Micro-Electrocatalytic Upgrading of Carbon Dioxide to Hydrocarbons

DOE Phase I SBIR
FY2016 Topic 18F Webinar

PI: Brian Skinn, Faraday Technology, Inc.

TPOC: José Figueroa

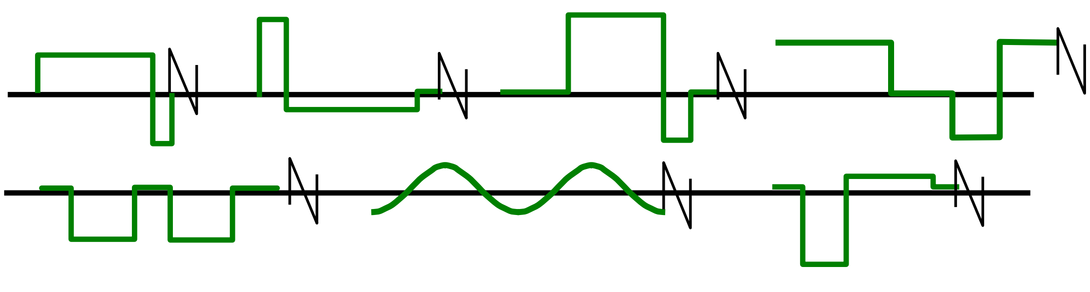
Contract No. DE-SC0015812

30 Aug 2016

Overview

- Faraday Company Introduction
- Program Overview
- Prior/Ongoing Work
- Program Description
- Activities to Date

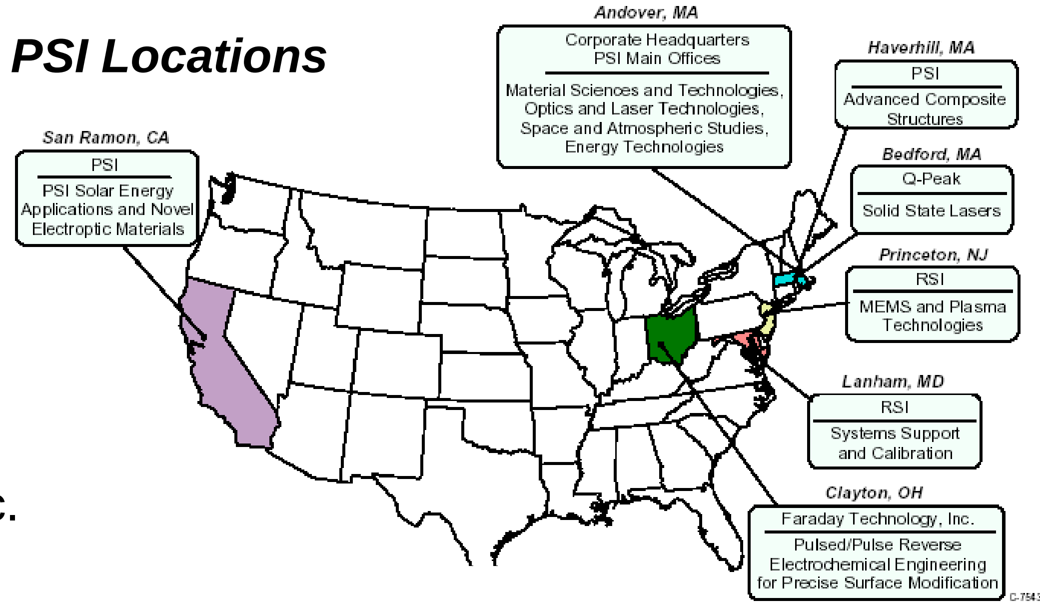
Introduction to Faraday Technology, Inc.

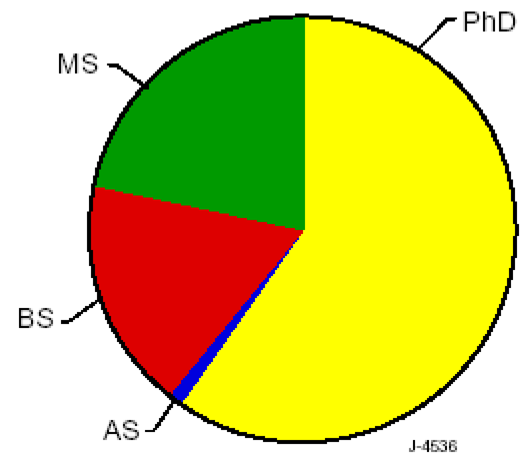


FARADAY TECHNOLOGY, INC.

- Electrochemical engineering processes and technologies – founded 1991
  - ~29 Issued Patents and ~15 Pending Patents in this area
  - www.FaradayTechnology.com
- Subsidiary of Physical Sciences, Inc. (Boston, MA) – acquired 2008
  - www.psicorp.com
- Collective employment ~140; ~90 MS/PhDs
- Annual revenue of ~ $40 million
- ~ 100 patents company-wide in numerous fields

PSI Locations





PSI Employees by Education

FARADAY TECHNOLOGY, INC.

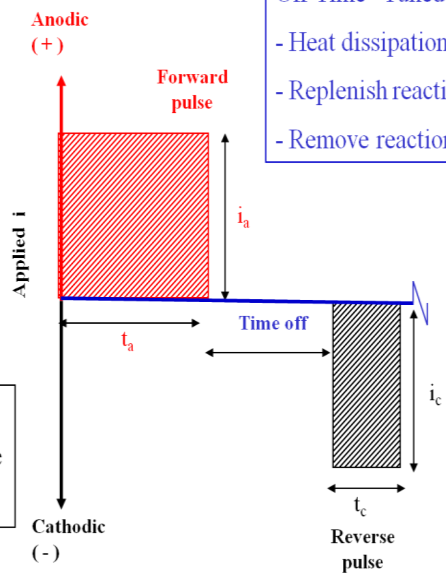
VISION - TECHNOLOGY PLATFORM

"…to be known as the company that changed the focus of electrochemical engineering from the art of complex chemistries to the science of pulse/pulse reverse electric fields…"

Electrochemical Machining, Polishing, Deburring, Through-Mask_Etching

Anodic Pulse "Tuned" to:
- Control current distribution
  - ➔ Eliminates need for viscous, low water content electrolytes

Off-Time "Tuned" to:
- Heat dissipation
- Replenish reacting species
- Remove reaction products



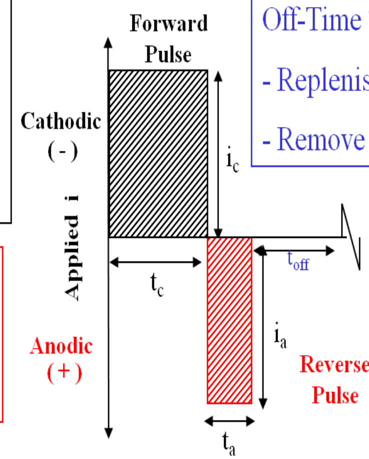
Cathodic Pulse "Tuned" to:
- Reduce oxide/depassivate surface
  - ➔ Eliminate need for HF

- 2008 Blum Scientific Achievement award for Pulse Reverse Surface Finishing
- 2016 R&D 100 Finalist for Nb ElectroPolishing

Electrodeposition/Plating

Cathodic Pulse "Tuned" to:
- Enhance mass transfer
- Control current distribution
- ➔ Simplify chemistry

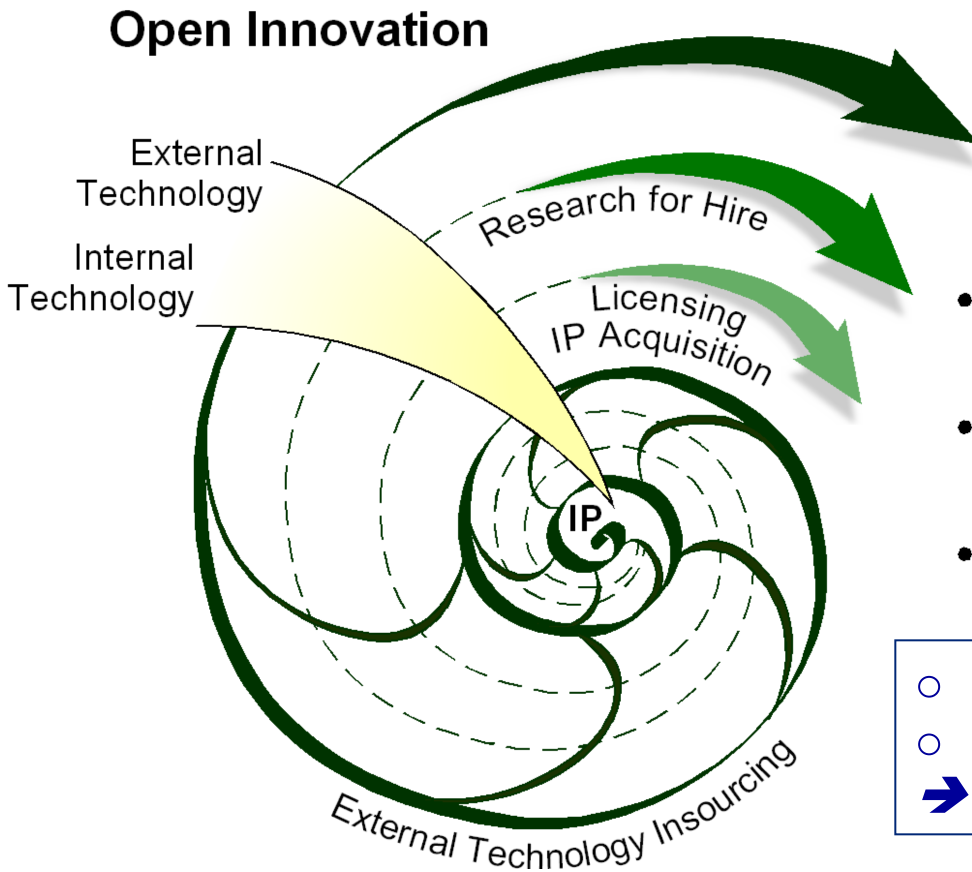
Anodic Pulse "Tuned" to:
- Remove H_2 effects
- ➔ Acidify interface



Off-Time "Tuned" to:
- Replenish reacting species
- Remove reaction products

- 2011 R&D 100 for Co-Mn Alloy Plating
- 2013 Presidential Green Chemistry Challenge award for Cr^{+3} Plating

OPEN INNOVATION



- Current Market
- New Market
- Competitor Markets

> ○ ***Licensed numerous patents***
> ○ ***Sold eight patents***
> ➔ ***Competitive Advantage***

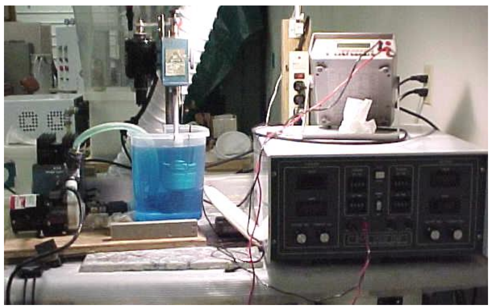
Investment Dollars — *Discovery* / *Research* → **Knowledge** — *Innovation* → **Market Dollars**

FARADAY'S TECHNOLOGY DEVELOPMENT

Technology development begins conceptually and is demonstrated at the bench-scale and developed through α/β-scale validation.

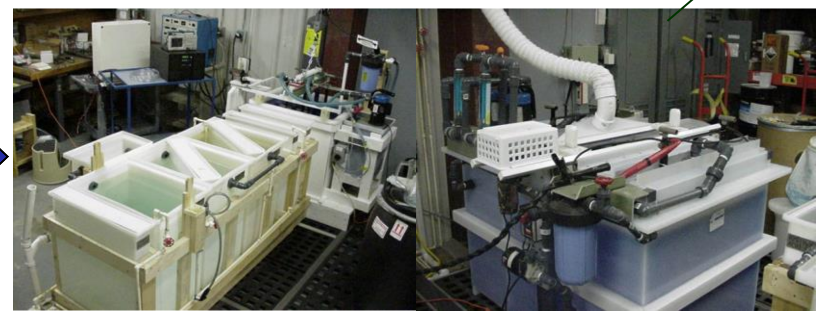
Technology/IP Alignment

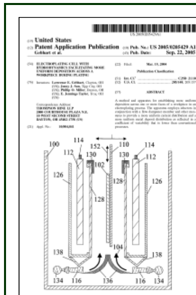
Pilot-Scale Validation



Bench-Top Feasibility

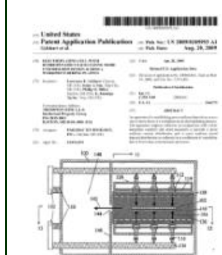
Cell → Design





IP: Issued 7,553,401 (6-30-09)

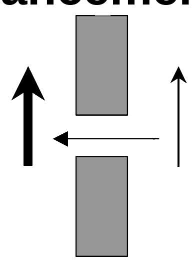
Production-Scale Validation

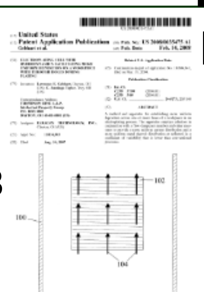


IP: Pending 12/431,030 (4-28-09)

Novel ← Flow

Further IP Enhancement





IP: CIP Pending 11/836,903 (8-10-07)

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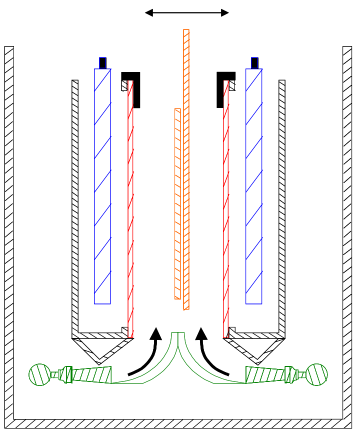
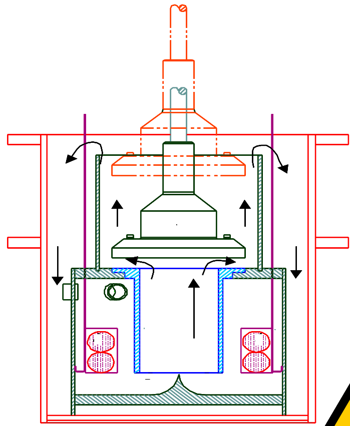
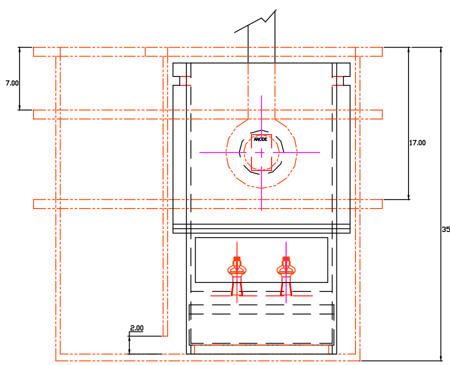
APPARATUS – PROCESS







Cell Geometry

Secondary and Tertiary Current Distribution:

Chemistry/Waveform Parameters, Temperature

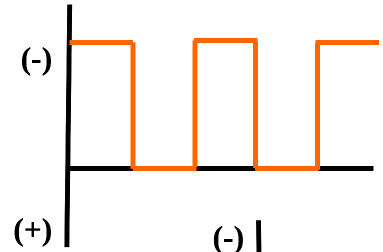
→ Throwing Power, Feature Size/Shape

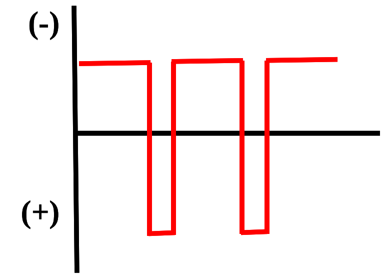
Primary Current Distribution:

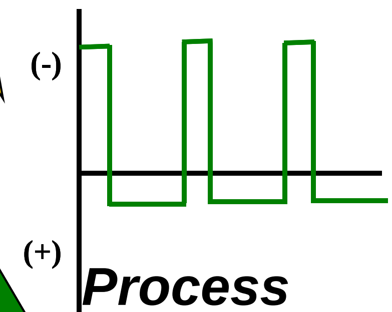
Agitation, Anode-Cathode Design and Spacing

→Panel Uniformity

→Must be Optimized Before Implementing Process



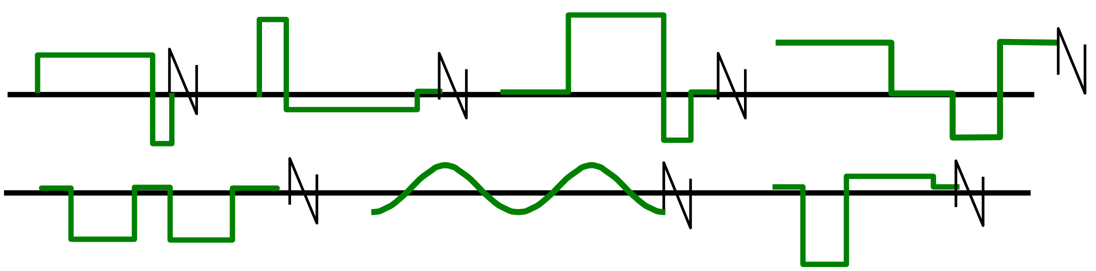




Process Parameters

Program Overview

Period of Performance: 13 Jun 2016 – 12 Mar 2017



Problem/Opportunity and Program Objective

- **Problem/Opportunity**
  - Conversion of carbon dioxide to high-value products using low-quality heat sources requires development of efficient conversion methods capable of high rates.

- **Objective**
  - The overall program goal is to establish the technical feasibility and scalability of FARADAYIC® techniques for electroreactor component and copper electrocatalyst fabrication, enabling efficient, high-rate conversion of carbon dioxide to hydrocarbons (e.g., ethylene)
    - Maximize product generation
    - Minimize H_2/CO/formate fractions
    - Minimize operating overpotential

Technical Approach

- Stackable-plate electroreactor for CO_2 → hydrocarbon (HC) conversion
- Novel activated-copper cathodic catalyst
- Commercial mixed-oxide anodic catalyst
- Exploit scalable, low-cost electrochemical fabrication methods
  - Electrodeposition & electrochemical through-mask etching

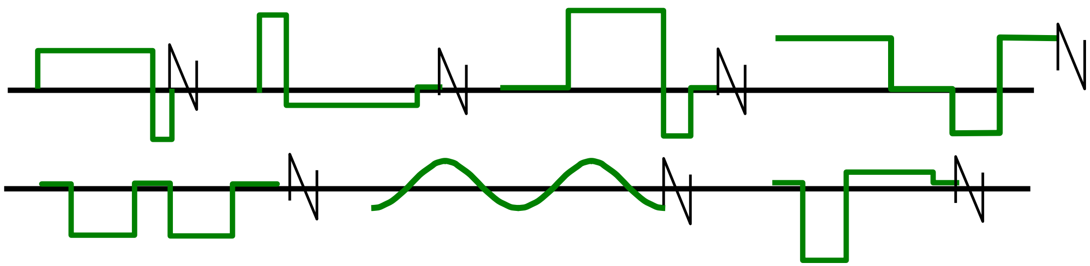
Project Team Members

- **Faraday**
  - Brian Skinn (PI)

- **DOE Personnel**
  - *TPOC*: José Figueroa
jose.figueroa@netl.doe.gov
412.386.4966
  - *Admin Contact*: Moriam Olowo
moriam.olowo@science.doe.gov
630.252.2121

- **Massachusetts Institute of Technology**
  - Fikile Brushett
    - Ph: 617.324.7400
    - Email: brushett@mit.edu

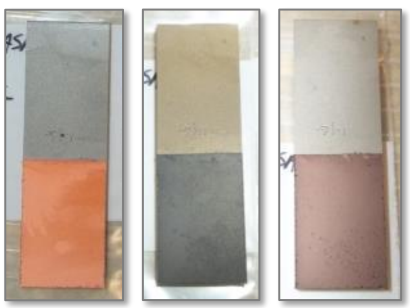
Prior/Ongoing Work

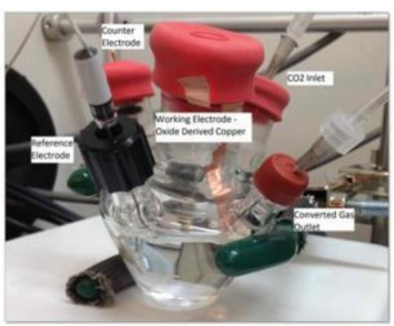


Prior Work: FARADAYIC® Copper ElectroCatalysis

- **FARADAYIC® Cu Deposition**
- **CO_2 Conversion to Hydrocarbons**
- **Microchannel Reactor Configuration**

Deposit Oxidize Reduce

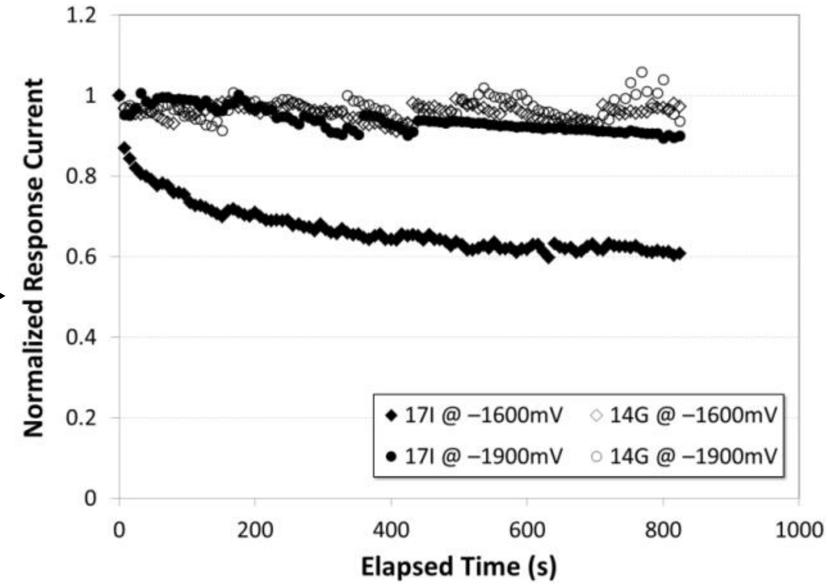


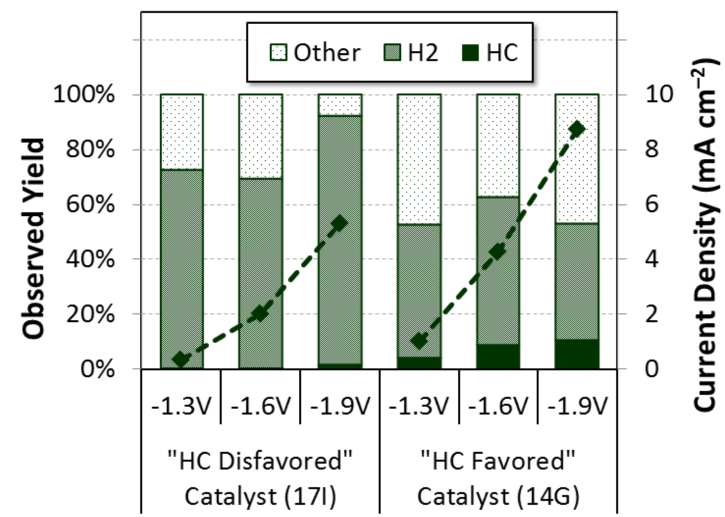


Chronoamperometry

&

GC Product Analysis





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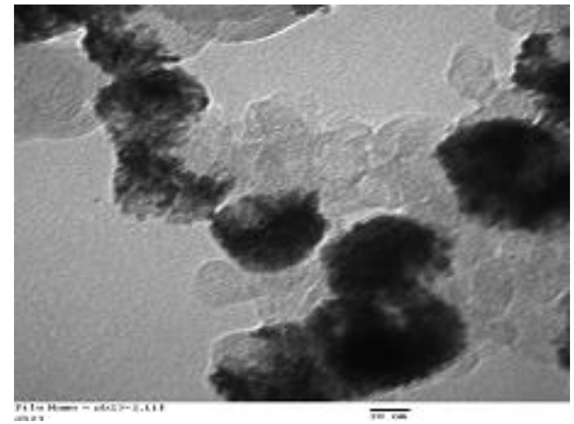
Prior Work: FARADAYIC® ElectroCatalyzation

- Low-loading deposition of Pt fuel cell catalyst
- Beta-scale batch system (NSF)
- Pilot-scale reel-to-reel system (OH)

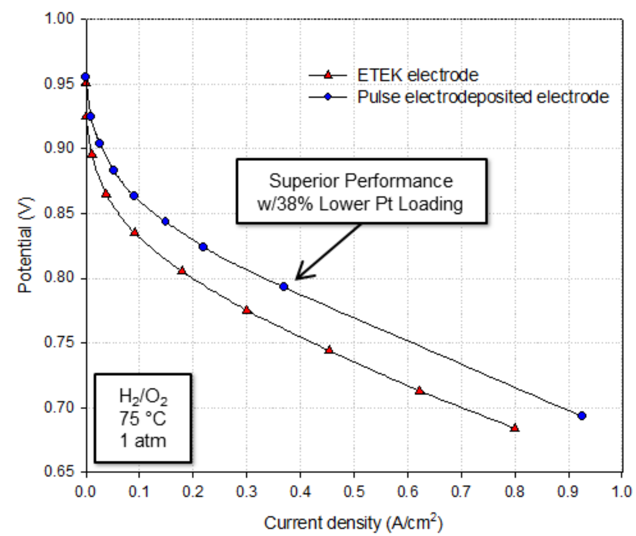
TEM of Pt on Carbon



Batch System **Continuous Reel-to-Reel**

U.S. Patent 6,080,504 Granted

Performance Comparison



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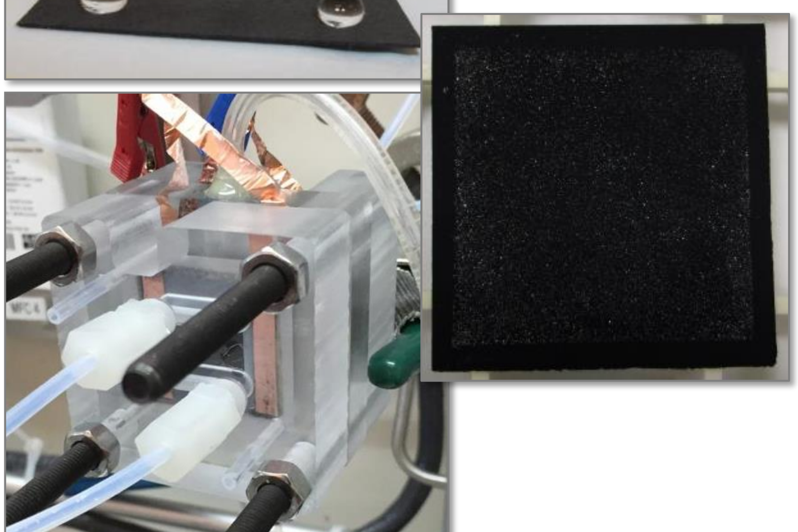
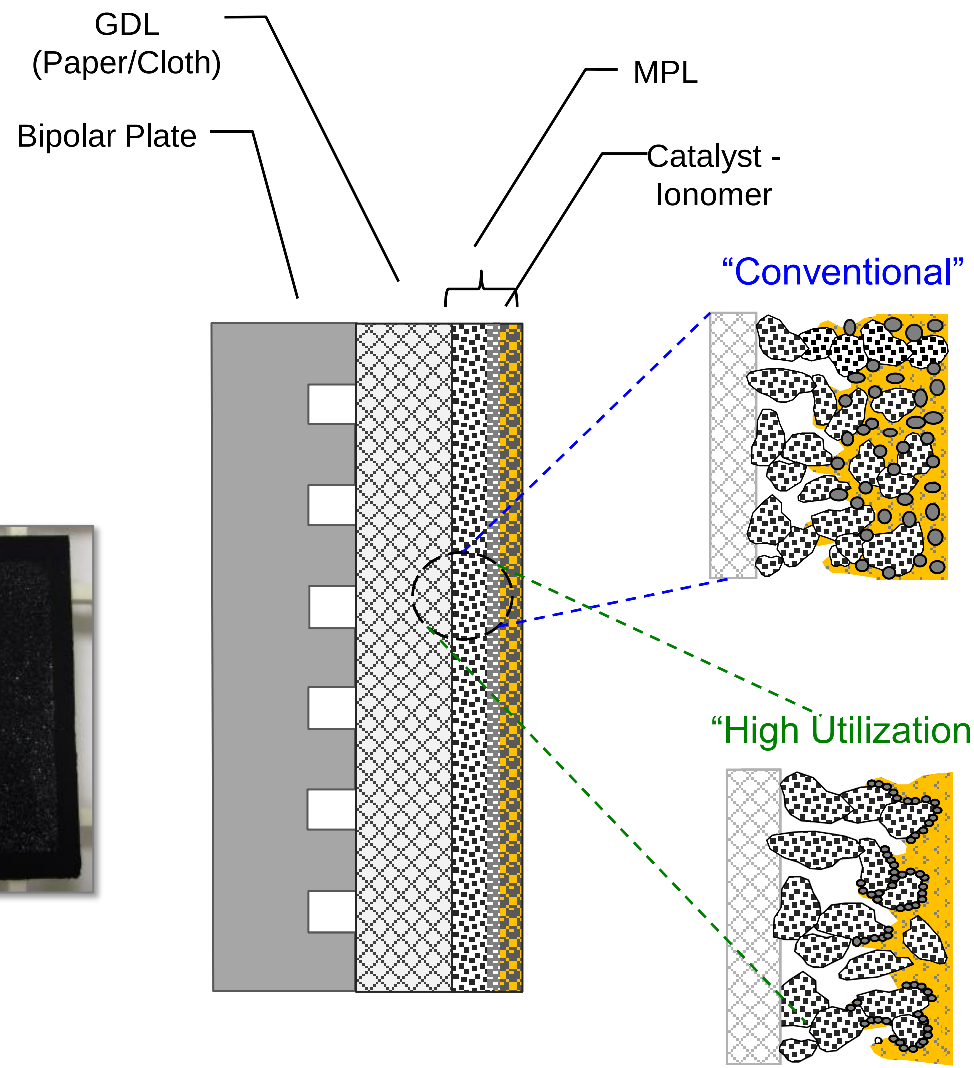
Ongoing Work: FARADAYIC® Tin Electrocatalysis

- **FARADAYIC® Sn Deposition**
- **CO_2 Conversion to Formate**
- **GDE-Based Electroreactor**





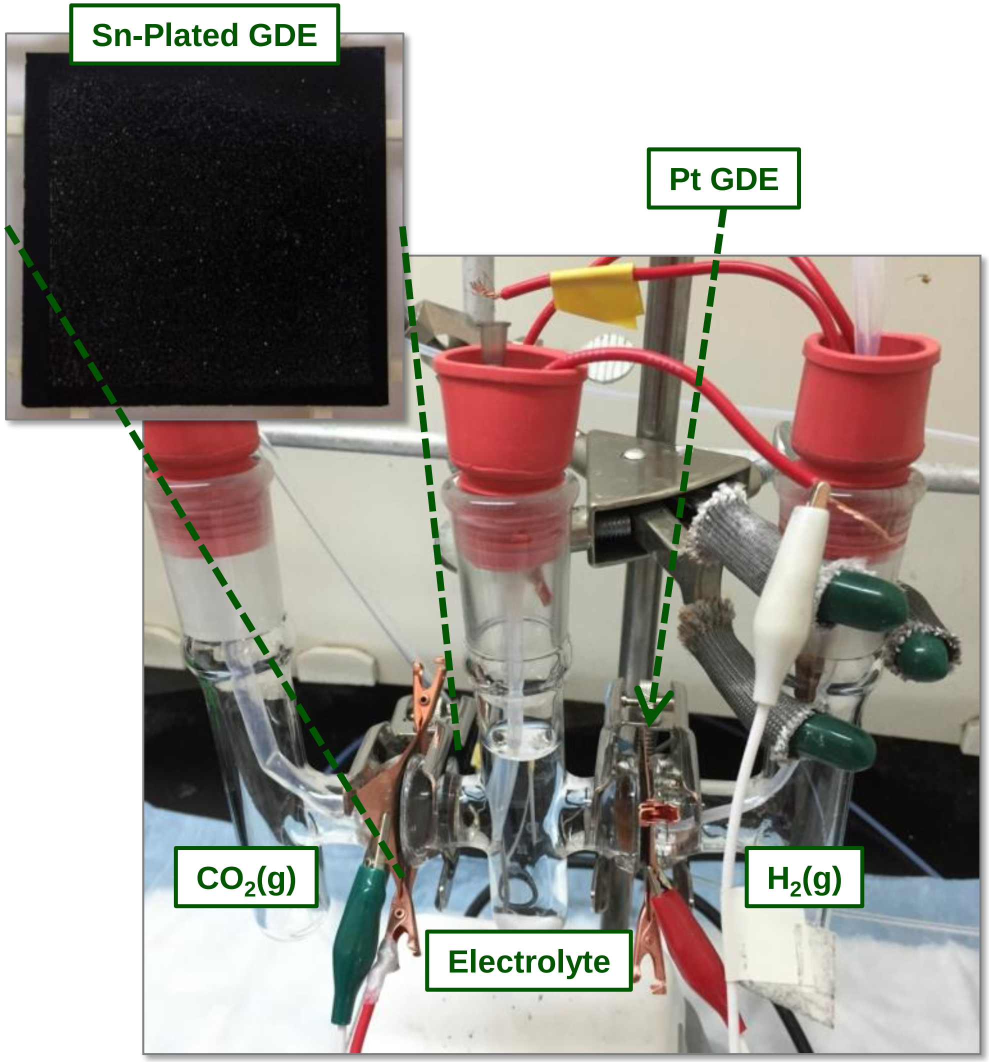
Ongoing Work: FARADAYIC® Tin Electrocatalysis

- Perform constant-potential electrolysis and measure:
  - Total response current
  - Formic acid production
    UV absorbance at 202 nm

- CO_2 flush gas behind GDE

- $Na_2CO_3 + Na_2SO_4$ electrolyte
  (pH ~ 10)

- H_2/Pt GDE counterelectrode used to reduce total cell potential

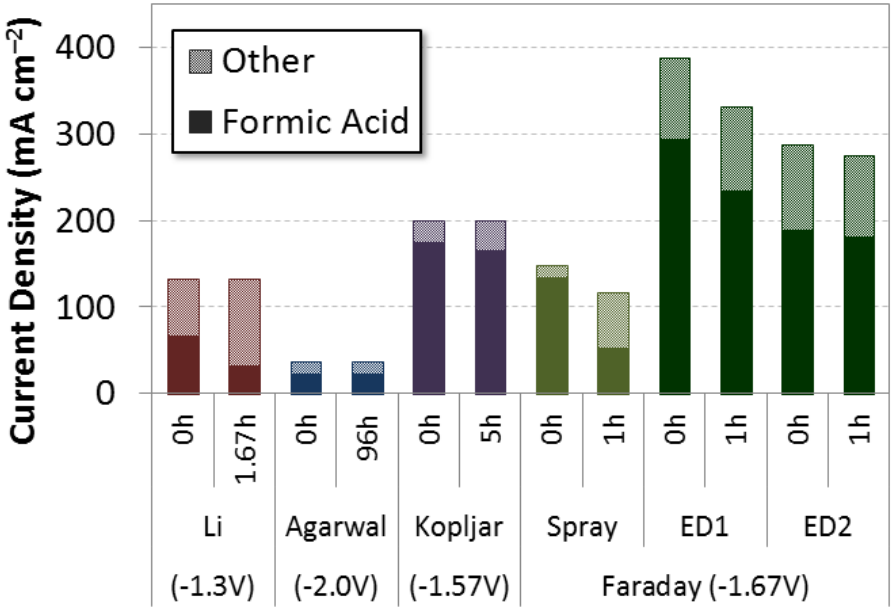


Ongoing Work: FARADAYIC® Tin Electrocatalysis

- Preliminary **FARADAYIC® ElectroDeposition (ED)** samples show significantly increased total and FA-efficient current densities relative to conventional **spray-coating method** and literature data
  - $j_{total} \geq 275$ mA cm^{-2}
  - %FA ≥ 70%

- Favorable short-term catalyst durability

- Significant potential for optimization
  - Ionomer loading
  - Sn electrocatalyst loading
  - Sn electrocatalyst ED parameters
  - GDE (GDL/MPL) parameters



(Half-cell potentials vs SHE)

Li and Oloman. *J Appl Electrochem* **35**: 955, 2005.

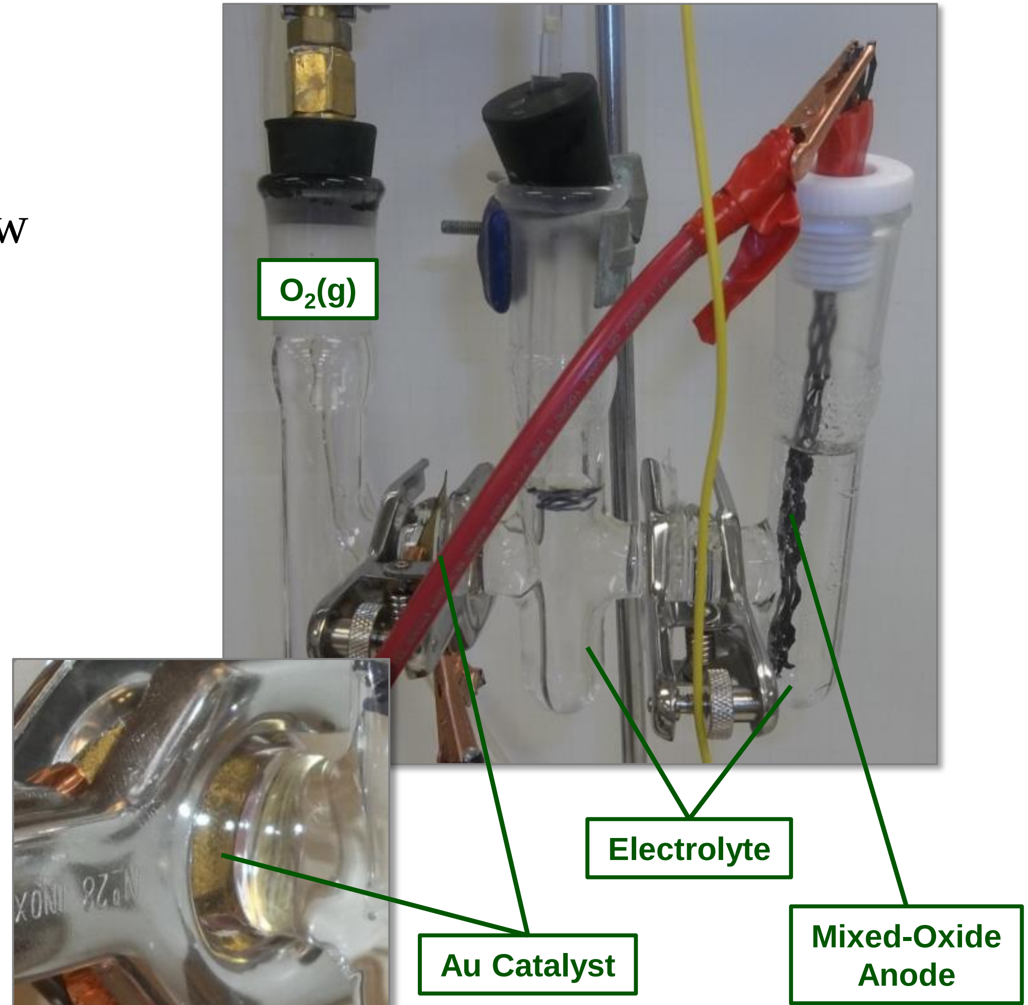
Agarwal et al. *ChemSusChem* **4**: 1301, 2011.

Kopljgar et al. *J Appl Electrochem* **44**: 1107, 2014.

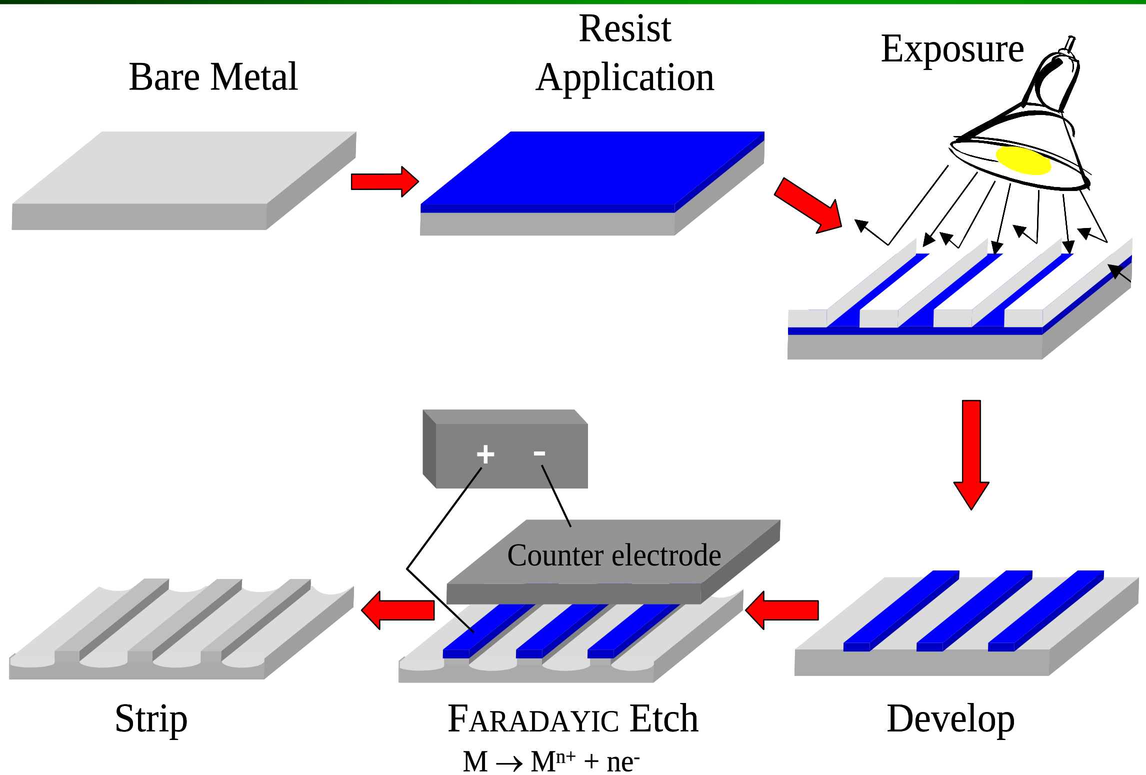
Ongoing Work: Electrochemical Peroxide Generation

- **Goal:** On-demand peroxide generation for disinfection of crew contact surfaces

- **Approach:**
  Au or C cathodic electrocatalyst
  Commercial mixed oxide anode

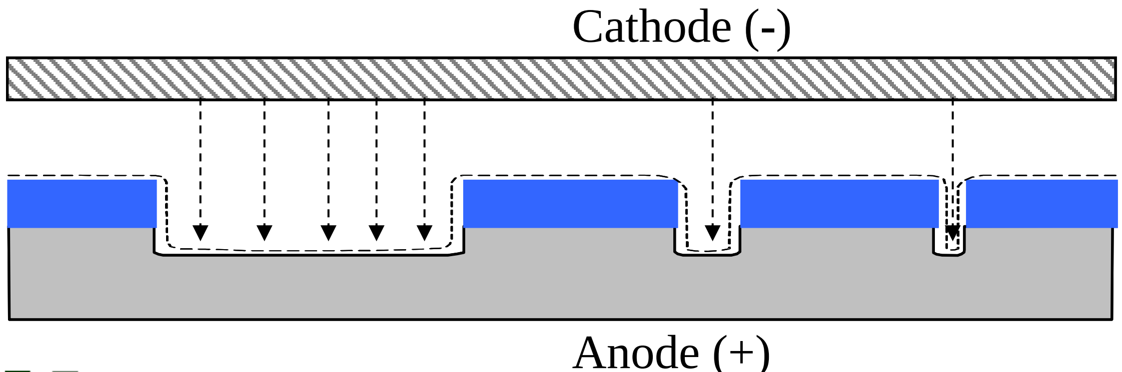


Prior Work: Through Mask ElectroEtching



ADVANTAGES

- **Same as chemical etching but also…**
- **Neutral salt or low concentration aqueous acid solutions for passive materials**
- **Superior surface finish**



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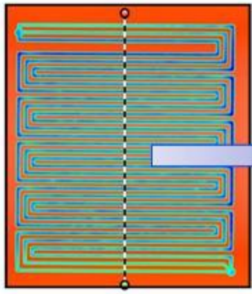
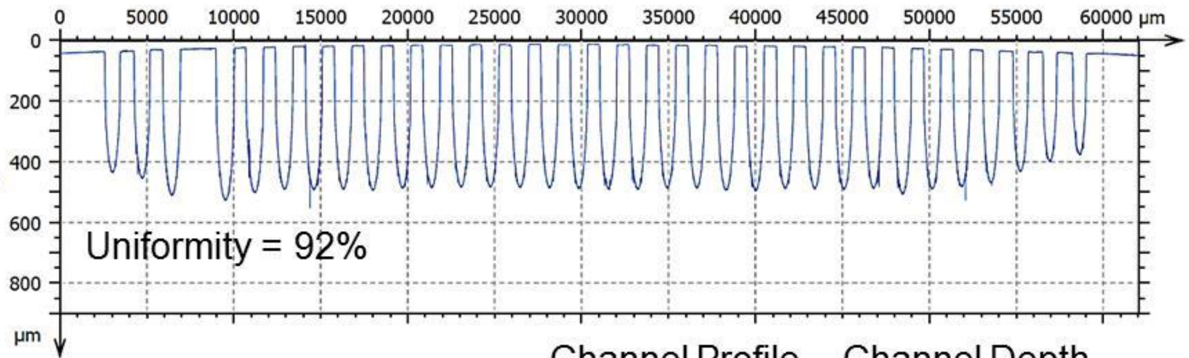
Prior Work: ElectroEtching Fuel Cell Bipolar Plates

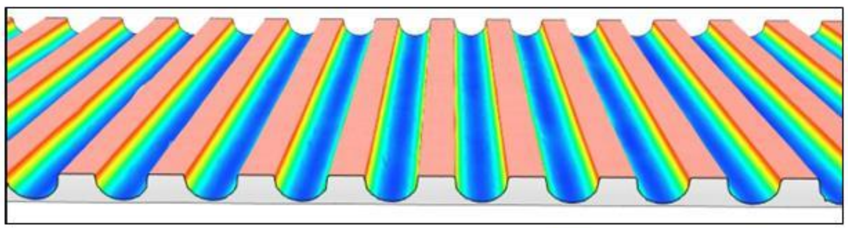
False Color Map



Extracted Channel Profile



3-D Image of Channels

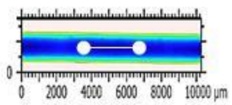


Channel Roughness

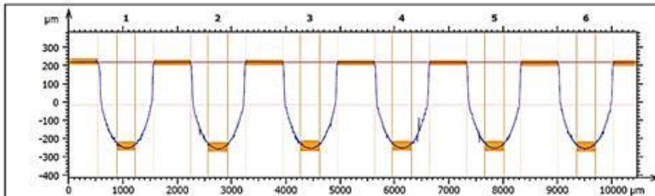
ISO 4287

Amplitude parameters - Roughness profile

Rp	0.508	µm
Rv	0.646	µm
Rz	1.154	µm
Ra	0.383	µm
Rq	0.422	µm

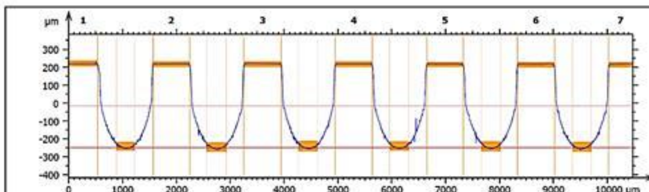


Channel Profile – Channel Depth



Parameters	Unit	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6
Width	µm	338.057	367.496	363.570	352.285	352.776	346.398
Maximum depth	µm	472.165	477.376	473.154	471.967	473.319	477.937
Mean depth	µm	462.455	465.274	462.020	461.324	462.156	464.561

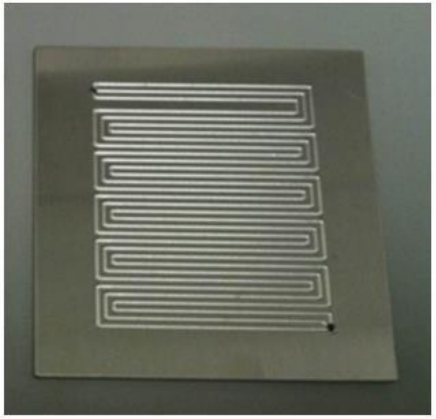
Channel Profile – Landing Width



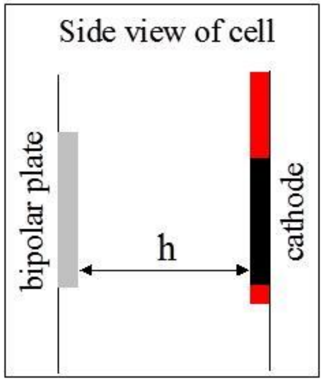
Parameters	Unit	Step 1	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7
Width	µm	535.788	683.964	689.852	687.398	684.945	683.964	437.168
Maximum height	µm	474.869	466.755	467.679	466.227	465.073	464.479	464.611
Mean height	µm	465.830	465.028	466.334	464.790	463.856	463.165	463.263

Prior Work: ElectroEtching Fuel Cell Bipolar Plates

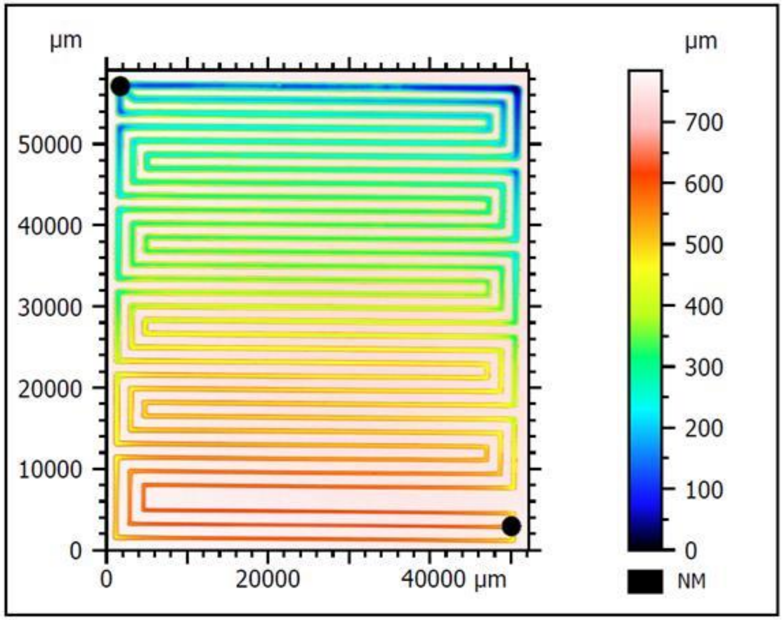
430 Stainless Steel
deep outlet/shallow inlet



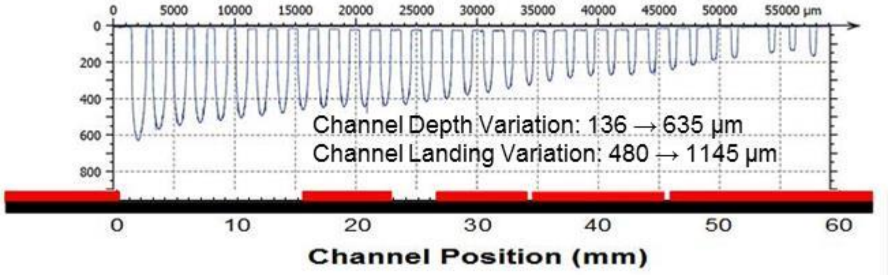
Counter electrode shielding
adjusted to control uniformity



False Color Map



Extracted Channel Profile deep outlet/shallow inlet



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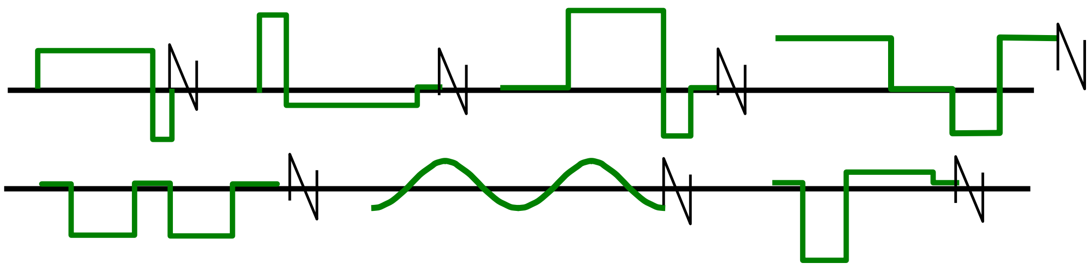
Program Description



Objective of Phase I

The Phase I objective is to demonstrate the potential for economical, scalable fabrication of stackable plate microchannel reactors exploiting activated copper electrocatalyst layers for CO_2 reduction to hydrocarbons.

The questions to be answered in the Phase I program are:

1. Can the potential for further ***enhancement in the hydrocarbon selectivity*** of activated copper electrocatalysts for CO_2 reduction be demonstrated?
2. Can a ***state-of-the-art wet ionic liquid electrolyte*** system be identified that shows potential to facilitate ***enhanced hydrocarbon selectivity*** in the CO_2 electroreduction system?
3. Can the potential be demonstrated for a microreactor stack system to ***provide CO_2 conversion performance and economical capability*** suitable for industrial-scale carbon emissions management?

Phase I Technical Approach

- For the Phase I program **Faraday** will:
  - Electrodeposit and thermally activate copper catalyst films
  - Revise/update thermal/electric/economic analysis (TEA)
  - Participate in ionic liquid evaluation/down-selection

- For the Phase I program **MIT** will:
  - Perform materials analysis of catalyst films
  - Perform electrocatalytic/electroanalytical tests on catalyst films
  - Participate in ionic liquid evaluation/down-selection

Program Tasks

- Kickoff Meetings
- Task 1: Copper Electrocatalyst Fabrication
- Task 2: Electrocatalysis Performance Evaluation
- Task 3: Electrocatalyst Materials Analysis
- Task 4: Ionic Liquid Selection/Evaluation
- Task 5: Techno-Economic Analysis
- Task 6: Reporting and Program Management

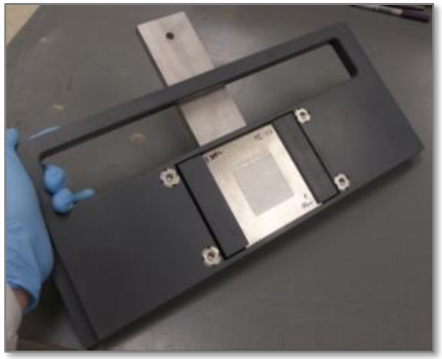
Task: Kickoff Meeting(s)

- **Faraday & DOE TPOC**
  - Engage TPOC
  - Identify DOE priorities
  - Held 3 Aug 2016
  - Poster presented at DOE NETL CCTP 2016 Meeting

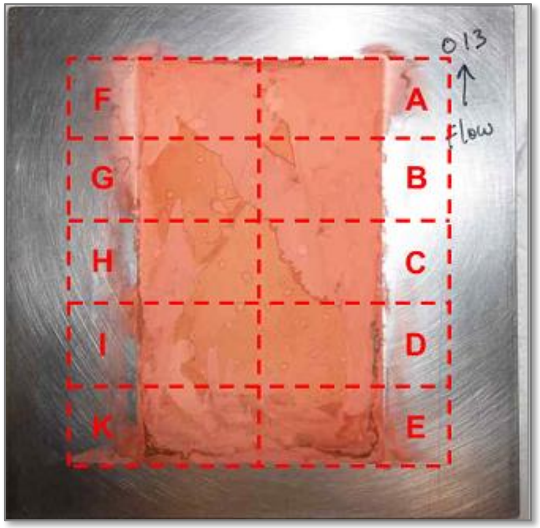
- **Faraday & MIT**
  - Review program goals
  - Identify / discuss milestones and completion targets
  - Synchronize work plans
  - Held 30 Jun 2016

Task 1: Copper Electrocatalyst Fabrication

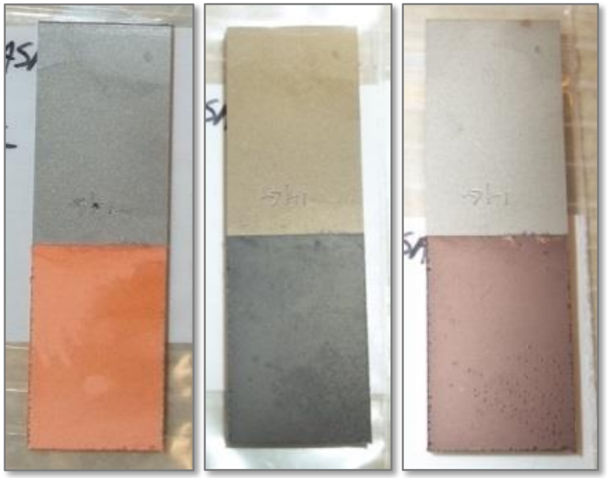
- Re-use NASA apparatus
- Plate on 4″ × 4″ SS304 panels
- Section panels into coupons
- Activate Cu by thermal oxidation & electrochemical reduction



Li and Kanan. *J Am Chem Soc* **134**: 7231, 2012



Deposit **Oxidize** **Reduce**



Task 1: Copper Electrocatalyst Fabrication

- FARADAYIC® ElectroDeposition Cell re-commissioned
- Three panels plated & sectioned into coupons
  - Identical waveform, different deposition durations (Cu film thicknesses)
- First set of coupons has been activated using best-performing protocol from NASA program
  - Twelve coupons (six as-plated, six activated) are in transit to MIT for testing

Deposit **Oxidize** **Reduce**

(1mm × 2mm plated area)

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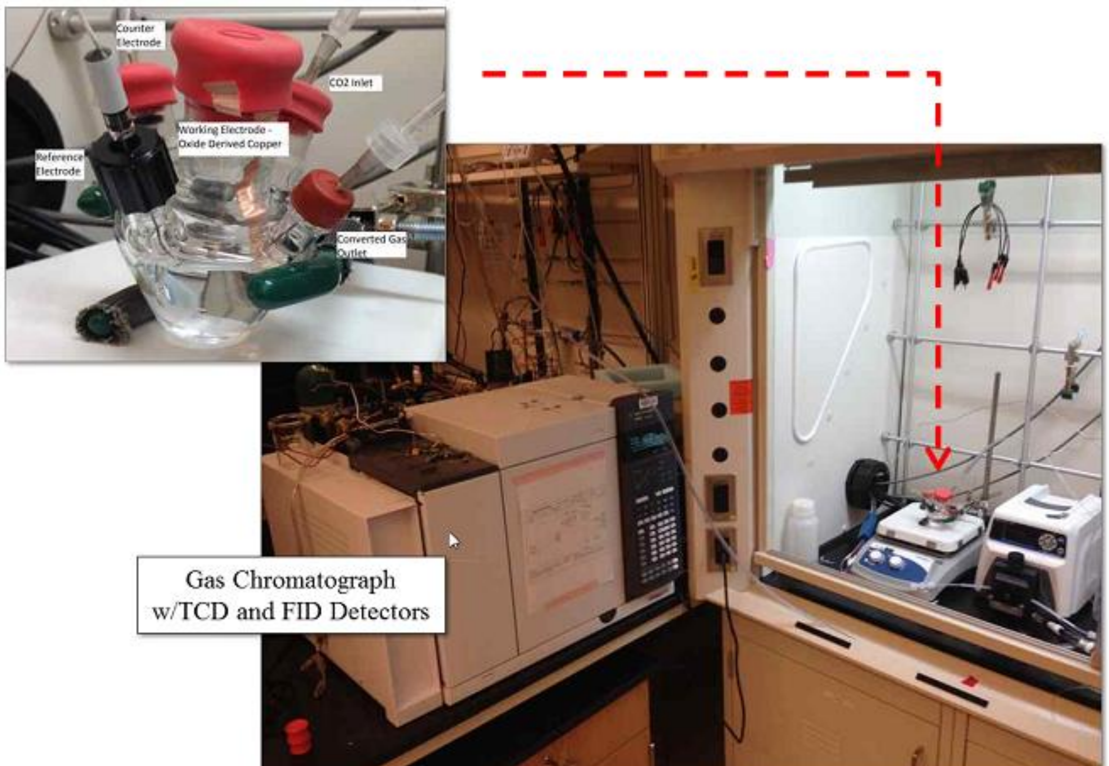
Task 2: Electrocatalysis Performance Evaluation

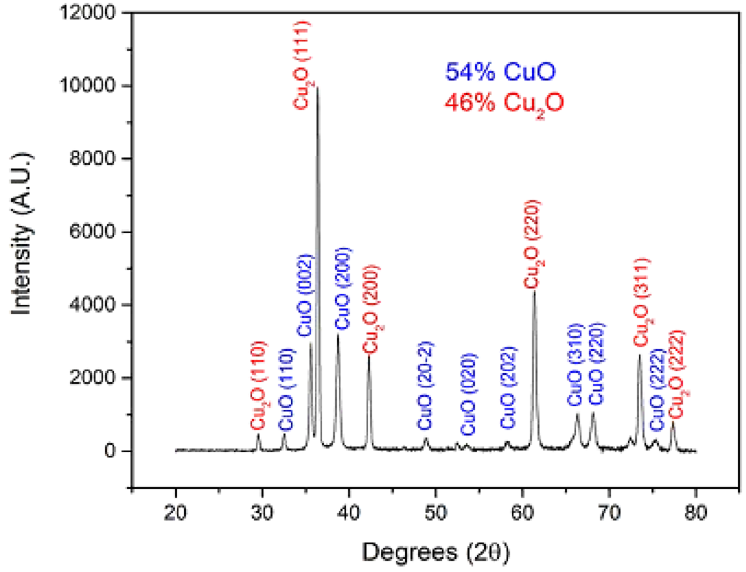
- Electroanalysis (CV, CA, etc.)
- GC assay of product gases
- UV/Vis analysis of formate (if formation suspected)



Task 3: Electrocatalyst Materials Analysis

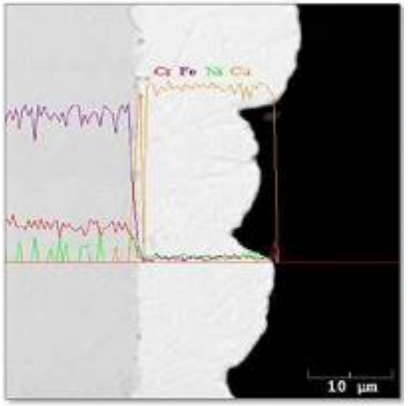
- XRD – Cu / Cu_2O / CuO content of films
- SEM/EDS – Morphology and composition

XRD

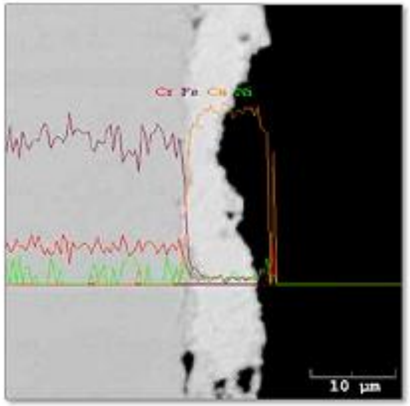


SEM/EDS

As-Plated



Oxidized



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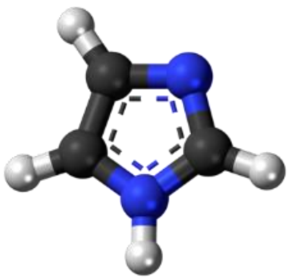
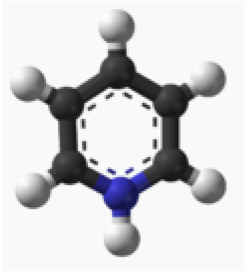
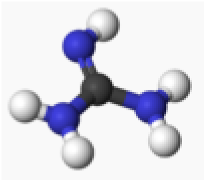
Task 4: Ionic Liquid Selection/Evaluation

- Imidazolium family selected for Phase I experimentation
- Key properties include:
  - *Physical*: Rheology, CO_2 solubility, HC solubility
  - (*Electro)chemical*: Stability, Potential window



- Preliminary research on other IL families
  - Pyridinium
  - Guanidinium
  - Others





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Task 5: Techno-Economic Analysis

- Spreadsheet model for power, material, etc. inputs
  - Estimate stack performance, footprint, etc

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QUALITY GUIDELINES

	A	B	C
1			
2	Assumed Overpotential Required:	0.5	V
3	Assumed Current Density	2	mA/cm^2 active area
4	Thermodynamic Potential Limit:	1.06	V
5	Electrons transferred per CO2 converted:	8	e/CO2
6	Coulombs to convert basis:	222.4559674	C/s
7	Power Required	347.0313091	W
8	Energy Consumed	347.0313091	J/s
9	Energy Consumed	29983.5051	kJ/day
10	Energy Consumed	8.328751418	kWh/day
11	Solar Panel Area Needed	17.35156545	m^2
12	Active Area of Catalyst	11.12279837	m^2
13	Est'd active channel wall part-perimeter	3.2	mm
14	Total channel arc length required	3475.87449	m

- Spreadsheet CapEx / OpEx model

Production Scales	EA/pCP	LRIP	MRCP
		OpEx	
		Part Geometry & Preparation	
Plates per Panel Row	3	4	4
Rows of Plates Per Panel	3	5	5
Panel Size	15"x15"	18"x24"	18"x24"
Stock Material Size	18"x18"	24"x24"	24"x24"
Metal cost per stock sheet	$38.97	$121.40	$121.40
Panels per sheet	1	1	1
Pre-Etch cuts per panel	2	1	1
Post-Etch cuts per panel	16	29	29

OpEx Outputs

Per-Plate Materials	[illegible]
Per-Plate Active Labor	[illegible]
Per-Plate Idle Labor	[illegible]
Per-Plate Shipping	[illegible]
Per-Plate Electricity	[illegible]
Per-Plate Total	[illegible]

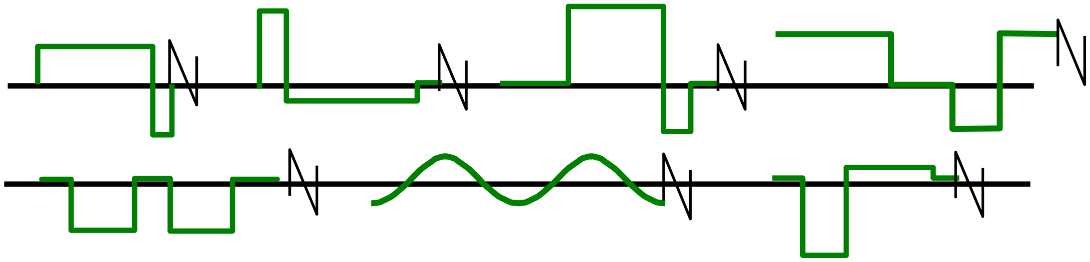
CapEx Outputs

Rectification	[illegible]
Tank(s) / Fixturing	[illegible]

Task 6: Reporting and Program Management

- Centered on the management of the project to ensure milestones and reporting requirements are met
- Contractual reporting requirements
  - Final report due 26 Mar 2017 (~2 weeks after program end)
- Faraday will convene periodic internal review meetings to assess program progress toward milestones/objectives
- Faraday will continue telephone/WebEx briefings with MIT partner and/or DOE program/technical staff

Questions/Comments



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