

# Electrocatalytic Reduction of CO<sub>2</sub> using Flow Cells with Gas Diffusion Electrodes

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**NREL's electrospinning system**

Diagram showing the electrospinning setup with components: Power Supply, AEM Junction, CEM, CL, GDL, Anode, and Cathode. Chemical reactions are shown:  $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$  at the anode and  $2H^+ + 2e^- \rightarrow H_2$  at the cathode. Water dissociation is also shown:  $2H_2O \leftrightarrow H_3O^+ + OH^-$ .

Photo of the Sonotek spray nozzle on top of the electrospinner drum.

**Sonotek spray nozzle on top of electrospinner drum**

Chemical structures for NREL's GEN 2 PFAEM - Perfluoroalkyl polymer and catalysts: Pt/C, Pt/C@G, Pt/C@GO, Pt/C@G@GO, Pt/C@G@GO@Pt/C, Pt/C@G@GO@Pt/C@G@GO@Pt/C.

Graph of EMV vs. i [mA/cm<sup>2</sup>] for various membranes: 2D BPM, 3D DC, 3D AC, 3D BC, 3D CD, 3D DE, 3D EF, 3D FG, 3D GH, 3D HI, 3D IJ, 3D JK, 3D LM, 3D NO, 3D OP, 3D PQ, 3D RS, 3D TU, 3D VW, 3D XY, 3D Z.

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## Bipolar membrane development

- Bipolar membranes (BPMs) prevent CO<sub>2</sub> (CO<sub>3</sub><sup>2-</sup>) and product crossover in CO<sub>2</sub> electrolyzers.
- BPMs maintain pH gradient permitting water oxidation to occur in alkaline environment where earth-abundant electrocatalysts can be used.
- Dual fiber electrospinning of NaFion and PFAEM results in a 3D interface that has higher mechanical stability and lower area specific resistance (better performance) than a 2D BPM
- Adding catalysts, like graphene oxide, to BPM interface lowers water dissociation resistance
- Electrospinning is a versatile platform that enables fabrication of an array of membrane architectures

## Component fabrication & device testing

Workflow from Powders to Mass Production:

- Powders:** Material Synthesis: Catalyst & Membrane Development
- MEA integration:** Coating, Spraying, Painting, Electrospinning, Lamination, Hot Press Transfer, Edge protection
- Performance Evaluation:** In-situ Diagnostics, PEMFC, AEMFC, Electrolyzer: Single Cell, Stacks, Spatial
- Roll-to-roll manufacturing:** Micro-gravure coating, Slot die coating
- Manufacturing Lab:** QC Diagnostic Development, Areal characterization, Roll-to-roll demonstration
- Electrochemical Characterization:** RDE & RRDE stations for Mass & Specific Activity, ECA, ORR; EQCM, Seiras

Graphs showing NECA, P/LC, Transport Phenomena, PGM-free, and KC Neyerlin's work.

- NREL's Energy Systems Integration Facility (ESIF) houses capabilities that span multiple scales and levels of integration – from materials synthesis to systems testing
- Over a decade of research in hydrogen fuel cells and water electrolysis systems has established an expertise and understanding needed to accelerate CO<sub>2</sub> electrolyzer development
- Techniques used to measure, model, and elucidate transport phenomena in gas diffusion electrodes in fuel cells can be applied to CO<sub>2</sub> electrocatalysis
- In-situ electrochemical diagnostics on devices that span mW - kW

**Designed and built world-class CO<sub>2</sub> 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) for H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, CO<sub>2</sub>
- HPLC with autosampler for liquid product analysis
- PEEK/PTFE backpressure (0-50 psig) regulators optimized for dual-phase flow
- Ambient to 85° C operation
- Safety N<sub>2</sub> purge
- Flammable gas leak detection
- Enclosure ventilation exceeds NREL standard for chemical fume-hoods

Specifications: Gas Delivery MFC's (5x humidified, 500 sccm to 3.5 sccm, 1x not humidified, expandable to 18 total), 8 PID Heater Control Loops, 4 PID Process Control Loops (pressure), Combustible Gas and CO Detection, Ventilated Enclosure (Toxic fume bottle storage), 8 Separate I/O channels (Both Digital/Analog), Add sensors/valves/peripherals with minimal effort, Online MicroGC (H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, CO<sub>2</sub>), On-line calibrations, 10 Channel stream selection.

Ellis Klein, Guido Bender

## CO<sub>2</sub> electrolysis test stands

- Testing CO<sub>2</sub> electrolyzers has more complex product analysis requirements than are needed for water electrolysis
- No commercially available test stands for CO<sub>2</sub> devices
- Experience gained from building and maintaining over a dozen fuel cell and water electrolysis test stands applied to design and assemble CO<sub>2</sub> electrolysis test stands
- Highly automated operation and on-line product analysis
- Standardized test bed to reproducibly evaluate and benchmark promising CO<sub>2</sub> reduction catalysts under conditions relevant to upscaling

Diagram of the CO<sub>2</sub> electrolysis cell with anode, BPM, and cathode. Predominant reaction of CO<sub>2</sub> = HCOOH, CO.

Graphs showing FE [%] vs. Time [h] for Formate+CO and Formate, and Voltage [V] vs. Current Density [A/cm<sup>2</sup>] for CSnOv032 (Sn32-Initial and Sn32-After 10 hrs).

Cell specifications: Anode (Temperature: 60 °C, Active area: 25 cm<sup>2</sup>), Cathode (Ni foam in 1 M KOH), BPM (2D BPM = Nafion+graphene oxide+AEM, FumaSep FBM), Faradaic Efficiency (HPLC for liquid product identification and quantification, GC for gas phase products).

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## Preliminary results: Formate

- Go/No-Go Milestone: "Demonstrate a CO<sub>2</sub> electrolyzer that has an area of 25 cm<sup>2</sup> and integrates a BPM with a catalyst-loaded MEA that can operate at over 150 mA/cm<sup>2</sup> for 10 hours with FE >80% non-hydrogen products"
- Targeted formate as the CO<sub>2</sub> reduction product for integration with biological upgrading to higher value products
- Hydrogen is the primary product without catholyte
- Starting to incorporate NiP<sub>2</sub> and Cu catalyst in cathode to achieve C-C products