High Efficiency Electrochemical Conversion of Carbon Dioxide to Ethylene (DE-FE-0031919)

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Project Manager
Dr. Naomi O'Neil

2022 Carbon Management
Project Review Meeting
August 16, 2022

DOE Share: $1,000,000
Cost Share: $250,000
Project Dates: 9/1/20-8/31/22

Outline

1. **Project Overview**

2. **Technical and Scientific Background**

   Catalysts of CO_2 reduction, C-C coupling pathway

3. **Progress of Project**

   Tandem electrodes and pulse electrolysis to maximize the production of C_2H_4

4. **Major Accomplishments**

Image Credit https://notes.nap.edu/2018/11/01/carbon-problem-manage-co2/

Project Overview: project objectives

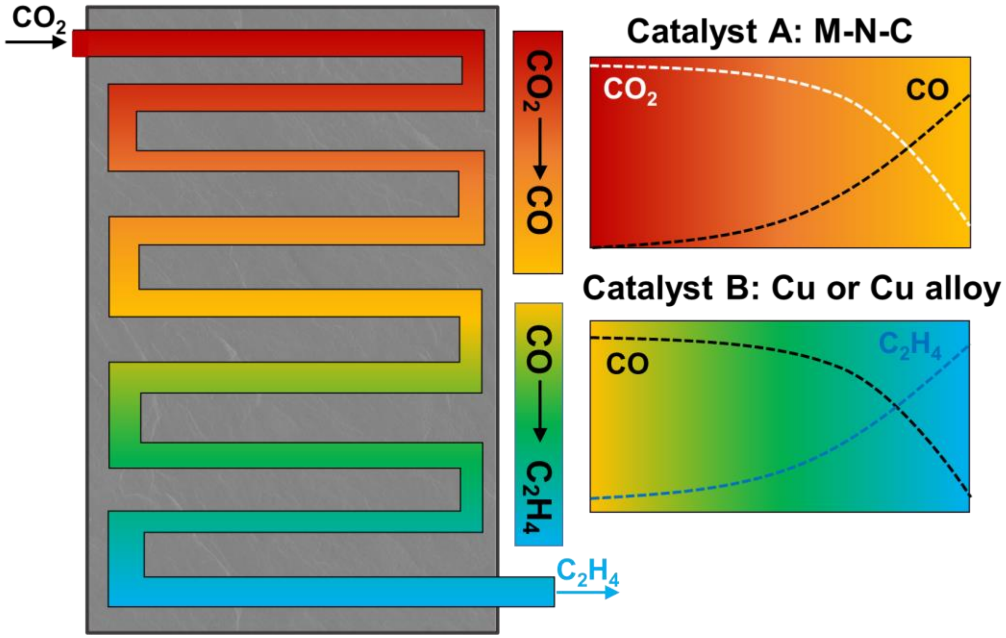
1) To design and fabricate tandem electrodes to direct the cascade reaction of $CO_2 \rightarrow CO \rightarrow C_2H_4$;

2) To develop a functionally graded catalyst layer in the tandem electrodes to balance the transport of electron, ions, and reactants;

3) To explore the pulse electrolysis technology to boost the production yield of C_2H_4 and lower the overpotential;

4) To demonstrate the MEA-type cell integrating the tandem electrodes for CO_2 pulse electrolysis.

Tandem CO_2 reduction in the gas diffusion electrode



Project Overview: budget, period, and participants

1. Project budget and period

- Funding: $1,000,000 DOE, $250,000 Cost Share
- Overall Project Performance Dates

  09/01/2020 to 08/31/2022 (1 year no cost extension was requested)

2. Project participants

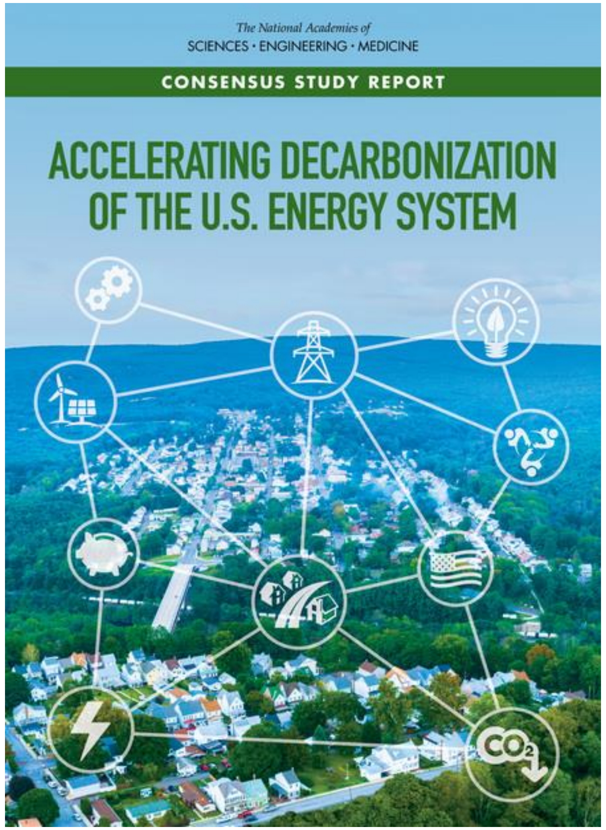
DOE/NETL
Project Manager
Dr. Naomi O'Neil

Principal Investigator
Dr. Xiao-Dong Zhou
University of Louisiana at Lafayette

Design of functionally graded catalyst layers, integration of MEA cell, and TEA and LCA
PI: Dr. Xiao-Dong Zhou
University of Louisiana at Lafayette

Development of catalysts, Design of tandem electrodes and pulse electrolysis protocol
Co-PI: Dr. Jingjie Wu
University of Cincinnati

Technical and Scientific Background



CLEAN
FUTURE

A massive, unprecedented challenge to our species

Not only dramatically and rapidly reduce global emissions of CO_2, but remove billions of tons of CO_2 from the earth's atmosphere and oceans by mid-century.

A historic opportunity

Madam Secretary of DOE, "We're really interested in carbon capture, use, and sequestration CCUS on all fossil fuels… you can't get to net-zero carbon emissions without CCUS."

CCUS **is arguably the largest economic opportunity of the next hundred years.**

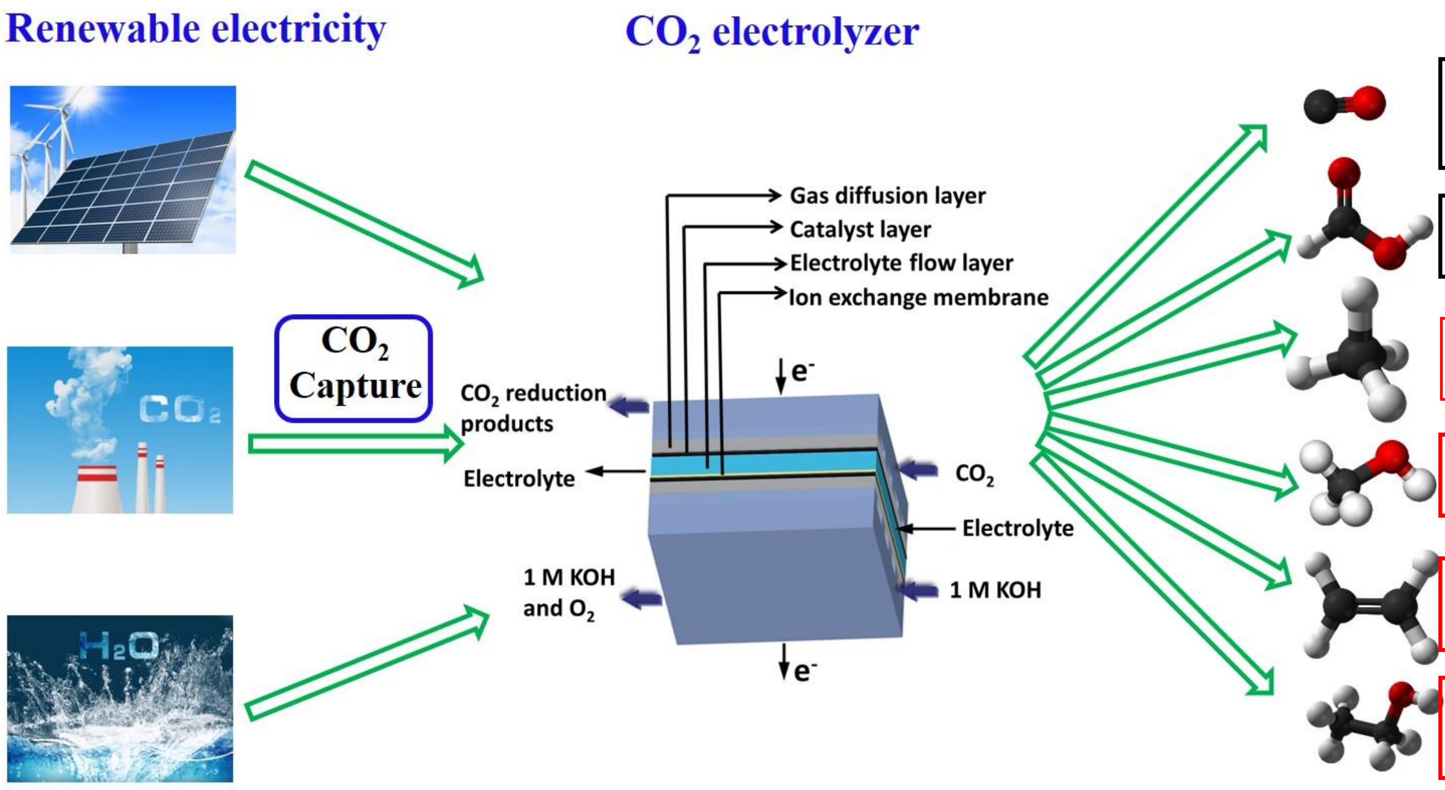
CO_2

- Supercritical CO_2
- Enhanced oil recovery
- Beverages & microcapsules

- Carboxylates & lactones
- Carbamates
- Urea or Isocyanates
- Biodegradable polymers

- Syngas, methane, ethylene
- Formic acid, methanol, etc

Electro-conversion of CO_2 to Chemicals: electrocatalysts

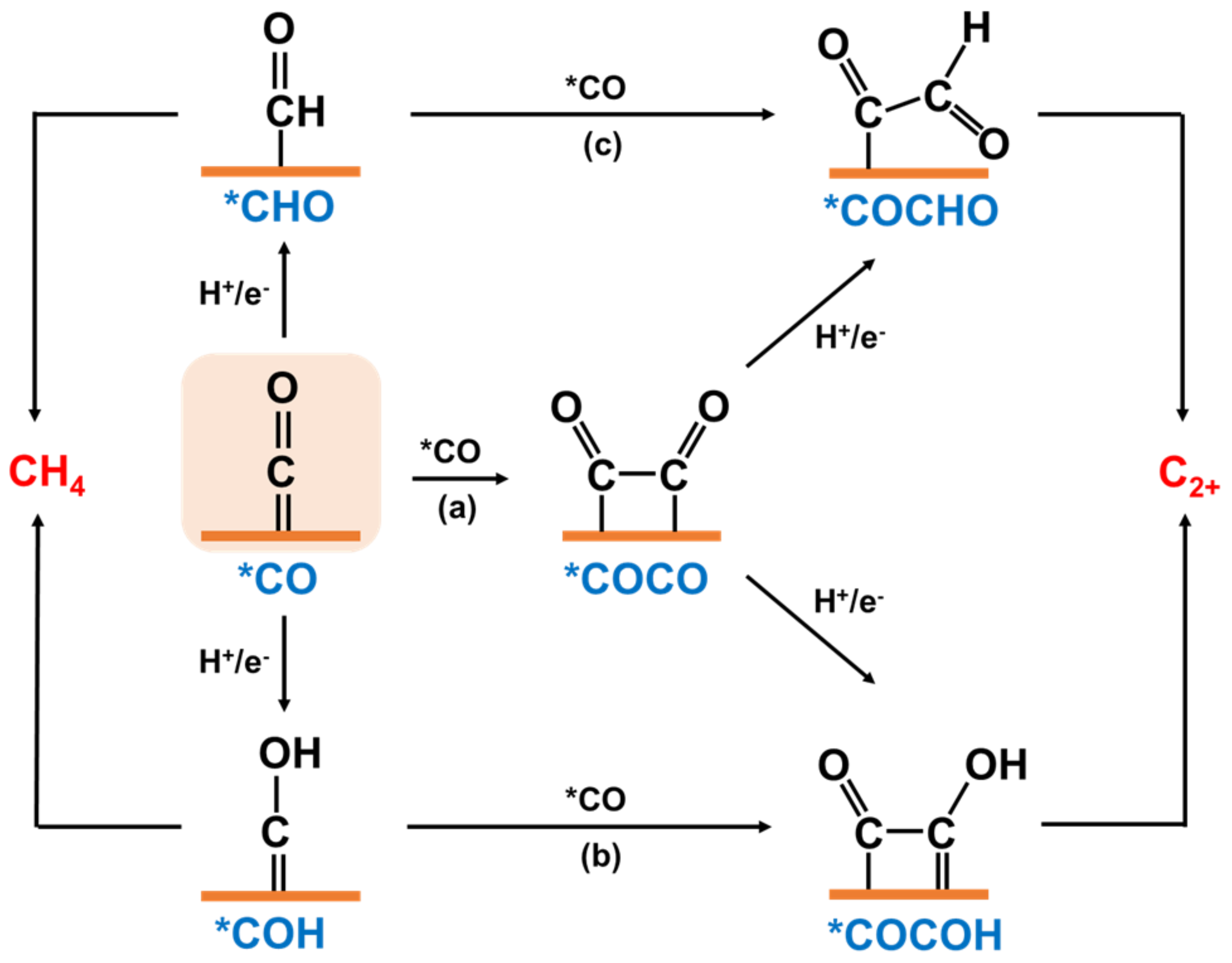


	State-of-art catalyst	Estimated market price (USD kg^{-1})	Estimated market size (Billion USD)
CO	Ag, Au, Zn, NCNTs, M-N-C	~1.20	2.7 - 3.2
HCOOH	Sn, Pb, In	0.40 - 0.90	0.62
CH_4	Cu	< 0.08	4.30
CH_3OH	Cu oxide	0.39 ~ 0.43	54
C_2H_4	Cu, NGQDs	0.80 - 1.10	155 - 248
C_2H_5OH	Cu, BN-nanodiamond	~0.52	110

- Modular processes that can be easily coupled with renewable electricity.
- Ease to scale-up to MW or GW plants.

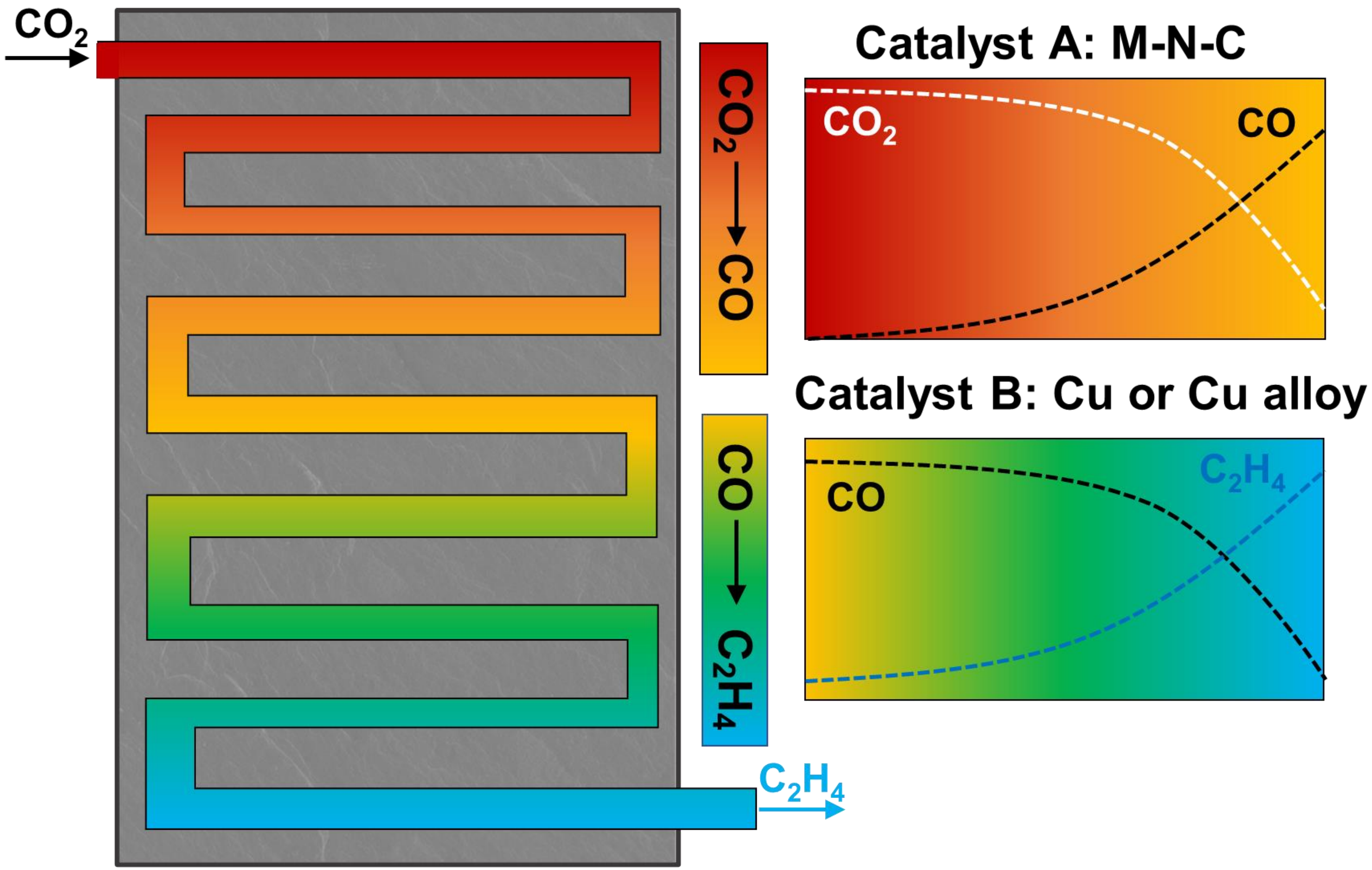
Electro-conversion of CO_2 to Chemicals: CO as the Key Intermediate for C_{2+} Products

Plausible C-C coupling pathways



- C-C coupling has various pathways, all of which involves CO.
- *CO has been identified a key intermediate for C_{2+} products formation.
- Increasing the *CO surface coverage enhances the C-C coupling kinetics according to the law of mass action.

How to Utilize the Intermediate $^{*}CO$ to Promote the formation of C_2H_4?



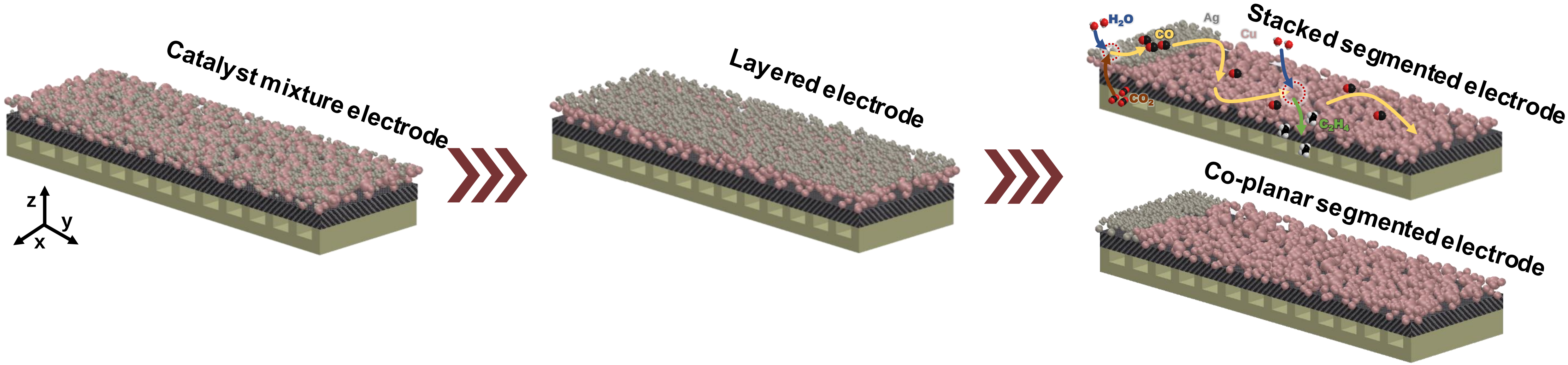
- Realize cascade reaction $CO_2 \rightarrow CO \rightarrow C_2H_4$ in one electrolyzer to simplify the reactor design.
- Maximize the CO utilization by using a tandem electrode design.

Project Progress: Tandem Electrodes

Conventional electrode

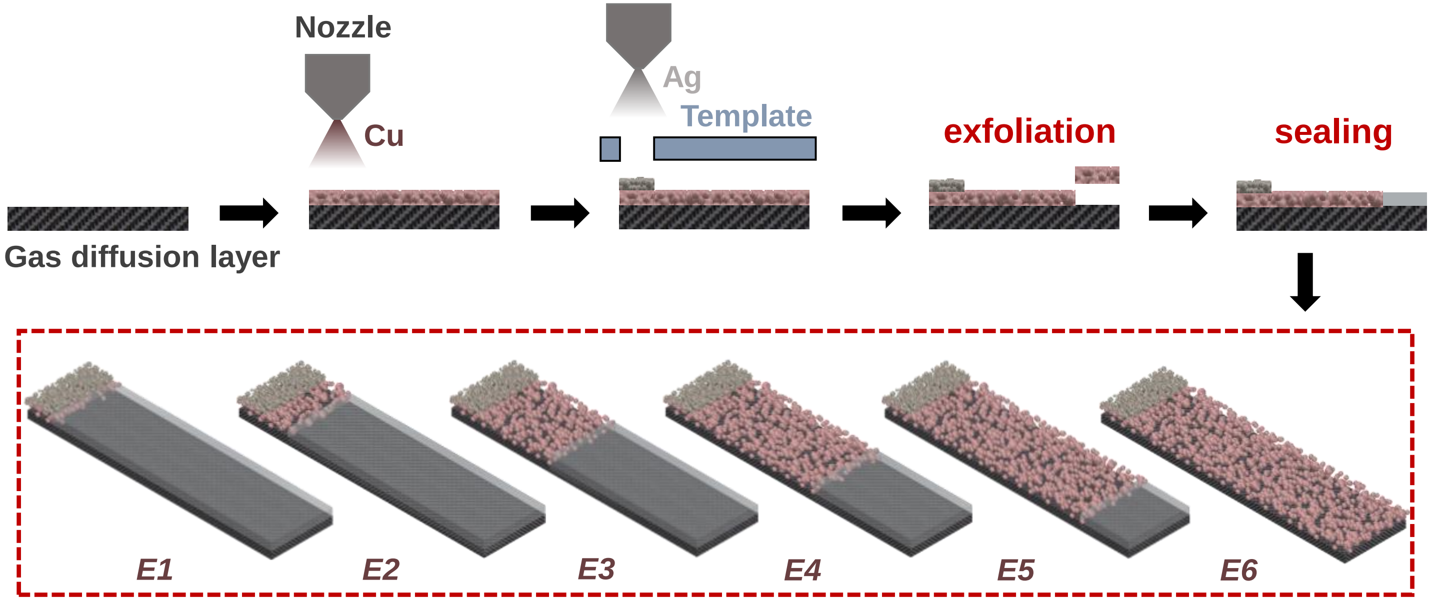
1st generation tandem electrode

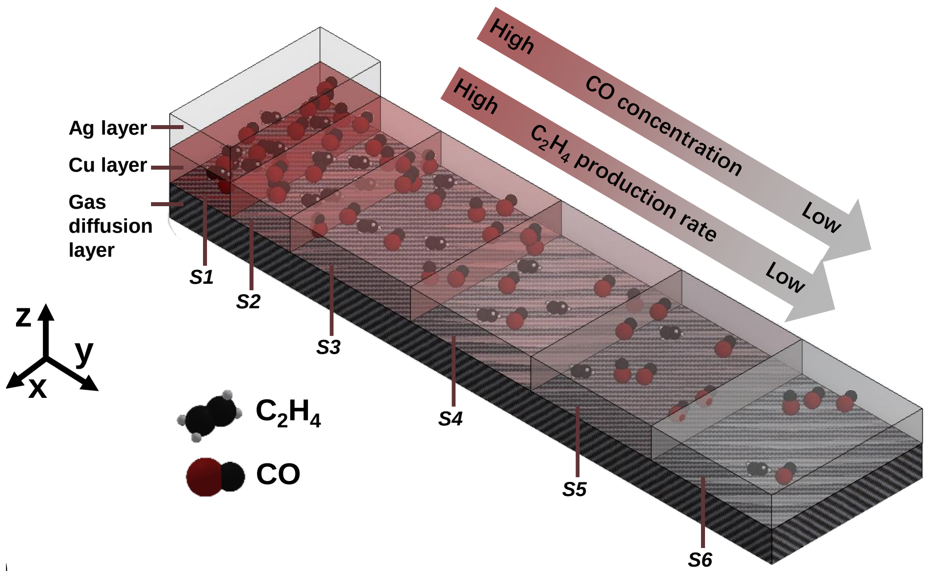
2nd generation tandem electrode

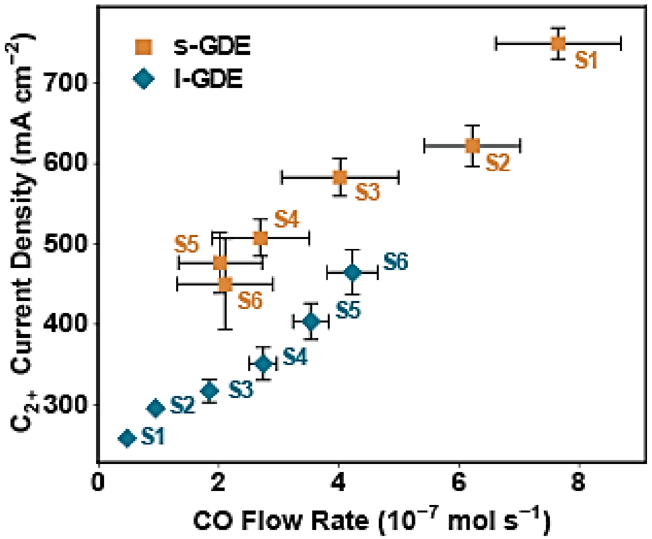


- Tandem electrode design principle: maximize the Θ_{*CO} at the Cu surface, leading to simultaneously maximized selectivity and productivity of C_2H_4 through cascade reaction $CO_2 \rightarrow CO \rightarrow C_2H_4$.
- Effectiveness: segmented > layered > tandem catalyst

Tandem Electrode Design: along-the-channel conversion of generated CO





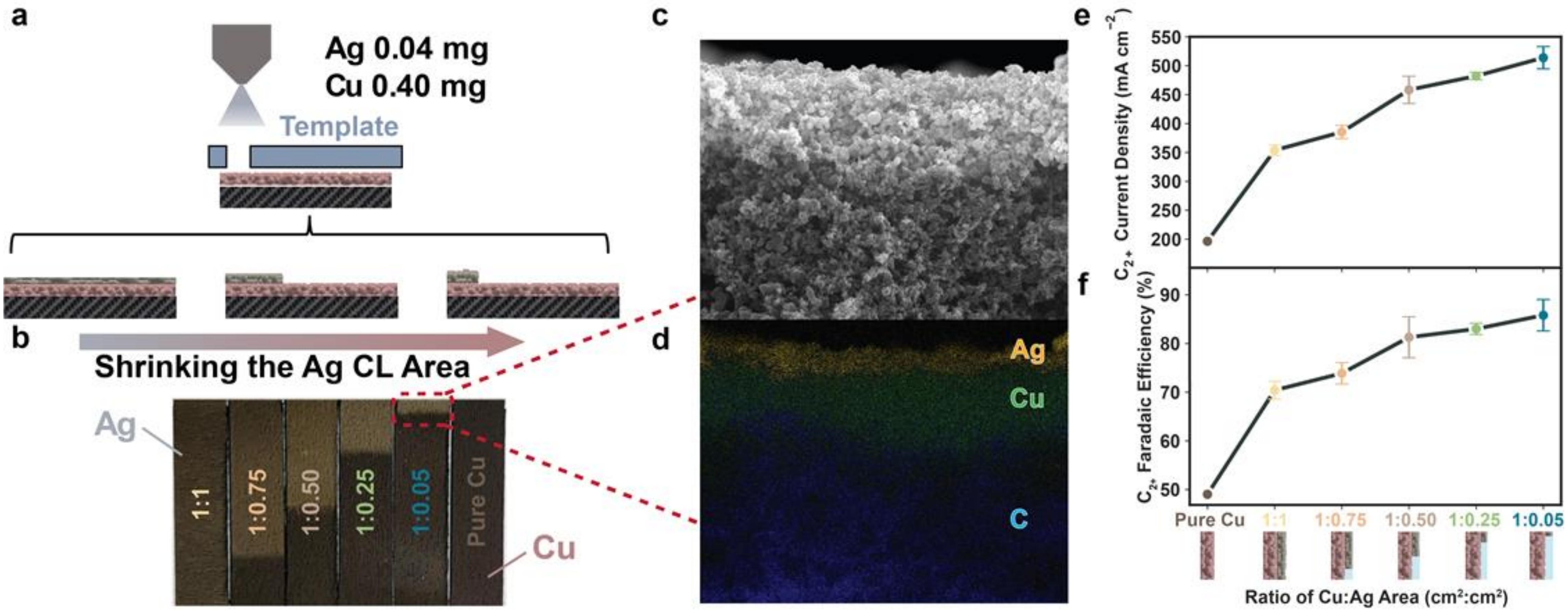


1) As CO concentration decreases down the length of the segmented GDE, C_{2+} productivity decreases as well.

2) Segmented GDE delivers higher CO concentration and C_{2+} productivity than layered GDE.

Nature Catalysis, 2022, 5, 202–211.

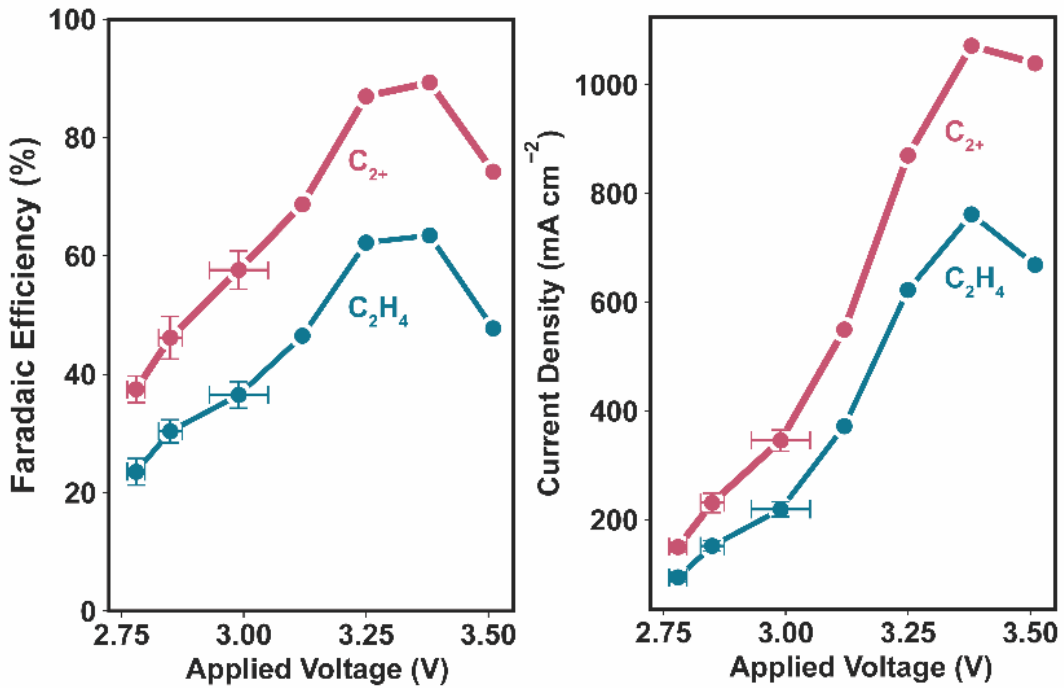
Tandem Electrode Design: optimal catalyst layer area ratio



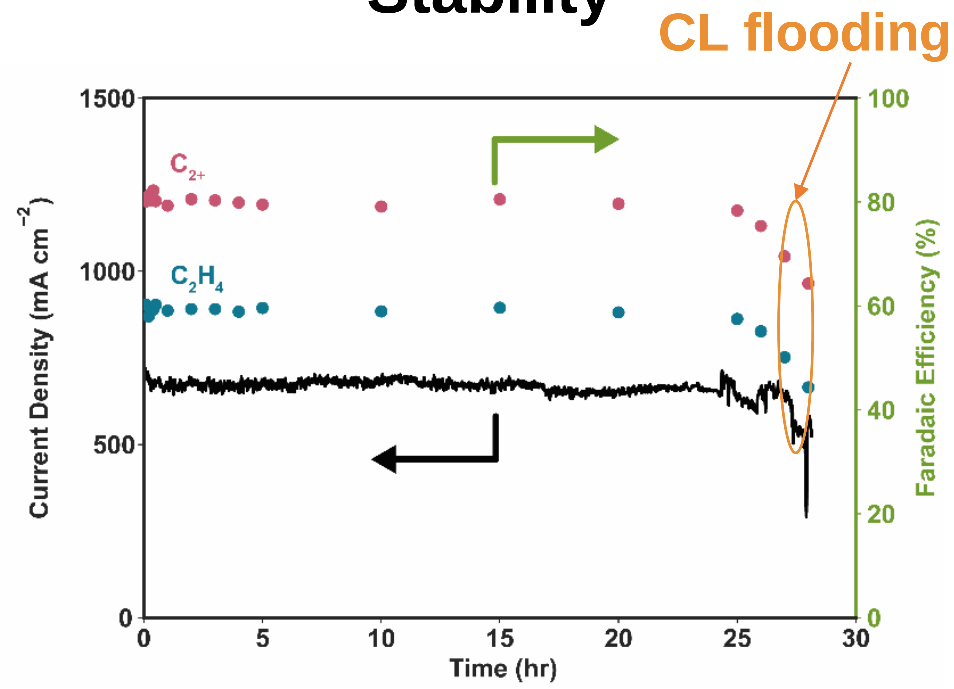
- **Shrinking Ag CL providing more concentrated CO for C-C coupling on the Cu CL, and thus yielding higher selectivity and productivity of C_{2+} products.**

Tandem Electrode Design: synergy between Cu and CO-generating catalyst

Activity and Selectivity

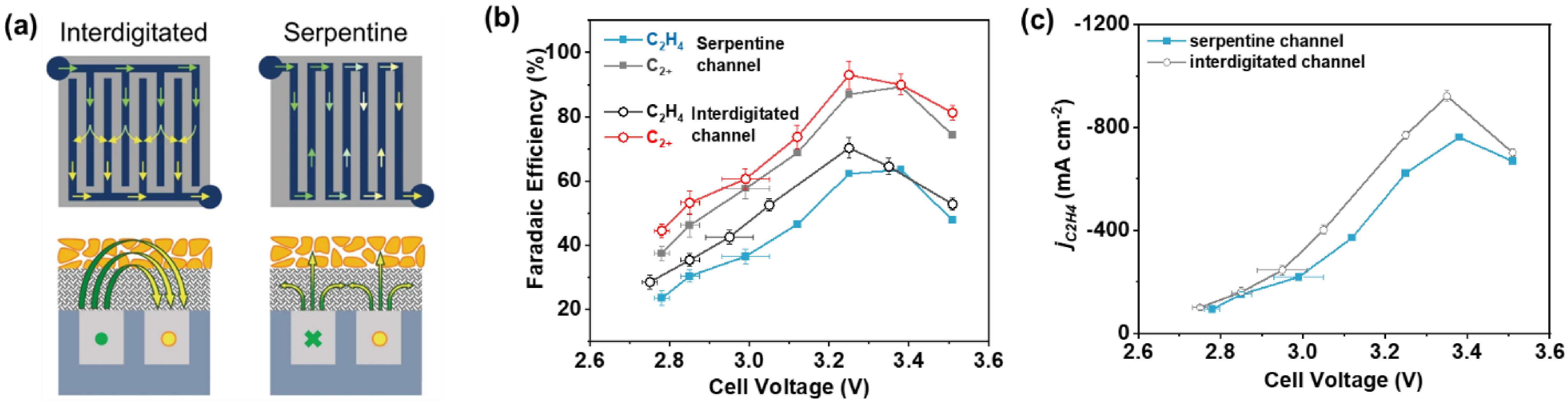


Stability



- Cu/Fe-N-C tandem electrode (Cu : Fe-N-C area ratio = 1 cm^2 : 0.05 cm^2) achieving 60% FE of C_2H_4 at current density > 1 A/cm^2 in a flow cell with a thin catholyte layer.
- Severe catalyst layer flooding limiting the long-term operation of tandem electrodes, especially at current density > 500 mA/cm^2.

Tandem Electrode Design: enhanced gas mass transport

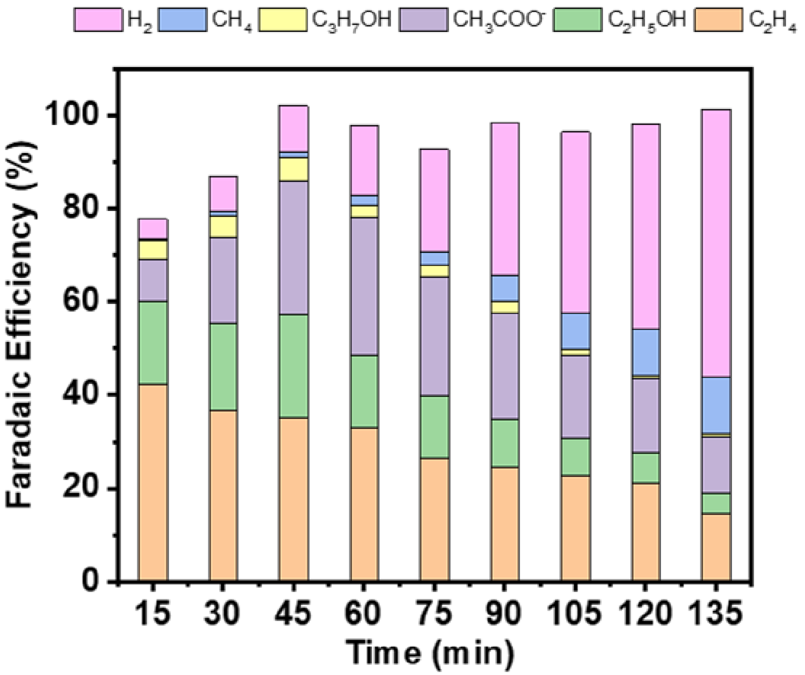


X. Feng et al., Nature Communications, 2011, 12, 136 .

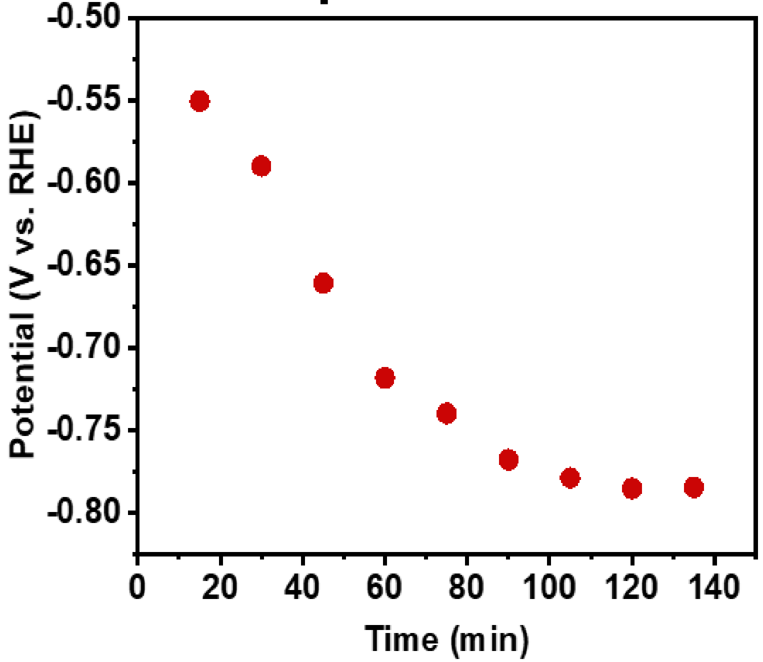
- **Interdigitated flow channel forces gas convection into the electrode and then exit to the outlet channels, enhancing mass transport of CO_2/CO into the catalyst layer.**
- **Maximum FE of C_2H_4 increased from 60% with serpentine flow field to ~70% with the interdigitated flow field at a partial current density of over 750 mA cm^{-2} on Cu/Fe-N-C tandem electrode.**

Tandem Electrode Design: flooding issue of current GDE structure

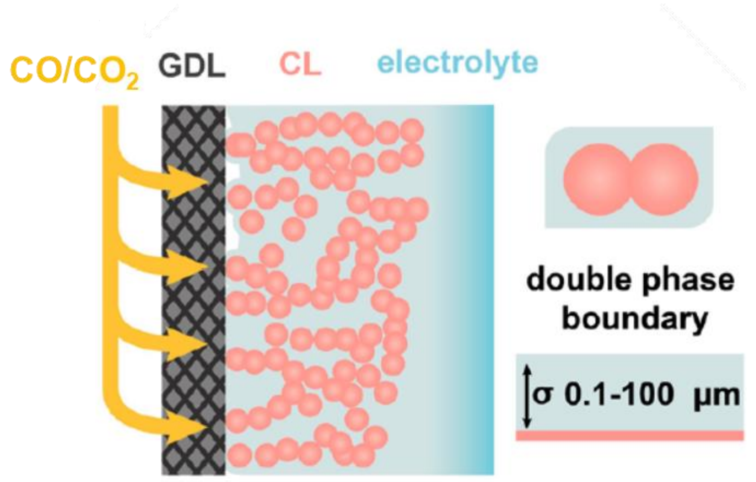
Decrease selectivity towards C_{2+}



Increase mass transfer polarization



Flooding model of CL

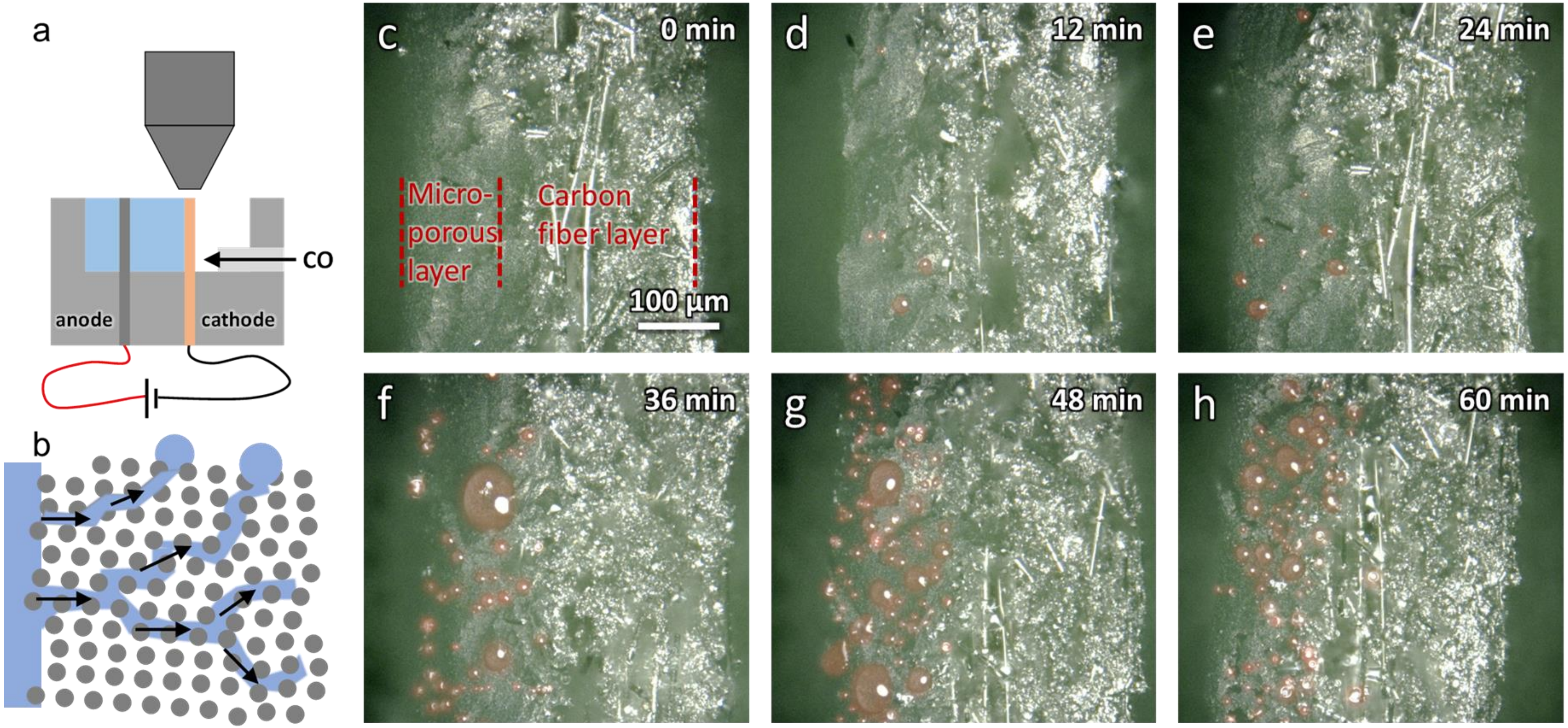


Galvanostatic electrolysis of CORR at 400 mA cm^{-2} on a GDE composed of SGL 39BB GDL and Cu CL

- Solubility in water at 1 atm and 25 °C: CO (0.98 mM) versus CO_2 (33 mM)
- CO reduction reaction (CORR) as the probe for catalyst layer flooding
- The current GDEs with structure and formulation adapted from PEMFC are prone to flooding in a short time, limiting the CO utilization efficacy.

J. Electrochem. Soc., 2022.

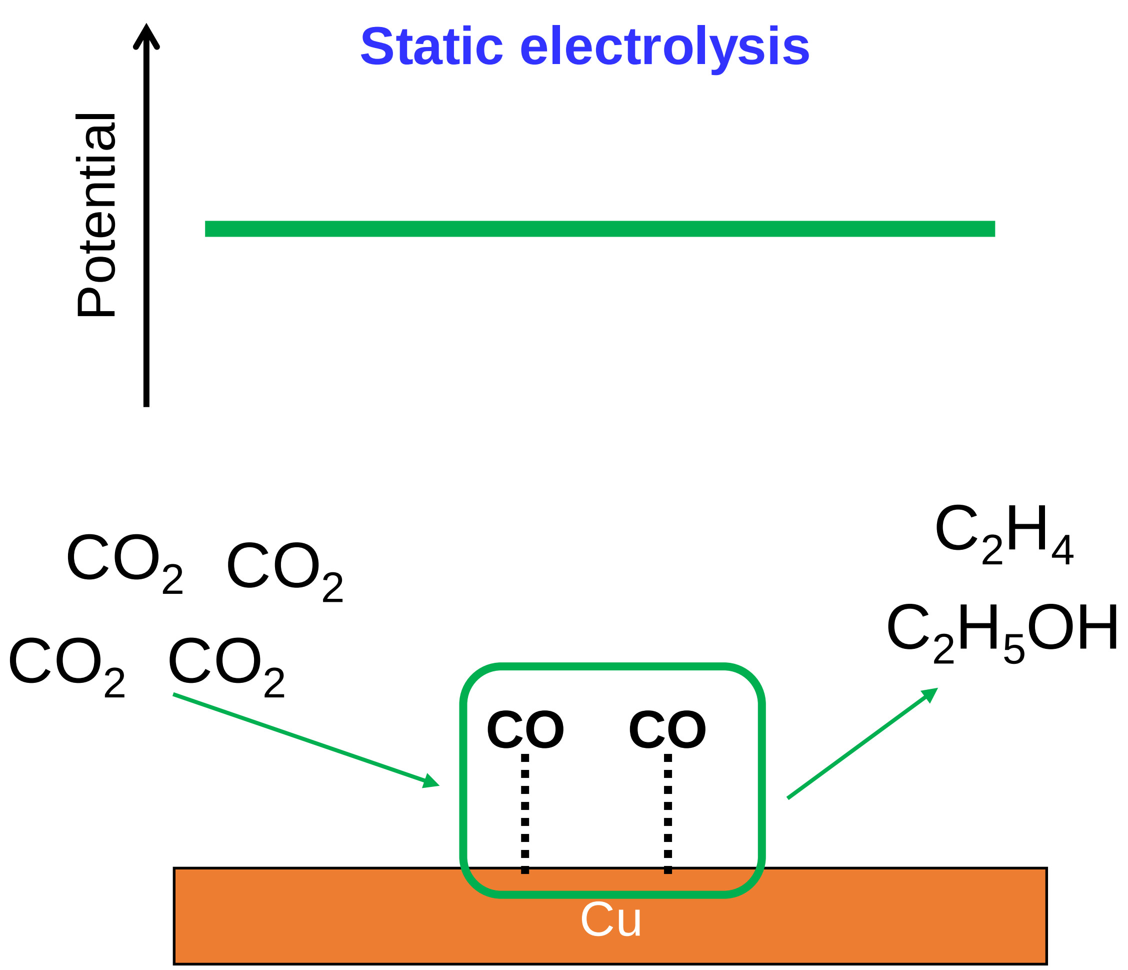
Tandem Electrode Design: flooding issue of current GDE structure

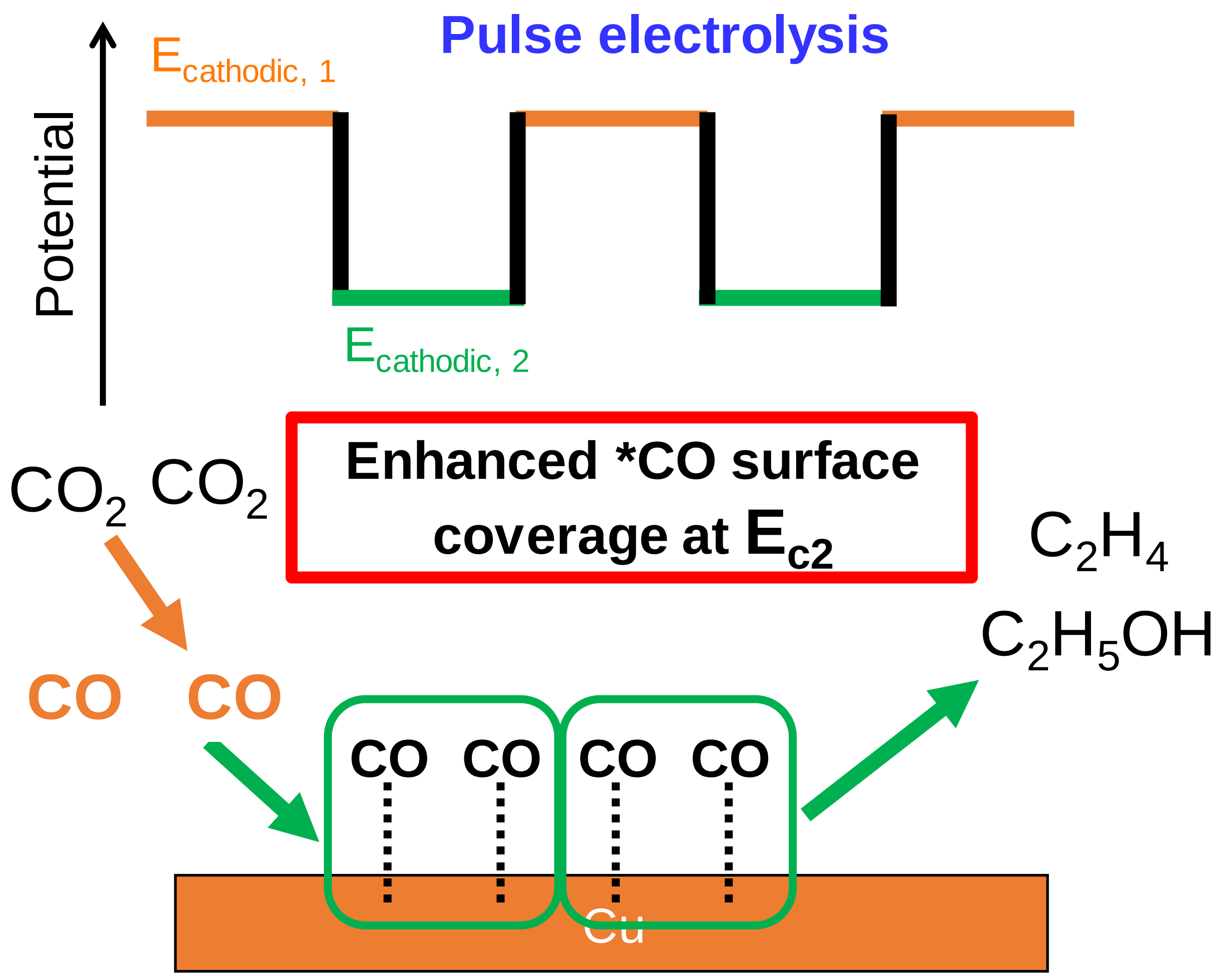


- **Flooding extends to gas diffusing layer.**
- **Design CL and GDL microstructures with effective water management is the focus of future work in order to increase the performance and stability of tandem electrodes.**

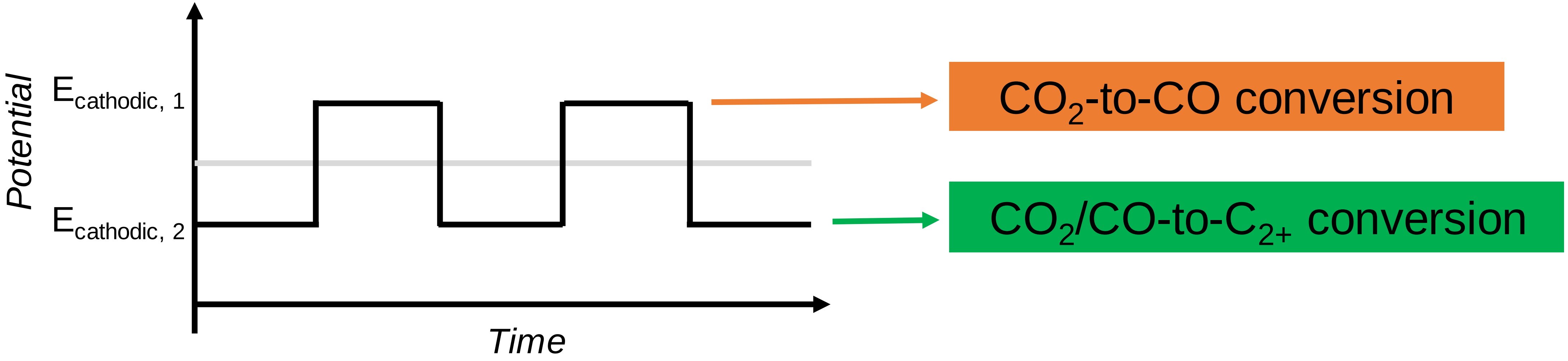
Project Progress: Pulse Electrolysis

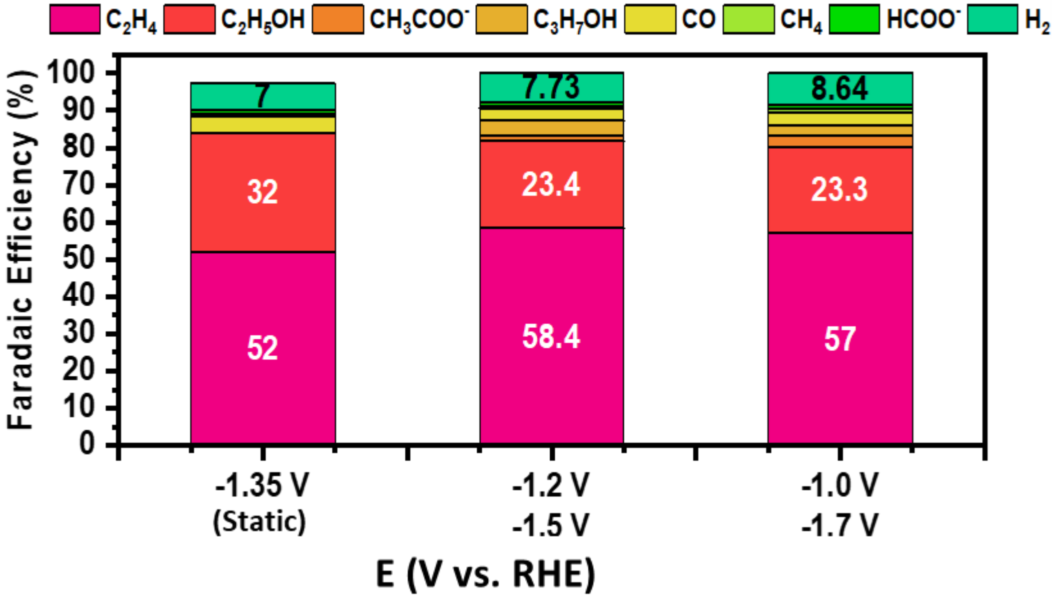
Control pulse potential: CO supply from CO-generation catalyst layer in the tandem electrode

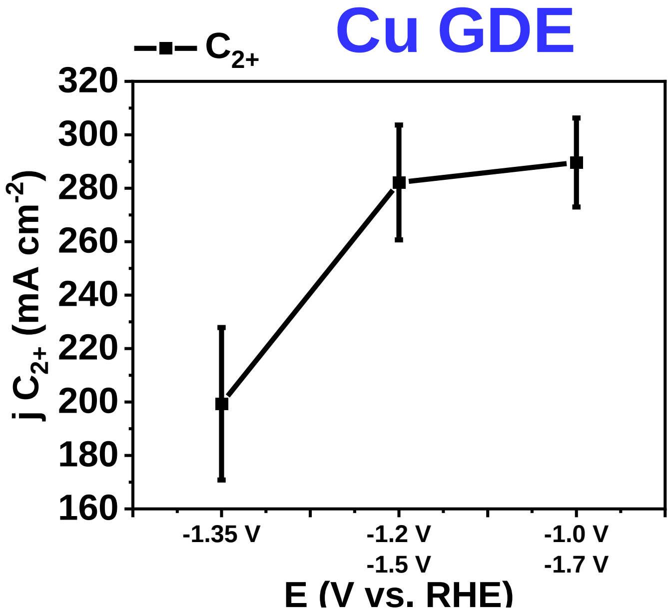




Pulse Electrolysis: enhancement of C_2H_4 selectivity and productivity on Cu GDE



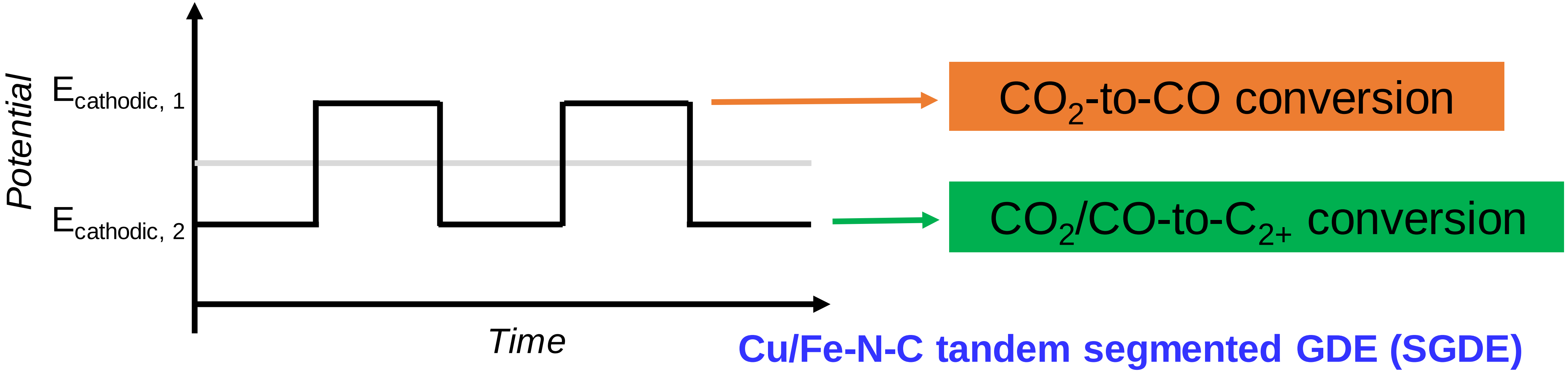




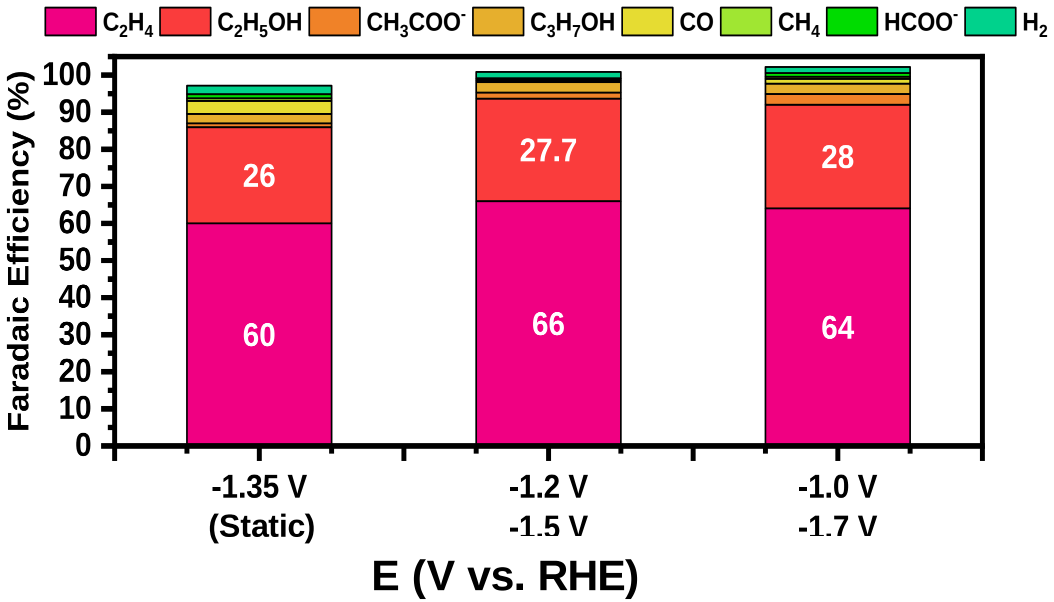
- Cathode potential without iR compensation.
- Faradaic efficiency and partial current density of C_{2+} and C_2H_4 enhances with pulse electrolysis.

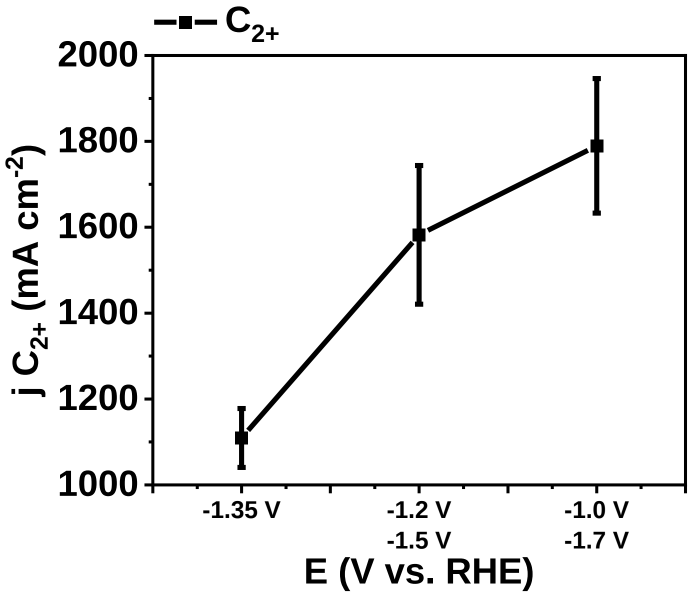
J. Electrochem. Soc., 2022.

Pulse Electrolysis: enhancement of C_2H_4 selectivity and productivity on Cu/Fe-N-C SGDE



Cu/Fe-N-C tandem segmented GDE (SGDE)

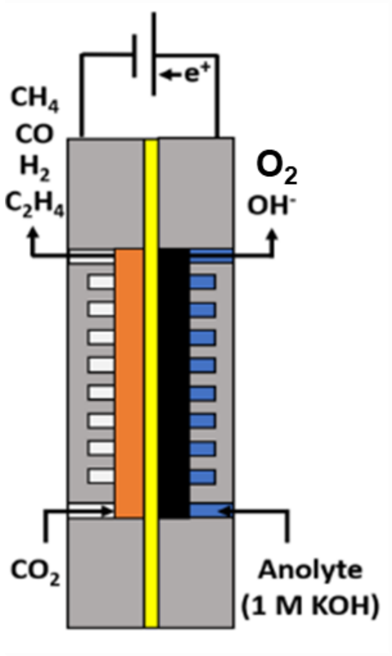


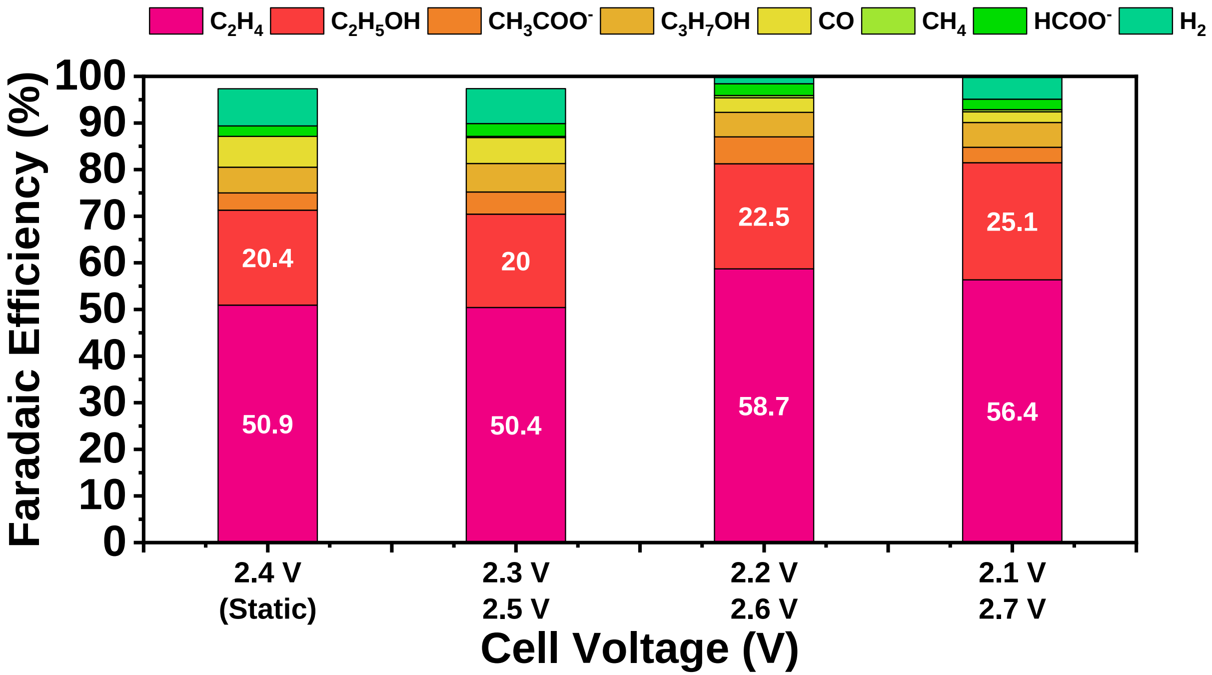


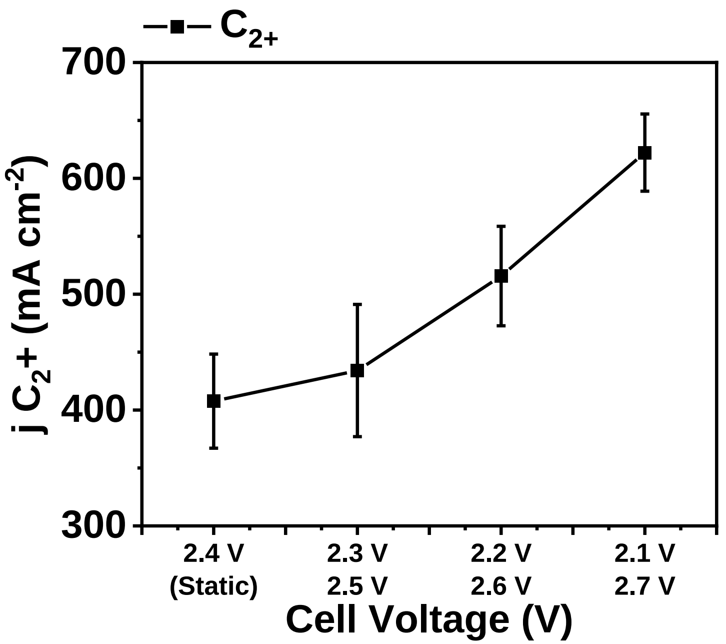
- Pulse electrolysis further promotes Faradaic efficiency and partial current density of C_{2+} and C_2H_4 on tandem SGDE.
- 66% FE of C_2H_4 at j_{C2H4} > 1100 mA cm^{-2}

Integration in a MEA cell: pulse electrolysis + tandem SGDE

Cu/Fe-N-C Tandem SGDE + Pulse Electrolysis + MEA Cell with a Serpentine Flow Field







- MEA cell shows lower selectivity of C_2H_4 and compared to flow cell due to the change of GDE surface micro-environment (e.g., local pH and water saturation in the GDE).
- Pulse electrolysis compensates the decline In the MEA cell, prompting the FE of C_2H_4 to 59% at a C_2H_4 partial current density of 340 mA cm^{-2}.

Project Progress: Milestone

Milestone Title and Description	Planned Completion Date	Actual Completion Date
Fabrication of tandem electrodes with a dimension > 2 × 2 cm^2	June 30, 2021	March 31, 2021
Achieving a current density > 0.5 A/cm^2 for the electrolysis	June 30, 2021	March 31, 2021
Achieving the cathodic energy efficiency of 50% at a current density of 0.5 A/cm^2	March 31, 2022	July 31, 2022
Achieving a selectivity of 90% towards ethylene at 1 A/cm^2	August 31, 2022	70% at 1 A/cm^2 by July 31, 2022

Summary

1. Major accomplishments

- Established the design principle of tandem electrodes
- Achieved 70% selectivity of C_2H_4 at 1 A cm^{-2} current density on segmented electrodes in the flow cell
- Developed pulse electrolysis protocol involving two reduction potentials and applied pulse electrolysis to tandem electrodes
- One formal patent for tandem electrodes was filed.

2. Future work

- Develop advanced Cu-based catalysts to increase the selectivity to C_2H_4
- Optimize the microstructure of catalyst layer to increase the CO flux and CO utilization efficiency in the tandem electrodes
- Intensify the process in the MEA cell
- Perform final TEA and LCA

Acknowledgment

Graduate students and postdocs at

University of Cincinnati

University of Louisiana Lafayette

Project Manager

Dr. Naomi O'Neil

National Energy Technology Laboratory

Thank You!

Appendix

			FY2021				FY2022			
			Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
1	1	Task 1. Project Management, Planning and Reporting								
2	2	Task 2. Design and fabricate tandem electrodes								
3	M2.1	Control over the size and distribution of Cu and C nanoclusters		◆ 01/30						
4	M2.2	Fabrication of tandem electrodes			◆ 05/30					
5	3	Task 3. Develop graded catalyst layers								
6	M3.1	Achieving catalyst layer with control over porosity and activity					◆ 01/30			
7	4	Task 4. Develop Pulsed Electrolysis Protocols								
8	M4.1	Identification key chemistry during pulsed electrolysis						06/01 ◆		
9	5	Demonstrate MEA-type cells for high efficiency conversion								
10	5.1	Integration of tandem electrodes into MEA-type cells								
11	M5.1	Current denstity > 500 mA/cm2					◆ 01/30			
12	M5.2	Achieving a selectivity of 90% for ethylene formation								09/01 ◆
13	6	Techno-economic analysis with technology gap analysis								
14	7	Life-cycle anlaysis								