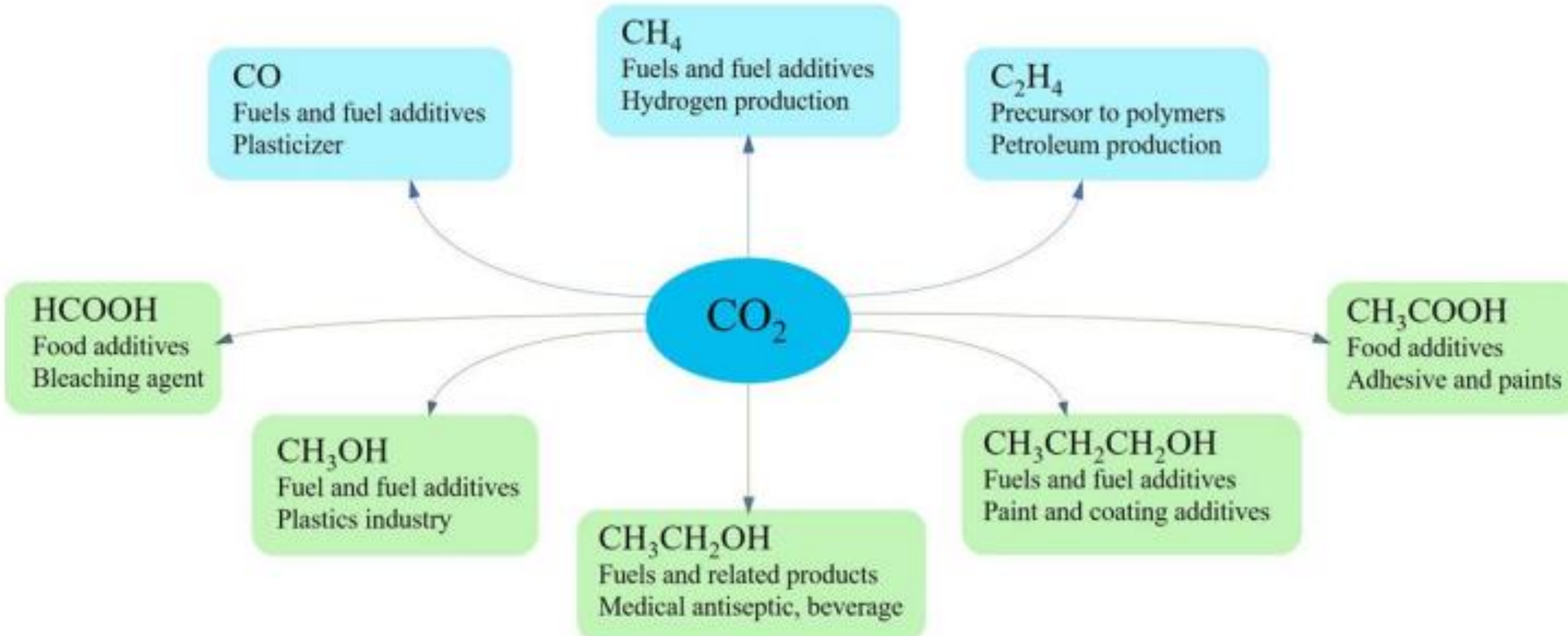
Literature Review: Assessing Reactor Design for Efficient Electrochemical CO_2 Reduction

Daniel A. Moreno

22 June 2021

Center for Applied Energy Research

Introduction – Why Electrochemical CO_2 Reduction?



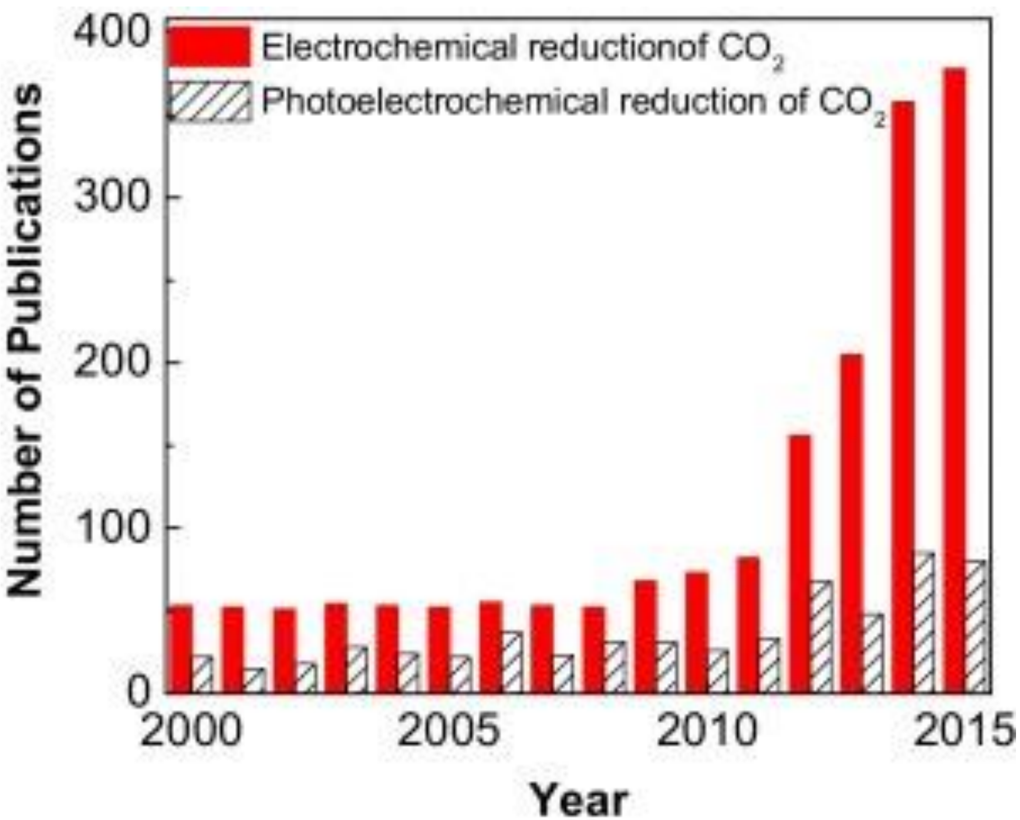
Lin R, Guo J, Li X, Patel P, Seifitokaldani A. Electrochemical reactors for CO2 conversion. Catalysts. 2020 May;10(5):473.

Conversion Method	Biochemical	Bioelectrochemical	Biophoto-electrochemical	Chemical	Electrochemical	Photochemical	Photo-electrochemical	Radiochemical
Reagent/ Energy Source	Bacteria	Enzyme, charge carrier, CO2 + oxoglutaric acid	Hv, light, enzyme + charge carrier	Mg2+, Sn2+, Na+	Electrons, protons	Hv, light	Hv, light, electrons	Gamma-radiation
Products	CH4	Isocitric acid	HCOOH	C, CO, Na2C2O4	CH4, HCOOH, HCHO	CO, HCOOH, HCHO	CO	HCOOH, HCHO

Adapted from: P.K. Scott. Sustainable and Green Electrochemical Science and Technology (Wiley, 2017).

Introduction – Why Electrochemical CO_2 Reduction?

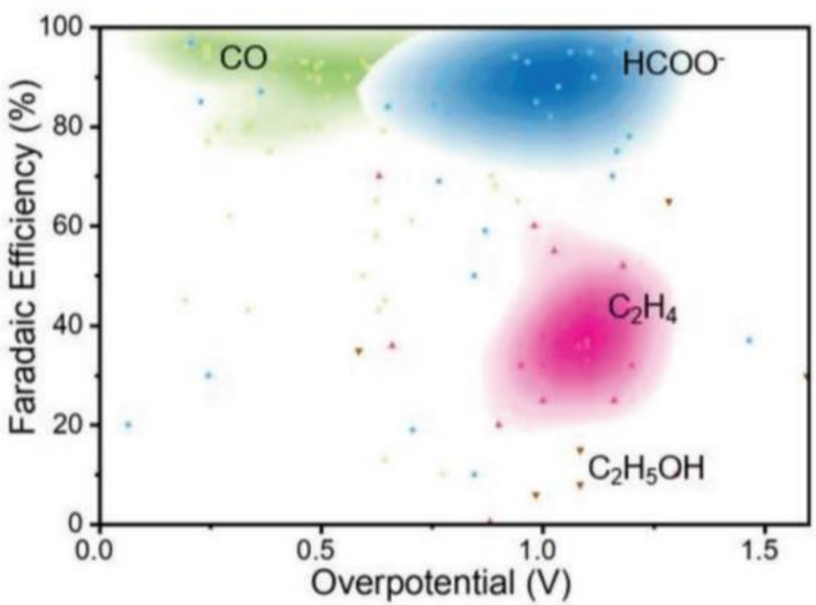
- ➢Process can operate under standard temperature & pressure conditions
- ➢Product selectivity can be tuned with appropriate electrode potential & catalysts
- ➢Can promote renewable energies to drive process
- ➢Low scale-up economy

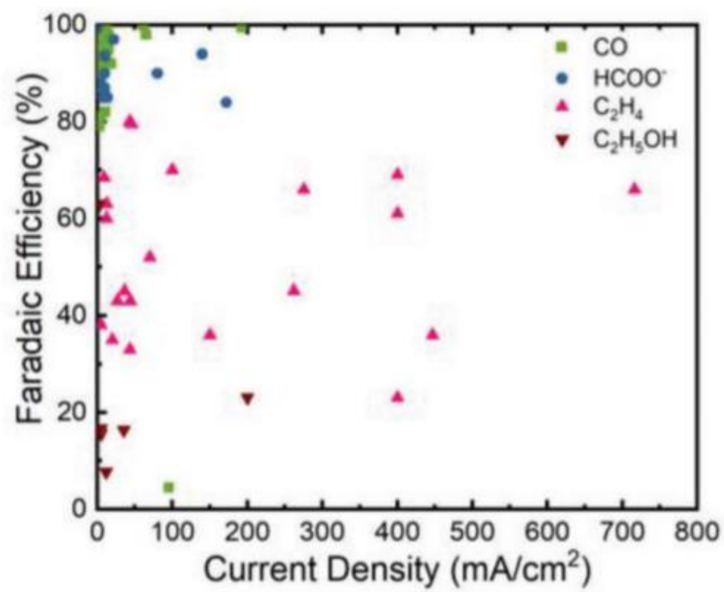


Kumar B, Brian JP, Atla V, Kumari S, Bertram KA, White RT, Spurgeon JM. New trends in the development of heterogeneous catalysts for electrochemical CO2 reduction. Catalysis today. 2016 Jul 15;270:19-30.

Long-Term Goals

- High current density/product rate
  - Industrial scale: 200 mA/cm^2 minimum
- Minimize overpotential – additional voltage required due to ohmic/mass transfer
- High long-term stability
- Large-scale operation in regions with high clean energy resources
- Optimized operating conditions (voltage, temperature, pressure) to maximize efficiency, minimize energy consumption

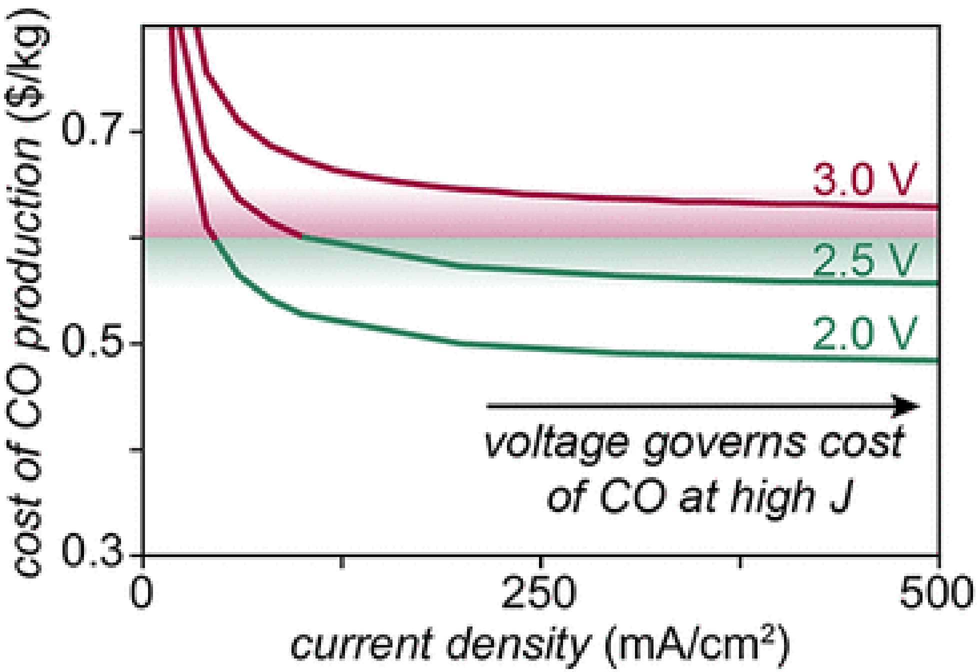




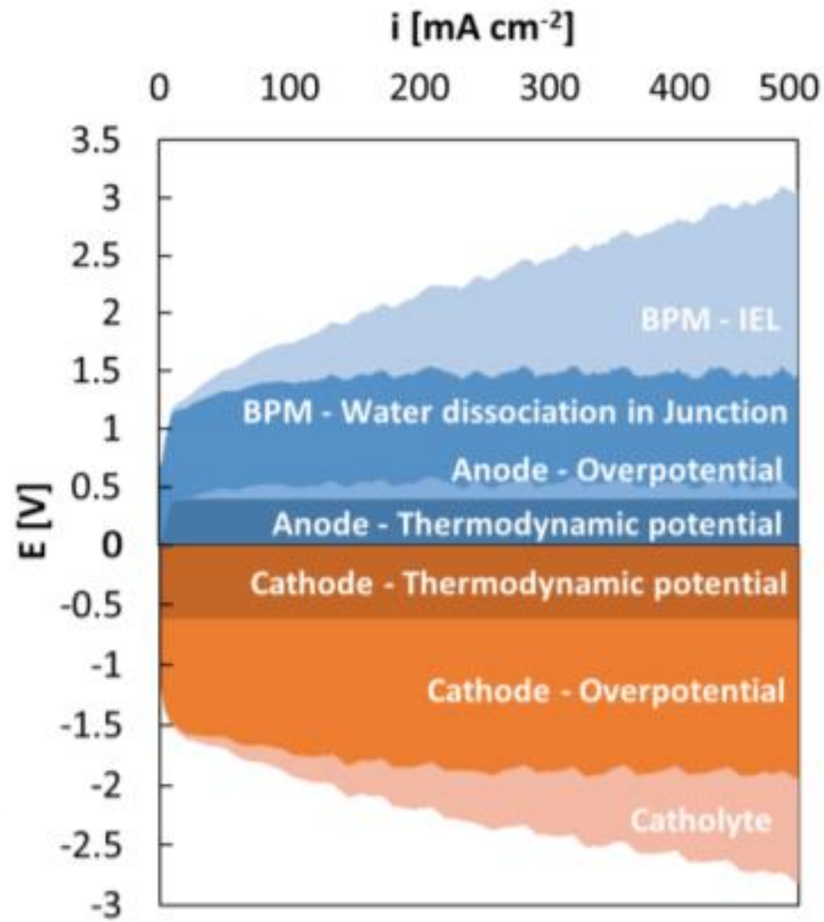
Kibria MG, Edwards JP, Gabardo CM, Dinh CT, Seifitokaldani A, Sinton D, Sargent EH. Electrochemical CO2 reduction into chemical feedstocks: from mechanistic electrocatalysis models to system design. Advanced Materials. 2019 Aug;31(31):1807166.

Energy Efficiency

- Energy consumption depends on both current and voltage, so a general design goal is to minimize overpotential
- Higher voltages not only increase cost, but also lead to stability issues

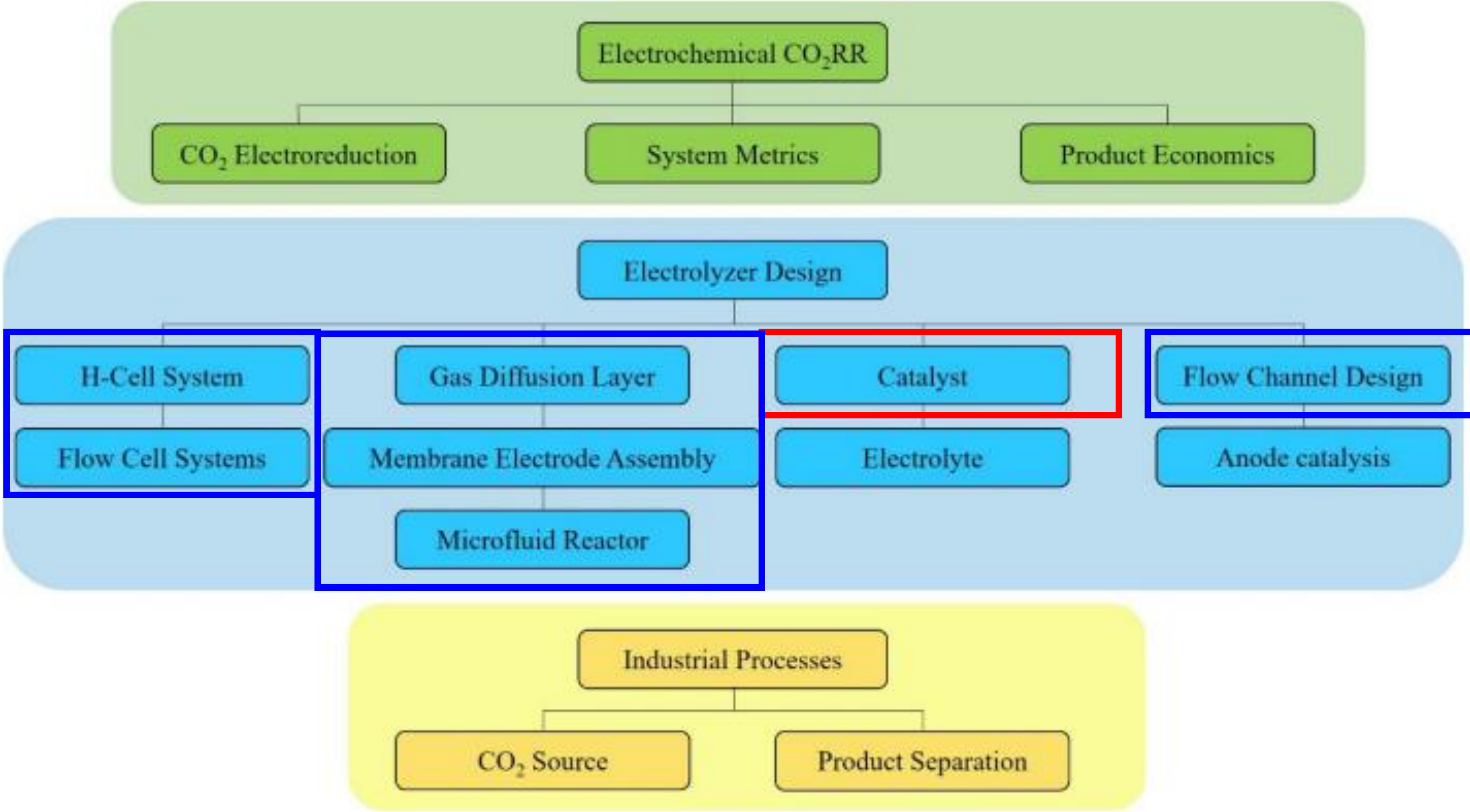


Salvatore D, Berlinguette CP. Voltage matters when reducing CO2 in an electrochemical flow cell. ACS Energy Letters. 2019 Dec 16;5(1):215-20.



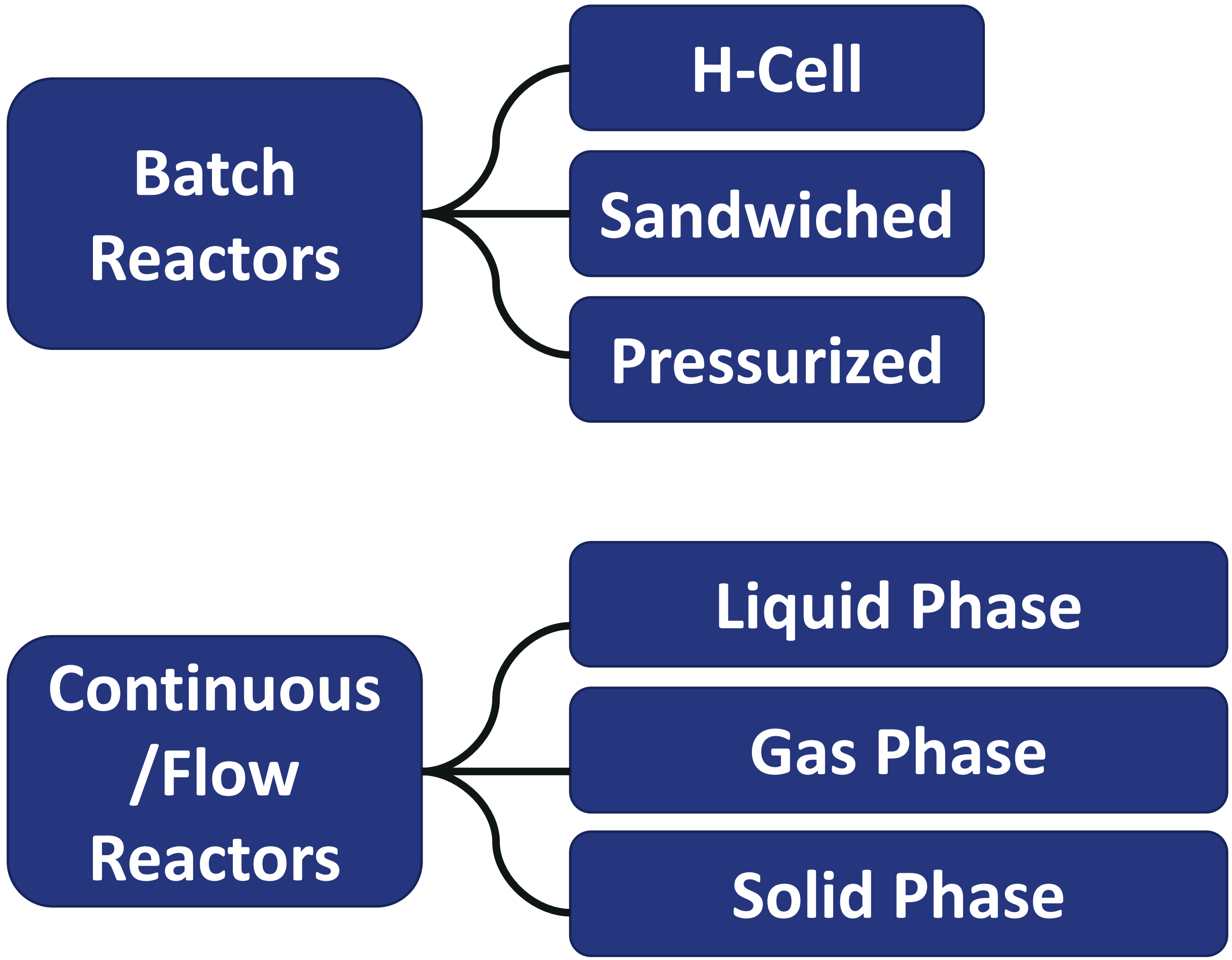
Chen Y, Vise A, Klein WE, Cetinbas FC, Myers DJ, Smith WA, Deutsch TG, Neyerlin KC. A robust, scalable platform for the electrochemical conversion of CO2 to formate: identifying pathways to higher energy efficiencies. ACS Energy Letters. 2020 May 11;5(6):1825-33.

Electrochemical Reactor Design



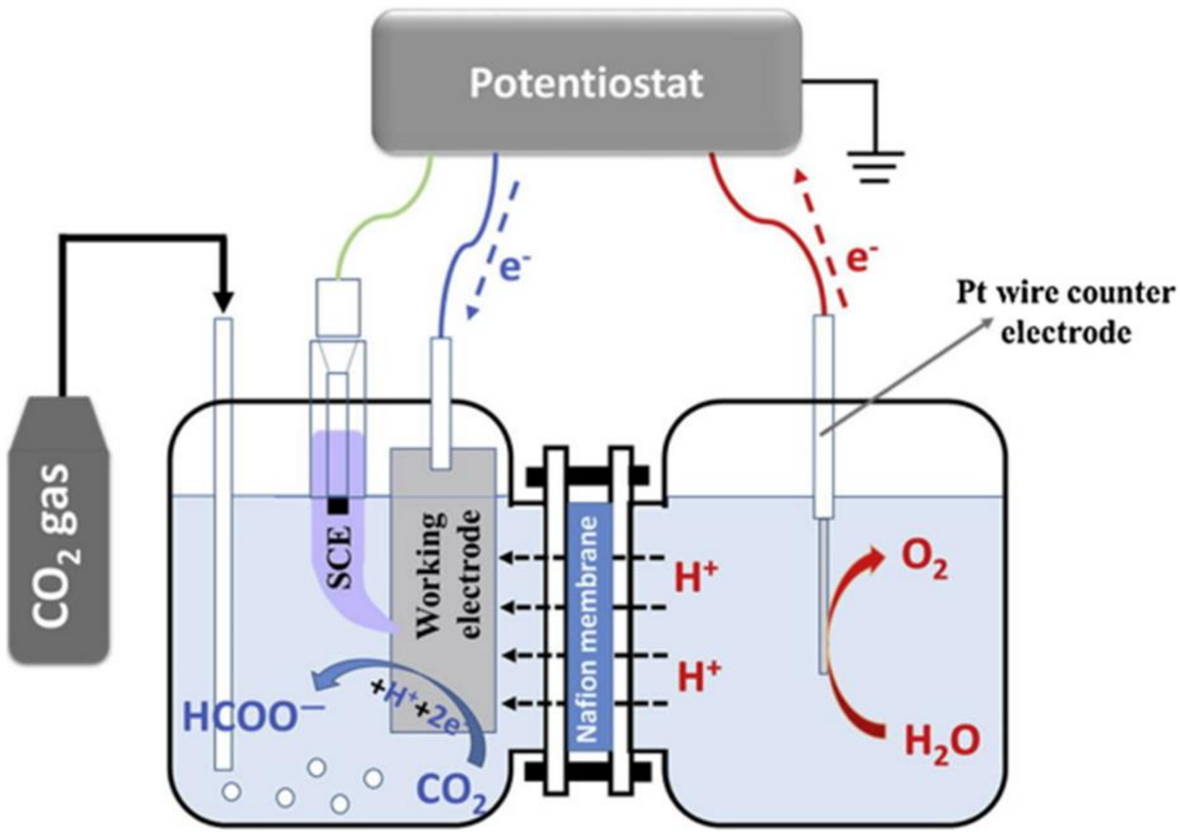
Lin R, Guo J, Li X, Patel P, Seifitokaldani A. Electrochemical reactors for CO2 conversion. Catalysts. 2020 May;10(5):473.

Types of Electrochemical Reactors



H-Cell Electrochemical Reactor

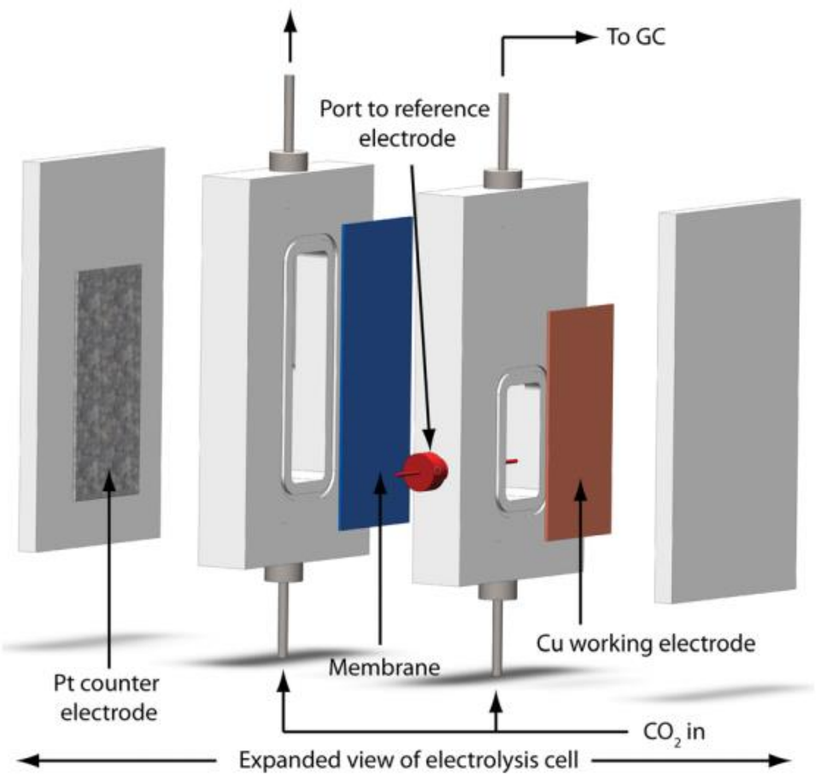
- Simplest form of operation
- Best for initially testing different catalysts/operating conditions
- Membrane used can either be cation exchange (Nafion), anion exchange, or bipolar, depending on chemical configuration



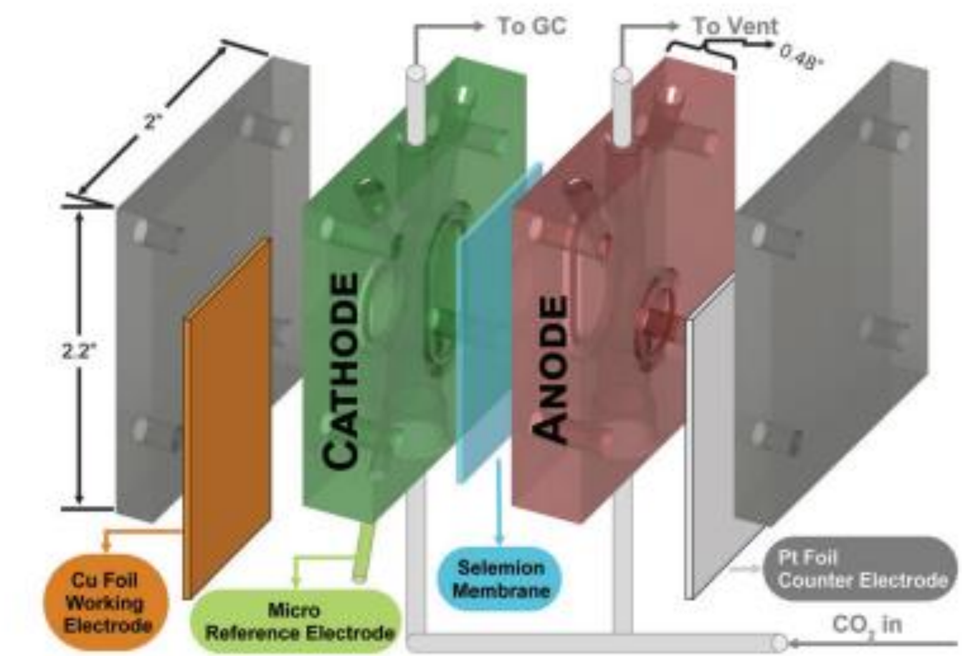
Zhao C, Wang J. Electrochemical reduction of CO2 to formate in aqueous solution using electro-deposited Sn catalysts. Chemical Engineering Journal. 2016 Jun 1;293:161-70.

Compressed "Sandwiched" Type of H-Cell

- ➢Higher **surface-to-volume (S/V)** ratio enables higher product concentrations and detections for carbon products
- ➢Lower volume also minimizes spacing within cell to decrease resistance
- ➢However, a smaller S/V can minimize bubble formation and pH changes



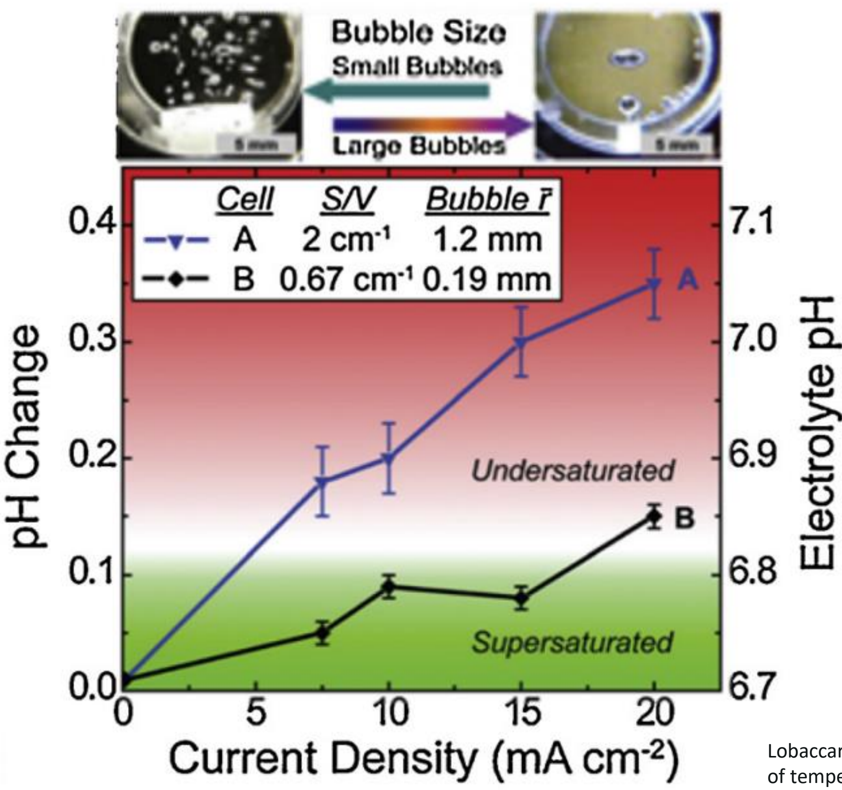
Kuhl KP, Cave ER, Abram DN, Jaramillo TF. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. Energy & Environmental Science. 2012;5(5):7050-9.

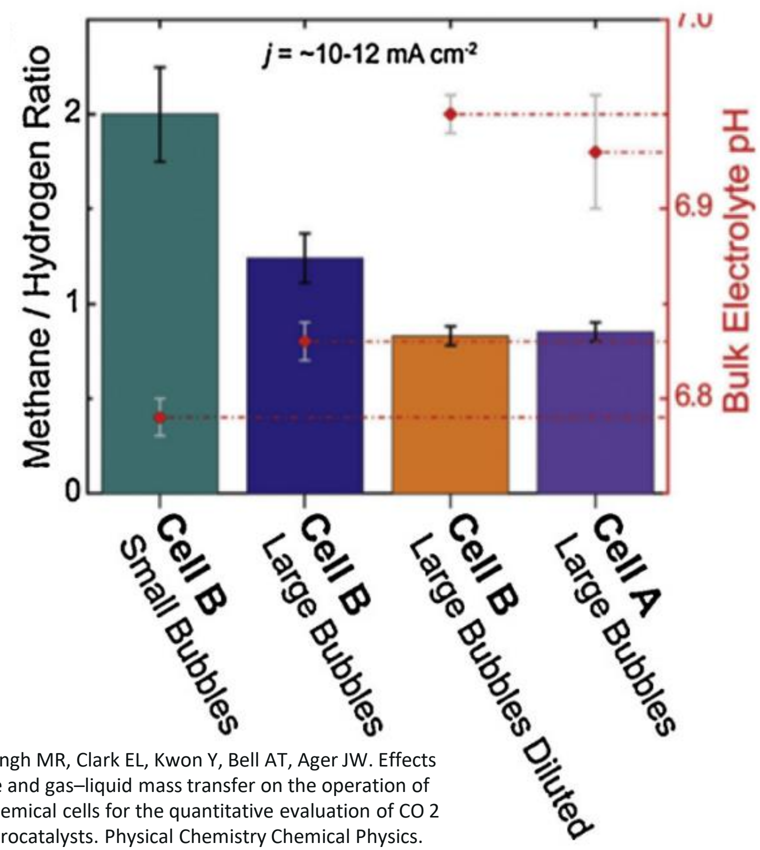


Lobaccaro P, Singh MR, Clark EL, Kwon Y, Bell AT, Ager JW. Effects of temperature and gas–liquid mass transfer on the operation of small electrochemical cells for the quantitative evaluation of CO 2 reduction electrocatalysts. Physical Chemistry Chemical Physics. 2016;18(38):26777-85.

Compressed “Sandwiched” Type of H-Cell

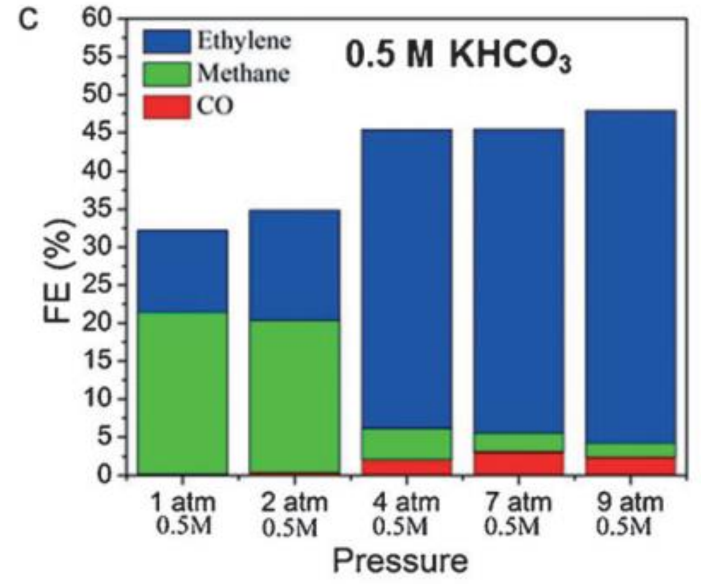
- Higher **surface-to-volume (S/V)** ratio enables higher product concentrations and detections for carbon products
- Lower volume also minimizes spacing within cell to decrease resistance
- However, a smaller S/V can minimize bubble formation and pH changes



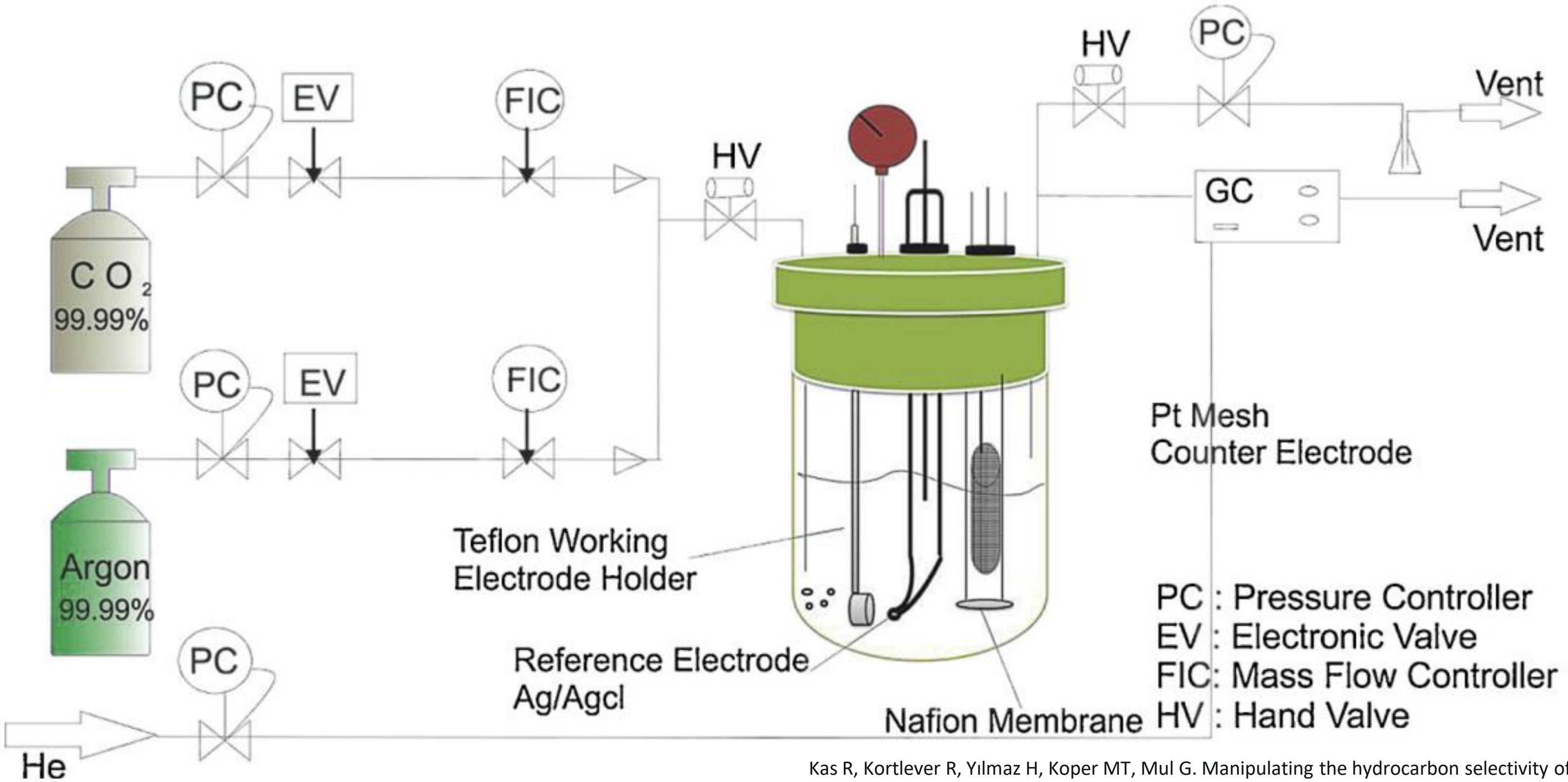


Lobaccaro P, Singh MR, Clark EL, Kwon Y, Bell AT, Ager JW. Effects of temperature and gas–liquid mass transfer on the operation of small electrochemical cells for the quantitative evaluation of CO 2 reduction electrocatalysts. Physical Chemistry Chemical Physics. 2016;18(38):26777-85.

Pressurized Batch Cell



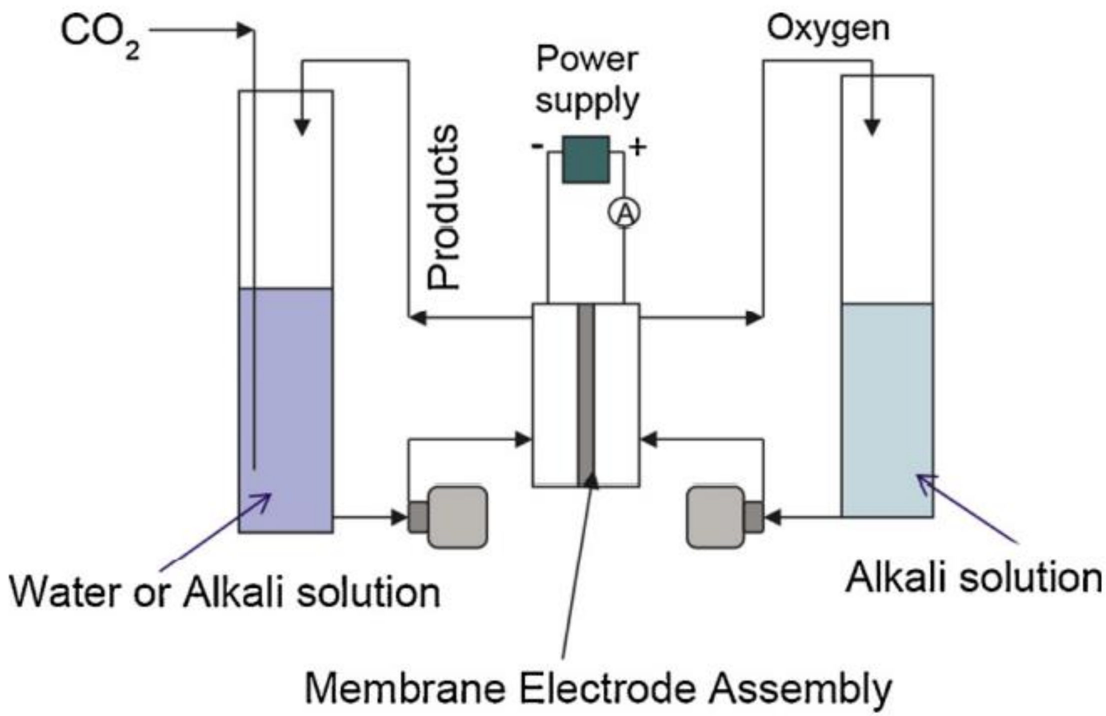
- ➢Can assess solubility limitations of CO_2 in aqueous solutions
- ➢Higher CO_2 pressure will lower system pH
- ➢Higher pressure not only improved current density and efficiency, but also changed product selectivity



Kas R, Kortlever R, Yılmaz H, Koper MT, Mul G. Manipulating the hydrocarbon selectivity of copper nanoparticles in CO2 electroreduction by process conditions. ChemElectroChem. 2015 Mar 11;2(3):354-8.

Flow Cells

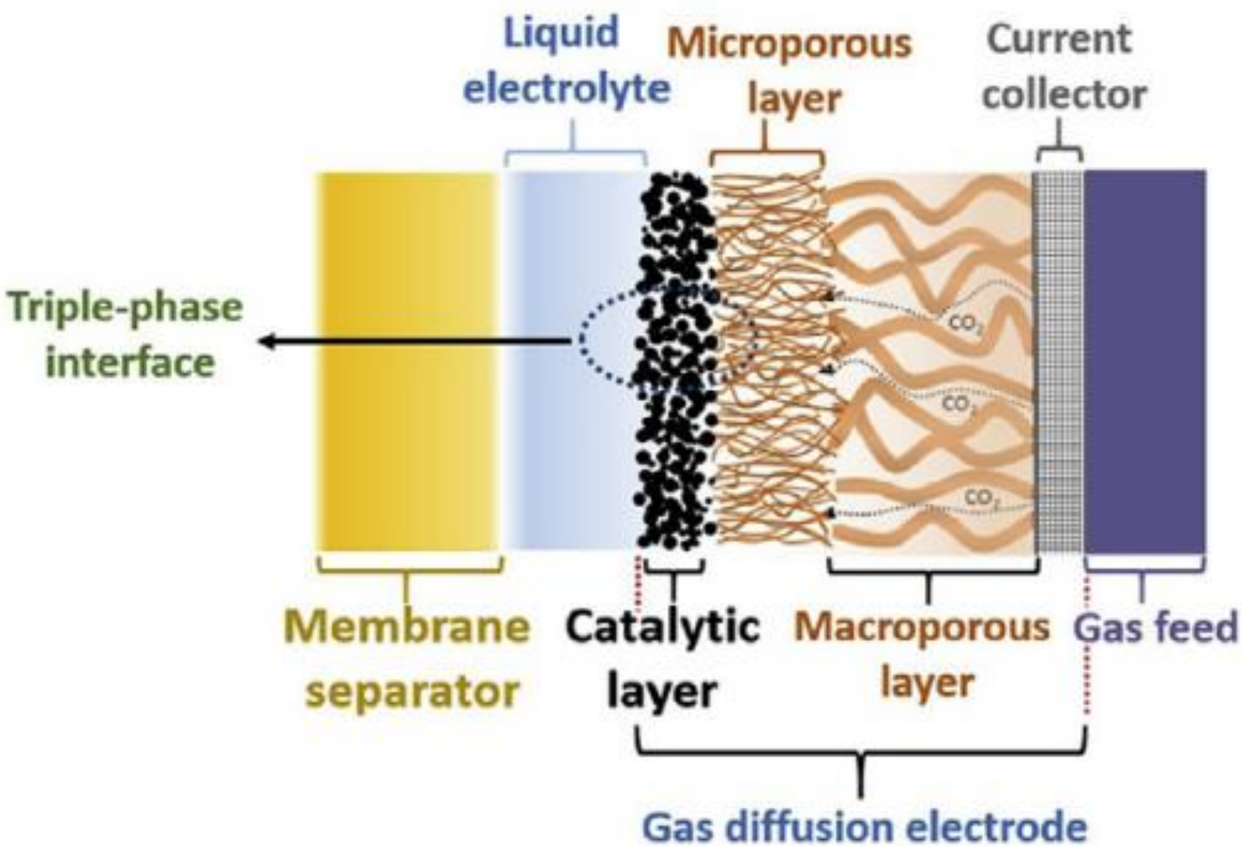
- Batch reactors generally mass transport limited (<45 mA/cm^2)
- Generally, flow cell design is adapted from existing literature in fuel cells and electrolyzers
- Flow cells recirculate solutions around the electrodes to maintain higher CO_2 concentrations and permit higher current densities
- Higher CO_2 loading is achieved by a **Gas Diffusion Layer (GDL)**



Narayanan SR, Haines B, Soler J, Valdez TI. Electrochemical conversion of carbon dioxide to formate in alkaline polymer electrolyte membrane cells. Journal of The Electrochemical Society. 2010 Dec 20;158(2):A167.

Gas Diffusion Layer

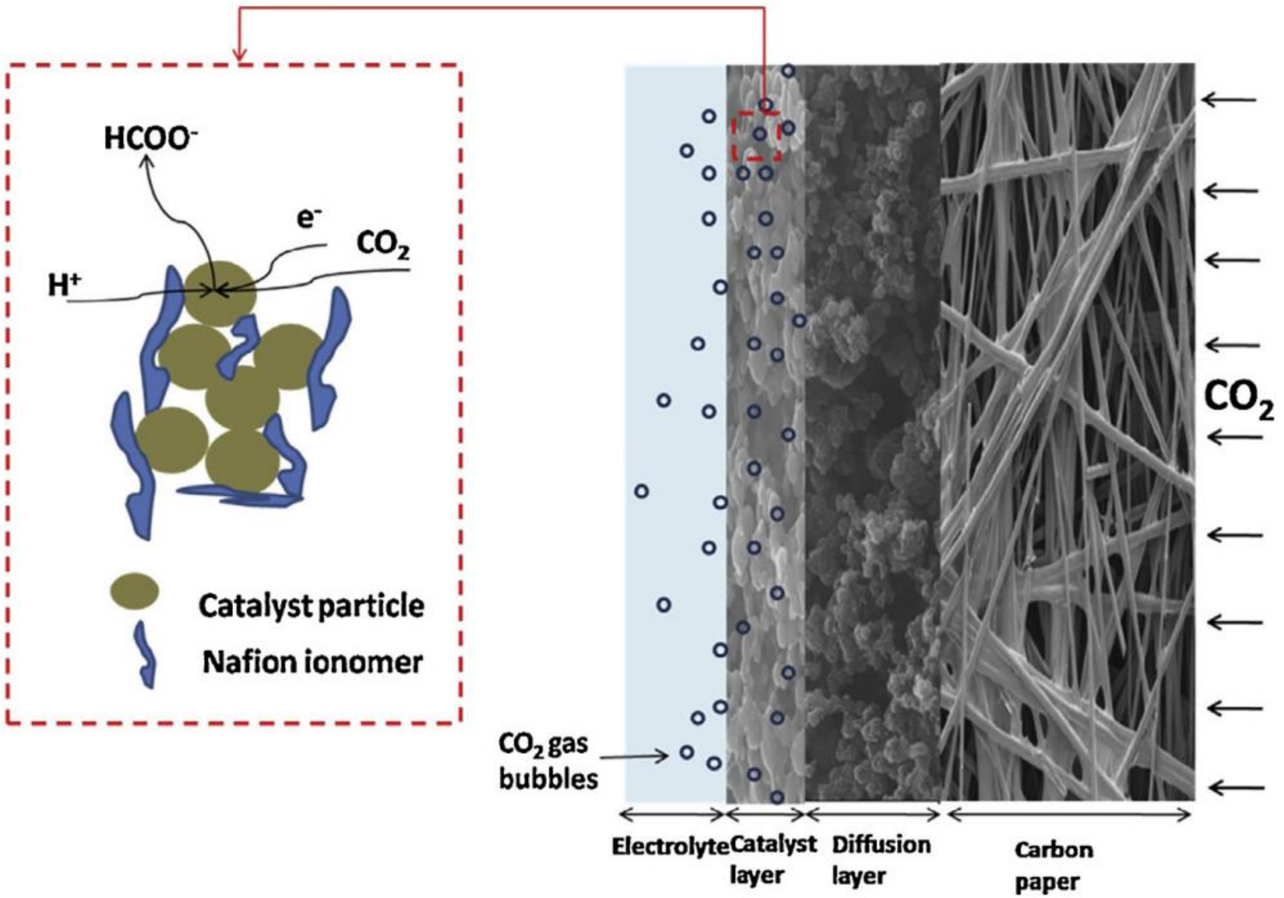
- Reduces diffusion path through the cell (µm to nm)
- Allows higher CO_2 saturation
- Gas purge through support layer minimizes agglomeration and blocking of catalysts, also facilitates the performance of the catalyst entirely



Yang Y, Li F. Reactor design for electrochemical CO2 conversion towards large scale applications. Current Opinion in Green and Sustainable Chemistry. 2020 Nov 26:100419.

Gas Diffusion Electrodes

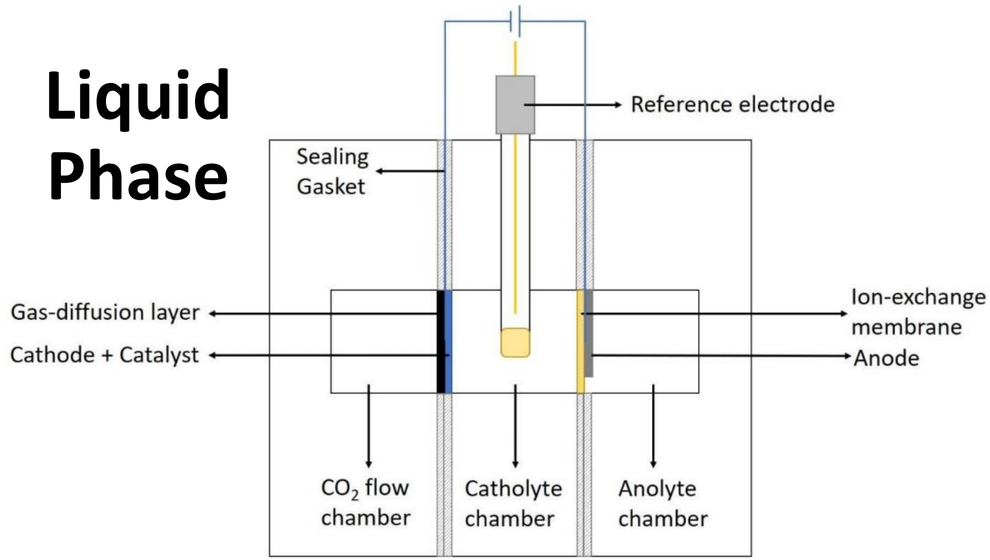
Electrode typically made of a carbon paper to diffuse gases through, while hydrophobic coating prevents water leakage



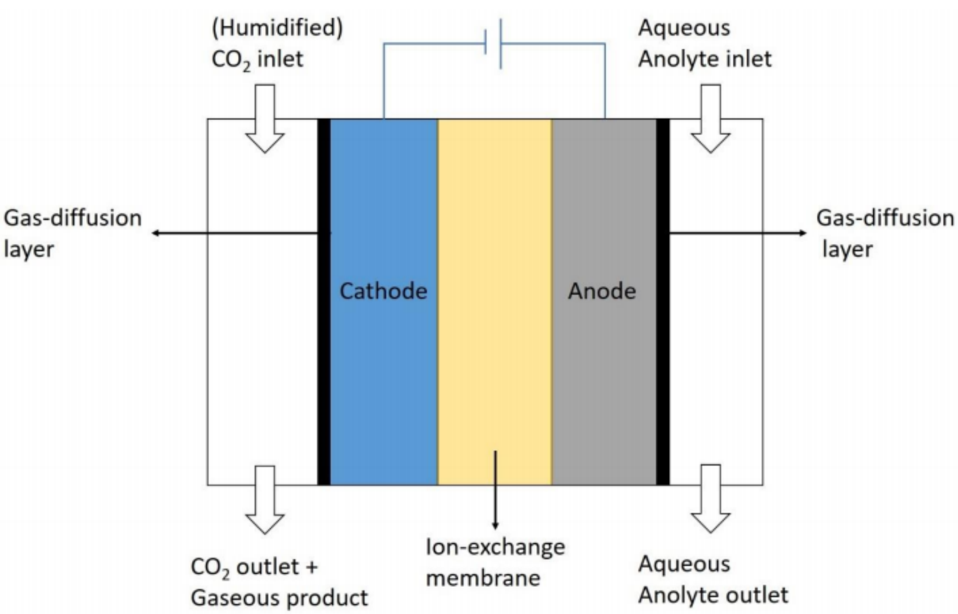
Wu J, Sharma PP, Harris BH, Zhou XD. Electrochemical reduction of carbon dioxide: IV dependence of the Faradaic efficiency and current density on the microstructure and thickness of tin electrode. Journal of Power Sources. 2014 Jul 15;258:189-94.

Types of Electrochemical Flow Cells

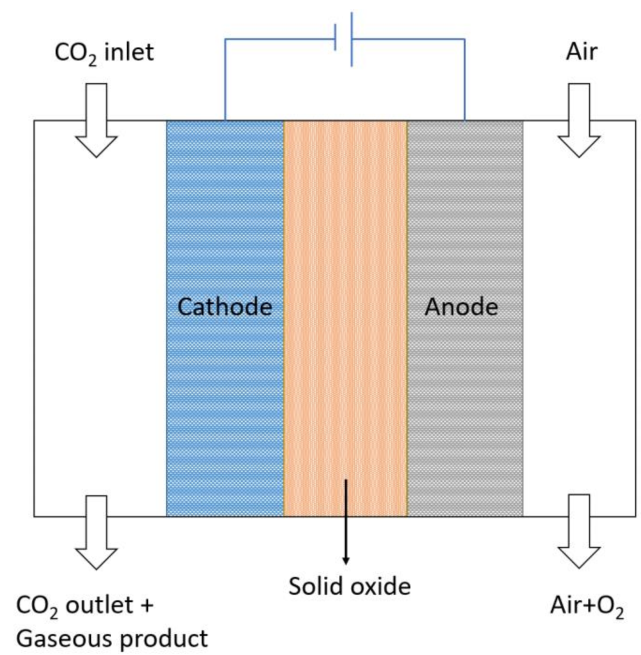
Liquid Phase



Gas Phase



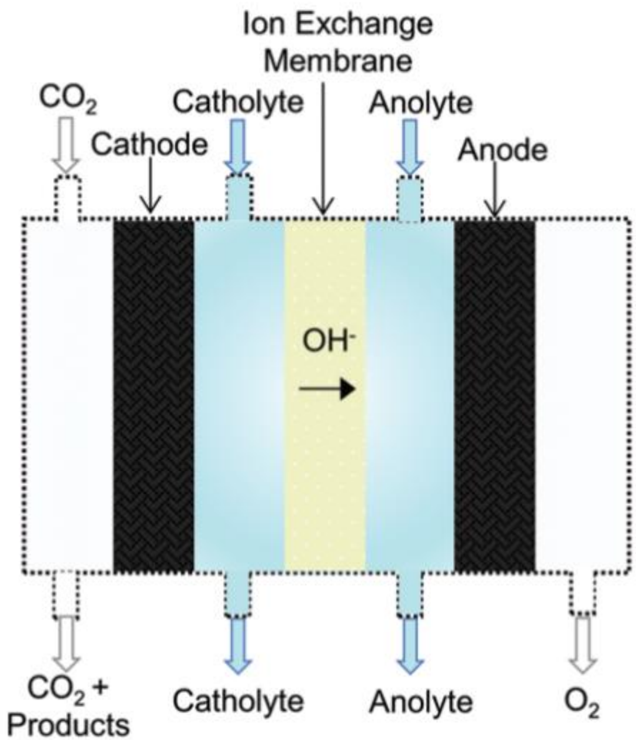
Solid Phase

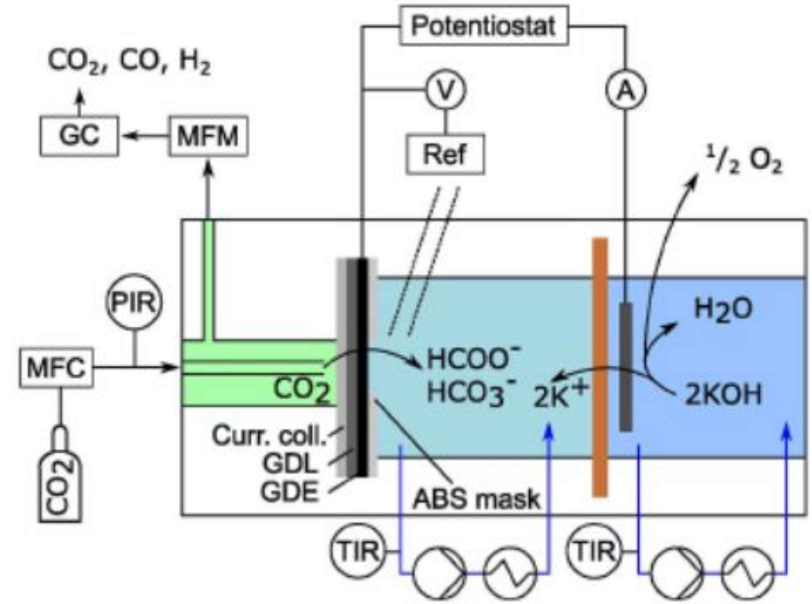


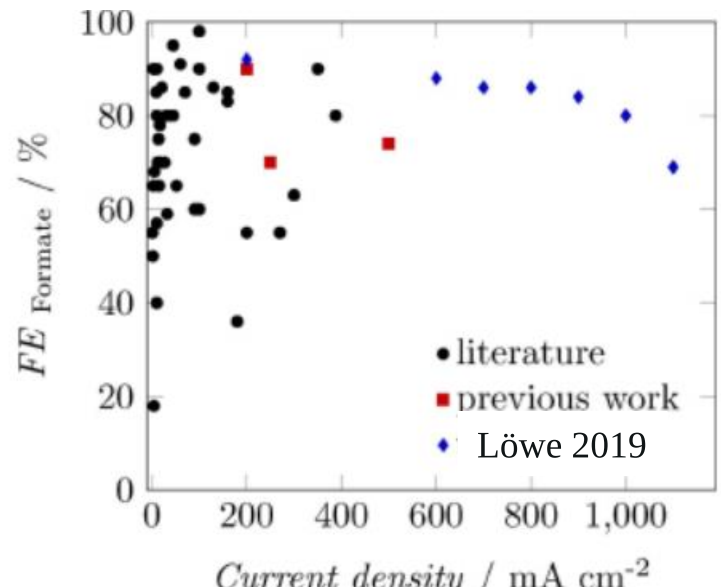
Lin R, Guo J, Li X, Patel P, Seifitokaldani A. Electrochemical reactors for CO2 conversion. Catalysts. 2020 May;10(5):473.

Liquid Phase Electrolyzer

- Three flow channels
- As with H-Cells, membrane used dependent on choice of catalysts and desired C products
- Produced current densities in excess of 1 mA/cm^2





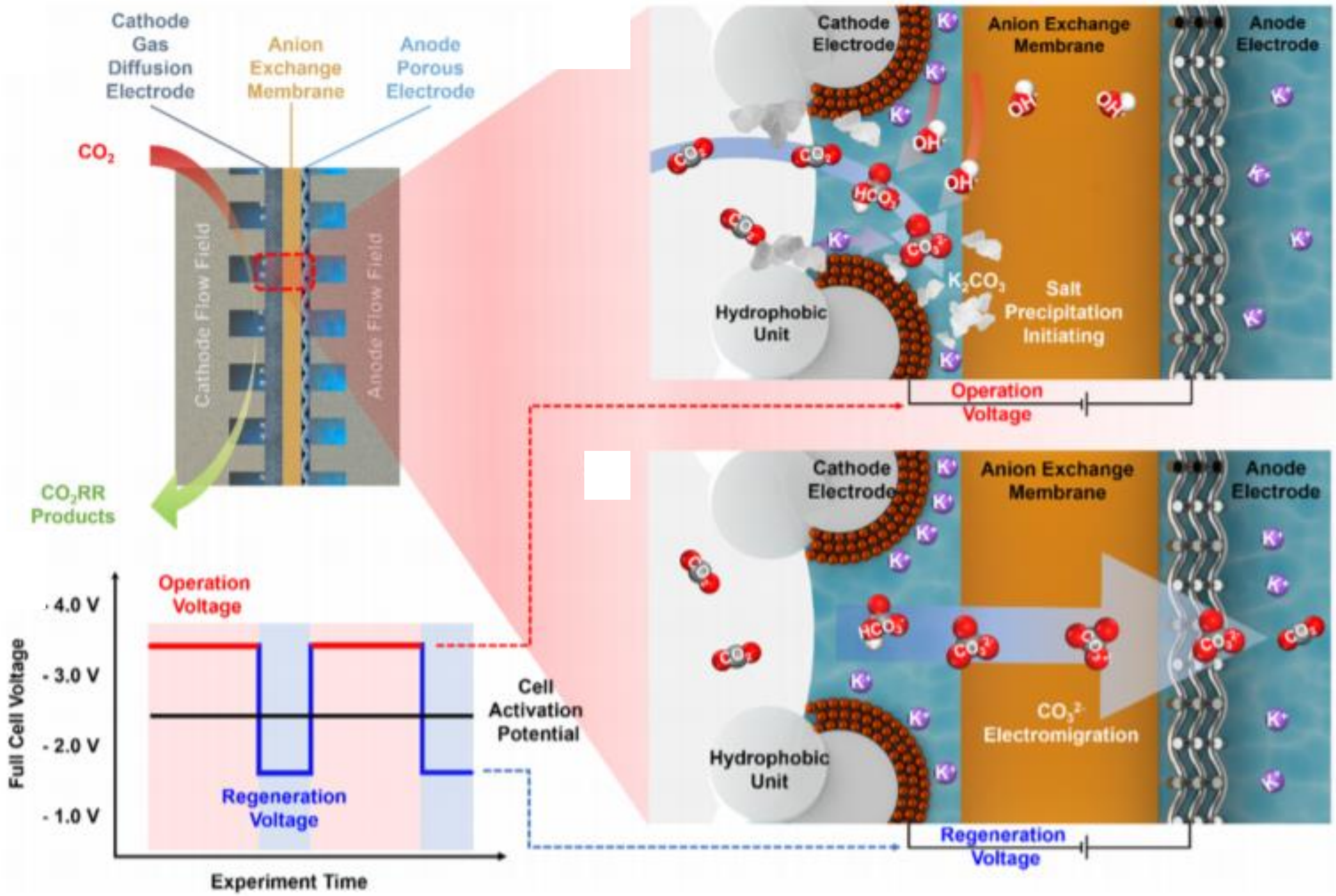


Kibria MG, Edwards JP, Gabardo CM, Dinh CT, Seifitokaldani A, Sinton D, Sargent EH. Electrochemical CO2 reduction into chemical feedstocks: from mechanistic electrocatalysis models to system design. Advanced Materials. 2019 Aug;31(31):1807166.

Löwe A, Rieg C, Hierlemann T, Salas N, Kopljar D, Wagner N, Klemm E. Influence of temperature on the performance of gas diffusion electrodes in the CO2 reduction reaction. ChemElectroChem. 2019 Sep 2;6(17):4497-506.

Liquid Phase Electrolyte: Challenges

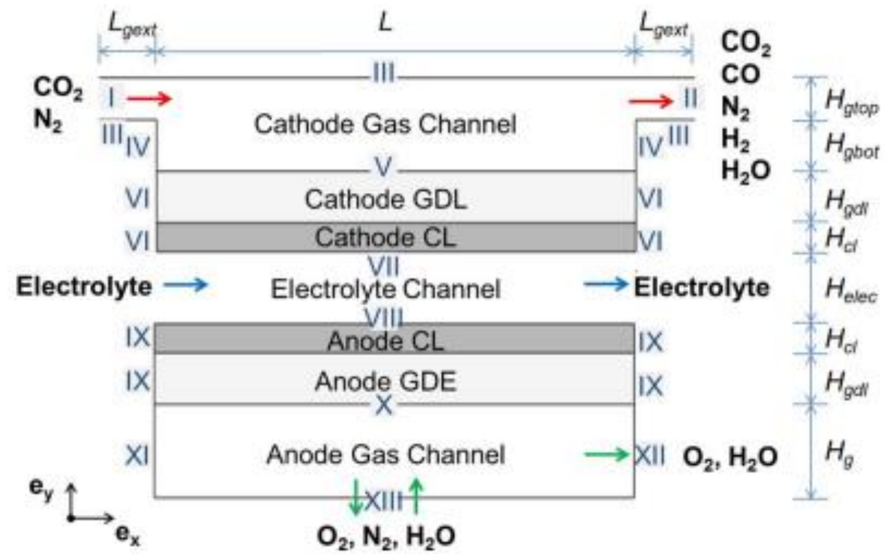
- Heavily depends on good GDE design
- May fail by flooding, impurity deposition on catalyst
- Precipitate formation on electrode

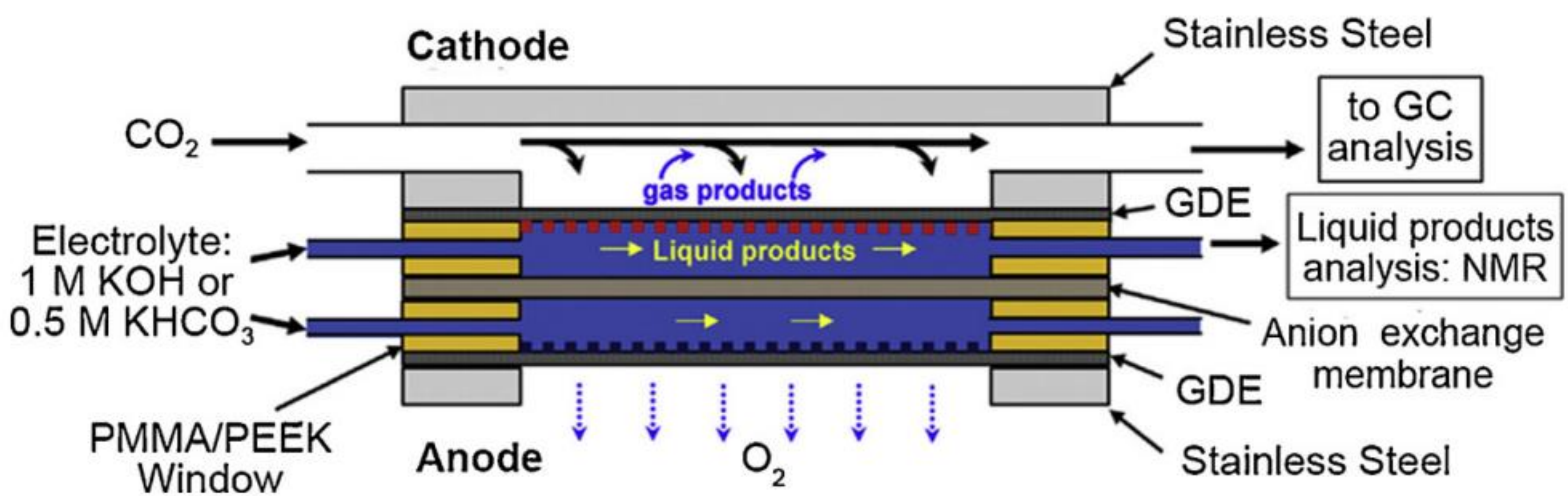


Xu Y, Edwards JP, Liu S, Miao RK, Huang JE, Gabardo CM, O'Brien CP, Li J, Sargent EH, Sinton D. Self-cleaning CO2 reduction systems: unsteady electrochemical forcing enables stability. ACS Energy Letters. 2021 Feb 2;6(2):809-15.

Microfluidic Flow Channels

- ➢Lower overall cell potential, maintains mass transport
- ➢Easy to model
- ➢Can be used as **membraneless** – employing laminar flow



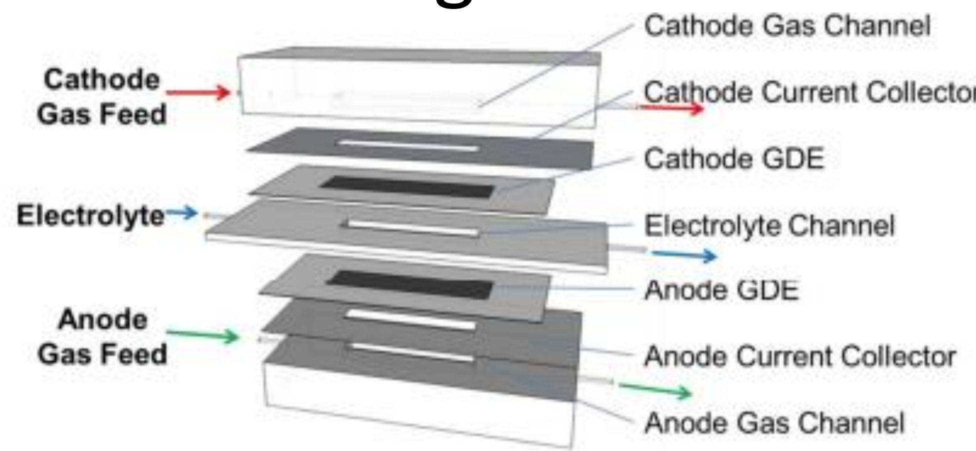


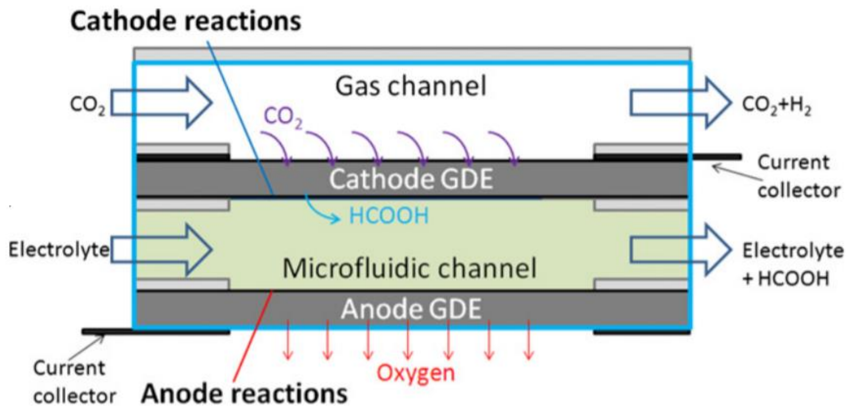
Rosen BA, Salehi-Khojin A, Thorson MR, Zhu W, Whipple DT, Kenis PJ, Masel RI. Ionic liquid–mediated selective conversion of CO2 to CO at low overpotentials. Science. 2011 Nov 4;334(6056):643-4.

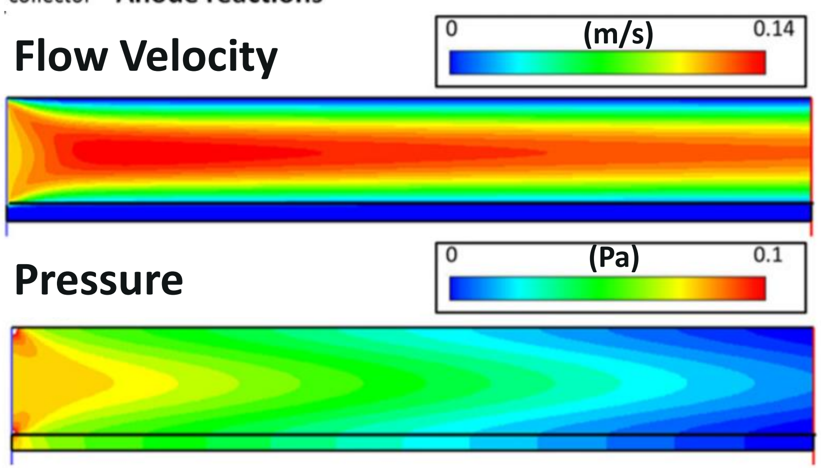
Wu K, Birgersson E, Kim B, Kenis PJ, Karimi IA. Modeling and experimental validation of electrochemical reduction of CO2 to CO in a microfluidic cell. Journal of The Electrochemical Society. 2014 Nov 4;162(1):F23.

Microfluidic Flow Channel Modeling

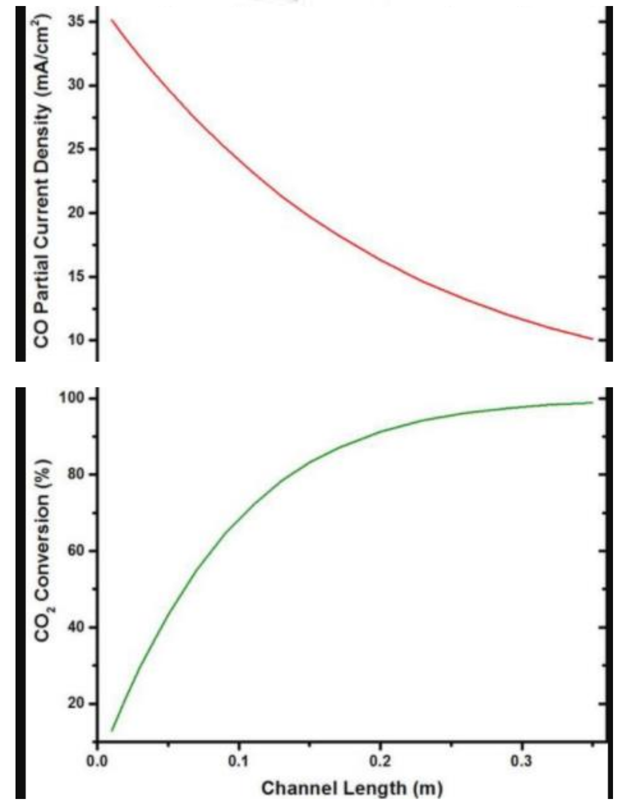
- ➢Geometry/configuration
- ➢Magnitude/direction of flow
- ➢Generally, challenged by pressure gradients within cell







Wang H, Leung DY, Xuan J. Modeling of a microfluidic electrochemical cell for CO2 utilization and fuel production. Applied energy. 2013 Feb 1;102:1057-62.



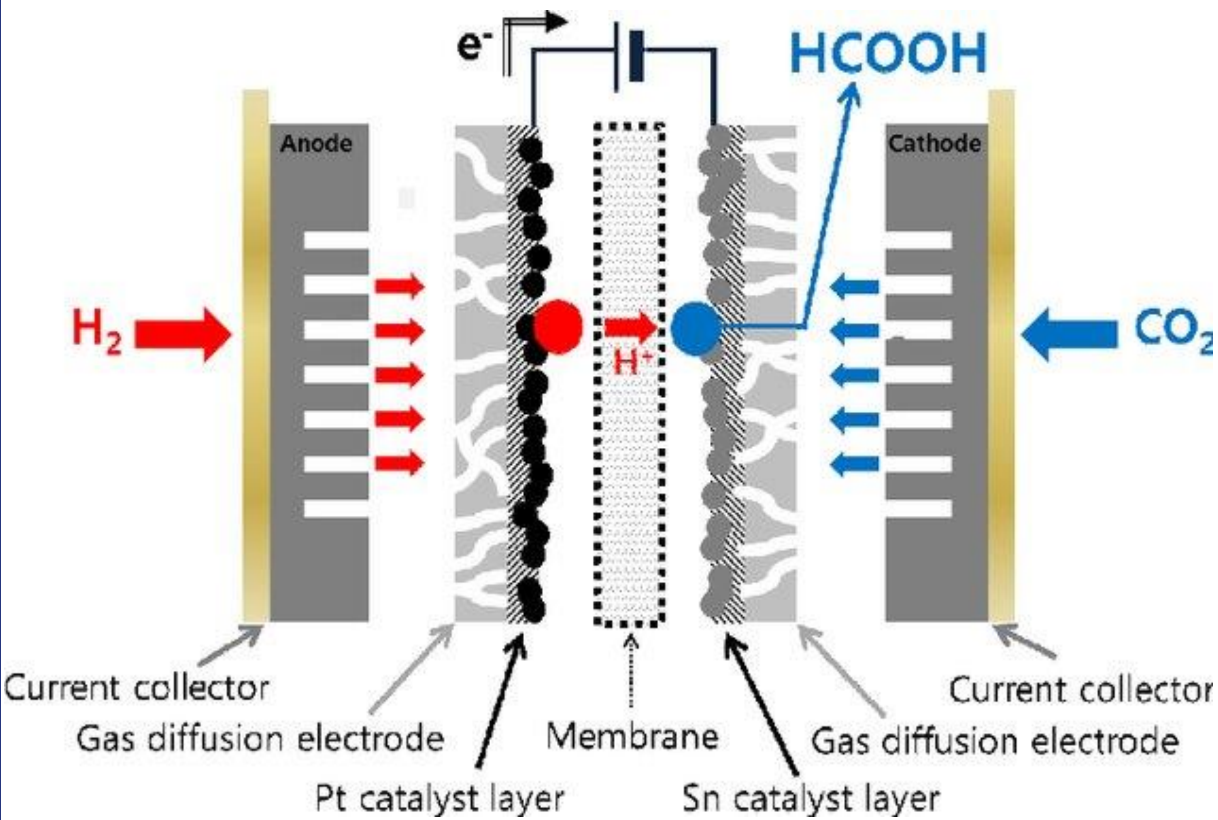
Wu K, Birgersson E, Kim B, Kenis PJ, Karimi IA. Modeling and experimental validation of electrochemical reduction of CO2 to CO in a microfluidic cell. Journal of The Electrochemical Society. 2014 Nov 4;162(1):F23.

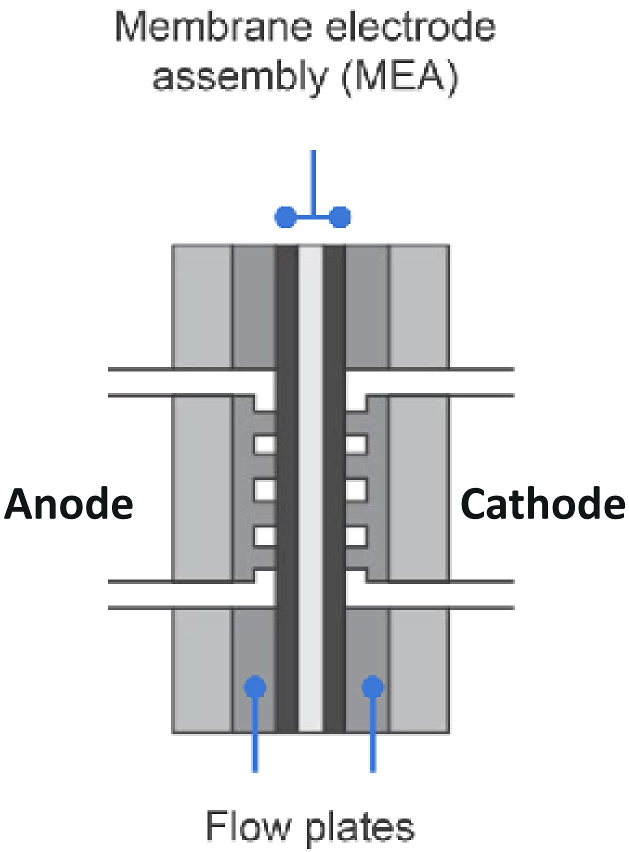
Center for Applied Energy Research

caer.uky.edu

Gas Phase Electrolyzer

- **Zero-gap configuration**: Cathode pressed directly against membrane – considered part of **membrane electrode assembly (MEA)**
- Trade-off of using pumps to humidity to hydrate membrane
- Maintains electrolyte purity in the absence of an electrolyte, prevents forming the carbonate/bicarbonate salts

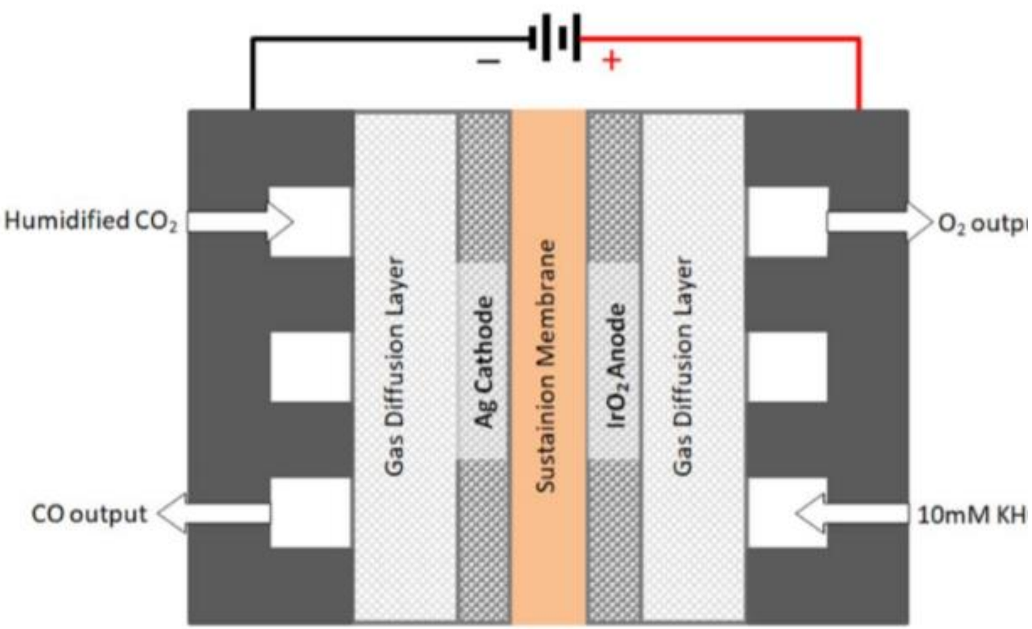




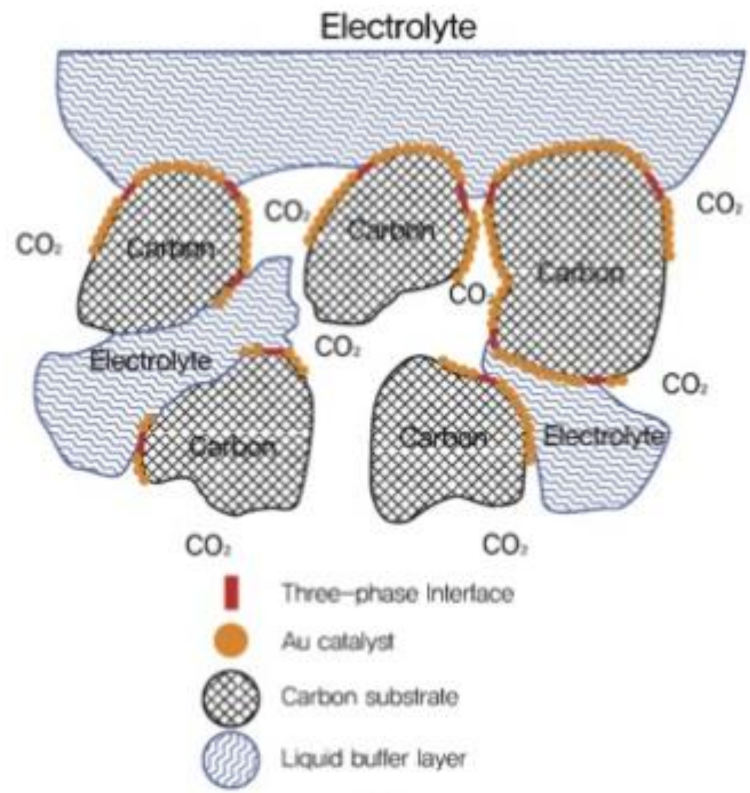
Lee S, Ju H, Machunda R, Uhm S, Lee JK, Lee HJ, Lee J. Sustainable production of formic acid by electrolytic reduction of gaseous carbon dioxide. Journal of Materials Chemistry A. 2015;3(6):3029-34.

Gas Phase Electrolyzer: Challenges

- Humidification of CO_2 is needed and must be carefully maintained to keep membrane active in MEA
- Liquid outlet from cathode can accumulate
- Acidification of electrolyte due to higher ion exchange, shifting reaction toward HER



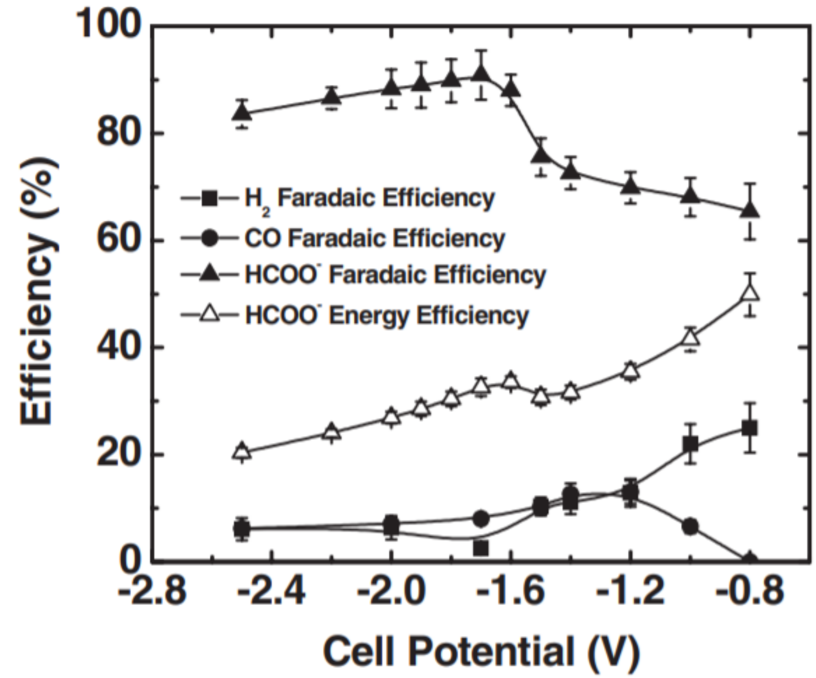
Liu Z, Yang H, Kutz R, Masel RI. CO2 electrolysis to CO and O2 at high selectivity, stability and efficiency using sustainion membranes. Journal of The Electrochemical Society. 2018 Nov 30;165(15):J3371.

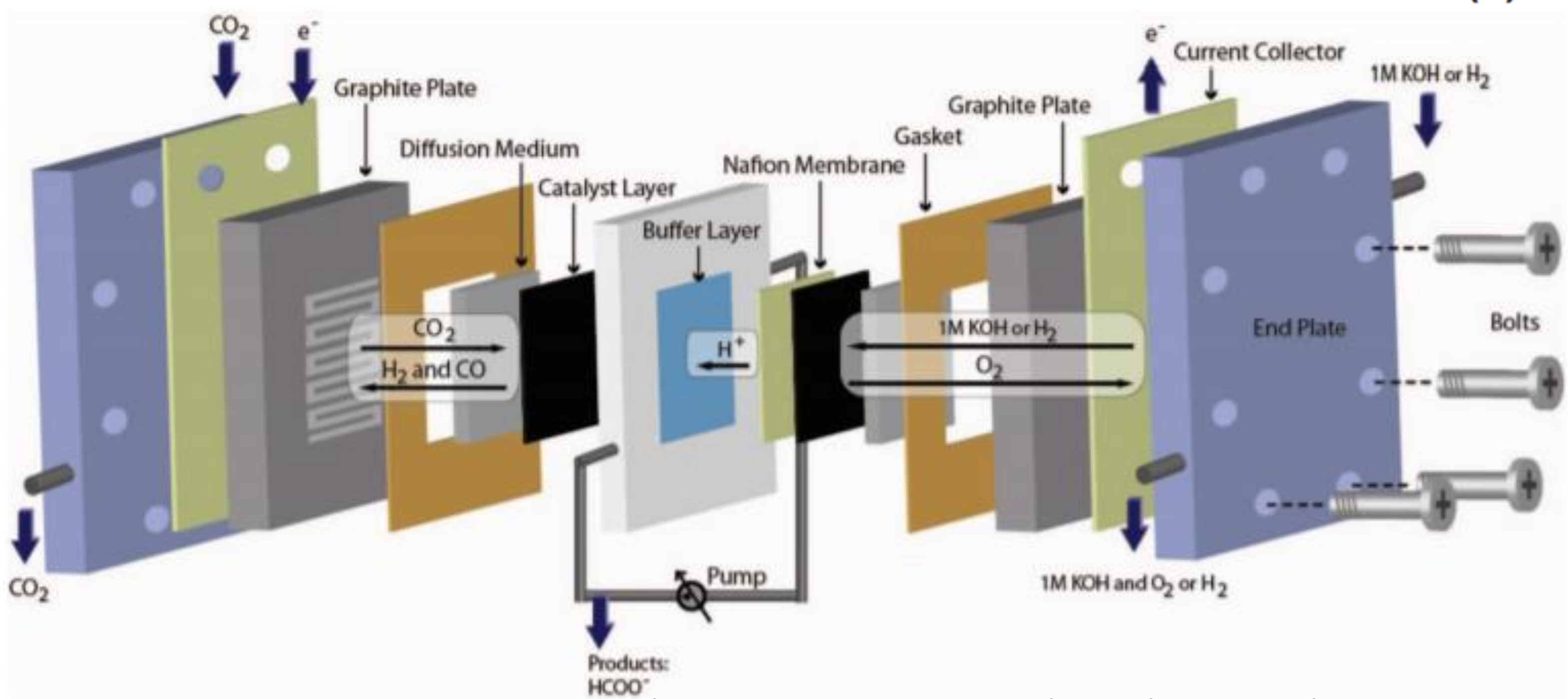


Park G, Hong S, Choi M, Lee S, Lee J. Au on highly hydrophobic carbon substrate for improved selective CO production from CO2 in gas-phase electrolytic cell. Catalysis Today. 2020 Sep 15;355:340-6.

Gas Phase Buffer Layers

- Mitigates issue of membrane wetting
- Enables adequate pH control in the system
- Can facilitate production of higher order C products

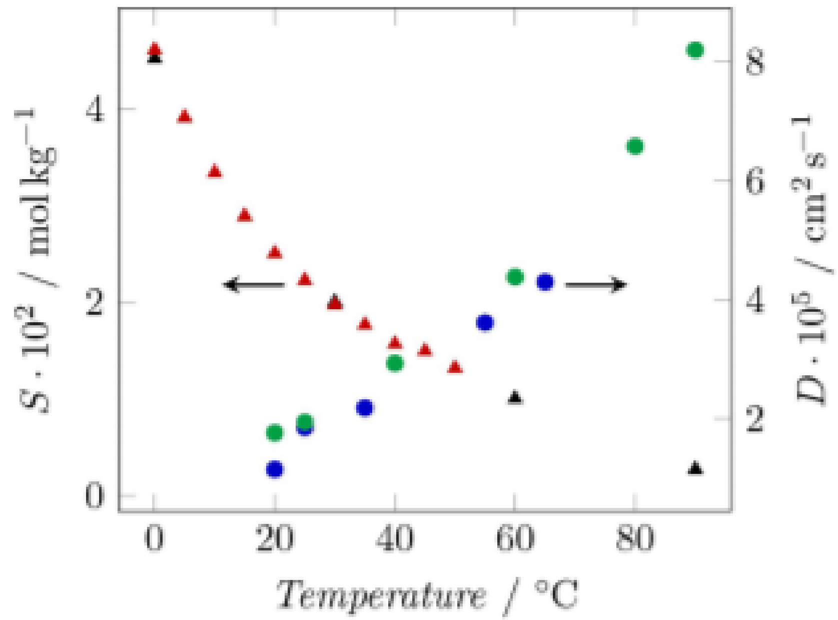


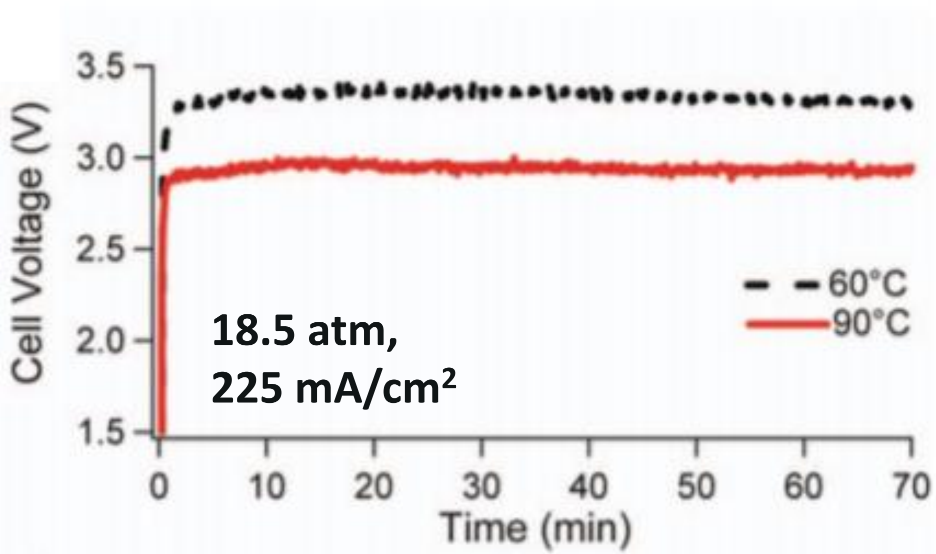


Wu J, Risalvato FG, Sharma PP, Pellechia PJ, Ke FS, Zhou XD. Electrochemical reduction of carbon dioxide: II. Design, assembly, and performance of low temperature full electrochemical cells. Journal of The Electrochemical Society. 2013 Jun 18;160(9):F953.

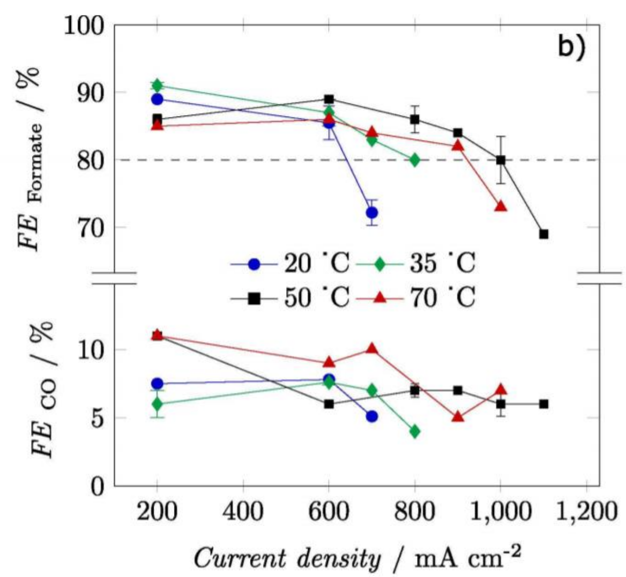
Increased Temperature Operation

- ➢Temperature decreases solubility, but enhances kinetics
- ➢Important consideration in large scale systems since ohmic losses contribute to heat **(Joule heating)**
- ➢Can be taken advantage of in more pressurized systems





Dufek EJ, Lister TE, Stone SG, McIlwain ME. Operation of a pressurized system for continuous reduction of CO2. Journal of The Electrochemical Society. 2012 Aug 14;159(9):F514.



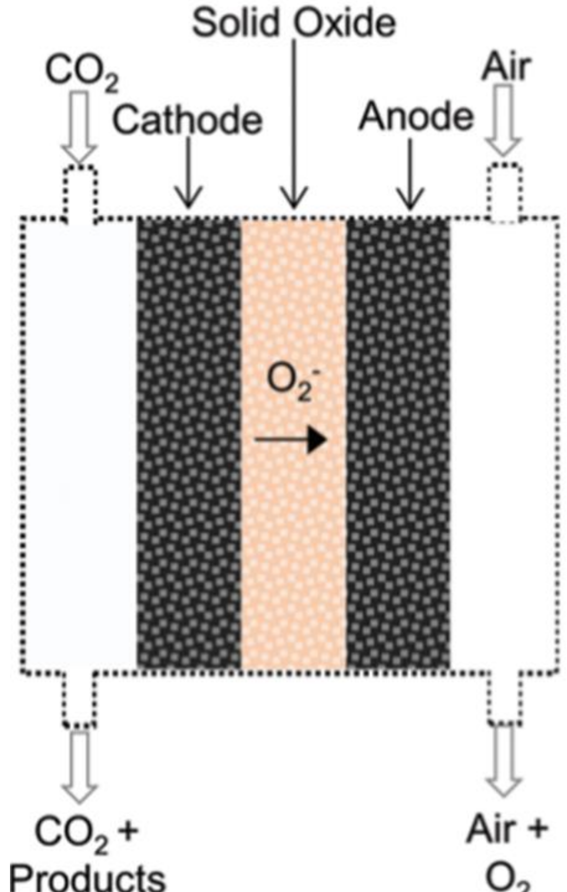
Löwe A, Rieg C, Hierlemann T, Salas N, Kopljar D, Wagner N, Klemm E. Influence of temperature on the performance of gas diffusion electrodes in the CO2 reduction reaction. ChemElectroChem. 2019 Sep 2;6(17):4497-506.

Center for Applied Energy Research

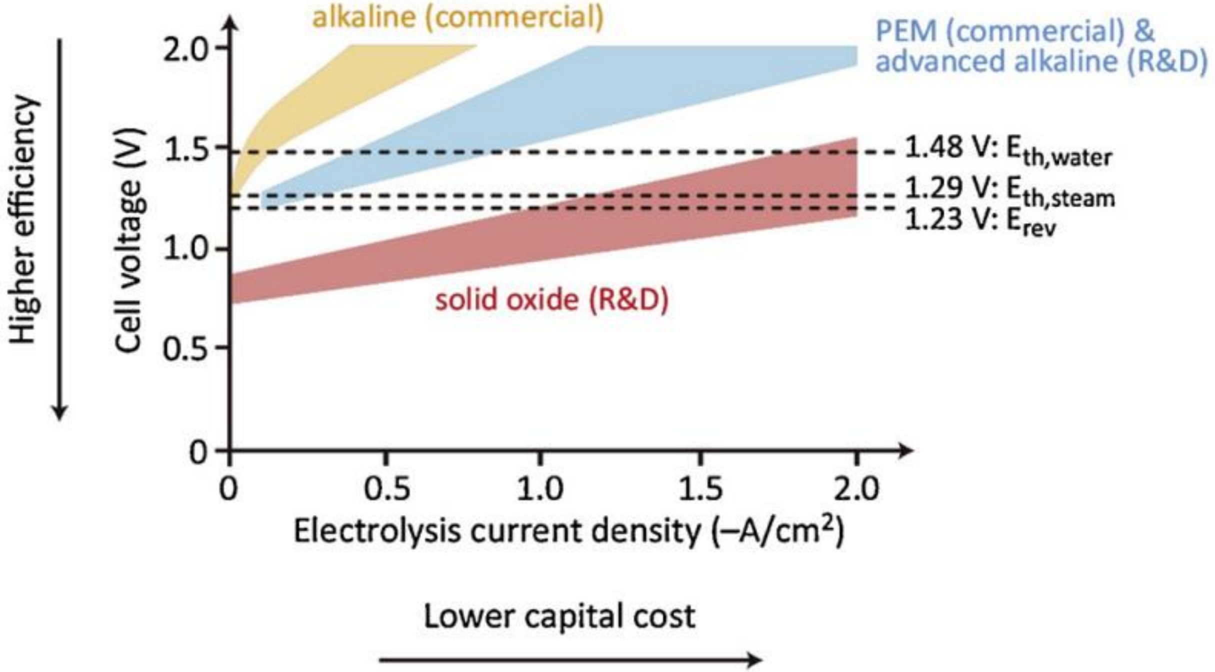
caer.uky.edu

Solid Phase Electrolyzer

- Zirconia/ceria/lanthanum-based oxides as solid electrolyte
- Ability to operate at higher temperatures (~600°C)
- Despite limited products (mostly CO), good selectivity and reliability
- No membranes needed



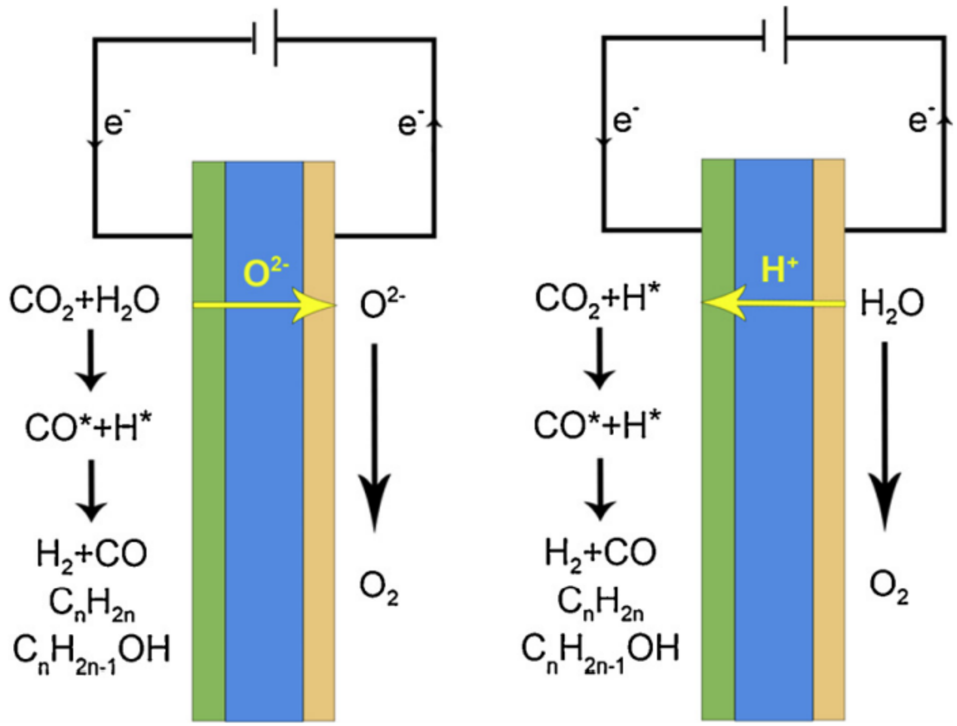
Kibria MG, Edwards JP, Gabardo CM, Dinh CT, Seifitokaldani A, Sinton D, Sargent EH. Electrochemical CO2 reduction into chemical feedstocks: from mechanistic electrocatalysis models to system design. Advanced Materials. 2019 Aug;31(31):1807166.



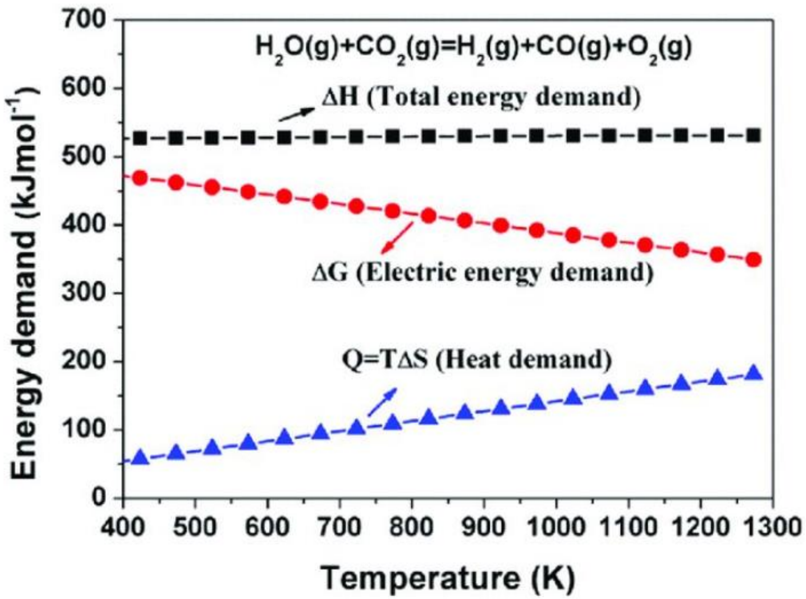
Graves C, Ebbesen SD, Mogensen M, Lackner KS. Sustainable hydrocarbon fuels by recycling CO2 and H2O with renewable or nuclear energy. Renewable and Sustainable Energy Reviews. 2011 Jan 1;15(1):1-23.

Solid Phase Electrolyzer: Operation

- Electrolyte either oxide or proton conducting
- Coupled with H_2O electrolysis to produce syngas
- Heat reduces electrical energy demand



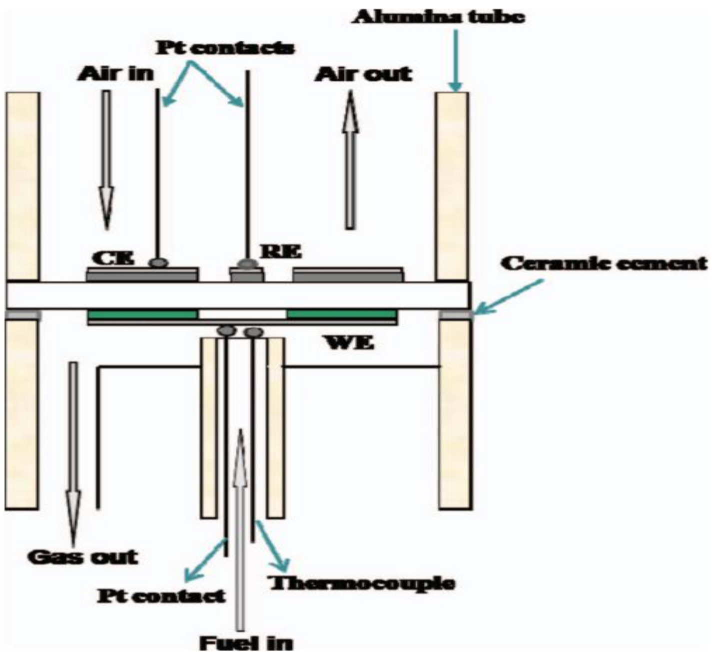
Zhang L, Hu S, Zhu X, Yang W. Electrochemical reduction of CO2 in solid oxide electrolysis cells. Journal of Energy chemistry. 2017 Jul 1;26(4):593-601.

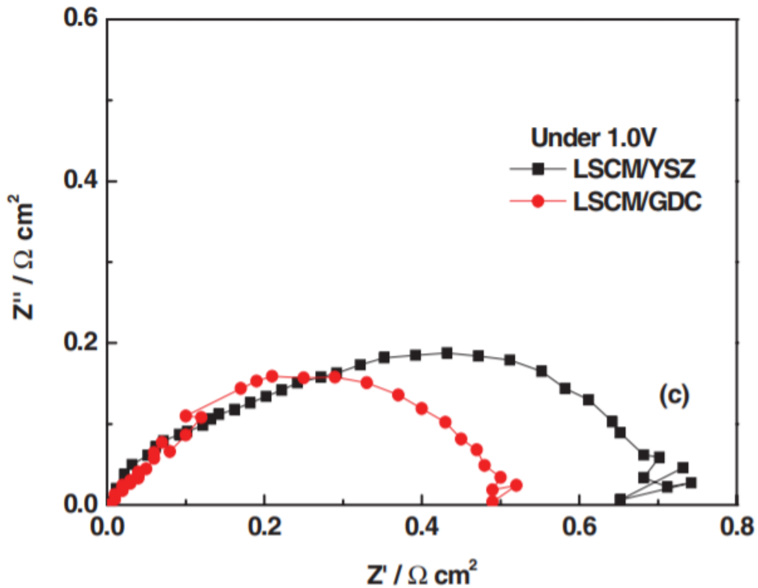


Wang Y, Liu T, Lei L, Chen F. High temperature solid oxide H2O/CO2 co-electrolysis for syngas production. Fuel Processing Technology. 2017 Jun 15;161:248-58.

Solid Phase Electrolyzer: Challenges

- Sensitivity to system degradation from CO_2 impurities
- Carbon deposition
- Extreme conditions to operate electrolyte



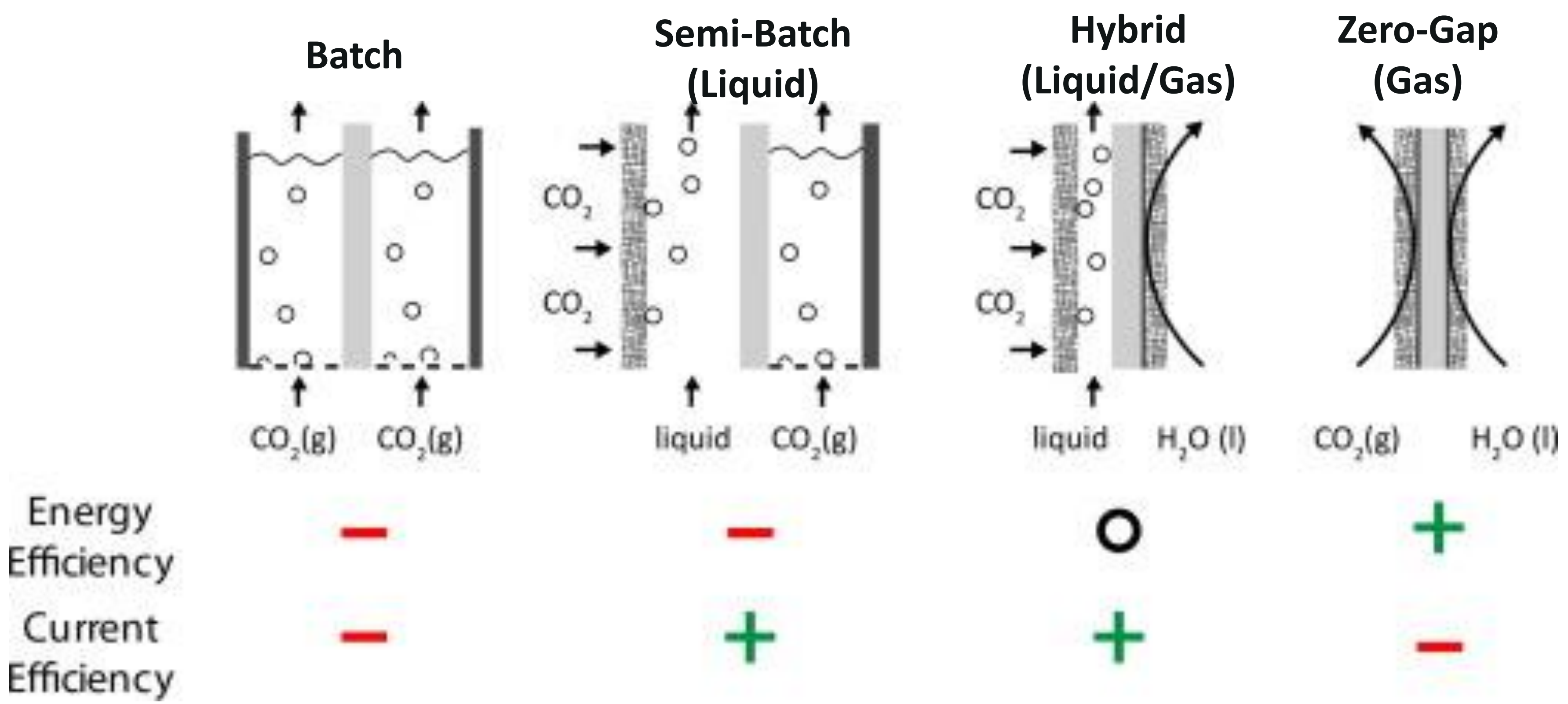


Yue X, Irvine JT. Alternative cathode material for CO2 reduction by high temperature solid oxide electrolysis cells. Journal of The Electrochemical Society. 2012 Jul 20;159(8):F442.

- Essentially, more research needed into electrodes to understand how to best operate solid-phase electrolyzers to form other carbon products at high current densities.
- Below 600°C, advantages of increased temperature may make solid-phase more profitable.

Putting it all together…

- This recent study looked at several different cell designs
- Operating temperature raised to 30°C to take advantage of enhanced kinetics
- Pressure ambient, but suggested up to 10 bar for solubility
- Hybrid configuration minimizes ohmic losses in gas phase, but maintains pH control and appropriate product formation in liquid phase



Vennekoetter JB, Sengpiel R, Wessling M. Beyond the catalyst: How electrode and reactor design determine the product spectrum during electrochemical CO2 reduction. Chemical Engineering Journal. 2019 May 15;364:89-101.

Overview

Cell Type	Pros	Cons
H-Cell	• Readily available, generally inexpensive • Good for catalyst/chemistry screening	• Limited by low current densities • Long diffusion pathways • Small-scale application only
Sandwiched Cell	• Better determination of liquid products • Lower resistance	• Bubble generation • Transport limited
Pressurized Cell	• Higher pressure enables greater CO_2 solubility	• Larger pH differences • Stronger construction materials needed
Liquid-Phase Flow	• Enables high current densities • Good control of system parameters • Membraneless microfluidic cells	• Ohmic losses • Flooding • Precipitate formation • Pressure gradients
Gas-Phase Flow	• Pumps not required • Lower ohmic loss • Controlled liquid extraction	• Requires humidified gases • Liquid accumulation • Acidification/HER competition
Solid-Phase Flow	• High temperature operation enhances kinetics • Membrane not required	• Mainly limited to CO, first-order carbon products

Summary

- Classification of electrochemical cells not always consistent
  - Many analogies can be drawn from existing electrochemical systems
  - Cell designs not as extensively compared for electrochemical CO_2 reduction as catalysts
- Temperature and pressure can be advantageous if varied to conditions modestly above ambient
  - Temperature in particular important due to heat generation in high current density systems
- Hybrid-phased electrolyzers may be the preferred route for optimizing current and energy efficiency
- More research needs to be done on solid-phase, can connect with liquid/gas phase

Questions?