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DOE "Carbon Capture Program" SBIR Project

A High-Efficiency Process for CO_2 Conversion to Hydrocarbon Fuels

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Giner, Inc.
Newton, MA

August 30, 2016

Giner Inc. Introduction

- Location: Newton, MA, 15 minutes to Boston downtown

- 42 years experience in electrochemical R&D, particularly in energy conversion and storage:
  - Fuel Cells
  - Electrolyzers
  - Batteries
  - Capacitors

Synergy of Giner Technologies

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

CO_2 Emission and Utilization

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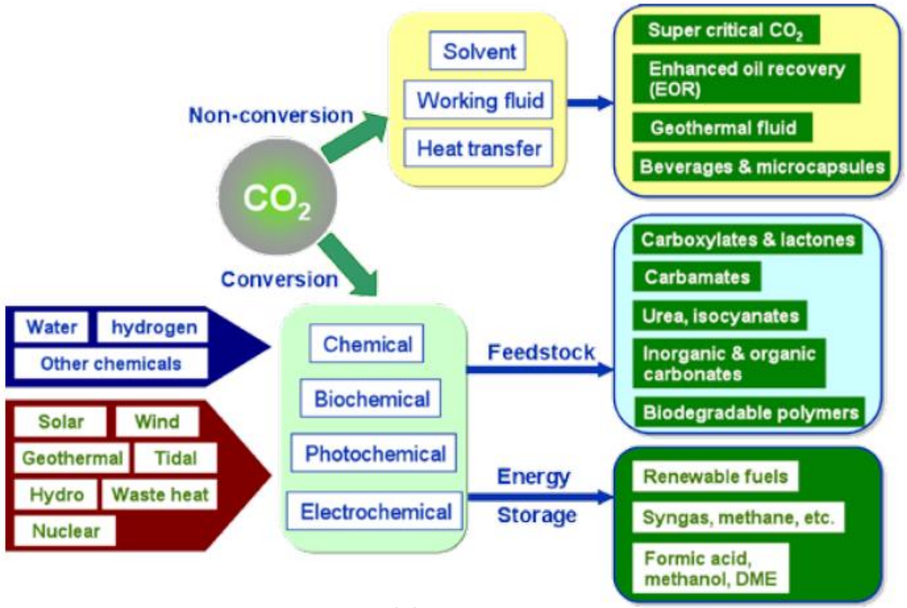
- Concern: Global CO_2 emissions from fossil fuel use were 35.9 gigatonnes (Gt) in 2014
- Key Driver: **Paris Agreement at COP 21 (2015)**

  - *President Barack Obama at the launch of COP21*

  - De-carbonization: reduce all U.S. Carbon emissions by half before 2050

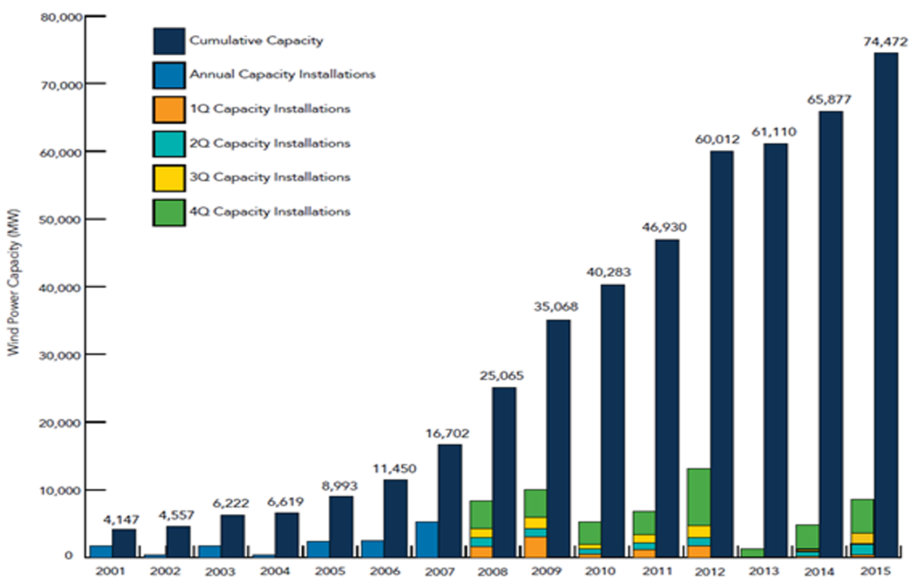
- Motivation: CO_2 capture and conversion to valuable chemicals



DNV, position 07-2011

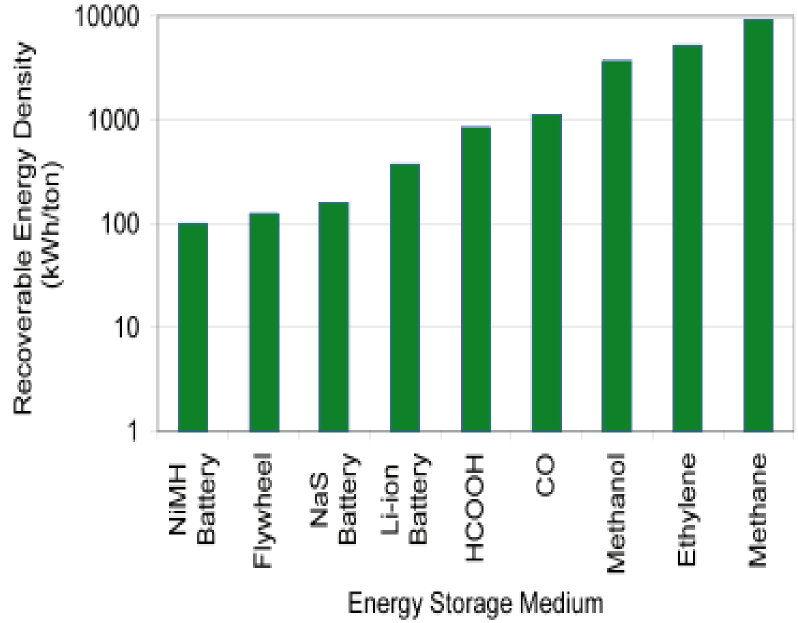
CO_2 to Hydrocarbon Fuels

Renewable energy installation keep climbing
and off-peak energy is not fully utilized



AWEA report, 2015

Methane: highest energy density



DNV, position 07-2011

- **Electrochemical Conversion of CO_2 to hydrocarbon fuels using off-peak renewables - A means of energy storage**

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CO_2 Electro-Reduction Processes

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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

Qiao, 2014
Appel, 2013

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
I	Hg	-1.51	5.0	0.0	0.0	0.0	0.0	0.0	99.5	0.0	99.5
I	Tl	-1.60	5.0	0.0	0.0	0.0	0.0	0.0	95.1	6.2	101.3
I	In	-1.55	5.0	0.0	0.0	0.0	0.0	2.1	94.9	3.3	100.3
I	Sn	-1.48	5.0	0.0	0.0	0.0	0.0	7.1	88.4	4.6	100.1
I	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
II	Ag	-1.37	5.0	0.0	0.0	0.0	0.0	81.5	0.8	12.4	94.4
II	Zn	-1.54	5.0	0.0	0.0	0.0	0.0	79.4	6.1	9.9	95.4
II	Pd	-1.20	5.0	2.9	0.0	0.0	0.0	28.3	2.8	26.2	60.2
II	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
III	Fe	-0.91	5.0	0.0	0.0	0.0	0.0	0.0	0.0	94.8	94.8
III	Pt	-1.07	5.0	0.0	0.0	0.0	0.0	0.0	0.1	95.7	95.8
III	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

Hori, 2008

Effective Catalysts for CO_2 to Methane

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Initial Studies for CO_2 Electroreduction

- **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

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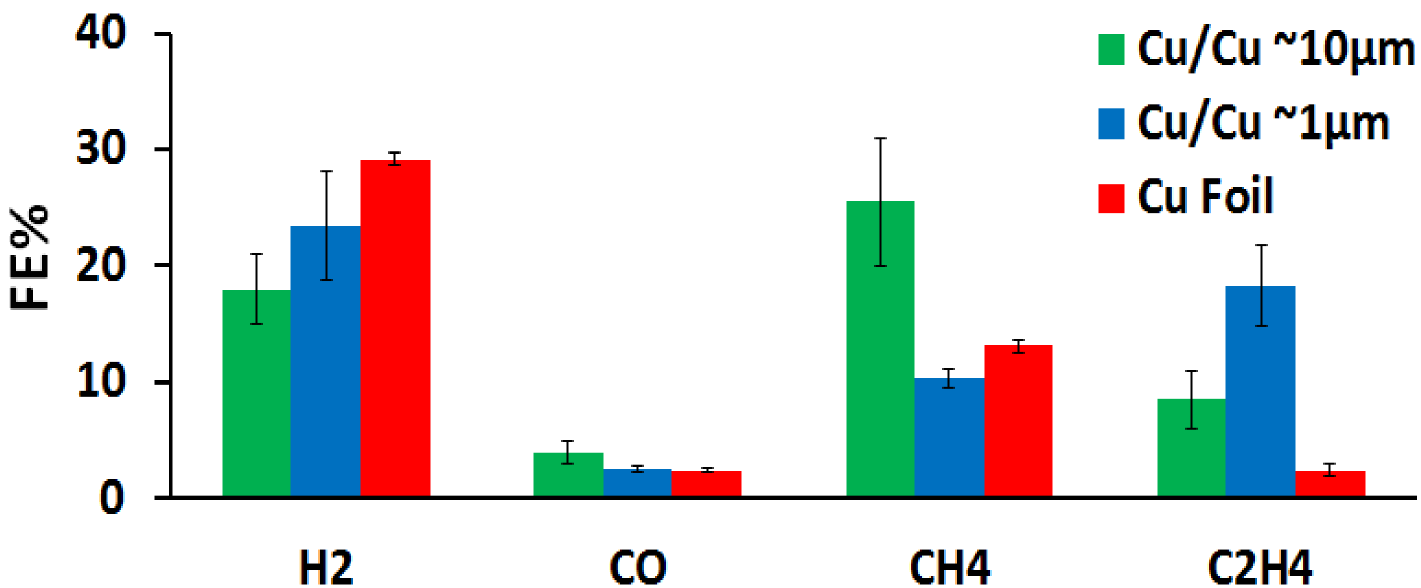
Cu electrocatalyst performance at -1.87V vs. RHE in CO_2-saturated 0.1M $KHCO_3$

Electrocatalyst	Gaseous Product Faradaic Efficiency				Gaseous Product Selectivity				Average Current Density (mA/cm^2)
	H_2	CO	CH_4	C_2H_4	H_2	CO	CH_4	C_2H_4	
Cu/Cu, ~10 μm thick	14.9%	2.9%	31.0%	10.6%	55%	11%	28%	6%	21
Cu/Ni, ~10 μm thick	34.3%	1.4%	7.6%	2.9%	90%	4%	5%	1%	21
Cu/Ti, ~10 μm thick	32.6%	2.0%	12.1%	9.1%	83%	5%	8%	4%	12
Cu/Cu, ~1μm thick	18.8%	2.2%	9.6%	21.8%	70%	8%	9%	13%	32
Bare Cu Foil	29.1%	2.5%	13.2%	2.4%					12

By changing the copper electrodeposition parameters, the product distribution can be altered.



Giner Previous Efforts

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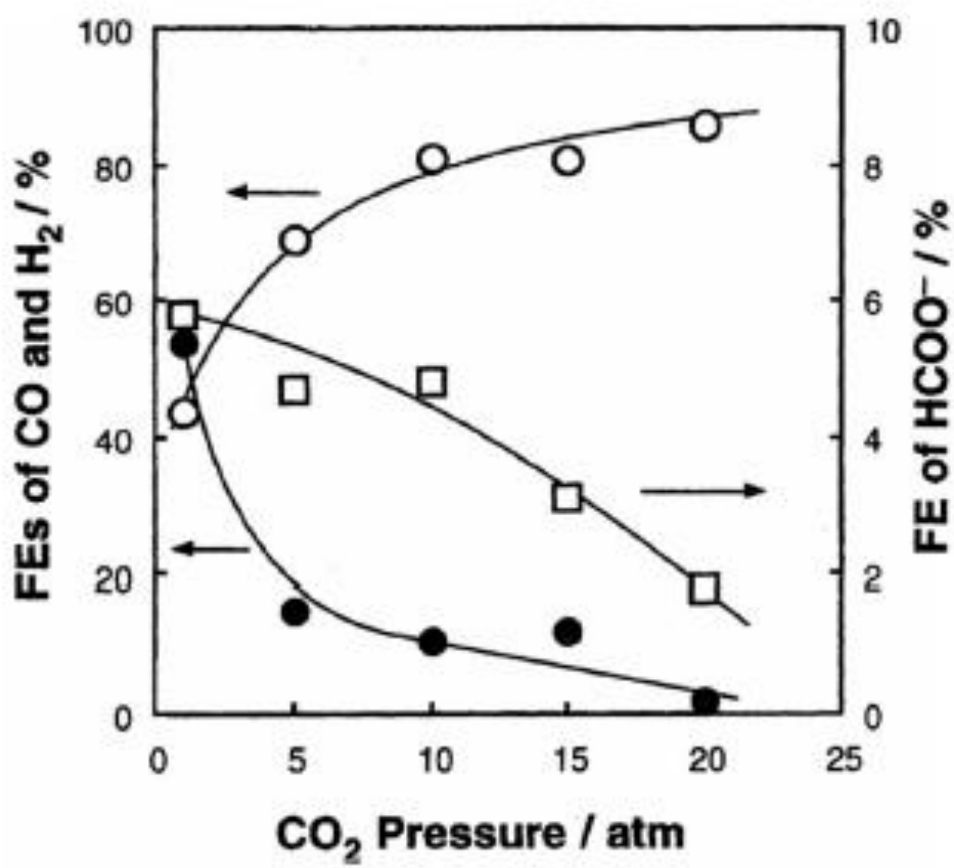
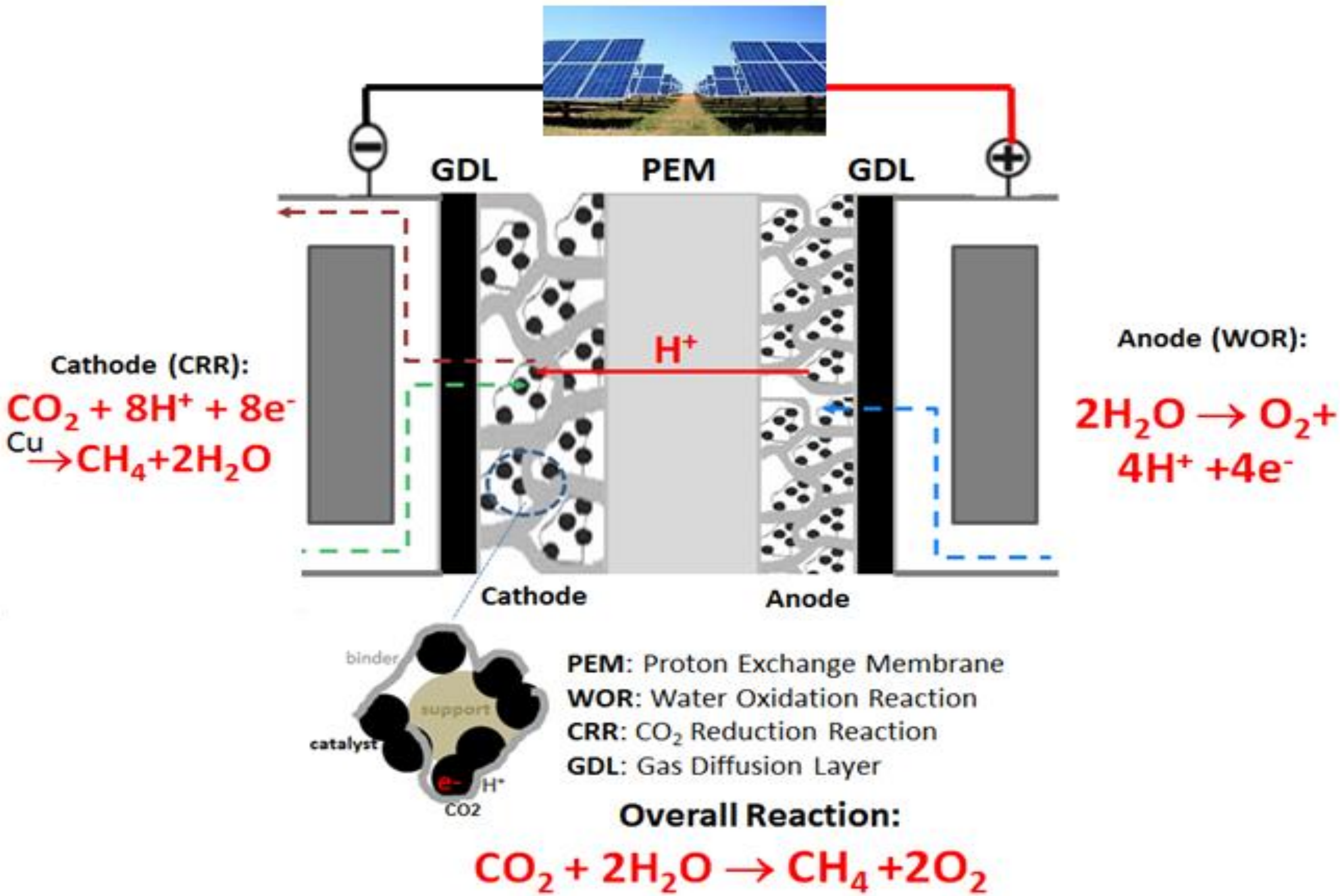
CO2 → Syn Gas



Dependence of Faradaic efficiencies of reduction products on the CO_2 pressure in the electrochemical reduction of CO_2 on a Ag-GDE at 300 mA/cm^2 in 0.5 mol/L $KHCO_3$.

Photograph of Giner's 8-cm^2 high-pressure (600-psig) CO_2 electroreduction cell.

Technical Approaches



Combine CCNY's direct CO_2 conversion catalyst development with Giner's expertise on electrolyzer cells and system design

Tasks and Milestones

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			X			X

Milestones

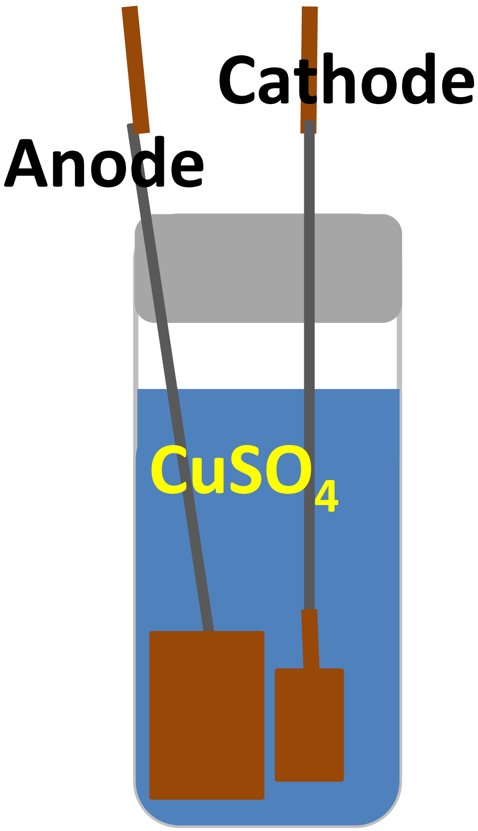
- Be able to operate the electrolyzer cell at a current density > 200 mA/cm^2 by Month 5
- Faradaic efficiency reaches 40% for the CH_4 formation by Month 9

Progress of Task 1:

Further Development of CO_2 Reduction Electro-catalysts

Electrochemical Cu Deposition: Scale Up

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



- **0.5M $CuSO_4$**: 80mL
- Catalysts: 2cm x 2.7cm
- Cu aux: 4cm x 4cm

Pre-treatment:

- 10 min Alumina 0.3µm
- 10 min Alumina 0.05µm
- 10 min Acetone
- 1 min HCl (10%): 4ml

Deposition Results

Optimizing scale up conditions – electrode positions result in differing qualities of Cu deposits

Front (0.5M $CuSO_4$) Back

vs.

Back (0.25M $CuSO_4$)

~1cm separation distance*

*Separation distance between Cu auxiliary and Cu catalyst

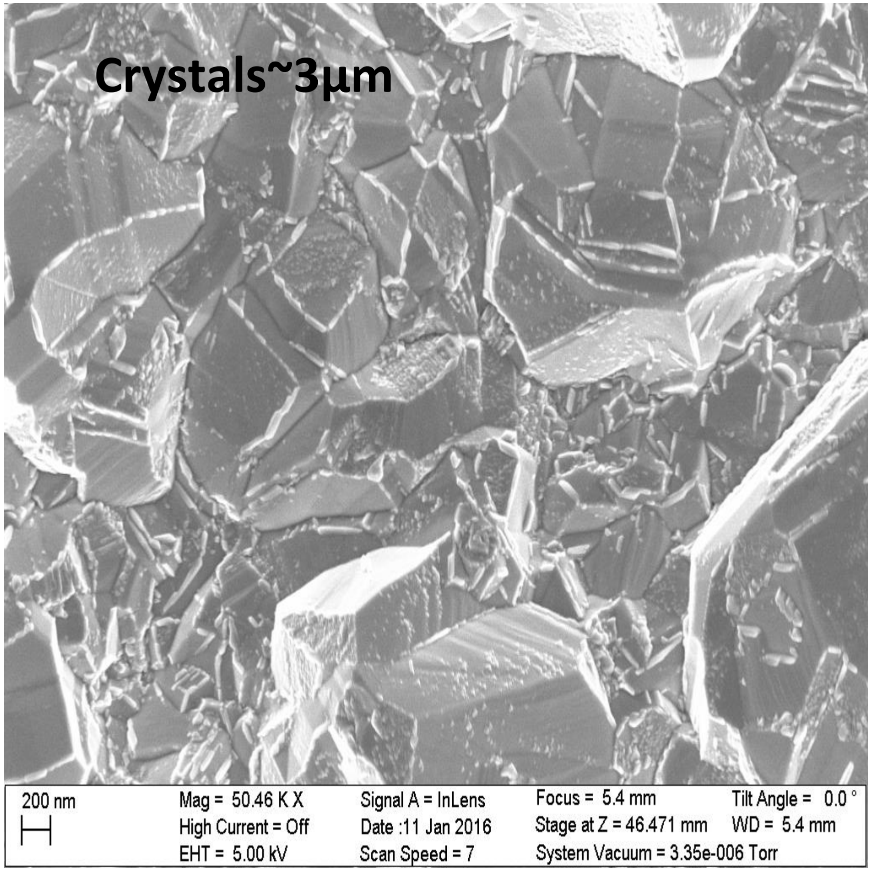
Deposition Results: Preliminary Small Scale

SEM Analysis:

21.43C x $0.35cm^2$ x 2= **15C**

Cu Morphology to Replicate

Cu/Cu (0.5cm x 0.7cm)



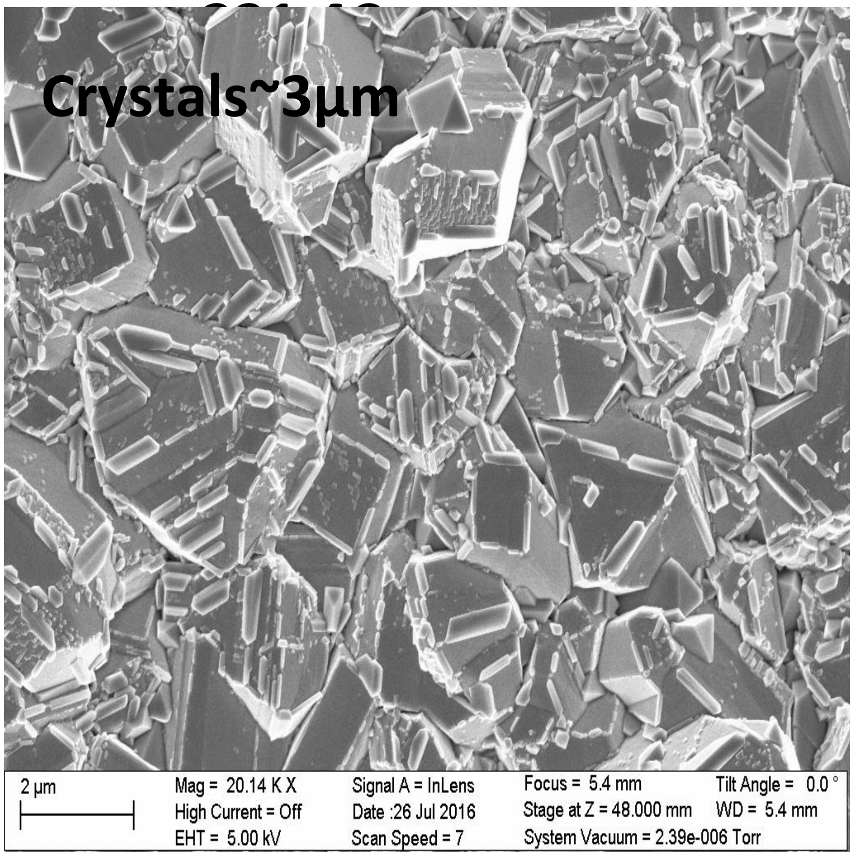
Deposition Results: Scaled Up (25 cm^2)

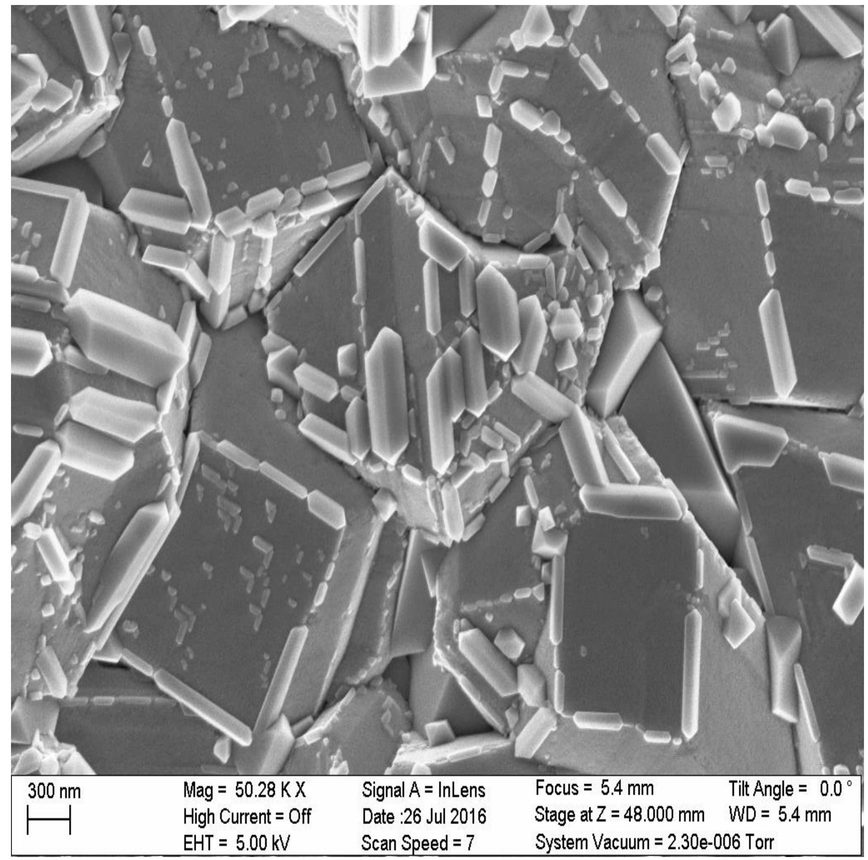
SEM Analysis:

21.43 C/cm^2 x 5.4cm^2 x 2=

0.5M $CuSO_4$

Cu/Cu (2cm x 2.7cm)





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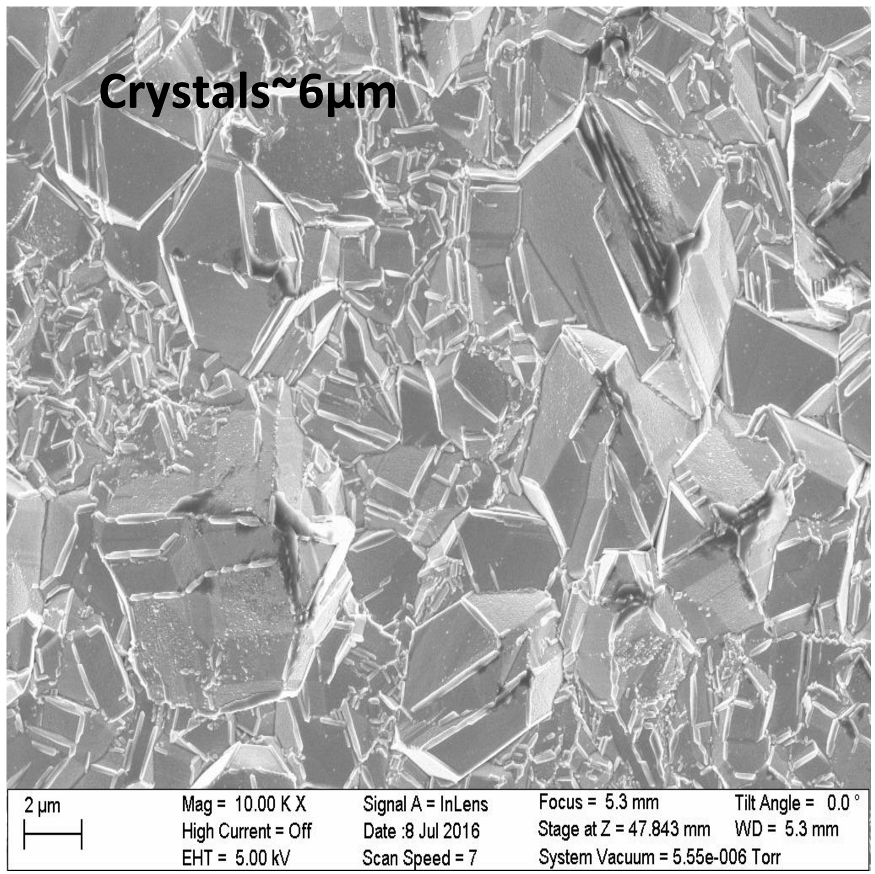
Deposition Results

SEM Analysis:

21.43 C/cm^2 x 5.4cm^2 x 2= **231.4C**

0.25M $CuSO_4$

Cu/Cu (2cm x 2.7cm)



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Deposition Results: Scale Up

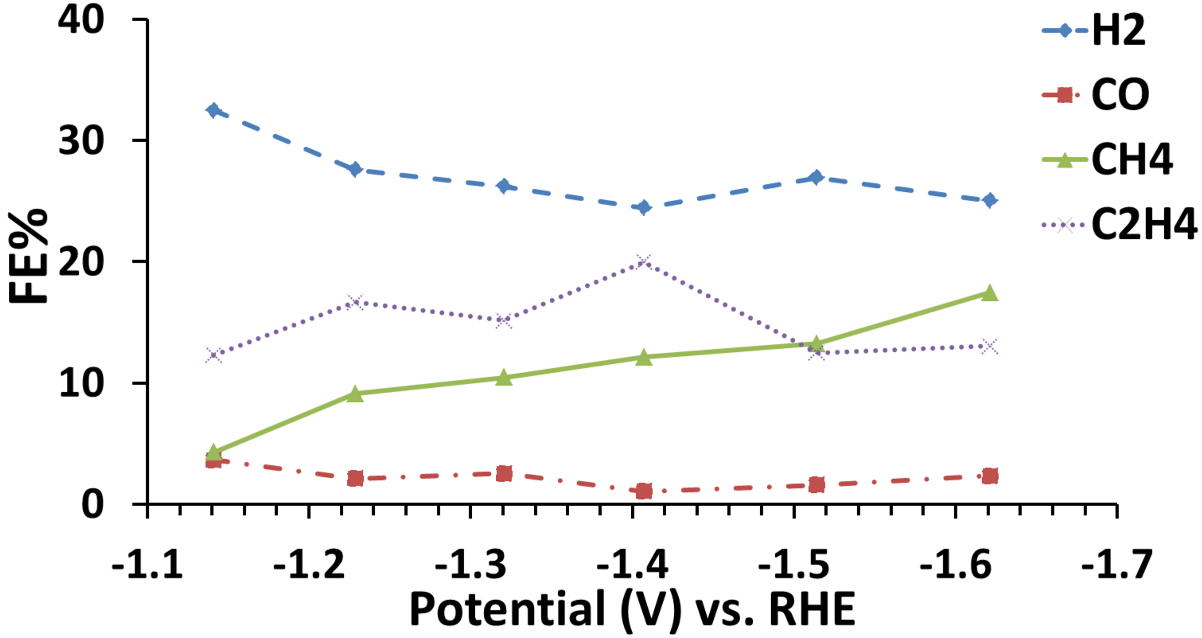
- Catalysts: 2cm x 2.7cm =5.4cm^2 (Min 5cm^2)
- ~1cm separation distance*

Reproducible depositions

21.43 C/cm^2	Size or Cu Crystals (~3µm)	Deviation from 100% deposition (Average)
Cu/Cu (0.25M $CuSO_4$)	**Crystals~6µm**	0.5%
Cu/Cu (0.5M $CuSO_4$)	**Crystals~3µm**	1.5%

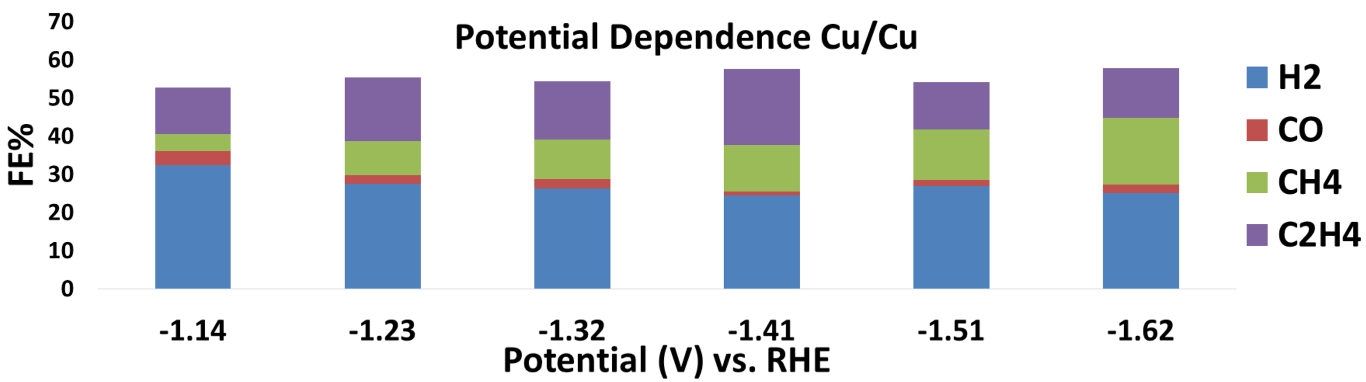
*Separation distance between Cu auxiliary and Cu catalyst

Evaluation of catalyst CO_2 Reduction performance – scaled up size



Catalyst deposition conditions:

-1V, 21.43 C/cm²



Differences between small and scaled-up electrodes likely due to increase in roughness factor from ~1.6 to ~3.1 with scale up

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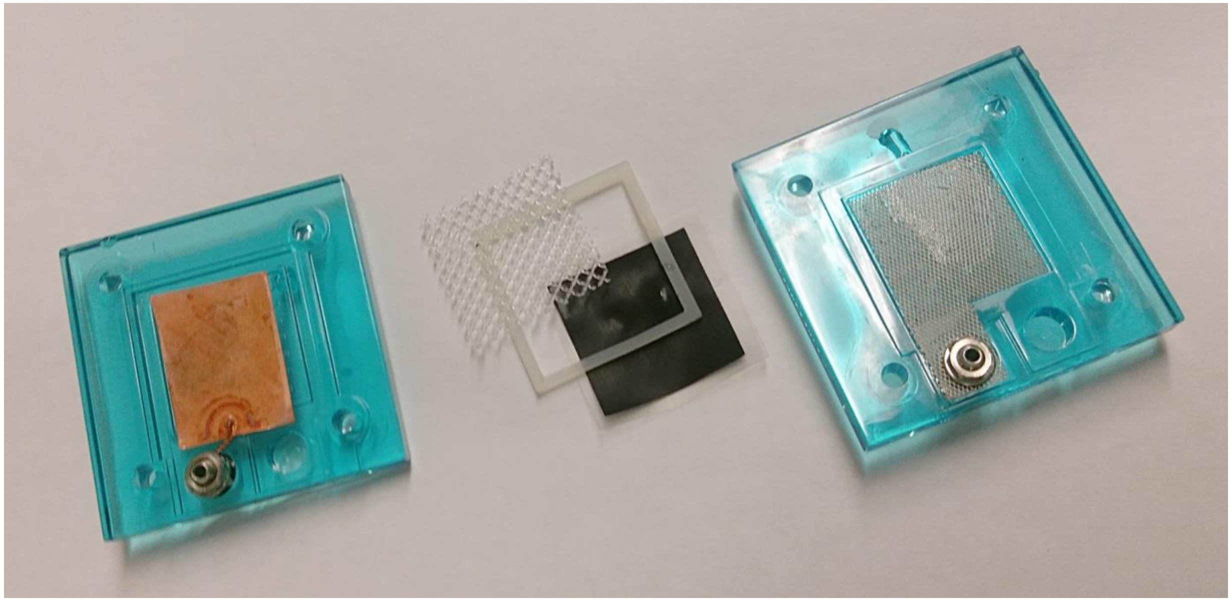
Progress of Task 2:

Conduction of Electrolyzer cells for CO_2 Conduction

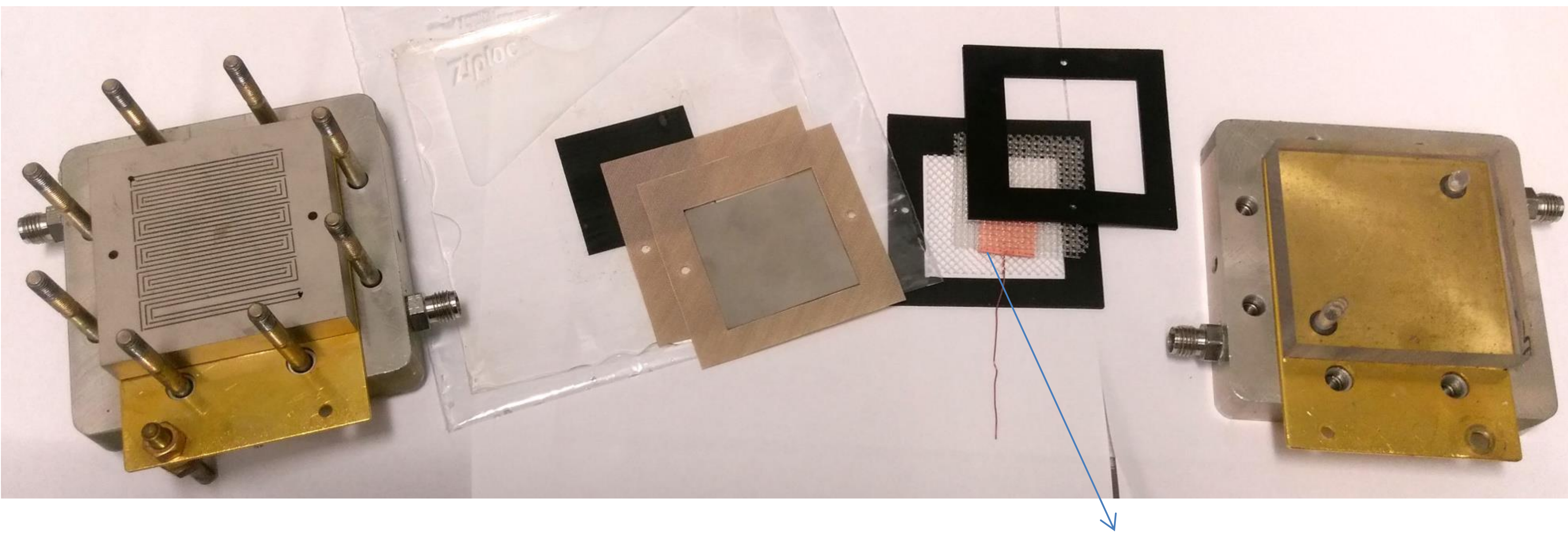
Horizon Mini Hardware



- Could not get a pressure tight seal

25cm^2 FCT Hardware

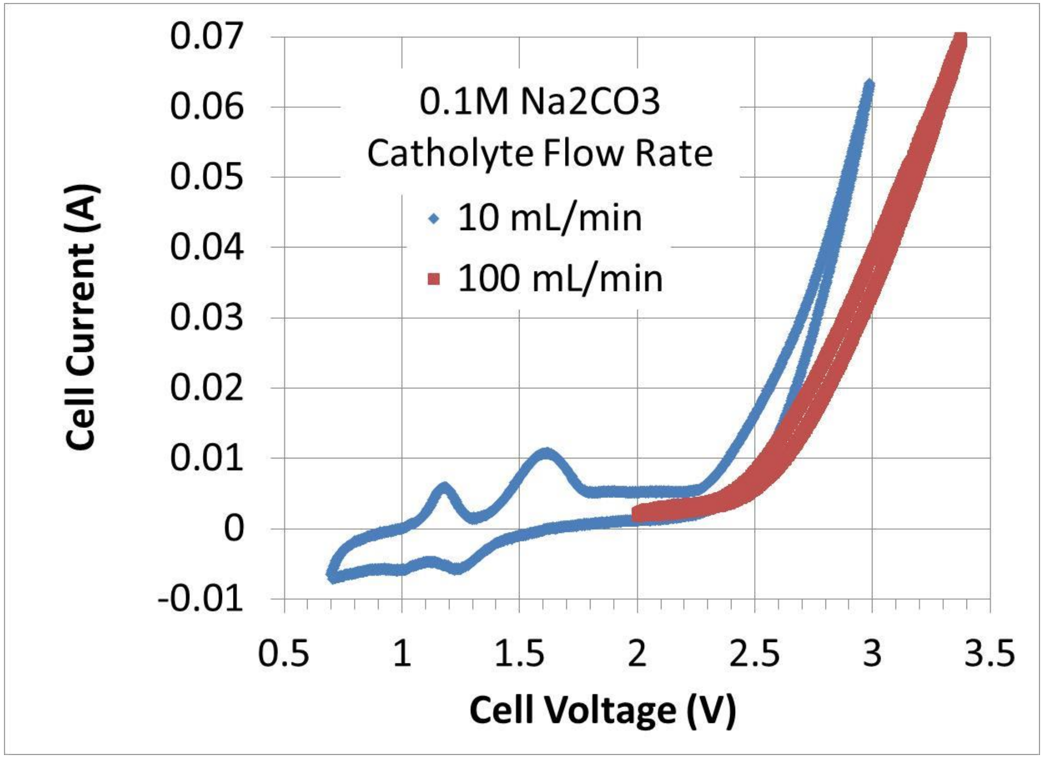
- Machined a plastic cathode block
- Used the foil's wire as the cathode lead, fed through rubber gaskets



CCNY 25cm2 Cathode Catalyst

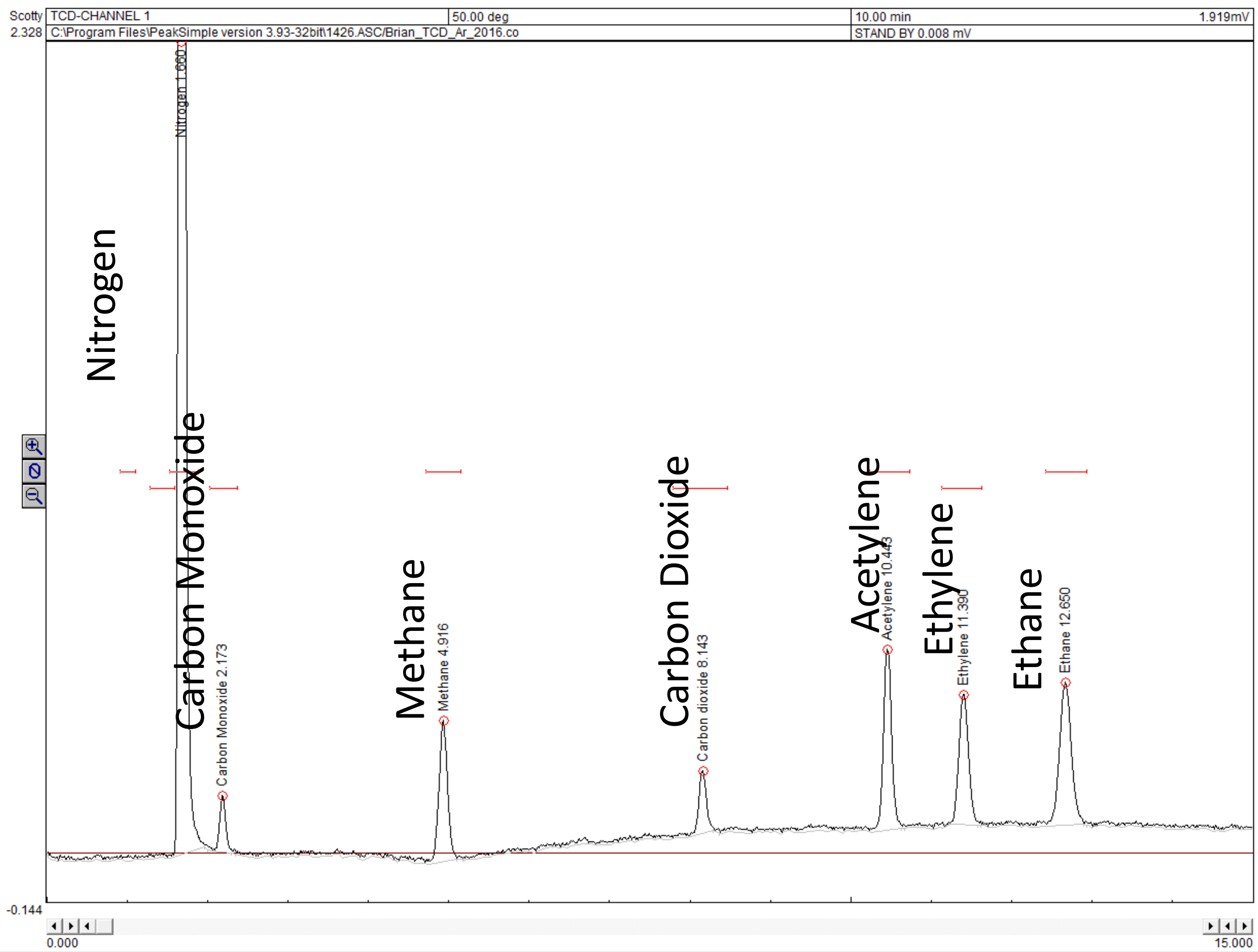
Initial CV Evaluation

- Hardware can tolerate high voltages without unexpected peaks
- Anode voltage is typically around 1.4V, so the cathode is reaching 1V before the reduction reaction begins
- Will switch catholytes to include gaseous CO_2 and retest



Proof that full cell can be constructed utilizing CCNY Cu electrodes.

GC Method Calibrated



GC is enabled to measurer all species involved

Summary

- Giner and CCNY collaborate on direct conversion of CO_2 to methane via electrochemical reduction
- CCNY successfully scale-up most effective Cu/Cu catalysts to 25 cm^2 and delivered to Giner
- Giner designed hardware and enabled GC, getting ready for electrolyzer cell test
- Project progress is well on the track of Task Schedule and Milestones

Project Management

- Bi-weekly meetings with CCNY to discuss project updated and direction
- Planned mutual site visits
- Midterm reports/presentation
- Communication with program manager

Acknowledgments

- Financial support from DOE SBIR Office

- DOE program manager Steve Mascaro

- Subcontractor
  - Dr. Elizabeth Biddinger at CCNY

- Giner Personnel
  - Brian Rasimick
  - Tom McCallum

Thank you!

Comments and Suggestions?!