

Electrochemical Reduction of CO₂ to Formic Acid Using Gas Diffusion Electrode Technology



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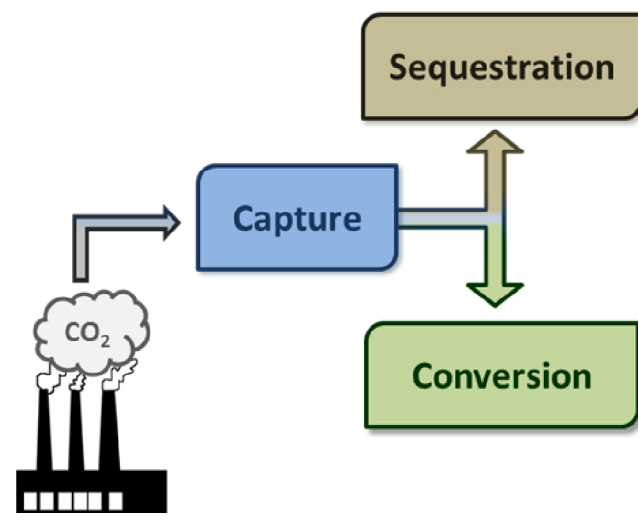
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Problem

- New technologies are needed to provide solutions for conversion of captured CO₂ as part of a multifaceted approach for mitigation and maintenance of greenhouse gas production.



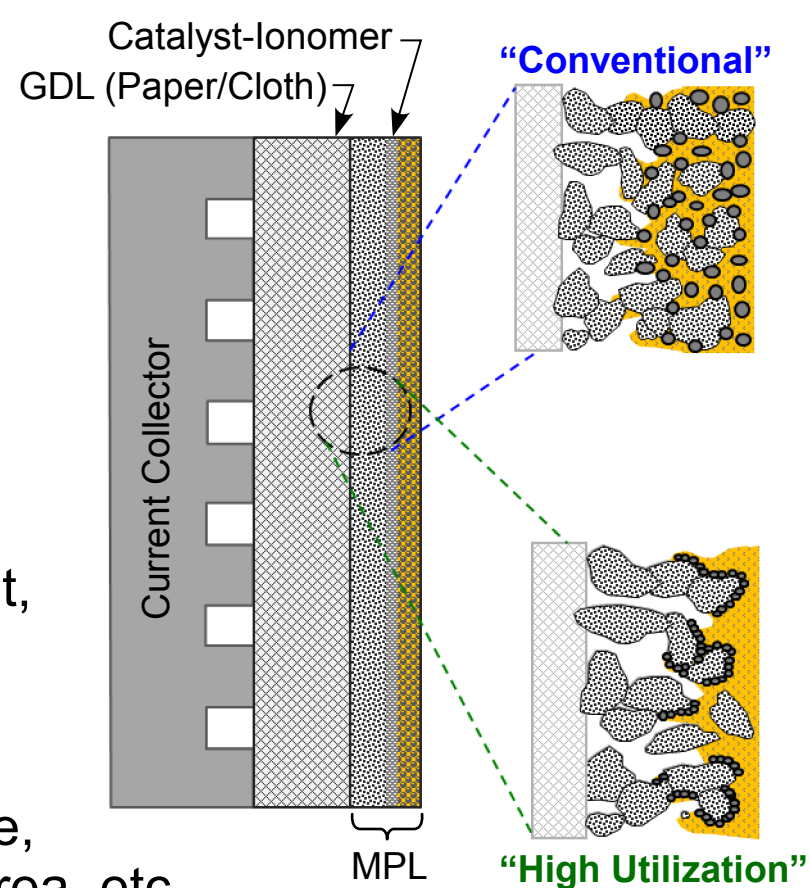
Technical Approach

- Gas diffusion electrode (GDE) based electroreactor for CO₂ conversion to formic acid (FA)
- Tin cathodic catalyst deposited by FARADAYIC[®] ElectroDeposition (ED)
- Commercial mixed-oxide anodic catalyst
- Exploit scalable, low-cost ED fabrication methods and MIT expertise in electrochemical analysis and reactor fabrication

High-Utilization Tin Catalyst via FARADAYIC[®] ElectroDeposition

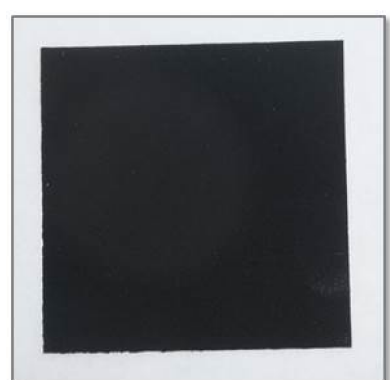
- Conventional methods use catalyst dispersed in ionomer suspension
 - Significant fraction of catalyst isolated from electrical contact and/or far from gas phase

- FARADAYIC[®] ElectroDeposition intrinsically produces electrically active catalyst = "High Utilization"
 - Smaller mass of applied catalyst, but with significantly enhanced per-mass catalytic efficiency
 - Waveform tuning also enables control over catalyst particle size, microstructure, active surface area, etc.



Catalyzed GDE Preparation

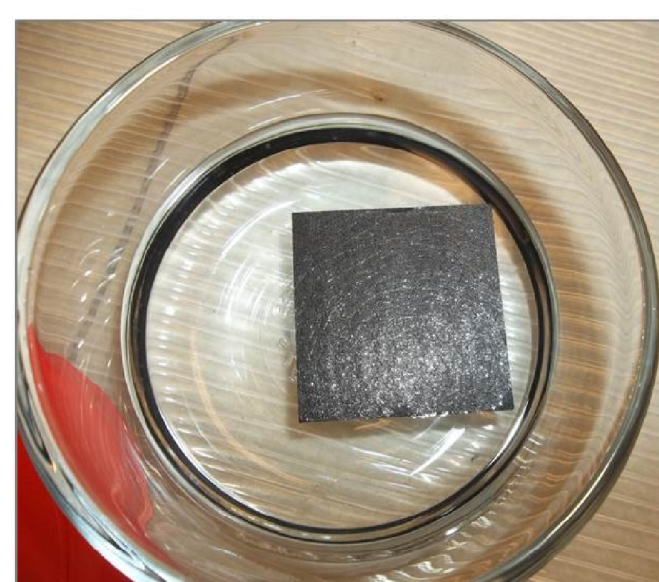
- Ionomer Application
 - Sigracet 39BC gas diffusion layer (GDL) with applied microporous layer (MPL)
 - Float 40mm x 40mm GDL square MPL-side down on ionomer dispersion in isopropanol



Front Side (MPL)

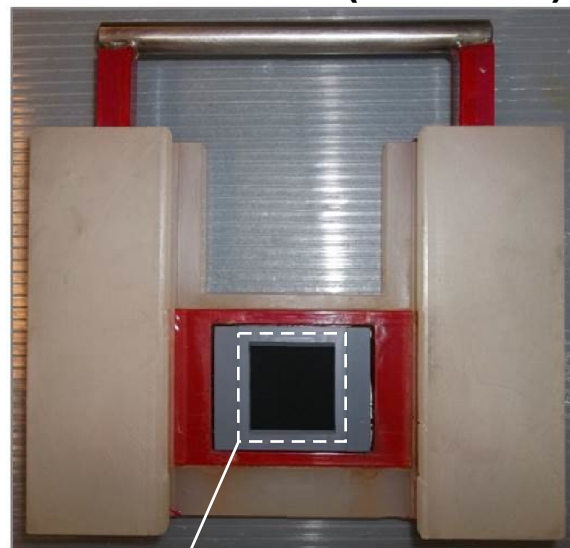


Reverse Side (Bare GDL)



- Sn ElectroDeposition – FARADAYIC[®] ElectroCell

Part & Holder (Cathode)



Ionomer-Treated GDL

Sn Sheet (Anode)



FARADAYIC[®] ElectroDeposition Cell

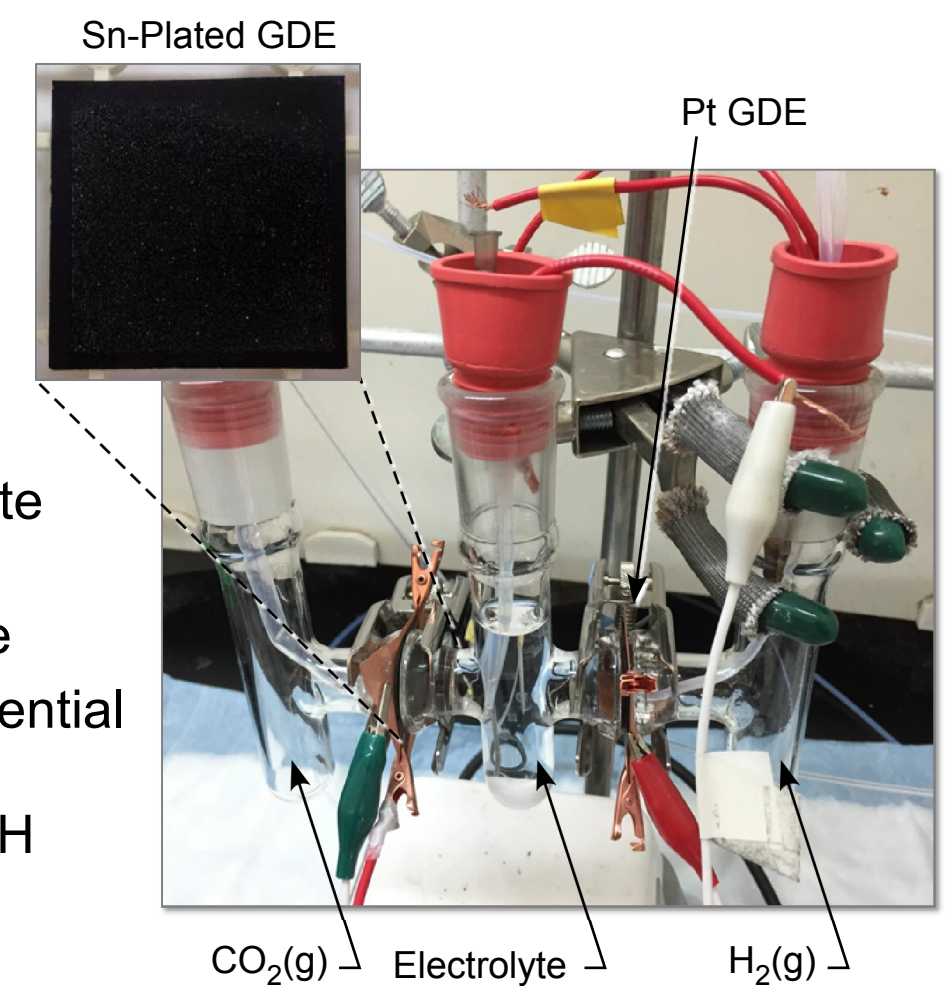


Tin Methanesulfonate Plating Electrolyte

Electrochemical Testing

- Perform electrolysis at constant half-cell potential and measure:
 - Total response current
 - Formic acid production
 - UV absorbance at 202 nm
- Apparatus Configuration
 - CO₂ flush gas behind GDE
 - Na₂CO₃ + Na₂SO₄ electrolyte (pH ~ 10)
 - H₂/Pt GDE counterelectrode used to reduce total cell potential
- Desired reaction:

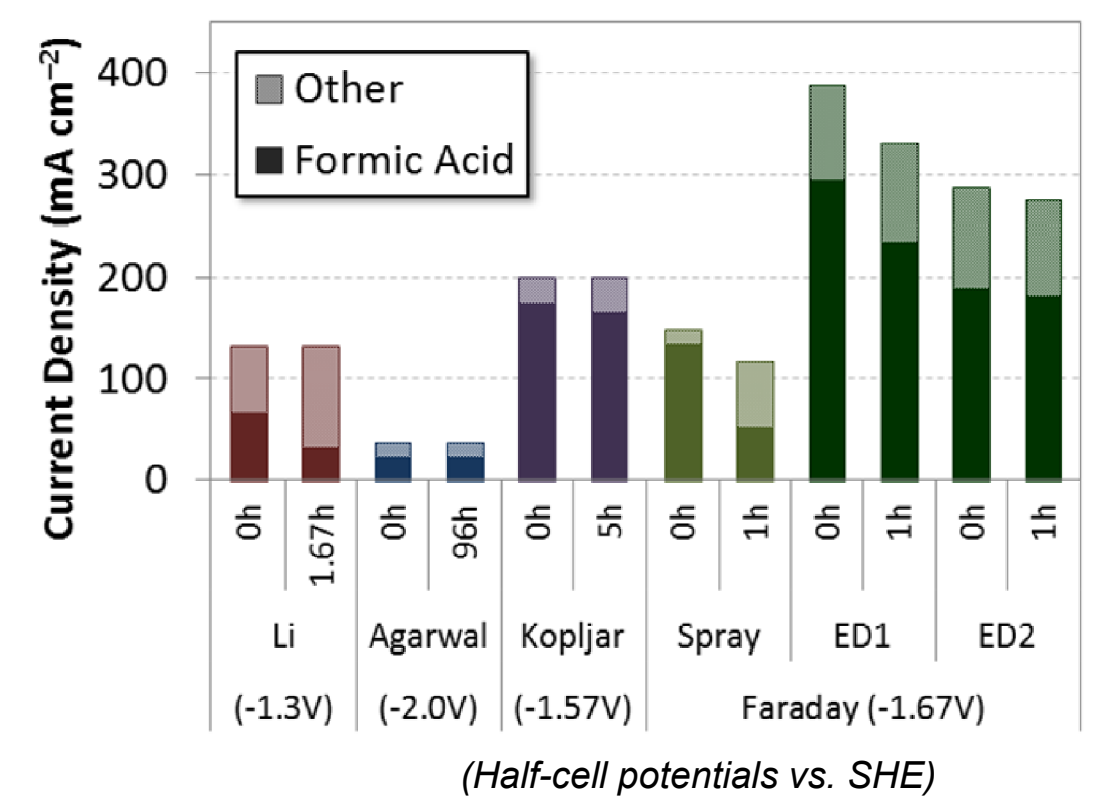
$$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$$



Preliminary Results

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

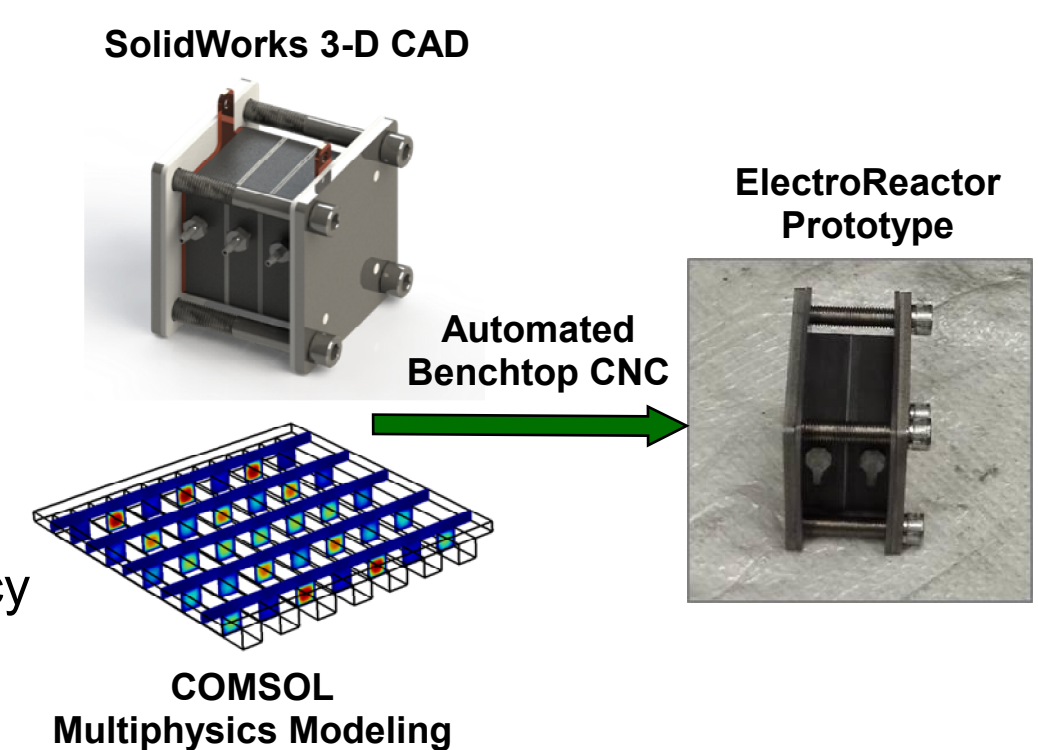
- Favorable short-term catalyst durability
- Ongoing optimization
 - Ionomer loading
 - Sn electrocatalyst loading
 - Sn electrocatalyst ED parameters
 - GDE (GDL/MPL) parameters



Li and Oloman. J Appl Electrochem 35: 955, 2005
 Agarwal et al. ChemSusChem 4: 1301, 2011
 Kopljar et al. J Appl Electrochem 44: 1107, 2014

Alpha-Scale Electroreactor

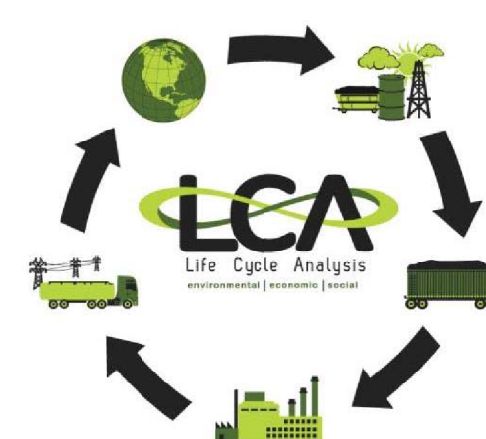
- Electroreactor design previously developed by MIT for CO₂ → CO conversion studies
- COMSOL modeling facilitates rapid design optimization to:
 - Increase energy efficiency
 - Minimize pressure drop
 - Maximize conversion



Economic / Scale-Up Analysis

Life Cycle Analysis

- Standard methodologies
 - EPA, DOE/NETL, etc.



Scale-Up Analysis

- Technology evaluation
- Market-entry / pre-commercial analysis

