

Electrochemical Reduction of CO₂ to Hydrocarbons in Microchannel Reactors with Ionic Liquids



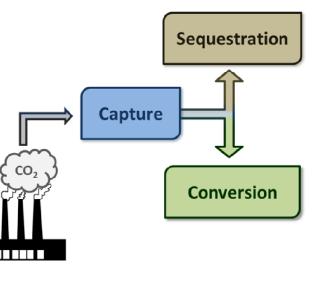
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Problem

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

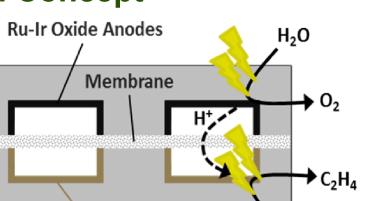


Technical Approach

- Stackable-plate electroreactor for CO₂ -> hydrocarbon (HC) conversion
- Novel activated-copper cathodic catalyst
- Commercial mixed-oxide anodic catalyst
- Exploit scalable, low-cost electrodeposition fabrication methods
- Power via Peltier-effect devices to exploit low-quality energy sources

Electroreactor Design Concept

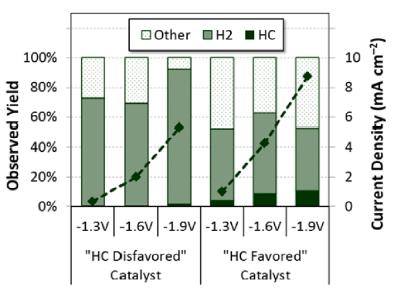
- FARADAYIC[®] Through-Mask Etching of reactor flow channels
- Cu cathodic catalyst
 - FARADAYIC[®] ElectroDeposition of copper
 - Optimized literature activation



CO₂

Prior Results

- Constant-potential electrolysis in CO₂-saturated 0.5 M aqueous NaHCO₃
- Catalyst preparation influences selectivity and total current density
- Hydrogen evolution still appreciable

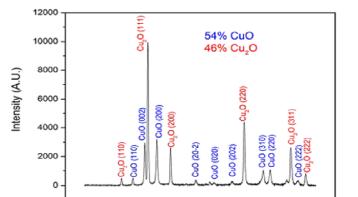


(All potentials vs. Ag/AgCl reference)

Electrocatalyst Materials Analysis

• XRD – Cu / Cu₂O / CuO content of films

XRD



- method
- Mixed metal oxide anodic catalyst
 - Standard application method: painting and thermal consolidation
 - Low overpotential for water oxidation
- Ion exchange membrane separator
- Wet ionic liquid electrolyte for enhanced CO₂ solubility and expanded electrochemical window

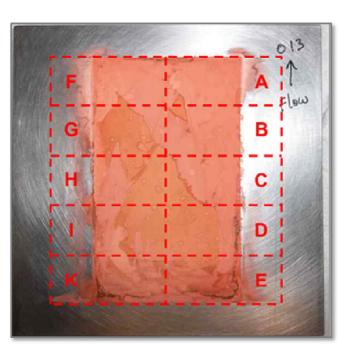


Activated Cu Cathodes

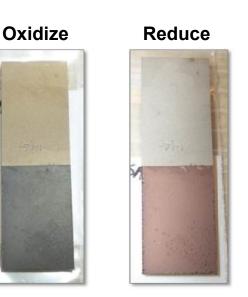
Copper Electrocatalyst Fabrication

- Deposit Cu on 4"× 4" SS304 panels
 - FARADAYIC[®] ElectroDeposition Cell
- Section panels into coupons
- Activate Cu by thermal oxidation and electrochemical reduction

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







Electrocatalysis Performance Evaluation

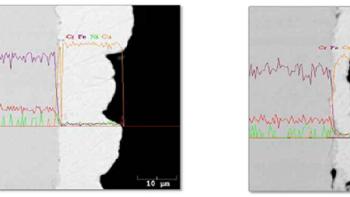


- SEM/EDS Morphology and composition



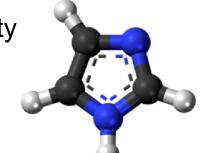




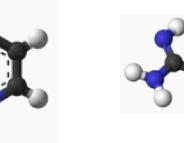


Ionic Liquid Selection/Evaluation

- Imidazolium family selected for Phase I experimentation
- Key properties include:
 - Physical: Rheology, CO₂ solubility, HC solubility
 - (Electro)chemical: Stability, Potential window



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



Thermal/Electrical/Economic Analysis

• Develop spreadsheet model for power, material, etc. inputs - Estimate stack performance, footprint, etc.

| | A | В | С |
|----|--|---------------------------|-------------------|
| | | | |
| 2 | Assumed Overpotential Required: | 0.5 | |
| 3 | Assumed Current Density | 2mA | /cm^2 active area |
| 4 | Thermodynamic Potential Limit: | 1.06 | |
| 5 | Electrons transferred per CO2 converted: | 8e/C | :02 |
| 6 | Coulombs to convert basis: | 222.4559674C/s | |
| 7 | Power Required | 347.0313091W | |
| 8 | Energy Consumed | 347.0313091J/s | |
| 9 | Energy Consumed | 29983.5051kJ/ | day |
| 10 | Energy Consumed | 8.328751418kW | h/day |
| 11 | Solar Panel Area Needed | 17.35156545m^ | 2 |
| 12 | Active Area of Catalyst | 11.12279837m [^] | 2 |
| 13 | Est'd active channel wall part-perimeter | 3.2mm | 1 |
| 14 | Total channel arc length required | 3475.87449m | |

• Electroanalysis (CV, CA, etc.) • GC assay of product gases • UV/Vis analysis of formate

- Optimization targets:
 - Hydrocarbon selectivity
 - Current density
 - Catalyst durability

Apply 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" |
| Netal 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 Output | OpEx Outputs | | |
|------------------------|--------------|--|--|
| Per-Plate Materials | \$15.08 | | |
| Per-Plate Active Labor | \$1.39 | | |
| Per-Plate Idle Labor | \$0.01 | | |
| Per-Plate Shipping | \$0.40 | | |
| Per-Plate Electricity | \$0.06 | | |
| Per-Plate Total | \$16.94 | | |
| | | | |

| CapEx Outputs | | | |
|---------------------|-----------|--|--|
| Rectification | \$580,430 | | |
| Tank(s) / Fixturing | \$40,000 | | |