DOE “Carbon Capture Program” SBIR Project Review

A High-Efficiency Process for CO_2 Conversion to Hydrocarbon Fuels

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Outline

- Introduction and background
- Executive Summary
- Preliminary Data
- Phase I accomplishments
- Phase II plan

Executive Summary

- Electrochemical conversion of CO_2 to methane and other fuels have been investigated using Cu based catalysts
  - Cu morphology was tailored for methane synthesis
  - Ability to tune gaseous product selectivity through morphology
- High CH_4 FE efficiency 42% has been achieved and electrical efficiency has been doubled
  - Ability to minimize H_2 efficiency while increasing CH_4 efficiency
  - Knowledge gained on gaseous products can be transferred to liquids products
- Current density ~ 50 mA/cm^2 (Cu area submerged for reduction) has been reached with CH_4 efficiency > 40%
  - 10 times increase compared to literatures
  - Increasing current decreased product selectivity of hydrocarbons
- Gas flow-Cell has been designed and fabricated and Phase II work and strategies have been proposed

Project Overview

Timeline

- Project Start Date: 6/13/2016
- Project End Date: 3/12/2017

Budget

- Phase I 150K

Partners

- Dr. Elizabeth Biddinger
  The City College of New York (CCNY)

Barriers Addressed

- Low conversion and efficiency for direct electro-reduction of CO_2 to hydrocarbon fuels

Technical Targets

- Further develop the CO_2 reduction catalysts for electrochemical reduction of CO_2 to hydrocarbon fuels
- Optimize operating conditions of electrolyzer cells to maximize the efficiency, selectivity and yield of hydrocarbon fuels
- Construct flow electrolyzer cells by integrating CO_2 reduction catalysts with other components

Background: CO_2 Electro-Reduction

Theoretical Electrode Potential

Primary Product	Reaction	Theoretical Electrode Potential at 1.0 atm CO_2, 25°C, Aqueous (V vs. NHE)
Hydrogen	$2H^+ + 2e^- \leftrightarrow H_2$	0.000
Carbon Anion Radical	$CO_2 + e^- \leftrightarrow CO_2^{\cdot -}$	-1.480
Carbon	$CO_2 + 4H^+ + 4e^- \leftrightarrow C_{(s)} + 2H_2O$	0.210
Formic Acid	$CO_2 + 2H^+ + 2e^- \leftrightarrow HCOOH$	-0.250
Carbon Monoxide	$CO_2 + 2H^+ + 2e^- \leftrightarrow CO + H_2O$	-0.106
Formaldehyde	$CO_2 + 4H^+ + 4e^- \leftrightarrow CH_2O + H_2O$	-0.898
Methanol	$CO_2 + 6H^+ + 6e^- \leftrightarrow CH_3OH + H_2O$	0.016
Methane	$CO_2 + 8H^+ + 8e^- \leftrightarrow CH_4 + 2H_2O$	0.169
Oxalic Acid	$2CO_2 + 2H^+ + 2e^- \leftrightarrow H_2C_2O_4$	-0.500
Oxalate	$2CO_2 + 2e^- \leftrightarrow C_2O_4^{2-}$	-0.590
Ethylene	$2CO_2 + 12H^+ + 12e^- \leftrightarrow CH_2CH_2 + 4H_2O$	0.064
Ethanol	$2CO_2 + 12H^+ + 12e^- \leftrightarrow CH_3CH_2OH + 3H_2O$	0.084

Catalyst and %FE

	Metals	E V vs. SHE	I mA/cm^2	Faradaic Efficiency %							
				CH_4	C_2H_4	EtOH	PrOH	CO	HCOO	H_2	Total
I	Pb	-1.63	5.0	0.0	0.0	0.0	0.0	0.0	97.4	5.0	102.4
	Hg	-1.51	5.0	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
	Tl	-1.60	5.0	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
	In	-1.55	5.0	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
	Sn	-1.48	5.0	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
	Cd	-1.63	5.0	1.3	0.0	0.0	0.0	13.9	78.4	9.4	103.0
II	Au	-1.14	5.0	0.0	0.0	0.0	0.0	87.1	0.7	10.2	98.0
	Ag	-1.37	5.0	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.4
	Zn	-1.54	5.0	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
	Pd	-1.20	5.0	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
	Ga	-1.24	5.0	0.0	0.0	0.0	0.0	23.2	0.0	79.0	102.0
III	Ni	-1.48	5.0	1.8	0.1	0.0	0.0	0.0	1.4	88.9	92.4
	Fe	-0.91	5.0	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
	Pt	-1.07	5.0	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
	Ti	-1.60	5.0	0.0	0.0	0.0	0.0	tr.	0.0	99.7	99.7
IV	Cu	-1.44	5.0	33.3	25.5	5.7	3.0	1.3	9.4	20.5	103.5

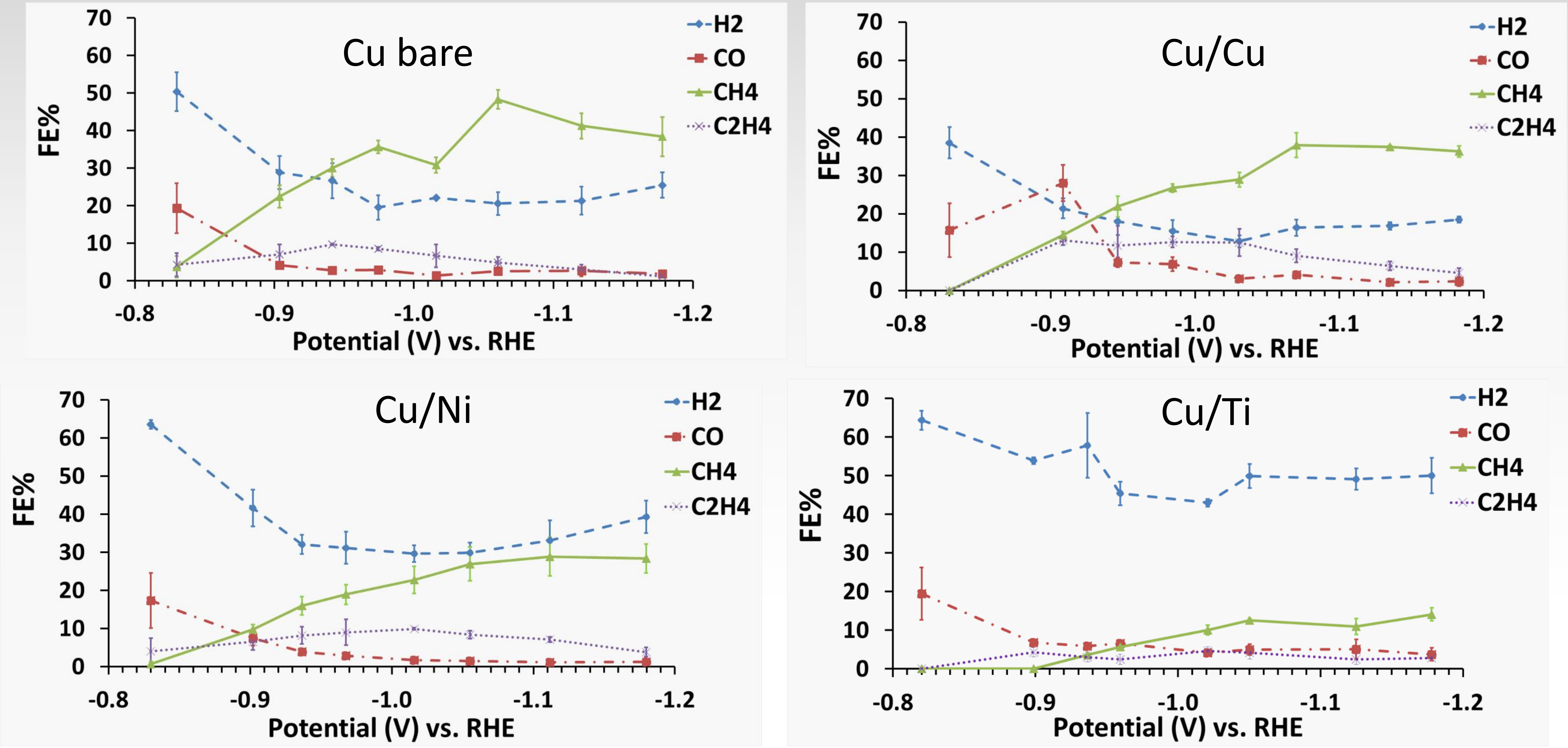
Y. Hori, in Modern Aspects of Electrochemistry, eds. C. G. Vayenas,, Springer, New York, 2008, vol. 42, pp. 89-189.

Effective Catalysts for CO_2 to Methane

Background: CO_2 Electro-Reduction

- **Chronocoulometry : -1V and the charge Q=(1.5-15C) or (2.43 C/cm^2- 21.43C/cm^2) 0.25M copper sulfate penta-hydrate ($CuSO_4$ $5H_2O$)**
- **Cathode: Cu, Ni, Ti , Anode: Cu flag**

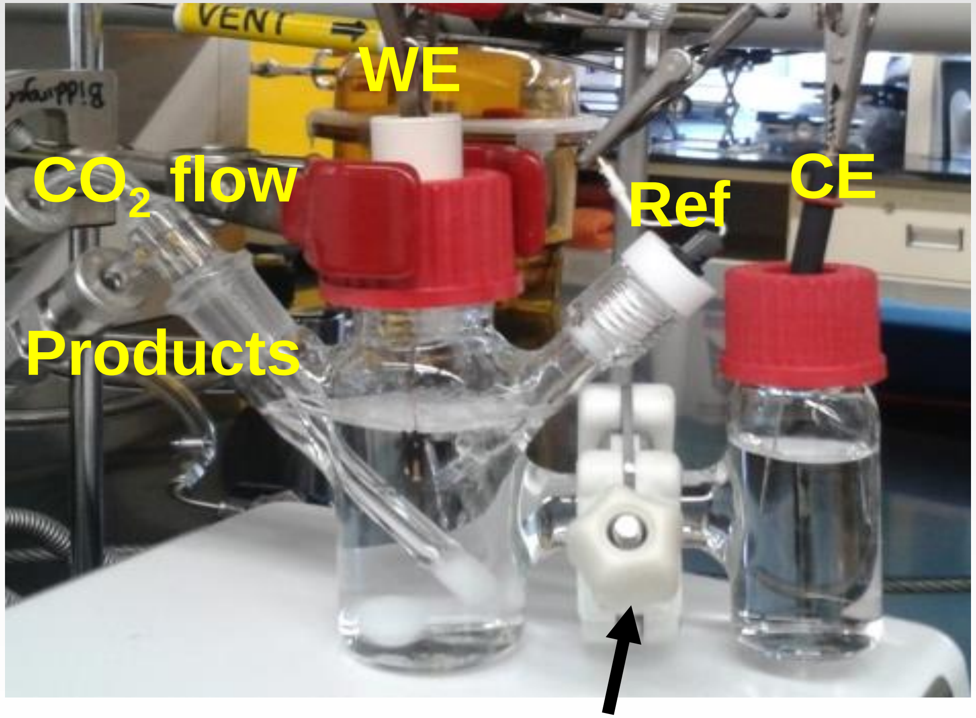
Catalysts for Electrochemical CO_2 Reduction



A. N. Karaiskakis and E. J. Biddinger, *Energy Technology*, 2016, **DOI: 10.1002/ente.201600583**.

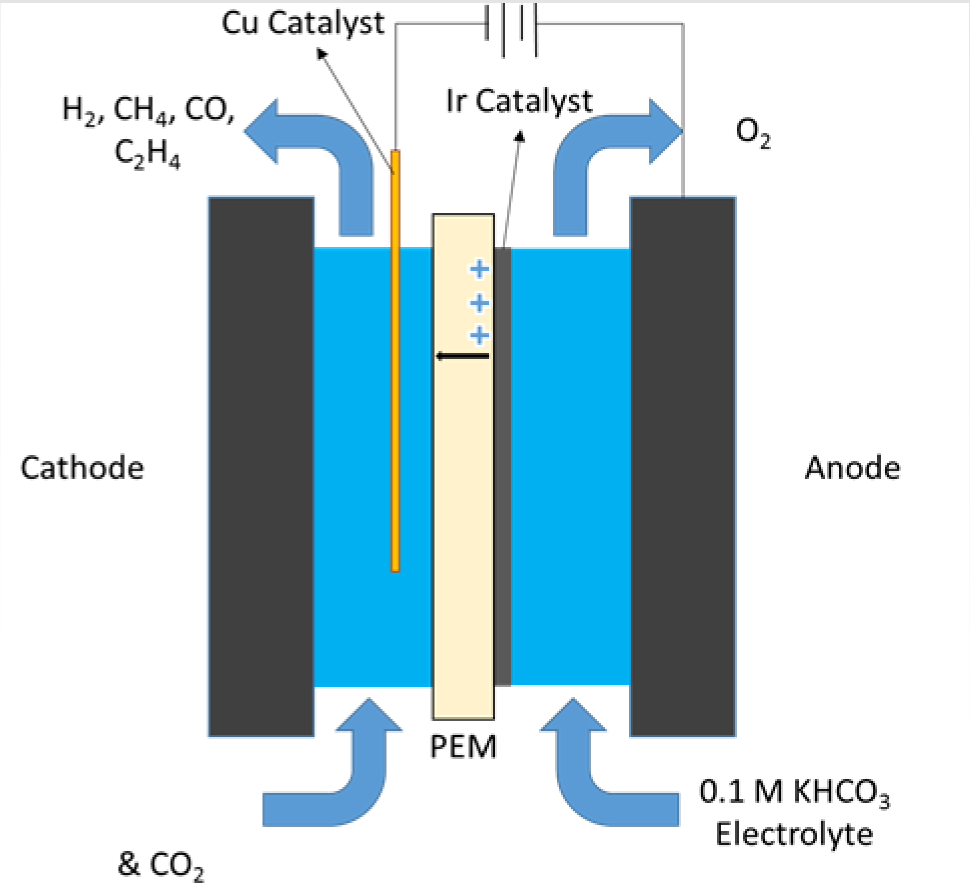
Technical Approaches

CCNY



Membrane (Nafion-212)

Giner



Tasks

Task	% Time	Month								
		1	2	3	4	5	6	7	8	9
1. Further develop CO_2 reduction electrocatalysts	25									
2. Construct electrolyzer cells for CO_2 conversion	20									
3. Optimize operating conditions of electrolyzer cells	40									
4. Perform the economic analysis of flow electrolyzer cells	10									
Report	5									X

CCNY- Giner Phase I Results

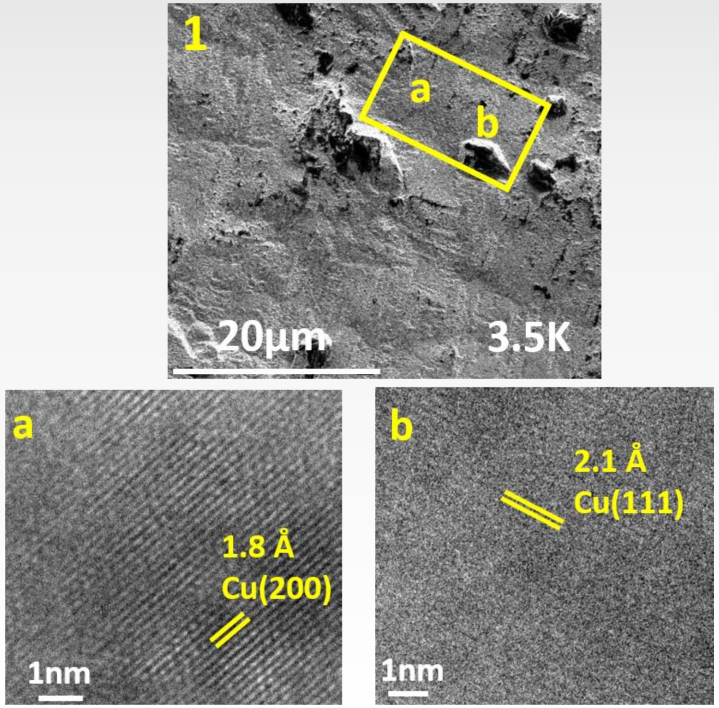
Key Questions

- What is the main factor that drives selectivity on rough polycrystalline Cu?
- Cu Reconstruction under CO_2 Electrochemical Conditions
- Result transfer from liquid cell to gas flow cells

Evaluation of Cu facet dependence

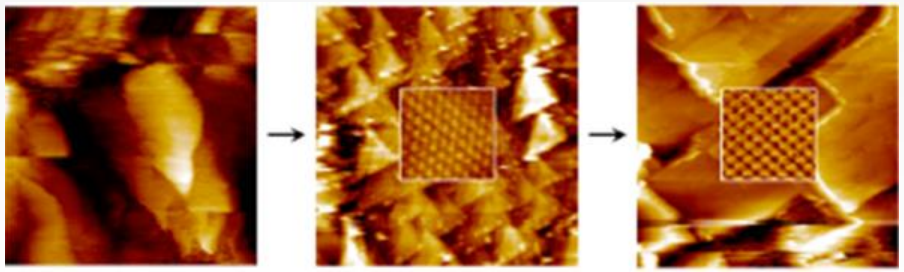
HRTEM- Reconstruction on the surface

Cu/Cu After CO_2 ELR



Alexandros N. Karaiskakis and Elizabeth J. Biddinger, *Energy Technology* **2016**, *DOI: 10.1002/ente.201600583R1*

- Cu/Cu surface areas (a) → Dominant Cu(200)
- Cu/Cu larger particles (b) → Dominant Cu(111)
- Cu foil substrate → Dominant Cu(200)



Operando EC-STM

Y.-G. Kim, J. H. Baricuatro, A. Javier, J. M. Gregoire, M. P. Soriaga, *Langmuir* **2014**, *30*, 15053-15056

Summary and Literature

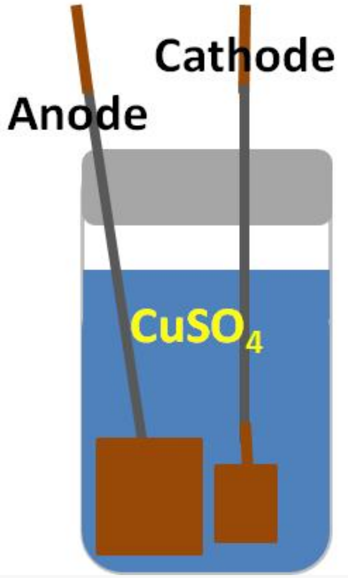
Main Hydrocarbon Product	Cu Facets	Reference
Cu Single crystal foil		
CH_4	Cu(111)	Hori
C_2H_4	Cu(100)	Hori
Cu rough polycrystalline		
CH_4	Dominant Cu(200), Secondary Cu(111)	Karaiskakis
C_2H_4	Dominant Cu(200), Secondary Cu(111)	Kas
C_2H_4	Dominant Cu(111), Secondary Cu(002)	Chen

Alexandros N. Karaiskakis and Elizabeth J. Biddinger, *Energy Technology* **2016**, *DOI: 10.1002/ente.201600583R1*

1. Catalysts Synthesis Method

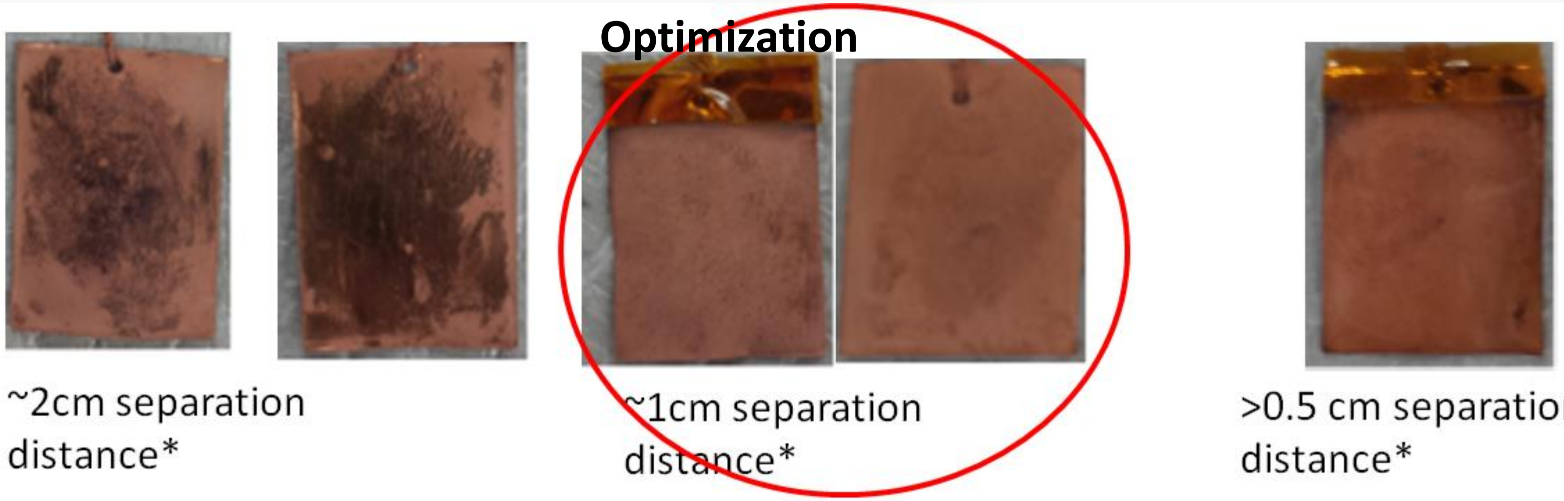
- **Synthesis Methodology - Electrodeposition:**
  - Rapid synthesis of nanomaterials
  - Low cost and Industrial usage
  - High purity products
  - Ability to use different substrates
- **Goal: Uniform reproducible deposition**
- **Evaluated factors**:
  - Distance between electrodes
  - Current density
  - Deposition reproducibility
  - Morphology

Electrodeposition Optimization



- **Charge (Q)**: 21.43 C/cm^2
- **Potential:** -1V

- $CuSO_4$: 80mL
- Catalysts: 2cm x 2.7cm
- Cu aux: 4cm x 4cm



~2cm separation distance*

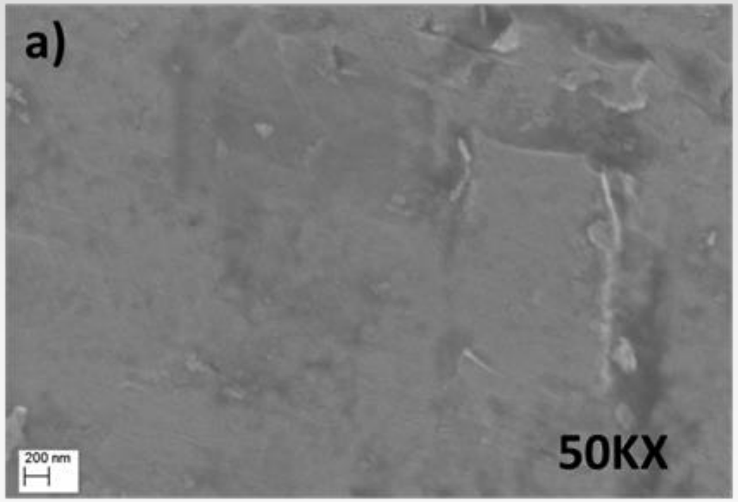
~1cm separation distance*

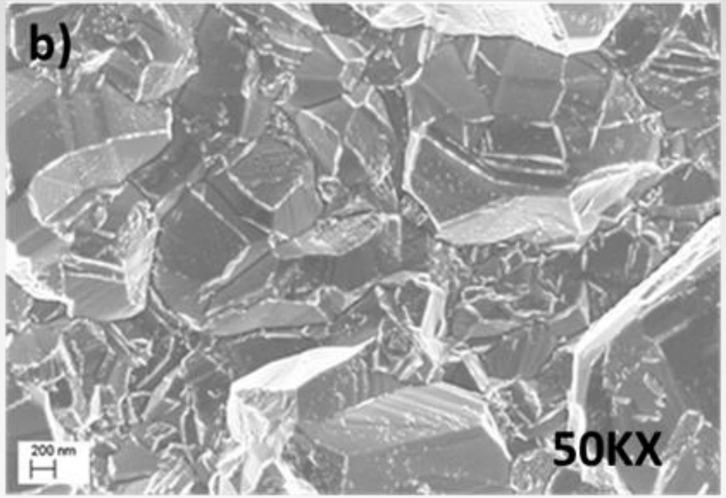
>0.5 cm separation distance*

*Separation distance between Cu auxiliary and Cu catalyst

Control over the Catalyst Morphology

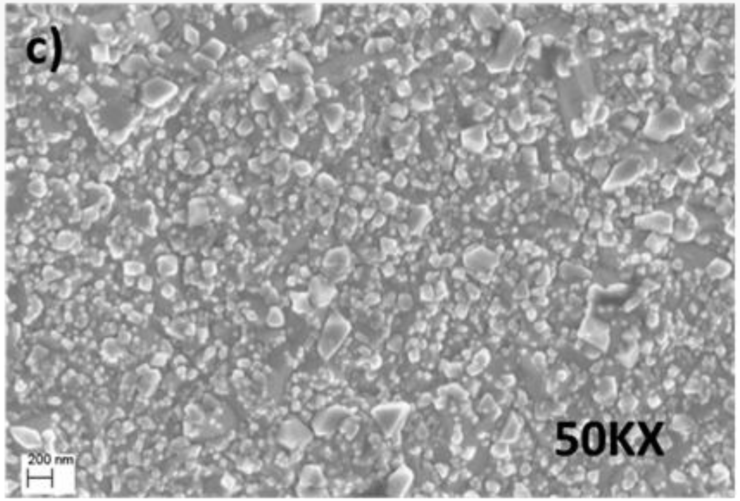
Cu bare



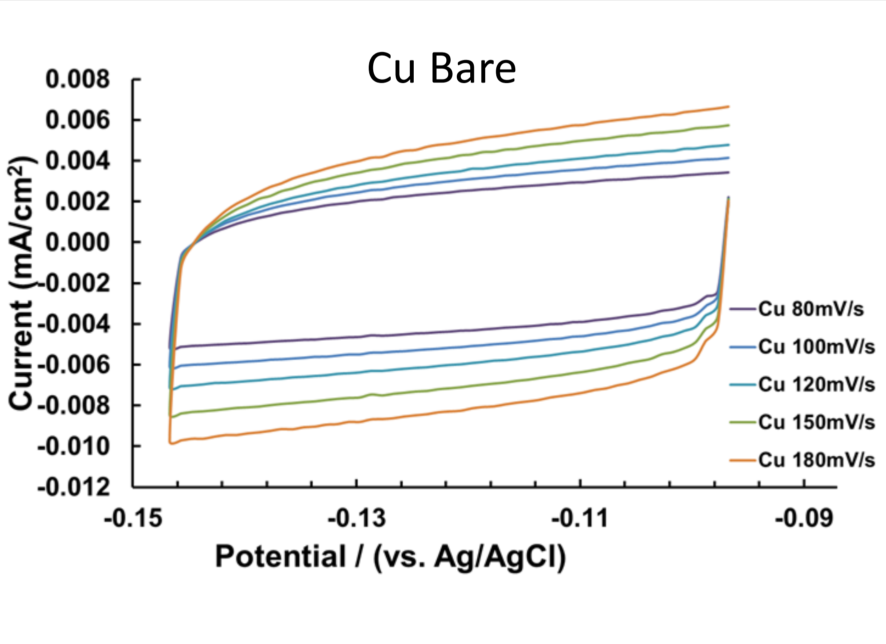


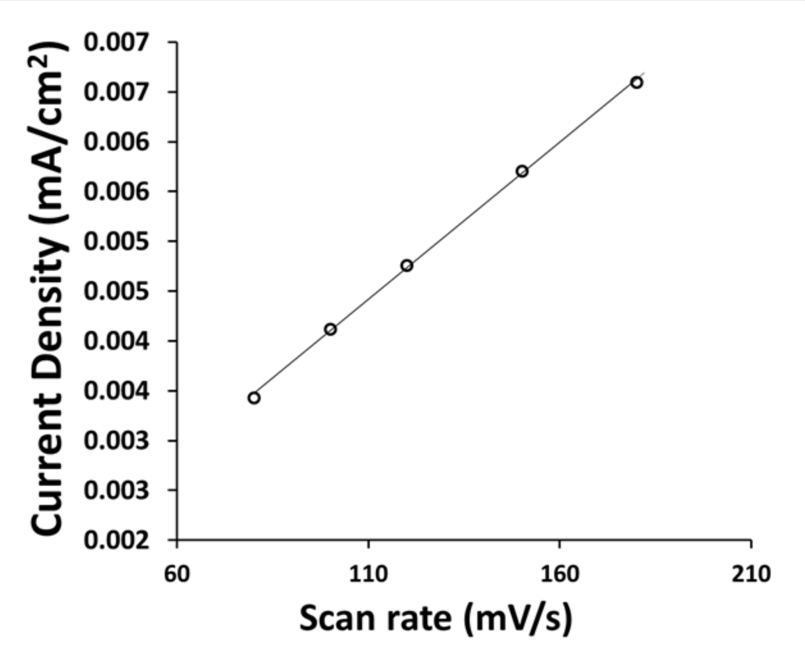
Cu/Cu:
~3μm crystals

Cu/Cu:
~300nm particles



Electrochemical Area Evaluation





Capacitance : $C = \frac{Current\ Density}{Scan\ Rate}$

$$Surface\ roughness = \frac{C}{C_o}$$

2. Controllable Product Selectivity

Evaluation of Roughness

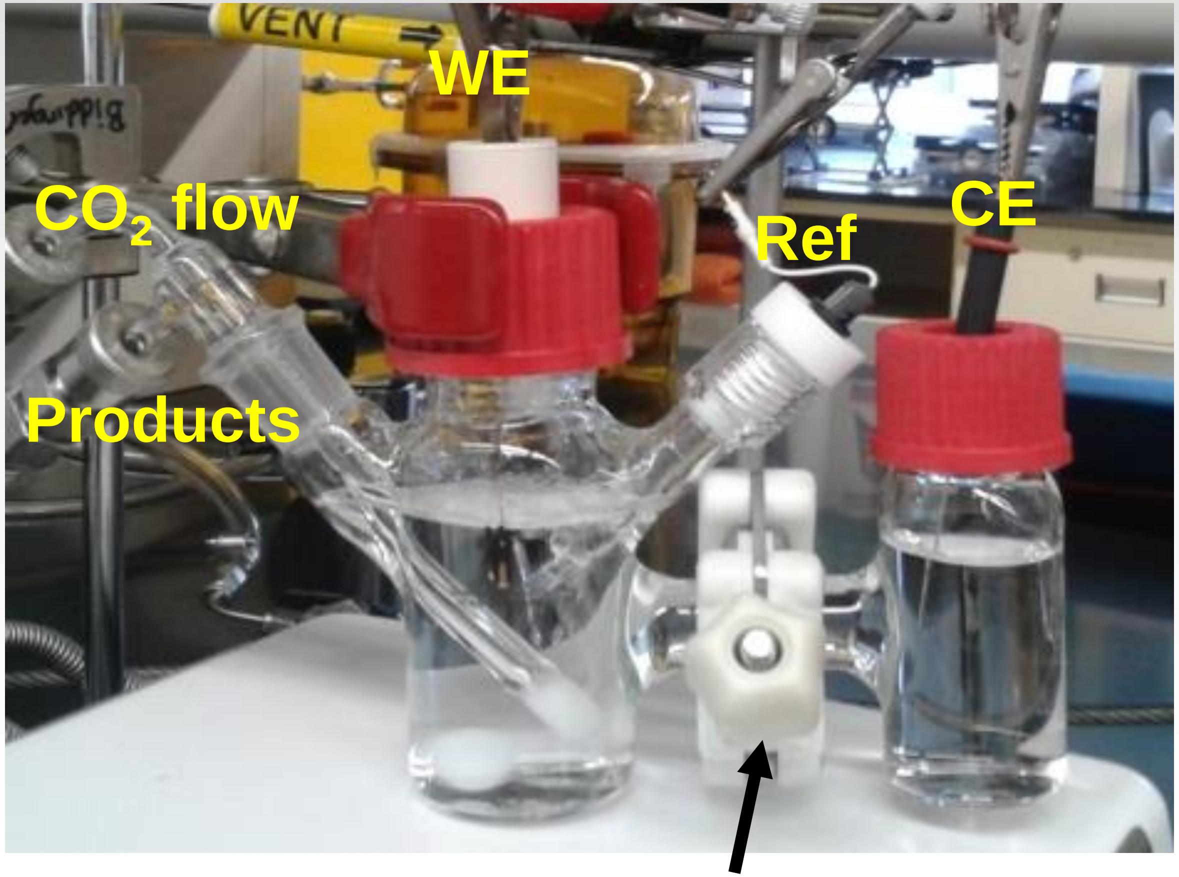
Capacitance and surface roughness factor of Cu-based catalysts

Catalyst	Capacitance (mF/cm^2) (± SD)	Surface roughness factor (± SD)
Cu-Bare	**0.030** ± 0.003	**1.0**
Cu/Cu(1)	**0.048** ± 0.005	**1.6** ± 0.2
Cu/Cu(2)	**0.173** ± 0.002	**7.8** ± 0.5

Cu/Cu(1), Cu/Cu(2) synthesized by electrodeposition - changing deposition characteristics

Alexandros N. Karaiskakis and Elizabeth J. Biddinger, *under preparation*

Experimental Set-up



Membrane (Nafion-212)

- Chronoamperometry :

  -1.6V to -2.4 V vs. Ag/AgCl

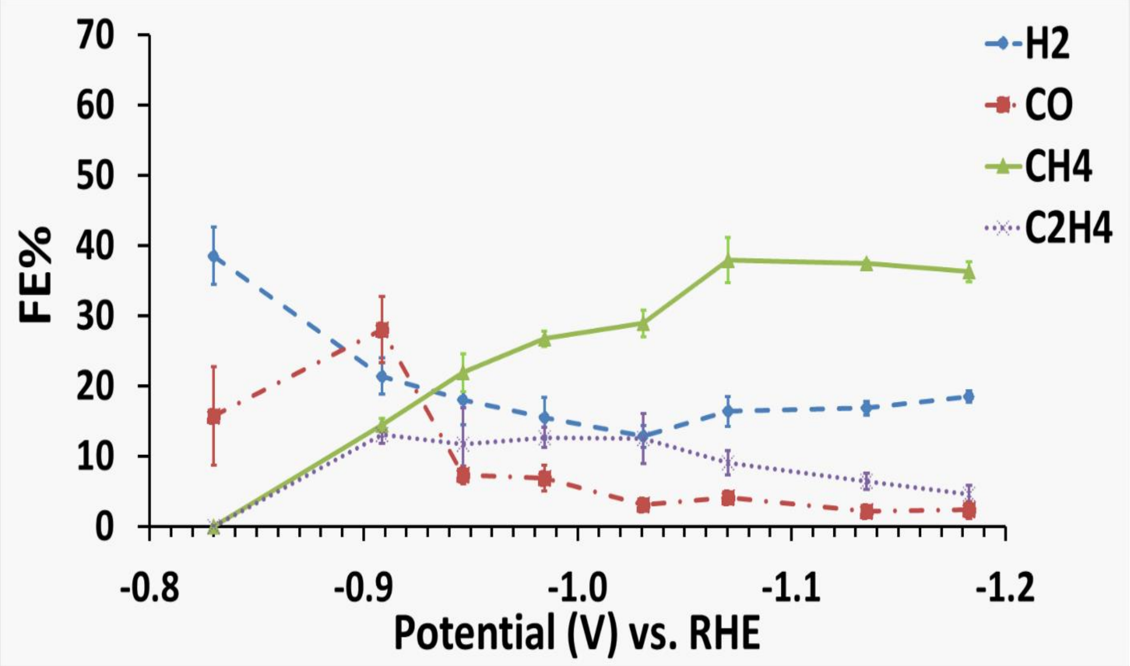
  WE: Cu, CE: Pt-mesh,

  Ref: Ag/AgCl (3M NaCl)

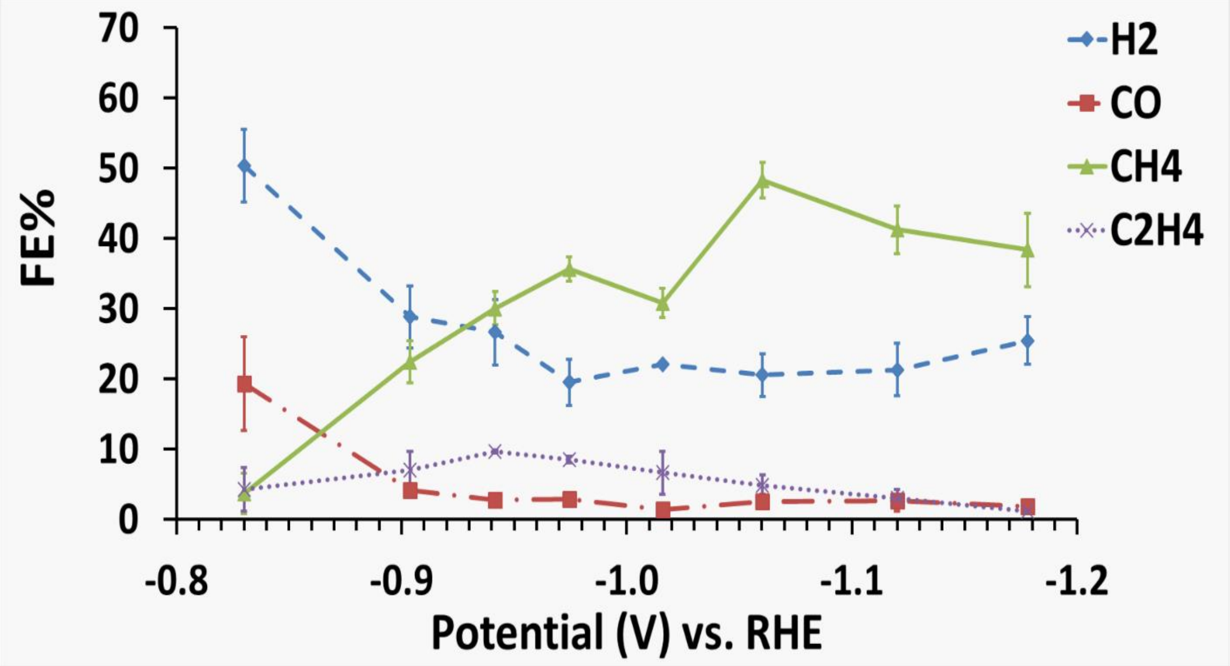
- 0.1M $KHCO_3$, CO_2 saturated
- pH: 6.8
- Temp: 25C and 1 atm
- Membrane: Nafion-212

Evaluation of Cu facet dependence

Cu/Cu → Dominant Cu(200), 2nd Cu(111)



Cu-bare → Dominant Cu(200)



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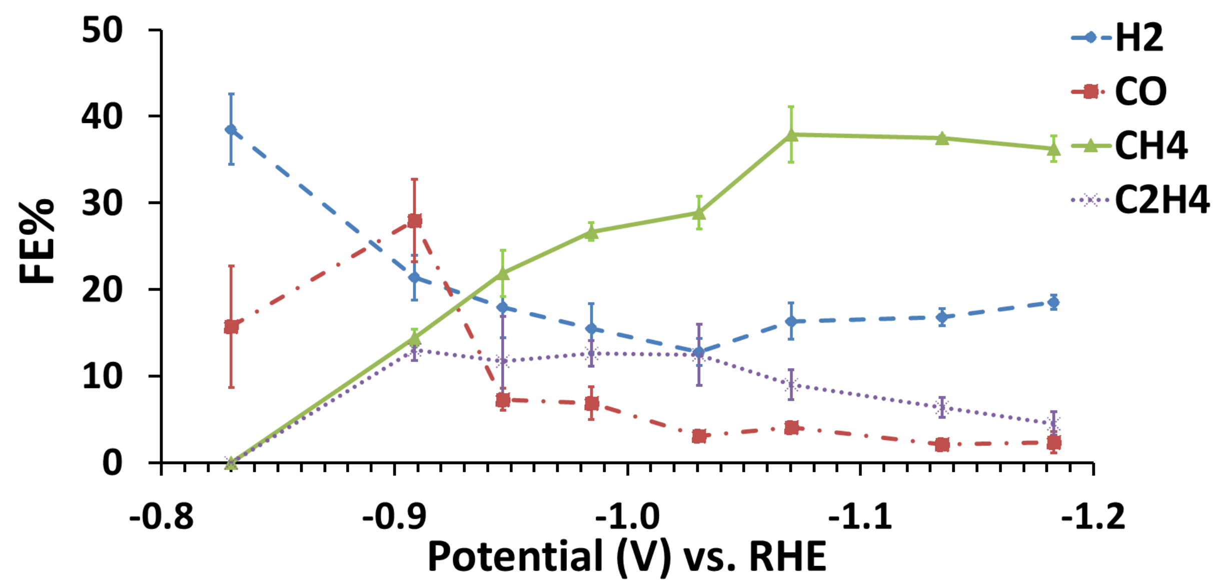
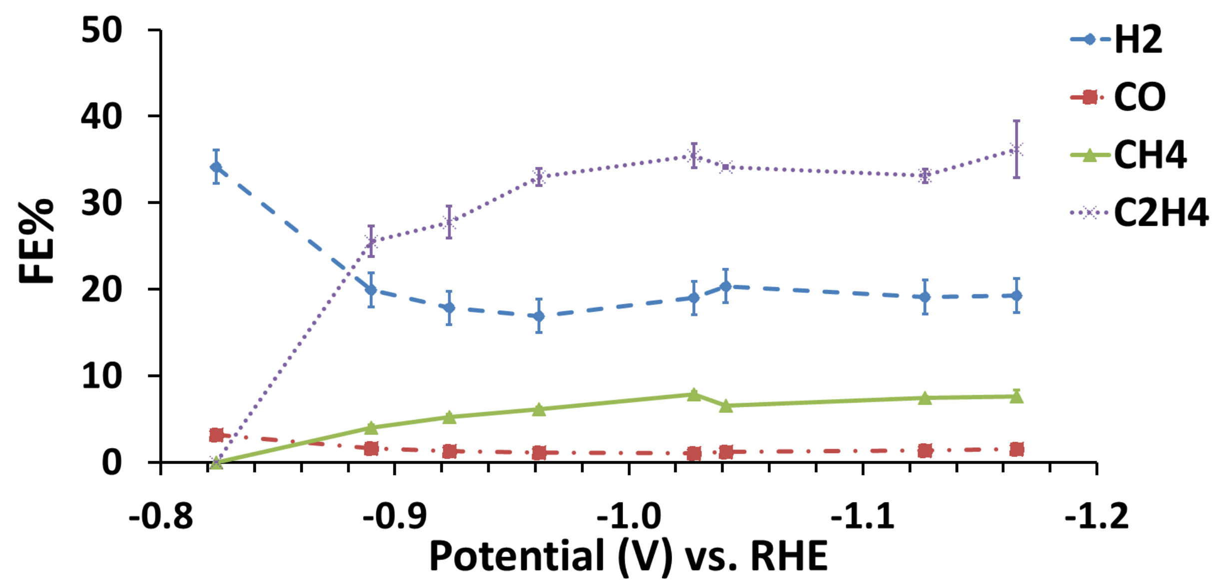
Impact of Roughness on FE

Cu/Cu(1) → Dominant Cu(200), 2nd Cu(111)
Roughness 1.6



Cu/Cu(2) → Dominant Cu(200), 2nd Cu(111)
Roughness 7.8



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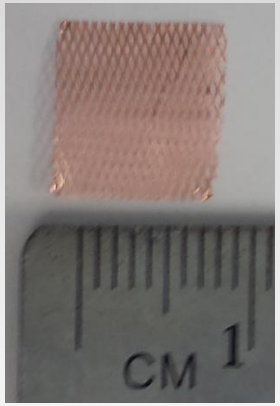
Alexandros N. Karaiskakis and Elizabeth J. Biddinger, *under preparation*

Catalysts' Shape Evaluation

Cu mesh used:

- $0.7\ cm^2$ (as Cu foil)-comparison purposes
- Based on surface density: 0.7cm x 1cm
- Wire attachment not possible→ 0.7cm x 9cm



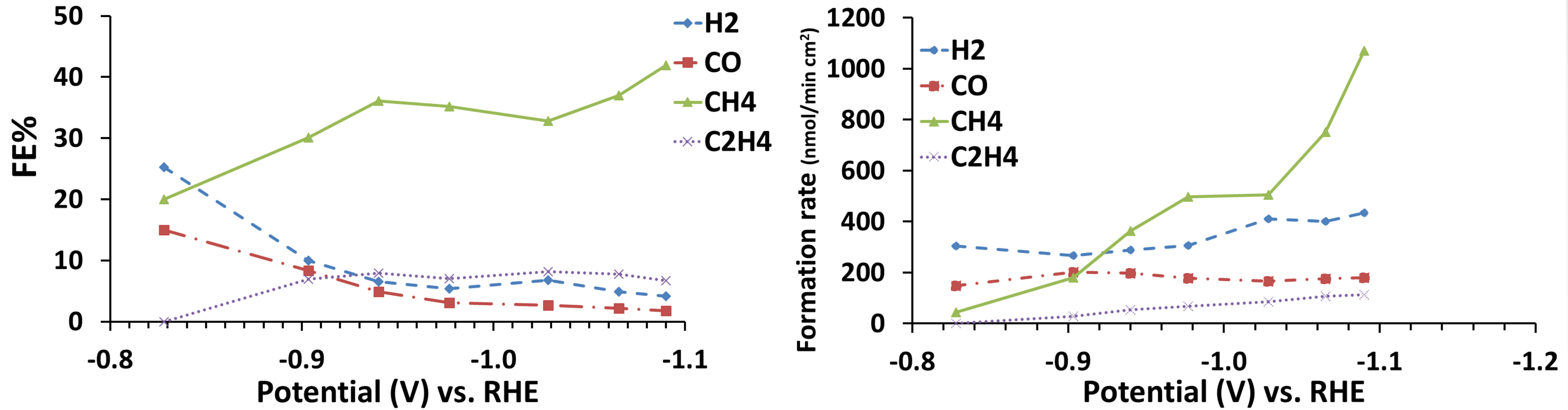
Capacitance and surface roughness factor of Cu-based catalysts

Catalyst	Capacitance (mF/cm^2)	Surface roughness factor
Cu mesh	0.032	1.01
Cu bare foil	0.033	1

Compared with: Cu bare foil

Improved CH_4 Formation Using Electro-polished Cu-mesh

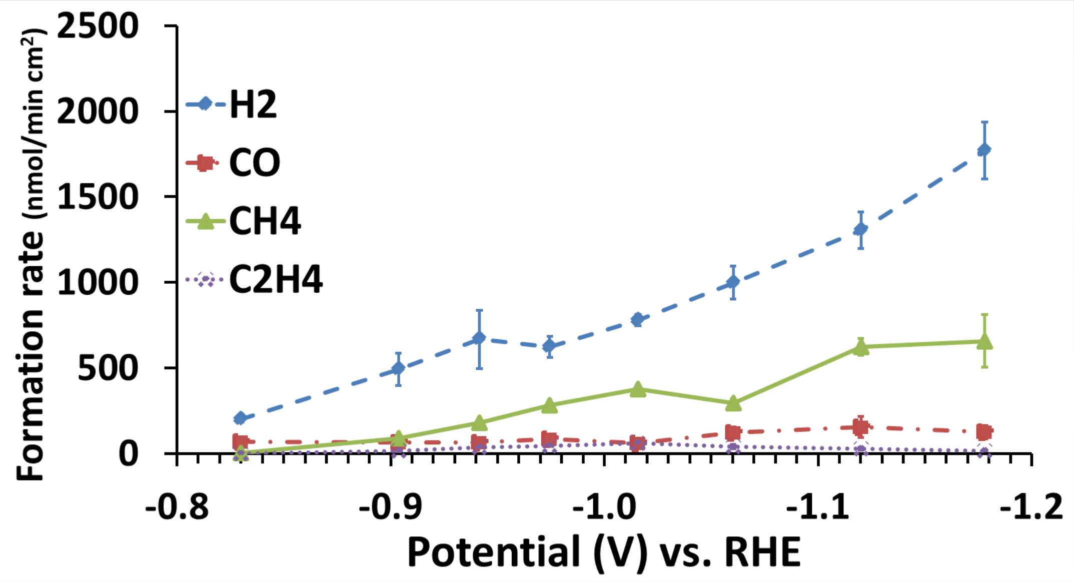
High performance ~40%FE CH_4



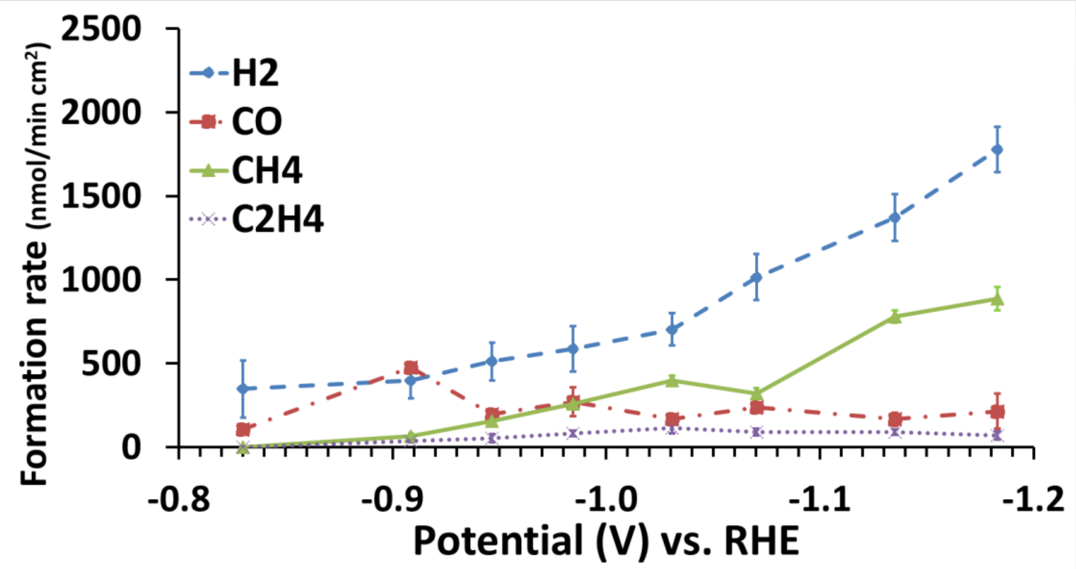
First time reported: lowest H_2 formation rates and CH_4 main product, not just FE

Comparison Between Cu Foil and Mesh

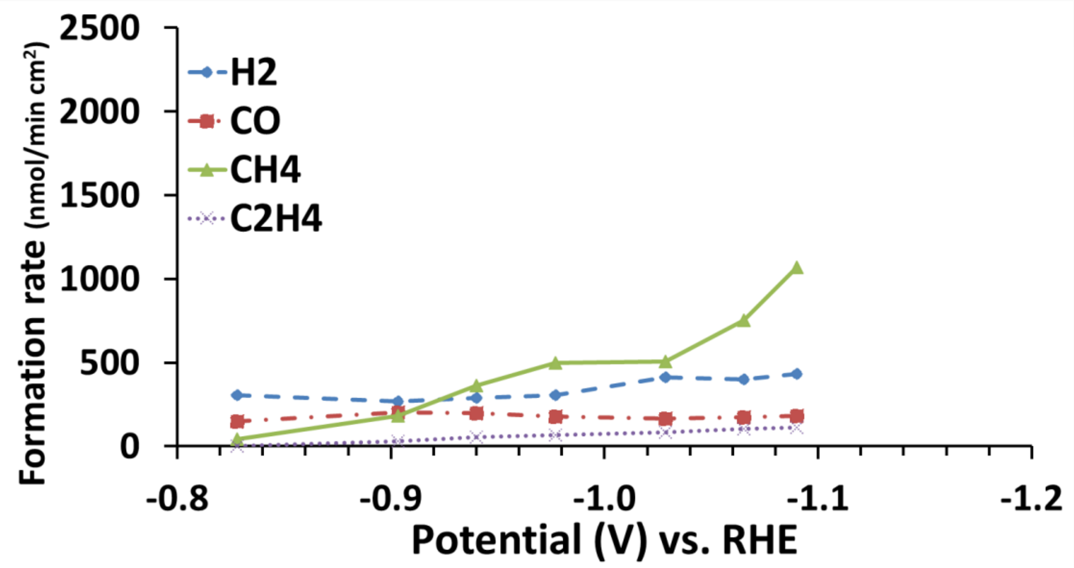
Cu-bare electropolished



Cu/Cu (Roughness 1.6)



Cu-mesh electropolished



Comparison Between Cu Foil and Mesh

Formation rates and current densities

Cu-bare electropolished | **Cu-mesh electropolished**

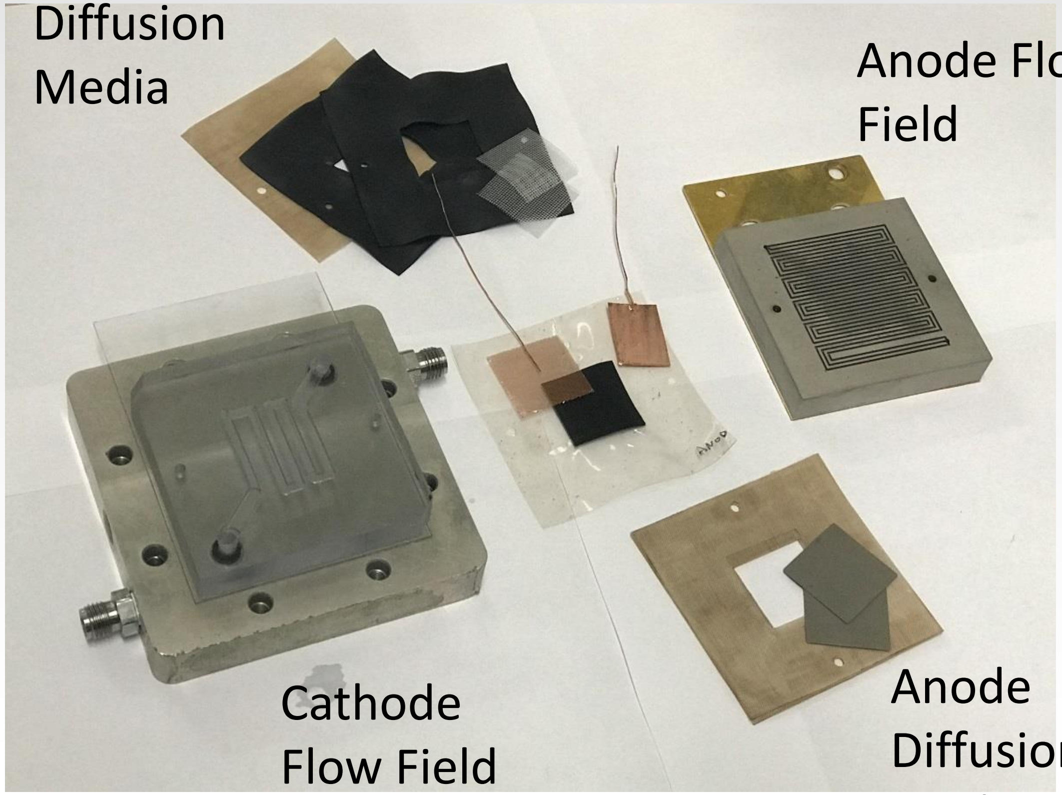
I(mA/cm2)	**23**
V vs. RHE	**-1.09**
Products	(nmol/min cm^2)
H2	734
CO	109
CH4	**558**
C2H4	27
Total	1427

I(mA/cm^2)	**33**
V vs. RHE	**-1.2**
Products	(nmol/min cm^2)
H2	1831
CO	221
CH4	**711**
C2H4	20
Total	2783

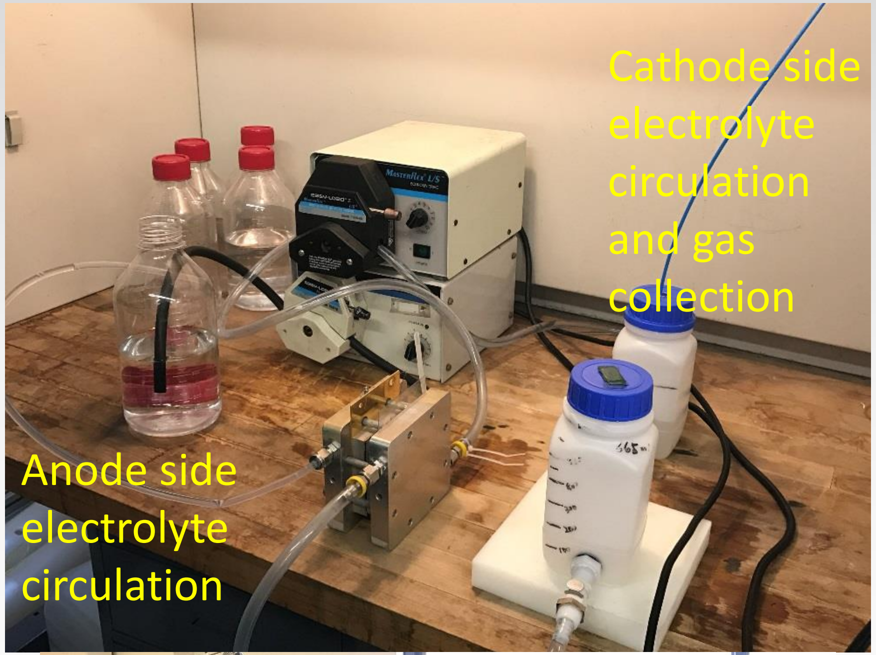
I(mA/cm^2)	**43**
V (reduction)	**-1.09**
Products	(nmol/min cm^2)
H2	433
CO	180
CH4	**1070**
C2H4	113
Total	1798

Current density (mA/cm^2), area of Cu exposed to electroreduction

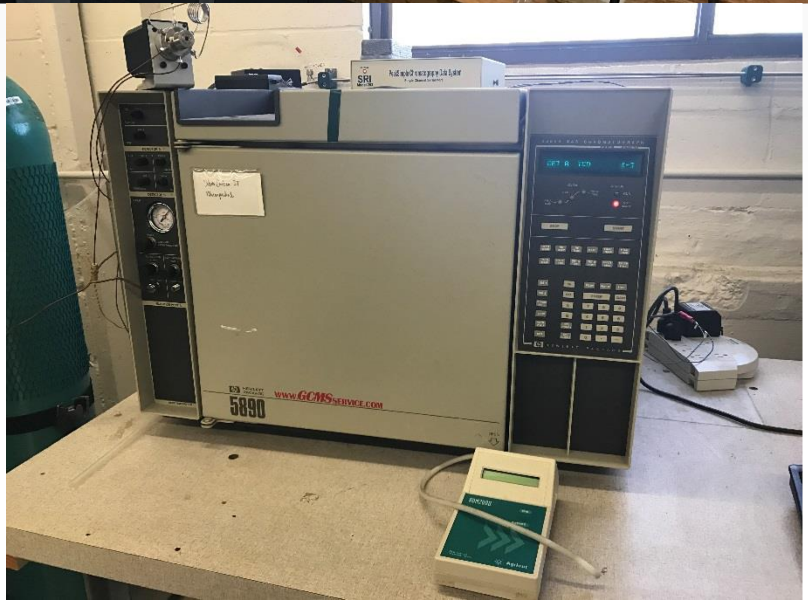
3. Giner Cell Configuration and Experiment Set Up



Cell Assembly



Experiment Setup



GC

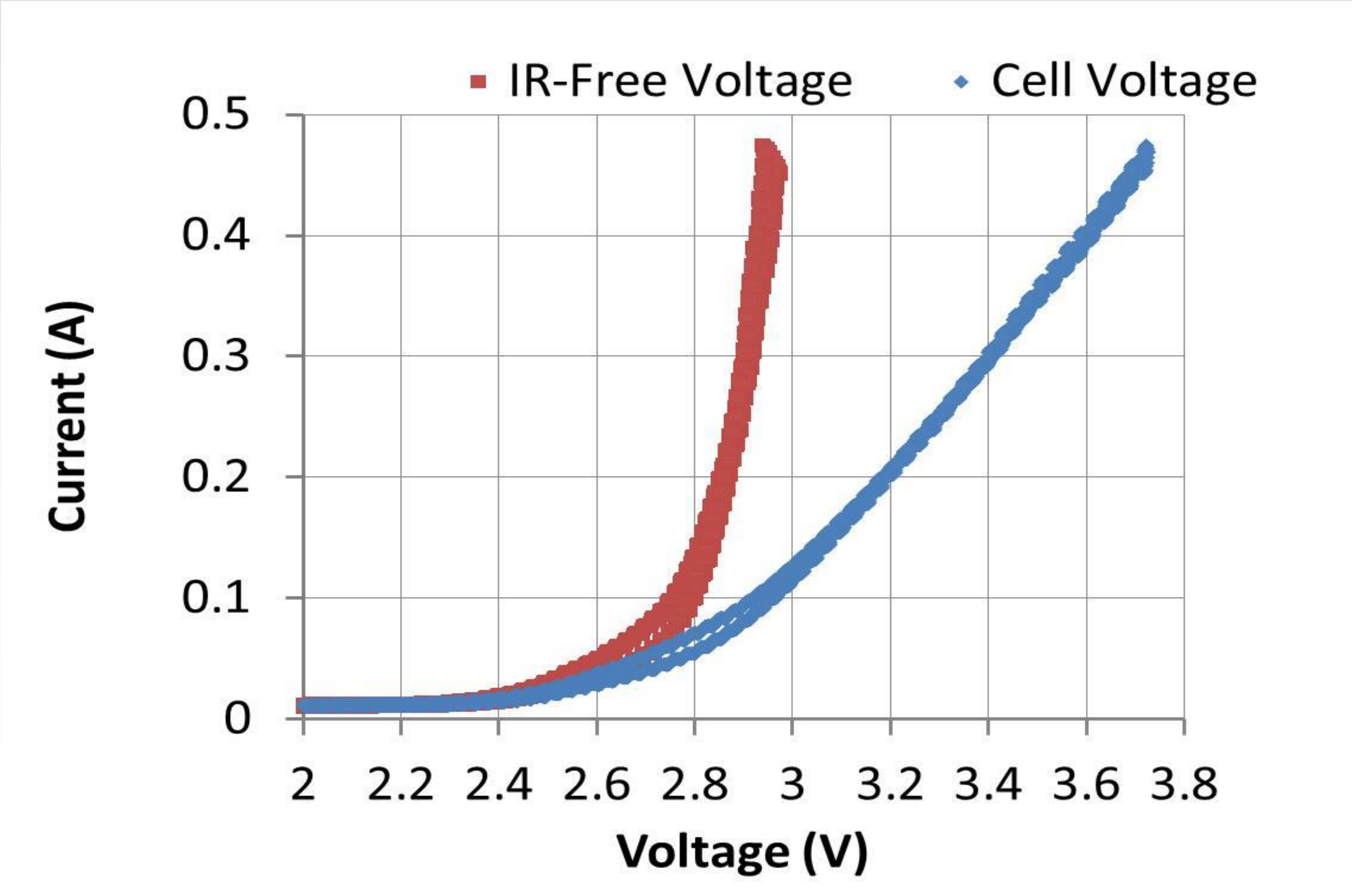
Optimizing Experiment Set Up

Build No.	Details and Changes	Comments
1	**Horizon Mini Hardware** 0.5 M $KHCO_3$ as electrolyte 2 cm x 2.7 cm Copper bare foil as catalyst and electrode	Cannot seal properly
2	**25cm^2 FCT Hardware w/ rubber gasket** 2 layers of 10 mil thick plastic mesh as diffusion media 10 mil Nafion membrane	Properly sealed but high cell resistance
3	**Reduced diffusion media thickness**	Cell resistance lowered by approx. 10%
4	**Reduced active area to confine electrolyte flow** **Reduced membrane thickness to 5 mil**	Cell resistance lowered by approx. 25%
5	**Gas collection set up change**	Easier gas sample collection and extraction
6	**Flow channels added**	Prevent port clogging; increased flow rate limit to test its impacts on cell performance; reduced cell resistance
7	**Gas flow cell with copper mesh against the Nafion membrane**	Eliminate the possibility of gas product dissolving in electrolyte

List of Tests Performed

Date	Catalyst	Date Received	Membrane	Set up	Diffusion Media	Flow rate	Voltage	Electrolyte	Temperature	Results
10/31/2016	Copper Bare Foil	Oct-16	N115	FCT	36 mil mesh	200	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.5	20	High cell resistance; poor cell performance; low methane FE%
11/2/2016	Copper Bare Foil	Oct-16	Akaline Membrane	FCT	36 mil mesh	200	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.5	20	Improved resistance; still very low methane FE%; move back to Nafion membrane
11/7/2016	Copper Bare Foil	Oct-16	N115	FCT	36 mil mesh	200	3.0; 3.2; 3.4; 3.6	0.5	20	Higher flow rate helped with cell resistance; clog issues; Methane FE% still low at low cell voltage
11/8/2016	Copper Bare Foil	Oct-16	N115	FCT	36 mil mesh	200	3.8; 4.0; 4.2; 4.4	0.5	20	Higher flow rate helped with cell resistance; clog issues; Methane FE% slightly improves
11/9/2016	Copper Bare Foil	Oct-16	N115	FCT	26 mil mesh	200	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.5	20	Reducing thickness of diffusion media leads to small decrease in cell resistance; methane FE% is not siginificantly affected
11/10/2016	Copper Bare Foil	Oct-16	N115	FCT	17 mil mesh	200	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.5	20	Reducing thickness of diffusion media leads to small decrease in cell resistance; methane FE% is not siginificantly affected
11/14/2016	Copper Bare Foil	Oct-16	N115	FCT	17 mil mesh	200	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.3	20	Reducing electrolyte concentration leads to increase in cell resistance; methane FE% increases noticeably.
11/15/2016	Copper Bare Foil	Nov-16	N115	FCT	17 mil mesh	200	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.1	20	Reducing electrolyte concentration leads to increase in cell resistance; methane FE% increases noticeably.
11/23/2016	Copper Bare Foil	Nov-16	N115	FCT	17 mil mesh	200	3.0; 3.2; 3.4; 3.6	0.1	20	Inconsistency is a problem between different runs; methane FE% are different with the same conditions; problem of poor control of the current set up
12/1/2016	Copper Bare Foil	Nov-16	N115	FCT	17 mil mesh	200	3.8; 4.0; 4.2; 4.4	0.1	20	Inconsistency is a problem between different runs; methane FE% are different with the same conditions; problem of poor control of the current set up
12/7/2016	Copper Bare Foil	Nov-16	N115	FCT	17 mil mesh	300	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.1	20	Carved out flow field on the cathode side of the cell on the previously used plastic block; improved maximum flow allowrance by 100%; increasing flow rate greatly reduced cell resistance;
12/12/2016	Copper Bare Foil	Nov-16	N115	FCT	17 mil mesh	400	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.1	20	increasing flow rate greatly reduced cell resistance; methane FE% is improved at the same time; H2 FE% is also improved as a result of overall cell activity improvement as flow rate increases
12/15/2016	Copper Bare Foil	Nov-16	N115	FCT	17 mil mesh	500	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.1	20	Methane FE% starts to drop while H2 FE% keeps increasing; high flow rate may impact selectivity but reducing resisdence time of the reactants inside the cell
1/9/2017	Copper Bare Foil	Nov-16	N115	FCT	17 mil mesh	400	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.1	20	Repeated experiment with same conditions but different flow rate than before as comparison; still existing issues on inconsistency and lack of controls on some unknown variables
1/11/2017	Cu/Cu	Oct-16	N115	FCT	17 mil mesh	400	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.1	20	No obvious changes to product FE%; the set up is the limitation still;
1/16/2017	Cu/Cu	Oct-16	N115	FCT	17 mil mesh	400	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.1	20	No obvious changes to product FE%; the set up is the limitation still;
1/18/2017	Copper Bare Foil	Jan-17	N115	FCT	17 mil mesh	400	3.0; 3.2; 3.4; 3.6; 3.8; 4.0; 4.2; 4.4	0.1	50	Cell Performance greatly reduced at high temperature; caused by low CO2 solubility
1/25/2017	Copper Bare Mesh		N115	FCT	17 mil mesh	400	3.0; 3.2; 3.4; 3.6	0.1	20	Show short time good performance; normal cell resistance; high current density; high methane FE%;
2/1/2017	Copper Bare Mesh		N115	FCT	17 mil mesh	400	3.8; 4.0; 4.2; 4.4	0.1	20	Suffers from catalyst deactivation high cell voltage; surface turns black very quickly under high voltage;
2/6/2017	Copper Bare Foil	Jan-17	N115	FCT	17 mil mesh	400	3.0; 3.2; 3.4; 3.6	0.1	20	Continuous investigation on improving consistency and catalyst conditions after runs
2/8/2017	Copper Bare Foil	Feb-17	N115	FCT	17 mil mesh	400	3.8; 4.0; 4.2; 4.4	0.1	20	Continuous investigation on improving consistency and catalyst conditions after runs
2/13/2017	Copper Bare Foil	Feb-17	N115	FCT	17 mil mesh	400	3.0; 3.2; 3.4; 3.6	0.1	20	Continuous investigation on improving consistency and catalyst conditions after runs
2/22/2017	Copper Bare Foil	Feb-17	N115	FCT	17 mil mesh	400	3.8; 4.0; 4.2; 4.4	0.1	20	Continuous investigation on improving consistency and catalyst conditions after runs

Initial Cell Test



Flow rate: 20ml/min; No flow field
Diffusion media: 36 mil plastic mesh
Membrane: N115
Cathode Catalyst: Copper Bare Foil

Higher current ≠ better performance

SUMMARY

1. Controllable Synthesis

Electrodeposition→ Roughness, Morphology

2. Tunable synthesis of catalysts based on desired product

Main products	Crystal orientation	Roughness	Particle size
40% CH_4 - 8% C_2H_4 (FE%)	Dominant Cu(200), Secondary Cu(111)	1.6 ± 0.2	3µm
36% C_2H_4 - 7% CH_4 (FE%)	Dominant Cu(200), Secondary Cu(111)	7.8 ± 0.5	300nm

3. Activity Improvement

Formation Rates of main products on Cu-based Catalysts (nmol/min cm^2)			
Catalyst	H_2	CH_4	C_2H_4
Cu-bare	1770	657	14
Cu/Cu (1.6 roughness) flag	1779	886	70
Cu/Cu (7.7 roughness) flag	1580	137	440
Cu-mesh bare	433	1070	113

SUMMARY (Cont'd)

High Activity Tunable Catalysts Based on Desired Product

1.	Ability to synthesize catalyst with the controllable deposition technique developed
2.	Knowledge gained on gaseous products can be transferred to liquids products
3.	The customer can select the desired product based on their needs

Proposed Phase II Work

- Further improve efficiency and formation rates of desired products through morphology control (deposition)
- Liquid products evaluation and control (ethanol and formic acid) based on knowledge gained (gaseous methane and ethylene)
- Cell design optimization modelling (COMSOL)
- Focus will be given to optimize single flow cell (25cm^2)
  - Flow field, gas diffusion, mesh vs. foil
  - Better gas and liquid composition sampling
  - Gas and liquid product analysis
- Short stack demonstration
  - A 6-cell (each 50 cm^2) will be delivered

Phase II Team

- CCNY:
  - Continued catalyst modification and scale-up using liquid cell;
- Giner:
  - Gas flow single cell and short stack design
- NREL
  - Integration w/ renewable energy
  - TEA and sensitivity studies

Project Management and Continuation

- Project review meeting on March 24;
- Final report will be submitted on March 27;
- Phase II proposal will be submitted on April 3

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