A Tandem Electrolysis Process for Multicarbon Chemical Production from Carbon Dioxide

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Area of Interest 1 – Synthesis of Value-Added Organic Products

Project title: A Tandem Electrolysis Process for Multi-carbon Chemical Production from Carbon Dioxide

Applicant Name: University of Delaware

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Principal Investigator: Feng Jiao Additional Team Member: Bri-Mathias Hodge, UC Boulder

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Federal Share: \$1,000,000 Cost Share: \$250,000 Total Estimated Project Cost: \$1,250,000



Introduction to CO₂ Electrolyzer



Reaction	E (V) vs. SHE
CO_2 + 2H ⁺ +2e ⁻ → 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 ⁻ → HCHO + H ₂ O	-0.48
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	-0.38
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0.24

Key components:

two electrodes (cathode & anode) one polymer membrane

 CO_2 electroreduction occurs on the cathode side, whereas the water oxidation reaction occurs on the anode side.

Technical Challenges:

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



Tandem electrolysis through CO intermediate



Decoupling of the electrolysis steps allows sustainable C₂₊ production



M. Jouny, W. Luc, & F. Jiao, Nature Catalysis 1, 748-755 (2018).



Schematic of Two-Step CO₂ Electrolysis Process





Two-Step Electrochemical Conversion of CO₂ to Alcohols





Electrolyzer subsystem performance



- A stable performance for the two-step process was achieved.
- ~80% CO FE for the first step and ~40% alcohol FE for the second step



Project Objectives and Approach

The objectives of this project include:

- designing a novel, high-performance carbon monoxide (CO) electrolysis reactor that produces <u>two concentrated product streams</u>, ethylene gas stream on cathode and acetate liquid stream on anode
- (2) constructing and assessing CO electrolysis multi-cell stack reactor prototype with a <u>90% carbon selectivity</u> and <u>a total power of 0.9 kW</u>
- (3) performing a <u>full techno-economic analysis (TEA) and a life-cycle assessment (LCA)</u> of the whole two-step carbon dioxide (CO_2) electrolysis technology for CO_2 utilization at a technology readiness level (TRL) 4

Our Approach:







A full mass balance analysis of the two-step CO_2 electrolysis system for acetate and ethylene co-production. Operating conditions for each electrolysis unit are also indicated.



	Units	Measured/Current Performance	Projected/Target Performance						
Synthesis Pathway Steps									
Step 1 (based on CO ₂)	mol ⁻¹	$2CO_2 \rightarrow 2CO + O_2$							
Step 2-1	mol ⁻¹	$2CO + 2H_2O \rightarrow C_2H_4 + 2O_2$							
Step 2-2	mol ⁻¹	$2CO + H_2O \rightarrow CH_2COOH + O_2$							
Source of external intermediate 1		Pure water							
Reaction Thermodynamics									
Reaction		Electrochemical reaction							
$\Delta {\sf H^o}_{\sf rxn}$	KJ/mol	Acetate: 873.2 Ethylene: 1323.1							
ΔG^{o}_{rxn}	KJ/mol	Acetate: 786.6 Ethylene: 1331.5					Acetate: 786.6 Ethylene: 1331.5		
Conditions		(range)	(range)						
CO ₂ Source		Pure CO ₂	Simulated CO ₂ source with common flue gas contaminants						
Catalyst		Cu (cathode)	Cu (cathode)						
		IrO _x (anode)	Ni-FeO _x or Co-Pi (anode)						
Pressure	bar	1-2	1-5						
CO ₂ Partial Pressure	bar	1	>0.9						
Temperature	°C	~25	30-70						
Performance		(range)	(minimum)						
Nominal Residence Time	sec	48-184	32						
Selectivity to Desired Product ^a	%	30-45	50 (Acetate) 80 (Acetate + ethylene)						
Product Composition		(range)	(optimal)						
Desired Product (Acetate)	mol%	15-25	40						
Desirable co-Product (Ethylene)	mol%	10-15	20						
Unwanted By-Products:	mol%								
Ethanol	mol%	2-4	<1						
1-Propanol	mol%	1-2	<1						
Carbon Monoxide	mol%	15-27	<10						
Hydrogen	mol%	>40 <30%							
Grand Total	mol%		100%						

Synthesis of Value-Added Organic Products *Technology Performance Data*



Techno-economic Analysis of CO₂ Electrolysis



- Survey the current state-of-the-art technology in the field for the past 5 years.
- Incorporate the current leading-edge performances into TEA.
- Evaluate the economic feasibility of electrochemical CO₂ conversion to products.
- Provide a roadmap for future research direction.



Roadmap to Market-competitive Production



- Overall, electricity cost is one of the key parameters in cost reduction for all products.
- With a current technology, C₁
 product production is
 economically viable, while C₂
 product production still
 demands tech enhancement.

Shin, H.#, Hansen, K. U.# & Jiao, F.* Techno-economic assessment of lowtemperature carbon dioxide electrolysis. *Nature Sustainability* (in press). doi: <u>10.1038/s41893-021-00739-x</u>



Project Management





Project Schedule and Milestones

Tack Name	Assigned Budget Period 1			Budget Period 2					
Task Name	Resources	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
Task 1.0 - Project Management and Planning	Team								
Task 2.0 - Development of Nanostructured Cu Catalysts	Jiao								
Subtask 2.1 - Synthesis of Nanostructured Cu with Desired Properties	Jiao								
Subtask 2.2 - Catalytic Tests of Nanostructured Cu for CO Electroreduction	Jiao								
Subtask 2.3 - Scale-up Synthesis of Nanostructured Cu Catalysts	Jiao								
Milestone A – Complete the Development of Nanostructured Cu Catalysts	Jiao								
Task 3.0 - Development of Anion-Exchange-Membrane-Based CO Electrolysis Reactor	Jiao								
Subtask 3.1 - Investigation of Anion Exchange Membranes	Jiao								
Subtask 3.2 - Fabrication of Anion-Exchange-Membrane-Based CO Electrolysis Reactor	Jiao								
Subtask 3.3 - Evaluation of Anion-Exchange-Membrane-Based CO Electrolysis Reactor	Jiao								
Milestone B – Complete the Development of Anion-Exchange-Membrane-Based CO Electrolysis Reactor	Jiao								
Decision Point 1	Team								
Task 4.0 - Integration and Evaluation of the Complete Electrolyzer System	Jiao								
Subtask 4.1 - Scale-up of CO Electrolysis Reactor with an Electrode Area of 100 $\rm cm^2$	Jiao								
Subtask 4.2 - Design and Fabrication of CO Electrolysis Multi-Cell Stack Reactor	Jiao								
Subtask 4.3 - Evaluation of CO Electrolysis Multi-Cell Stack Reactor	Jiao								
Subtask 4.4 - Durability Test of CO Electrolysis Multi-Cell Stack Reactor	Jiao								
Subtask 4.5 - Flue Gas Compatibility Test of CO Electrolysis Multi-Cell Stack Reactor	Jiao								
Milestone C – Complete the Development of CO Electrolysis Multi-Cell Stack Reactor	Jiao								
Task 5.0 - Techno-Economic Analysis and Life-Cycle Assessment	Hodge								
Subtask 5.1 - Techno-Economic Analysis	Hodge								
Subtask 5.2 - Life-Cycle Assessment	Hodge								
Milestone D – Complete the Techno-Economic Analysis and Life-Cycle Assessment	Hodge								
Decision Point 2	Team								



Key Decision Points

Task/ Subtask	Milestone Title & Description	Planned Completion Date	Verification method
Task 2.0	Milestone A – Complete the Development of Nanostructured Cu Catalysts	02/28/2021	Documented performance data
Task 3.0	Milestone B – Complete the Development of Anion-Exchange- Membrane-Based CO Electrolysis Reactor	08/31/2021*	Photograph of the prototype and documented performance data
Task 4.0	Milestone C – Complete the Development of CO Electrolysis Multi-Cell Stack Reactor	08/31/2022	Photograph of the prototype and documented performance data
Task 5.0	Milestone D – Complete the Techno-Economic Analysis and Life-Cycle Assessment	08/31/2022	Documented analysis results

* A 3-month no-cost time extension was requested.



Acknowledgements





Project manager: Andrea T. McNemar



Thank you