Industrially scalable waste CO_2 reduction to useful chemicals and fuels

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National Renewable Energy Laboratory

May 2020

DOE Hydrogen and Fuel Cells Program
2020 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: $2,055,000
  - Total recipient share: $55,000 (Rutgers cost share)
  - Total federal share: $2M
  - Total DOE funds spent*: $1,600k

* As of 5/01/20

Barriers

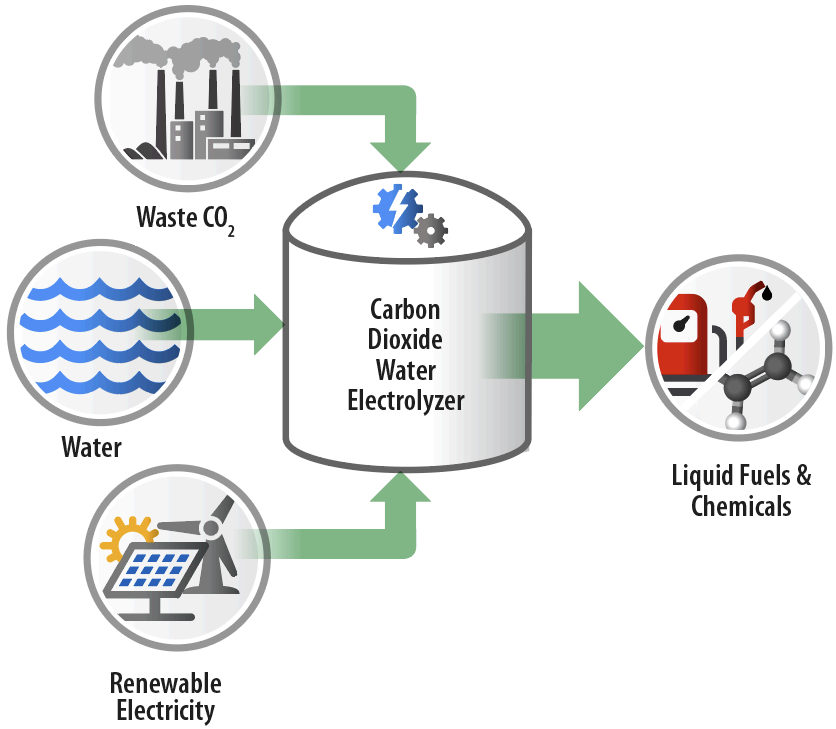
- CO_2 reduction selectivity
- CO_2 electrolyzer current density
- CO_2 electrolyzer stability

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.

Relevance & impact

- End of project goals:
  - Area: 25cm^2 (5 times larger than state of the art)
  - Current density: 500 mA/cm^2
  - Stability: Over 80% FE for 100 hours
  - Bipolar membrane: Maximize CO_2 utilization and perform water oxidation in alkaline environment for non-precious oxygen evolution catalysts
- Relevance to H_2 production targets: Similar processes to water electrolysis
  - Anode: oxygen from water splitting
  - Cathode: Hydrogen is formed from protons and electrons but is bound to carbon, liquid storage of renewable electrons
  - Electrochemical routes to syngas. H_2 co-production with CO, top off with H_2 from water electrolysis if necessary.

Approach

Research focus areas

Membrane:
- 3D Bipolar membrane interfaces by electrospinning–add particles
- Active water management

Electrode:
- Binary and ternary cathode structures

Catalysts:
- Incorporate known (Sn, Cu) catalyst in a relevant electrode architecture
- Develop new (NiP) catalysts
- Drop in anode catalysts from AEM electrolysis research

Microstructure characterization and simulation:
- Nano-CT characterization and modeled ensemble properties

Modeling:
- Fluent, COMSOL

In-situ diagnostics
- Use electrochemical techniques to probe component properties under variable operating conditions

Research team responsibilities

NREL

- Develop gas diffusion electrodes to overcome mass transport limitations of aqueous electrolyte to achieve A/cm^2 instead of mA/cm^2
- Synthesize bipolar membrane to allow water oxidation in alkaline electrolyte where earth-abundant water oxidation catalysts can be used
- Establish finite element model to understand performance and inform future designs

Los Alamos National Lab

- (Spendelow) Engineer new binary and ternary cathode electrode architectures to manage reactants and multi-phase products

Argonne National Lab

- (Myers, Ahluwalia) Electrode and membrane microstructure (nano-CT) characterization and modeling

Rutgers University

- (Dismukes) Ni_xP_y catalyst synthesis and incorporation for products with C-C bonds

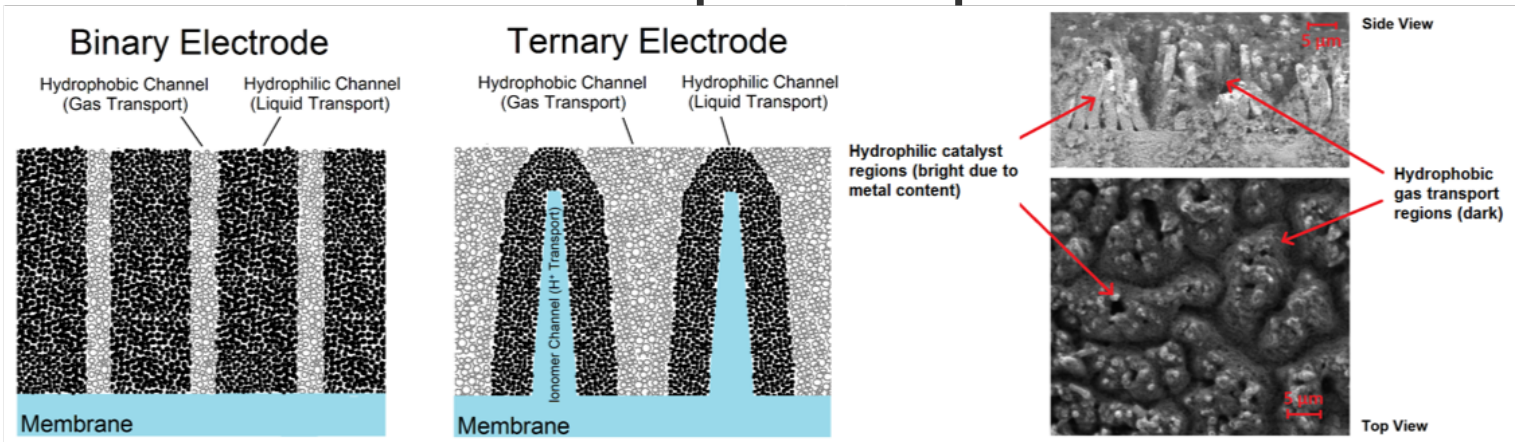
Approach

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 carbonate/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

Current year milestones and GNG criteria

FY20 Milestones

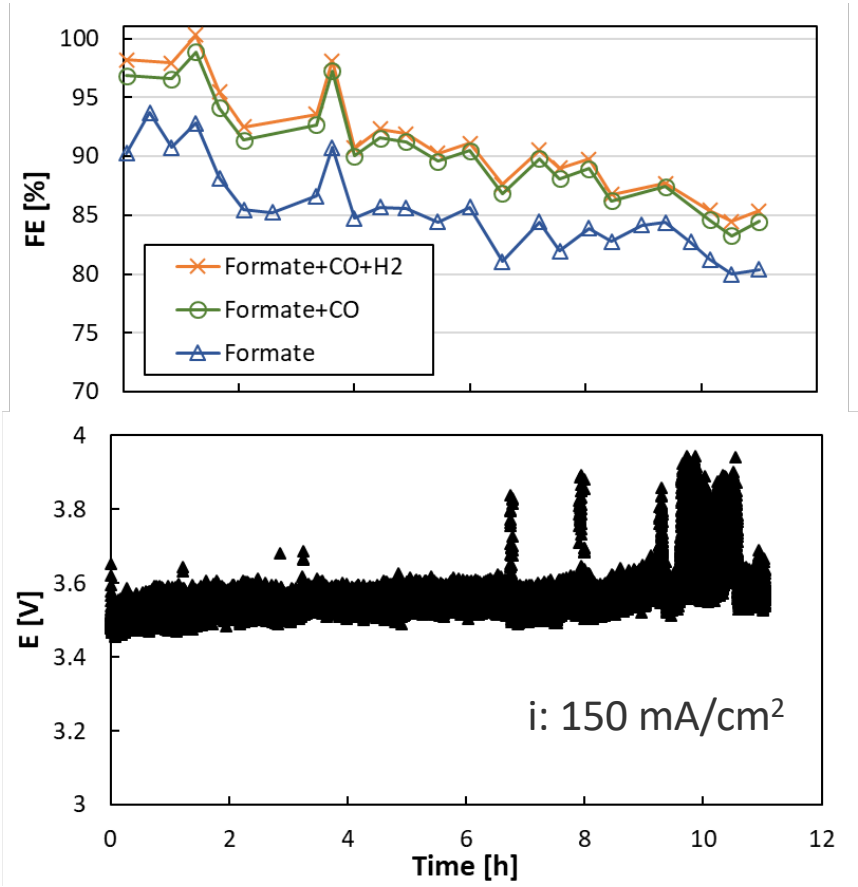
Due Date	Milestones, Deliverables, or Go/No-Go Decision	Criteria	Status
12/30/2019	Assess **BPM stability** as a function of catholyte and anolyte electrolyte composition	Identify a BPM configuration and electrolyte that achieves >15 hr durability in no more than 10% loss in membrane conductivity.	Complete
3/31/2020	Assemble full **MEA with NiP catalysts** and assess CO2E performance with BPM under variable operating conditions	CO2E with NiP catalysts evaluated in NREL's test station to determine faradaic efficiency and product selectivity	Complete
6/30/2020	Evaluate **new binary electrode structures**, a set of three configurations with varying aspect rations obtained from LANL	Test the faradaic efficiency, energy efficiency, and single pass CO_2 conversion efficiency of three different binary electrodes under operation in a CO2E at 100%, 50%, and 4% CO_2.	On-track
9/30/2020	Demonstrate a CO_2 electrolyzer	Demonstrate a **CO_2 electrolyzer** that is at least **25 cm^2** , integrates a BPM, advanced electrode, and catalyst-loaded MEA that can operate at **500 mA/cm^2 or greater for 100 hours with faradaic efficiency >80% to liquid products**.	On-track

Accomplishments and Progress

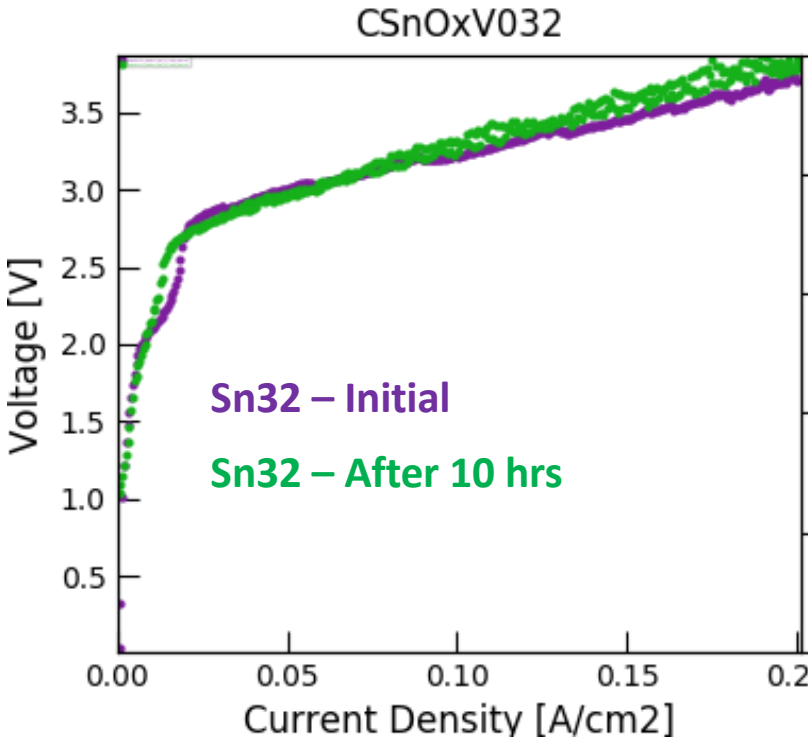
Met Go/No-Go (September 2019) metric using large-area CO_2 to Formate Flow Cell

G/NG: Demonstrate a 25 cm^2 CO_2 electrolyzer that integrates a BPM and a catalyst-loaded MEA that can operate at 150 mA/cm^2 for 10 hours with a Faradaic efficiency (FE) >80% non-hydrogen products.

25 cm^2, Ni foam anode, 0.5 mg/cm^2 SnO_2 on C, Fumasep FBM, 1M KOH, 0.5 M K_2SO_4



stable operation



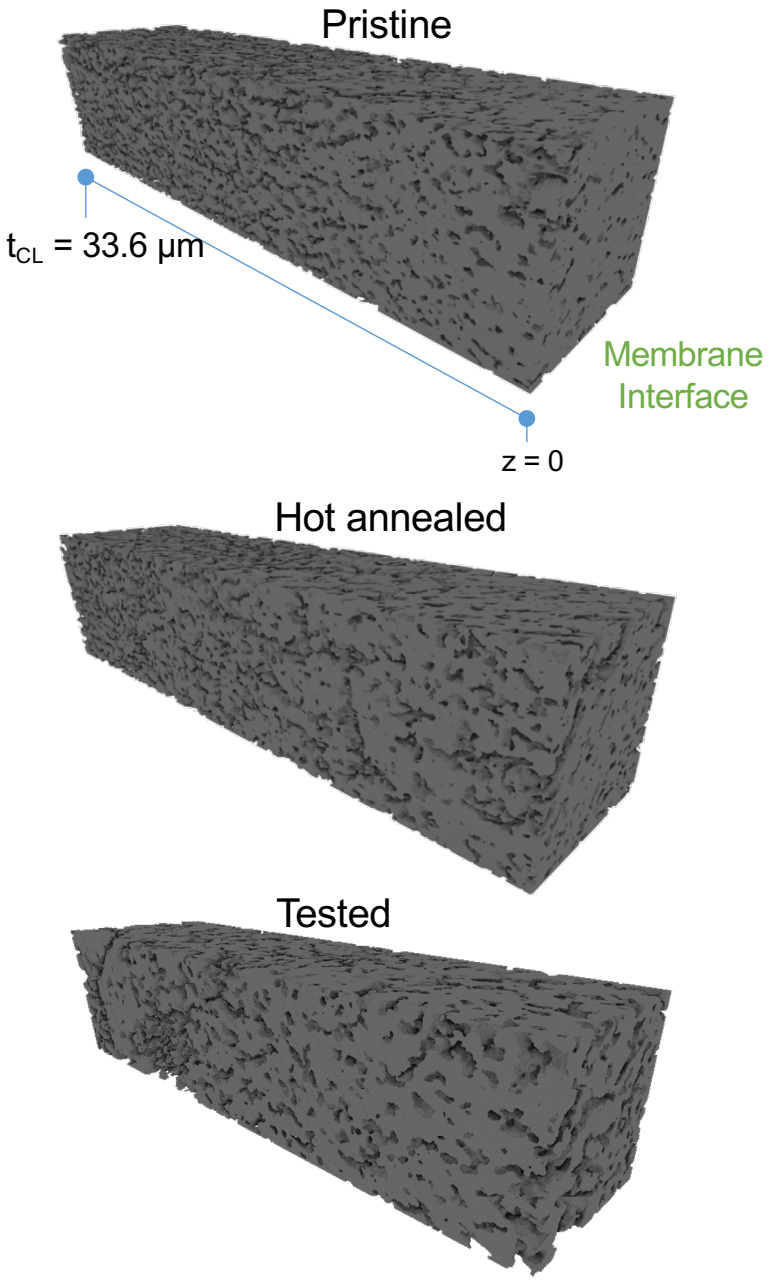
Large scale, no precious metals

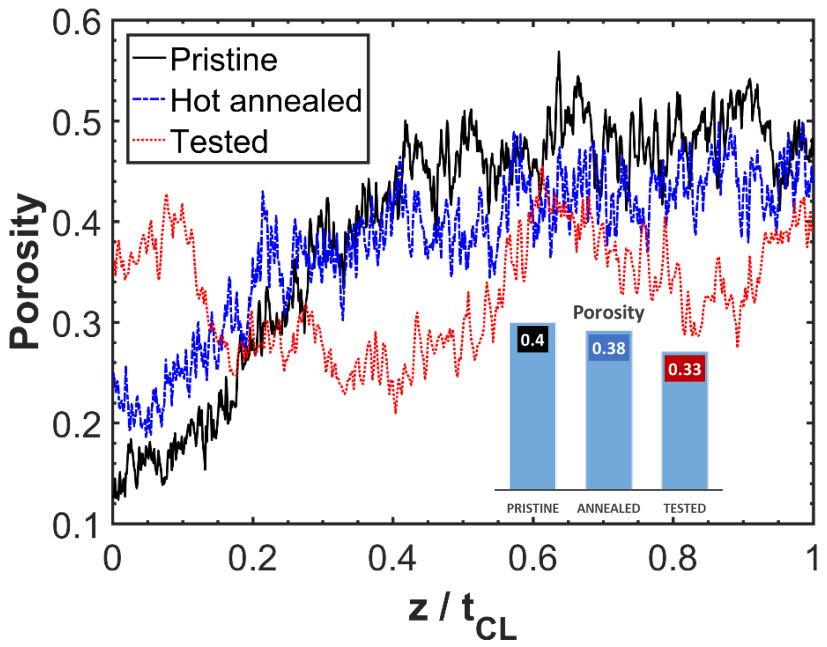
Yingying Chen, Ashlee Vise

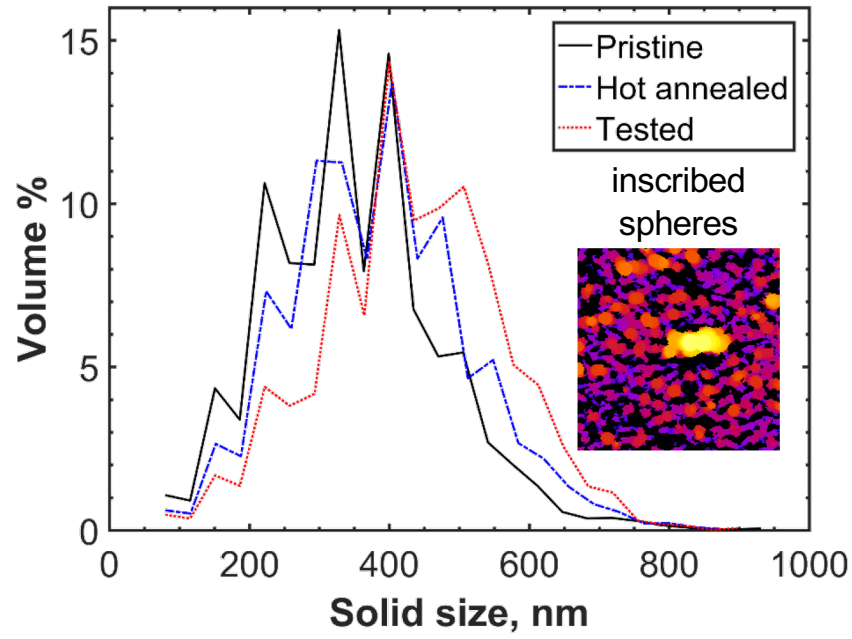
Accomplishments and Progress:

Nano computed tomography on SnO_2 electrodes NREL used to make Go/No-go milestone

Testing for 11 hours decreases porosity and increases solid size



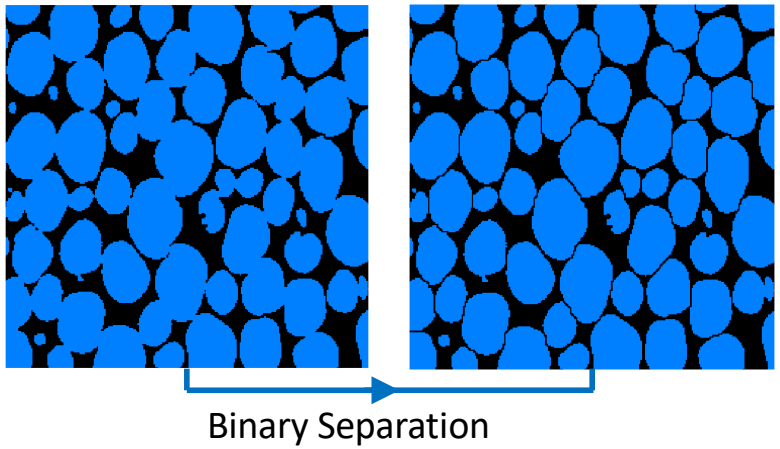


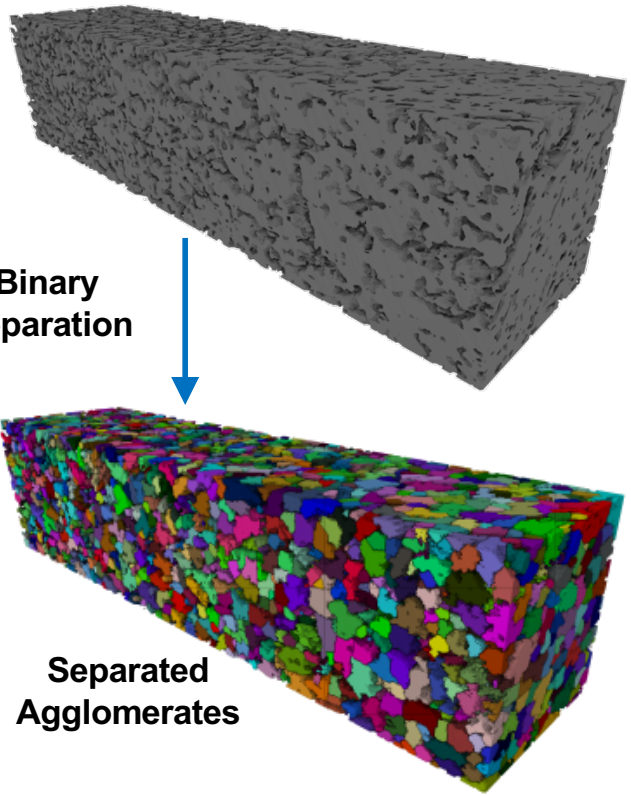


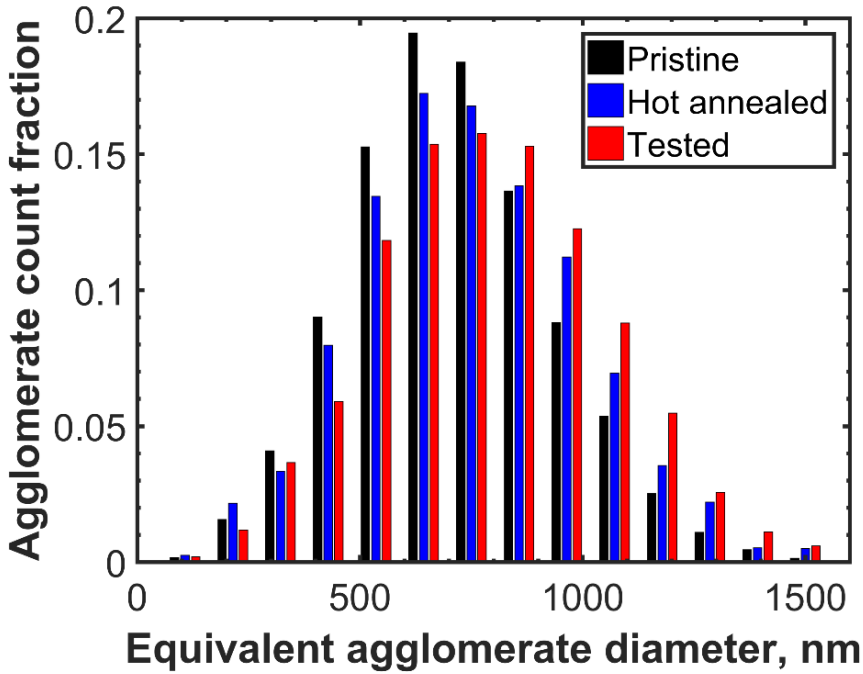
Debbie Myers, Rajesh Ahluwalia, Firat Cetinbas

Accomplishments and Progress: Argonne National Lab

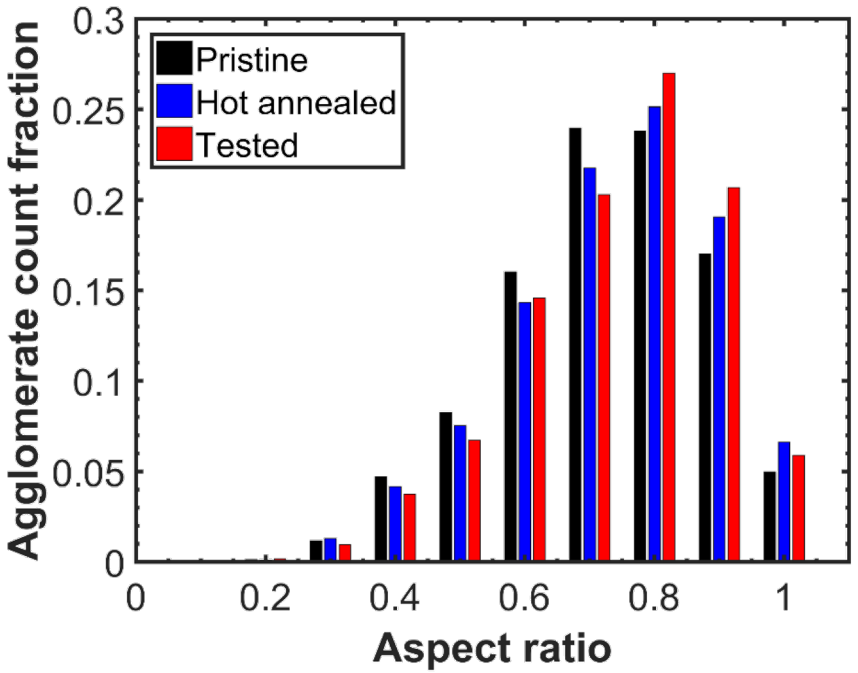
Nano computed tomography on SnO_2 electrodes NREL used to make Go/No-go milestone







Testing for 11 hours increases equivalent agglomerate diameter and increases aspect ratio



Debbie Myers, Rajesh Ahluwalia, Firat Cetinbas

Accomplishments and Progress: Rutgers University

CO_2 reduction catalyst Ni_2P particle size and facet control

2018 High-temp phosphidization route:
N_2 BET surface area: **0.1 m^2/g**
PXRD crystallite size: 200-1000 nm

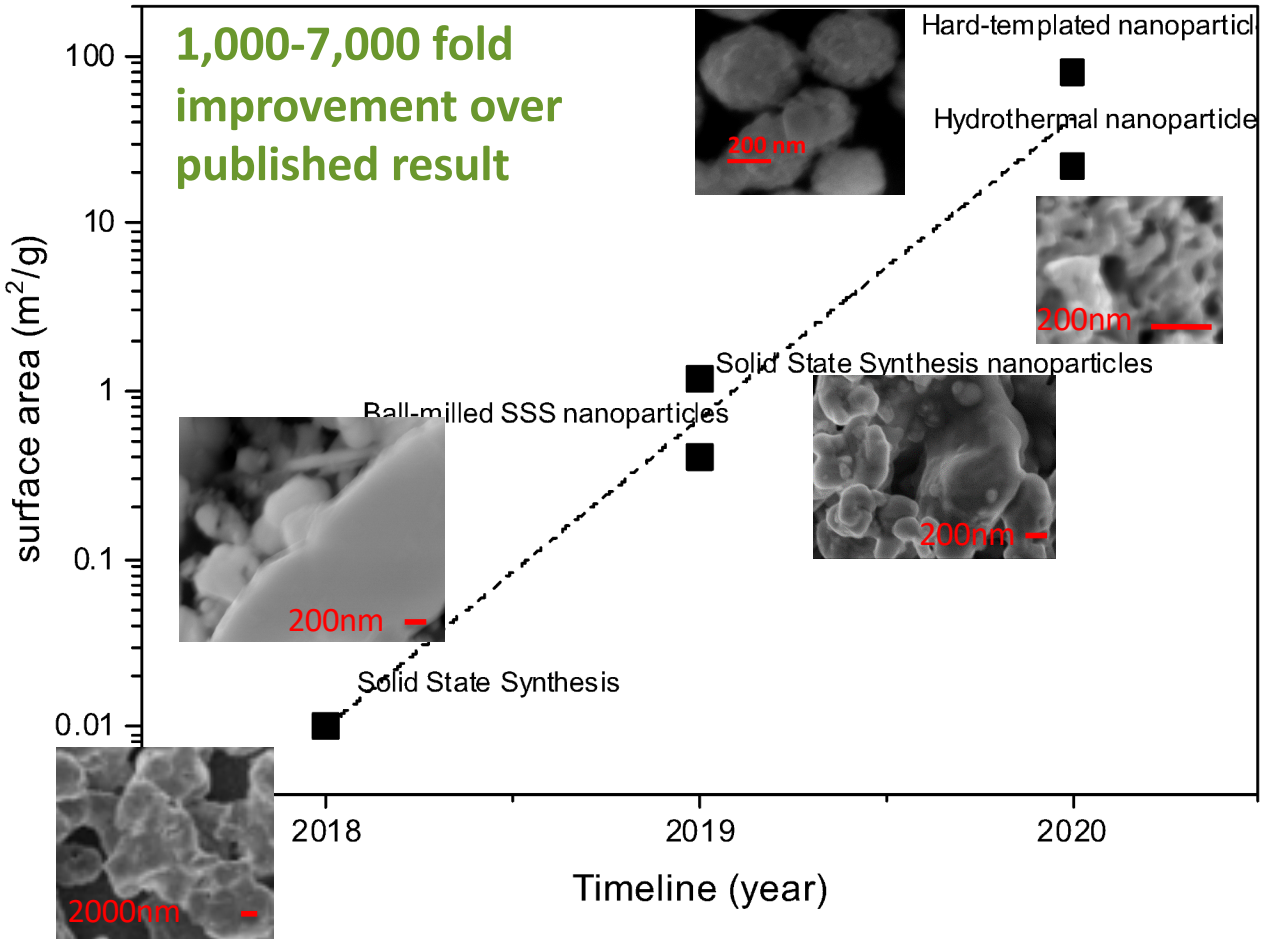
↓ Use nanoparticle precursor (Benchmarking RU)

2018-19 Red-temp phosphidization route:
N_2 BET surface area: **1.2 m^2/g**
PXRD crystallite size: 40-60 nm

↓ Ball milling at NREL (Benchmarking RU)

2019-20 Post-synthesis ball milling:
N_2 BET surface area: **0.4 m^2/g**
PXRD crystallite size: ~21 nm

↓ Ligand stabilized low temperature growth (Benchmarking NREL)



2020 Low temperature solution synthesis:
N_2 BET surface area: **22 m^2/g**
PXRD crystallite size: ~11 nm
(Benchmarking RU)

→ Hard-templated low temperature growth

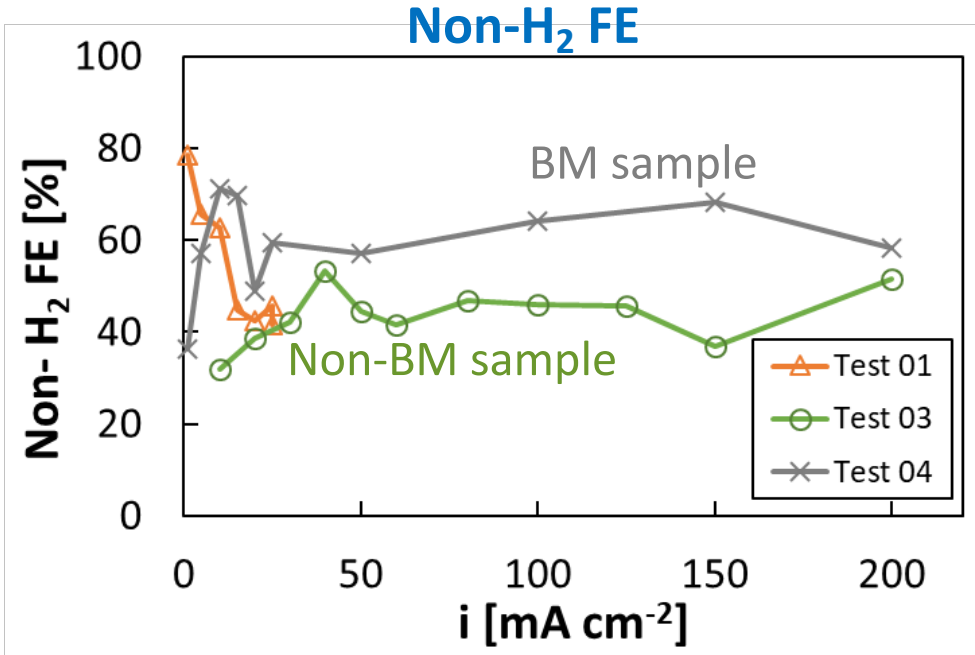
2020 Low temperature hard-templated solution synthesis:
N_2 BET surface area: **77 m^2/g**
PXRD crystallite size: ~33 nm
(Benchmarking RU underway)

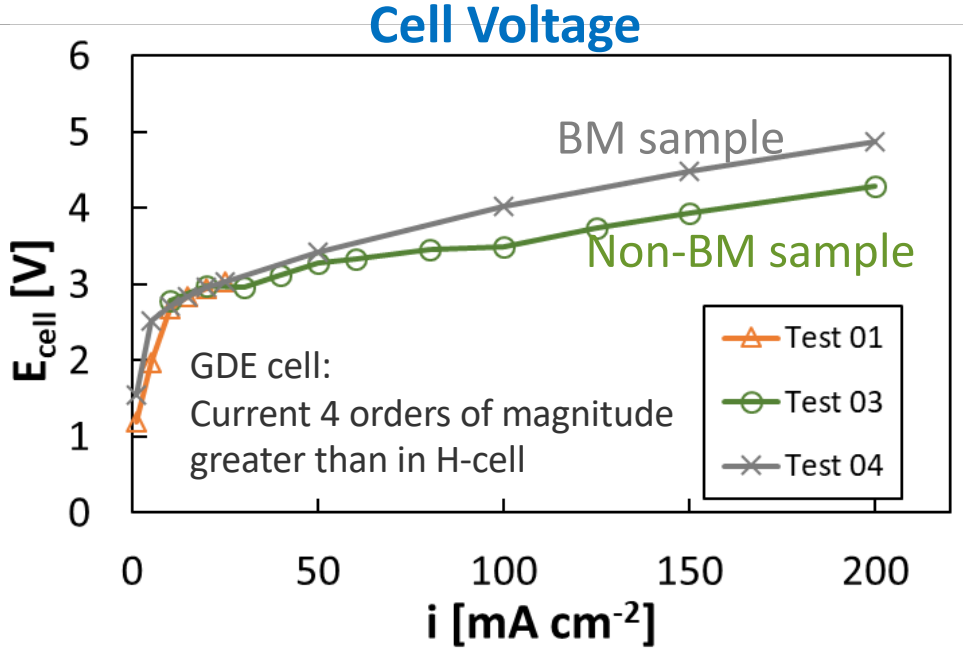
Rutgers University (RU):Charles Dismukes, Anders Laursen, Karin Calvinho, Yifei Li, Mahak Dhiman

Accomplishments and Progress

NREL benchmarking of Rutgers catalysts

Current focus area: manipulating CO_2 reduction product selectivity with catalysts and tuning their local environment
Challenge: increase energy efficiency by lower cell voltage via thinning/eliminating electrolyte layer
Testing conditions: Ni_2P (solid-state synthesis) nanoparticle catalysts – hand painted on Sigracet 39BC GDL 0.5 mg/cm^2, 0.4 M K_2SO_4 at 40 ml/min catholyte, CO_2 through flow field at 2 L/min, Ni foam anode, 1 M KOH at 50 ml/min anolyte, Fumasep FBM membrane, 60 ^oC





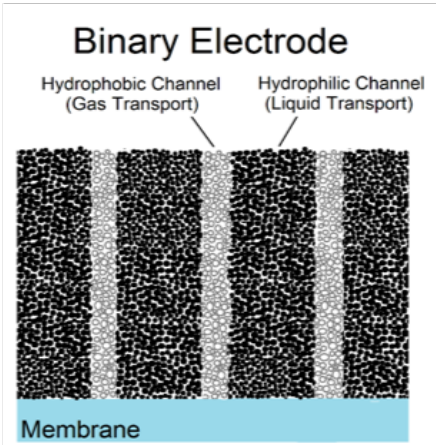
Ball-milled (BM) catalyst (Test 04) shows higher non-H_2 FE, and slightly higher cell voltage

Test#	Ball-milled?	I:C ratio
01	No	0.5
03	No	0.6
04	Yes	0.6

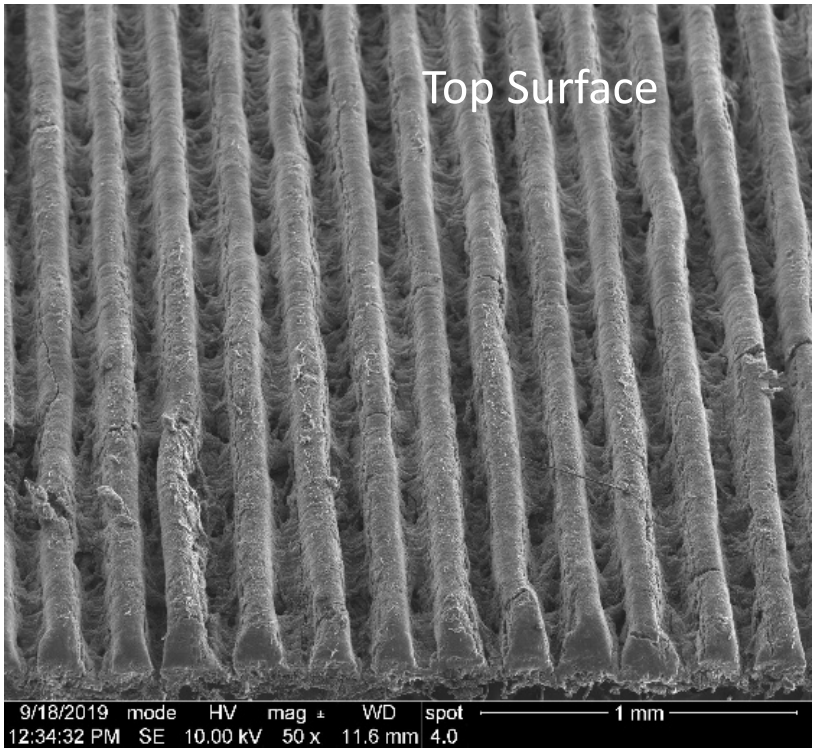
- While ball milling resulted in a decreased surface area - and therefore decreased currents at a fixed potential - the treatment also resulted in an increased CO_2 reduction product selectivity
- HPLC instrument difficulties have prevented liquid product analysis
- GC used to quantify H_2

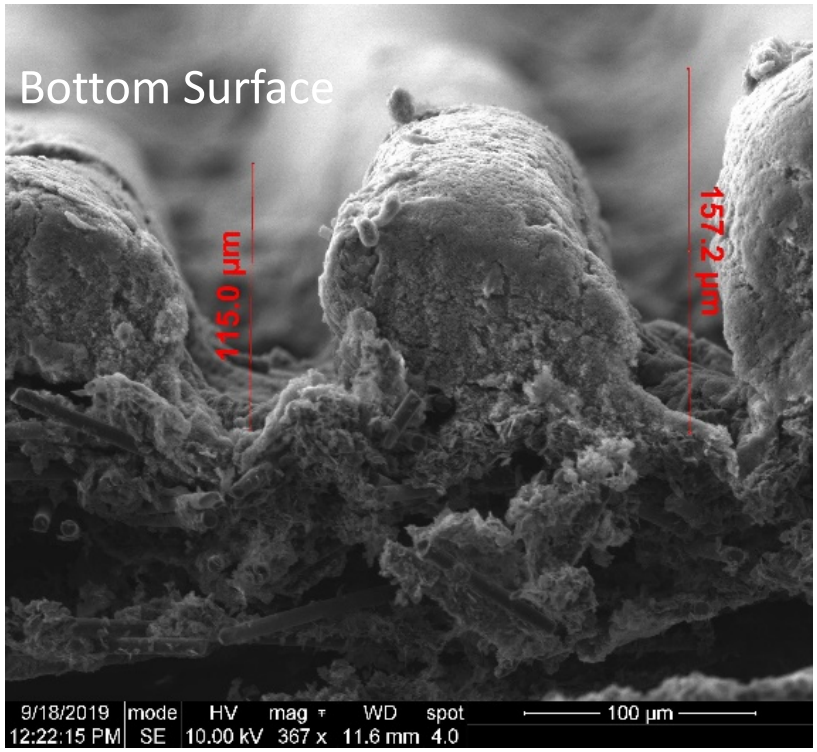
Yingying Chen, Ashlee Vise

Accomplishments and Progress: Los Alamos National Lab



- Prepared 100 µm tall hydrophobic MPL channel on carbon paper GDL (29BA)
- Some catalysts Ag/C deposited at LANL some at NREL



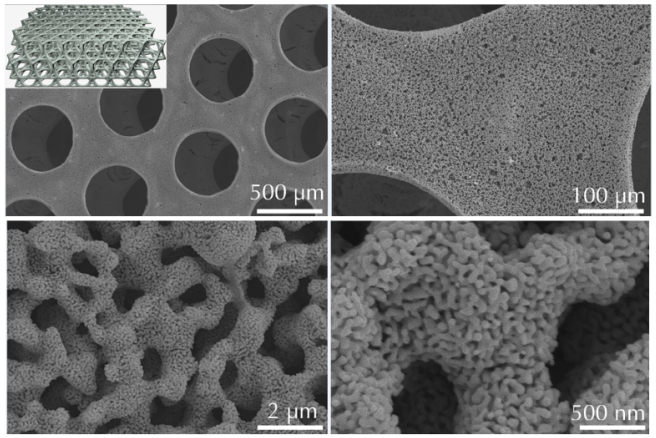


Aman Uddin, Tanvir Arman, and Jacob Spendelow

Accomplishments and Progress: Los Alamos National Lab

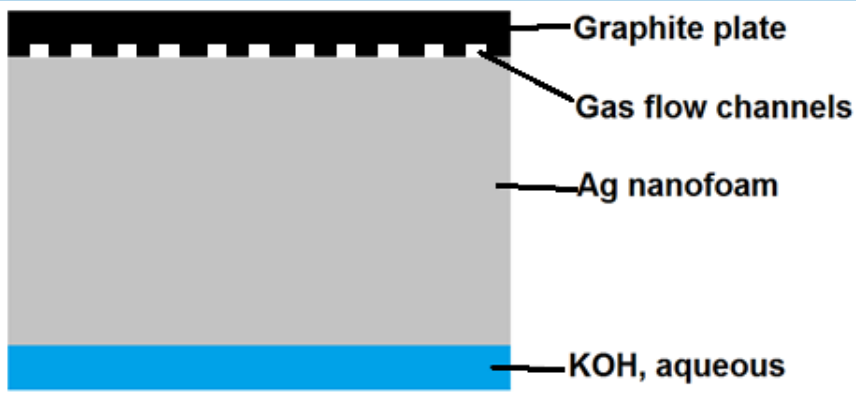
- 3D printed Ag nanofoam monolith that could serve both as electrode and flow field

Hierarchical Ag nanofoam

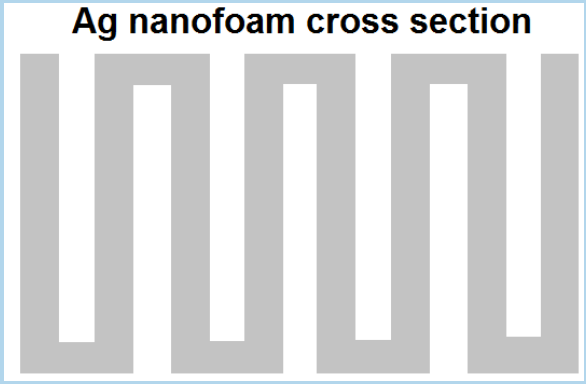


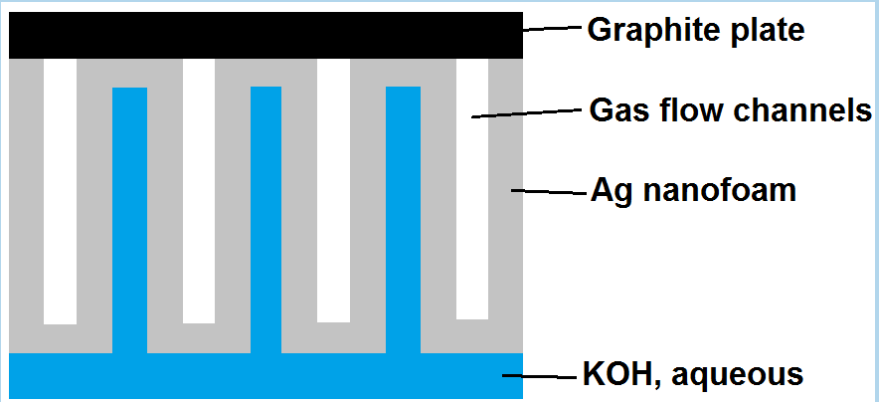
Initial approach: uniform Ag foam

Test various and thicknesses



Advanced approach: Ag foam as combined electrode and flowfield

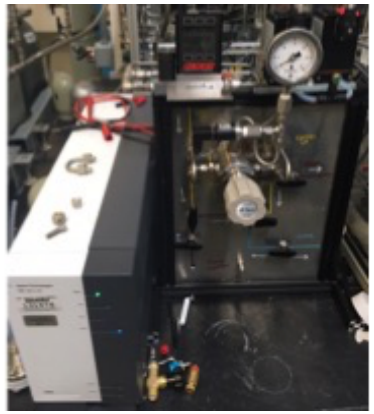




Aman Uddin, Tanvir Arman, and Jacob Spendelow

Accomplishments and Progress

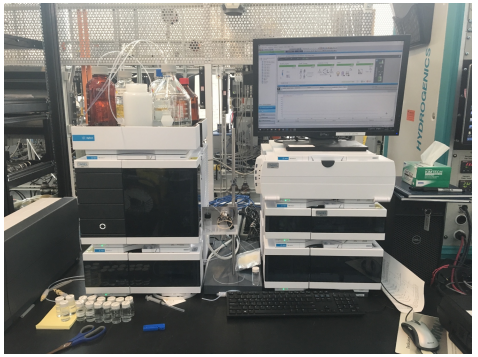
GC with sampling manifold



Designed and built world-class CO_2 test stands

- Anode and cathode can flow liquid (0-100 mL/min) or gas (0-4 SLPM)
- In-line automated gas sampling (two Agilent 490 MicroGCs)
  - H_2 , CO, CH_4, C_2H_4, CO_2
- HPLC with autosampler for liquid product analysis
- PEEK-PTFE backpressure (0-60 psig) regulators optimized for dual-phase flow
- Ambient to 85 °C operation
- Safety N_2 purge
- Flammable gas leak detection
- Enclosure ventilation exceeds NREL standard for chemical fume-hoods

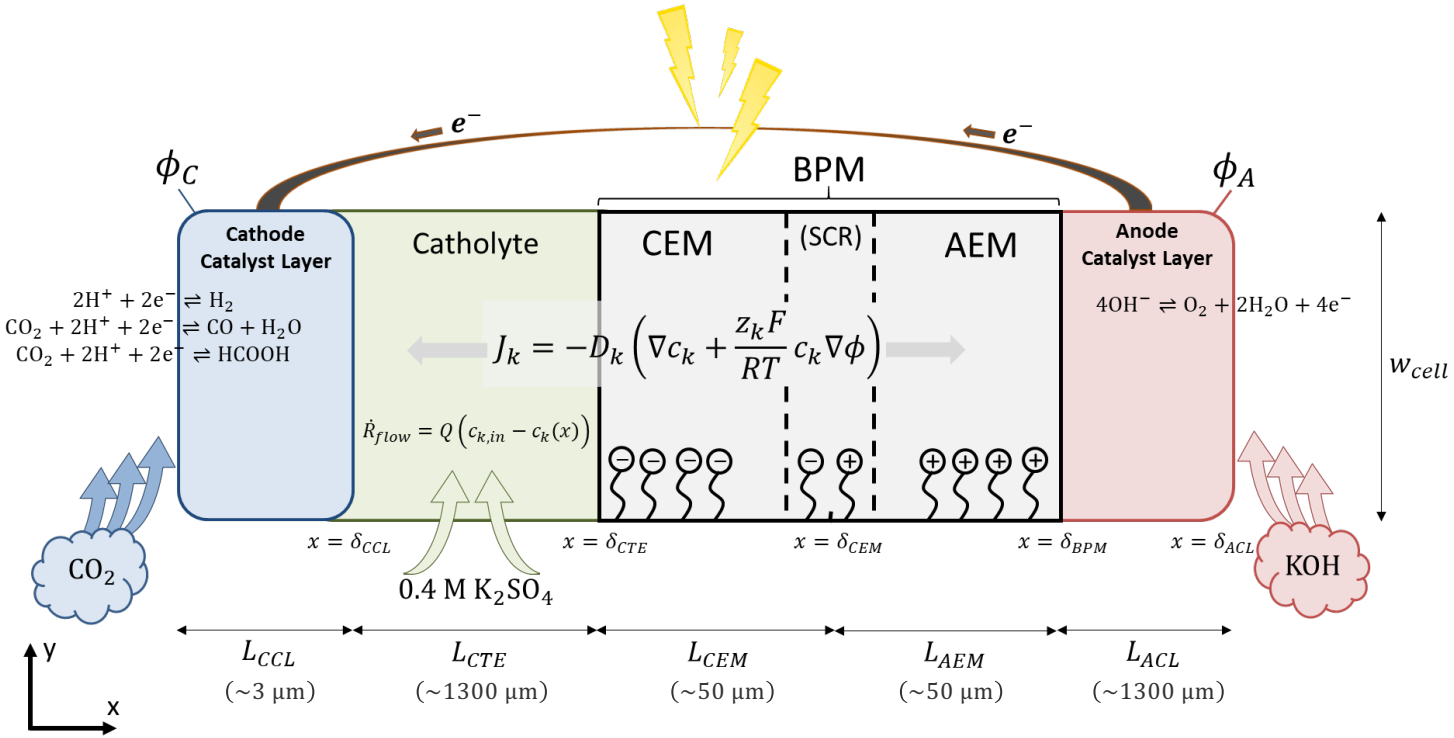
HPLC with autosampler



Ellis Klein

Accomplishments and Progress

Finite element coupled multi-physics (COMSOL) modeling of conditions at boundary layers in the CO_2 electrolysis cell



Species: $(8 + \phi)$

$H^+, OH^-, CO_2, K^+, SO_4^{2-}, HSO_4^-, CO_3^{2-}, HCO_3^-, \phi$

Reactions:

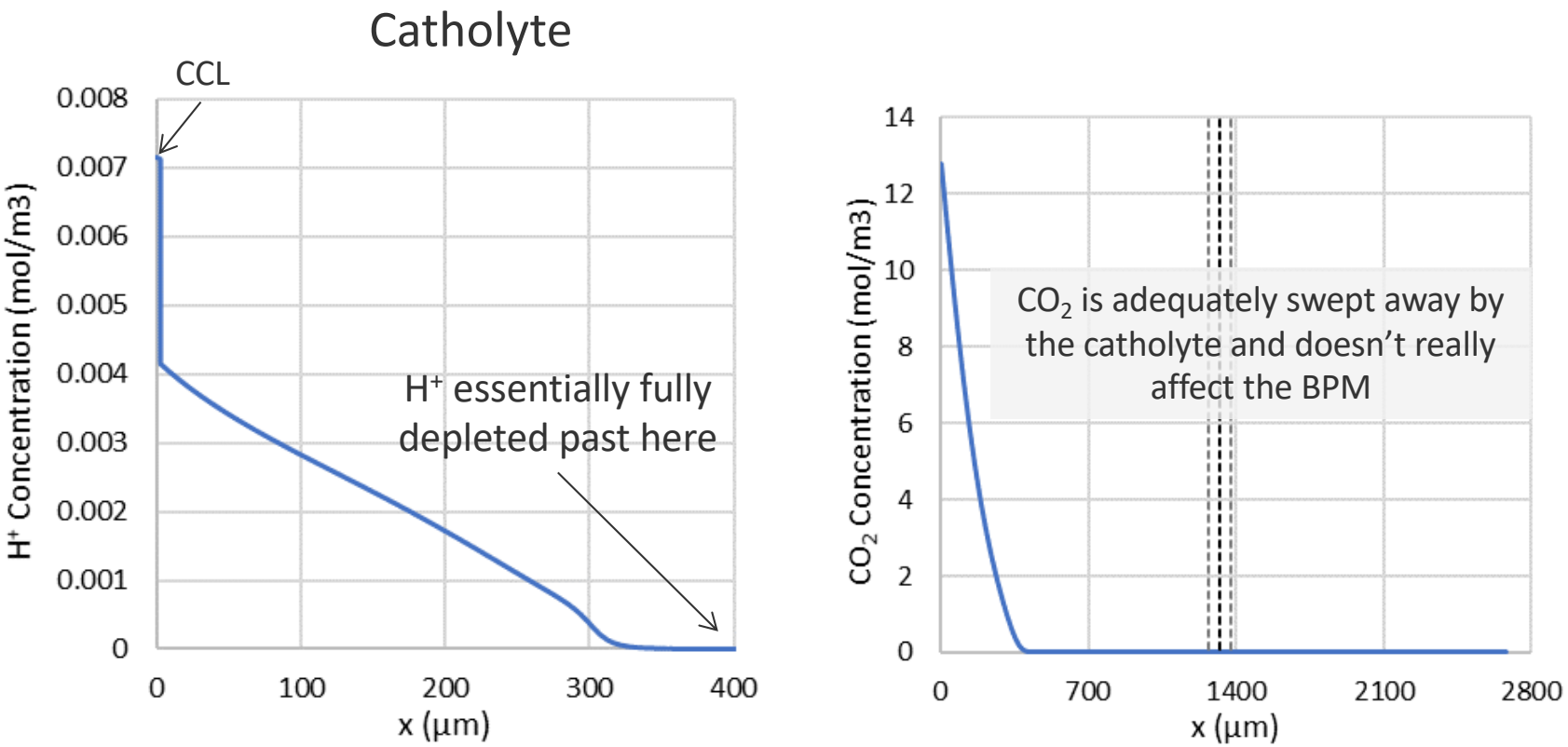
$$H_2O \rightleftharpoons H^+ + OH^-$$
$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$
$$CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$$
$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$$
$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$
$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O$$

Goal: understand the roles of mass transport of products and reactants, liquid water flow, electrochemical reaction kinetics, and charge and heat transfer on device performance. Ultimately, explain and predict the influence of CO2E component modifications on overall device performance

Jake Wrubel, Liam Witteman, Zhiwen Ma

Accomplishments and Progress

Modeling species distributions at open circuit



- Species distributions can be used to identify ideal reactor configurations
  - Proton concentrations are useful when designing the catholyte buffer layer thickness – maybe we don't need 1.27 mm
- Next modeling task: calculate concentration profiles under high current conditions and use results to further inform reactor geometry, dimensions, flow rates, etc.

Jake Wrubel, Liam Witteman, Zhiwen Ma

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- The project lacks industrial collaboration. In the absence of an industrial viewpoint, the team may develop technology that may not translate into industrial practice.
  - This is a lab call project and participation with outside entities is limited. We regularly engage with industry through unofficial channels for input on the relevance of our approach to their chemistry and processes.

- While the reuse of CO_2 may be impactful, it is difficult to determine the extent of the impact without a technoeconomic analysis. The analysis should compare the cost of producing the target products electrochemically versus thermochemically. Investigators should include the market size along with other relevant factors in their consideration.
  - Technoeconomic analysis is outside the scope of this project. However, this analysis has been recently published by our colleagues in the Bioenergy Science and Technology directorate at NREL.

    EnergyEnviron.Sci., 2020, **13**, 472–494.

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 CO_2 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 year 1)
  - 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

Future works

- Continue testing NiP and Cu catalysts targeting C-C products (C_2H_4, C_2H_5OH)
- Push for higher current densities without sacrificing selectivity, stability, or energy efficiency
  - Electrode development/morphology
  - Reactor hardware
  - Bipolar membrane improvements
  - Incorporate LANL's advanced electrode structures

Any proposed future work is subject to change based on funding levels

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

- Summary of current accomplishments
  - Have gotten to 500 mA/cm^2 (not shown)
  - 25 cm^2, leading the field in terms of scale
  - Starting from scratch, exceeded state of the art in 1 year
  - World-class capabilities established

Thank You

www.nrel.gov

NREL/PR-5900-76876

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.