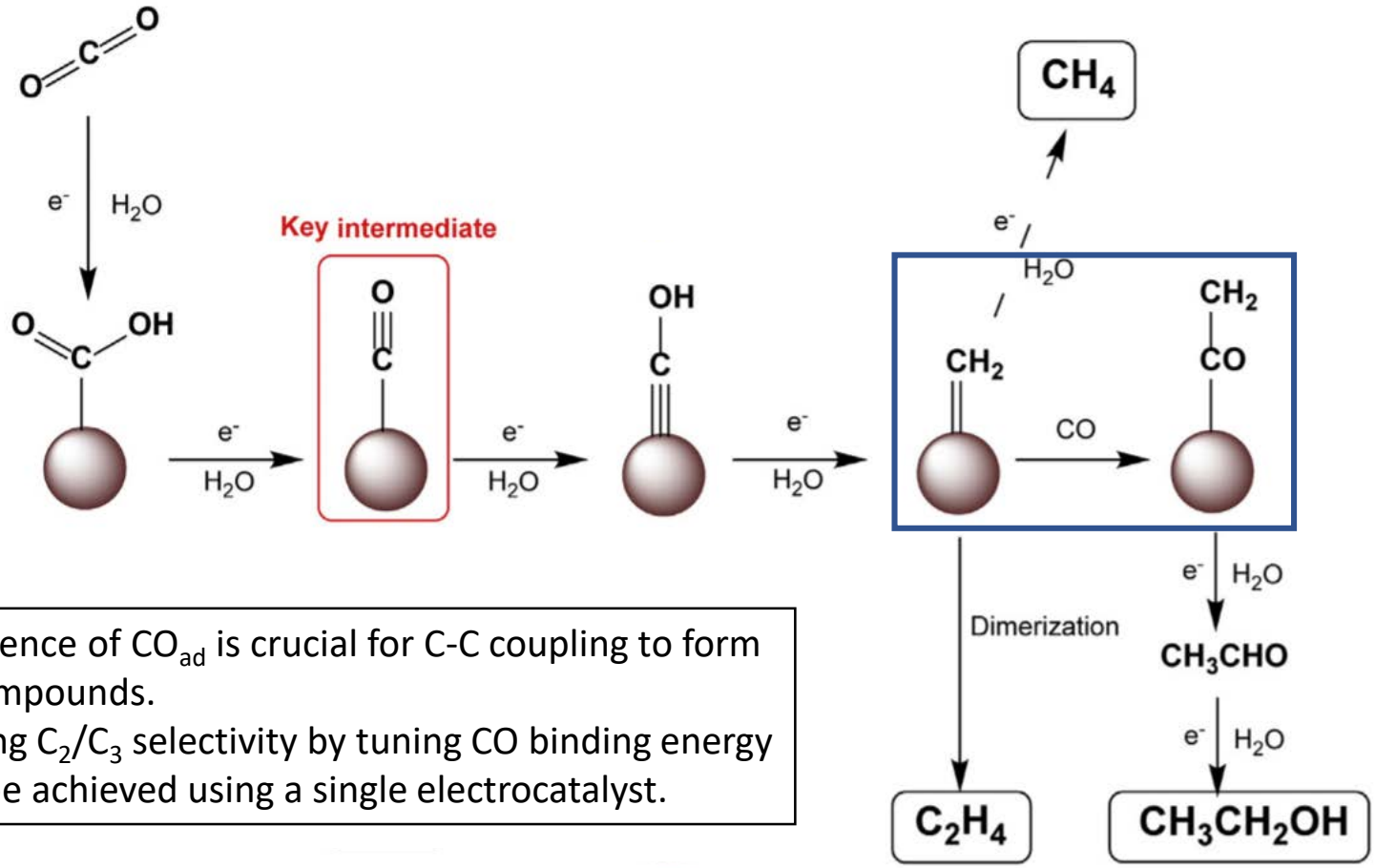
No single electrocatalyst can convert CO_2 into ethanol with an appreciable performance.

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

CO_2 to Alcohols

Copper is the only metal that can catalyze CO_2 conversion to hydrocarbons in aqueous.

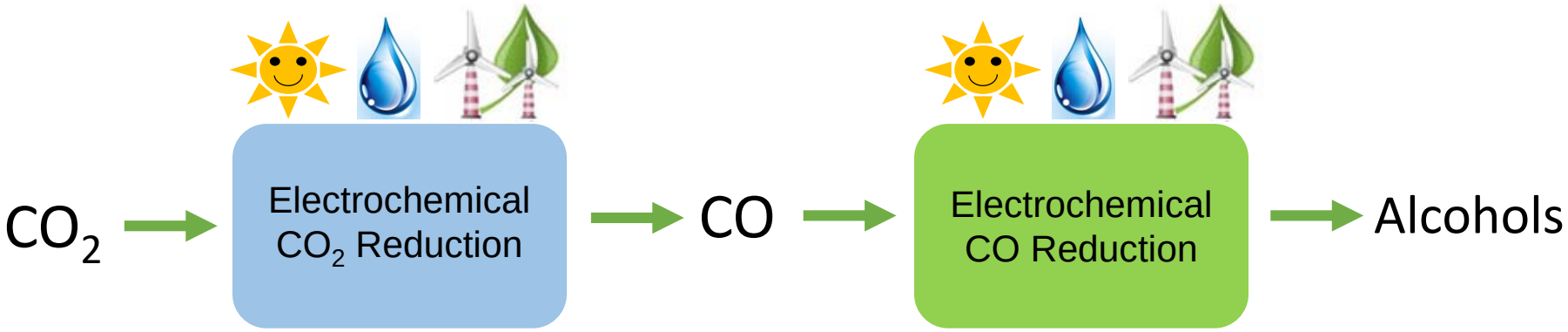
Proposed mechanism:

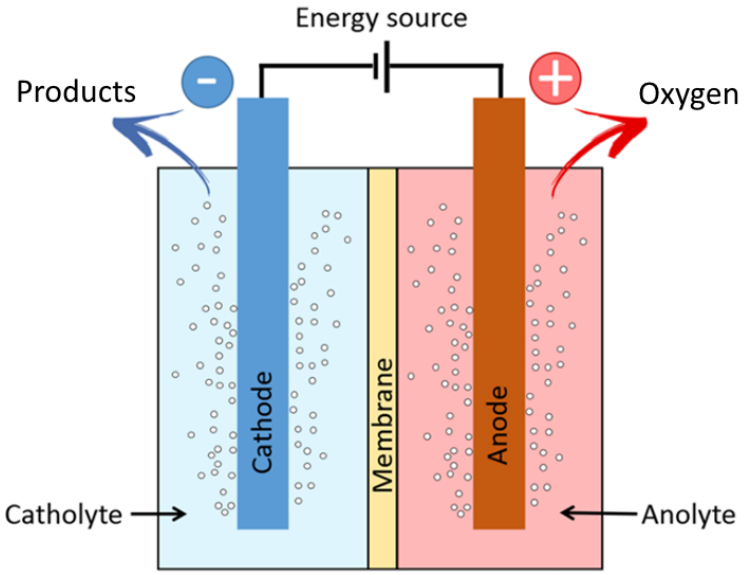


- The presence of CO_{ad} is crucial for C-C coupling to form C_2/C_3 compounds.
- Enhancing C_2/C_3 selectivity by tuning CO binding energy cannot be achieved using a single electrocatalyst.

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

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: $2CO_2 \rightarrow 2CO + O_2$

Subsystem: CO electrolyzer
Cathode reaction: $2CO + 8H^+ + 8e^- \rightarrow C_2H_6O + H_2O$
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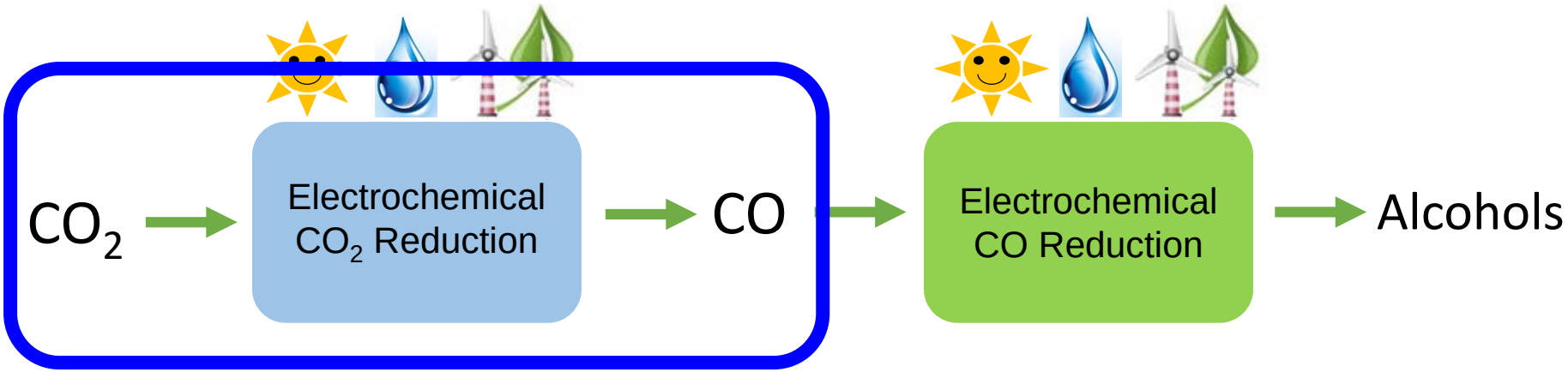
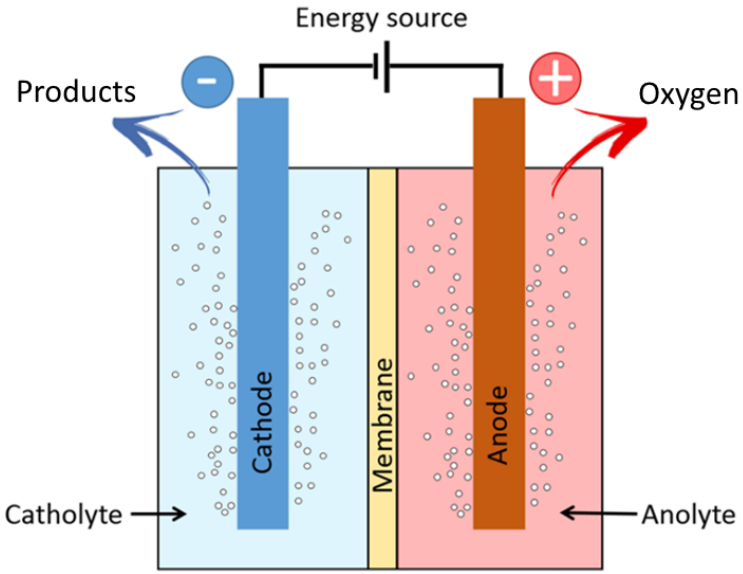
Overall reaction: $2CO + 3H_2O \rightarrow C_2H_6O + 2O_2$

Proposed Two-stage Process and its Chemistry





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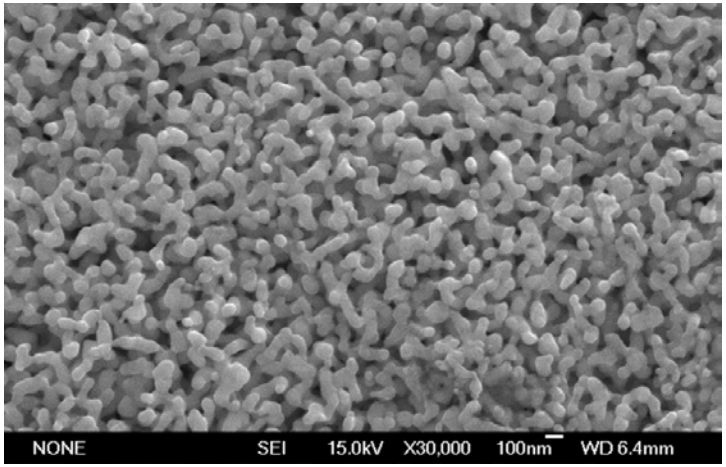
CO_2-to-CO electrolyzer prototype



- Nanoporous Ag – SOA CO_2-to-CO catalyst
- 36 electrochemical cells arranged in 6 stacks
- 22A @ 3V

On-going Research: CO_2-to-CO Electrolyzer 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

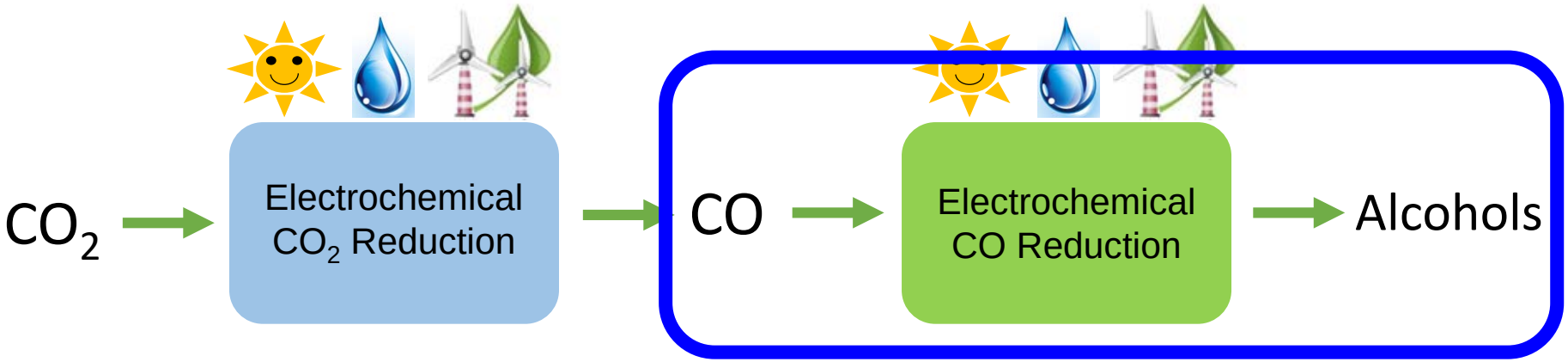
Subtask 2.4: Development of Gas/Liquid Contactor and Gas/Liquid Separator
- CO_2 delivery to catalyst (active site)
- Product separation

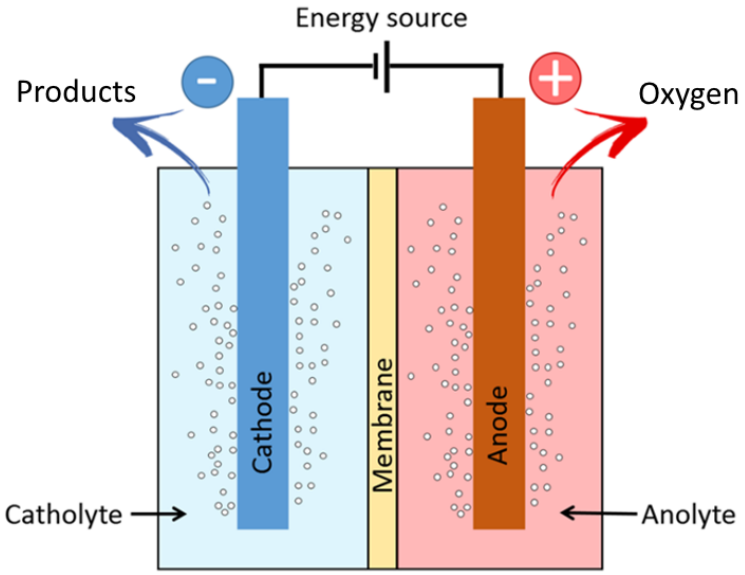
Subtask 2.5: Fabrication of CO_2 Electrolyzer Subsystem
- Scale up
- Integration

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

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: $2CO_2 \rightarrow 2CO + O_2$

Subsystem: CO electrolyzer

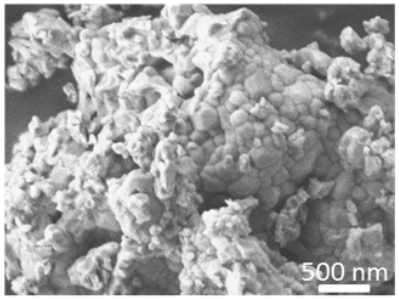
Cathode reaction: $2CO + 8H^+ + 8e^- \rightarrow C_2H_6O + H_2O$

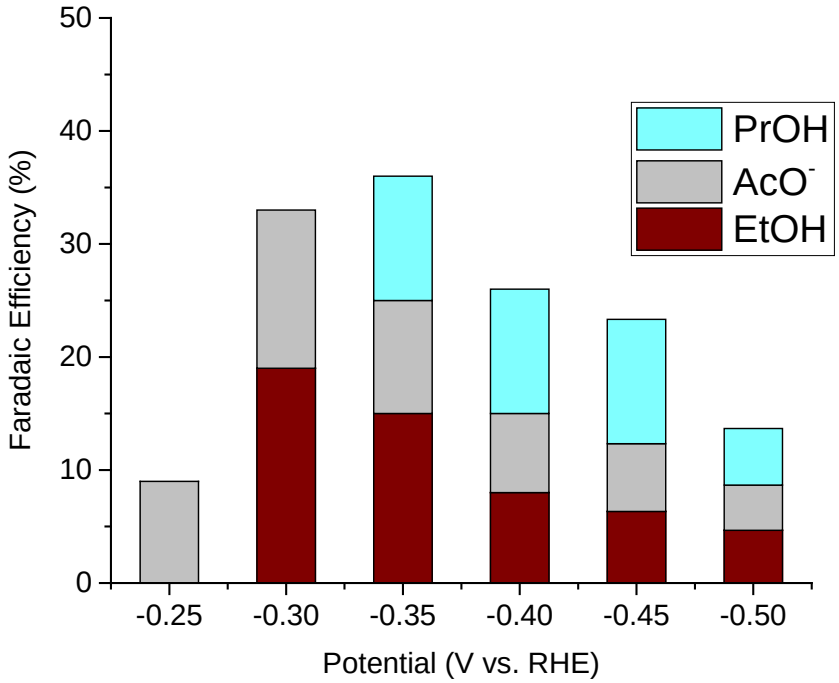
Anode reaction: $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

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

Cu Catalyst 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).



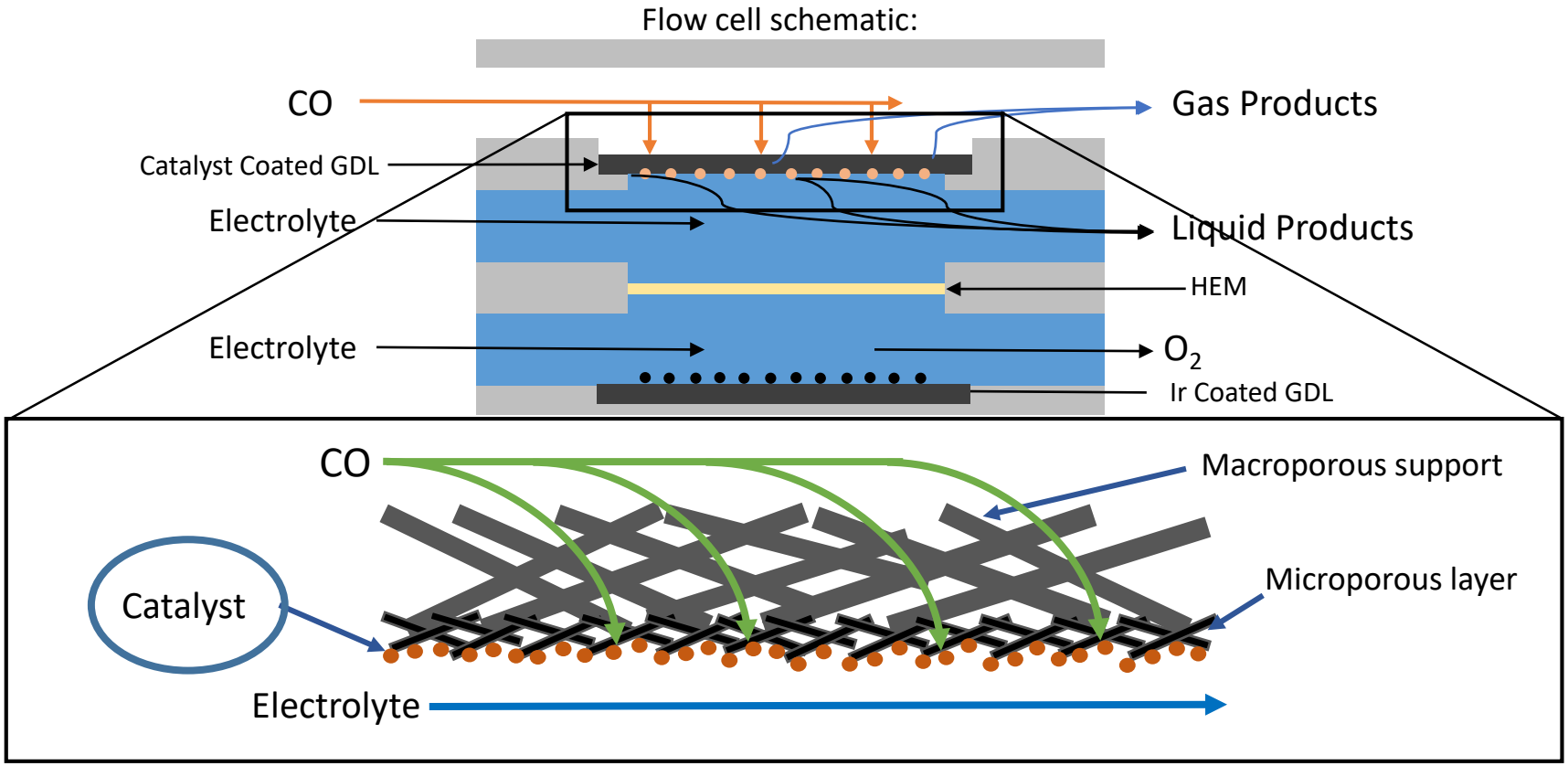


Batch test:
0.1 M KOH electrolyte

- Selective towards alcohols at moderate overpotentials
- Max. current density: 0.5 mA/cm^2 with n-PrOH selectivity of 10%
- Batch test: 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.



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

On-going Research: Development of CO Electrolyzer

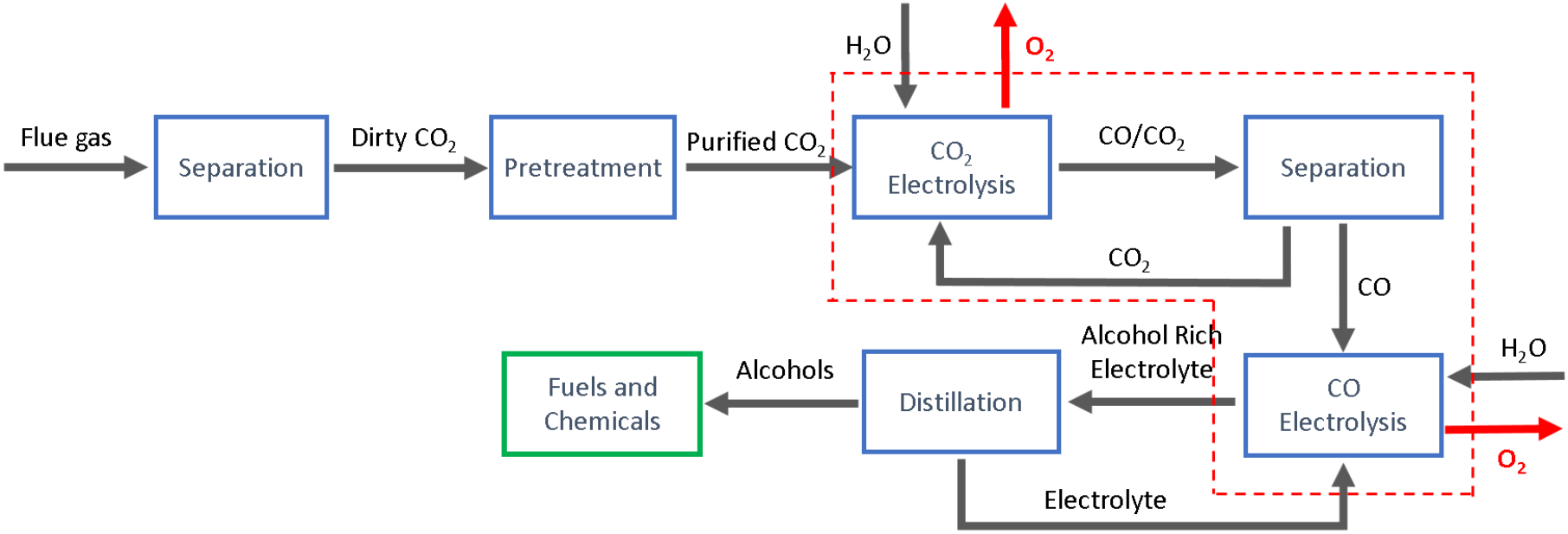
Subtask 3.1: Conceptual Design of CO Electrolyzer Subsystem
- Process control & optimization

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

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
- Techno-economical analysis and life cycle analysis

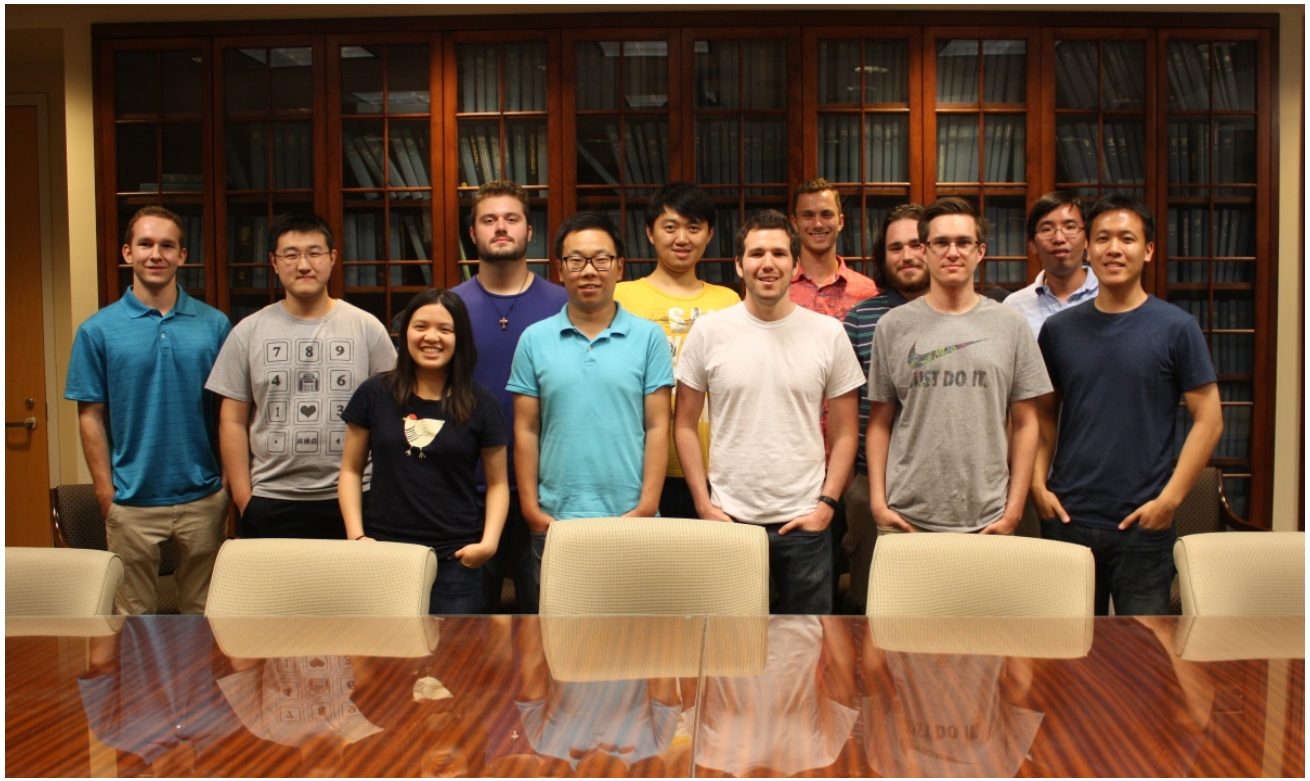
Project Schedule and Milestones

				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

Acknowledgements



NATIONAL ENERGY TECHNOLOGY LABORATORY

Project manager:

Ted McMahon (NETL)

Thank you