CO_2 Reduction and Upgrading for e-Fuels Consortium

U.S. DEPARTMENT OF ENERGY

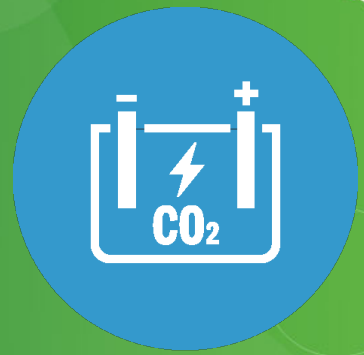
DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Efficient Scalable CO_2 Reduction to Formate (CO_2 Electrolysis)

2.3.4.301

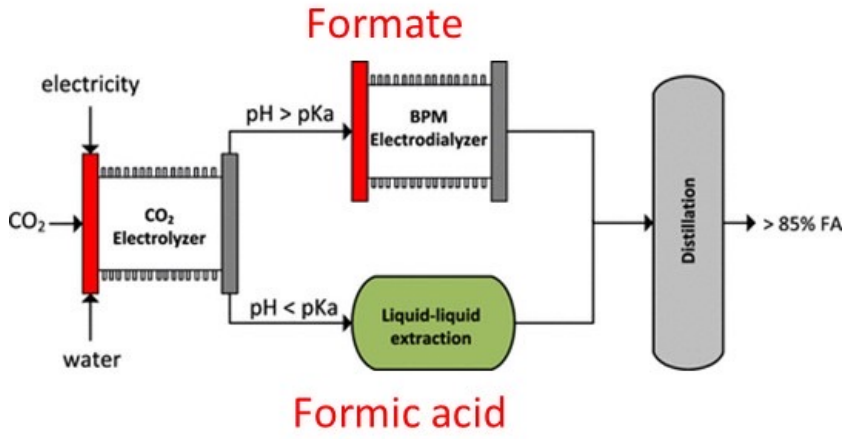
PI – K.C. Neyerlin (NREL)

4-6-2023



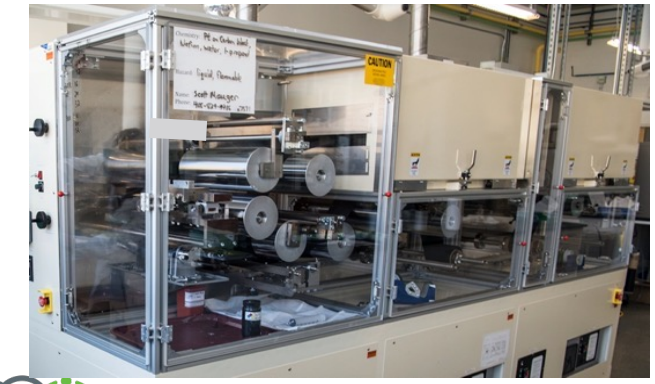
Project Overview

- Produce formate/formic acid utilizing scalable manufacturing and electrochemical processes and components that integrate into current and future infrastructure while enabling durable operation at high current density.

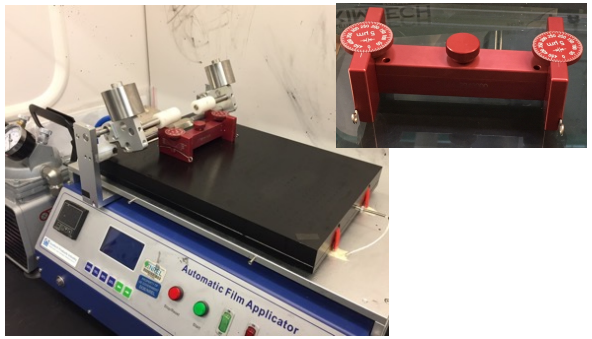


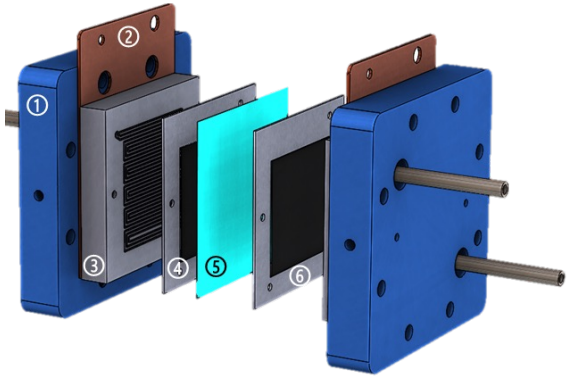
>200 cm^2 cell stacks

Roll-to-Roll (R2R)



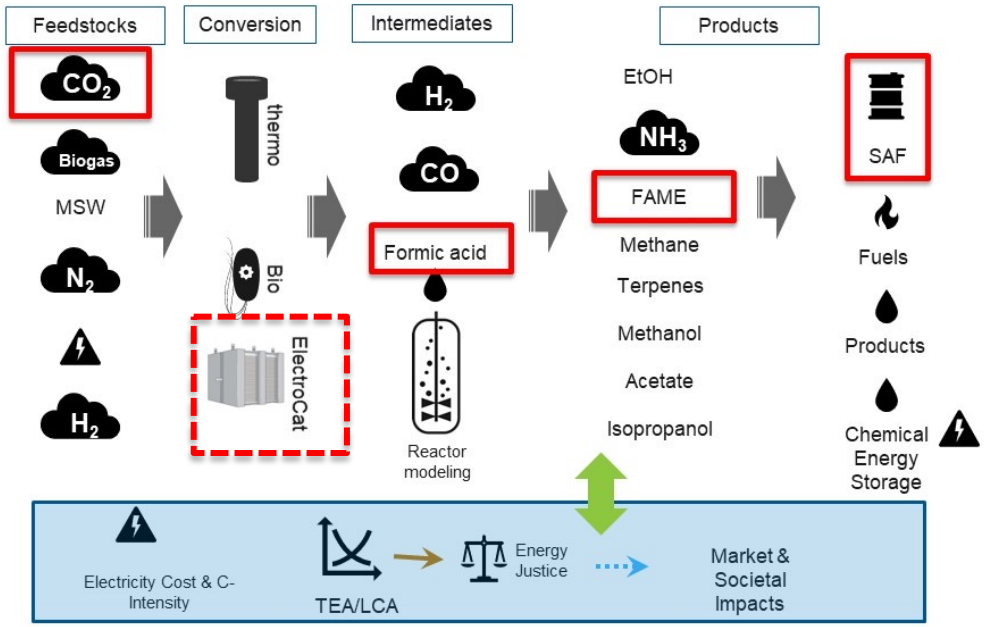
Automatic Film Applicator





25 cm^2 cells

Project Overview



- Need to consider impact of electrolyzer design and product(s) on downstream processes
- Overall cost dependent on product type as well as current density, cell voltage and FE
- Direct FA production only cost competitive at low cell voltages
- <u>None of this matters without durability</u>

Project Overview

Milestone Name/Description	Criteria	End Date	Type
TEA connection	Joint with WBS#2.1.0.506 and WBS#2.1.0.507 to complete baseline TEA from CO2 to formate (or formic acid) and provide a summary of analysis findings to assist upcoming R&D activities.	12/31/2022	QPMR
Biological handoff	Joint with WBS# 2.3.2.121 collect formate/formic acid effluent to be utilize for subsequent biological conversion. Target conditions that approach the 7M formic acid concentrations required for subsequent utilization by bacteria. Current level of production yields 0.08 M formic acid.	12/31/2022	QPMR
Durability/ Energy Efficiency	For membrane electrode assembly architectures demonstrate improved FE retention over catholyte-free baseline for 10 hrs utilizing at least a 25 cm^2 area cell operating at $\geq$ 200 mA/cm^2. Starting FE should be >70%. Provide a breakdown of voltage improvements associated with novel device development.	3/31/2022	QPMR
Durability interrogation	For at least a 25 cm2 cell having operated for at least 10 hrs at $\geq$ 200 mA/cm^2, apply electrochemical diagnostics and microscopy (e.g. TEM) to elucidate the degradation of electrochemical interfaces and catalyst particles with and without a catalyst support. Characterization should include elucidation of particle mobilization to the membrane and resulting electrode particle size distributions.	6/30/2022	QPMR
Incorporation of non-oxidizing anode catalyst from ANL	Incorporate anode electrocatalysts (developed within this project) that have previously demonstrated the ability to mitigate oxidation of formate/formic acid, into at least a 25 cm^2 device. Demonstrate enhanced recovery of formate/formic acid over baseline configurations while operating at 200 mA/cm^2.	9/30/2022	Annual

Name/Description	Criteria	Date	
Scaleup	For at least a 50 cm^2 active area cell at $\geq$ 200 mA/cm^2 demonstrate improved at least 70% FE to formate for 50 hrs.	3/31/2023	Go/no-go

1. Approach

- Develop electrochemical diagnostics and models to assess current SOA for electrochemical production of formate/formic acid and inform device design
- **Start with commercially available materials (catalysts/membranes/ionomers) to glean information with scalable and reproducible results**
- Utilize $\geq$25 cm^2 cells for testing (akin to fuel cells and H_2 electrolysis) to facilitate scale up
- **Initiate material integration using methods that project towards R2R processes**
- Understand failure modes and mitigate with **both engineering and material solutions**
- Provide scalable platforms in parallel with **characterization/mitigation**

1. Approach - Project Team and Responsibilities

- Scalable processes and components that integrate into current and future infrastructure while enabling durable operation at high current density.

NREL (Transforming ENERGY)

- Modeling
- Electrode Integration
- Device development
- Ink formulation and coating translation
- Durability studies
- Coordination with consortium efforts

(e.g. TEA, biological conversion, larger durability efforts)

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Leiming Hu
Jacob Wrubel
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Prantik Saha
Kun Lou
Wilson Smith
Tim Van Cleve
Fry Intia
Ellis Klein
Holly Gadpaille
Cole Delery

Argonne NATIONAL LABORATORY

- Development of electrocatalysts that limit anodic formic acid oxidation
- Characterization using X-ray scattering to inform degradation processes
- Catalyst development for alternative oxidation processes
- Automation of high-throughput synthesis

Deborah Myers
Magali Ferrandon
Ahmed A. Farghaly
Xiaoping Wang

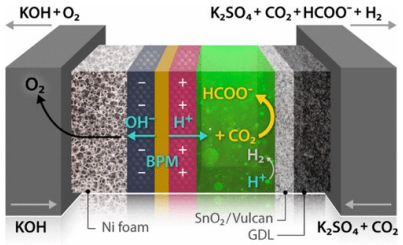
Oak Ridge National Laboratory

- Characterization of catalyst, electrode and membrane through microscopy

Dave Cullen

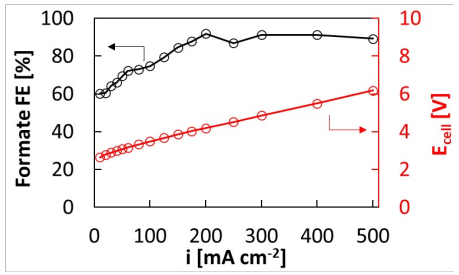
1. Approach - Electrochemical Options

BPM w/ Catholyte [1]

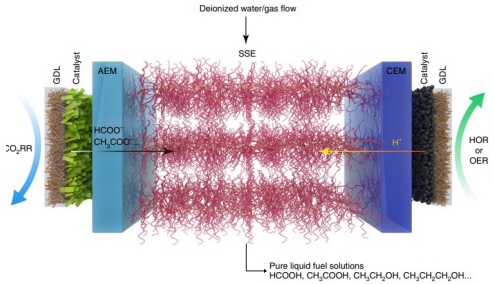


- Low energy efficiency
- Durability issues with gas/liquid interface
- Low formate concentrations
- BPM degradation

+ High potential CO_2 utilization



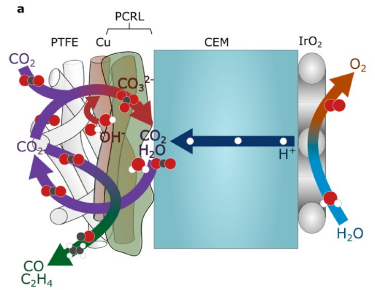
BPM w/ Solid Electrolyte [2]



- Low energy efficiency (OER)
- Ir on anode (OER)
- Yet to be proven at scale
- Additional material requirements

+ High potential CO_2 utilization
+ Concentrated formic acid production
+ Low cell voltage when combined with HOR

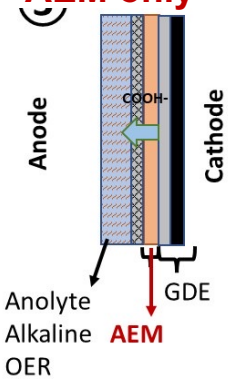
CEM w/ AEM overlayer [3]



- Requires Ir on anode (OER)
- Complex design,
- High formic acid concentrations could affect durability at scale

+ High potential CO_2 utilization
+ Potentially concentrated formic acid production
+ Low cell voltage when combined with HOR
+ CEMs a known commodity

AEM only



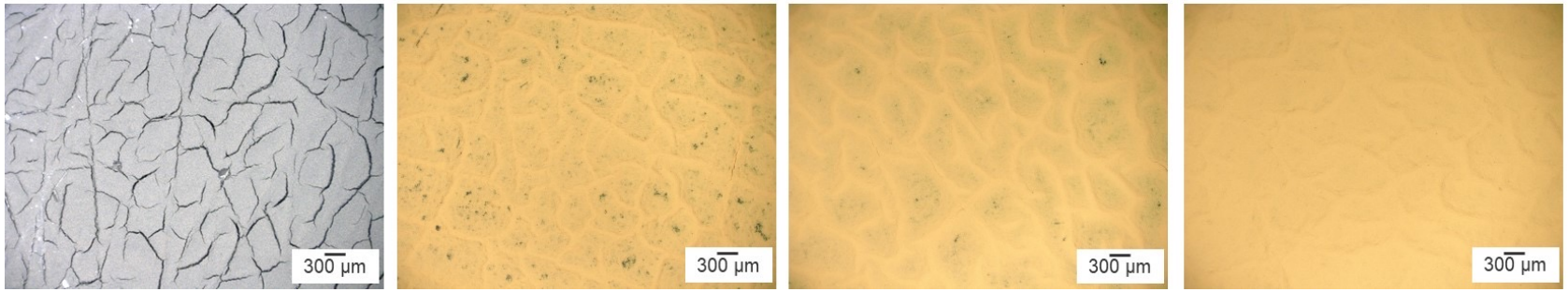
- Low CO_2 utilization
- Salt formation and instability
- Possible product oxidation

+ Simple design
+ No precious metal use

- ➢ In order to couple with biological processes concentrated formic acid is desired
- ➢ Operational robustness/durability is the limitation
- ➢ Need to consider complexity of design

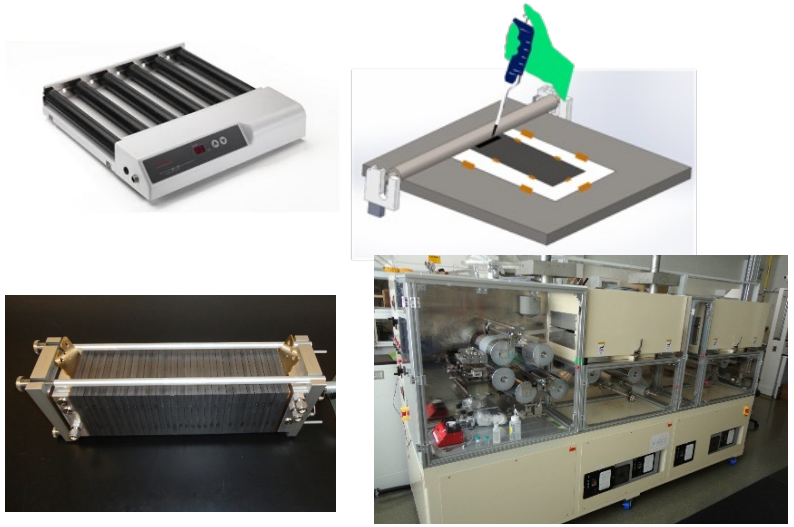
[1] Chen Y, Vise A, Klein W E, et al. ACS Energy Letters, 2020, 5(6): 1825-1833.
[2] Xia C, Zhu P, Jiang Q, et al. Nature Energy, 2019, 4(9): 776-785.
[3] O'Brien C P, Miao R K, Liu S, et al. ACS Energy Letters, 2021, 6(8): 2952-2959.

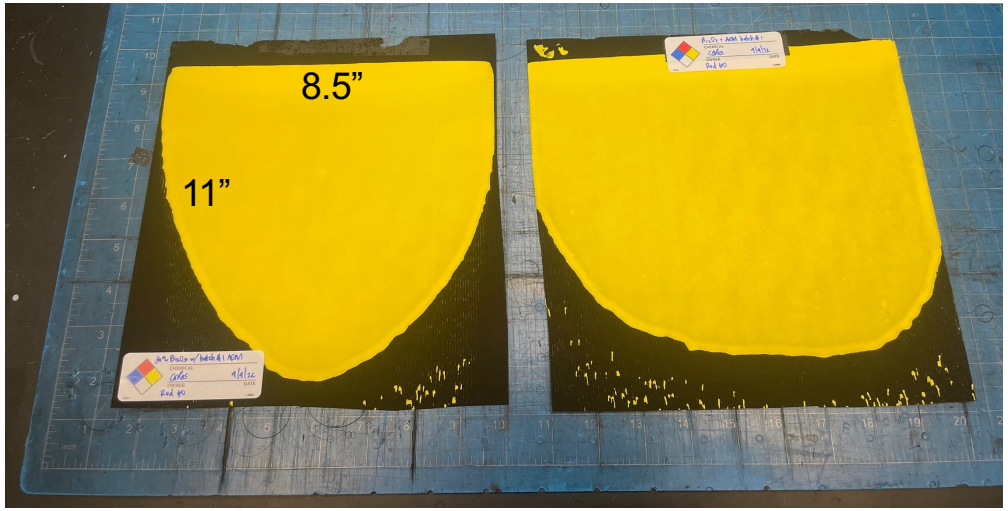
2. Progress – Scalable Electrode Fabrication



Cracked MPL/substrate

➢ Ink formulation and processing effect catalyst coatability





2. Progress and Outcomes (Modeling)

➢ Nernst-Planck Poisson Model

Governing Equations

Species Conservation:

$$\frac{\partial c_k}{\partial t} = -\frac{\partial}{\partial x}(J_k) + \dot{R}_k$$

Species Flux:

$$J_k = -D_k\left(\frac{\partial c_k}{\partial x} + \frac{z_k F}{RT} c_k \frac{d\phi}{dx}\right)$$

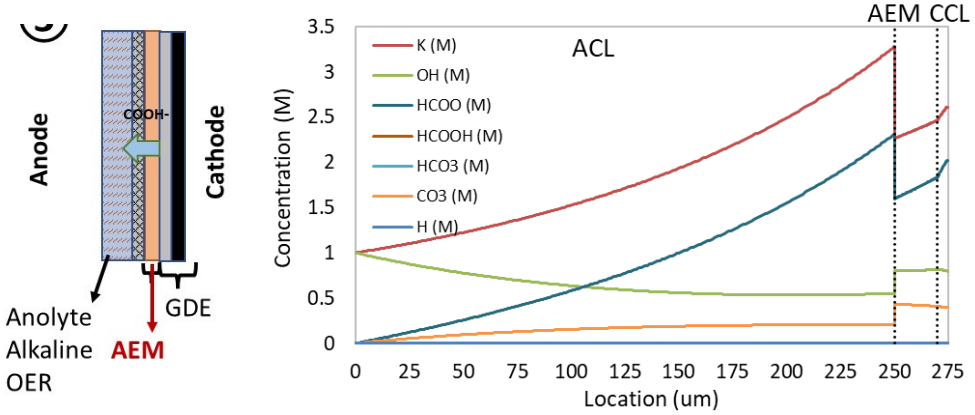
Potential (in ion-conducting phases):

$$\frac{d^2\phi}{dx^2} = -\frac{F}{\varepsilon}\sum_k z_k c_k$$

where k = $CO_{2(aq)}$, H^+, OH^-, HCO_3^-, CO_3^{2-}, $HCOO^-$, HCOOH, K^+

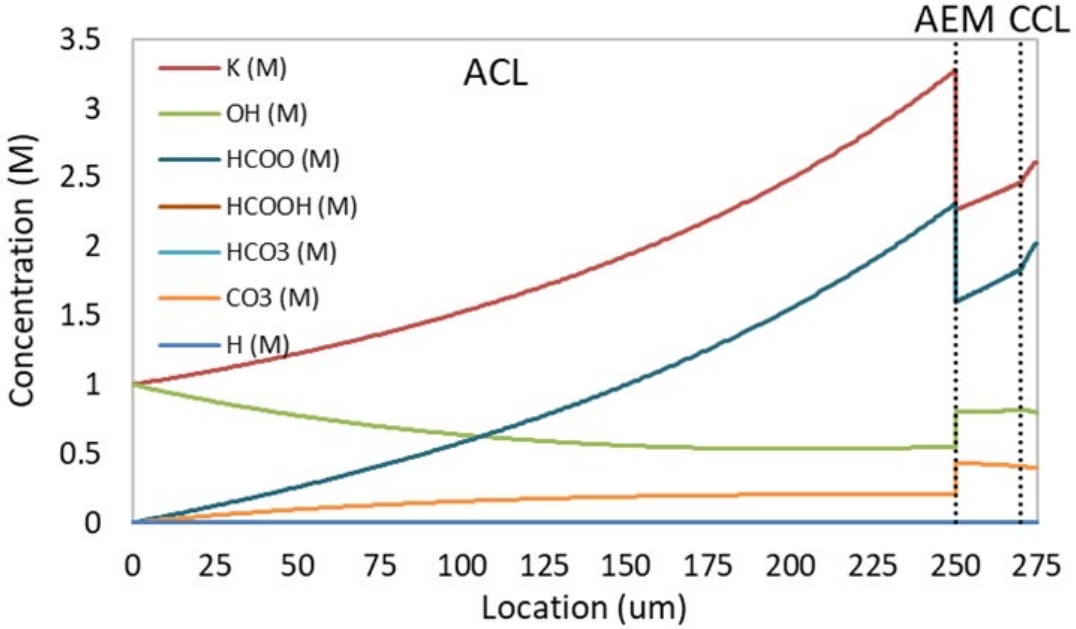
➢ 1-D (AEM example)

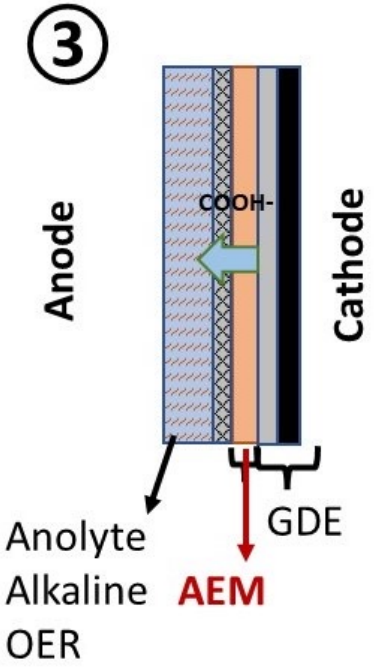
Chemical Reactions	
$CO_{2(aq)} + H_2O \rightleftharpoons H^+ + HCO_3^-$	$HCO_3^- + OH^- \rightleftharpoons H_2O + CO_3^{2-}$
$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$HCOOH \rightleftharpoons H^+ + HCOO^-$
$CO_{2(aq)} + OH^- \rightleftharpoons HCO_3^-$	$H_2O \rightleftharpoons H^+ + OH^-$
Electrochemical Reactions	
Cathode	Anode
$2H^+ + 2e^- \rightleftharpoons H_2$	$2OH^- \rightleftharpoons H_2O + 2e^- + 1/2\,O_2$
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	$\mathbf{HCOOH \rightleftharpoons CO_2 + 2H^+ + 2e^-}$
$CO_{2(aq)} + 2HCO_3^- + 2e^- \rightleftharpoons CO + H_2O + 2CO_3^{2-}$	
$CO_{2(aq)} + H_2O + 2e^- \rightleftharpoons HCOO^- + OH^-$	

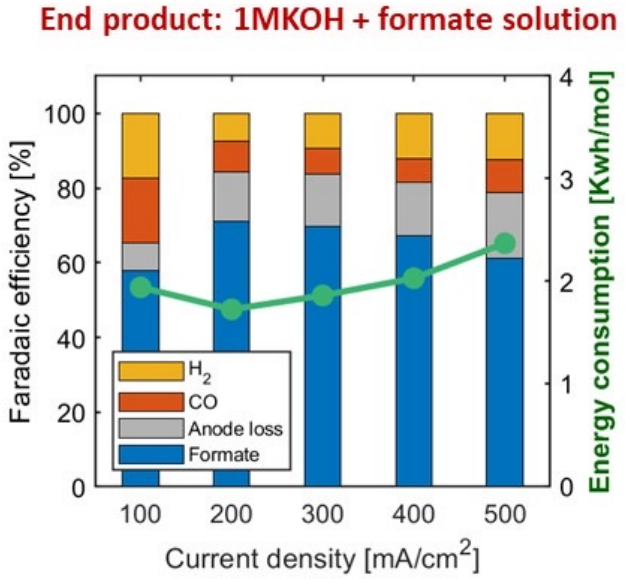


- Thin AEM architecture (with anolyte) can result in low voltages and high FE to formate
- Formate produced remains in anion form ($HCOO^-$) and collects on the anode

2. Progress and Outcomes





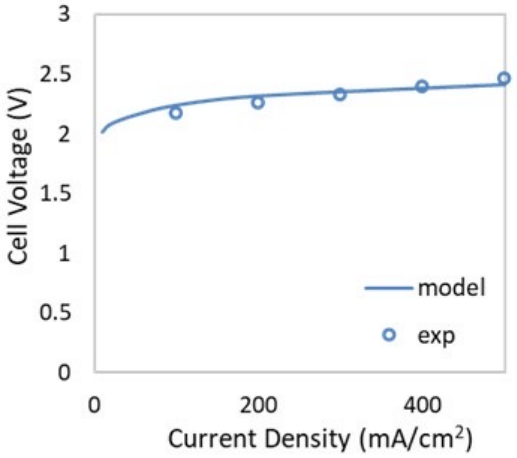


Thin AEM architecture (with anolyte) can result in low voltages and high FE to formate

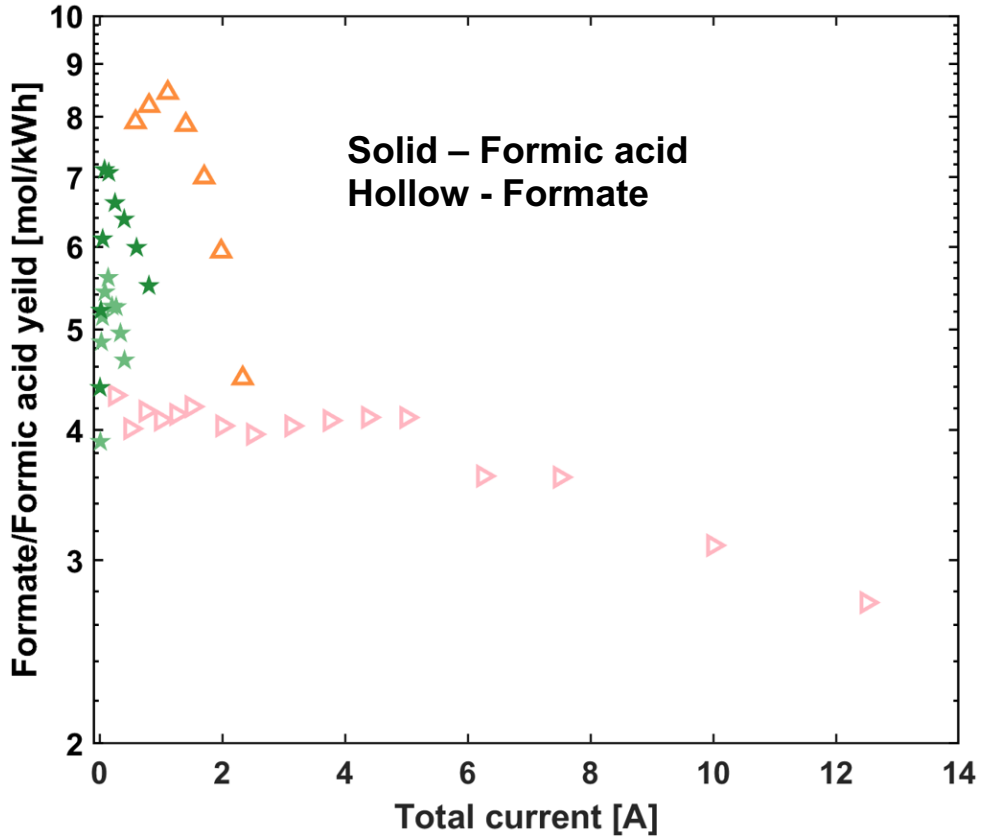
- **Apparent oxidation of formate at anode due to high OER potentials**

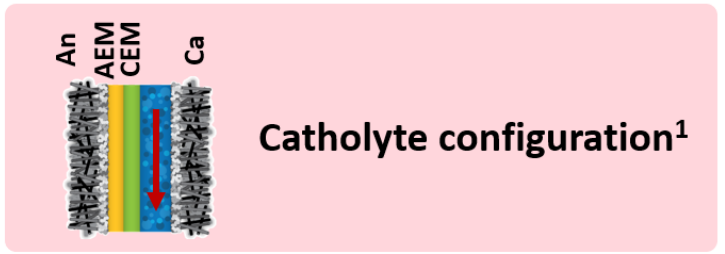
Formate produced remains in anion form ($HCOO^-$)

- **No way to produce HCOOH with this setup alone**



2. Progress and Outcomes

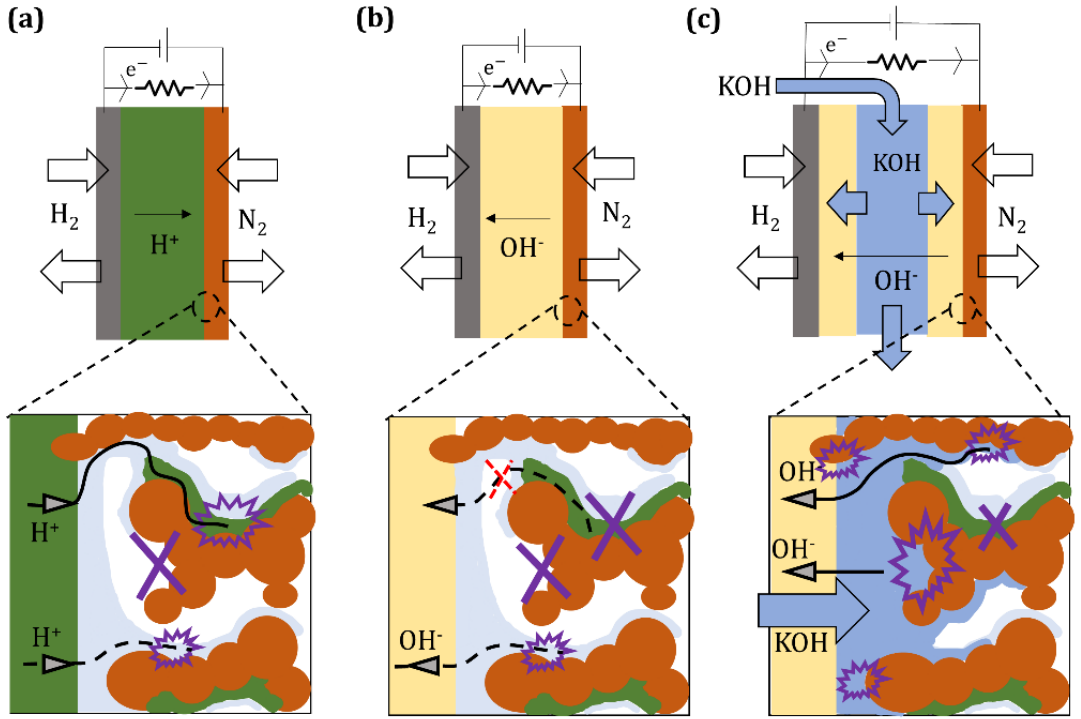


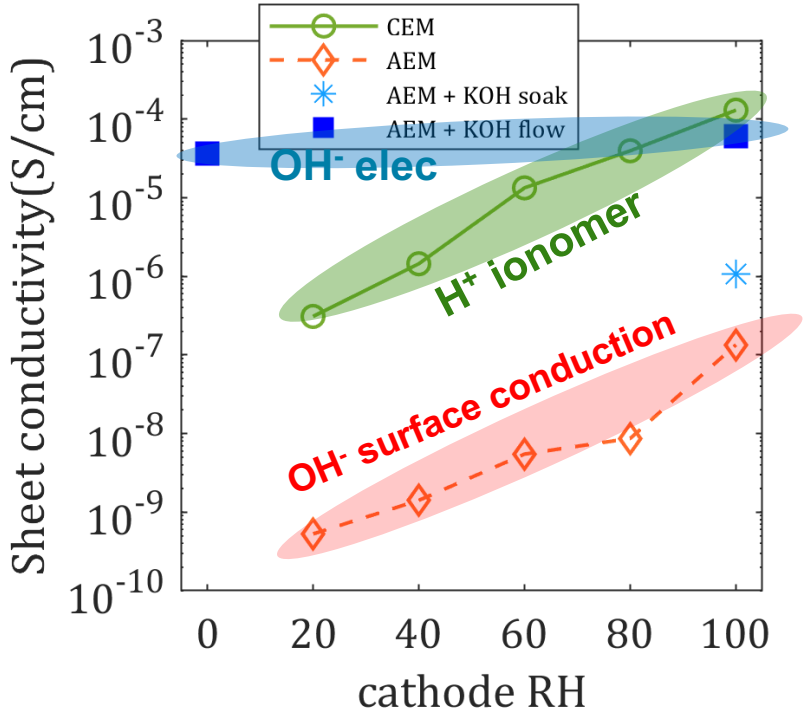


- Low production per energy input
- Most configurations result in formate/formic acid oxidation
- Limited durability (data not shown) due to salt formation
- Unclear roles for catholyte/anolyte and component needs

2. Progress and Outcomes

- Models suggested DI water on anode (instead of KOH) to produce formic acid - failed during experimental assessment





- Anolyte provides necessary access to electrochemical sites and improves bulk ionic conductivity in systems with zero-gap cathodes
- Goal is then to improve cathode layer conductivity, eliminate formation of HCOOK, reduce formic acid oxidation at anode

Published work - Saha et al. JECS 2023 doi: 10.1149/1945-7111/acb01d

2. Progress and Outcomes

Perforated membrane configuration

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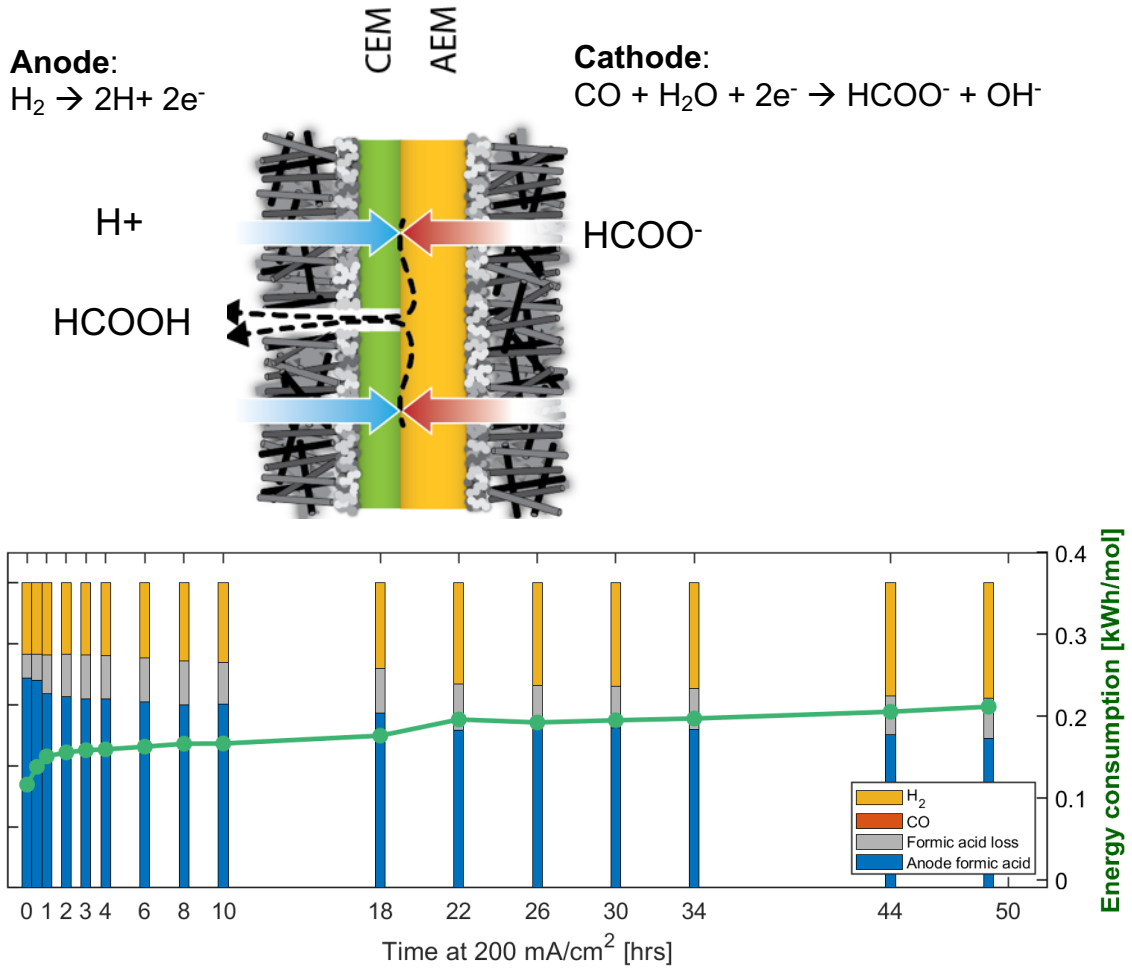
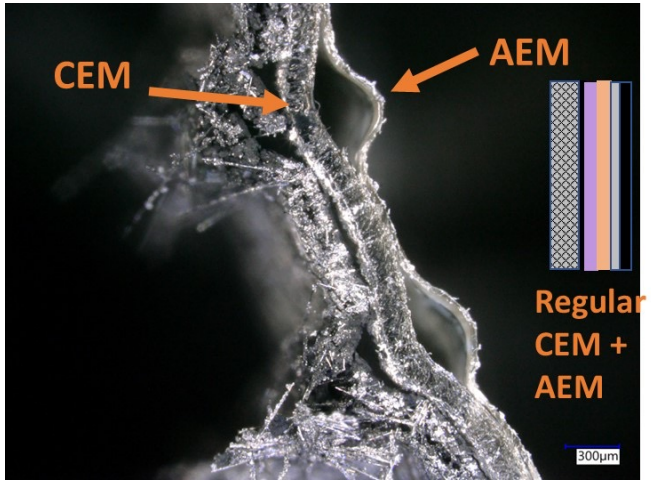
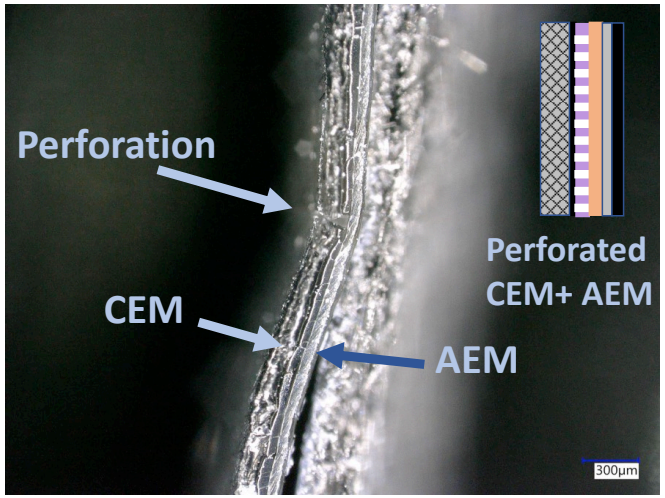


Traditional bipolar membrane



Perforated membrane configuration



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Potential (in ion-conducting phases):

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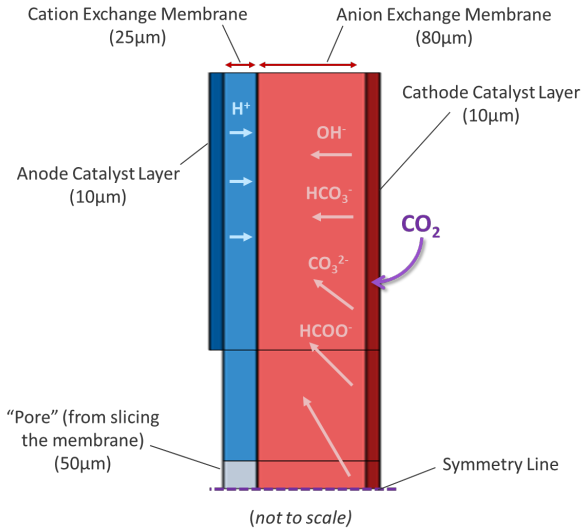
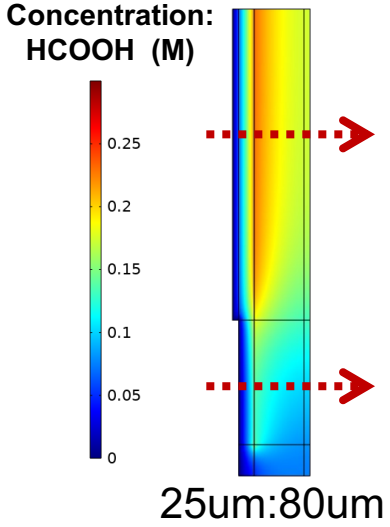
➢ 2-D (novel composite mem)





Chemical Reactions	
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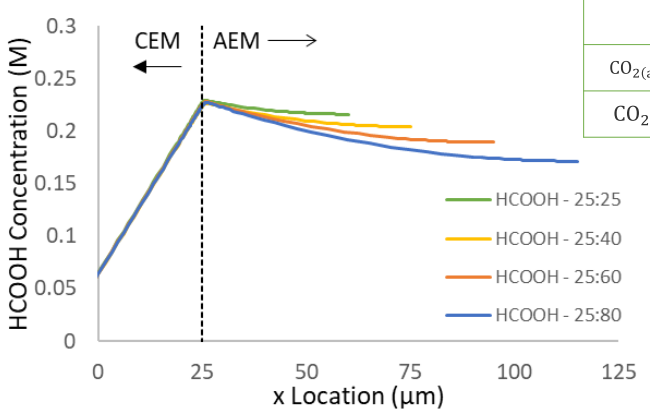
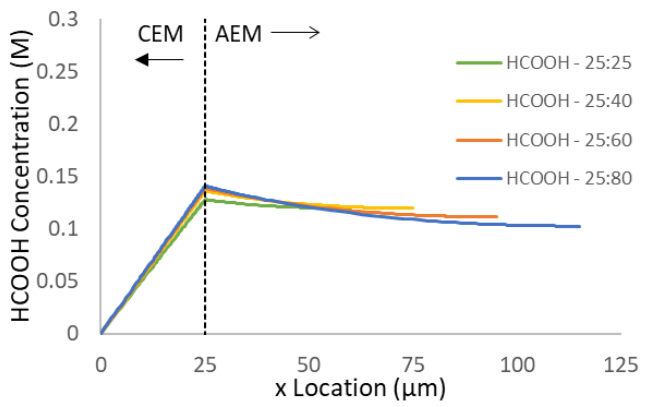
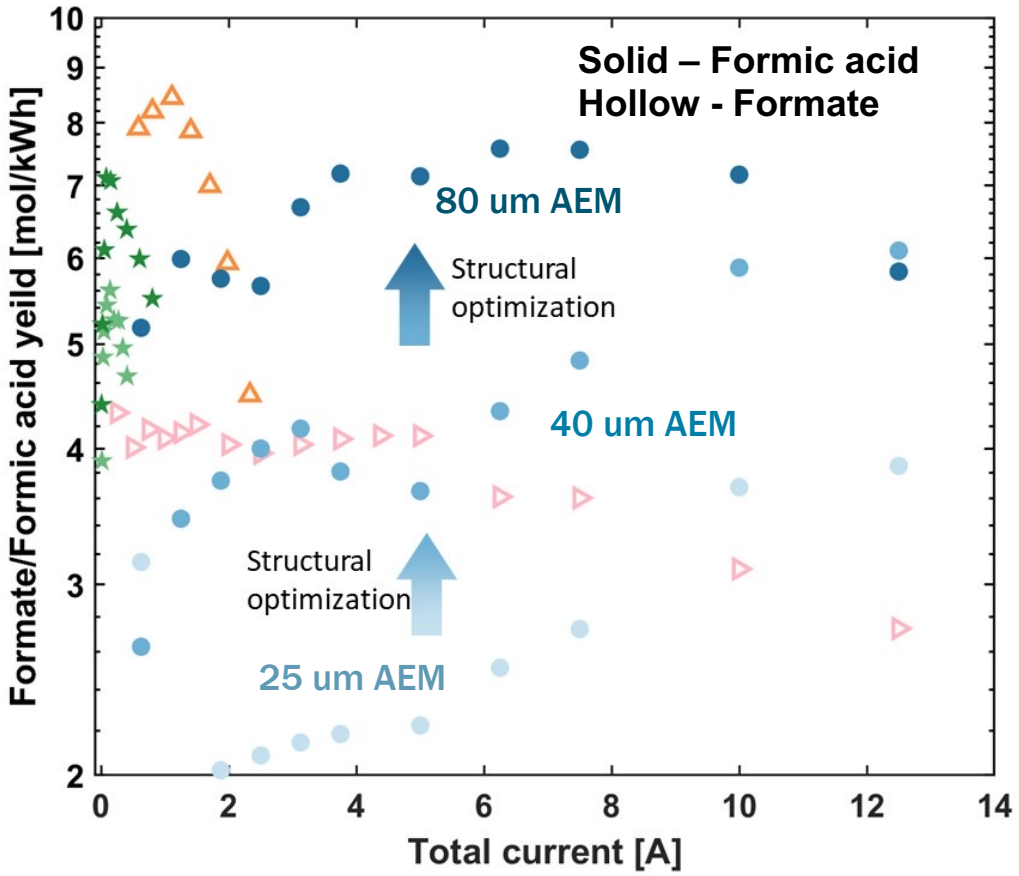
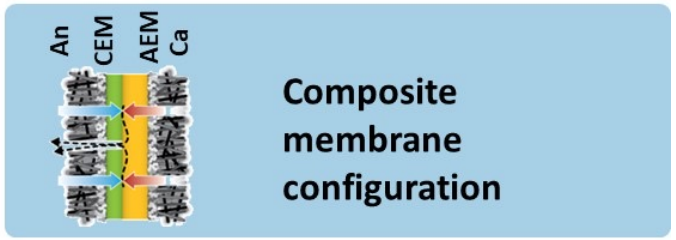




➢ Thicker AEM membranes reduce product accumulation on cathode

2. Progress and Outcomes

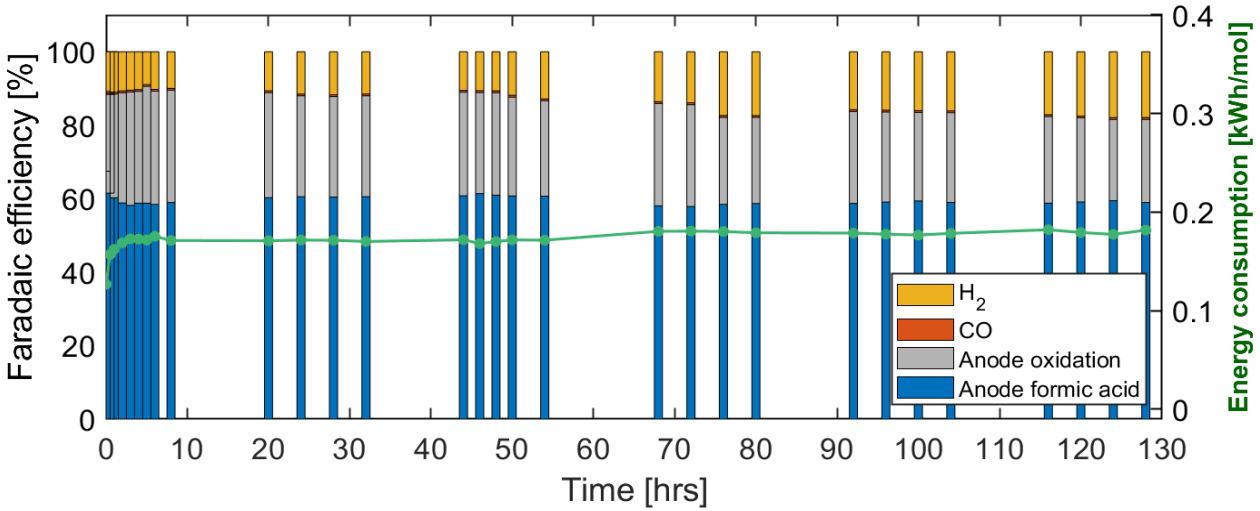


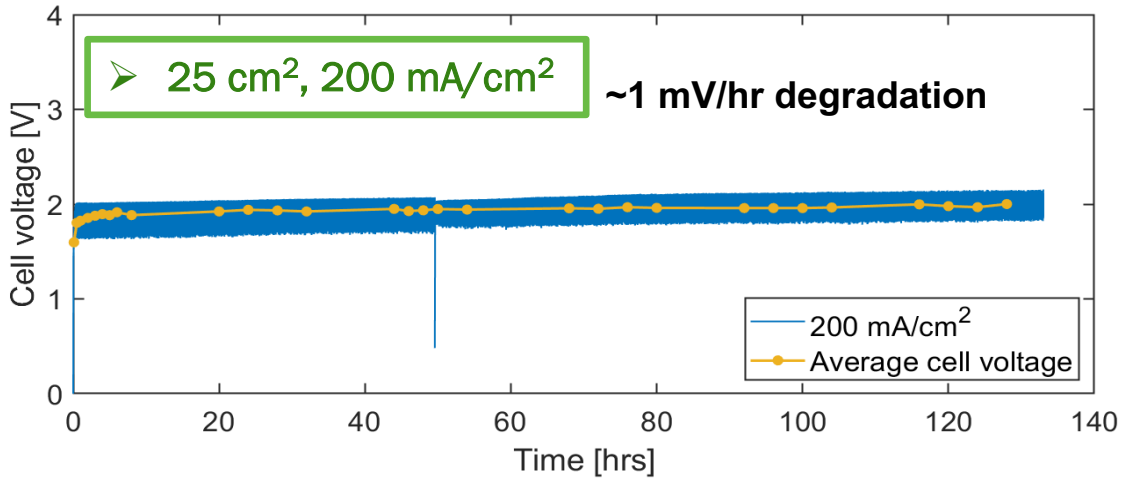


U.S. Application No. **63/386,711**. 2022

[1] Chen Y, Vise A, Klein W E, et al. [J]. ACS Energy Letters, 2020, 5(6): 1825-1833.
[2] Lee W, Kim Y E, Youn M H, et al. Angewandte Chemie International Edition, 2018, 57(23): 6883-6887.
[3] Xia C, Zhu P, Jiang Q, et al. Nature Energy, 2019, 4(9): 776-785.

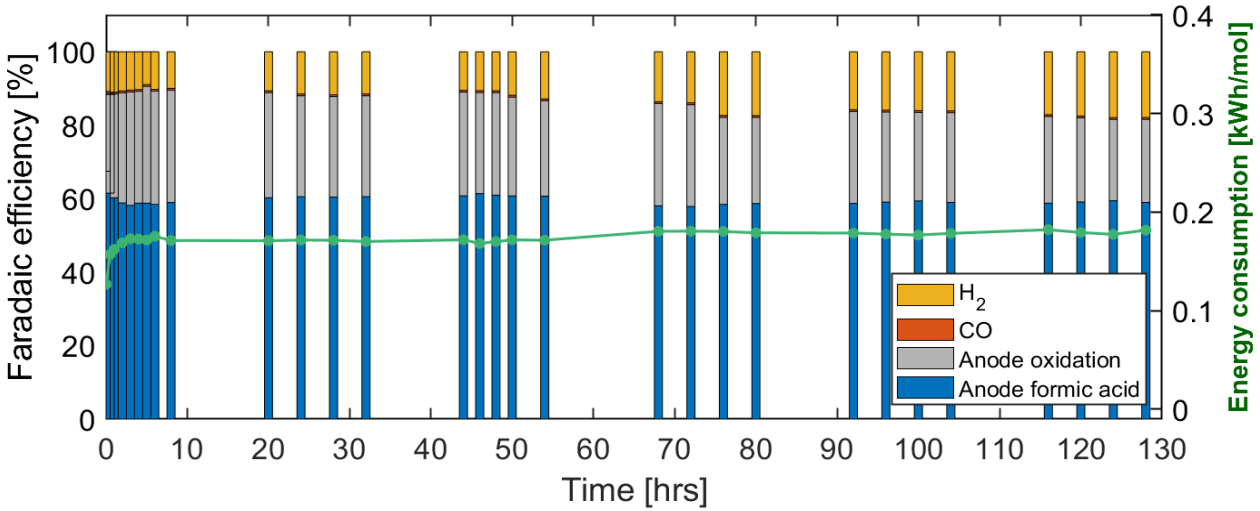
2. Progress and Outcomes

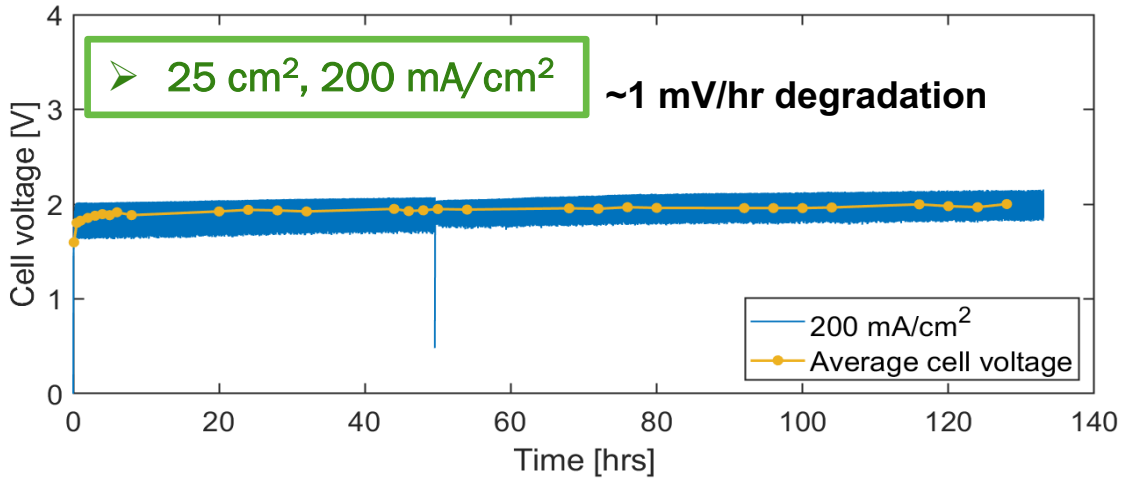


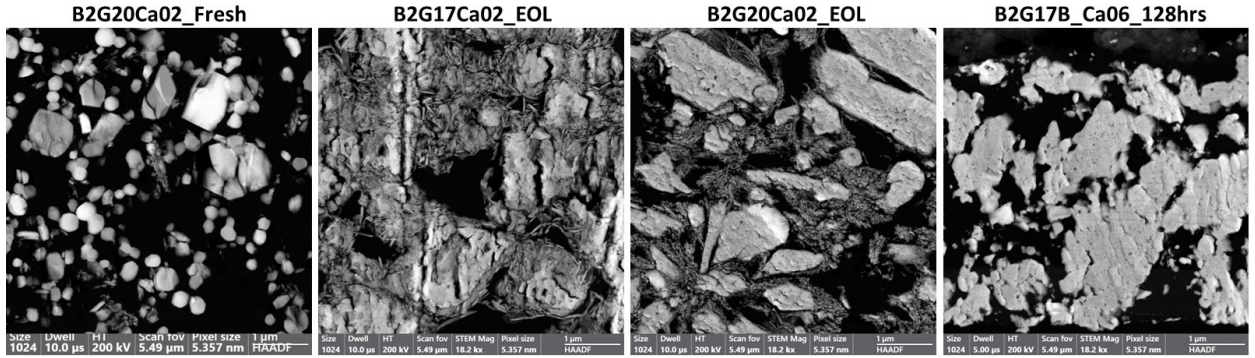


➢ Formic acid oxidation at anode reduces energy efficiency

2. Progress and Outcomes







- ➢ Formic acid oxidation at anode reduces energy efficiency
- ➢ Notable catalyst degradation and reduction throughout testing

2. Progress and Outcomes

- Nanoengineered encased platinum catalysts to suppress anode formic acid oxidation
- ROI filed, ANL Ahmed A. Farghaly and Deborah J. Myers "Nanoengineered Catalyst for Improving the Faradaic Efficiency of Energy Conversion and Electrolysis Systems."

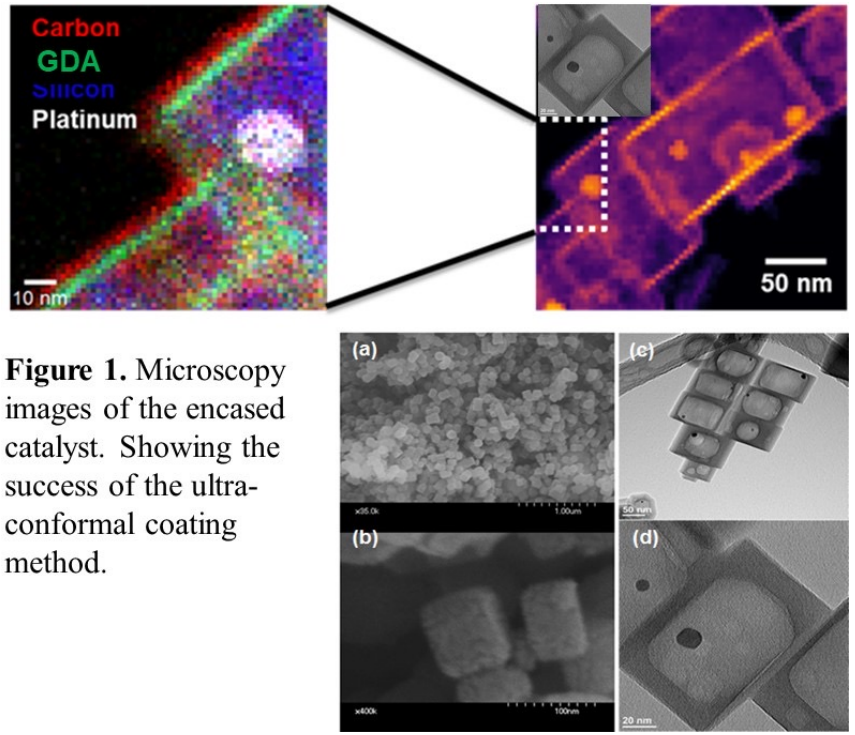
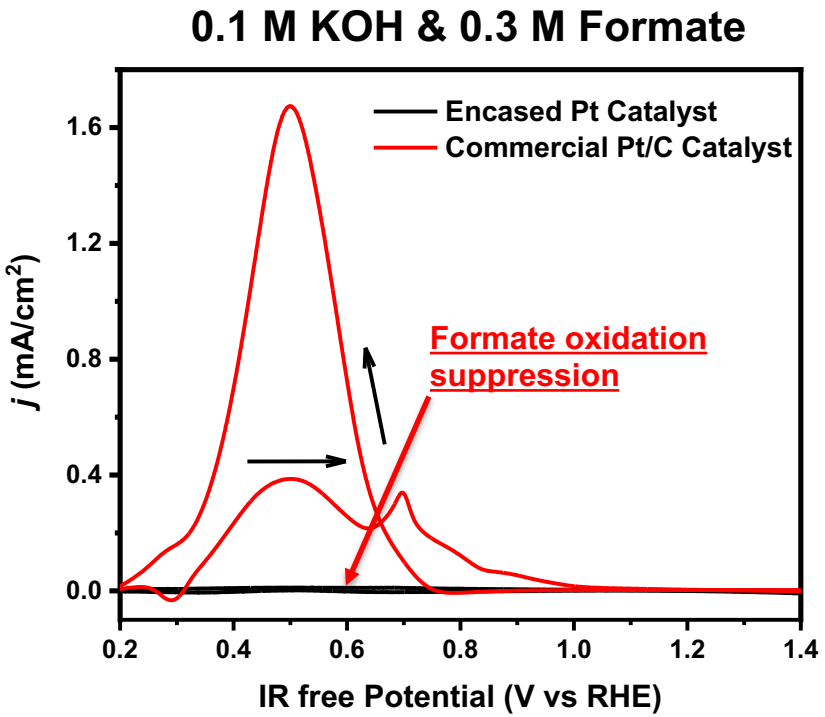


Figure 1. Microscopy images of the encased catalyst. Showing the success of the ultra-conformal coating method.

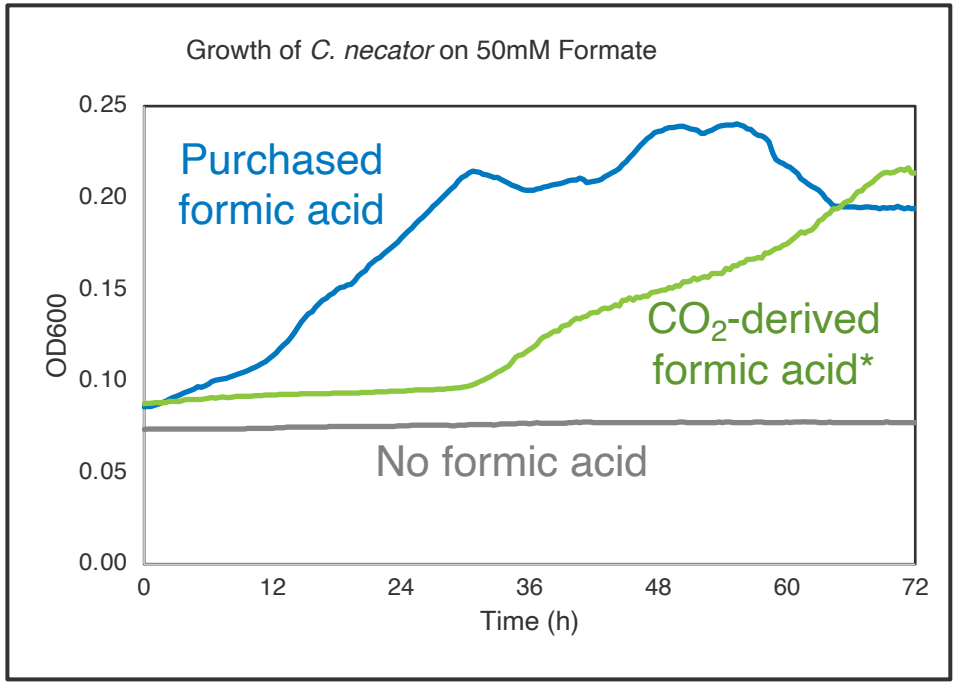


- NREL received 500 mg of catalyst material on 2/2/2023 to incorporate into MEA

3. Impact

- Utilizing commercially available materials and a novel device design, enabled operation for ~130 hrs in a 25 cm^2 cell operating at 200 mA/cm2 and 2 V
- Distributed effluent (99% formic acid at 0.08 M) to WBS# 2.3.2.121
- Shared all performance and durability data with TEA efforts WBS# 2.1.0.506 & WBS# 2.1.0.507
- Can be coupled with intermittent electricity to increase carbon utilization – risk mitigation to CO hazards, liquid intermediate (safe/stable)…

***Results from C. Johnson WBS 2.3.2.121**



Patent Application Filed: Hu L, Neyerlin KC., inventors. A new type of electrochemical device for high energy efficient CO2 to formic acid conversion. US 63/386,711. 2022.

ROI filed, ANL Ahmed A. Farghaly and Deborah J. Myers "Nanoengineered Catalyst for Improving the Faradaic Efficiency of Energy Conversion and Electrolysis Systems."

A. Farghaly (submitted)

L. Hu (submitted)

P. Saha, D. Henckel, F. Intia, L. Hu, T. Van Cleve, K.C. Neyerlin "Anolyte enhances catalyst utilization and ion transport inside a CO2 electrolyzer cathode." J. Electrochemical Society. 2022; doi: 10.1149/1945-7111/acb01d

K.C. Neyerlin "COxR – Electrochemical Conversion and Capabilities" The Mines/NREL Carbon Capture and Utilization Workshop – Colorado School of Mines

K.C. Neyerlin – "Electrocatalyst/ionomer interactions and CO2 product selectivity" Telluride Science Research Conference

Summary

- Examined the impact of operating conditions on device performance and durability (NREL)
- Utilized XAFS to examine BOT and EOT cathode electrodes (ANL)
- Characterized a series of 22 different BOT and EOT samples (ORNL)
- Distributed effluent (99% formic acid at 0.8 M) to WBS# 2.3.2.121 (NREL)
- Modified device operation and anode configuration to reduce formic acid oxidation (NREL)

Quad Chart Overview

Timeline
- 1/1/2022
- 12/31/2024

	FY22 Costed	Total Award
DOE Funding	1 mill	1.4 mill
Project Cost Share*		

TRL at Project Start:2-3
TRL at Project End:4-5

Project Goal

Develop novel membrane electrode assembly (MEA) architectures (i.e. no catholyte) to enable the robust and efficient production of formate/formic acid using scalable electrode fabrication techniques. Approaches will also be focused on enable the recovery of concentrated products for subsequent use in biological conversion.

End of Project Milestone

250 cm^2 cell, $\geq$ 200 mA/cm^2, $\geq$80% FE to formate/formic acid for at least 500 hrs with $\geq$30% single pass conversion

Project Partners*

- ANL - Ahmed Farghaly, Debbie Myers, Magali Ferrandon
- ORNL – David Cullen

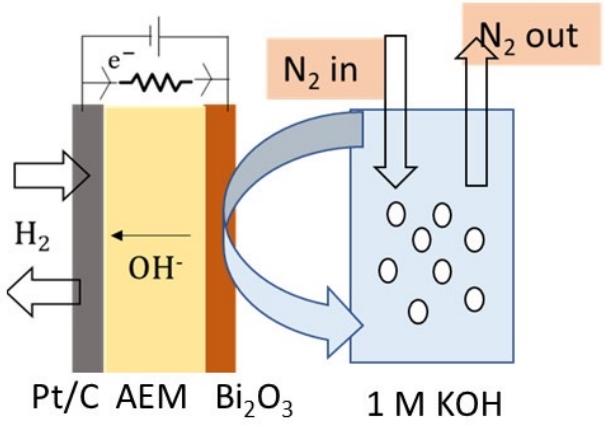
Thank You

Attribution / Disclaimer

CO_2 Reduction and Upgrading for e-Fuels Consortium

U.S. DEPARTMENT OF ENERGY

Experiment design (schematic)



Cell materials:

hardware- CO_2 hardware
cathode- Bi_2O_3 with HNN8
anode- Pt/C with low I:C
membrane- Versogen 80 µm
electrolyte- 1 M KOH
circulation rate- 20 mL/min

EIS: 0.1 V DC + 0.01 V AC
KOH flow stopped during EIS

Electrode degradation

- Apply -1.0 V with KOH flow on (reduction in presence of KOH)
- KOH increases catalyst utilization and OH^- conduction inside CL to accelerate the reduction process, and hence degradation
- Also mimics the CO_2 reducer setup used in this project
- N_2 purges out CO_2 and prevents

EIS experiment results

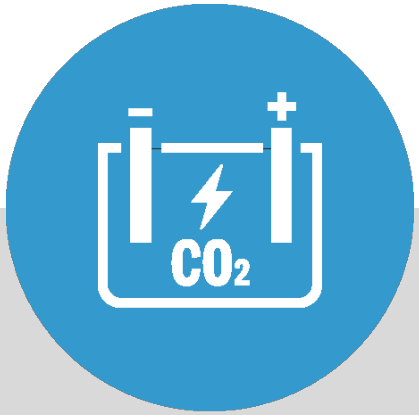
Ageing	C_{sheet}(µF/cm²)	R_{sheet}(Ω-cm²)	R_Ω(Ω-cm²)
BOT	4975.67 ± 11.44	1.51 ± 0.5	0.37 ± 0.01
1 hr reduction	10784 ± 367.54	11.74 ± 0.62	0.17 ± 0.01
4.5 hrs reduction	10742 ± 356.77	13.88 ± 0.42	0.15 ± 0.01

Conclusions:

1. R_Ω decreases because of increased hydration with time
2. Capacitance increases after reduction, trend clearly opposite of what was observed with SnO_2 (both supported and unsupported)
3. OH^- transport resistance increases. Trend similar.

Slide Title

- Analysis and Modeling



- CO2 Electrolysis

- Biological Upgrading