Electrochemical Reduction of Carbon Dioxide to Useful Chemicals

Carbon Capture Team
SBIR Kick-Off Meeting
May 12, 2017

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Contract No.: DE-SC0017105
Contractor Name: Mainstream Engineering Corporation
Contractor Address: 200 Yellow Place, Rockledge FL 32955

Mainstream Engineering Corporation
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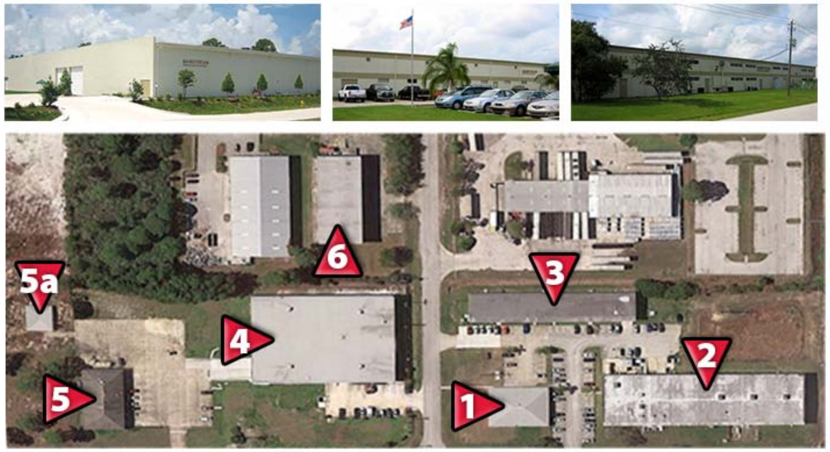
Agenda

- Background on Mainstream
- Project overall technical approach
- Project work plan

Mainstream Engineering Corporation

- Small business incorporated in 1986
- 100+ employees
- Mechanical, chemical, electrical, materials and aerospace engineers
- 100,000 ft^2 facility in Rockledge, FL
- Laboratories: electric power, electronics, materials, nanotube, physical and analytical chemistry, thermal, fuels, internal combustion engine
- Manufacturing: 3- and 5- axis CNC and manual mills, CNC and manual lathes, grinders, sheet metal, plastic injection molding, welding and painting



1 - ENGINEERING OFFICES
2 - RESEARCH and DEVELOPMENT
3 - RESEARCH and DEVELOPMENT
4 - PRODUCTION FACILITY
5 - PRODUCT DEVELOPMENT
5a - MAINSTREAM EBEAM
6 - ADMINISTRATIVE OFFICES

- **Basic Research, Applied Research & Product Development**
- **Transition from Research to Production (Systems Solution)**
- **Manufacture Advanced Products**

Mission Statement

To research and develop emerging technologies.
To engineer these technologies into superior quality, military and private sector products that provide a technological advantage.

SBIR Successes and Awards

- **95% DOD Commercialization Index**
- **SBIR spinoffs – QwikProduct Line**
- **SBIR spinoffs – Military Product Line**
- **Honors**
  - 2014 DOE's SBIR/STTR Small Business of the Year
  - 2013 Florida Excellence Award by the Small Business Institute for Excellence in Commerce
  - Winner Florida Companies to Watch
  - Blue Chip Enterprise Initiative Awards
  - Job Creation Awards
  - Two SBA's Tibbetts Awards for Commercialization
  - State of Florida Governor's New Product Award
  - SBA's Small Business Prime Contractor of the Year for the Southeastern U.S.
  - SBA's Administrator's Award for Excellence

Solutions Through Advanced Technology®
MAINSTREAM ENGINEERING

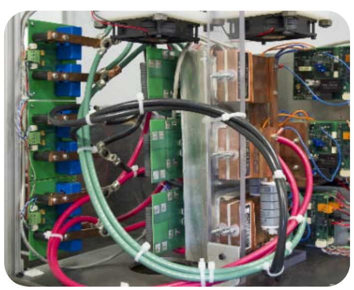
Mainstream's Focus Areas

THERMAL CONTROL

- High Heat Flux Cooling
- Thermal Energy Storage
- Directed Energy Weapons
- Rugged Military Systems

TURBOMACHINERY

- Compressors
- Turbines
- Bearings/Seals
- Airborne Power Systems

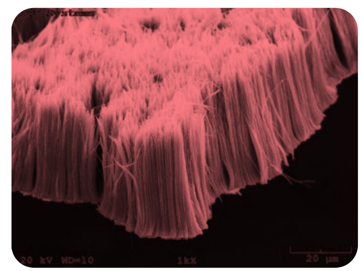


POWER ELECTRONICS

- High Speed Motor Drives
- Hybrid Power Systems
- Solar/Wind Electronics
- Pulse Power Supplies
- Battery Chargers

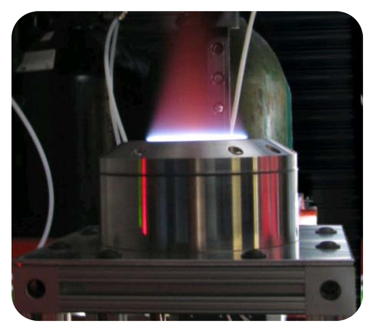
ENERGY CONVERSION

- Combustion
- Diesel/JP-8 Engines
- Biomass Conversion
- Alternative Fuels
- Fuel Cells



MATERIALS SCIENCE

- Thermoelectrics
- Batteries/Ultracapacitors
- Hydrogen Storage
- E-Beam Processing
- Nanostructured Materials



CHEMICAL TECHNOLOGIES

- Heat Transfer Fluids
- Catalysis
- Chemical Replacements
- Water Purification
- Chemical Sensors

Using CO_2 as a Chemical Feedstock

- **CO_2 use as a chemical feedstock is an attractive strategy for CO_2 capture and value recovery**
- **It use is limited by the high thermodynamic stability of CO_2**
- **Only a small fraction of CO_2 is used since conventional synthesis requires**
  - High temperatures and pressures to activate the CO_2
  - The use of reactive substances such as epoxides and amines to produce cyclic carbonates and carbamates
  - The use of complex reactive catalysts and organometallic reagents such a Grignard reagents which create significant waste streams

Electrosynthesis as a Path to CO_2 Utilization

- **Electroreduction uses clean electrons to replace the hazardous reducing agents to activate CO_2**
- **Electrosynthesis is a viable alternative to**
  - avoiding the dangerous, energy-intensive, high waste-producing, conventional chemical approaches
- **Two possible approaches**
  - A direct election transfer process at the electrode
  - Use of an intermediate species to transfer the activated CO_2 to the organic precursor

Electrosynthesis as a path to CO_2 Utilization

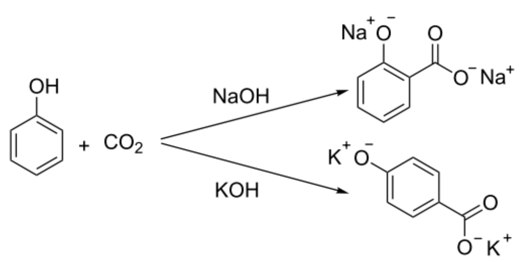
- **The direct reduction of CO_2 produces a path to the electrosynthesis of fuels such as formic acid, methanol, methane or higher hydrocarbons**
  - At present these are typically low value intermediates

$$CO_2 + H^+ + 2\,e \rightarrow HCOO^-$$

$$CO_2 + 8\,H^+ + 8\,e \rightarrow CH_4 + 2\,H_2O$$

$$2CO_2 + 12\,H^+ + 12\,e \rightarrow C_2H_4 + 4\,H_2O$$

- **An alternative approach is to capture the CO_2 by inserting it into an organic precursor to form a carboxylic acid**
  - Carboxylic acids are valuable and important precursors used in polymers, pharmaceuticals, agrichemicals and cosmetics

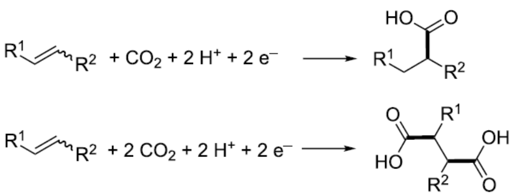


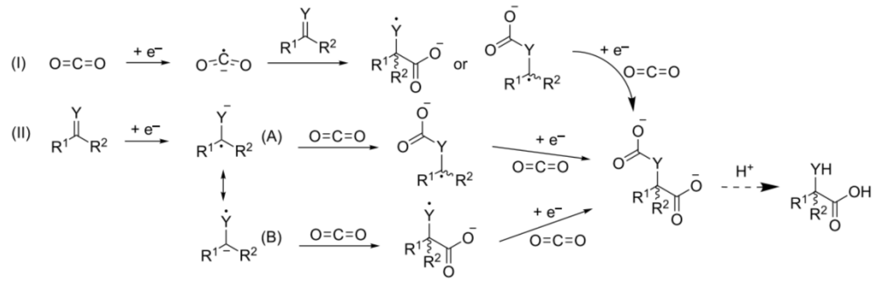
Precursor of aspirin

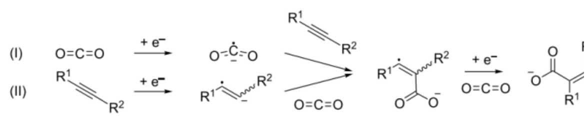
Precursor for polyester

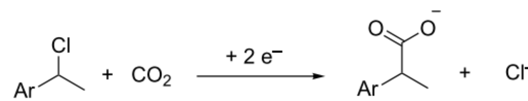
Currently produced by Kolbe-Schmidt process using high temperatures and pressures

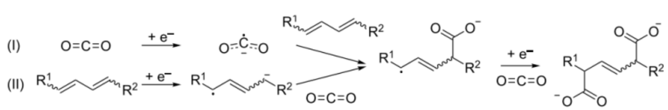
Electrosynthesis of Carboxylic Acids

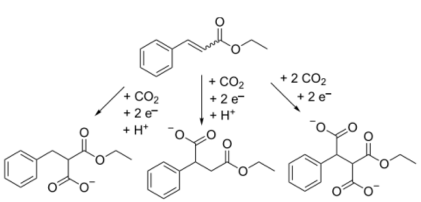








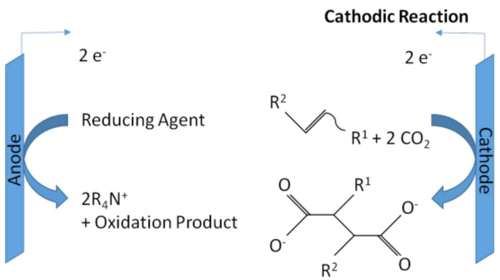




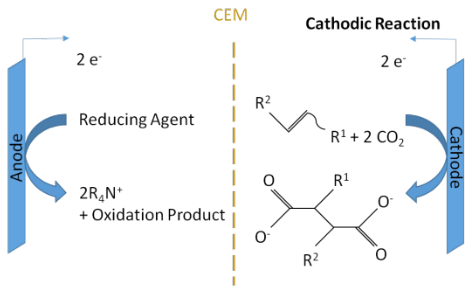
A wide range of electrosynthesis routes are possible to produce industrially useful intermediates

Phase I Technical Approach

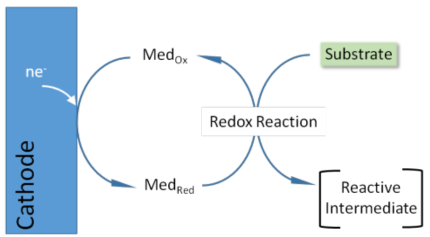
- **The electrode and cell design are critical to maximize**
  - Target product yield
  - Electrochemical or Faradaic efficiency
  - Reaction rate
- **Direct vs indirect electrosynthesis – equally benefit from Mainstreams gas diffusion electrode approach**



Undivided Cell



Divided Cell



Indirect/Mediated Electrosynthesis

Direct Electrosynthesis

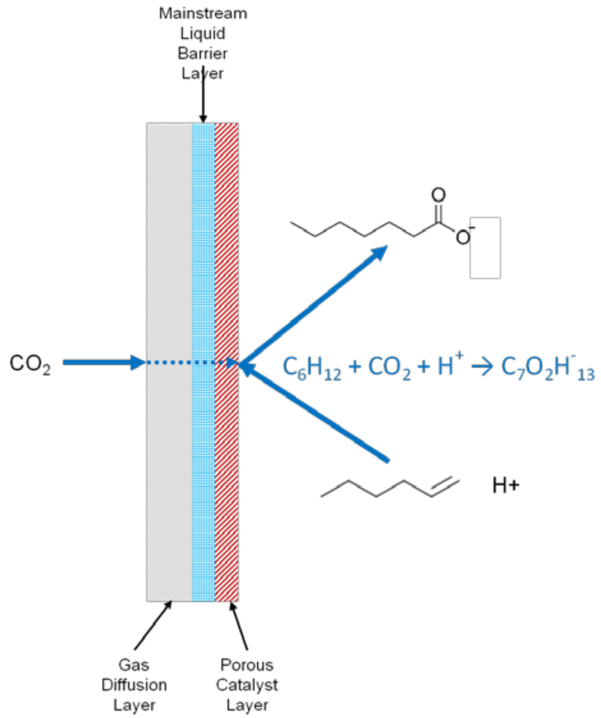
Phase I Technical Approach

- **Electrode design parameters**
  - Choice of electrode material or electrocatalyst
    - Overpotential – low for the target reaction and high for solvent decomposition
    - Selectivity for target reactions
    - High current density for the target reaction
  - Electrode design
    - High active area to maximize reaction rate
    - Mass transport of both CO_2 and reactants to the active sites
      - Maximizing selectivity, yield and efficiency
  - Direct vs. Indirect synthesis
    - Direct electron transfer at the electrode surface is simpler
      - The rate may be limited by reactant mass transport and access
    - Indirect synthesis mimics biological processes and uses a redox species to transfer the CO_2

Phase I Technical Approach

Leverage Mainstreams liquid fuel cell electrode fabrication

- **Gas diffusion electrode approach to overcome CO_2 solubility and mass transport**
- **Integrating a dense liquid barrier layer to prevent solution loss**
- **Porous catalyst layer with controlled**
  - Pore structure for gas and solution access
  - Catalyst particle size
  - Loading



Phase I Work Plan

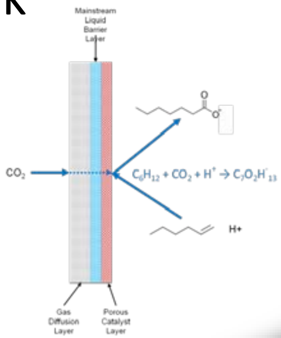
- Task 1: Selection, synthesis, and optimization of electrocatalysts and mediators
- Task 2: Fabrication of a cathode structure for the reduction of CO_2
- Task 3: Integration of the cathode structure into a single cell test cell
- Task 4: Measurement of overall efficiency and durability for CO_2 conversion in electrolysis
- Task 5: Preliminary design and modeling of system for the capture of CO_2

Task 1: Selection of Electrocatalysts and Mediators

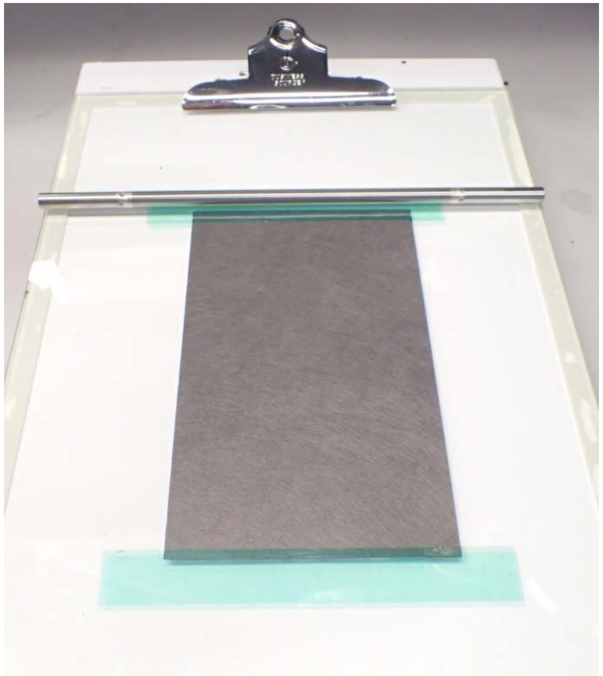
- **Screen electrode materials and catalysts for the selective insertion of CO_2 into key precursors**
- **Electrodes fabricated by direct deposition onto carbon fiber paper**
- **Initial screening using electroanalytical techniques**
  - cyclic voltammetry, chronoamperometry and electrochemical impedance.
- **The preferred strategy is direct electrochemical reaction at the electrode but indirect will be considered to maximize the reaction rate**

Task 2: Fabrication of a cathode structure for the reduction of CO_2

- **Electrode designed to optimize CO_2 access to the active sites**
  - Base electrode is carbon fiber paper
  - Incorporate liquid barrier layer to minimize electrolyte loss and flooding
  - The catalyst layer deposition will be optimize to control the active surface for both CO_2 and reactant access
  - Electrode deposition using scalable screen printing or rod coating techniques
  - Electrocatalyst structure is controlled by optimizing the ink composition and coating parameter
    - Solvent and binder
    - Additives pore formers, surfactants viscosity modifiers
    - Coating thickness
    - Solids loading
    - Drying conditions



Reproducible Electrode Structures Have Been Fabricated



Highly uniform, high viscosity coating solutions

Meyer rod coating provides a scalable process for depositing the liquid barrier layer

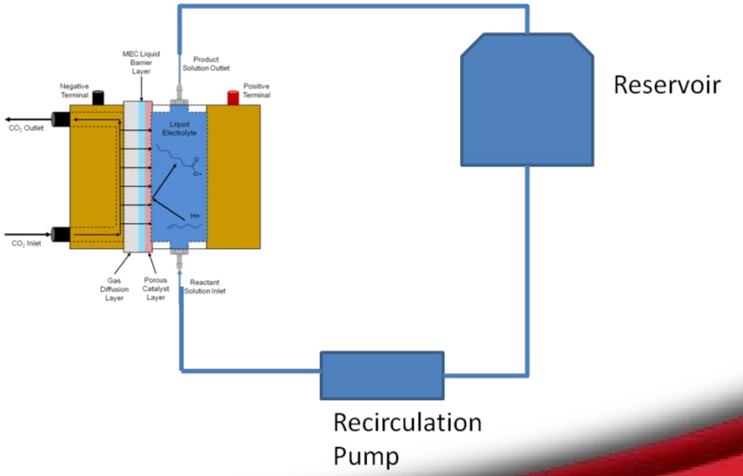
Reproducible electrode structures produced with various catalysts.

Task 3: Integration of the Cathode Structure into a Single Cell System

- **The gas diffusion electrode structure has been incorporated into a flow cell design**
- **Both divided and undivided cell structures will be examined**
  - Focus in Phase I is on the cathode design and chemistry
  - Anode chemistry will be optimized to maximize the cathode CO_2 utilization yield and rate
- **Synthesis routes based on direct and indirect electrosynthesis can be examined**
- **Designs will be created without sacrificial anodes**
  - Lends itself to continuous processing and minimizes waste handling
  - In Phase II, paired synthesis using the anode to produce additional products can be evaluated

Task 4: Efficiency and Durability for CO_2 Conversion

- **Electrochemical performance will be measured using a range of conditions**
  - CO_2 pressure
  - Temperature
  - Cell voltage and current density
- **Performance will be monitored by**
  - Tracking the overpotential
  - Monitoring the charge passed
  - Products distribution – measured using Gas chromatography (GC/MS and quantitative)
- **Key metrics include**
  - Current or Faradaic efficiency
  - Product yield
  - Reaction selectivity



Preliminary Design and Modeling of System for the Capture of CO_2

- **The reaction efficiency metrics will be used to develop a reactor design and economic evaluation**
  - Model will compare the energy requirements
  - Target product economics – through competing reactions
- **Design will incorporate expected**
  - Extraction and purification
  - Energy requirements

Program Schedule

	Task Name	Month 1	Month 2	Month 3	Month 4	Month 5	Month 6	Month 7	Month 8	Month 9
Task 1 :	Selection, synthesis and optimization of optimal redox catalysts and mediators									
Task 2 :	Fabrication of a cathode structure for the reduction of CO_2									
Task 3 :	Integration of the cathode structure into a single cell test cell.									
Task 4 :	Measurment of overall efficiency and durability for CO_2 conversion in electrolysis									
Task 5 :	Preliminary design and modeling of system for the capture of CO_2									

Summary

At the completion of the Phase I contract, Mainstream will have accomplished the following:

- **Developed electrode structures and a cell design for the efficient direct reduction of CO_2**
- **Established the efficiency, yield and rate of electrosynthesis of key model and molecules of interest**
- **Developed a preliminary design and techno-economic model for the utilization of CO_2 to produce key carboxylic acids.**