High Efficiency Electrochemical Conversion of CO_2 to C_2H_4

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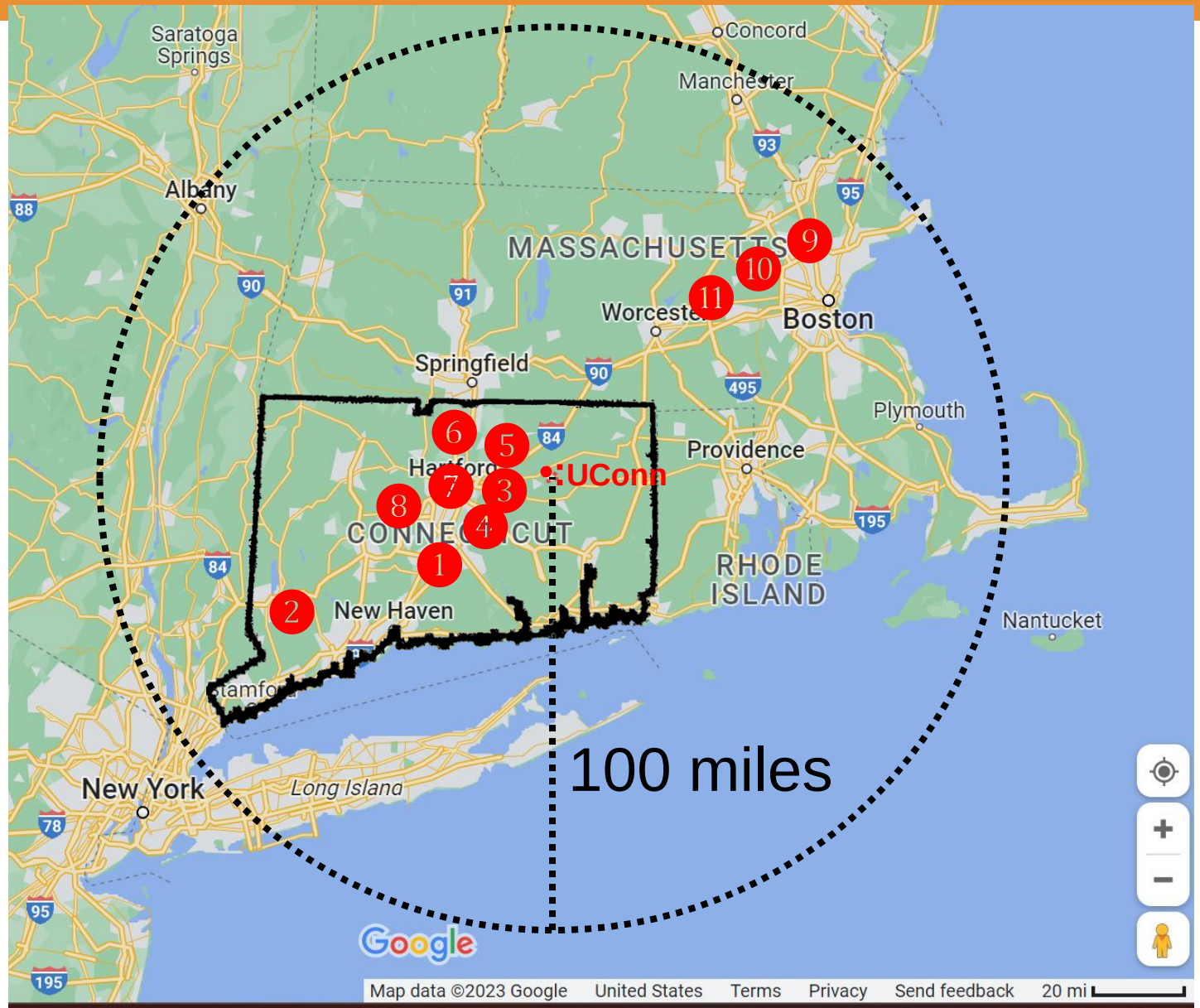
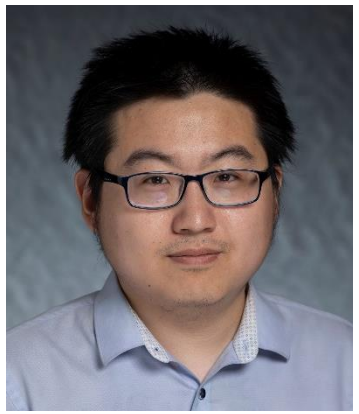
UConn – Carbon Neutrality by 2030



1: Nel Hydrogen
2: FuelCell Energy
3: Raytheon Technology Research Center
4: Pratt & Whitney
5: Connecticut Center for Advanced Tech
6: Infinity Fuel Cell & Hydrogen
7: Doosan Fuel Cell (HyAxiom)
8: Connecticut Green Bank

9: Envision Energy
10: Plug Power Electrolyzers
11: Giner Inc

Team Members –
Electrochemical Transformation



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Outline

1. **Technical and Scientific Background**
   Catalysts of CO_2 reduction, C-C coupling pathway

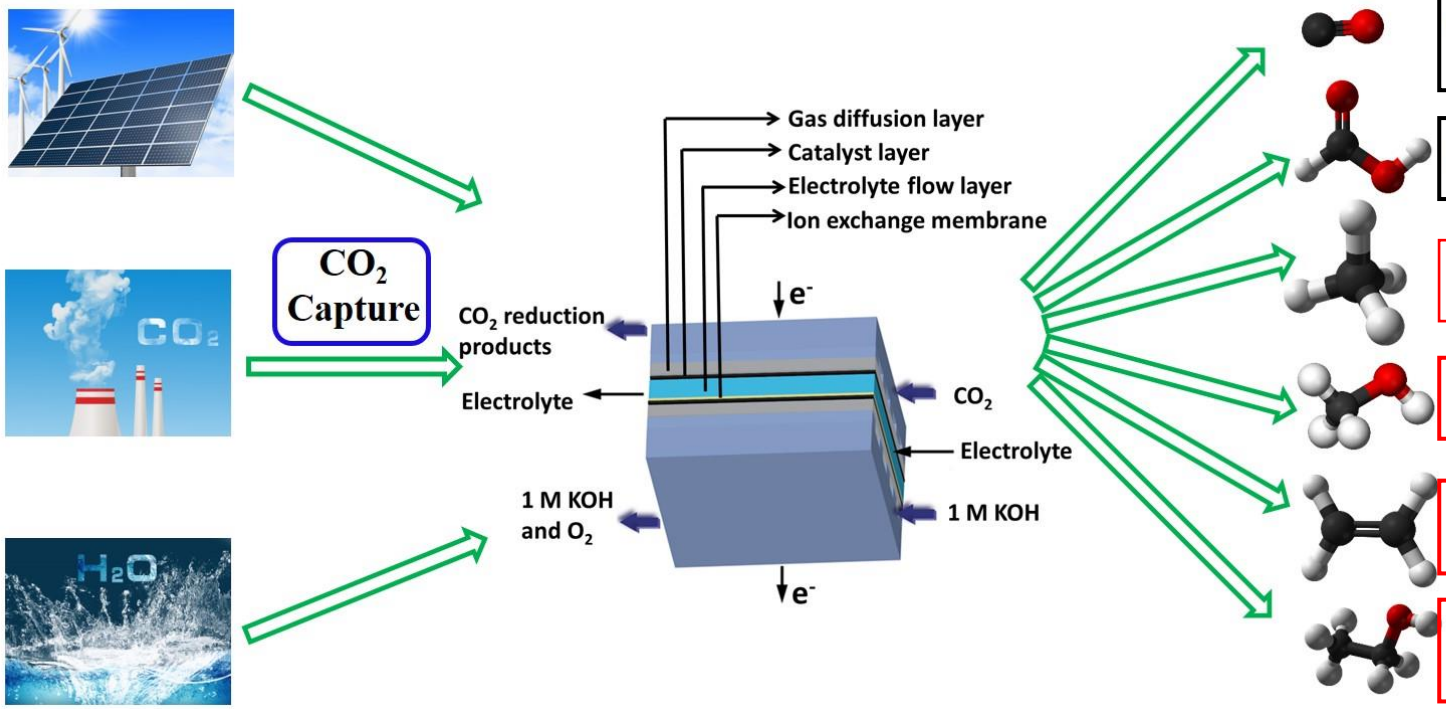
2. **Factors for an electrodes to promote the formation of C_2H_4**

3. **Tandem Electrodes**

4. **Pulsed Electrolysis**

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

Electro-conversion of CO_2 to Chemicals: Electrocatalysts



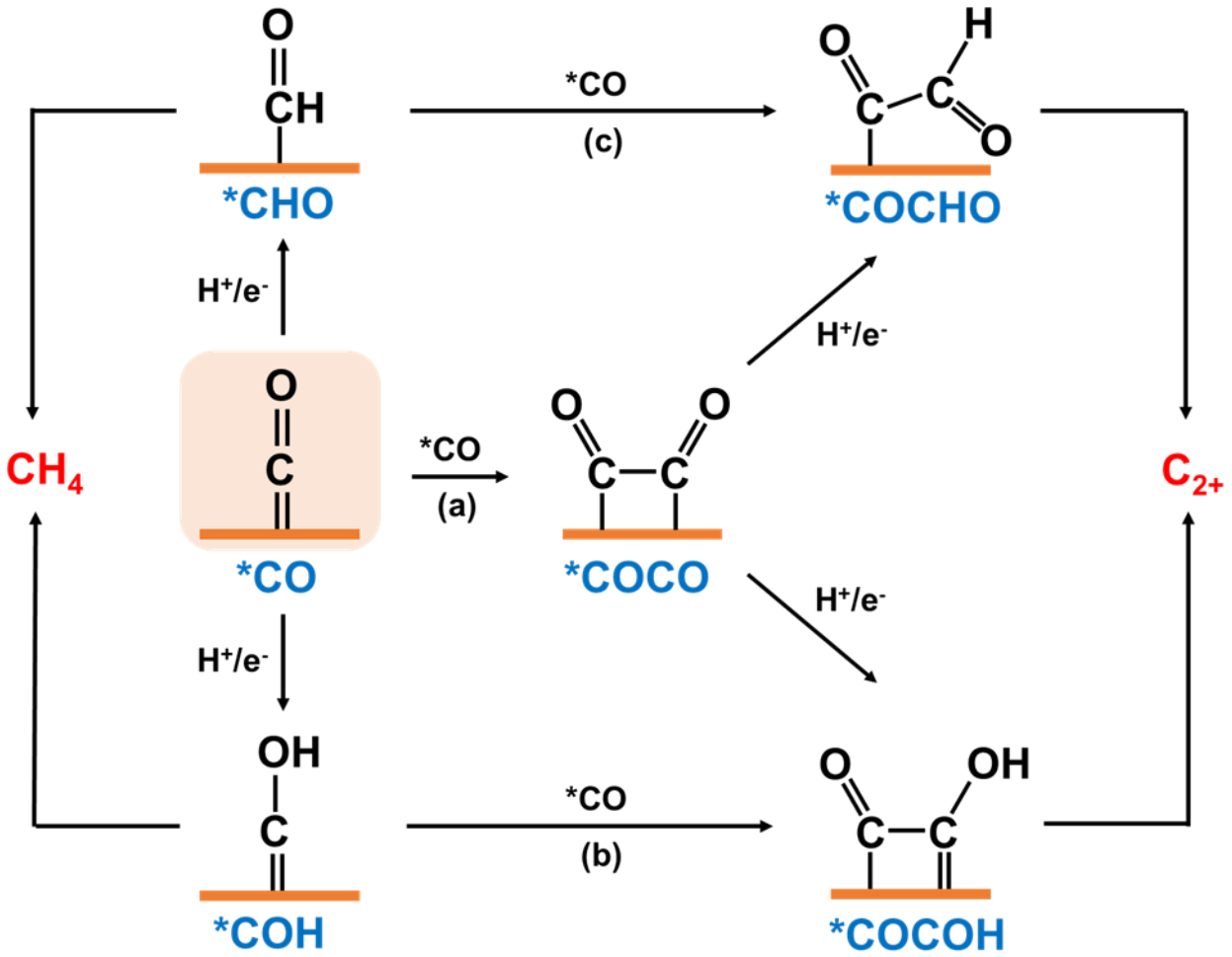
	State-of-art catalyst	Estimated market price (USD kg^{-1})	Estimated market size (Billion USD)
CO	Ag, Au, Zn, NCNTs, M-N-C	~1.20	2.7 - 3.2
HCOOH	Sn, Pb, In	0.40 - 0.90	0.62
CH_4	Cu	< 0.08	4.30
CH_3OH	Cu oxide	0.39 ~ 0.43	54
C_2H_4	Cu, NGQDs	0.80 - 1.10	155 - 248
C_2H_5OH	Cu, BN-nanodiamond	~0.52	110

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

Electrode Development

Electro-conversion of CO_2 to Chemicals: CO as a 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.

Zhao, Martirez, and Carter, PNAS, 2022
Garza, Bell, and Head-Gordon, ACS Catalysis, 2018

Research Objectives

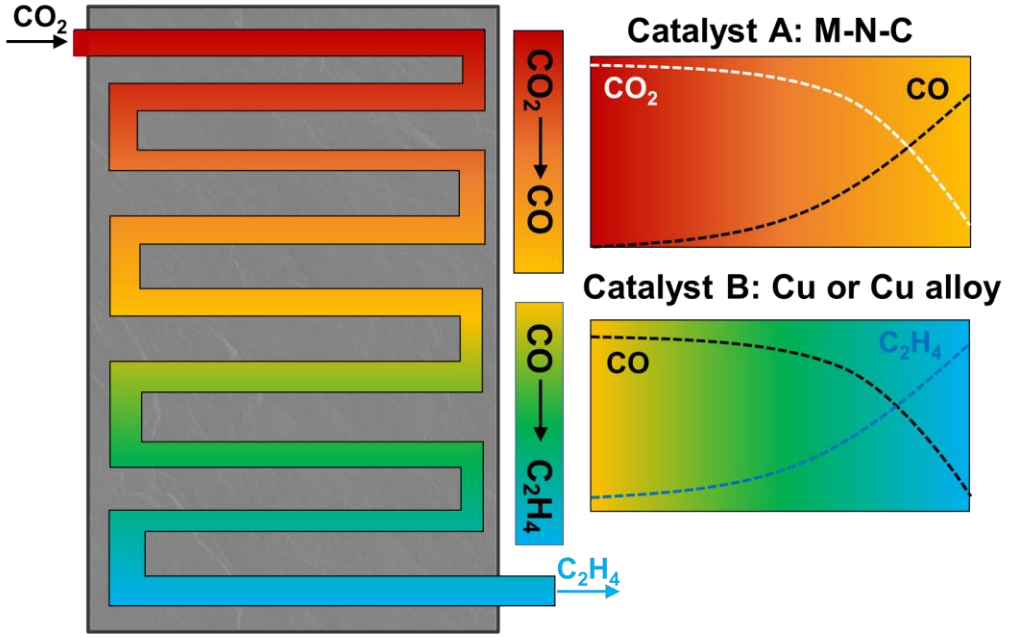
1) To design and fabricate tandem electrodes to direct the cascade reaction of $CO_2 \rightarrow CO \rightarrow C_2H_4$;

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

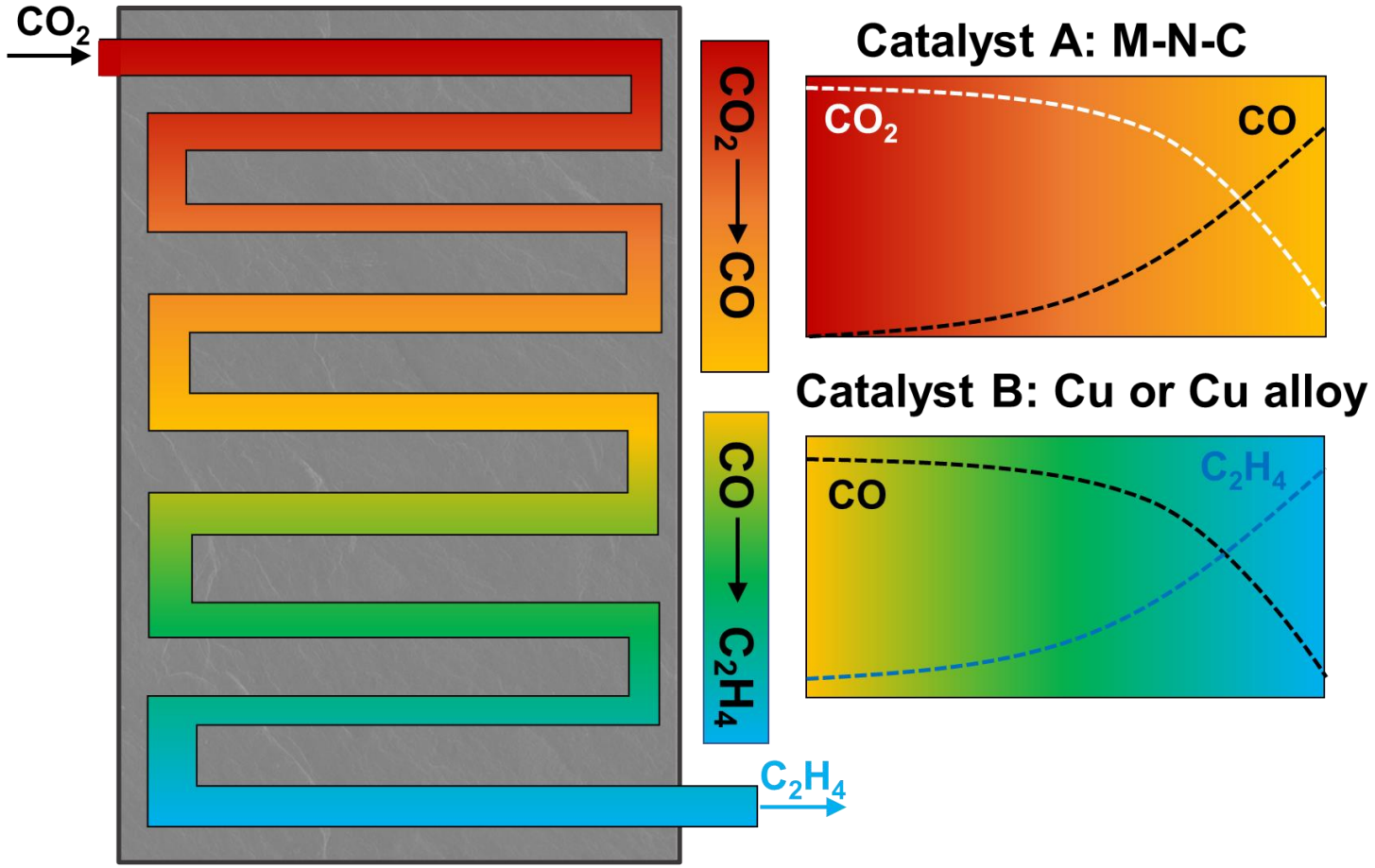
3) To explore the pulse electrolysis technology to boost the production yield of C_2H_4 and lower the overpotential;

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



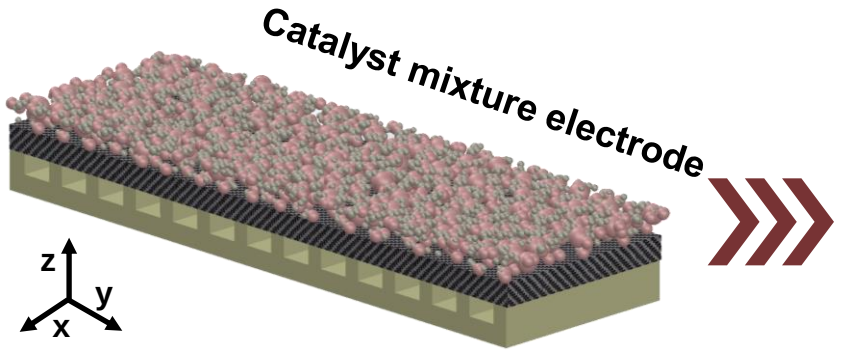
How to Utilize the Intermediate *CO to Promote the Formation of C_2H_4?



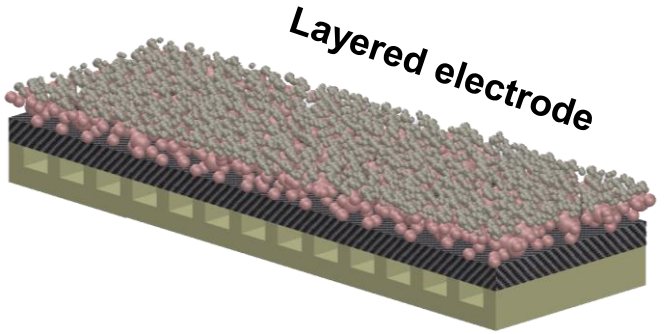
- Realize cascade reaction $CO_2 \rightarrow CO \rightarrow C_2H_4$ in one electrolyzer to simplify the reactor design.
- Maximize the CO utilization by using a tandem electrode design.

Tandem Electrodes

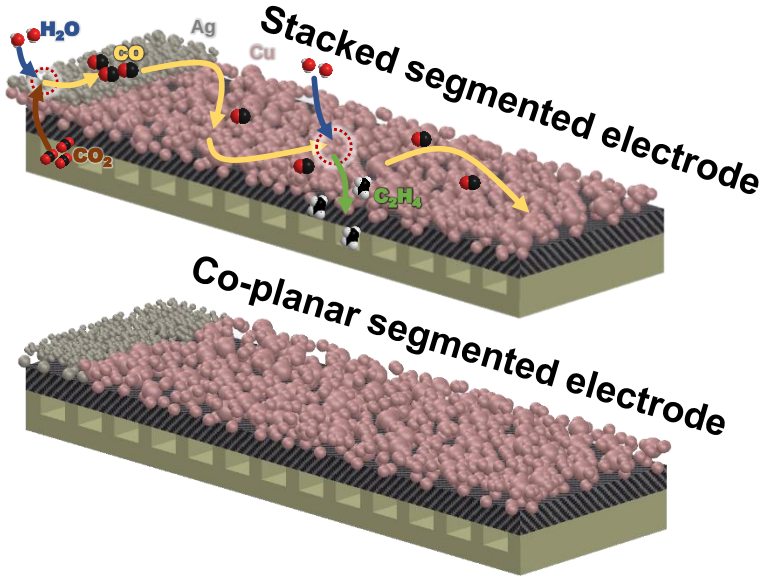
Conventional electrode



Layered electrode

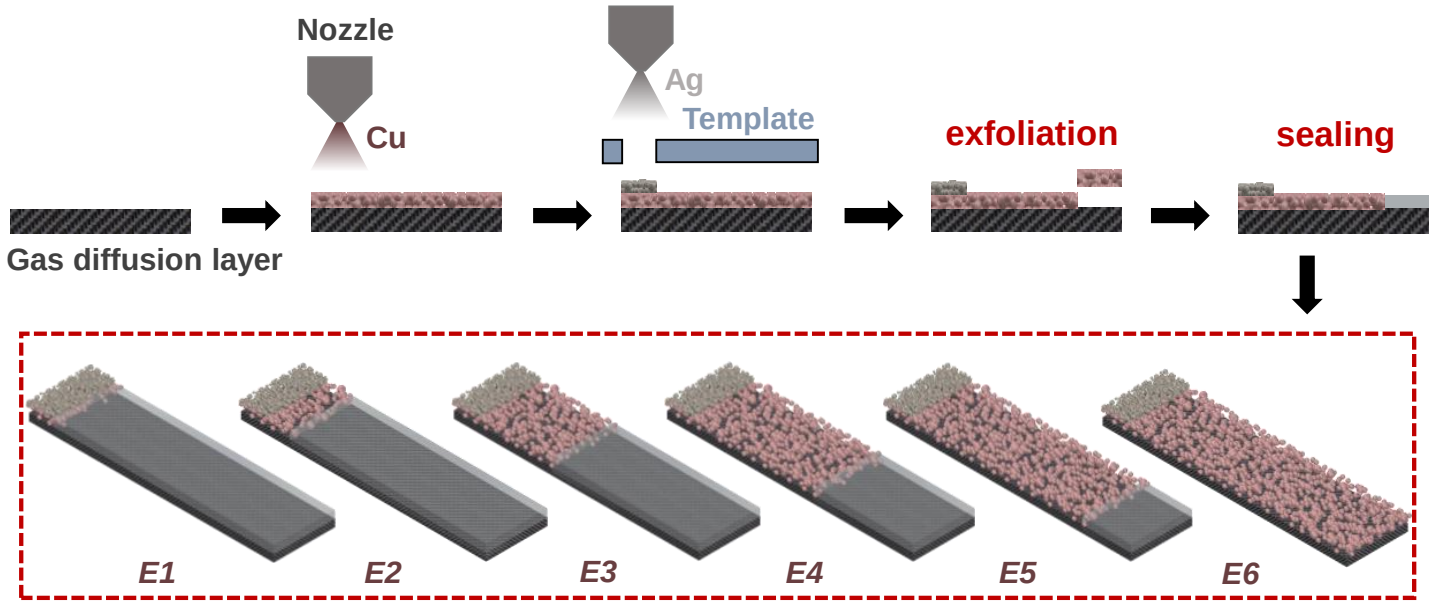


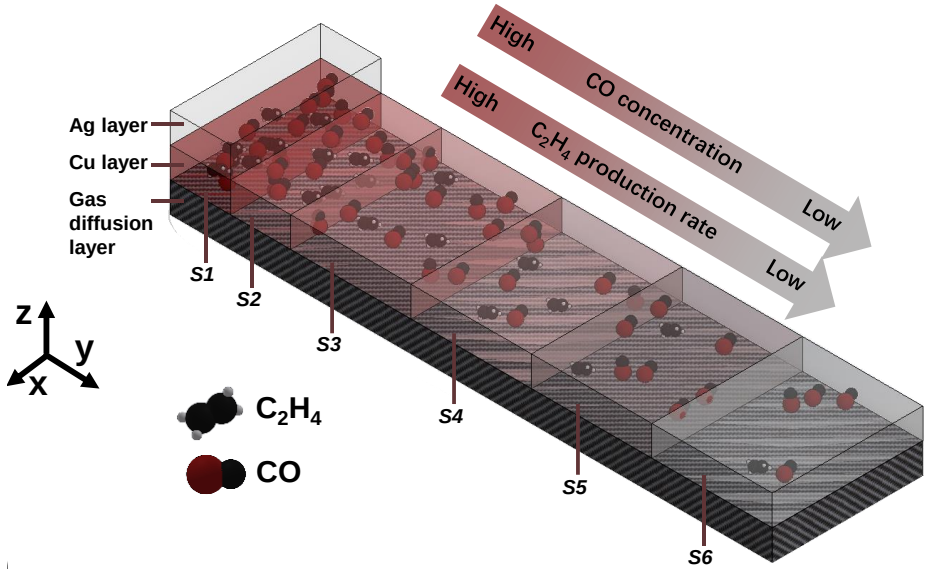
Tandem electrode



- Tandem electrode design principle: optimize 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

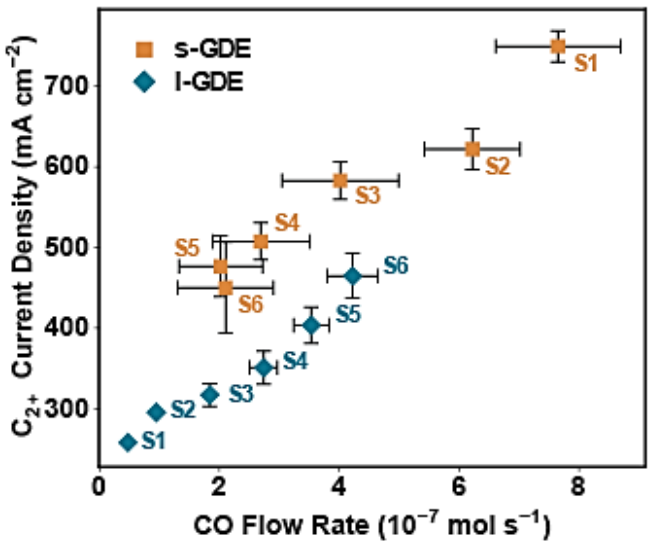
What's the role for the Ag on the conversion of C2+ products?





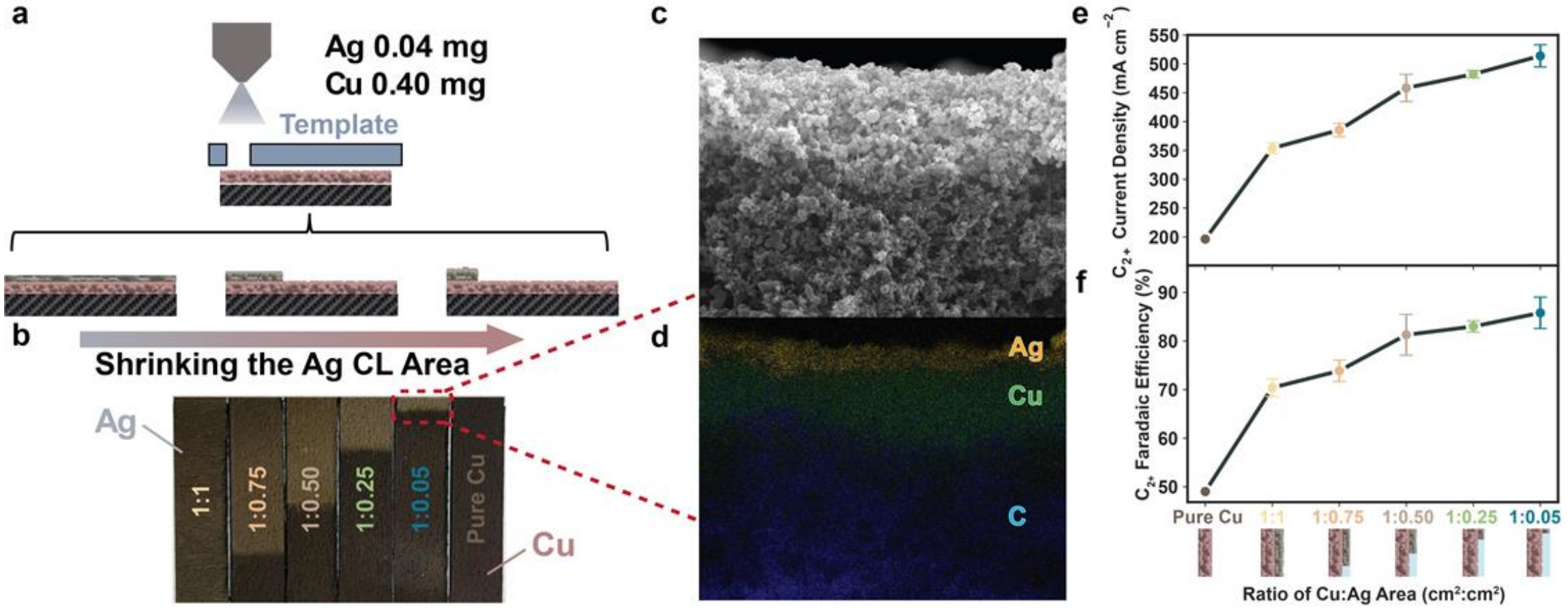
1) As CO concentration decreases down the length of the segmented GDE, C_{2+} productivity decreases as well.

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



Nature Catalysis, 2022, 5, 202–211.

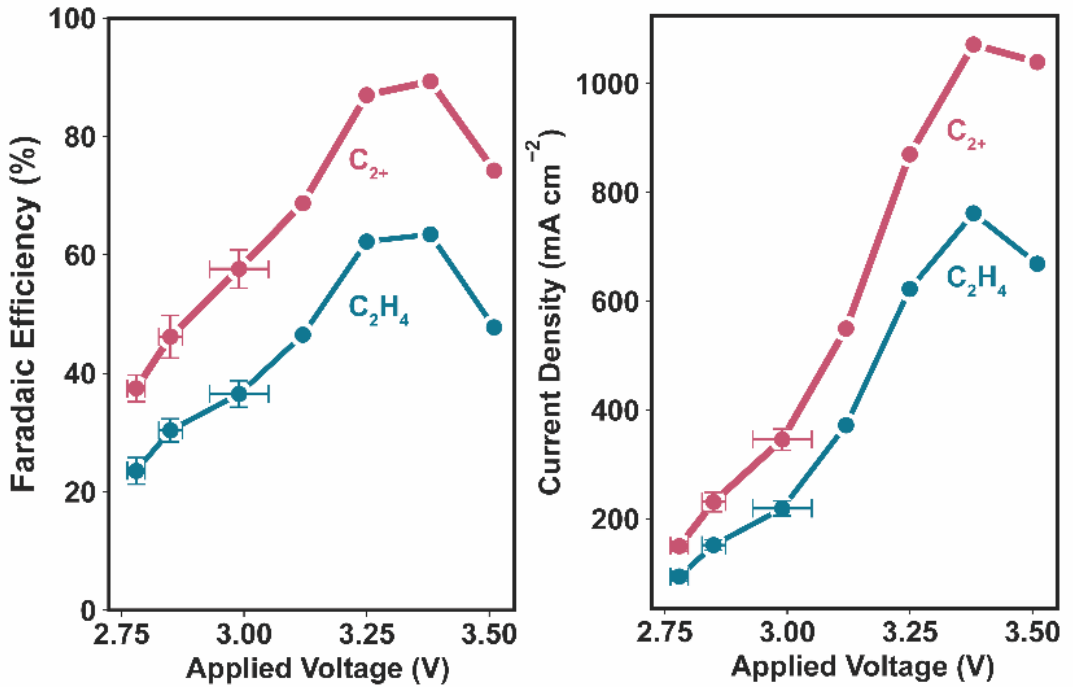
What's the role Ag/Cu exposure area ratio on FE and current desity for C2+ products?



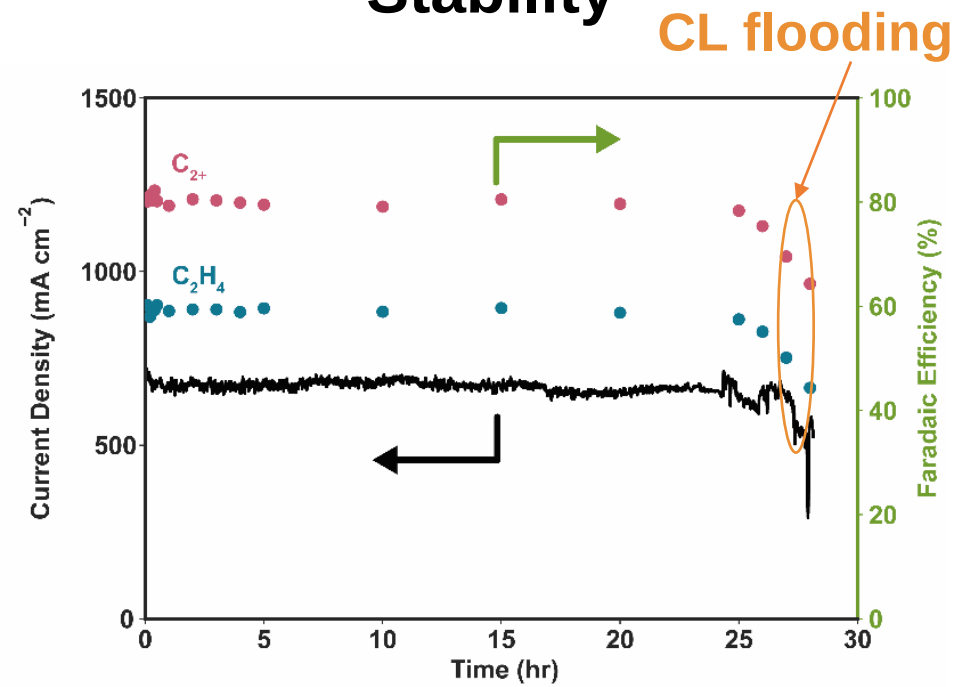
- **Shrinking Ag CL providing more concentrated CO for C-C coupling on the Cu CL, and thus yielding higher selectivity and productivity of C_{2+} products.**

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

Activity and Selectivity

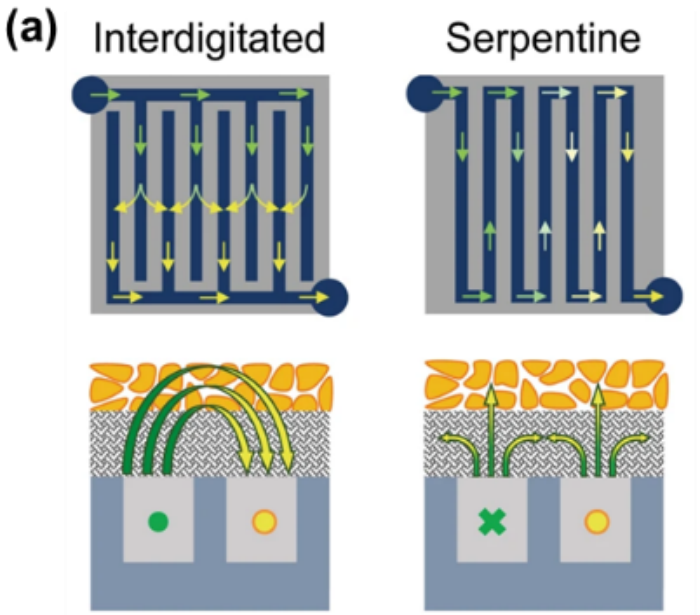


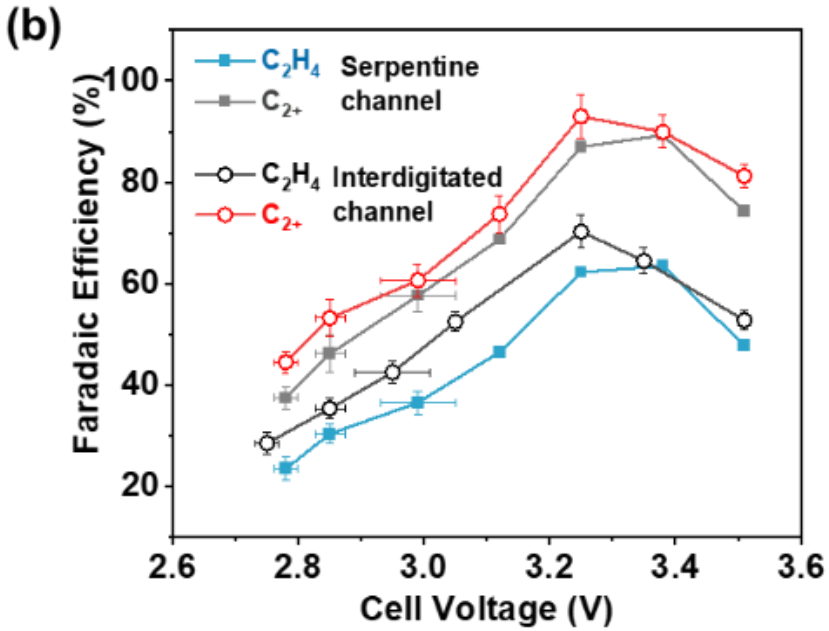
Stability

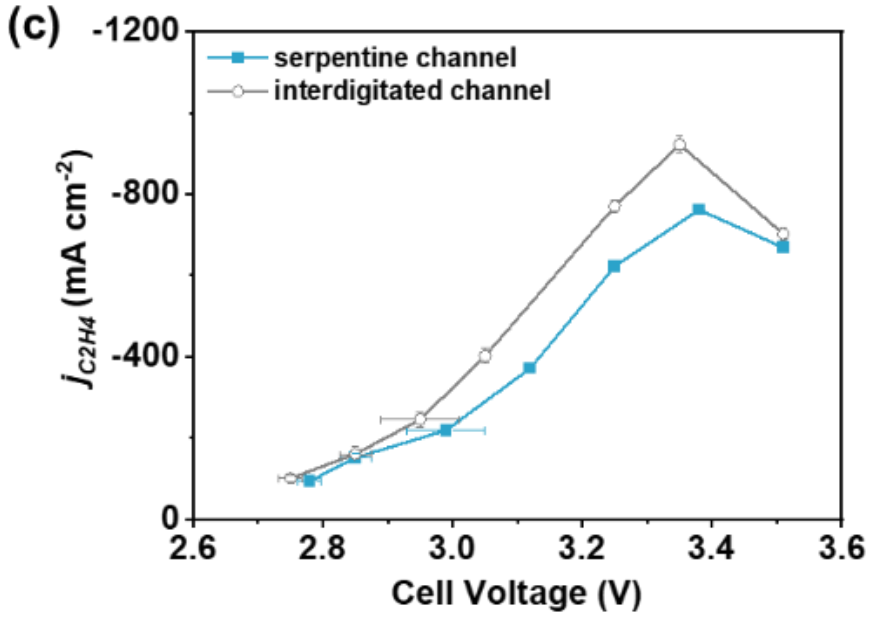


- **Cu/Fe-N-C tandem electrode (Cu : Fe-N-C area ratio = 1 cm² : 0.05 cm²) achieving 60% FE of C_2H_4 at current density > 1 A/cm² in a flow cell with a thin catholyte layer.**
- **Severe catalyst layer flooding limiting the long-term operation of tandem electrodes, especially at current density > 500 mA/cm².**

Tandem Electrode Design: enhanced gas mass transport





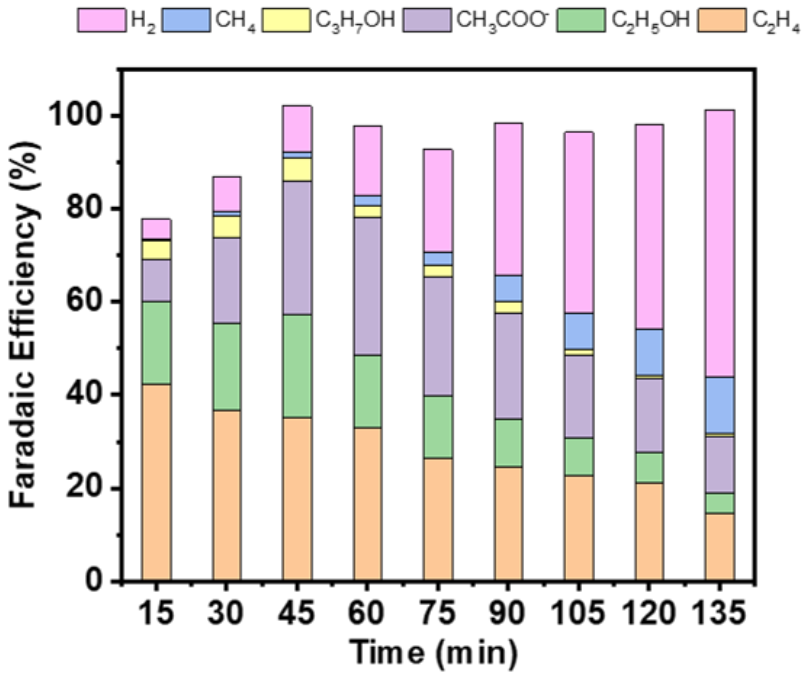


X. Feng et al., Nature Communications, 2011, 12, 136 .

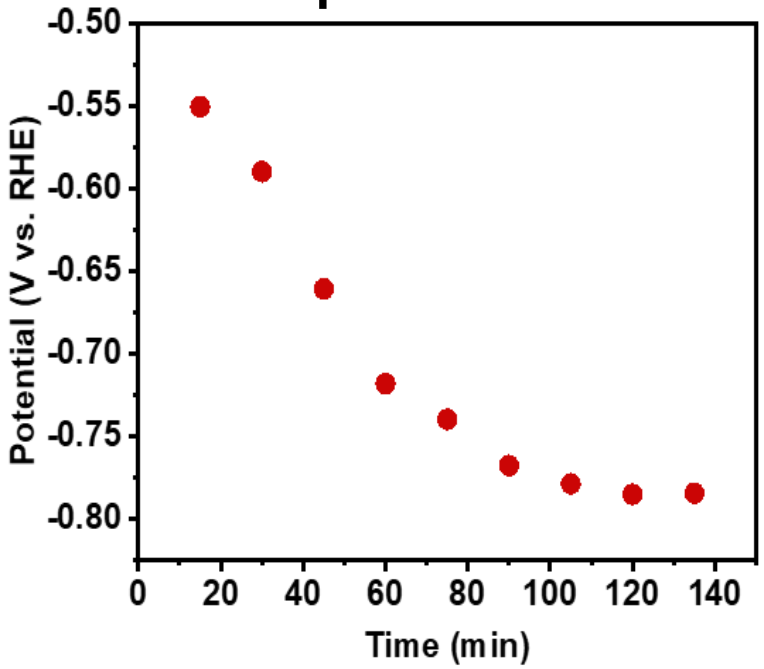
- **Interdigitated flow channel forces gas convection into the electrode and then exit to the outlet channels, enhancing mass transport of CO_2/CO into the catalyst layer.**
- **Maximum FE of C_2H_4 increased from 60% with serpentine flow field to ~70% with the interdigitated flow field at a partial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

Tandem Electrode Design: flooding issue of current GDE structure

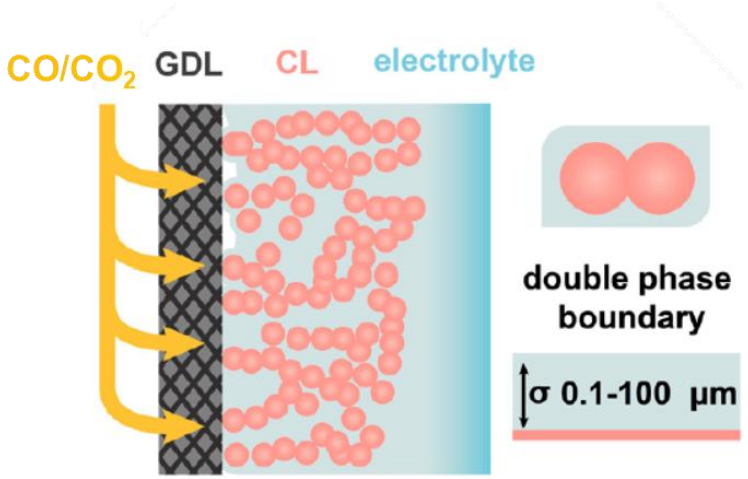
Decrease selectivity towards C_{2+}



Increase mass transfer polarization



Flooding model of CL

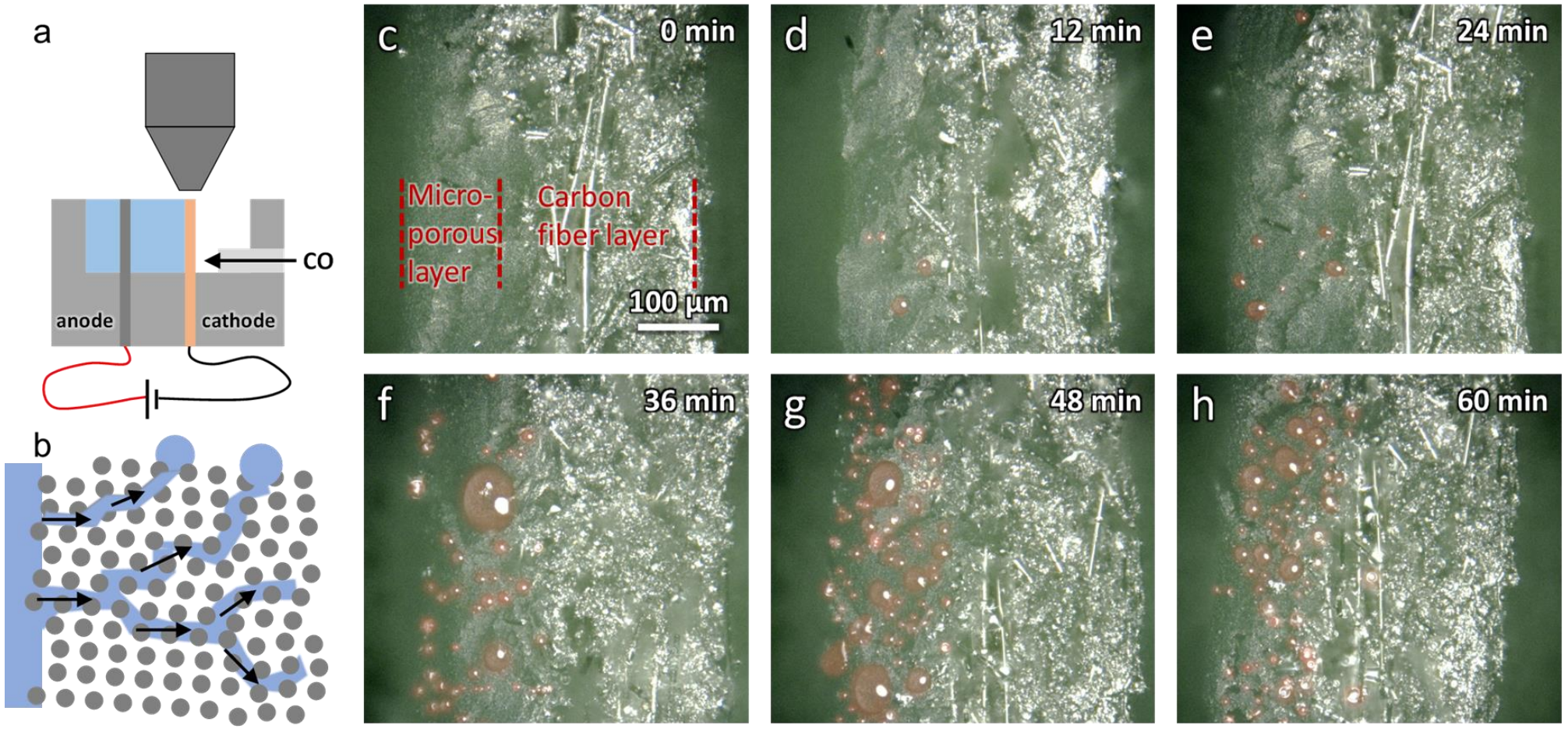


Galvanostatic electrolysis of CORR at 400 mA cm^{-2} on a GDE composed of SGL 39BB GDL and Cu CL

- **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

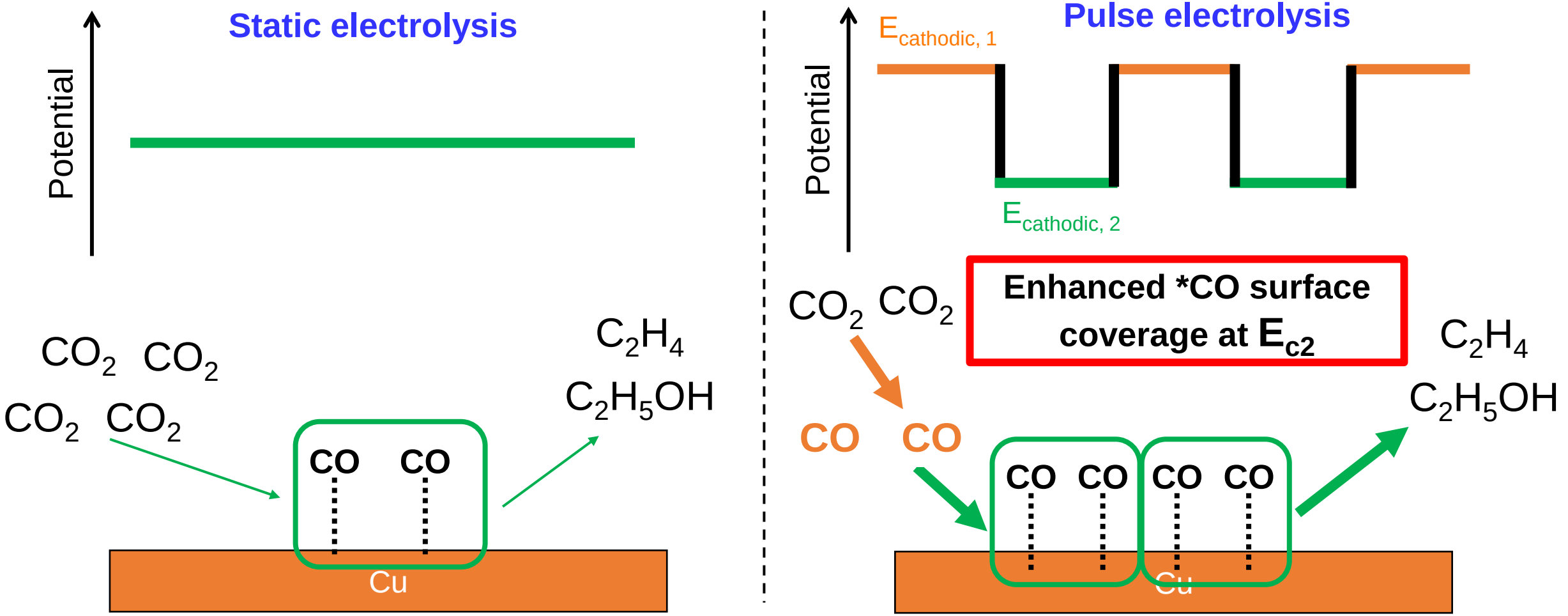


- **Flooding extends to gas diffusing layer.**
- **Design CL and GDL microstructures with effective water management is the focus of future work in order to increase the performance and stability of tandem electrodes.**

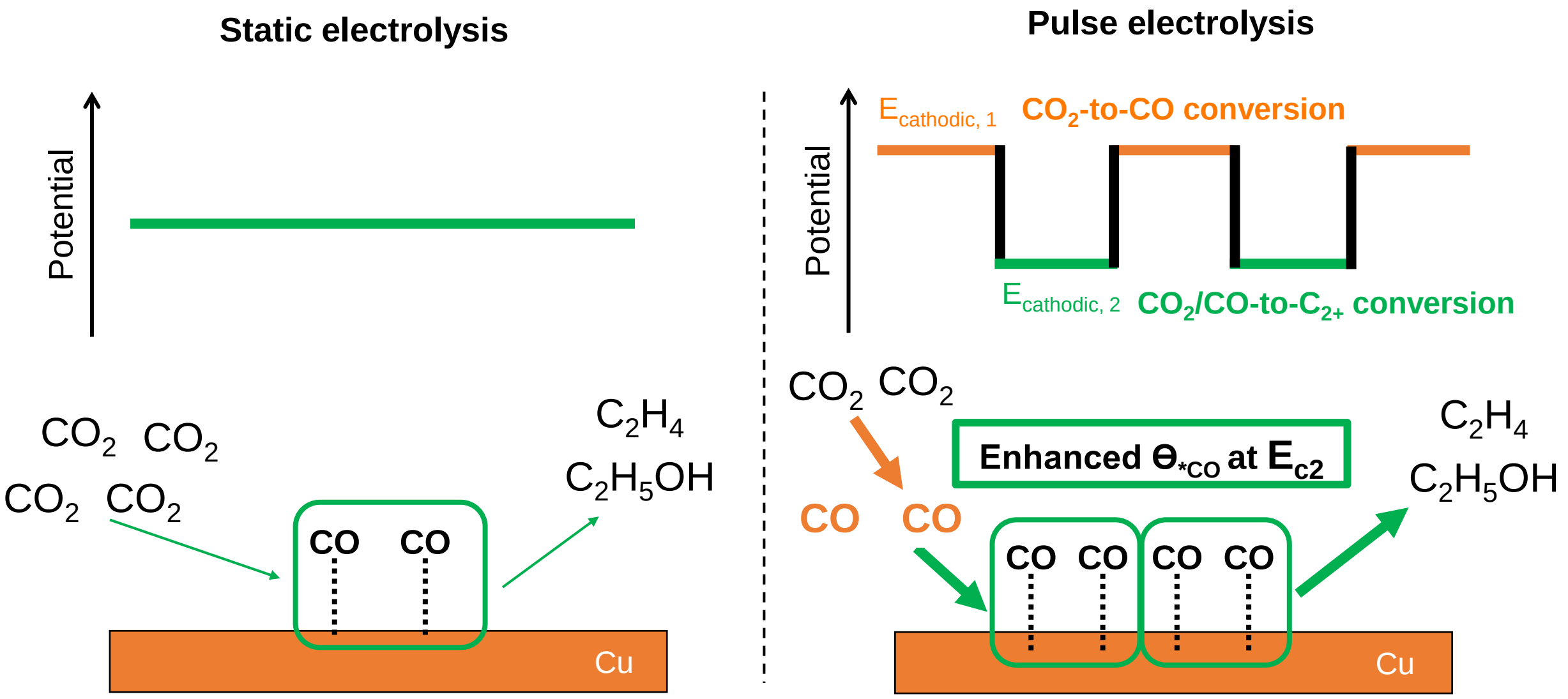
Pulse Electrolysis

Project Progress: Pulse Electrolysis

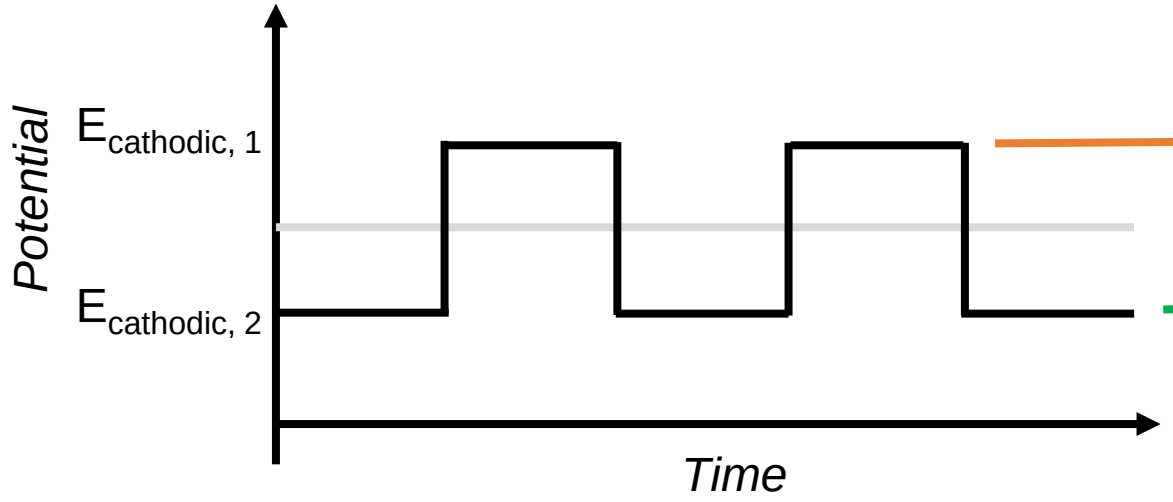
Control pulse potential: CO supply from CO-generation catalyst layer in the tandem electrode



Project Progress: Pulse Electrolysis

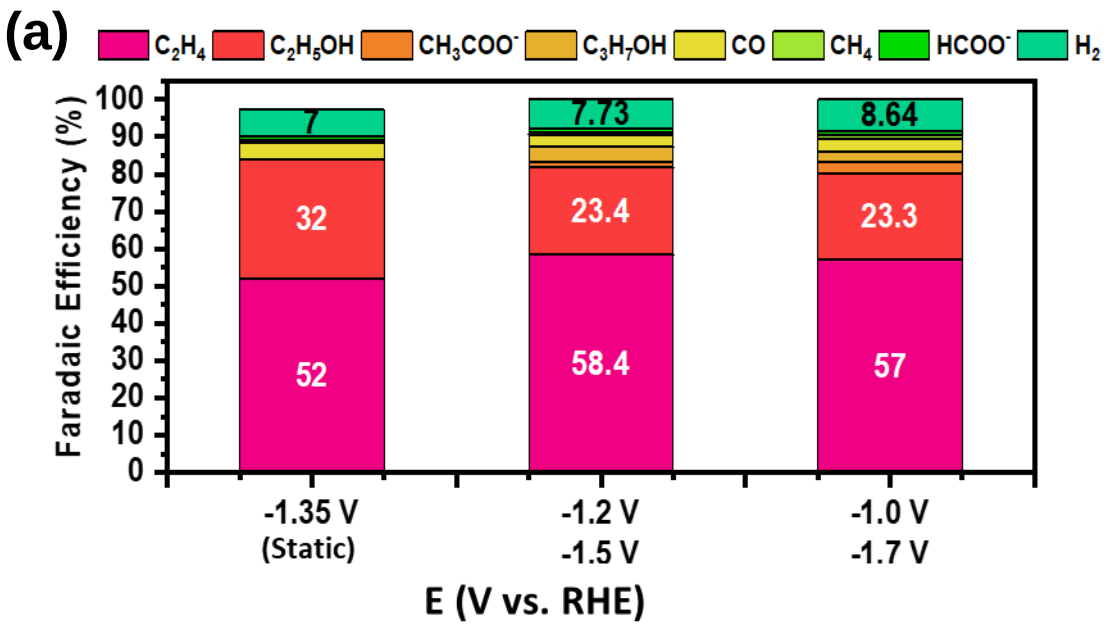


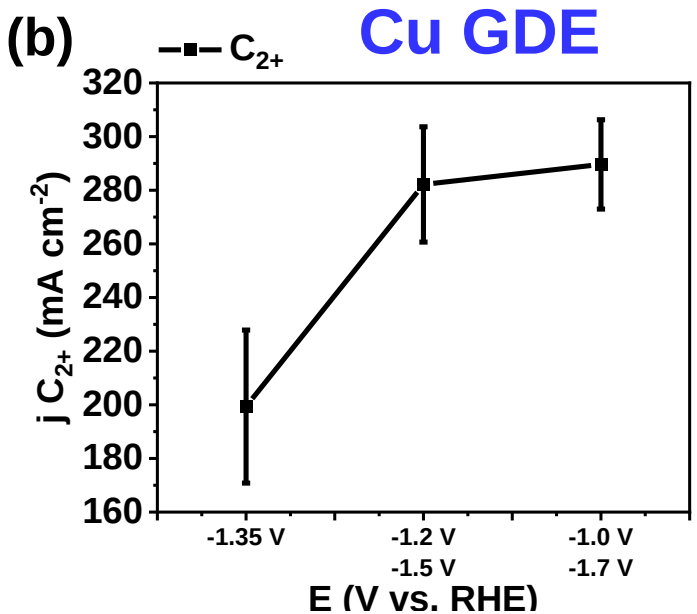
Pulse Electrolysis: enhancement of C_2H_4 selectivity and productivity on Cu GDE



CO_2-to-CO conversion

CO_2/CO-to-C_{2+} conversion

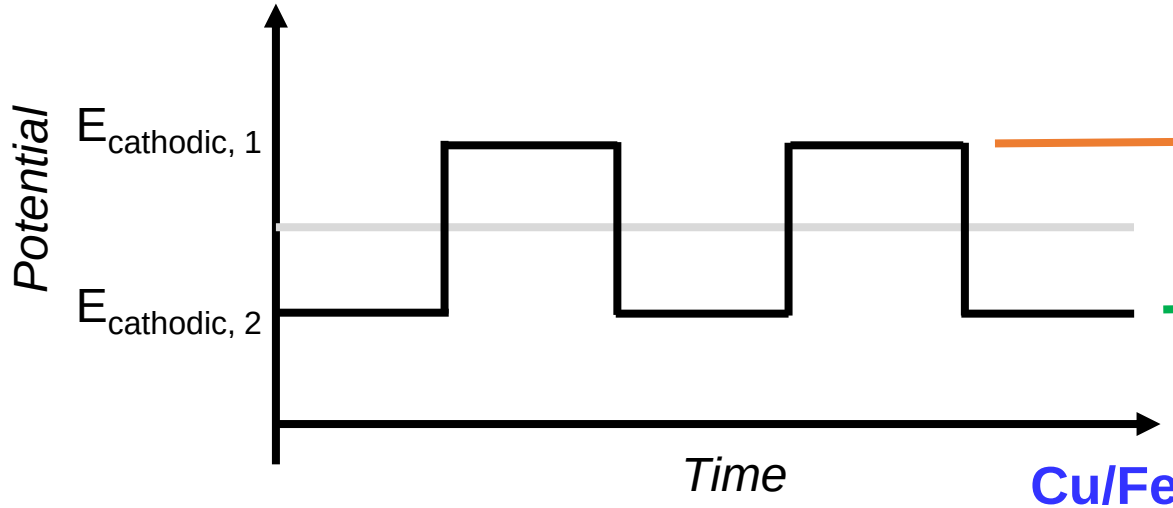




- Cathode potential without iR compensation.
- Faradaic efficiency and partial current density of C_{2+} and C_2H_4 enhances with pulse electrolysis.

J. Electrochem. Soc., 2022.

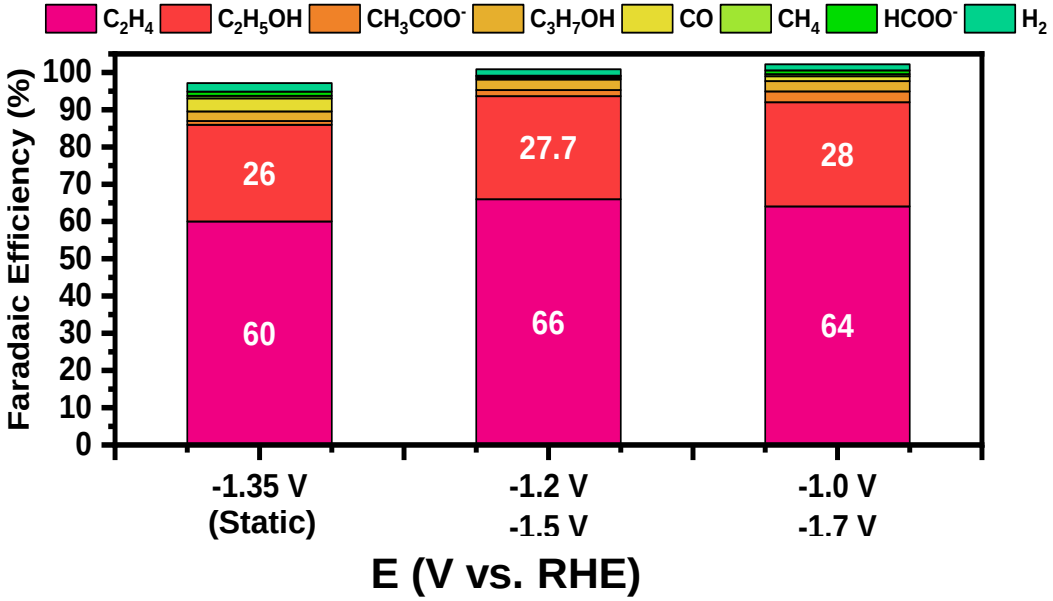
Pulse Electrolysis: enhancement of C_2H_4 selectivity and productivity on Cu/Fe-N-C SGDE

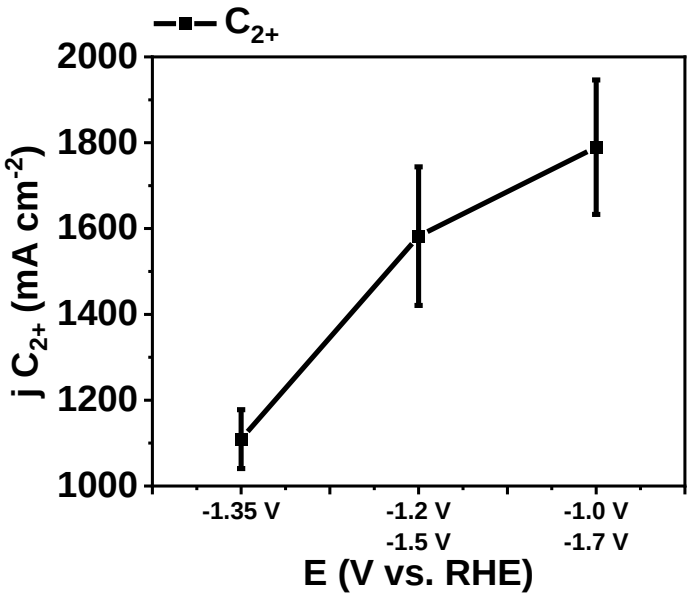


CO_2-to-CO conversion

CO_2/CO-to-C_{2+} conversion

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

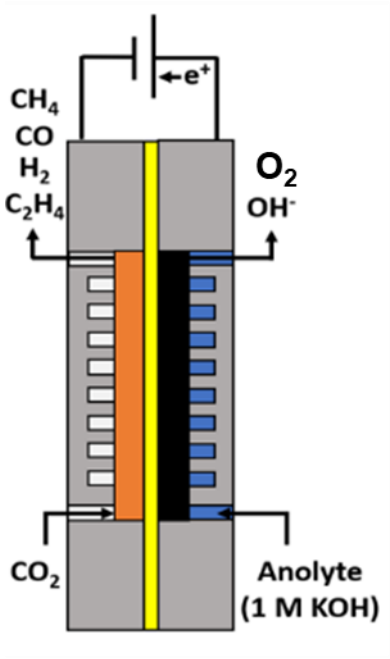


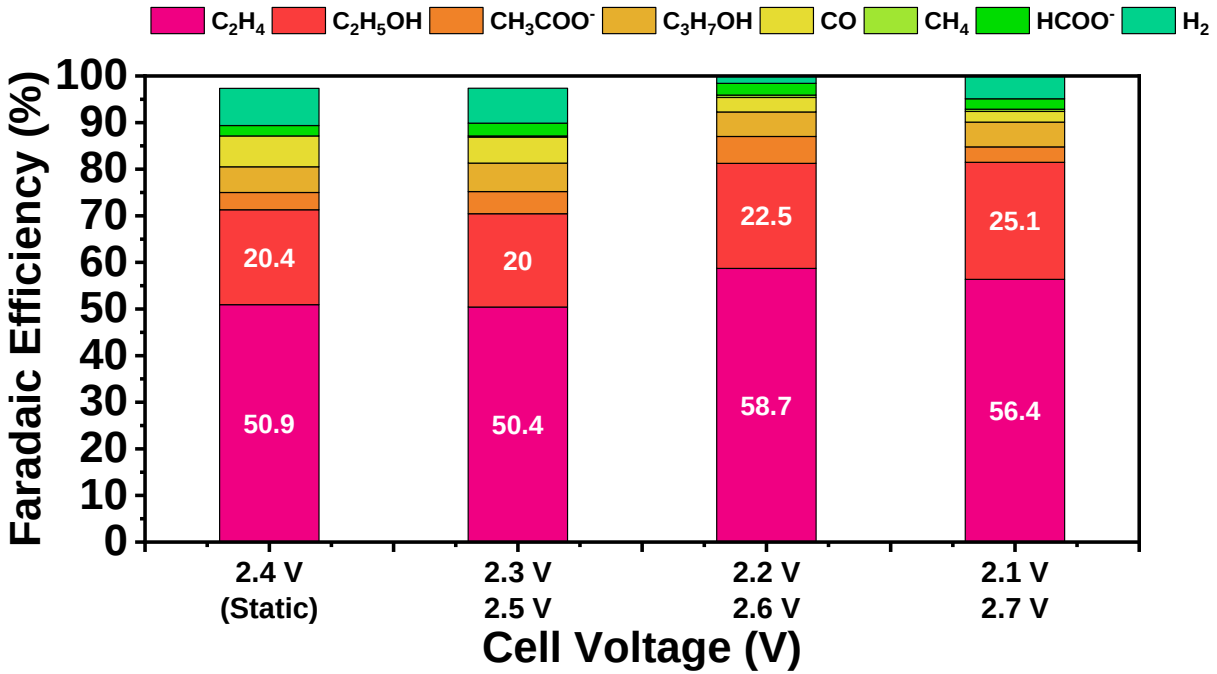


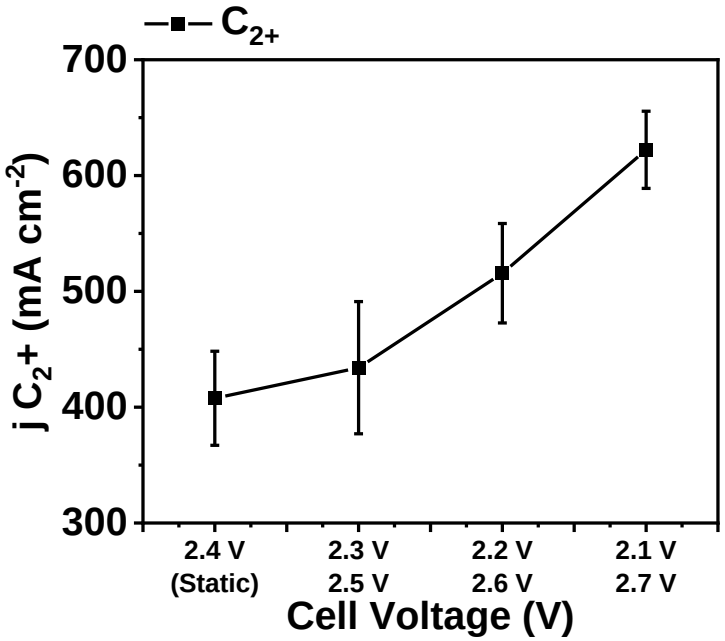
- Pulse electrolysis further promotes Faradaic efficiency and partial current density of C_{2+} and C_2H_4 on tandem SGDE.
- 66% FE of C_2H_4 at j_{C2H4} > 1100 mA cm^{-2}

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}.

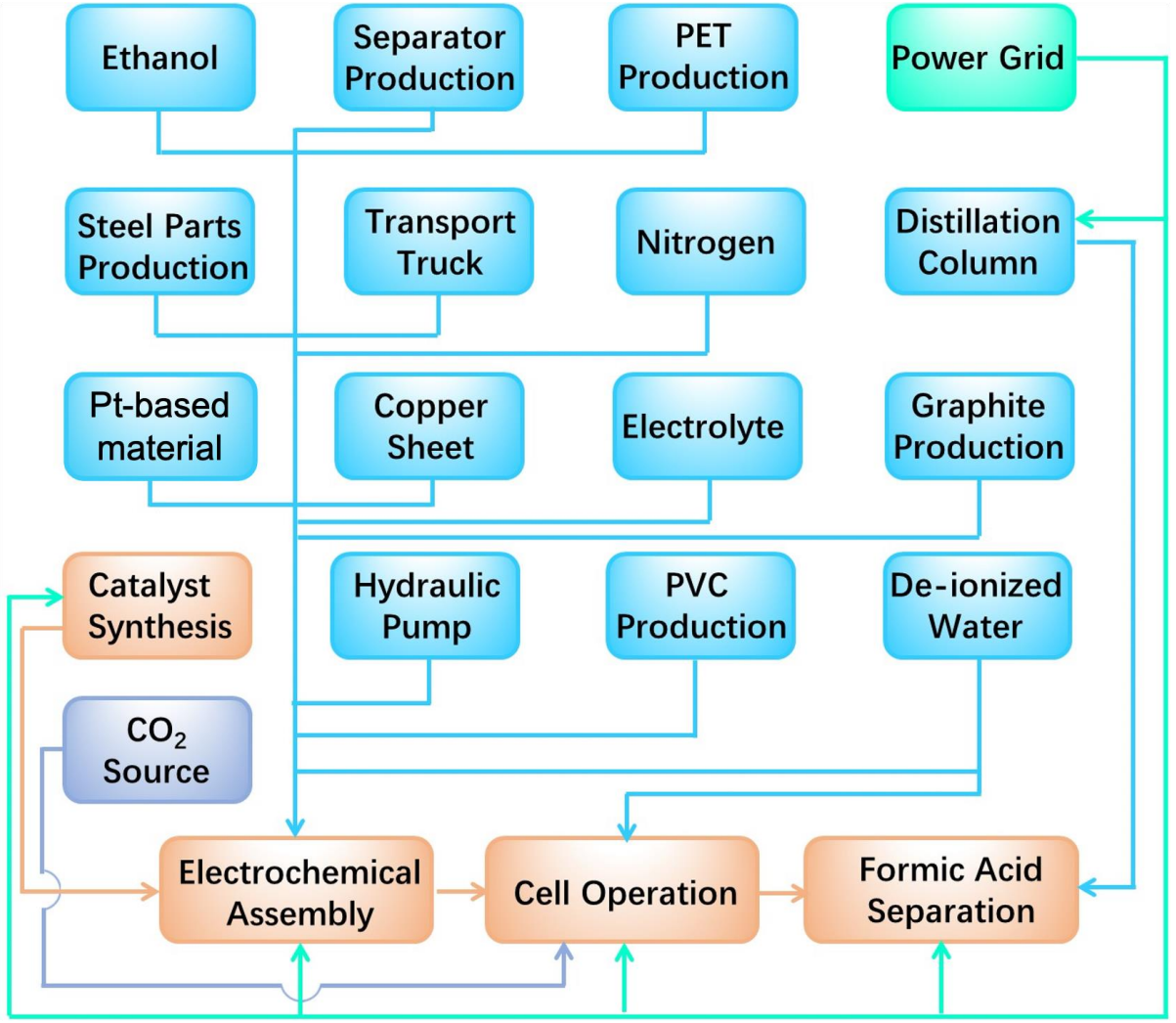
LCA/TEA Analysis

Life Cycle Assessment of CO_2 Conversion

Goal and motivations

1. We completed a cradle-to-gate life cycle assessment of assembling and operating an electrochemical cell to perform conversion of previously captured carbon dioxide (CO_2), followed by product separation
2. The goal is to investigate the the environmental impact and predict ways of decreasing carbon emissions for manufacturing and using carbon capture and utilization (CCU) technologies
3. We successfully built a model to investigate the environmental impact as a function of number of operation parameters.
4. We envisage that this LCA study will provide guidance and information regarding aspects of CCU technologies which may require optimization under the environmental point of view.

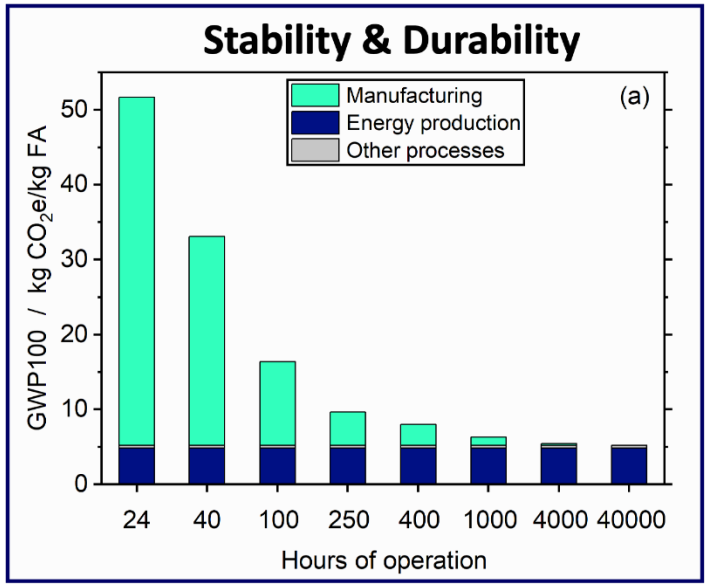
The LCA model

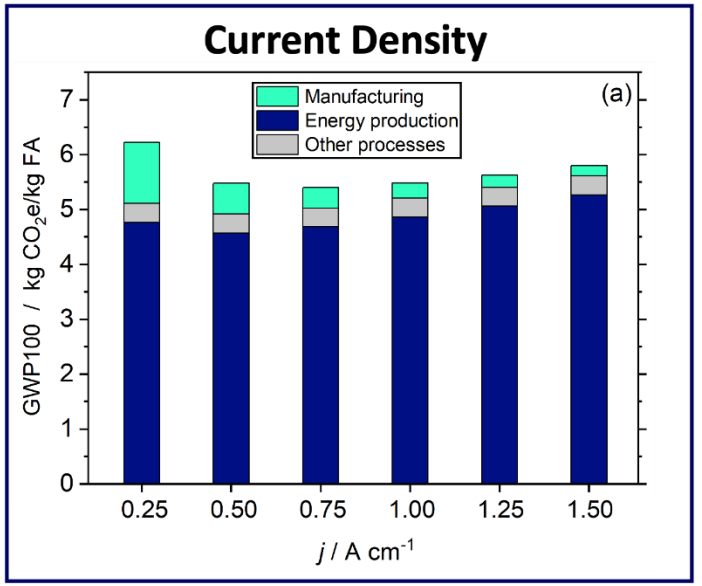


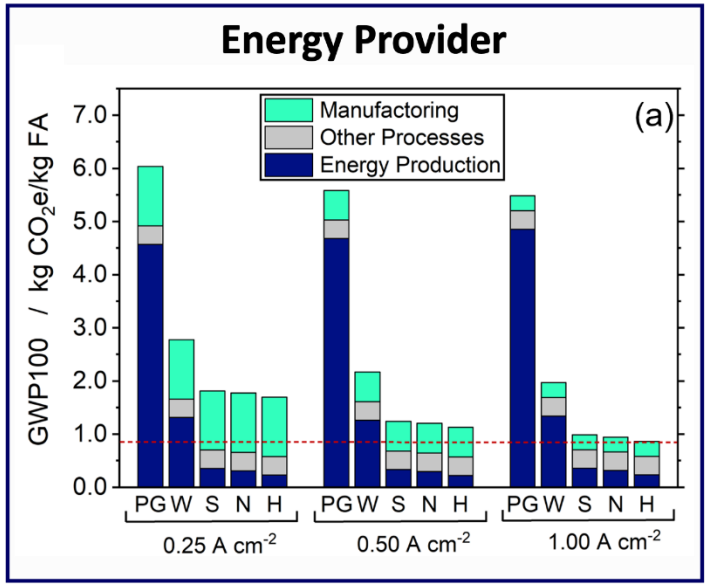
Life Cycle Assessment of CO_2 Conversion

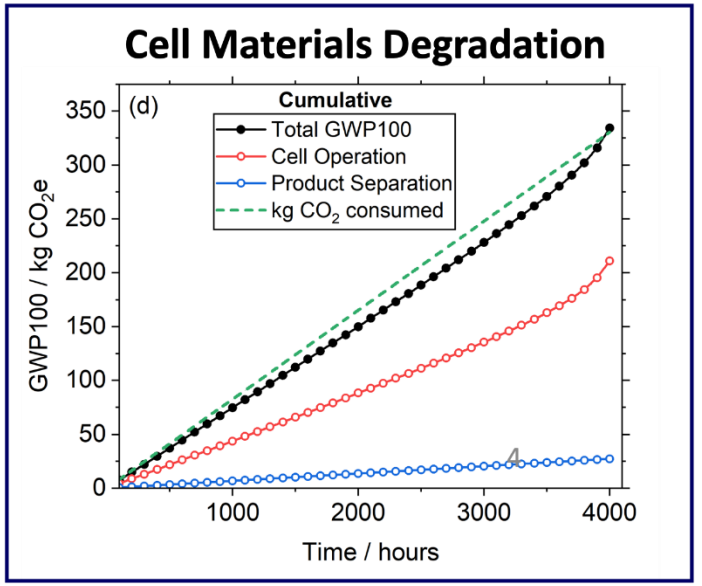
Results and Discussion

1. Stability/durability and operation variables (current density or cell voltage) have high impact on the carbon emissions.
2. The optimal parameters include stable operation for at least 4,000 hours at (ultrahigh) current densities (0.50 - 1.00 A cm^{-2}).
3. Through use of renewable energy sources zero carbon emissions may be achieved only if high cell performance conditions are met.
4. The cumulative carbon emissions were predicted during the entire life cycle of the system (4,000 hours), while modelling cell aging and corresponding decline in performance. Here, the use of renewable energy is of outmost importance to achieve climate change mitigation.







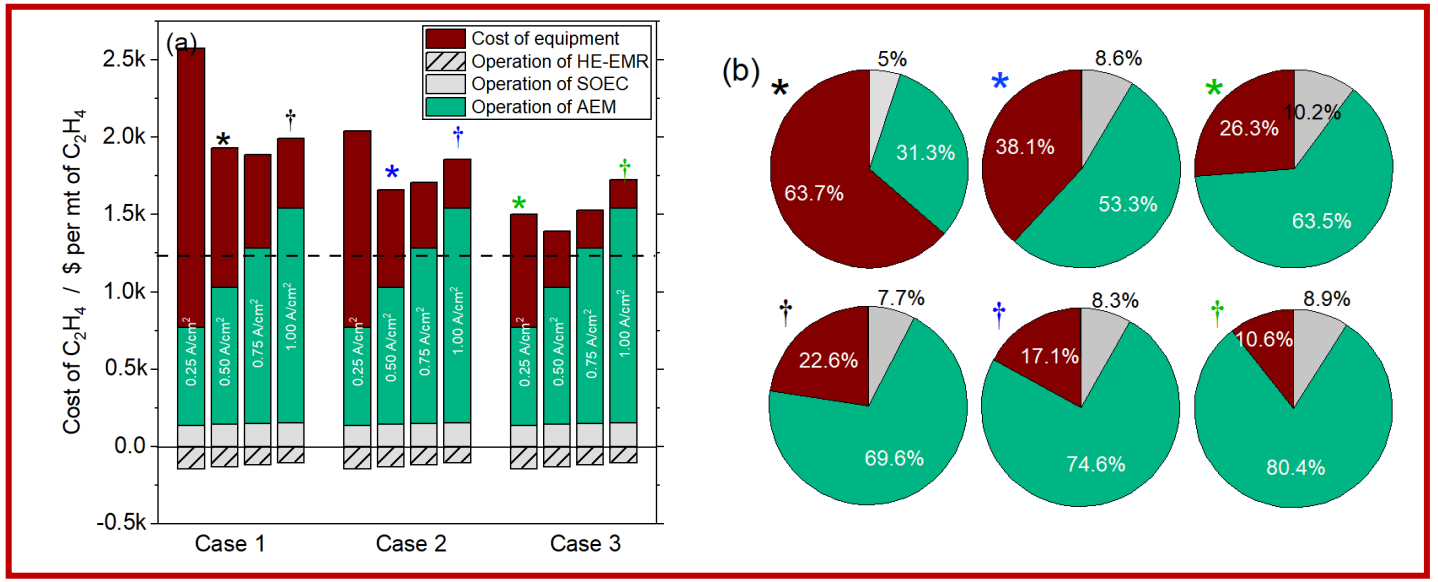


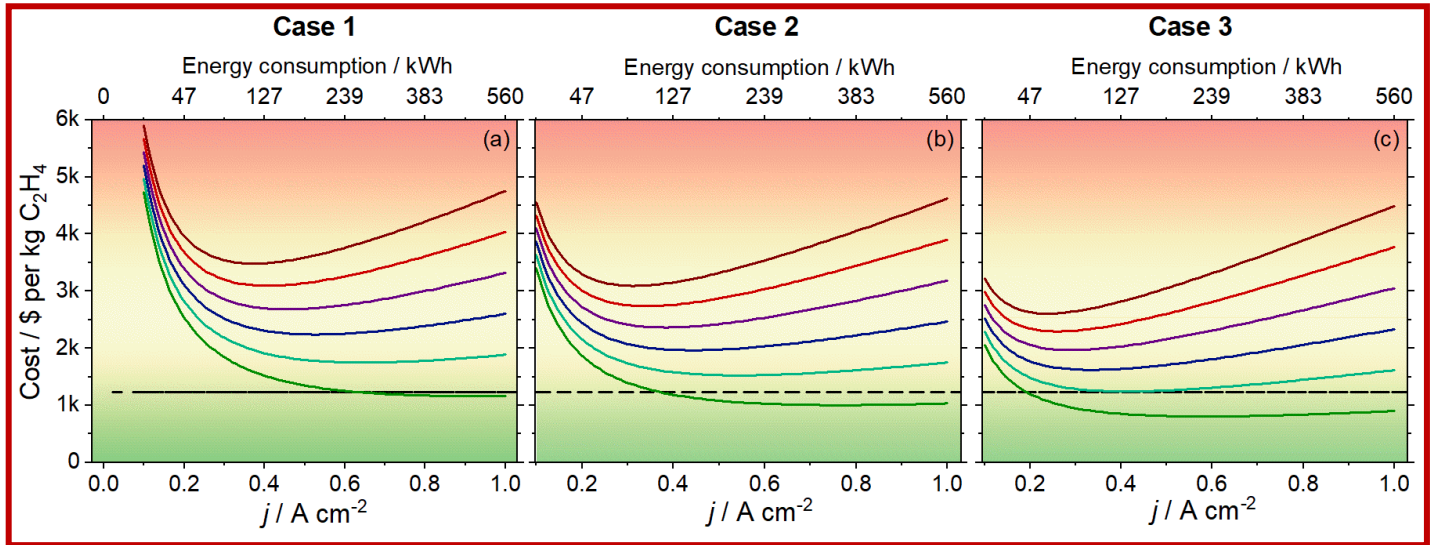
Technoeconomic Analysis of CO_2 to Ethylene

Results and Discussion

1. Reducing the area-specific resistance of an AEM reactor and achieving a high selectivity for ethylene (>50%) have the potential to significantly lower the product cost.
2. Operation of carbon capture unit allows reduction in production cost up to ~30%.
3. Cost of equipment is not negligeable and can contributes up to ~28% to the overall production cost (60% of which is attributed to the AEM)
4. With renewable electricity of $0.02-0.04/kWh, competitive production costs of ethylene are achievable.
5. From LCA studies, when renewable energy is used, conversion of CO_2 to ethylene yield to negligible environmental impact and allows achieving negative emissions.

Equipment cost & Current density

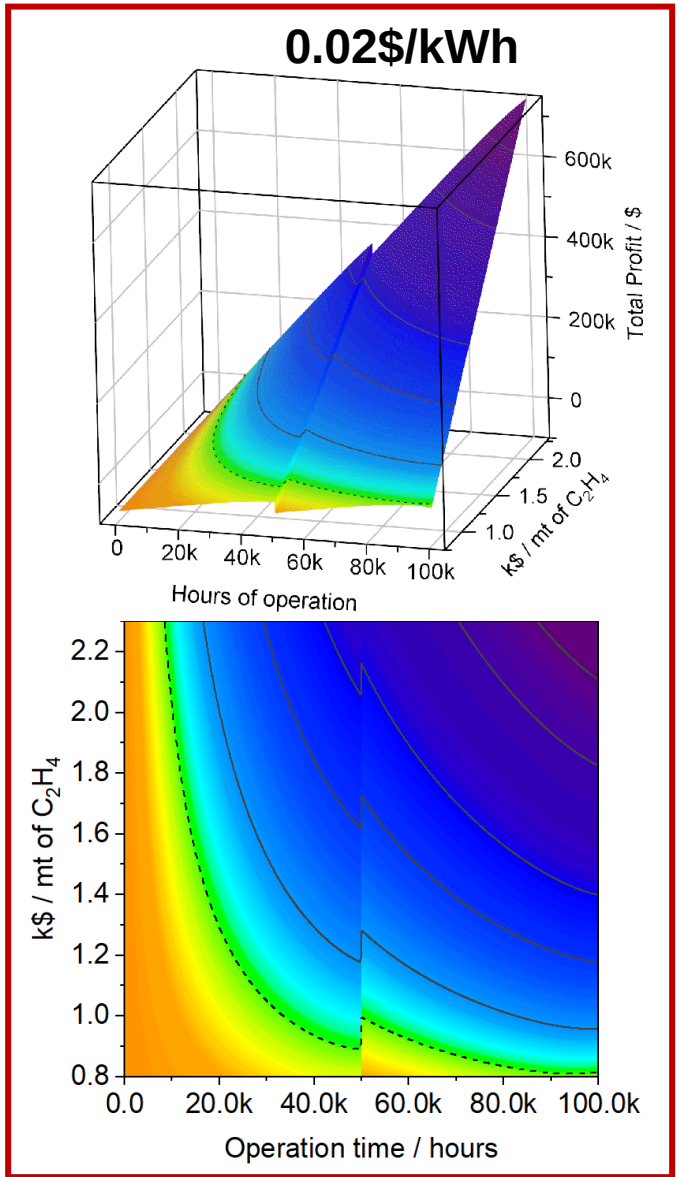


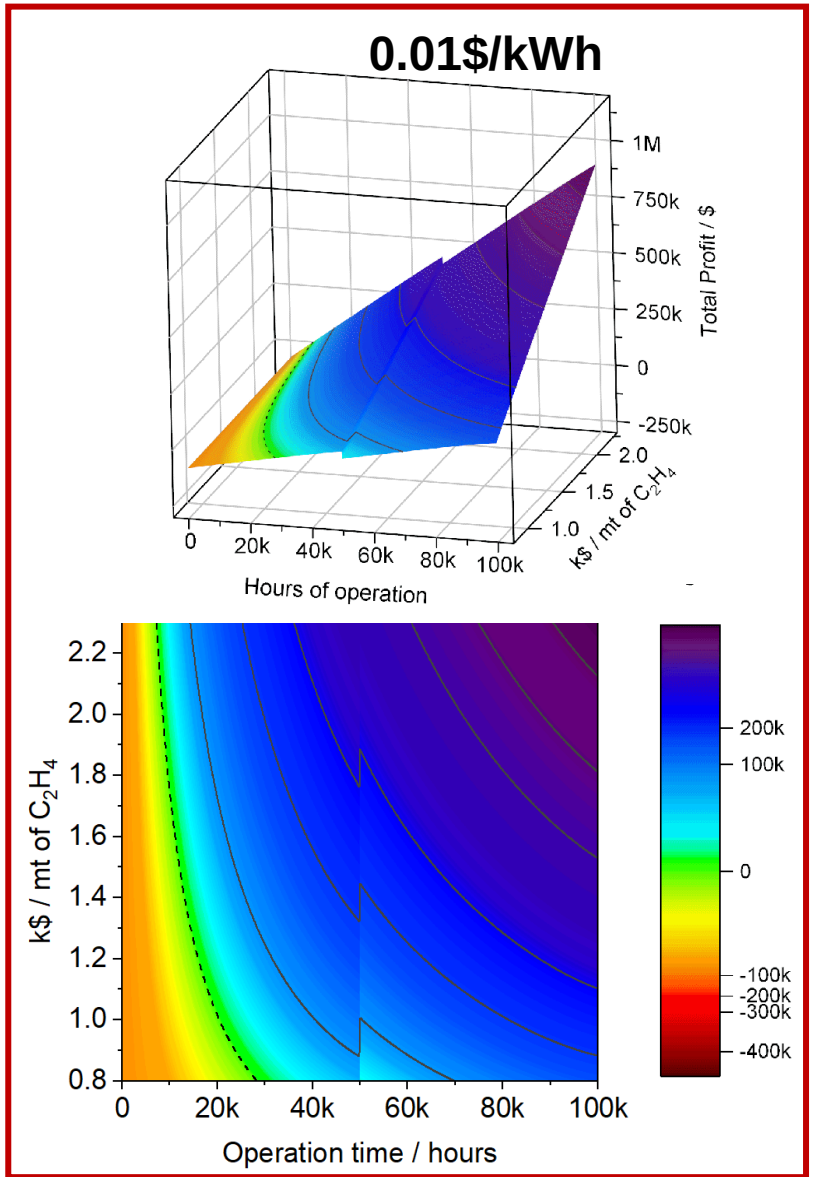


Technoeconomic Analysis of CO_2 to Ethylene

Profit Analysis

1. Total profit for production of ethylene using the modelled set-up for CO_2 capture and electrolysis, accounting for degradation of cell performance over operation time.
2. The profit is dictated by the energy consumption and its cost, as well as the projected market price of ethylene.
3. For cost of electricity 0.01$/kWh, positive value of the total profit are observed at competitive prices of ethylene, when the set-up operates for longer then 20,000 hours





Summary and 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.

- 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