
Industrially Scalable Waste CO₂ Reduction to Useful Chemicals and Fuels

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Overall Objectives

- Develop an electrochemical device that can convert carbon dioxide (CO₂) to fuels.
- Use a gas diffusion electrode (GDE) as the cathode to overcome mass transport limitations, allowing gas-phase CO₂ to be fed, to achieve current densities in the 100s of mA/cm².
- Invent new bipolar membranes (BPMs) and membrane architectures that are optimized for the unique operating conditions of a CO₂ electrolyzer.
- Evaluate the influence of various cathode electrocatalysts on CO₂ product selectivity.
- Integrate and evaluate each discrete component as part of the system to understand its complex interactions and role in process performance.

Fiscal Year (FY) 2019 Objectives

- Establish a gas-phase CO₂ electrolyzer device platform and protocols for evaluating promising catalysts at industrially relevant current densities.

- Fabricate BPMs from Nafion and NREL's proprietary perfluorinated anion exchange ionomer that have 3-D interfaces from dual electrospinning or other templated approaches.
- Develop a coupled multi-physics finite element model to explain and predict the influence of component modifications on CO₂ electrolyzer performance.
- Synthesize NiP catalysts that have demonstrated suppression of hydrogen and selectivity for conversion of CO₂ to liquid products (Rutgers).
- Develop a recipe for catalyst ink that is compatible with ultrasonic spray application to electrodes.
- Conduct NiCoFe synthesis and develop a recipe for catalyst ink for ultrasonic spray deposition in electrodes.

Technical Barriers

There are currently no codified technical barriers for CO₂ electrocatalytic conversion devices in the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.¹ This project addresses the following technical barriers for CO₂ electrolyzers:

- Stability under extended operation
- Scale or size of the active area of the membrane electrode assembly
- Product selectivity
- Energy efficiency
- Reactant and product crossover.

Technical Targets

This project is conducting studies on membrane, catalyst, and electrode design to develop CO₂ electrolyzers that, in the first year, meet the following targets:

- Current density: 150 mA/cm²

¹ <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

- Stability: 10 h of continuous operation at 150 mA/cm²
- Faradaic efficiency: Greater than 80% conversion to non-hydrogen products
- Device active area: 25 cm².

FY 2019 Accomplishments

- Demonstrated electrospun BPMs with water dissociation particles that had lower water dissociation resistance than commercially available BPMs, which led to better performance.
- Established a preliminary coupled multi-physics finite element model that is based on a

simple CO₂ electrolyzer that correlates mass transport of products and reactants, liquid water flow, electrochemical reaction kinetics, and charge and heat transfer to describe device performance.

- Established a CO₂ electrolyzer test stand with in situ electrochemical diagnostics and Faradaic efficiency analysis capabilities.
- Built and tested a CO₂ electrolyzer that integrated a BPM in a 25 cm² SnO₂ catalyst-loaded membrane electrode assembly that operated at over 150 mA/cm² for 10 hours with a Faradaic efficiency >80% to formate production.

INTRODUCTION

The goal of this project is to develop an electrochemical device that can convert CO₂ to fuels, like what the Haber-Bosch chemical process did for the nitrogen fixation reaction. Rudimentary CO₂ electrolyzers have been proven at a lab scale but need current densities to go from mA/cm² to A/cm² to be relevant.

A successful outcome would significantly improve the scalability of CO₂ electrolyzers while lowering the temperature and pressure of fuel synthesis reactors. This project is aligned with the H₂@Scale vision in which hydrogen is an enabler that can contribute to overall goals for energy security, resilience, and economic growth. Hydrogen is key to this concept, first as protons from water dissociation at the BPM interface, then as a charge carrier to balance the flow of renewable electrons, and eventually as the host of those renewable electrons in C-H bonds comprising an energy-dense fuel.

APPROACH

The first R&D challenge we plan to address is the mass transport task of getting a gaseous reactant to a solid/liquid interface at a high rate. We will use a GDE as the cathode (allowing gas-phase CO₂ to be fed) to achieve current densities in the 100s of mA/cm². The second main R&D challenge is developing new membranes and membrane architectures that are optimized for the unique conditions of a CO₂ electrolyzer. We plan to develop new BPMs tailored for such applications. The third major R&D challenge is the catalysts. For CO₂ reduction to become a scalable industrial process, product selectivity is needed. This can be done by controlling local reaction rates through judicious catalyst selection. The last major R&D challenge is the integration of all these components into a working device/process. It is necessary to evaluate each discrete component as part of the system to understand its complex interactions and role in process performance.

RESULTS

This year we made and tested a variety of BPMs to evaluate their ability to sustain high current densities. These initial experiments were four-electrode tests in which water electrolysis was performed at constant currents in 10 mA/cm² increments between a platinum anode and cathode while two reference electrodes monitored the potential drop between either side of the BPM. The compartment facing the anion exchange membrane was filled with 1 M KOH while the cation exchange membrane compartment contained a 1 M H₂SO₄ electrolyte. Good membrane performance is characterized by a low dependence of the potential difference on current density between the two sides of the BPM. Poor water dissociation at the BPM interface is often blamed for increasing the potential drop across the BPM. Application of water dissociation catalysts to the BPM interface can enhance the water dissociation rate and reduce the potential drop. This effect has been observed by others in planar or 3-D BPM junctions. We tested two configurations: first by spraying graphene oxide particles onto a 2-D planar interface, and second by introducing graphene oxide particles to the electrospinning ionomer precursors to yield anion exchange membrane and cation exchange membrane

nanofibers with a coating of catalytic particles. We compared our BPMs to the commercially available standard, Fumasep FBM, to observe how catalyst application and enhancement of the interfacial area influenced performance under electrolysis conditions. It is clear that an uncatalyzed interface, made by simply pressing an anion exchange membrane and cation exchange membrane, leads to huge potential losses across the BPM compared to the Fumasep FBM. An uncatalyzed 3-D electrospun interface appears to have a similar effect as introducing catalyst to a planar BPM interface (Figure 1 left). Two different loadings of catalysts were tested in the planar configuration: $2D = 0.002 \text{ mg/cm}^2$ and $0.2 = 0.2 \text{ mg/cm}^2$, with the latter having performance close to that of Fumasep FBM, for which the catalyst loading is unknown (Figure 1 right). The catalyzed 3-D junction exhibits a performance similar to that of the Fumasep and catalyzed 2-D BPMs; however, the open-circuit voltage is offset compared to the planar form factors. We believe this is due to co-ion crossover, which we plan to further investigate.

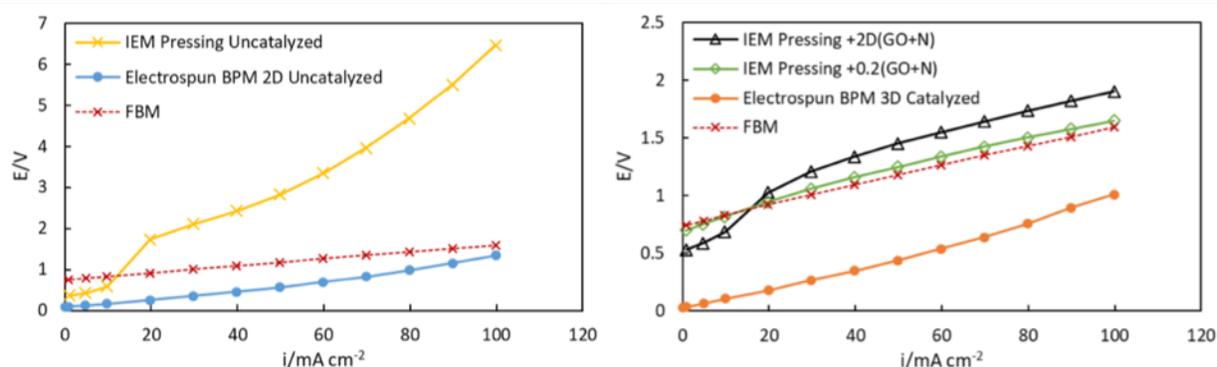


Figure 1. BPM potential drop under conditions of water electrolysis. The chart on the left shows an uncatalyzed BPM compared with Fumasep FBM and an uncatalyzed electrospun BPM junction. The chart on the right demonstrates that the introduction of 0.002 mg/cm^2 graphene oxide catalyst to the 2-D interface (black) can improve the performance, while 0.2 mg/cm^2 loading (green) yields performance similar to that of Fumasep FBM (red). The catalyzed 3-D junction (orange) exhibits performance similar to that of Fumasep FBM with a voltage offset.

We developed a recipe to integrate CO_2 reduction catalyst into GDEs. Based on our experience with fuel cell and electrolyzer electrodes, we inferred a formulation and procedure for putting SnO_2 nanoparticles on a GDE to serve as the cathode to reduce CO_2 to formate. First, we tried testing without a cathode buffer layer between the BPM and SnO_2 -loaded electrode but found very low CO_2 conversion rates. With this understanding, we tested a few different electrolytes to encourage the CO_2 reduction reaction at the cathode and suppress the hydrogen evolution reaction. We found that K_2CO_3 and KOH (both 0.5 M) led to near immediate failure via delamination of our BPMs. We did not observe this detrimental effect using $0.5 \text{ M K}_2\text{SO}_4$ as our catholyte, and this electrolyte allowed us to achieve high rates of conversion to formate. The water oxidation reaction was performed on nickel foam with flowing 1 M KOH . We used this configuration—flowing $0.5 \text{ M K}_2\text{SO}_4$ catholyte—for optimizing CO_2 electrolyzer performance and to meet the criteria in our go/no-go decision. Utilizing our CO_2 test stands we optimized the catalyst loading with respect to Faradaic efficiency and found 0.5 mg/cm^2 of SnO_2 nanoparticles yielded the highest conversion rate of CO_2 to formate. This level of catalyst loading was used to run the CO_2 electrolyzer for 11 hours at a constant current density of 150 mA/cm^2 while measuring the Faradaic efficiency over the duration of the run (Figure 2).

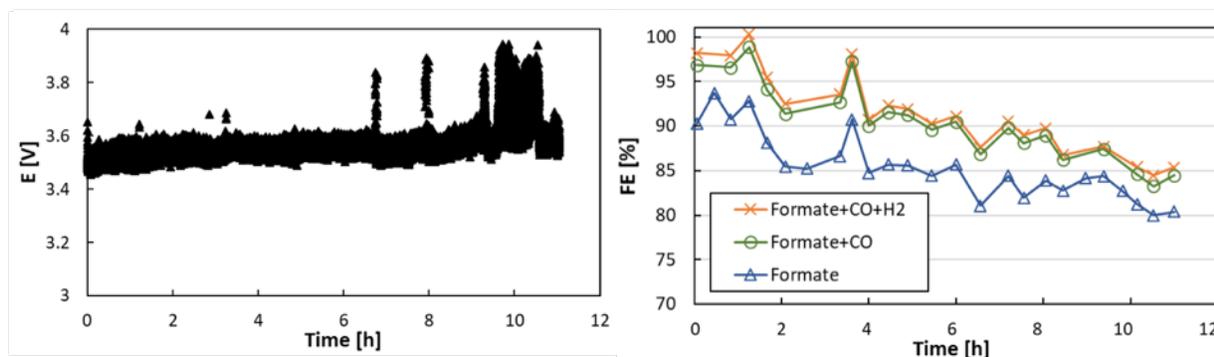


Figure 2. The left panel shows the cell voltage necessary to maintain 150 mA/cm^2 over the 11 hours of testing the SnO_2 -loaded 25-cm^2 membrane electrode assembly. The right panel shows the Faradaic efficiency (FE) to various products over the duration of the test.

CONCLUSIONS AND UPCOMING ACTIVITIES

This project made good progress in FY 2019 and achieved rather aggressive performance targets for a CO_2 electrolyzer. This upcoming year we will focus on making carbon-carbon bonds by incorporating copper catalysts in the cathode. We will also focus on simultaneously increasing the active area to 100 cm^2 , durability to 100 hours, and current density to 500 mA/cm^2 .

FY 2019 PUBLICATIONS/PRESENTATIONS

1. Todd Deutsch, “Electrocatalytic Reduction of CO_2 in Gas-Phase Electrolyzers: Moving Towards a Relevant Use of CO_2 ,” Invited talk presented at the 235th Electrochemical Society (ECS) Meeting, Dallas, TX, May 30, 2019.