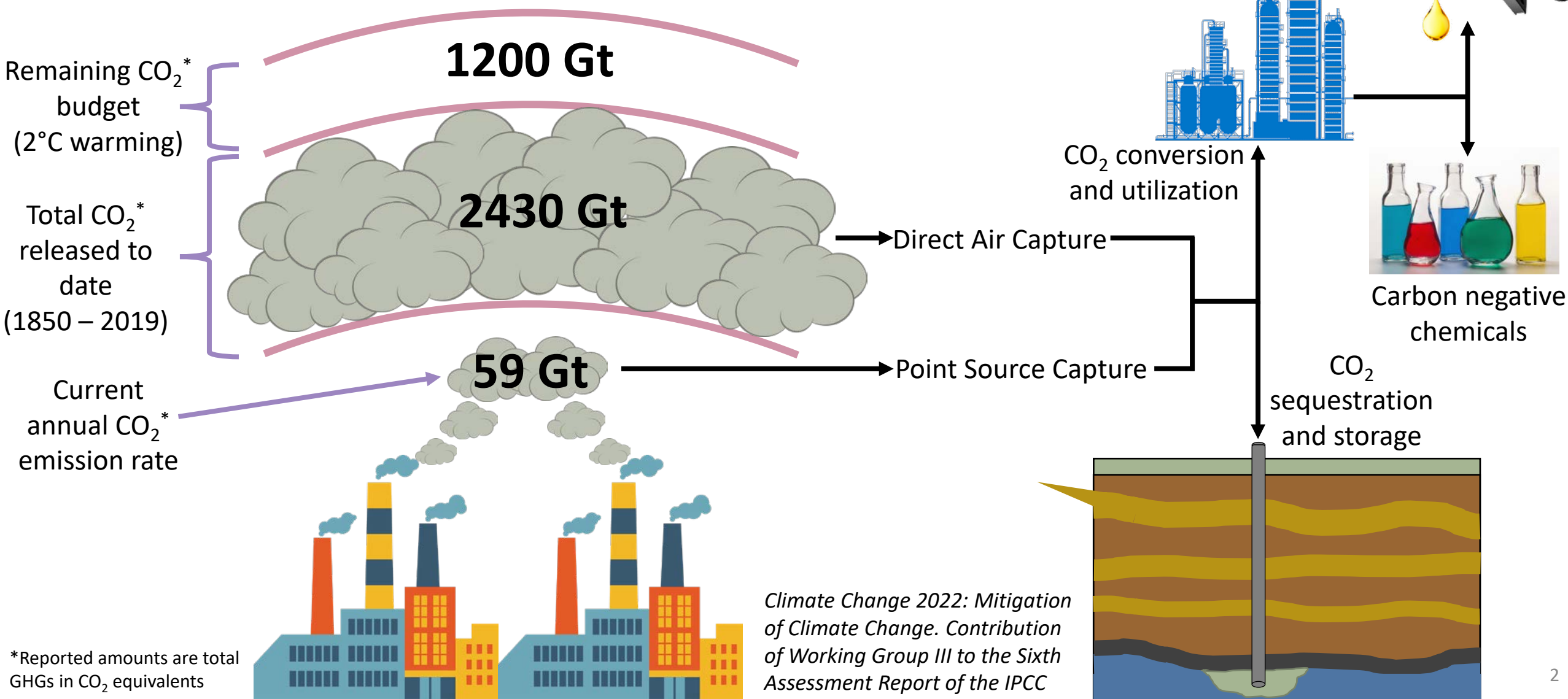


Carbon Corrosion in CO₂ Electrolysis Systems

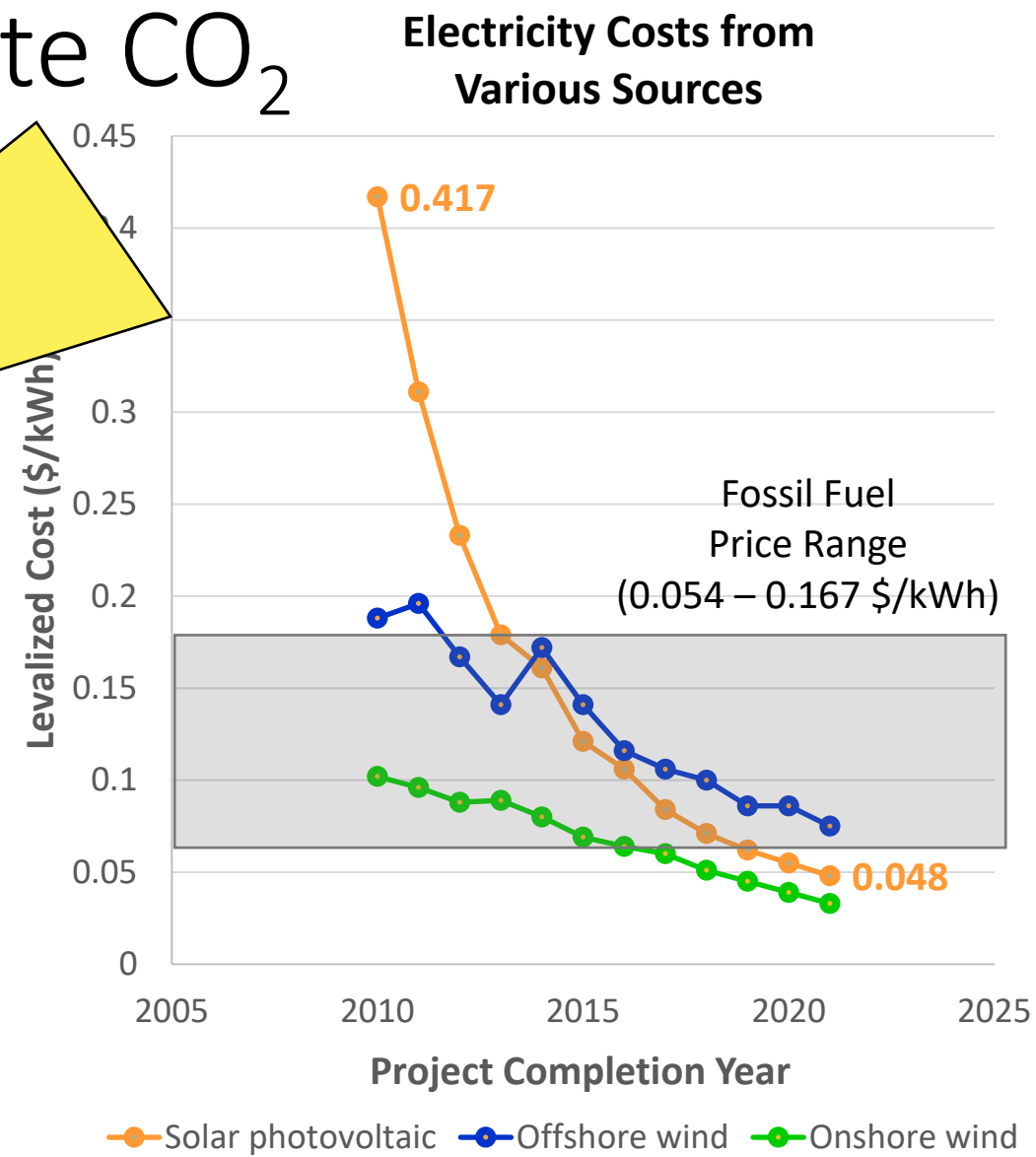
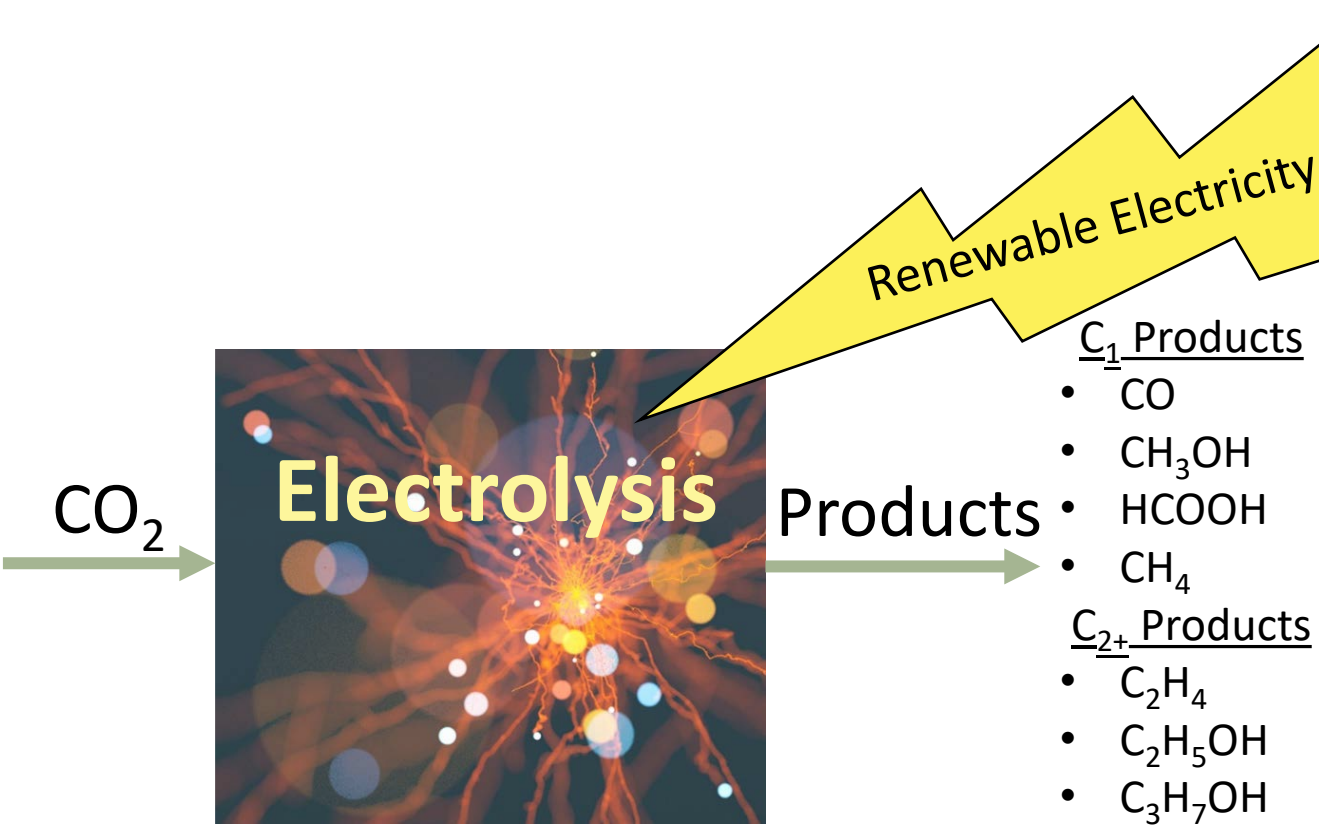
Mathew Rasmussen, Jack Ferrell
ACS Spring 2023
3/26/23

CO₂ budgets are nearing capacity for achieving climate goals



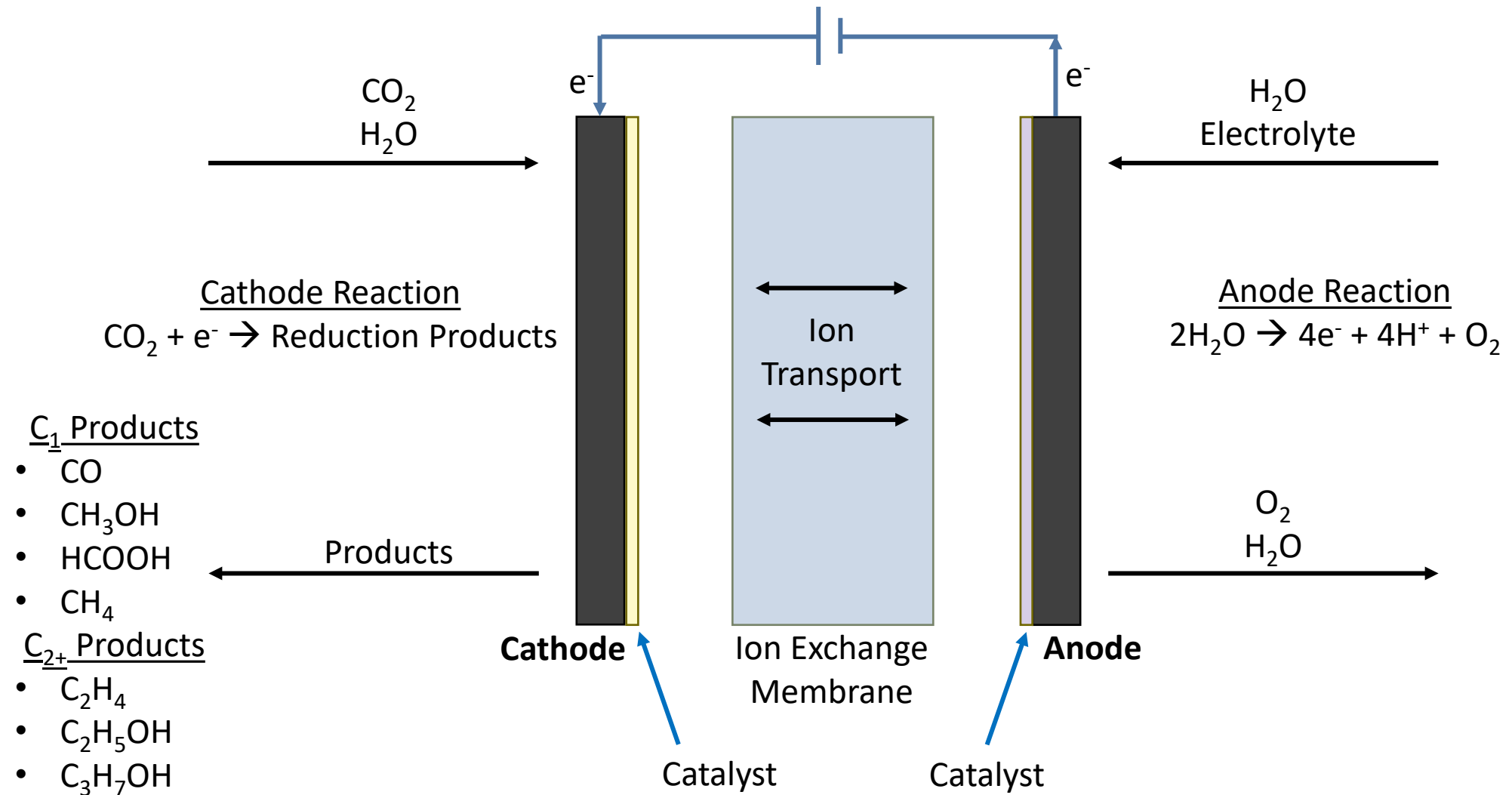
*Reported amounts are total GHGs in CO₂ equivalents

Electrochemical conversion is a promising pathway for utilizing waste CO₂

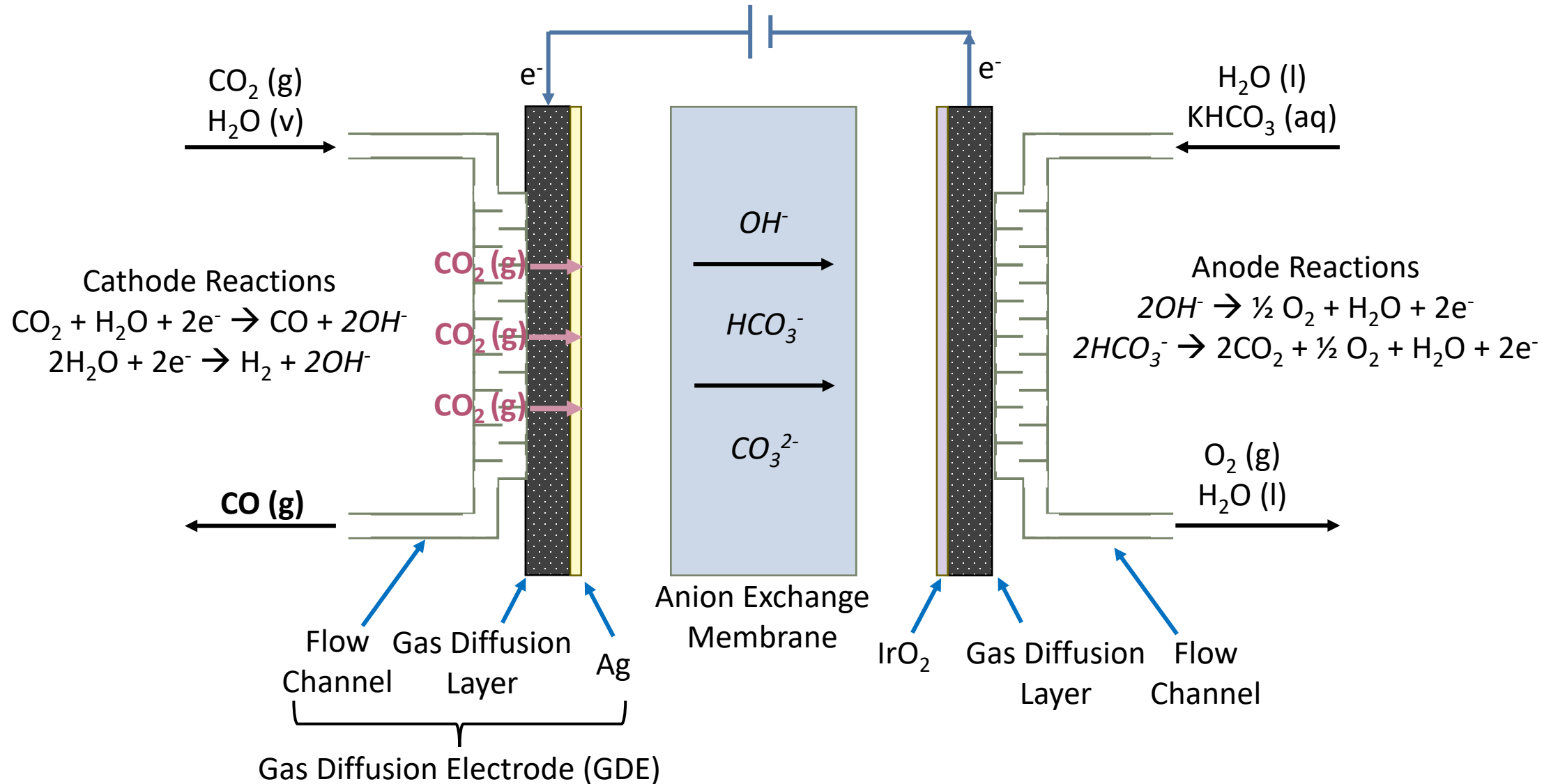


Adapted from: IRENA (2022), Renewable Power Generation Costs in 2021, International Renewable Energy Agency, Abu Dhabi.

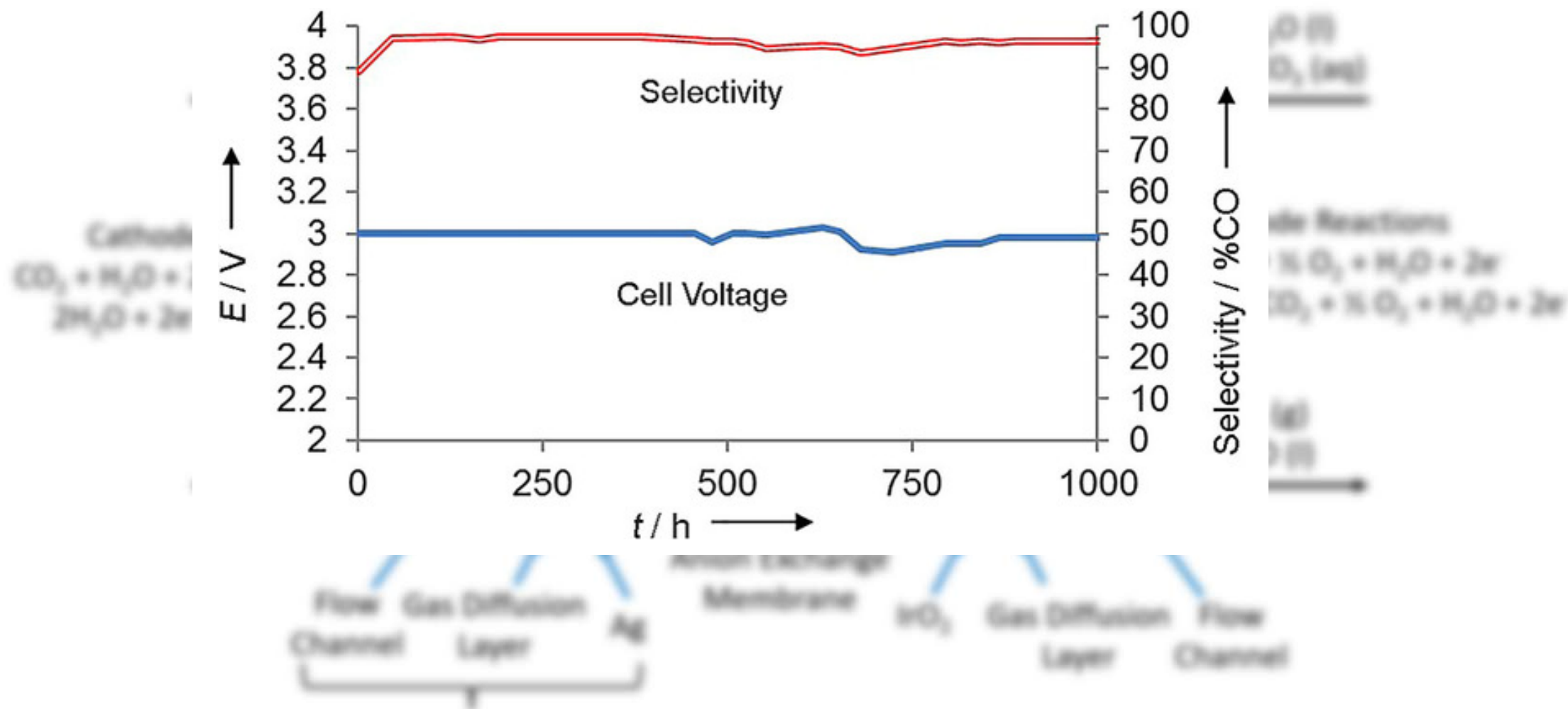
How does CO₂ electrolysis work?



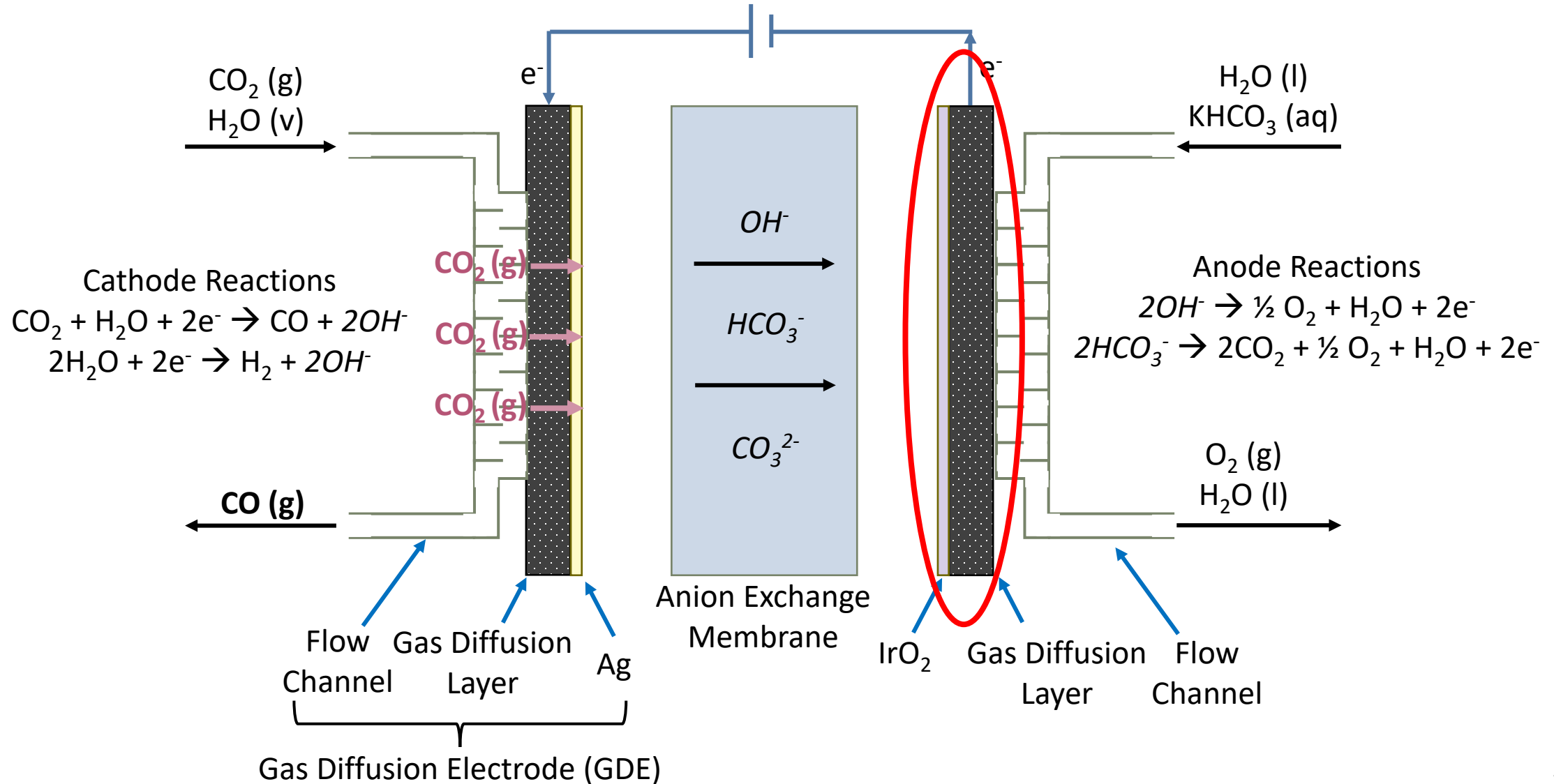
Membrane Electrode Assembly (MEA): state of the art electrolyzer design



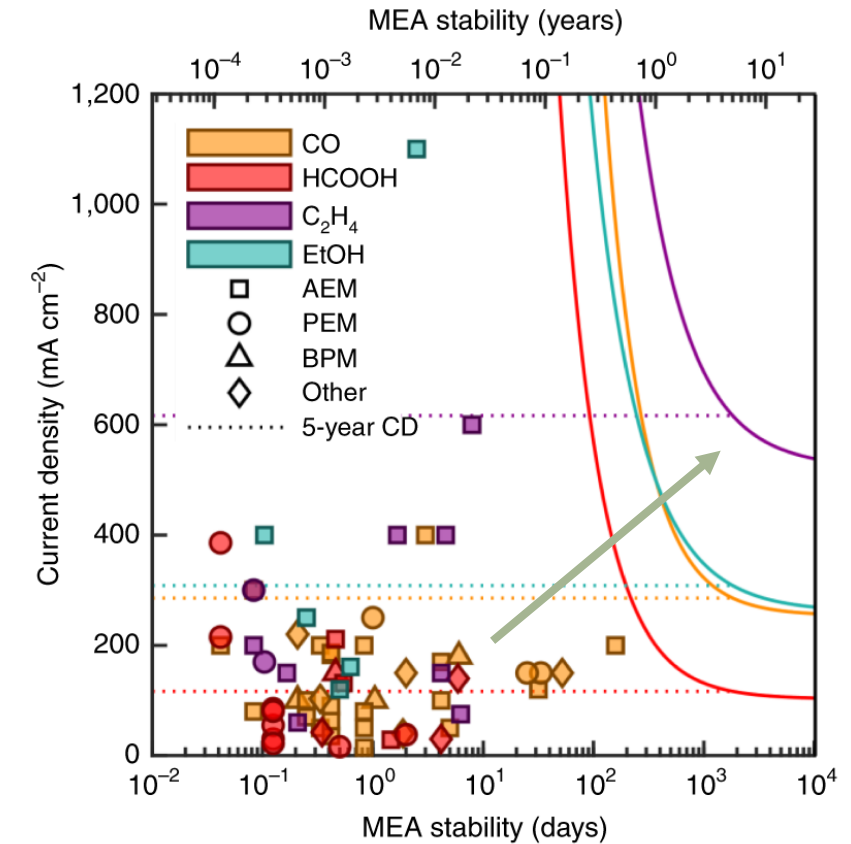
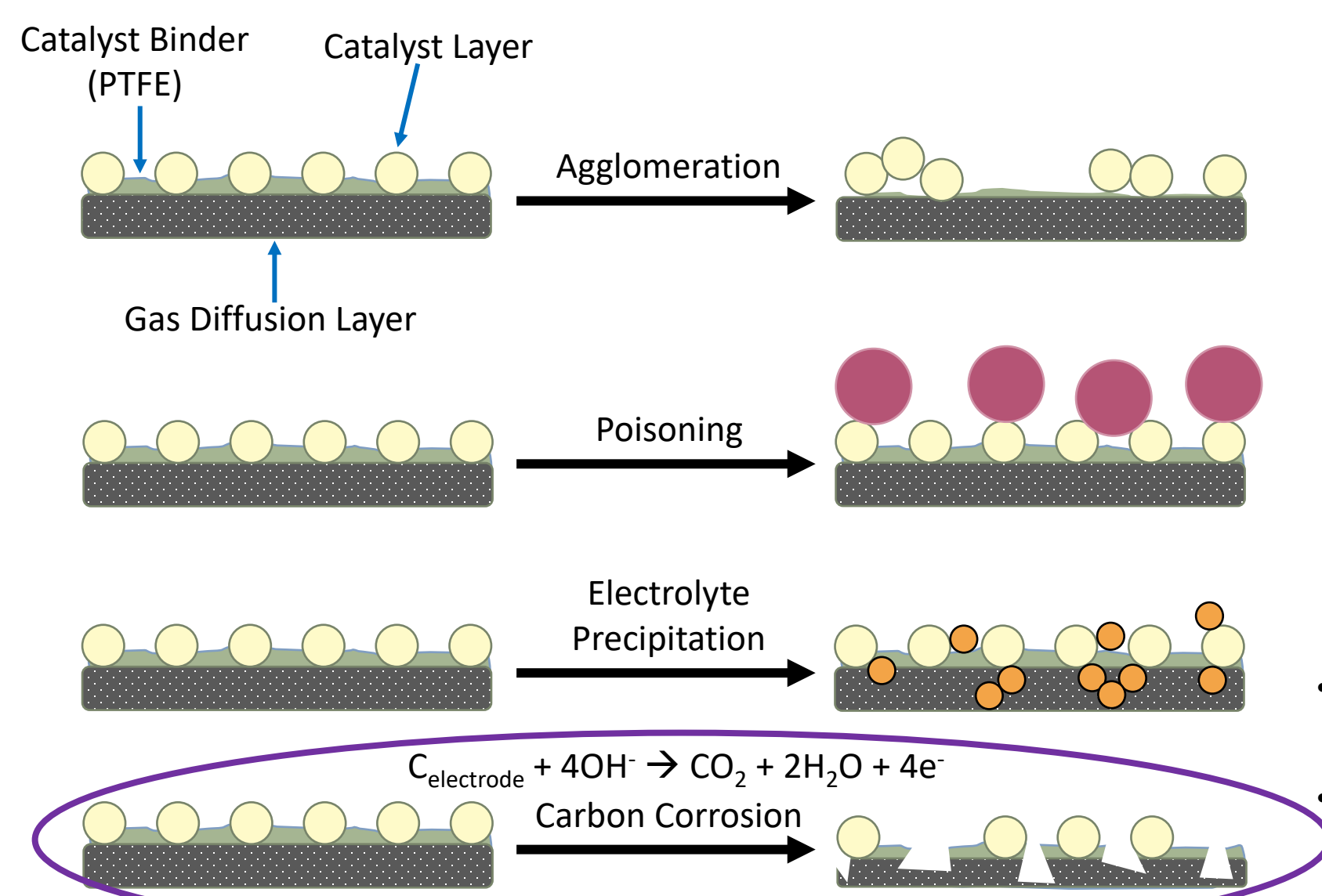
Dioxide Materials demonstrated 1000hr+ operation of MEA for reduction of CO₂ to CO



Membrane Electrode Assembly (MEA): state of the art electrolyzer design

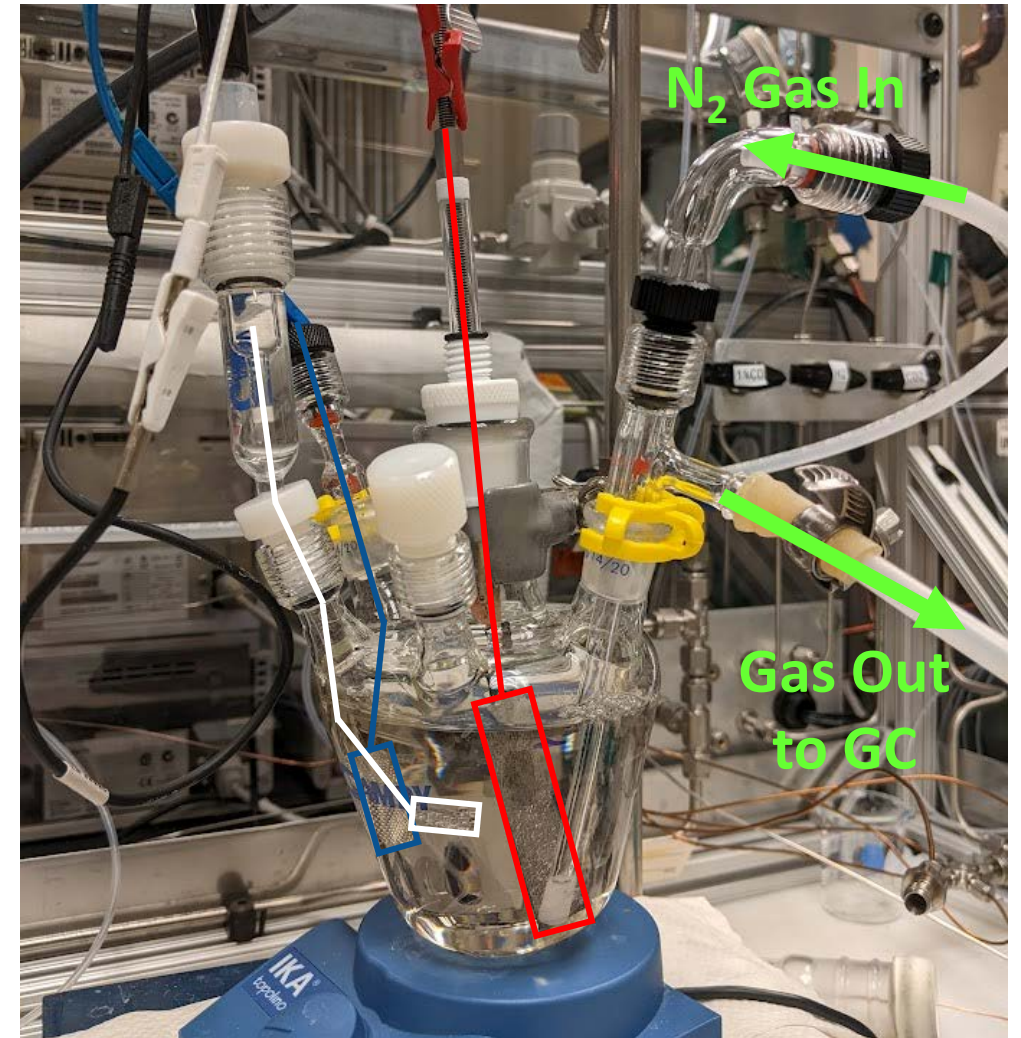
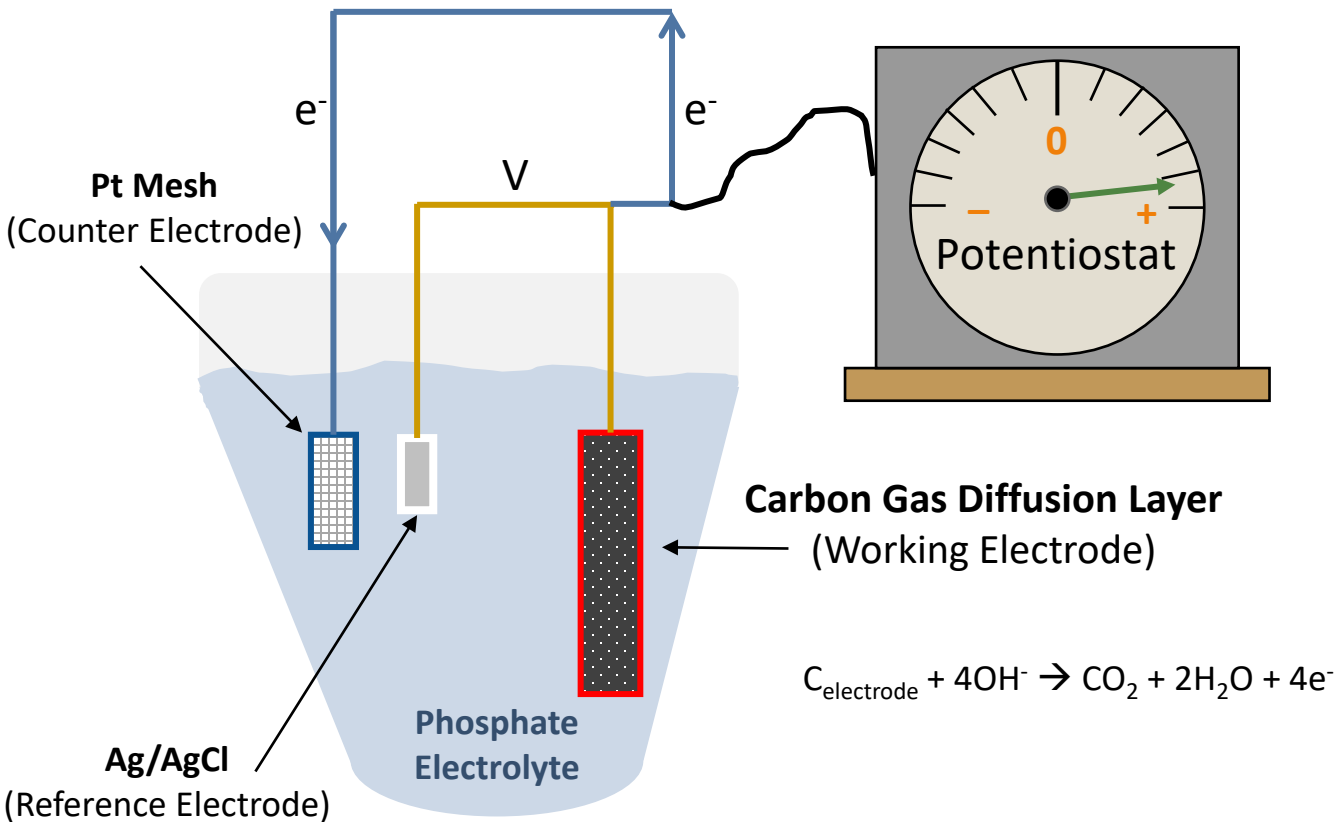


Stability and deactivation of MEA electrolyzers



- “At a minimum, stability to at least 100 days is a good first target for a prototype electrolyser”
- “We also propose industrially relevant benchmarks: 5-year stability of electrolyser components...”

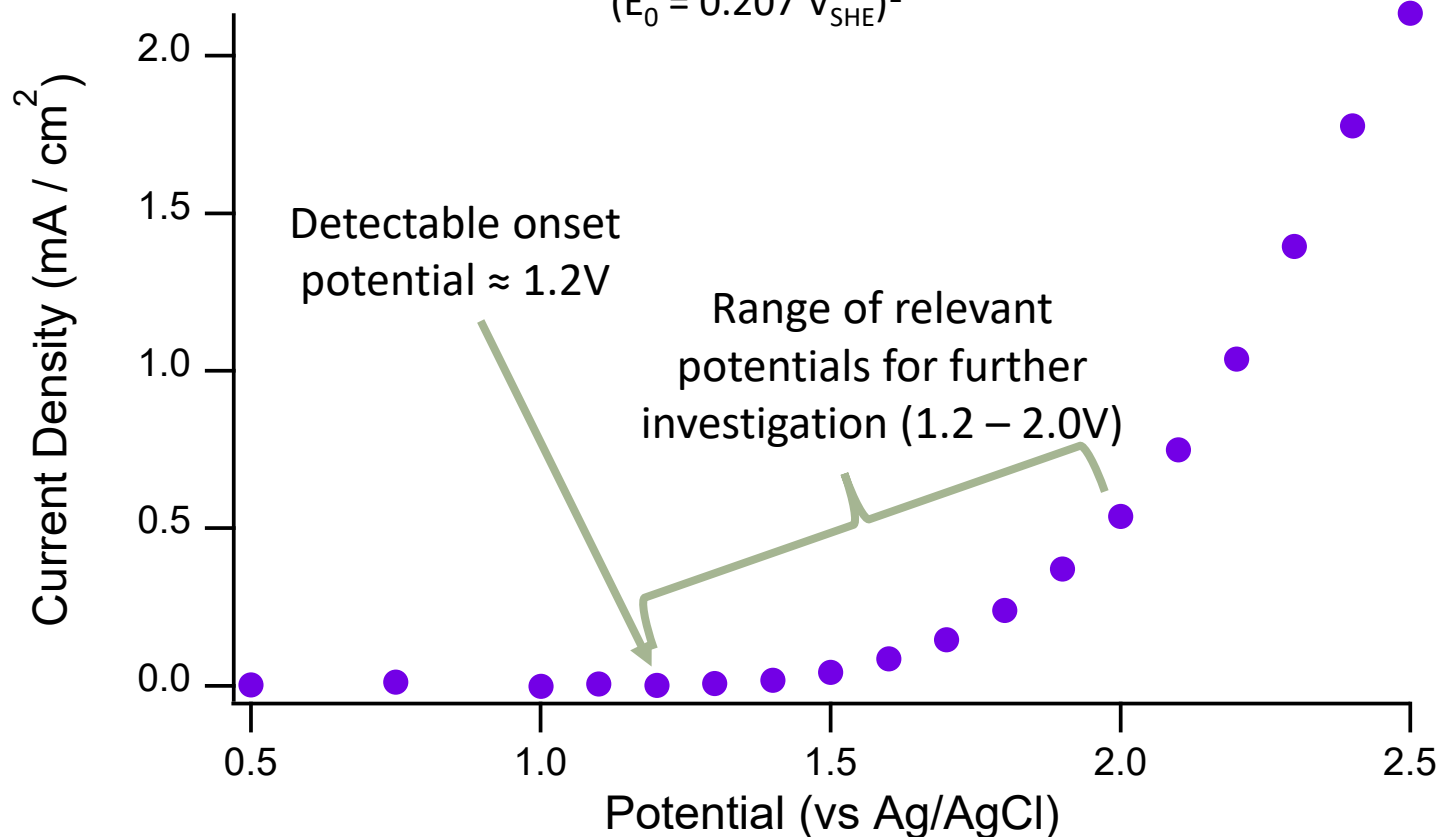
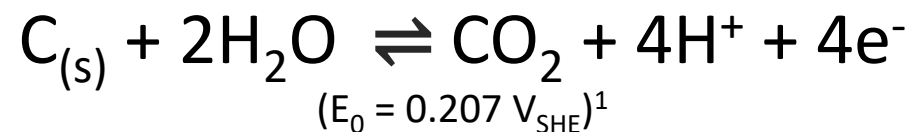
Controlled carbon corrosion experiment setup



- Simple three electrode setup
- Gas diffusion layer (no catalyst layer) exposed to oxidizing potentials
 - Samples cut from AvCarb GDS5130 gas diffusion layer
- Phosphate ($\text{K}_2\text{HPO}_4/\text{KH}_2\text{PO}_4$) electrolyte solution utilized

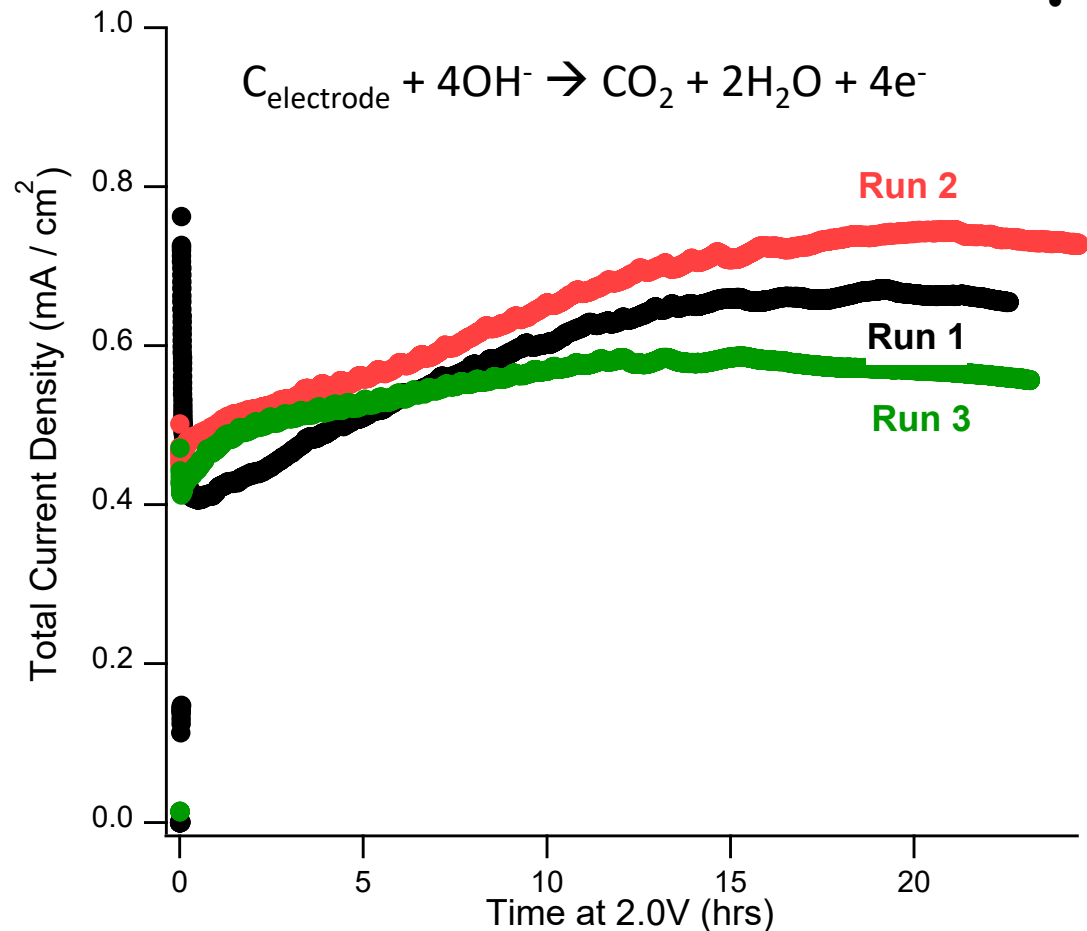
Voltage ramp determined relevant range of potentials for investigation

- Tested voltages increments from 0.5 – 2.5V
 - Phosphate buffer solution (5mM, pH~9)
 - 7.5cm² sample cut from AvCarb GDS5130 gas diffusion layer
- Voltages of at least 1.25V on the cathode are expected for CO₂ electrolysis in MEA during operation at reasonable current densities²
 - 1.23V at 50 mA/cm² (ref 2)
 - 1.43V at 200 mA/cm² (ref 2)



1. Varcoe, J. R., Atanassov, P., Dekel, D. R., Herring, A. M., Hickner, M. A., Kohl, P. A., Kucernak, A. R., Mustain, W. E., Nijmeijer, K., Scott, K., Xu, T., & Zhuang, L. (2014). Anion-exchange membranes in electrochemical energy systems. *Energy & Environmental Science*, 7(10), 3135–3191.
2. Salvatore, D., & Berlinguette, C. P. (2020). Voltage Matters When Reducing CO₂ in an Electrochemical Flow Cell. In *ACS Energy Letters* (Vol. 5, Issue 1, pp. 215–220). American Chemical Society.

Significant corrosion and good repeatability demonstrated at 2.0V



- Same conditions used for each test
 - Cell filled with phosphate buffer solution (5mM, pH ~ 9)
 - 7.5cm² samples cut from carbon AvCarb GDS5130 gas diffusion layer
 - Each sample held at 2.0V (vs. Ag/AgCl) for ~24hrs

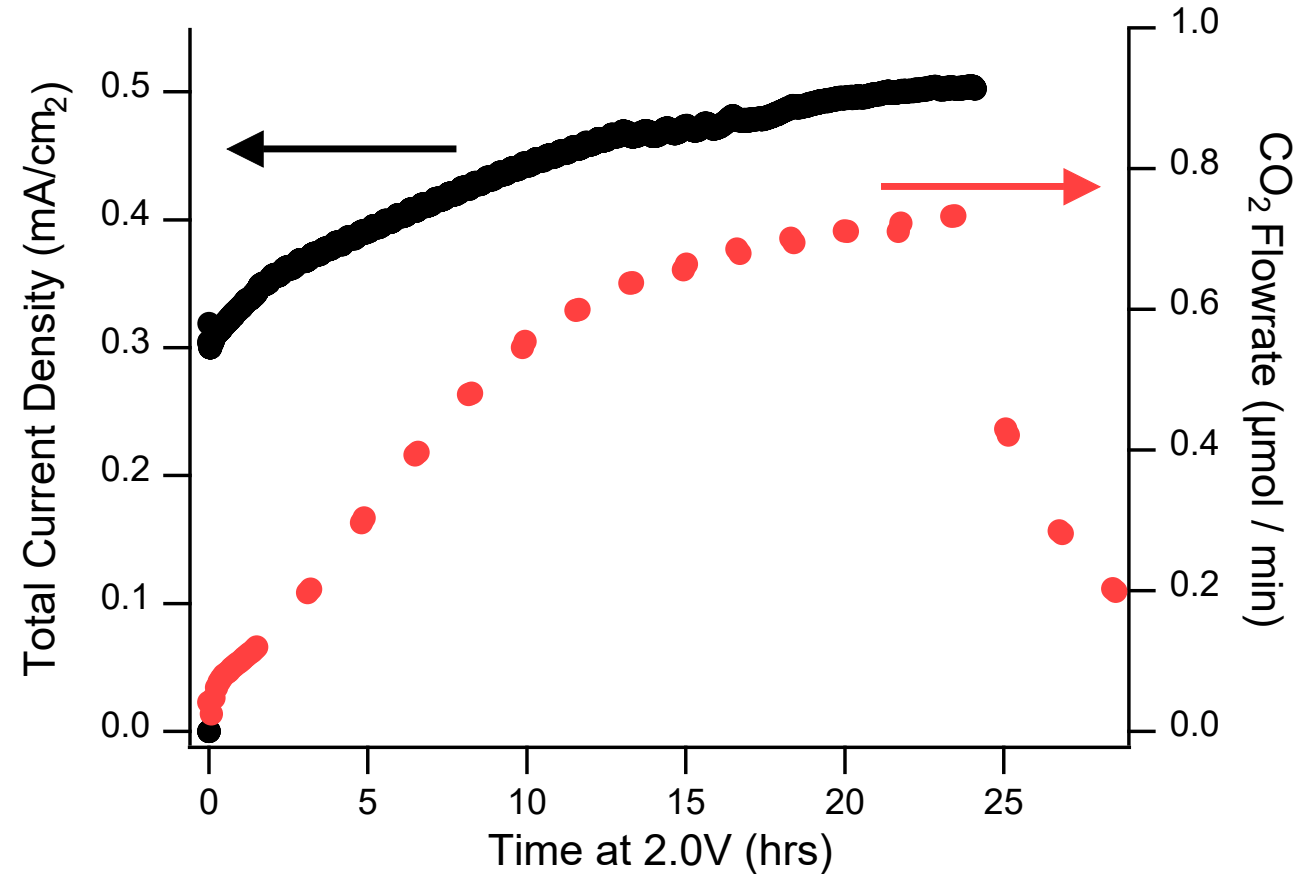
	Run 1	Run 2	Run 3
Initial Electrode Mass	0.0655 g	0.0697 g	0.0588 g
Final Electrode Mass	0.0574 g	0.0611 g	0.0515 g
Total Mass Loss	0.0081 g	0.0086 g	0.0073 g
% Mass Loss	12.36 %	12.34 %	12.41 %

Average % Mass Loss = 12.37 ± 0.04%

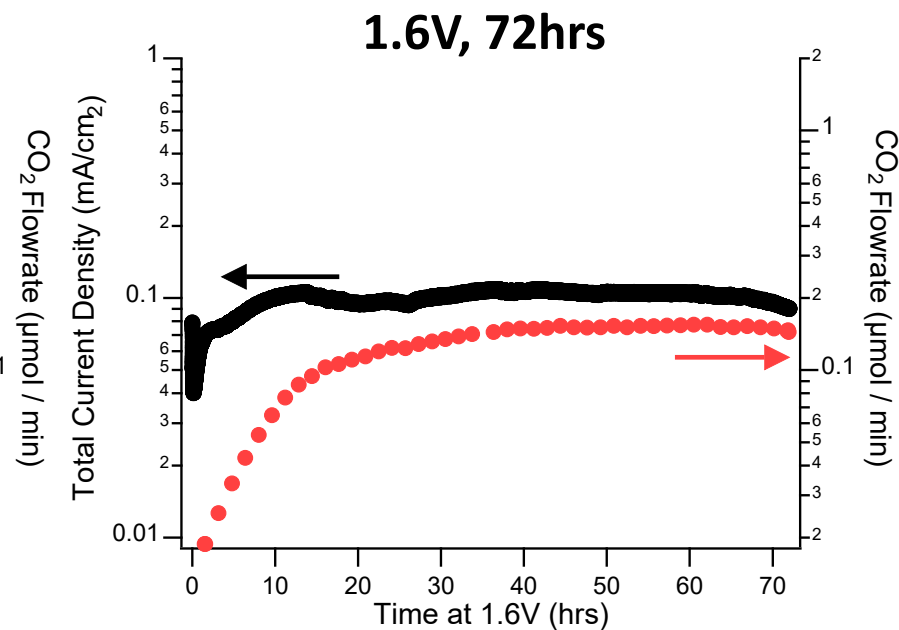
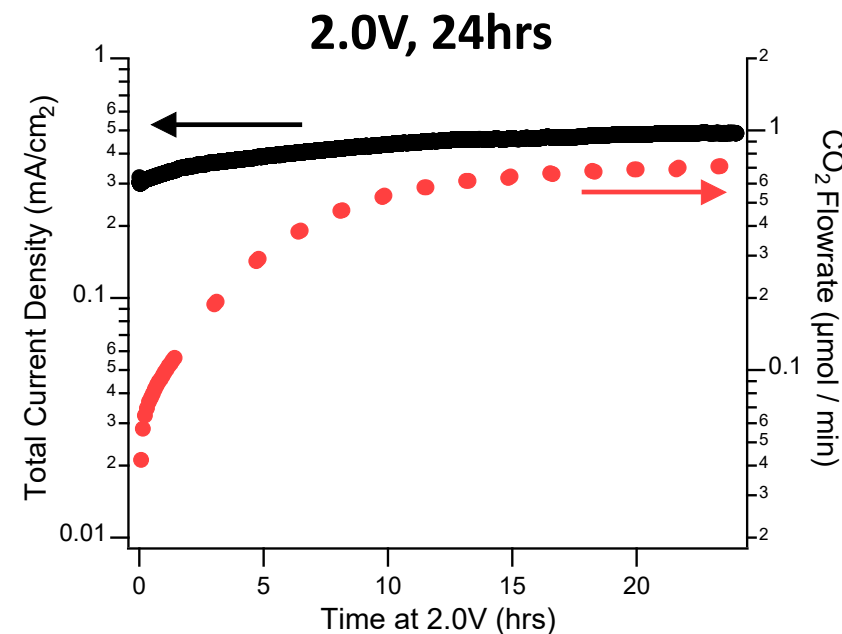
GC-detected CO₂ and potentiostat-measured current give reasonable estimate of mass loss

- 15sccm N₂ sweep gas used to bring corrosion products (CO₂) to GC
- Area underneath CO₂ detection curve and current density curve calculated by discrete integration

Measurement Type	Mass Loss	% Error from Measured Loss
Measured Mass Change	0.0091g	—
Potentiostat Estimate	0.0113g	24%
GC Estimate	0.0100g	10%



Even at lower voltages, carbon corrosion causes significant degradation within days of operation



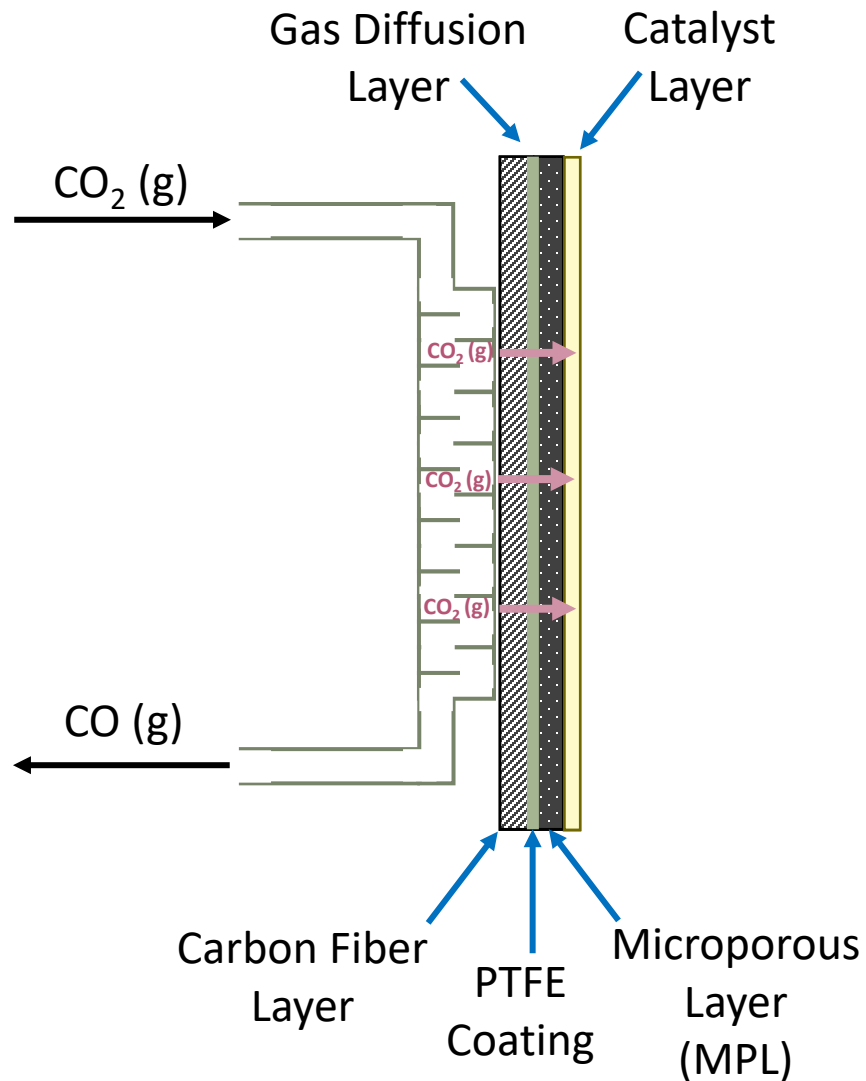
1.2V, 168hrs

Measurement Type	Mass Loss
Measured Mass Change	0.0091g
% Mass Change	10.9%
Potentiostat Estimate	0.0113g
GC Estimate	0.0100g

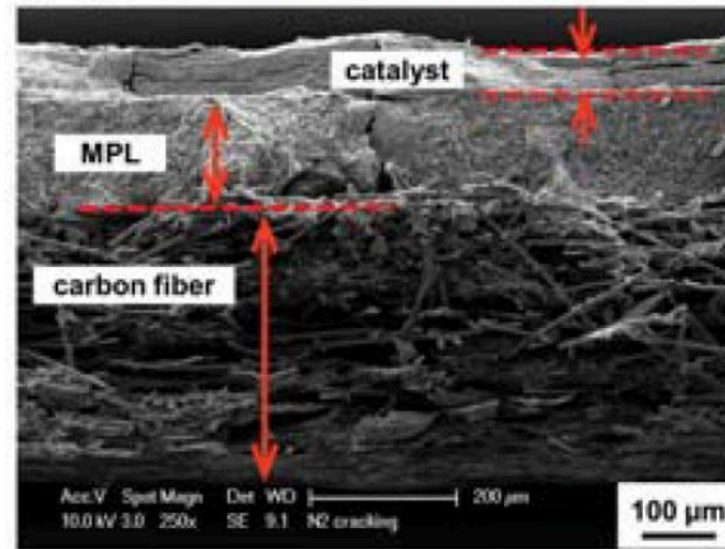
Measurement Type	Mass Loss
Measured Mass Change	0.0070g
% Mass Change	8.5%
Potentiostat Estimate	0.00793g
GC Estimate	0.00701g

Measurement Type	Mass Loss
Measured Mass Change	
% Mass Change	
Potentiostat Estimate	
GC Estimate	

Structure of gas diffusion layer (GDL)



(a1) SEM cross-section

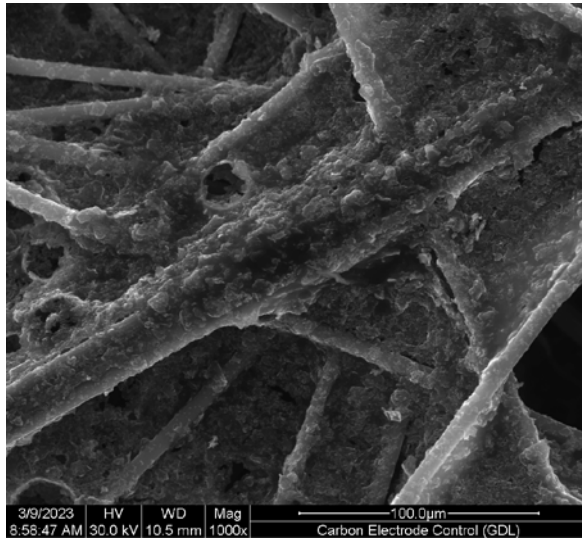


Only difference from our material is that we have no catalyst layer!

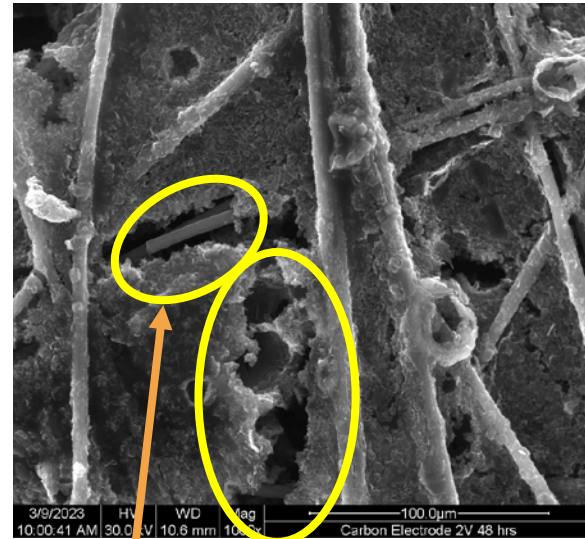
From Reference 1

SEM + EDS images of fresh vs corroded samples

Fresh Electrode (1000X)
Fiber Layer

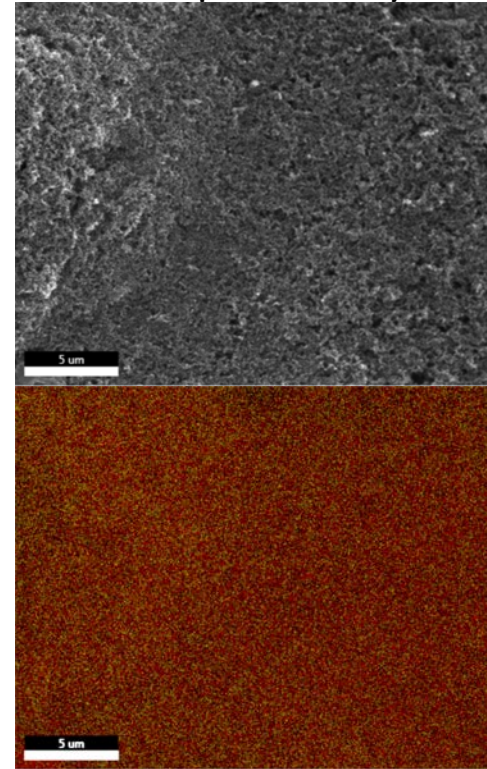


Corroded Electrode (1000X)
Fiber Layer
2V, 48hrs, KHCO_3



Degradation of interstitial region
Fracturing of carbon fibers

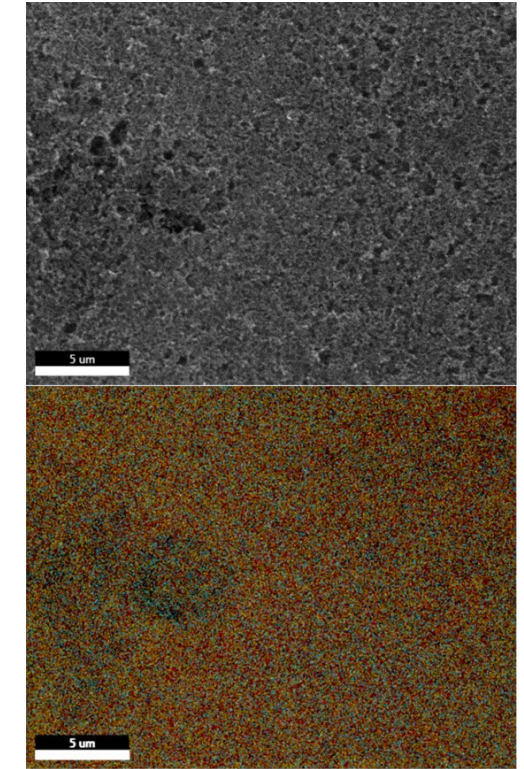
Fresh Electrode (5000X)
Microporous Layer



Element	Weight %
C K	72.94
F K	27.06

C:F Ratio = 2.70

Corroded Electrode (5000X)
Microporous Layer
2V, 48hrs, KHCO_3



Element	Weight %
C K	50.58
O K	8.20
F K	38.97
K K	2.24

C:F Ratio = 1.30

Conclusions and Future Plans

- Method developed to observe and quantify carbon corrosion in controlled environment
- Future experiments will probe effect of catalyst layer (IrO_2) on carbon corrosion
 - Studies suggest that presence of catalyst layer may suppress corrosion
- Determined that significant carbon corrosion occurs at potentials as low as 1.2V (vs. Ag/AgCl)
 - Electrode would last on the order of weeks (not years) under these conditions

Questions?

- Acknowledgements
 - Wilson McNeary (MEA testing)
 - Todd Vinzant (SEM-EDS images)



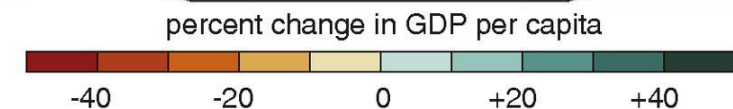
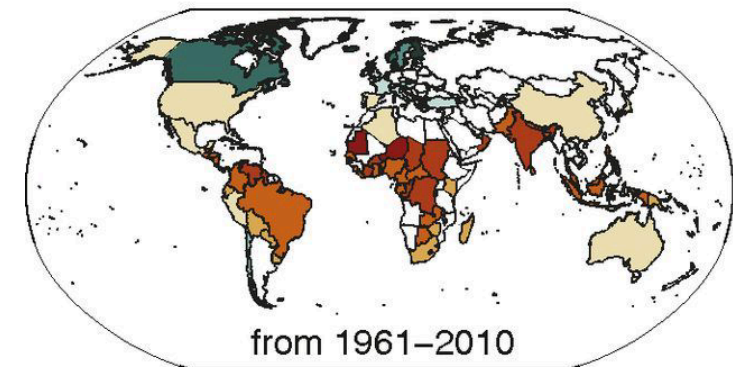
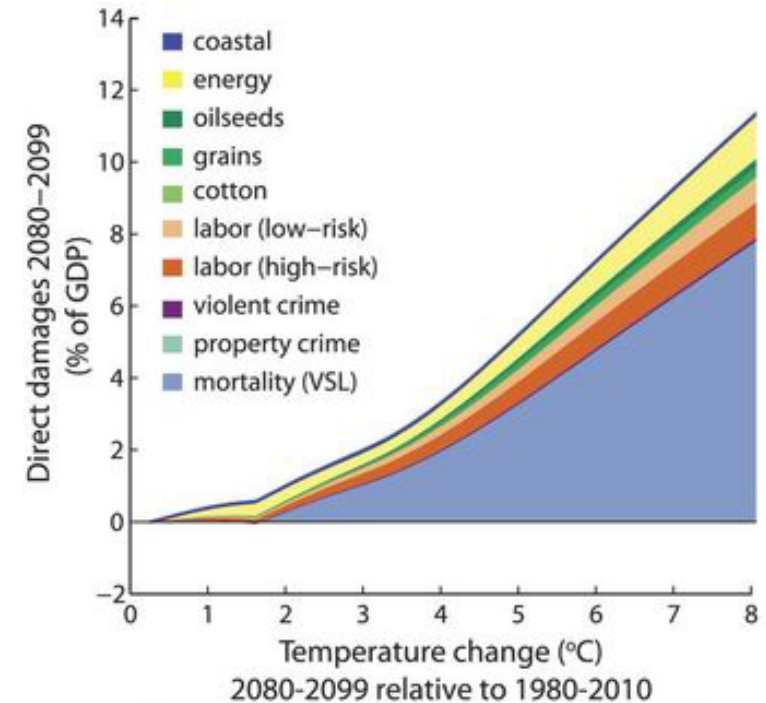
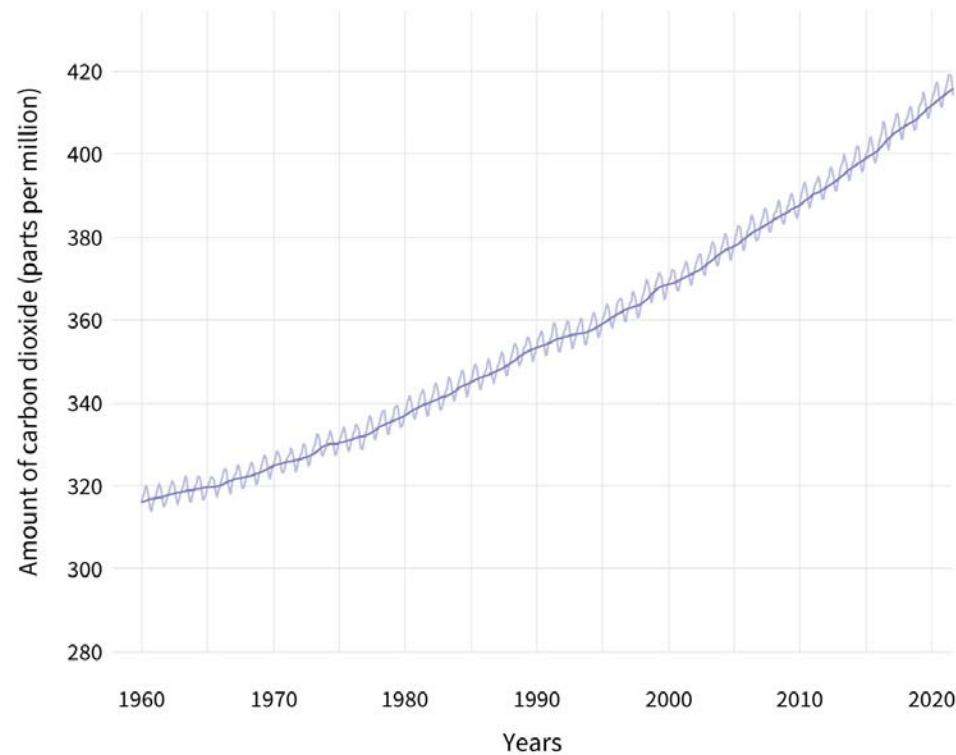
CO₂ Reduction and Upgrading
for e-Fuels Consortium
U.S. DEPARTMENT OF ENERGY

NREL/PR-5100-85759

This work was authored 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 U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy 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.

Rising levels of CO₂ and effects on environment

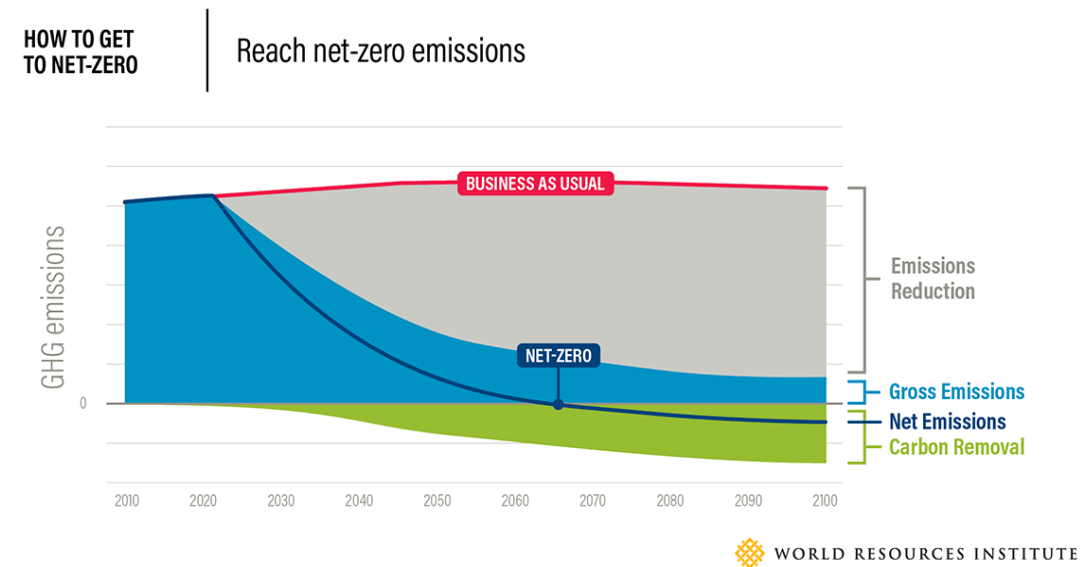
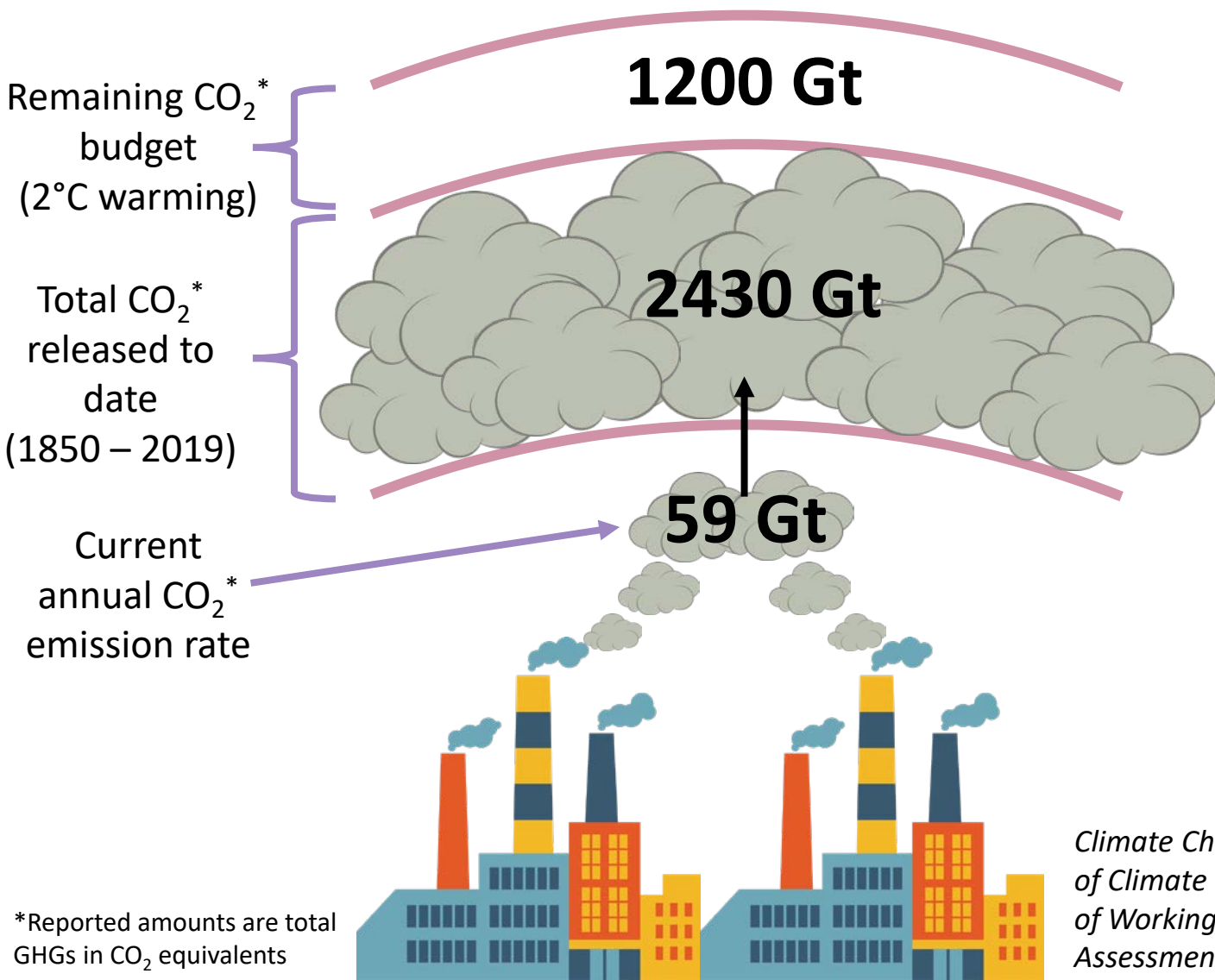
ATMOSPHERIC CARBON DIOXIDE (1960-2021)



Hsiang, S., Kopp, R., Jina, A., Rising, J., Delgado, M., Mohan, S., Rasmussen, D. J., Muir-Wood, R., Wilson, P., Oppenheimer, M., Larsen, K., & Houser, T. (2017). Estimating economic damage from climate change in the United States. *Science*, 356(6345), 1362–1369.

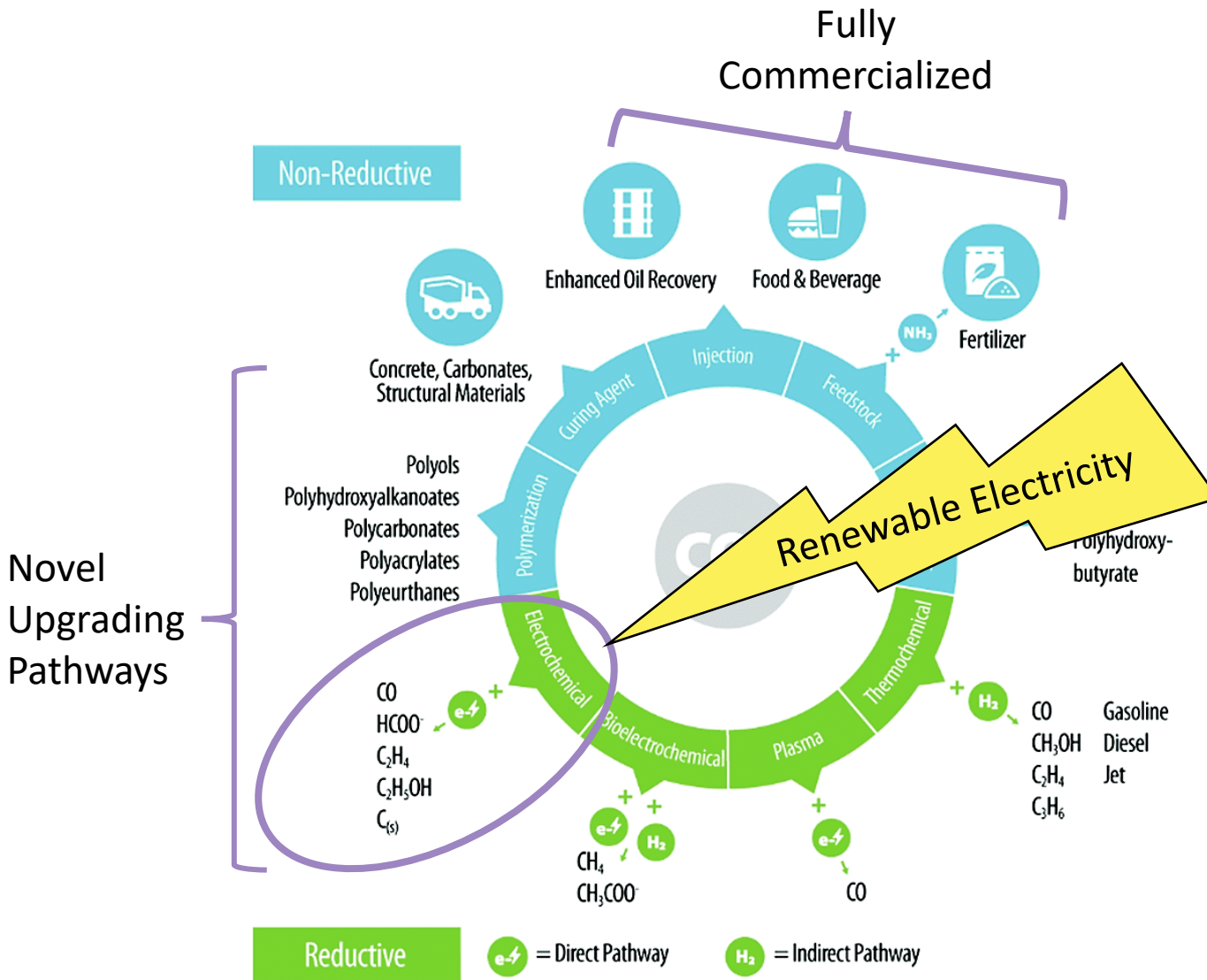
Diffenbaugh, N. S., & Burke, M. (2019). Global warming has increased global economic inequality. *Proceedings of the National Academy of Sciences of the United States of America*, 116(20), 9808–9813.

Global CO₂ budgets are nearing capacity

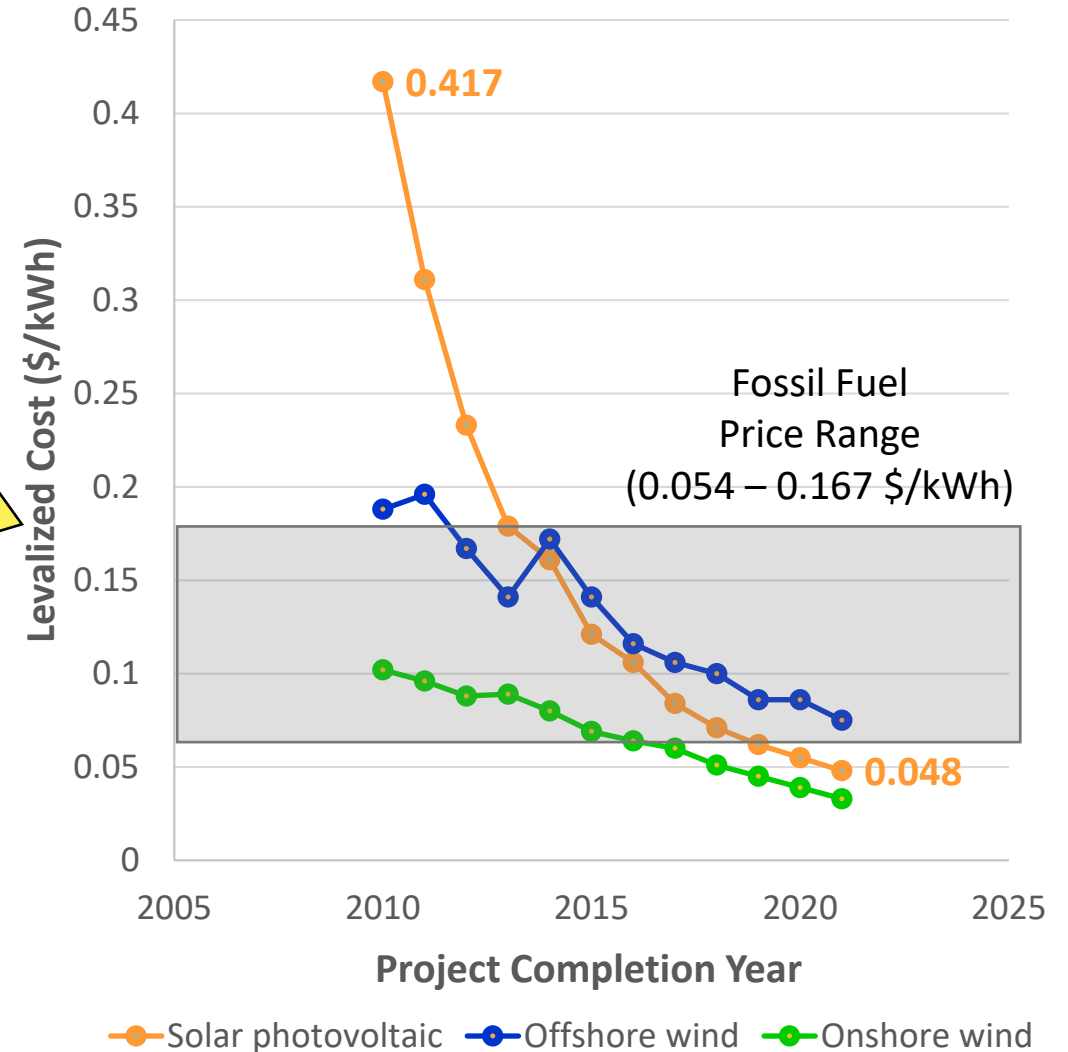


Climate Change 2022: Mitigation of Climate Change. Contribution of Working Group III to the Sixth Assessment Report of the IPCC

CO₂ Utilization Pathways



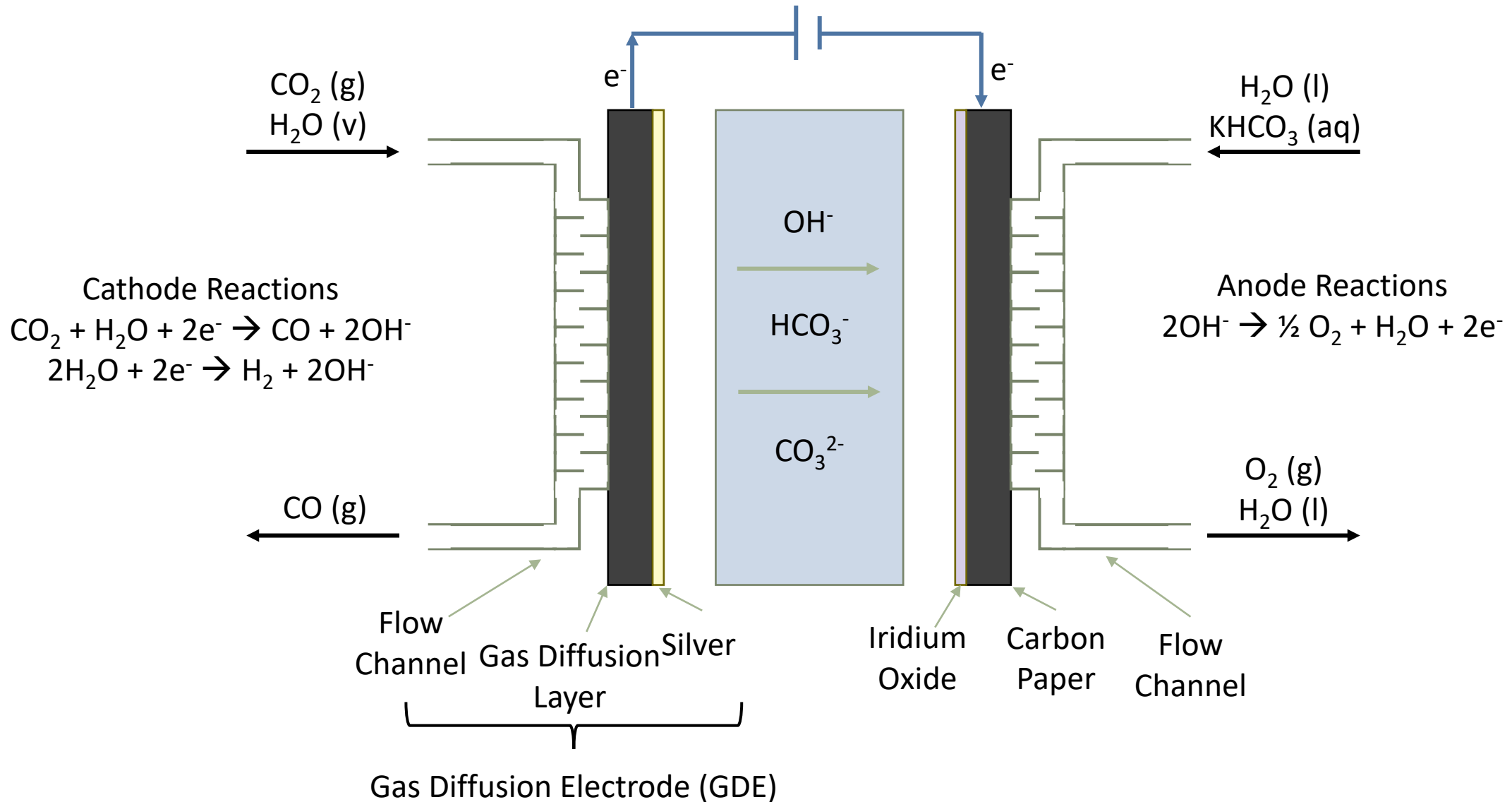
Electricity Costs from Various Sources



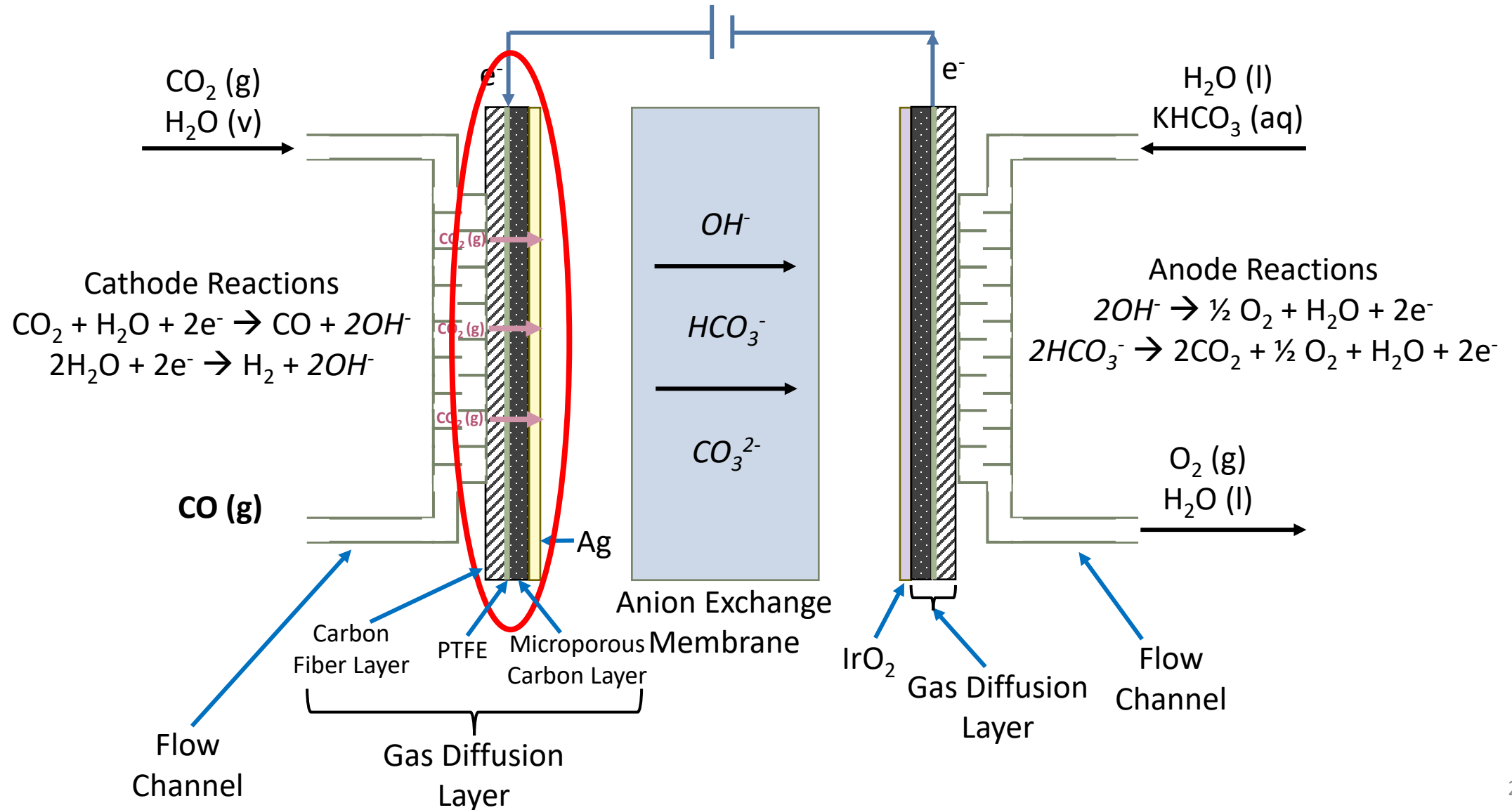
Adapted from: Transforming the carbon economy: challenges and opportunities in the convergence of low-cost electricity and reductive CO₂ utilization. *Energy & Environmental Science*, 13(2), 472–494.

Adapted from: IRENA (2022), Renewable Power Generation Costs in 2021, International Renewable Energy Agency, Abu Dhabi.

State of the art

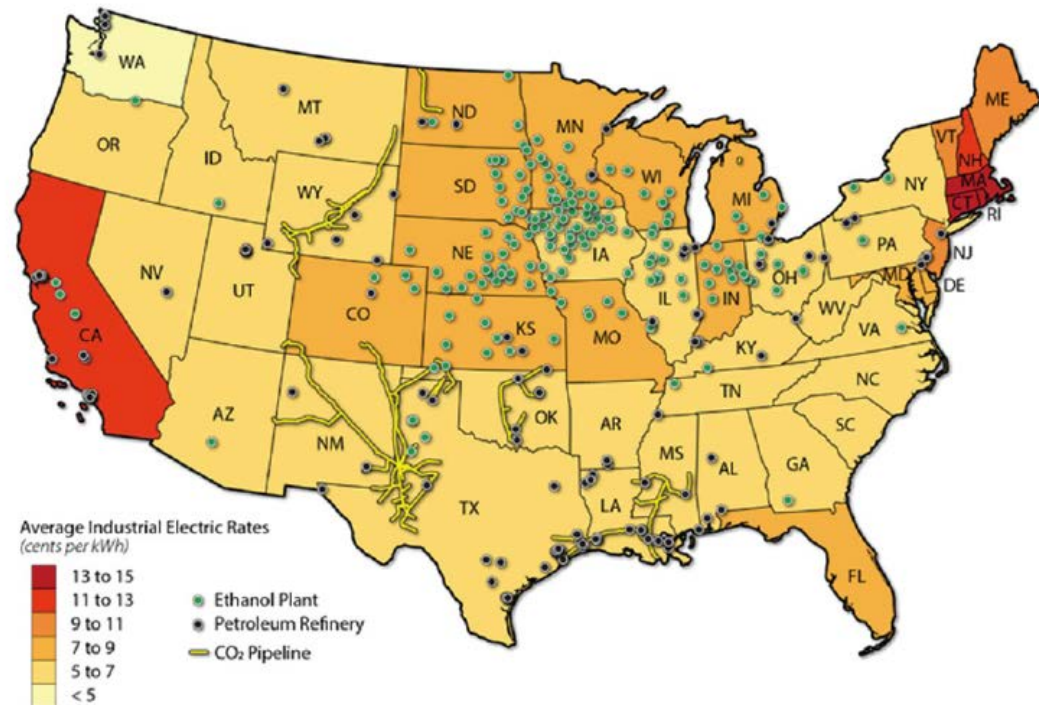


Membrane Electrode Assembly (MEA): state of the art electrolyzer design



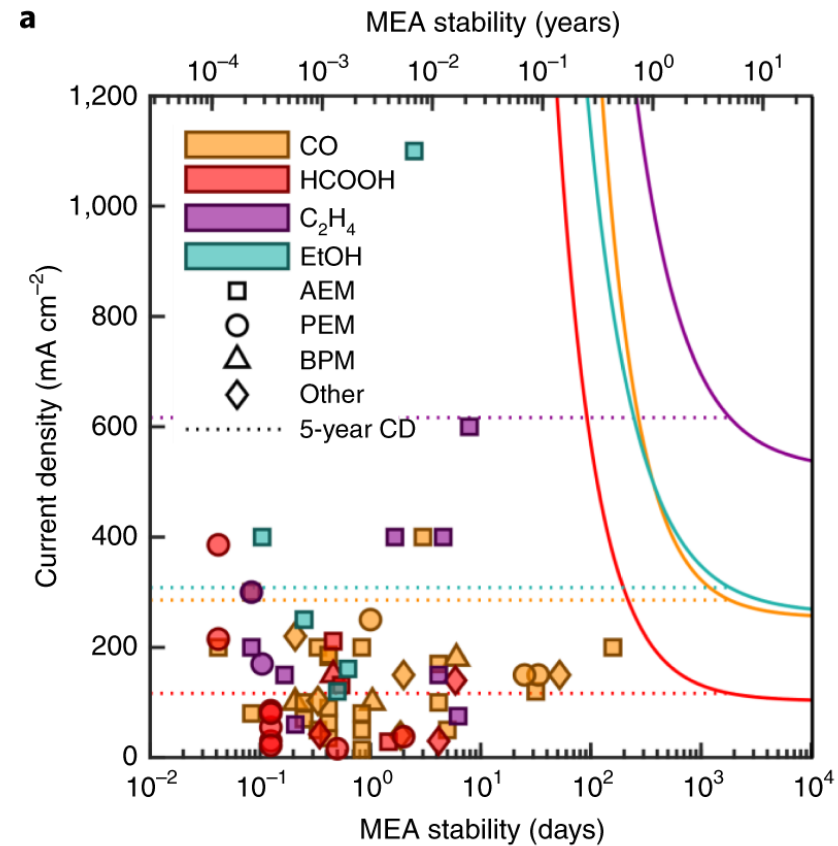
Distributed ethanol refineries represent promising point sources for CO₂ capture/utilization

- Ethanol fermentation facilities provide nearly pure CO₂ streams (~99%) with low capture costs¹
 - \$20-22 per ton¹
- Opportunity for near-term deployment of electrochemical CO₂ reduction

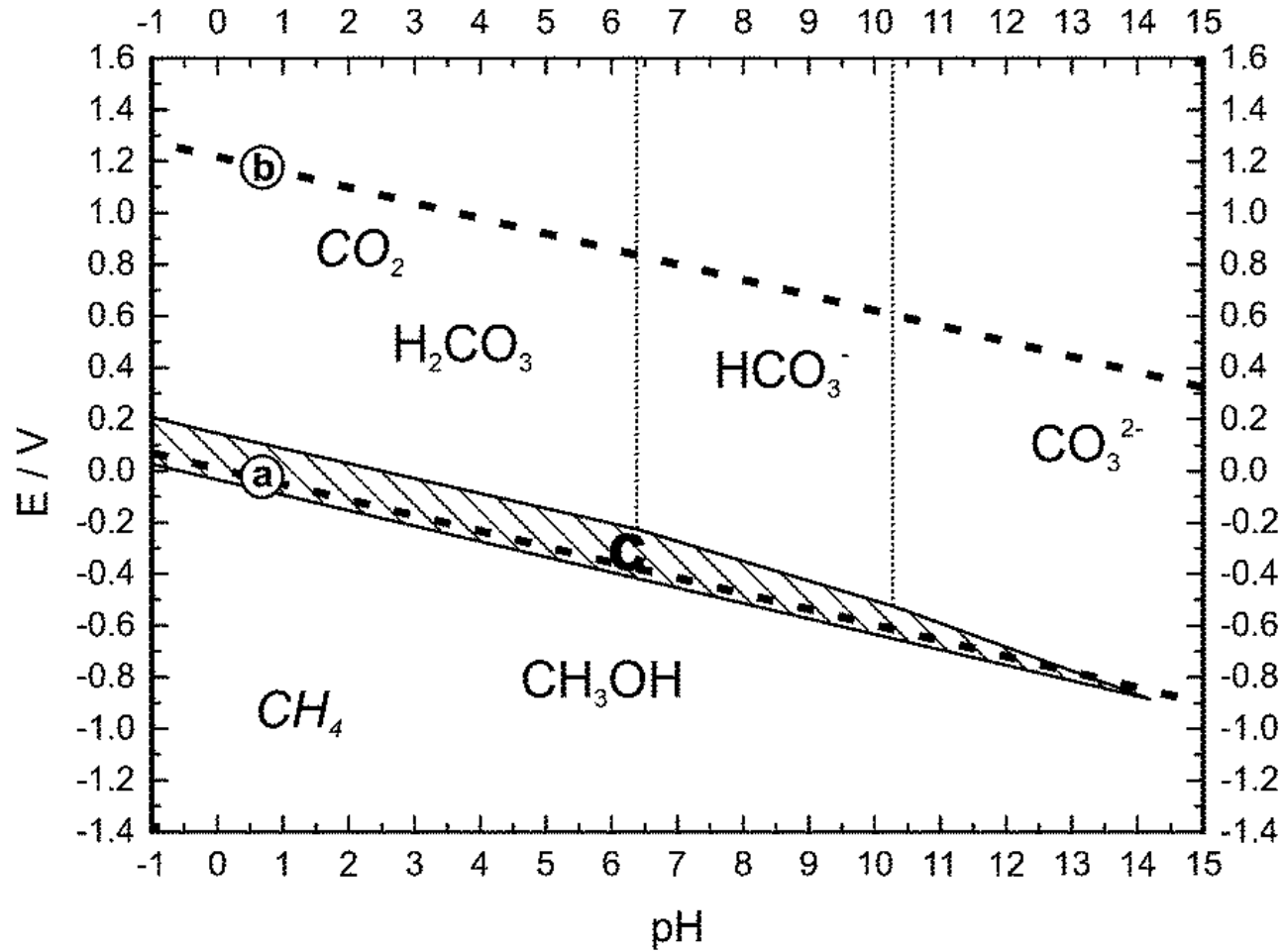


From Reference 1

MEA stability targets

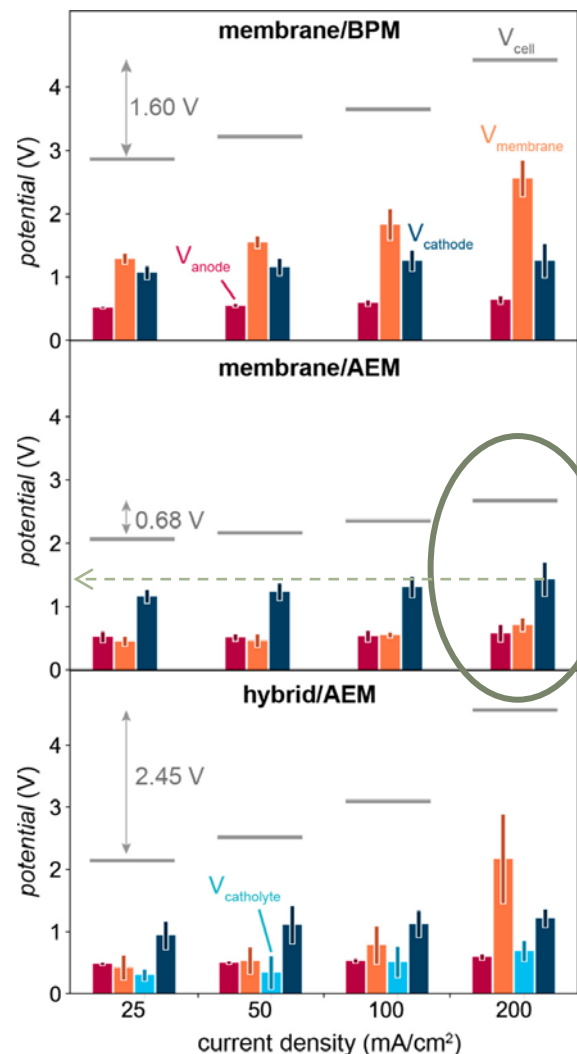
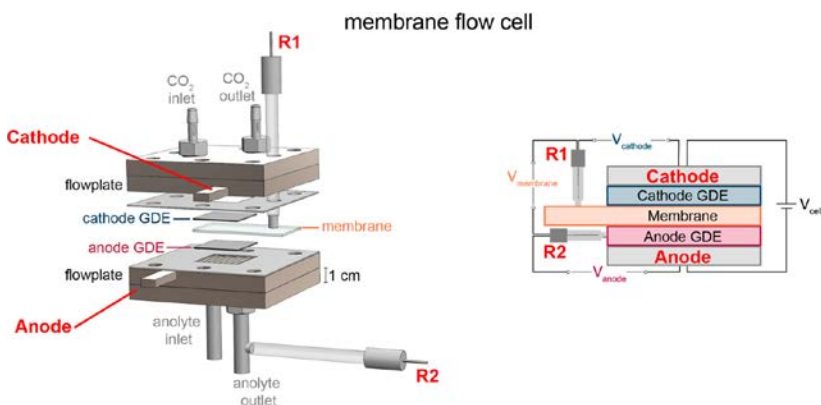


Pourbaix diagram for carbon



Cathode potentials under realistic CO₂ electrolysis conditions (1.2V+) are likely to cause corrosion

MEA setup for measuring voltage across specific components across specific components



- For anion exchange membrane (AEM)-type electrolysis cells, the cathode potential is likely at least 1.25V (vs. Ag/AgCl), depending on the overall cell potential
 - Overall cell potentials of 3V are a common benchmark
- Our experiments revealed measurable corrosion rates at 1.2V (vs. Ag/AgCl)
 - Higher cathode potentials may be experienced during startup/shutdown or when operating at high current densities (>200mA/cm²)

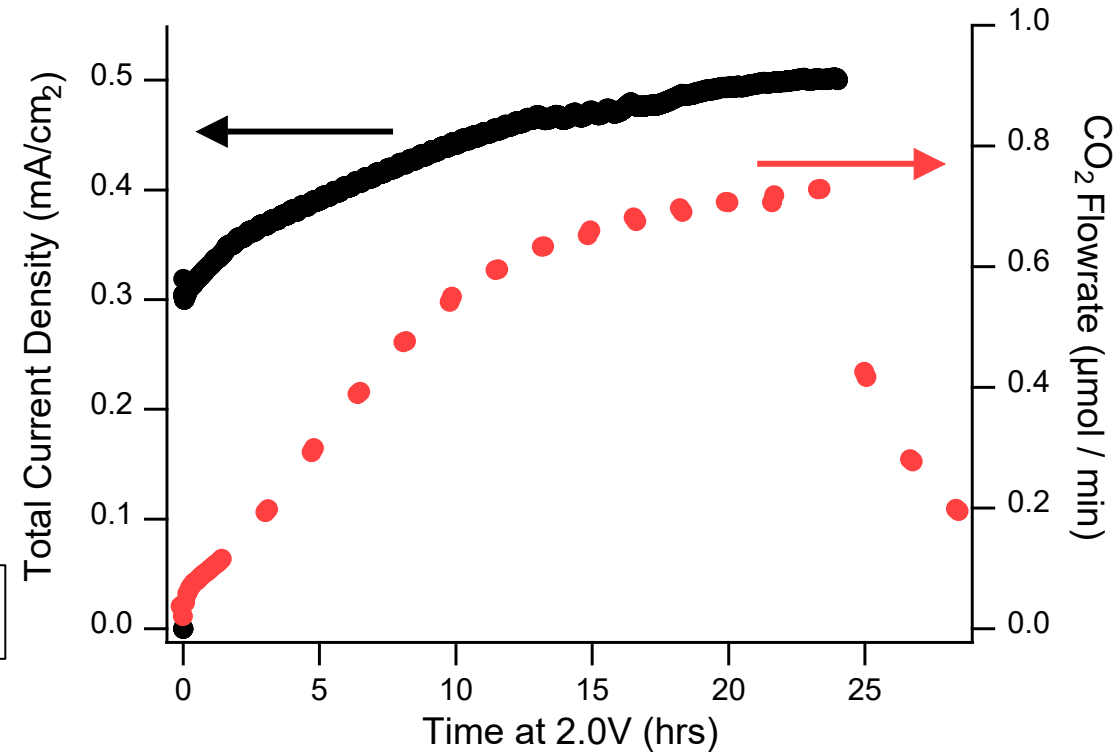
GC-detected CO₂ and potentiostat-measured current give reasonable estimate of mass loss

- 15sccm N₂ sweep gas used to bring corrosion products (CO₂) to GC
- CO₂ detected by GC used to estimate carbon corrosion mass loss according to the following equation:

$$GC \text{ Estimated Mass Loss} = \text{Sweep Gas Flowrate} * \Sigma \frac{CO_2 \text{ GC Peak Area}}{\text{Response Factor}} * \Delta t * MW_{CO_2}$$

- Potentiostat current used to estimate carbon corrosion according to the following equation:

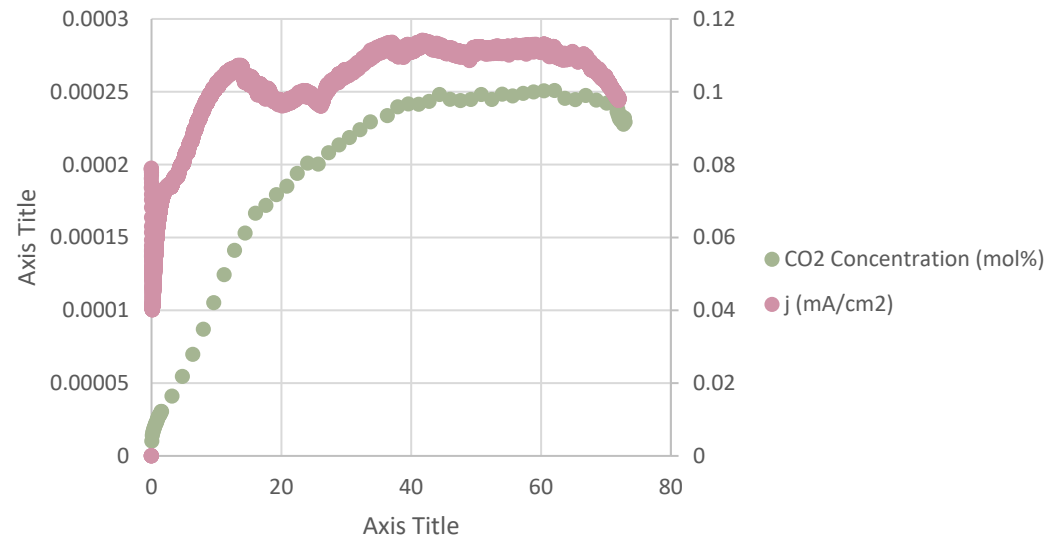
$$Potentiostat \text{ Estimated Mass Loss} = \Sigma \frac{Potentiostat \text{ Current (C/s)}}{96485 \frac{C}{mol e^-}} * \frac{1 mol CO_2}{4 mol e^-} * \Delta t * MW_{CO_2}$$



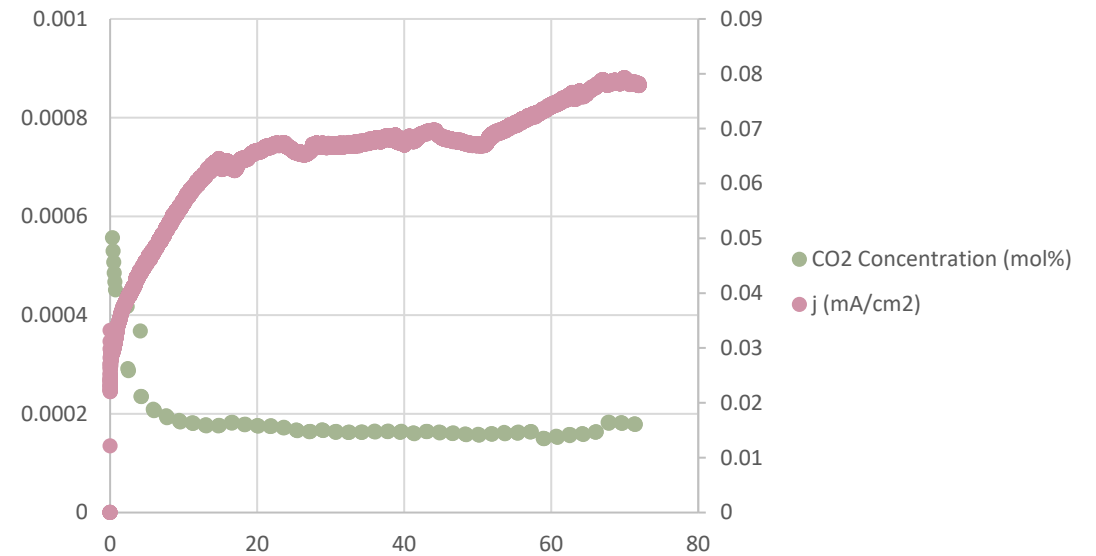
Measurement Type	Mass Loss	% Error from Measured Loss
Measured Mass Change	0.0091g	–
Potentiostat Estimated	0.0113g	24%
GC Estimated	0.0100g	10%

Phosphate vs KHCO_3 at 1.6V

Phosphate Solution



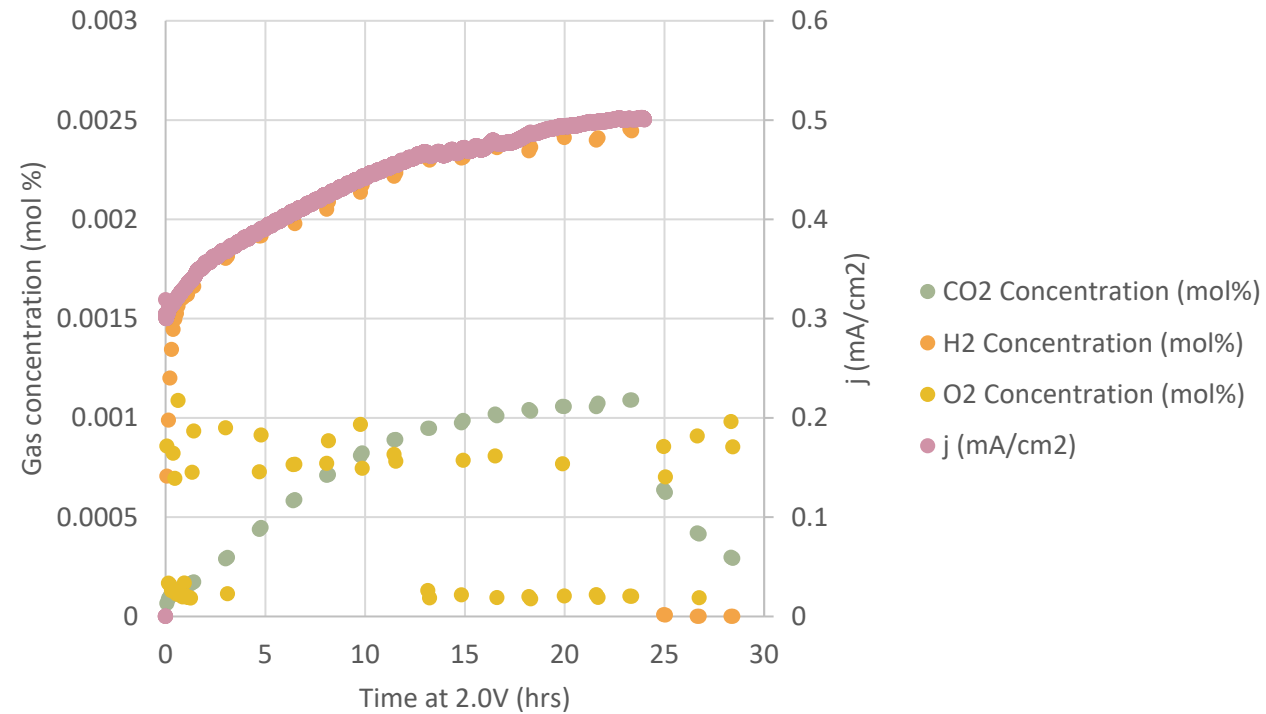
KHCO_3 Solution



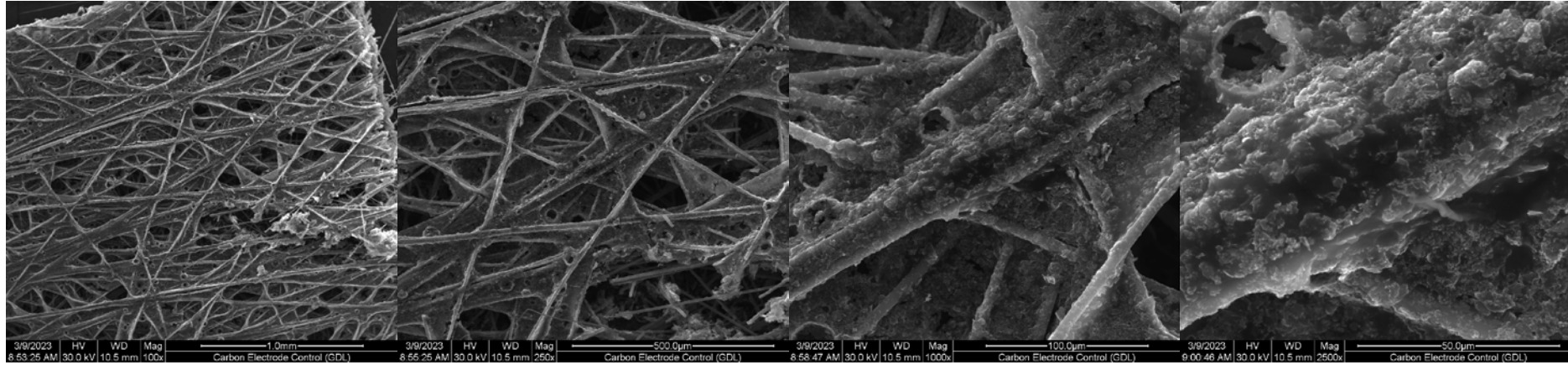
Measured Mass Loss		
Initial Electrode Mass =	0.0821 g	
Final Electrode Mass =	0.0751 g	
Mass Carbon Lost =	0.007 g	
% Mass Lost =	8.5%	

Measured Mass Loss		
Initial Electrode Mass =	0.0838 g	
Final Electrode Mass =	0.0795 g	
Mass Carbon Lost =	0.0043 g	
% Mass Lost =	5.1%	

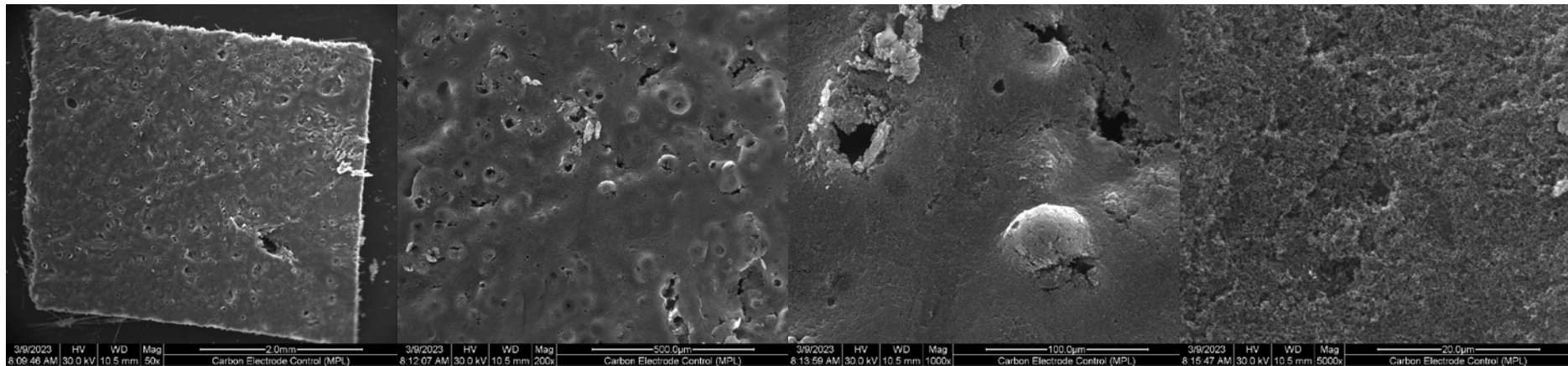
Slide of H₂, O₂, N₂, and CO₂ conc



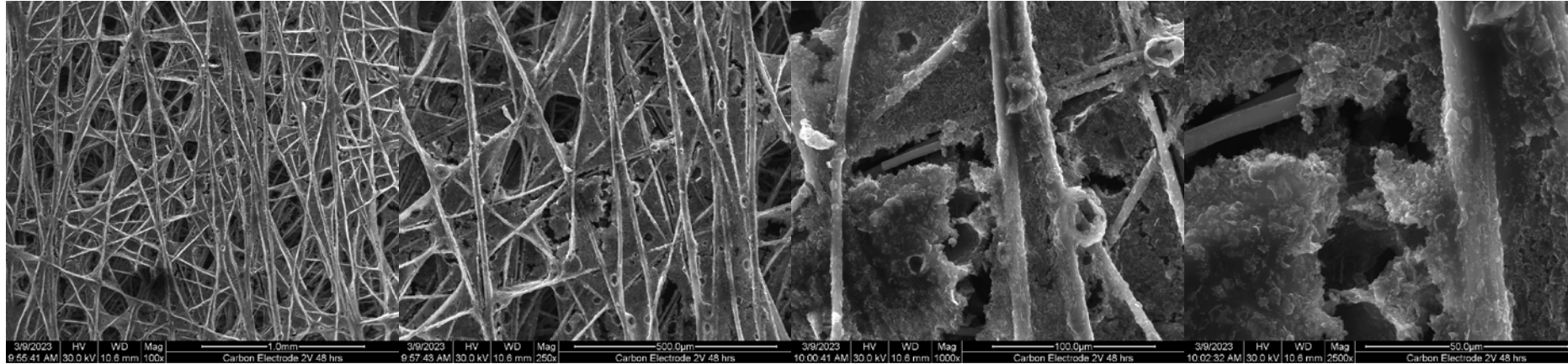
Fresh – Carbon fiber layer



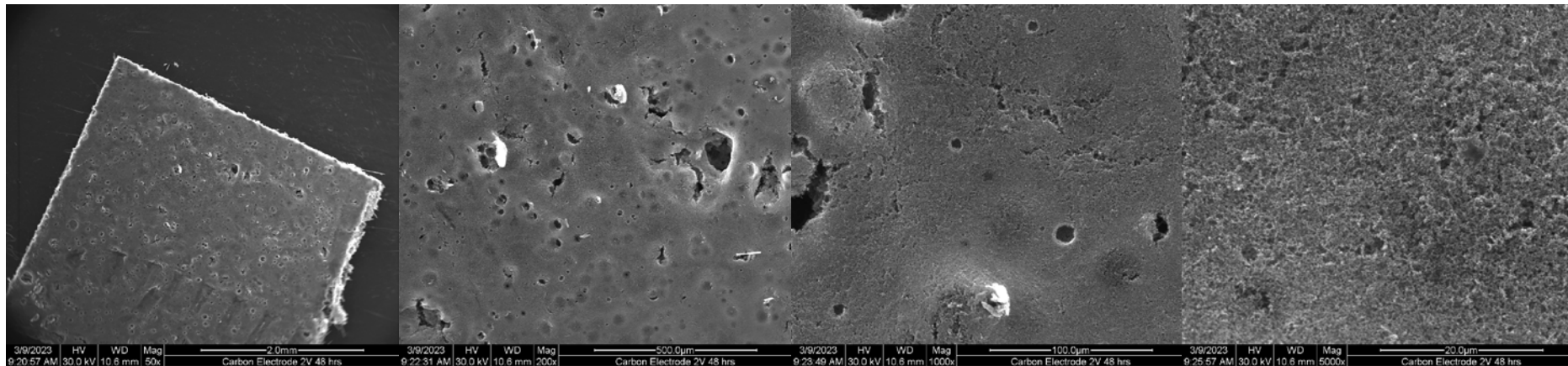
Fresh – Microporous layer



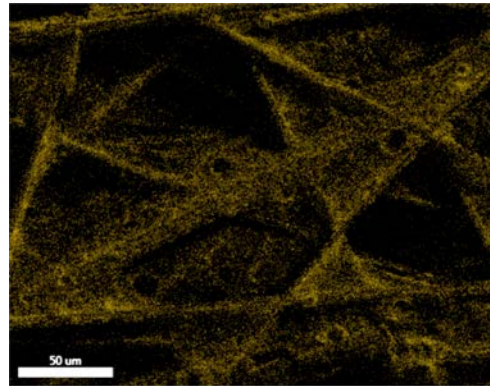
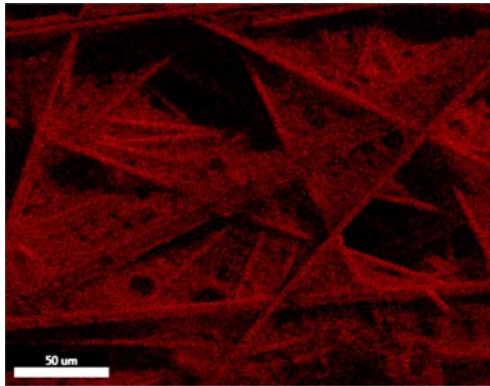
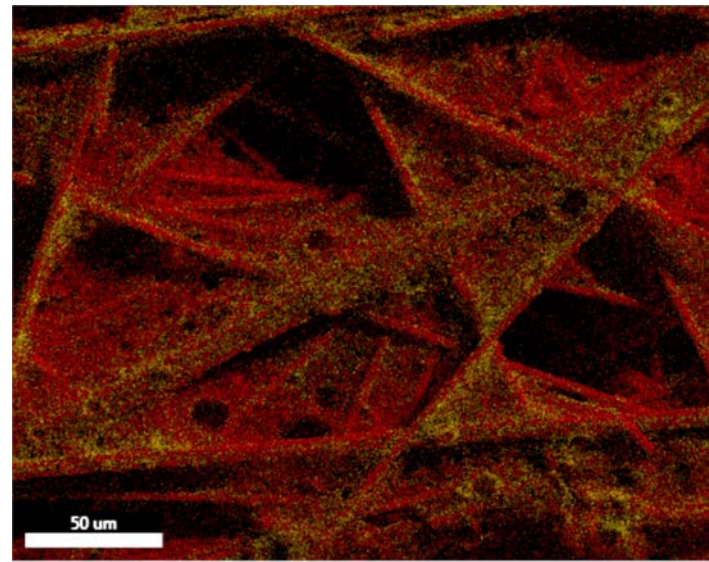
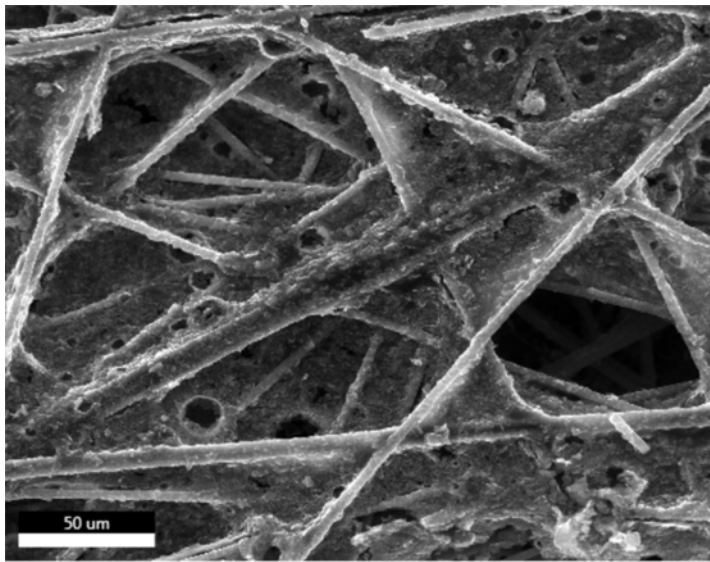
Spent – Carbon fiber layer



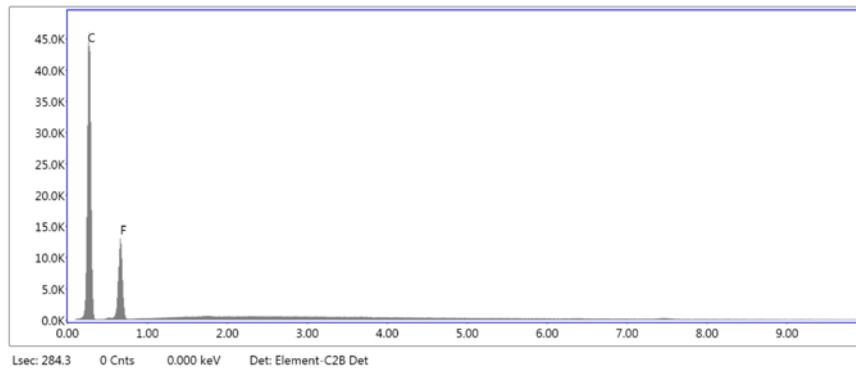
Spent (2V, 48hrs, KHCO₃) – Microporous layer



Fresh Electrode Fiber Layer

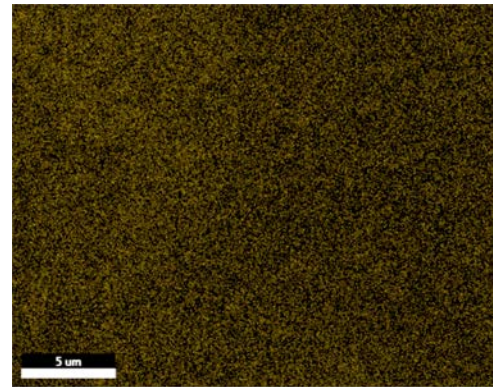
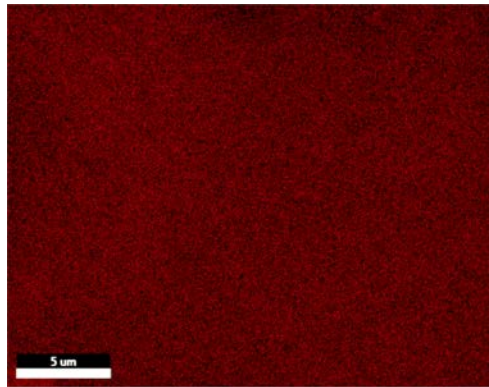
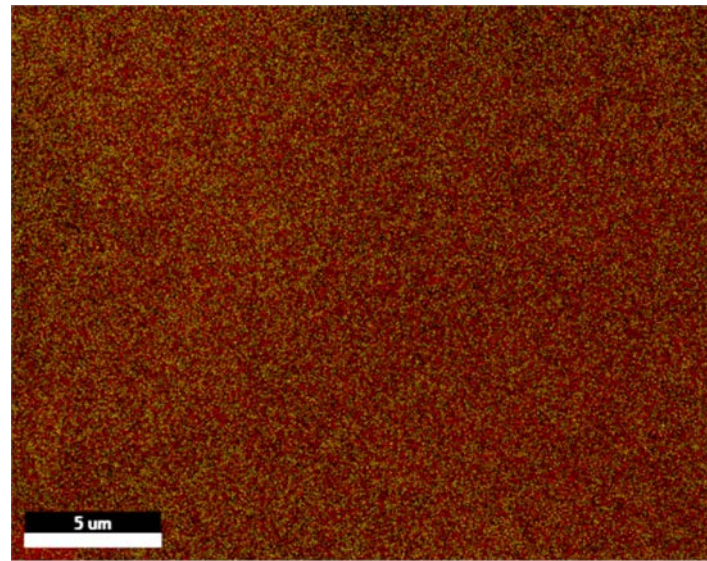
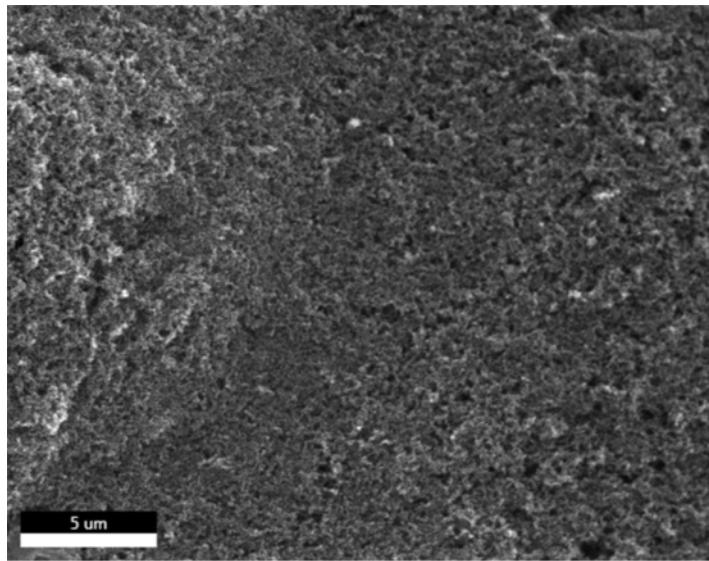


75% C K
25% F K

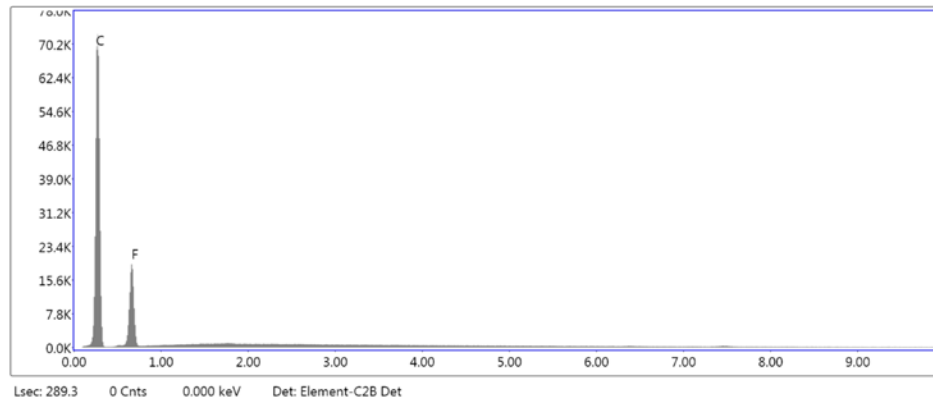


Element	Weight %
C K	72.18
F K	27.82

Fresh Electrode Microporous Layer

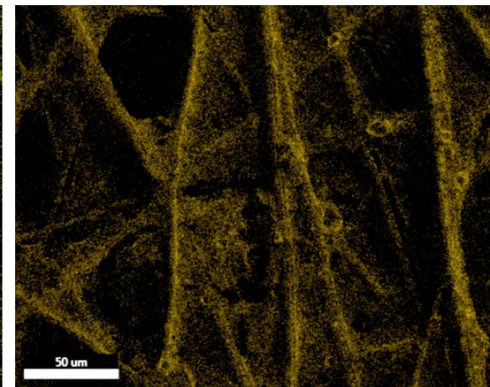
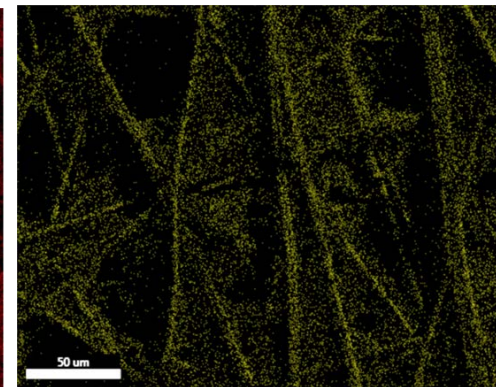
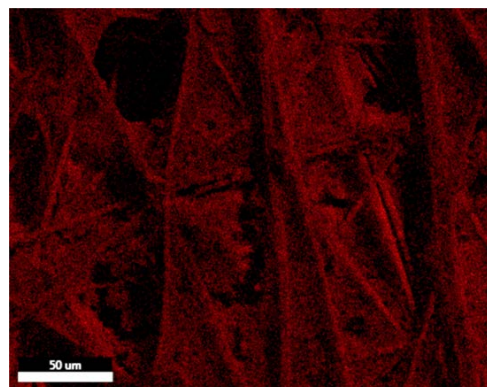
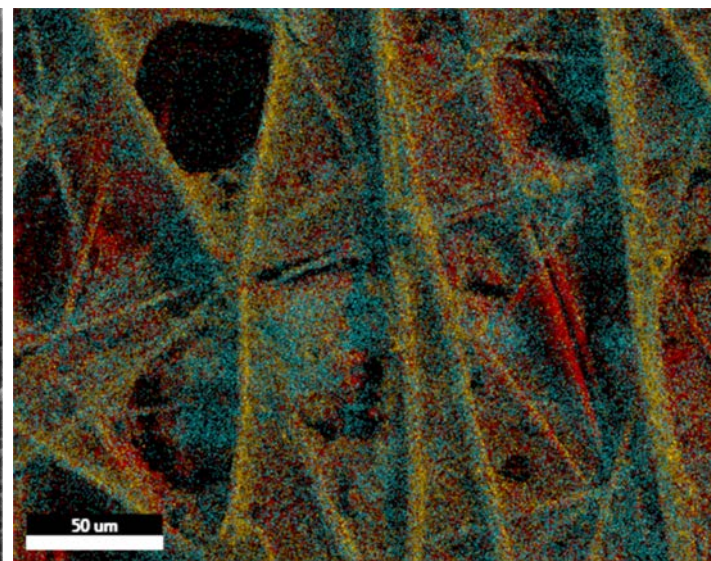
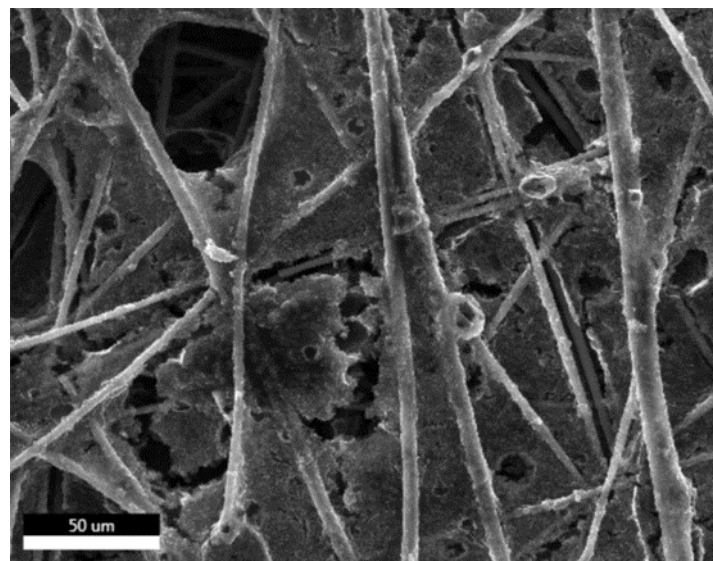


75% C K
25% F K

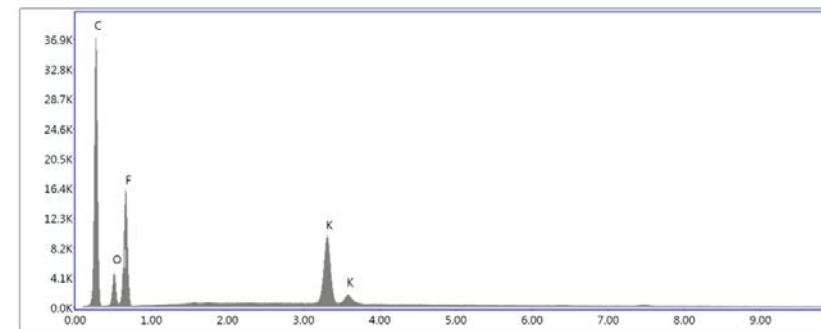
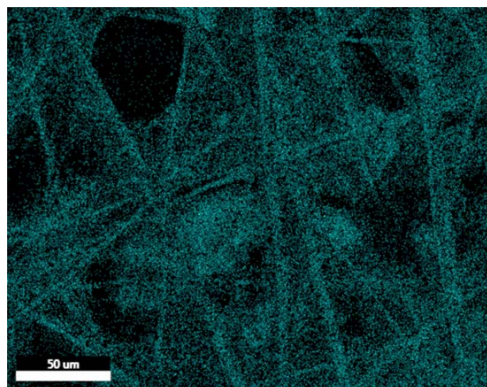


Element	Weight %
C K	72.94
F K	27.06

Spent Electrode Fiber Layer (2V, 48hrs, KCHO_3)

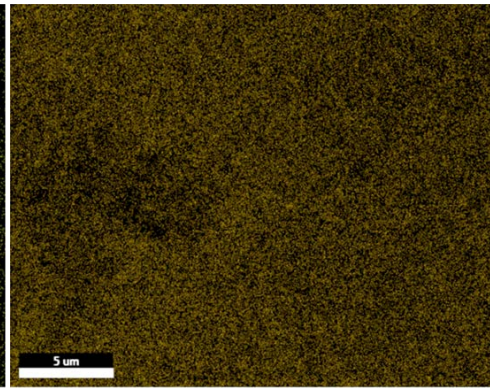
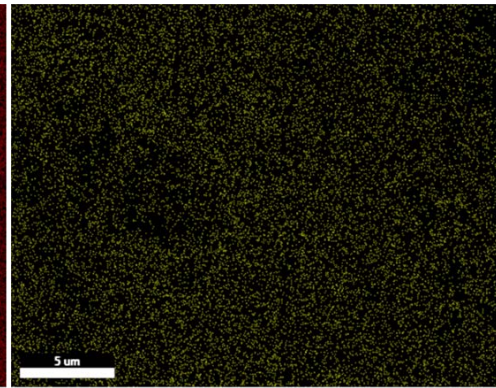
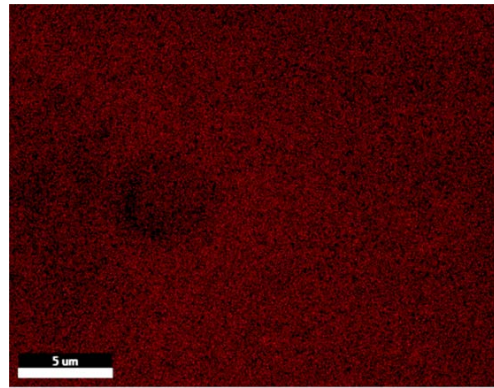
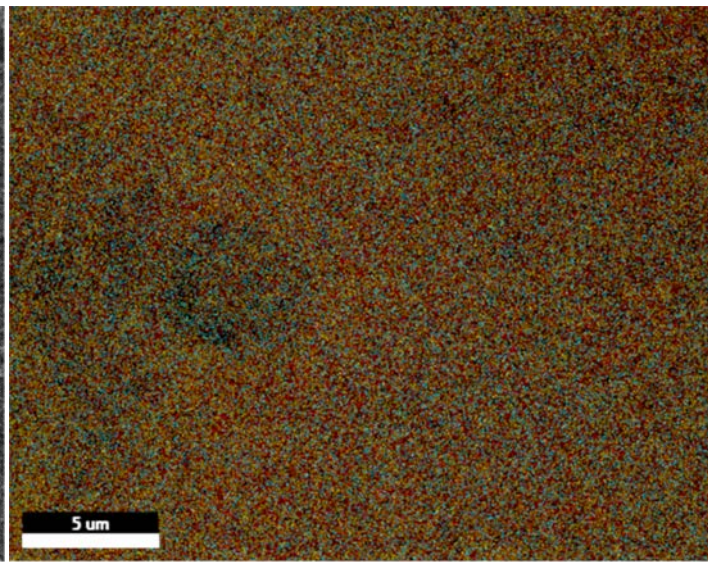
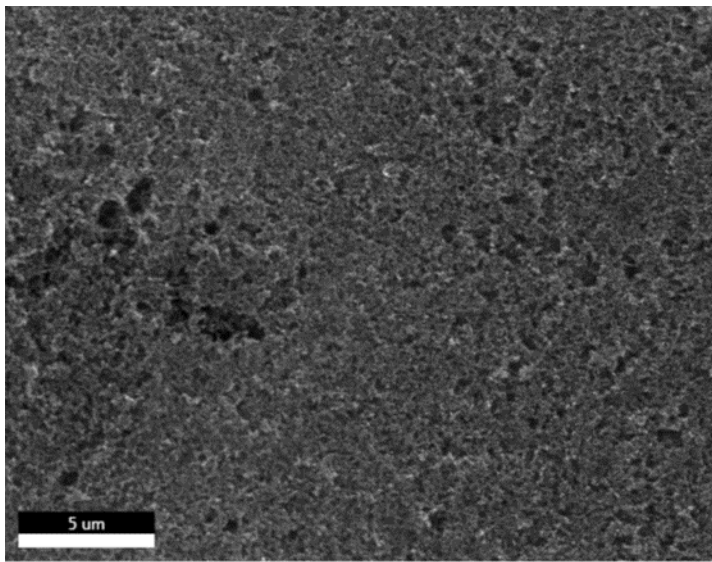


- 41% C K
- 6% O K
- 25% F K
- 28% K K

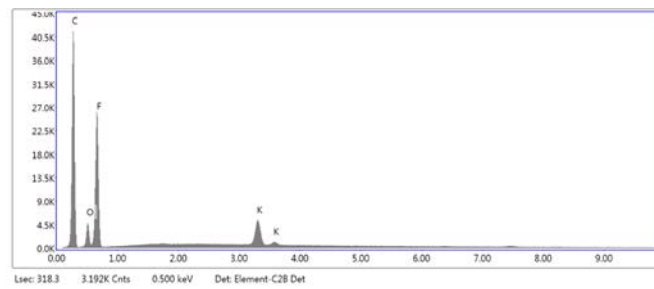
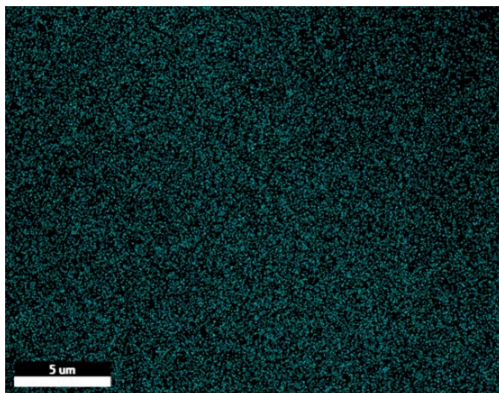


Element	Weight %	Atomic %
C K	51.21	62.61
O K	11.30	10.37
F K	32.58	25.18
K K	4.92	1.85

Spent Electrode Microporous Layer (2V, 48hrs, KCHO₃)



- 42% C K
- 6% O K
- 38% F K
- 14% K K

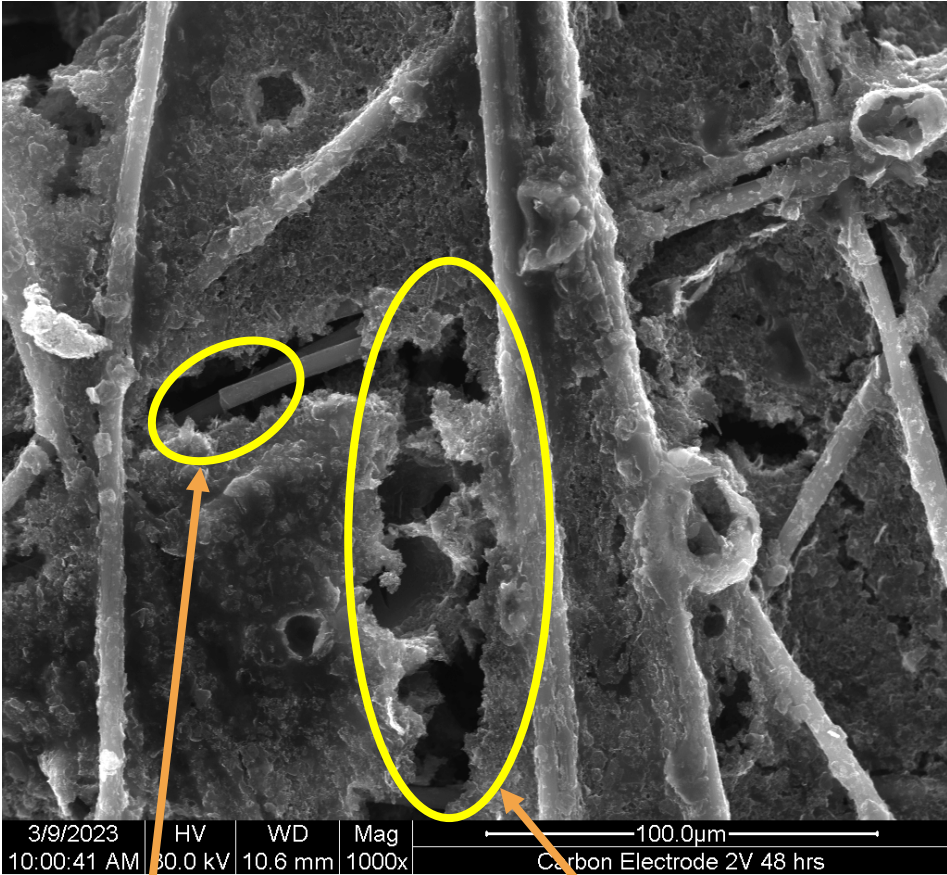


Element	Weight %	Atomic %
C K	50.58	61.63
O K	8.20	7.50
F K	38.97	30.02
K K	2.24	0.84

Fresh Electrode (1000X)
Fiber Layer



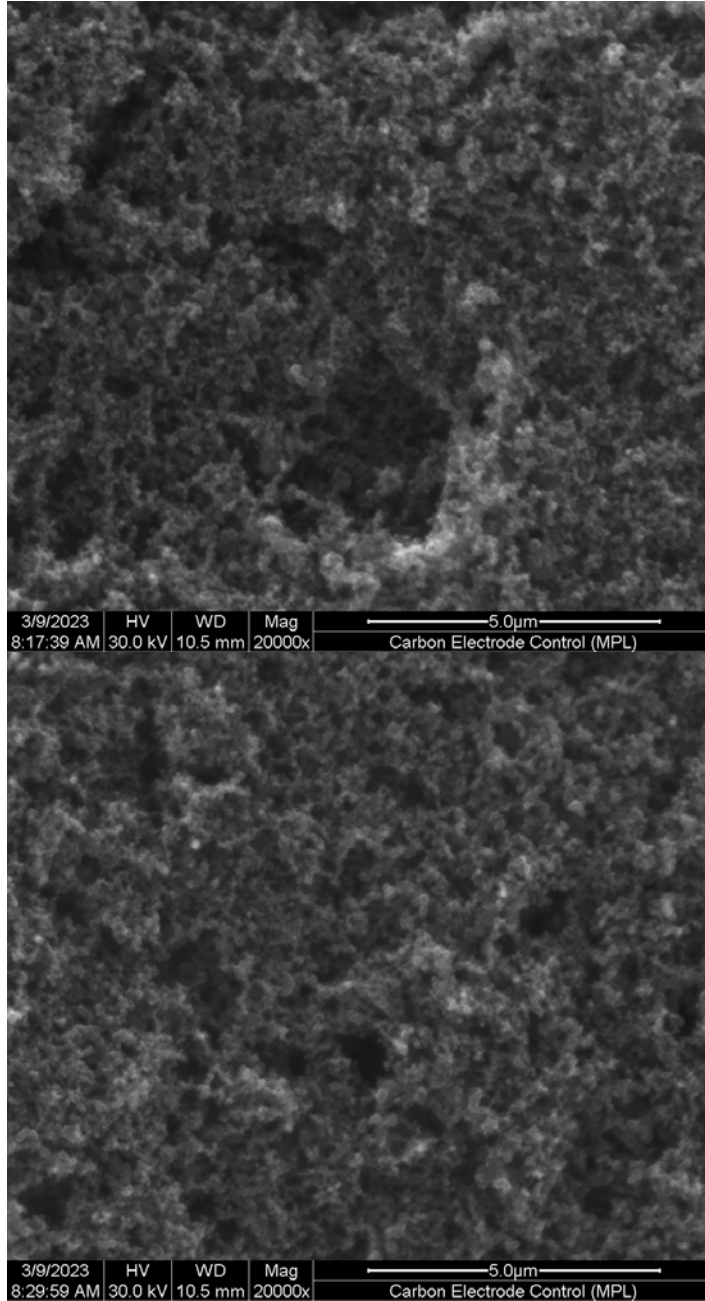
Corroded Electrode (1000X)
Fiber Layer
2V, 48hrs, KHCO₃



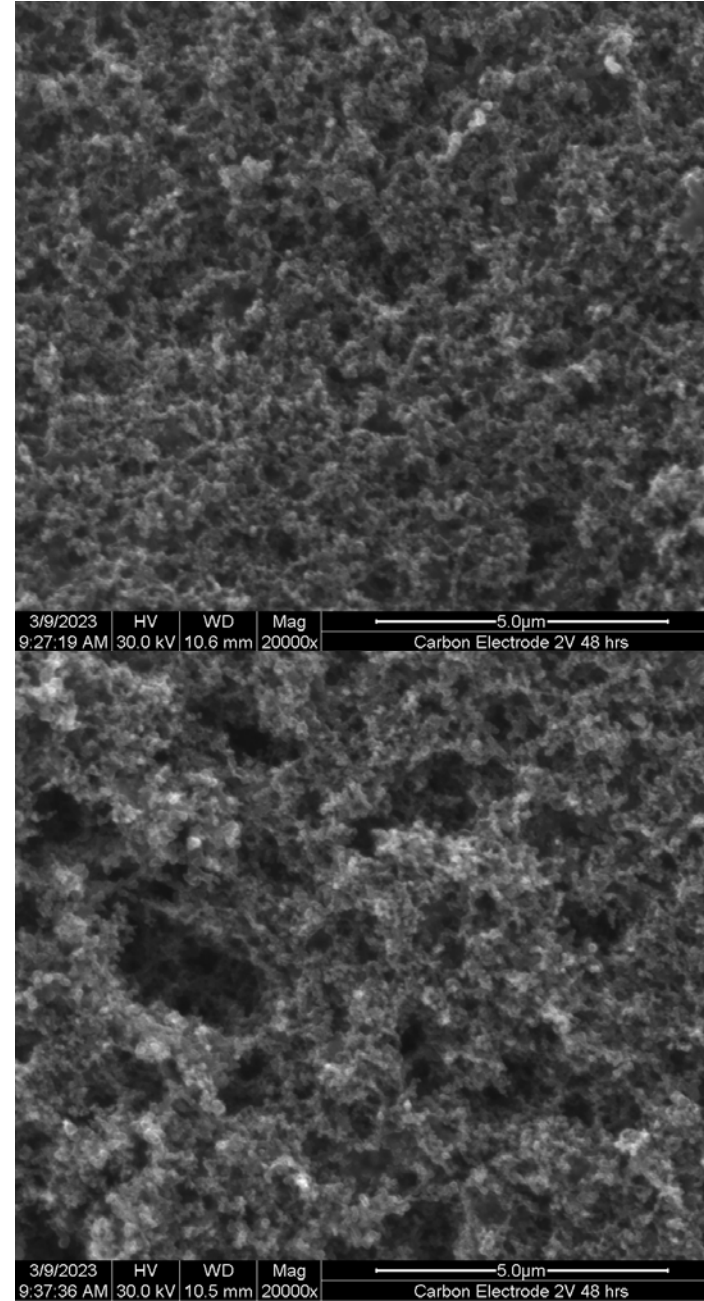
Fracturing of
carbon fibers

Degradation of
interstitial region

Fresh Electrode (20,000X)
Microporous Layer

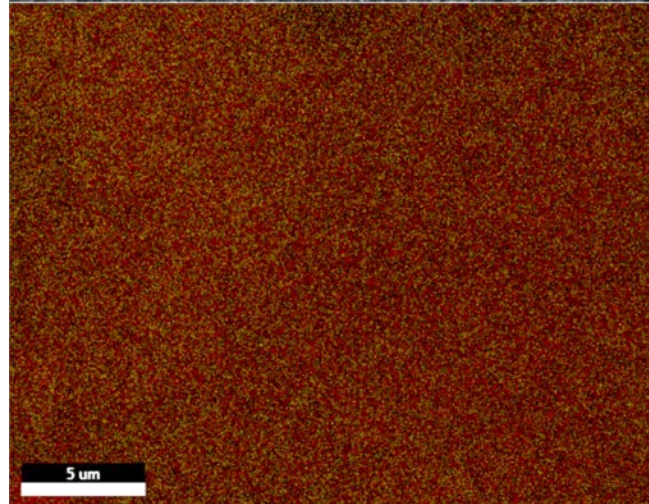
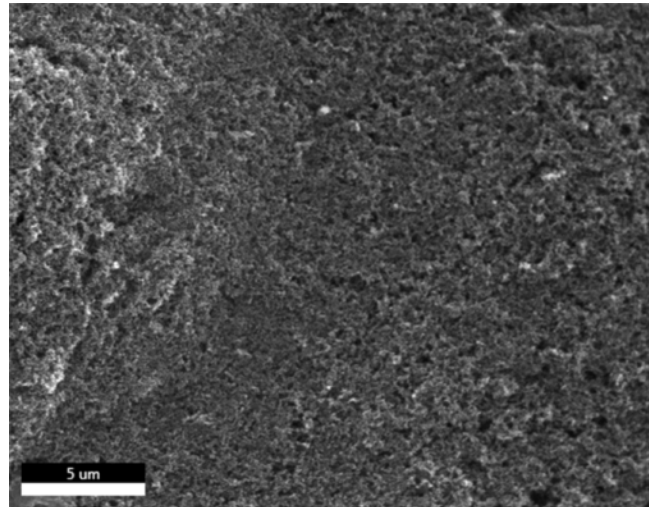


Corroded Electrode (20,00X)
Microporous Layer



- Hard to see a significant difference here
- Maybe some more pockmarks on the corroded sample(?)
- A cross-sectional view may be informative

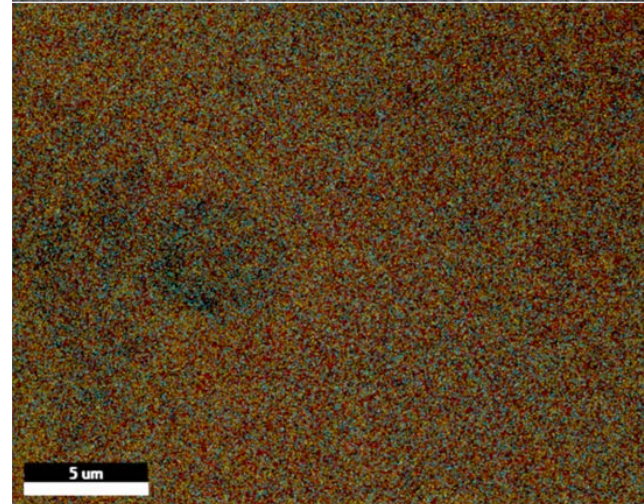
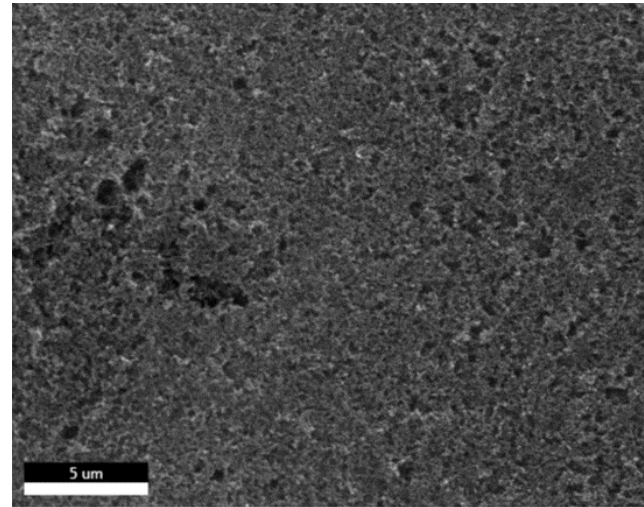
Fresh Electrode
Microporous Layer



Element	Weight %
75% C K	72.94
25% F K	27.06

C:F Ratio = 2.70

Corroded Electrode
Microporous Layer



Element	Weight %
42% C K	50.58
6% O K	8.20
38% F K	38.97
14% K K	2.24

C:F Ratio = 1.30

- EDS shows evidence of cavities in the surface/subsurface
- C:F ratio dramatically decreases after corrosion
 - Carbon layer being removed reveals PTFE coating