NREL
Transforming ENERGY

Industrially scalable waste CO_2 reduction to useful chemicals and fuels

Todd Deutsch, KC Neyerlin, Yingying Chen, Zhiwen Ma, Ellis Klein
National Renewable Energy Laboratory
April 30, 2019

DOE Hydrogen and Fuel Cells Program
2019 Annual Merit Review and Peer Evaluation Meeting

Project ID: p178

Overview

Timeline and Budget

- Project start date: 10/01/18
- Project end date: 09/30/20
- Total project budget: $2,110,000
  - Total recipient share: $110,000 (Rutgers cost share)
  - Total federal share: $2M
  - Total DOE funds spent*: $350k

* As of 3/01/19

Barriers

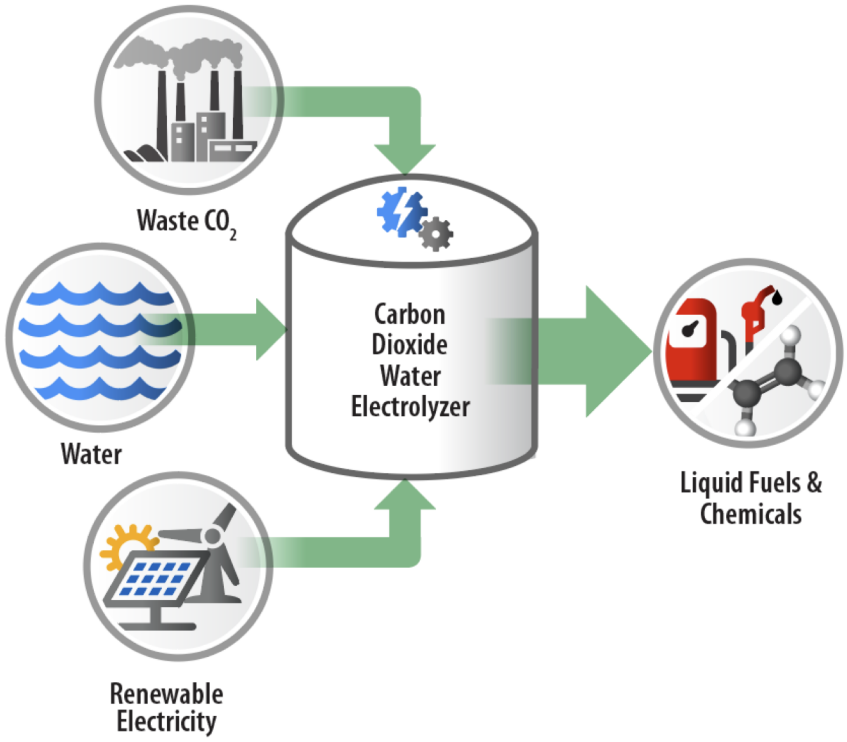
- CO_2 reduction selectivity
- CO_2 electrolyzer current density
- CO_2 electrolyzer stability

Partners

- Rutgers – Charles Dismukes
  - NiP catalysts for CO_2 reduction
  - Subcontract
- LANL – Jacob Spendelow
  - Advanced electrode structures
- ANL – Debbie Myers, Rajesh Ahluwalia
  - Nano-CT: electrode microstructure characterization and simulation

Relevance

- The goal of this project is to develop an **electrochemical device** that can do for the **carbon dioxide (CO_2) to fuels and chemicals** process what the Haber-Bosch process did for the nitrogen fixation reaction. That is, develop a reactor that accelerates the rate of the limiting reaction steps so that devices operate at power densities commensurate with the rate of point-source CO_2 emissions.
- Such a reactor could use this waste product as the backbone to **store inexpensive renewable electricity as hydrogen and carbon bonds** in the form of high-density liquid fuels and valuable chemicals. The **hydrogen atoms would come from water oxidation delivered as protons and electrons via electrolysis**.



- This electrochemical process could greatly improve the energy efficiency and selectivity compared to thermochemical processes starting from water and CO_2.

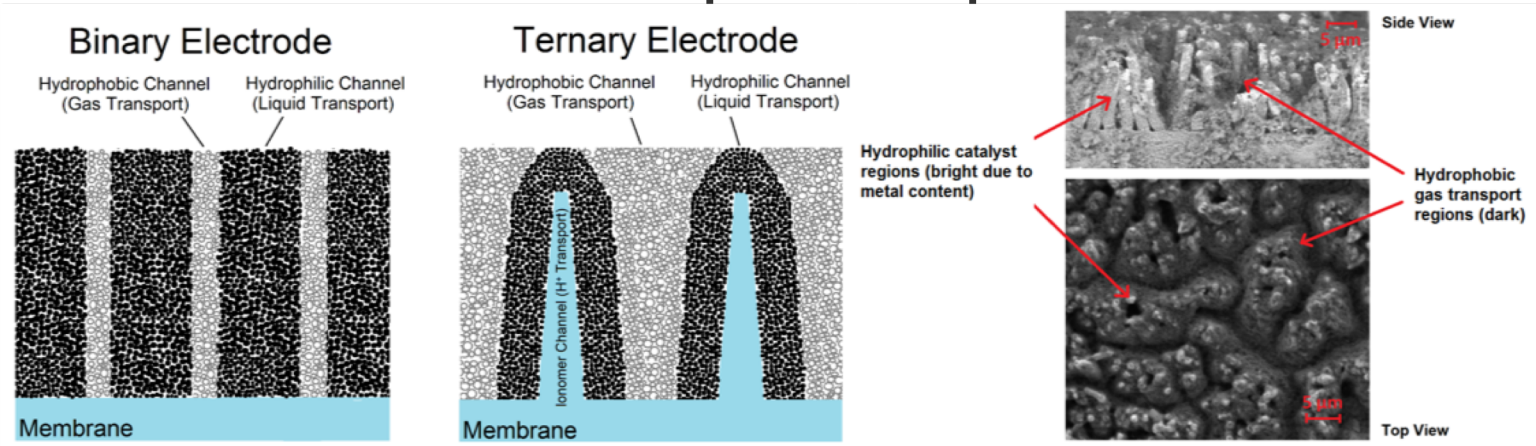
Approach

Tackle 4 significant *Research & Development* challenges

1) **Mass transport**
   - In the most commonly studied H-cells, CO_2 reduction current density is limited to ~30 mA/cm^2 by the *low aqueous solubility* of CO_2 (~30 mM)
   - Use *gas diffusion electrodes* (GDEs) to increase access of CO_2 to cathode
   - *Use membrane electrode assemblies* (MEAs) to achieve A/cm^2
2) **Advanced membranes and membrane architectures**
   - *Bipolar membranes* (BPMs), a hybrid or anion/cation exchange membranes can maintain a pH gradient and hinder product crossover
   - Electrospin the BPM interfacial layer to increase junction area and lower area specific resistance
   - Apply *water dissociation catalysts* and incorporate *active water management* schemes to keep membranes from drying out at high current densities
3) **Catalysts**
   - Product selectivity in CO_2 reduction is crucial for making cost-effective process
   - Instead of developing new catalysts, *benchmark known catalyst in industrially-relevant conditions*: Cu – cathode, NiCoFe – anode
   - Working with *Rutgers University on promising NiP-based catalysts*
4) **Component integration**
   - Assemble components into working devices and perform *in-situ electrochemical diagnostics*
   - Development of new *CO_2 electrolysis test stands* and *real-time product analysis*

Approach

Additional techniques and capabilities



- **LANL: Advanced CO_2 cathode transport structures**
  - Distinct hydrophilic catalyst channels (H_2O, liquid fuel product, H^+, and e- transport) and hydrophobic channels (CO_2 and gaseous fuel product transport)
- **ANL: Electrode microstructure characterization and simulation**
  - Nano-scale synchrotron X-ray computed tomography (nano-CT) characterization
  - Experimental effort to prepare samples and collect data; modeling effort to reconstruct the nano-CT data to extract the relevant membrane properties
- **NREL: Finite element multi-physics device modeling**
  - 2D modeling (COMSOL, Fluent) will be applied to deconvolute the roles of mass transport of products and reactants, liquid water flow, electrochemical reaction kinetics, and charge and heat transfer on device performance

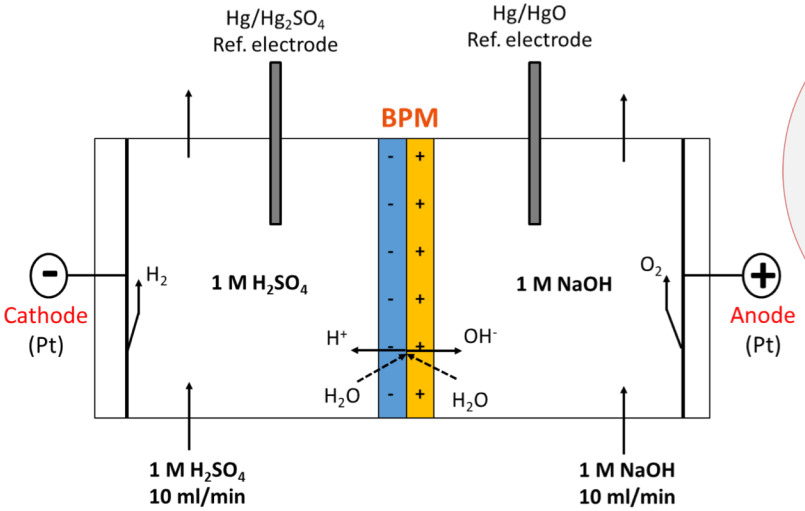
Approach

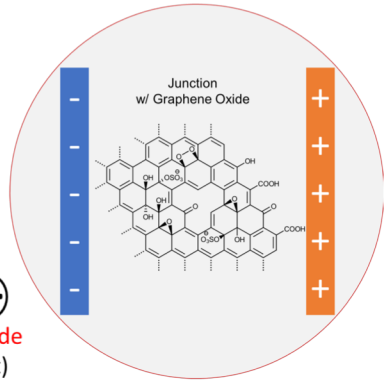
FY19 Milestones

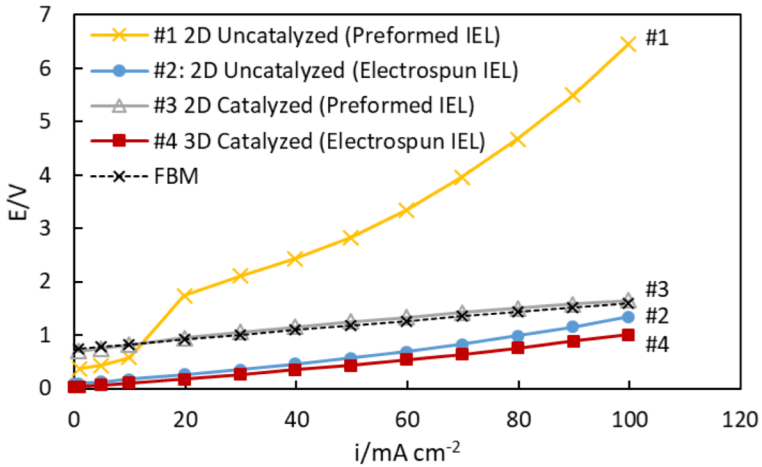
Milestone		
Q1	Demonstrate electrospun bipolar membrane with water dissociation particles and evaluate performance against planar and uncatalyzed electrospun membrane interfaces.	Completed
Q2	Establish a preliminary coupled multi-physics finite element model that is based on a simple CO_2 electrolyzer that correlates mass transport of products and reactants, liquid water flow, electrochemical reaction kinetics, and charge and heat transfer to describe device performance.	Completed
Q3	Establish a CO_2 electrolyzer test stand with in-situ electrochemical diagnostics and FE analysis capabilities.	On-track
Q4	Show NiP CO2R catalysts on GDE attaining > 10 h operation @ ≥ 25 mA/cm^2: Develop a process for stable deposition of advanced NiP CO2R catalysts onto GDE-electrode attaining > 10 h continuous operation at ≥ 25 mA/cm^2 and < 5% increase in half-cell potential. Achieve > 50% selectivity into C product(s) vs HER.	On-track
	G/NG: Demonstrate a CO_2 electrolyzer that integrates a BPM, binary electrode, and catalyst-loaded MEA that can operate at over 150 mA/cm^2 for 10 hours with FE >80% non-hydrogen products.	On-track

Accomplishments and Progress

Q1 milestone: Demonstrate electrospun bipolar membrane with water dissociation particles and evaluate performance against planar and uncatalyzed electrospun membrane interfaces.

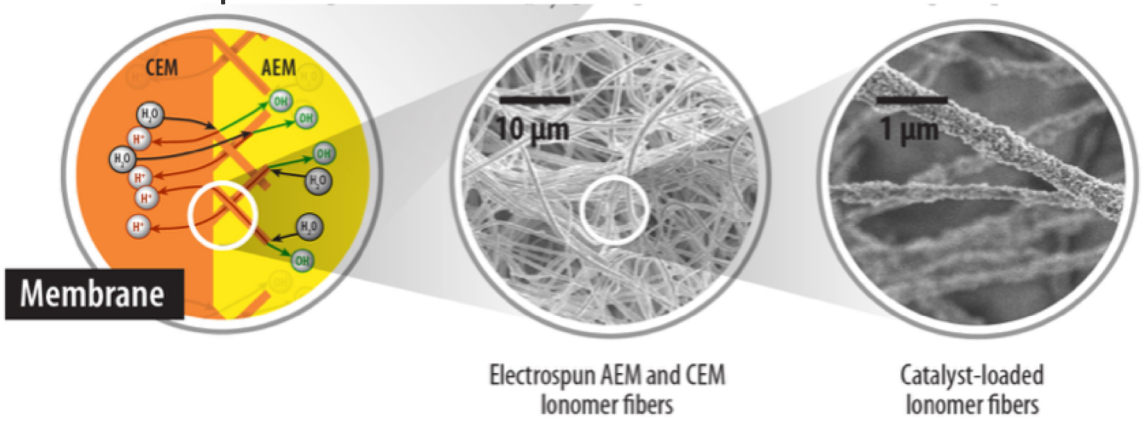


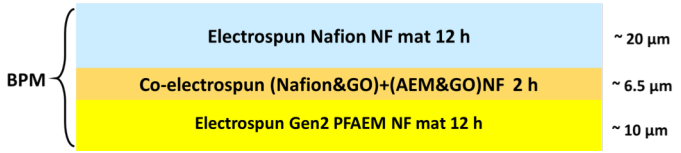




Bipolar membrane potential drop under conditions of water electrolysis. Electrospun BPMs without/with 3D catalyzed junction (#2 and #4), and BPMs made by pressing 2 planar membranes together without/with catalyst in junction (#1 and #3).

Tested bipolar membranes in flow cell

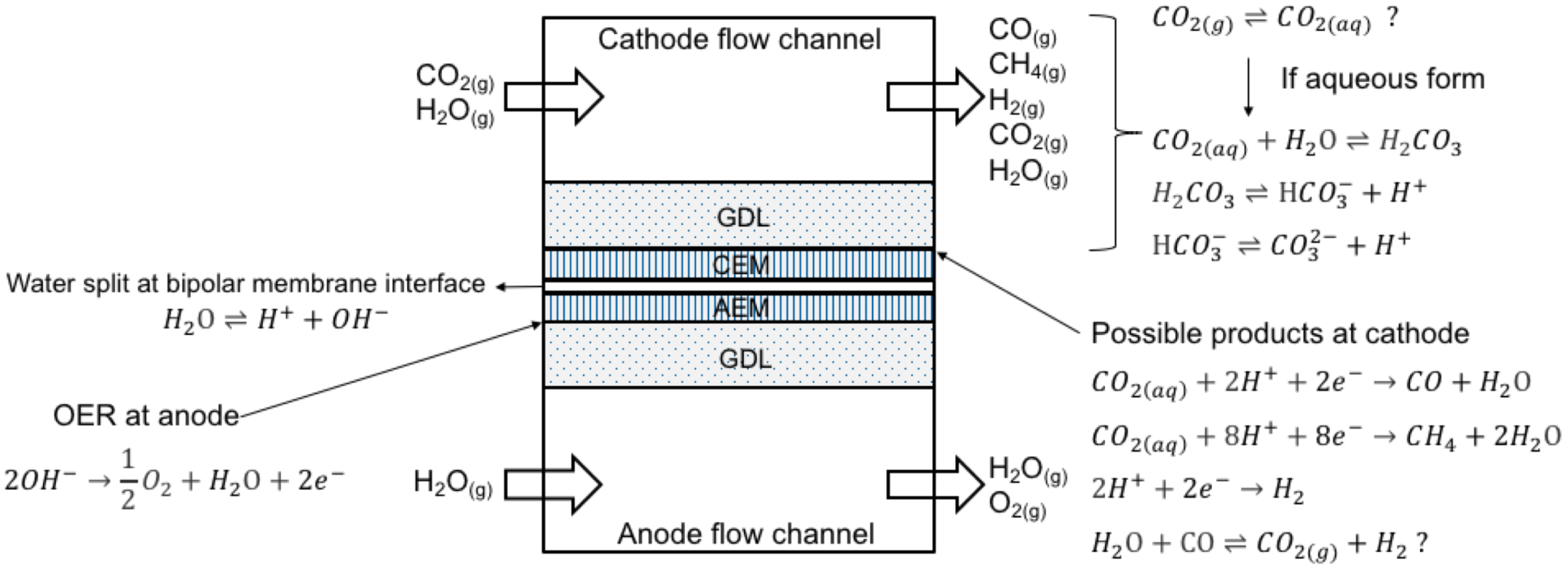




- **Successfully fabricated electrospun BPM with 3D dual-fiber junction incorporating graphene oxide in ionomer spinning solution as water dissociation catalyst, and achieved a similar performance with Fumasep FBM**
- **Application of catalyst to BPM junction significantly decreases the water dissociation resistance**

Accomplishments and Progress

Q2 milestone: Establish a preliminary coupled multi-physics finite element model that is based on a simple CO_2 electrolyzer that correlates mass transport of products and reactants, liquid water flow, electrochemical reaction kinetics, and charge and heat transfer to describe device performance.

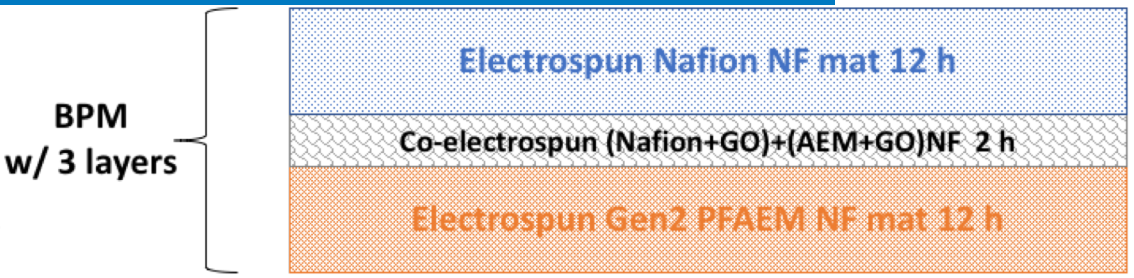


First question: What is the maximum current density achievable if diffusion alone is replenishing water dissociated and electro-osmotically dragged away from the interfacial layer?

Comprehensive model developed, plan is to publish in peer-reviewed journal

Accomplishments and Progress

Prepared samples for nano-CT (analysis pending)



BPM=Nafion NF 12 h + (Nafion+graphene oxide)(AEM+graphene oxide)NF 2 h + PFAEM NF 12 h

#1. After vapor for 15 min each side & press at 3.4 MPa 60°C for 2 min (~30-35 µm)

- Structure of the electrospun BPM ready for testing

#2. Pristine BPM nanofiber mat (~100 µm)

- Structure of the pristine electrospun BPM

#3. After in IPA vapor for 15 min each side (~60-70 µm)

- Fiber structure change after the exposure to IPA vapor

#4. BPM after testing, dried

- Durability of the electrospun BPM

#5. Co-electrospun (Nafion+graphene oxide)(AEM+graphene oxide)NF 2 h, pristine

- Structure of the pristine 3D junction

#6. (Nafion+C)NF 3 h, pristine

- More robust and thicker electrospun fiber mat to look into pristine fiber mat structure

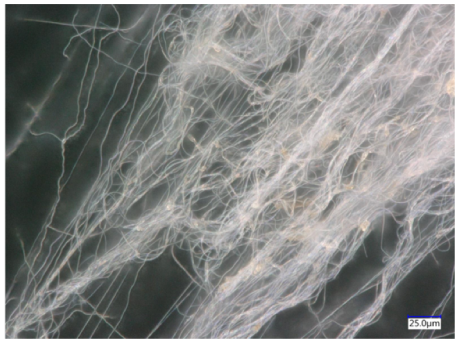
#7. Co-electrospun (Nafion+graphene oxide)(AEM+graphene oxide)NF 2 h, after vapor & press on Nafion

- Structure of the 3D junction after treatment

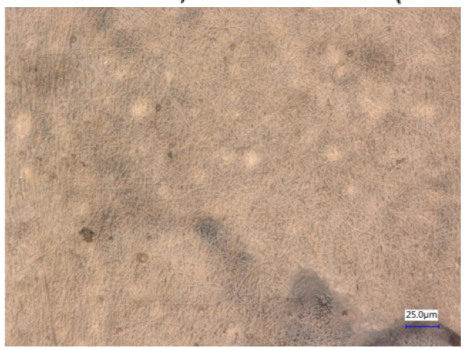
#8. (Nafion+C)NF 3 h, after vapor & press on Nafion

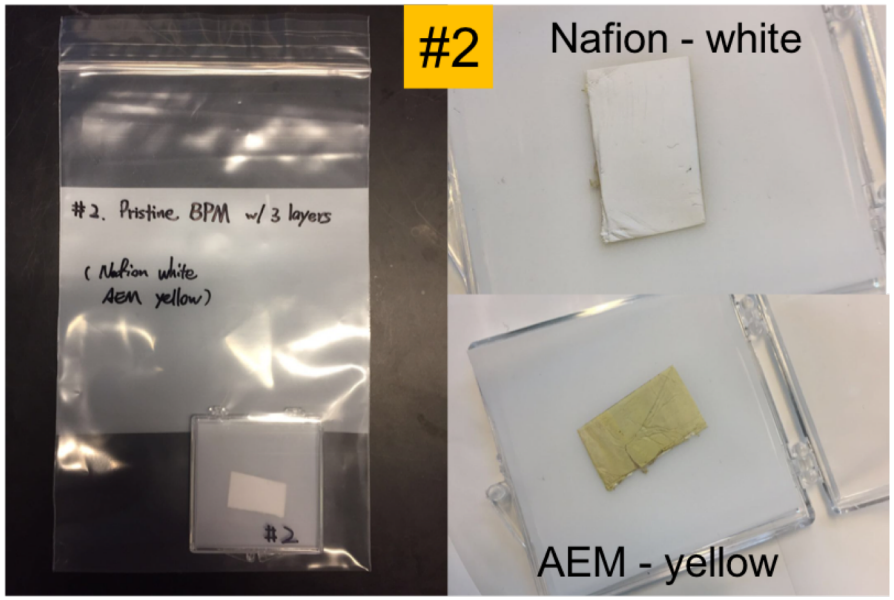
- More robust and thicker electrospun fiber mat to look into treated fiber mat structure

Pristine nanofiber mat



→ Solvent vapor to melt the fibers (~60-70 µm)
→ Press at 3.4 MPa, 60°C for 2 min (~30~35 µm)





Accomplishments and Progress

Designed and built a CO_2 electrolysis test stand

- Gas-fed cathode and alkaline aqueous anode feed.
- Cell, pumps, liquid feed solution and sample collection is housed in a ventilated enclosure due to the toxicity of expected products.
- The anode liquid feed consists of an entirely PTFE wetted pump, a custom Nickel-200 heat exchanger and all PTFE or PFA plumbing components, capable of 0-100mL/min flow rate and temperatures up to 80°C.
- A DI water purge option is used to remove corrosive liquids from the plumbing components and cell before a researcher disconnects a cell.
- The gas-fed cathode consists of 0-4 SLPM Mass Flow Controller, humidifier bottle with automatic drain and refill, and separate heat zones for humidifier bottle and gas line.
- Both anode and cathode feature a backpressure system that utilize chemically resistant PTFE and PEEK backpressure regulators optimized for dual phase flow.
- The cell is supplied power a Bio-Logic HCP-1005 High Current Potentiostat/Galvanostat/EIS instrument.
- Pressure, gas flow and cell power are controlled through a computer. Temperature and liquid flow are set manually.
- The stand is controlled by a programmable logic controller (PLC) which monitors safety features and is programmed to respond accordingly.

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- This project was not reviewed last year

Collaboration and Coordination

- Los Alamos National Lab – Jacob Spendelow
  - Sub-recipient ($250k/yr)
  - Federal laboratory
  - Within or outside of the DOE Hydrogen and Fuel Cells Program
  - Develop advanced CO2 cathode structures
- Argonne National Lab – Debbie Myers, Rajesh Ahluwalia
  - Sub-recipient ($150k/yr)
  - Federal laboratory
  - Within the DOE Hydrogen and Fuel Cells Program
  - Electrode nano-CT characterization and simulation
- Rutgers University – Charles Dismukes
  - Subcontract ($100k/yr, cost-share $55k/yr)
  - University
  - Within DOE Hydrogen and Fuel Cells Program (HydroGEN PEC awardee)
  - Synthesis and characterization of NiP-based CO_2 electrocatalysts for CO_2 electrolyzer cathodes
- NREL's anion ionomer development program
  - Federal lab
  - Within DOE FCTO
  - Provide this project PFAEM polymer, we provide characterization results
- NREL's MEA fabrication, fuel cell and electrolysis characterization groups
  - Federal lab
  - Within DOE FCTO
  - Maintain equipment for MEA fabrication as well as fuel cell and electrolyzer test stands that enable performance evaluation of BPM devices

Remaining Challenges and Barriers

- Achieving BPMs with sufficient performance and durability to sustain high currents (A/cm^2)
- Coupling CO_2 test stands with analytical techniques to observe product distributions in real time
- Benchmarking catalyst CO_2 reduction product distributions under operational conditions
- Controlling local pH on triple-phase cathode reaction sites to inhibit hydrogen evolution at potentials necessary for high current densities
- Understanding CO_2 electrolyzer tolerance to pollutants typically encountered in CO_2 point sources

Proposed Future Work

- Continue working on BPMs: increase throughput and scale
- Build more CO_2 test stations with state-of-the-art analytical capabilities
- Test catalysts in MEAs to see if product distributions and reaction mechanisms derived from aqueous cells translate to industrially-relevant conditions
- Incorporate LANL's advanced electrode structures
- Integrate Rutgers' NiP catalyst in CO_2 electrolyzers
- Perform nano-CT to understand the microstructure of electrodes
- Develop multi-physics model that could predict optimal operating conditions for desired products

Technology Transfer Activities

- Engage external parties (biorefineries, energy companies) to seek collaborative research or licensing opportunities
- "Electrolyzer for point source recycling of CO_2 emissions" U.S. provisional patent application corresponding to NREL Record of Invention (ROI) No. 18-107 was filed on August 1, 2018 at the United States Patent & Trademark Office (USPTO) and has received Application No. 62/713,114

Summary

- This is a new, highly collaborative lab-call project
- Despite the challenges of starting and staffing a new program, we have made good progress in the first six months
  - The pace of headway should increase with recent postdoc hires
  - The project is synergistic with ongoing research in fuel cells and electrolyzers at the various labs
- A successful outcome will result in several opportunities for interaction/collaboration/licensing with commercial entities

Thank You

www.nrel.gov

Publication Number

This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Fuel Cell Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.