Electrocatalytic processes for CO_2 utilization:

Technological status and economic prospects

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Reuse

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Outline

- **Introduction**
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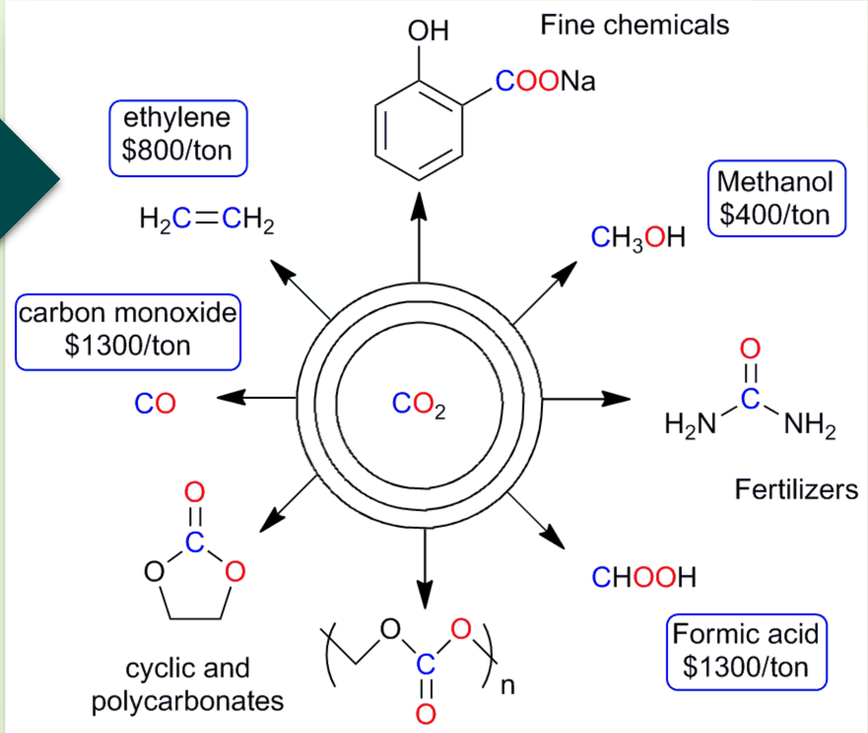
- **Electrochemical reduction of CO_2 process**
  - Essentials and technologies for electrochemical CO_2 conversion
- **Factors affecting on electrochemical reduction of CO_2**
- **Direct conversion of capture liquids**
- **Economic prospects of electrochemical CO2 conversion**
- **Advantages, challenges and prospects of electrochemical CO_2 conversion**

CO_2 reduction to value-added products

- **Global annual demand: 200 Mt**
  - **110 Mt of CO_2 are used annually in the production of chemicals**
  - **The rest is needed for:**
    - enhanced oil recovery
    - preservative and beverage additive
    - fire suppression
    - coolant or solvent
- **Annual production: 24 Gt**

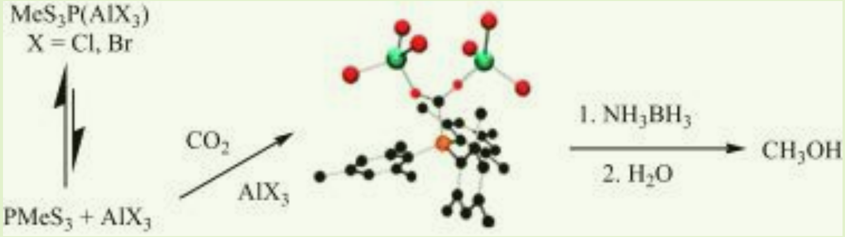


Processes to convert CO_2 into chemicals/fuels

Reuse

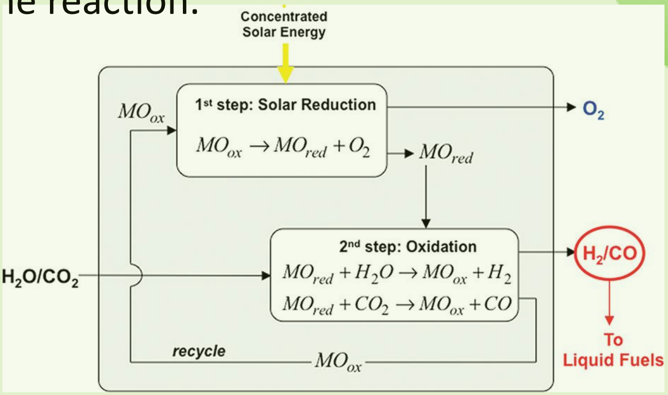
A. Stoichiometric reactions

They do not need any external thermodynamic energy inputs to proceed as they are not non-spontaneous reactions, and use only chemicals potentials to drive the reaction.



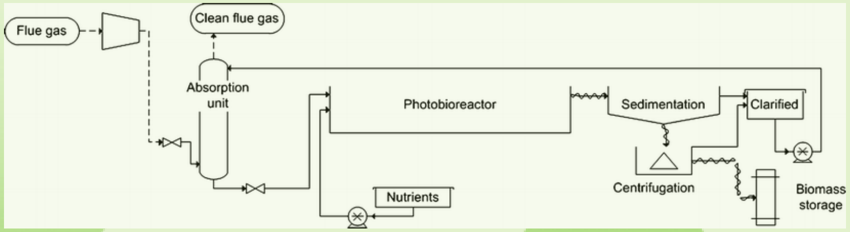
B. Thermo-chemical reactions

They utilize external energy in the form of heat to drive the reaction.



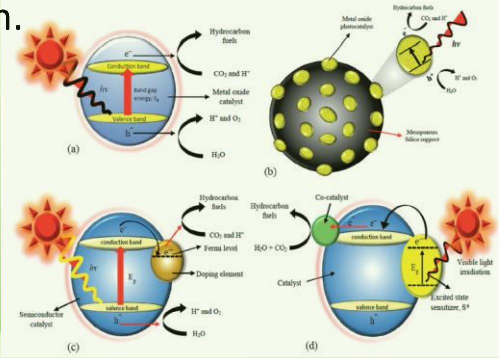
C. Biochemical processes

Use of microalgae for bio-fuels production.



D. Photocatalytic reactions

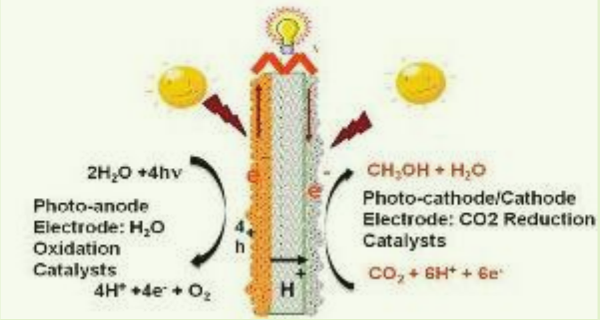
The transformation of CO_2 into fuel by using solar light irradiation.



Processes to convert CO_2 into chemicals/fuels

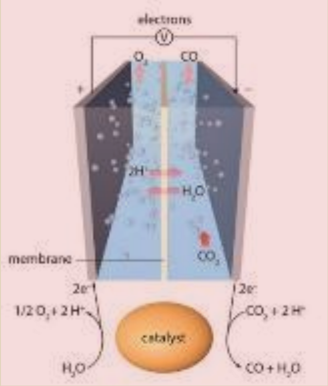
E. Photo-electrochemical (PEC) reactions

Use of semiconductors as anode/cathode electrodes. Yield highly reduced and selective CO_2 reduction products (methanol, ethanol, etc.), at lower overpotentials.

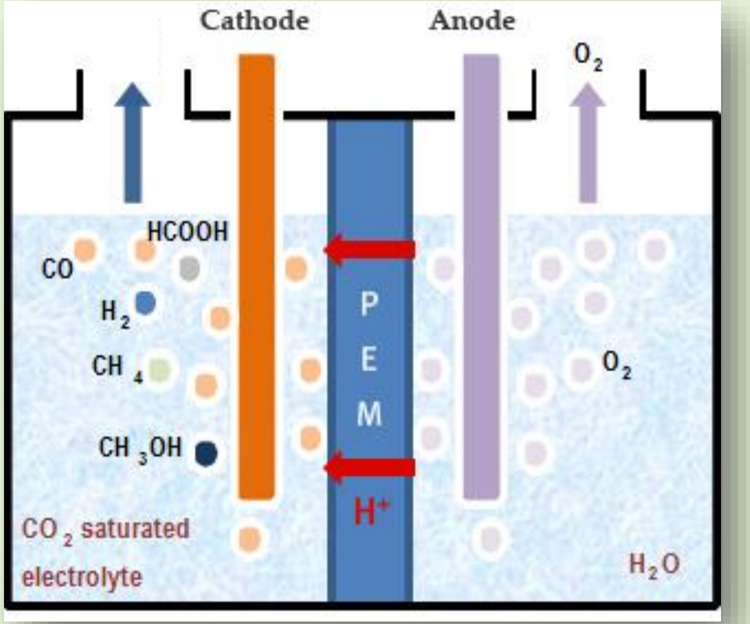


F. Electrochemical reductions

Use of electric energy (potential) to reduce CO_2 into chemical and/or fuels.



Essentials of electrochemical reduction of CO_2



$$E^0_{cell} = E_{cathode} - E_{anode}$$

Electrochemical CO_2 conversion process:

Cathode reaction: $CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$

Anode reaction: $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$

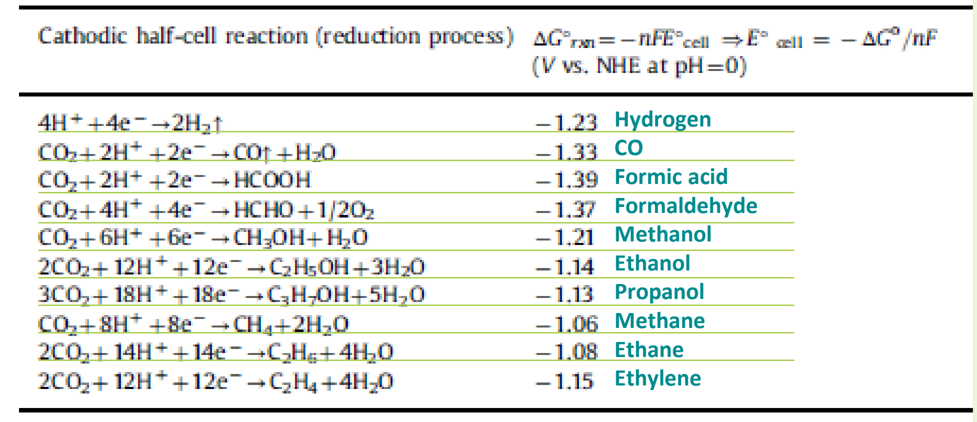
Overall reaction: $CO_2 \rightarrow CO + 1/2O_2$

The CO_2 reduction reaction usually competes with the hydrogen evolution reaction (HER):

$$2H^+ + 2e^- \rightarrow H_2$$

Essentials of electrochemical reduction of CO_2

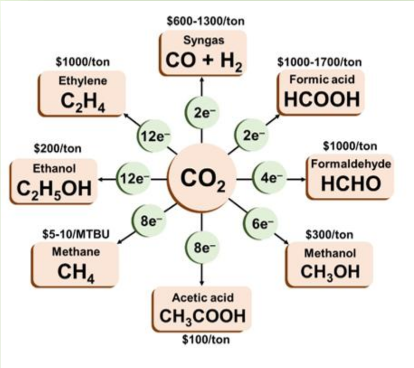
The half-cell reactions of cathode during electrochemical CO_2 reduction



Cathodic half-cell reaction (reduction process)	$\Delta G^\circ_{rxn} = -nFE^\circ_{cell} \Rightarrow E^\circ_{cell} = -\Delta G^\circ/nF$ (V vs. NHE at pH=0)	
$4H^+ + 4e^- \rightarrow 2H_2\uparrow$	−1.23	Hydrogen
$CO_2 + 2H^+ + 2e^- \rightarrow CO\uparrow + H_2O$	−1.33	CO
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	−1.39	Formic acid
$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + 1/2O_2$	−1.37	Formaldehyde
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	−1.21	Methanol
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_5OH + 3H_2O$	−1.14	Ethanol
$3CO_2 + 18H^+ + 18e^- \rightarrow C_3H_7OH + 5H_2O$	−1.13	Propanol
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	−1.06	Methane
$2CO_2 + 14H^+ + 14e^- \rightarrow C_2H_6 + 4H_2O$	−1.08	Ethane
$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$	−1.15	Ethylene

Potential products of CO_2 electroreduction:

Carbon monoxide (CO)
Formic acid (HCOOH) or formate ($HCOO^-$)
Methanol (CH_3OH) or ethanol (C_2H_5OH)
Methane (CH_4) or Ethylene (C_2H_4)
Formaldehyde (CH_2O)
Oxalic acid ($H_2C_2O_4$) or oxalate ($C_2O_4^{2-}$)



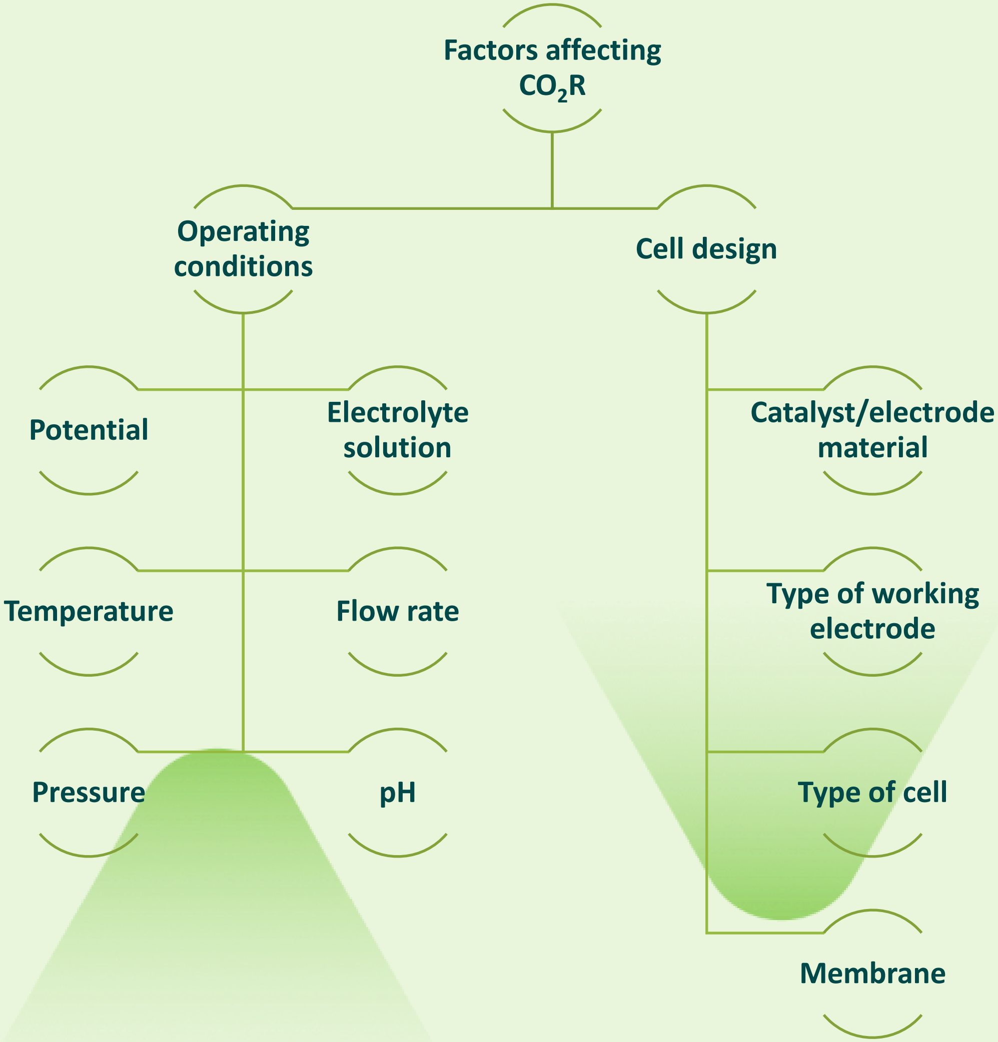
➲ In **thermodynamics**, the Gibbs free energy of CO_2 reduction (**ΔG_{rxn}=-n·F·E_{cell}**) is always positive at medium and high pH range, hence, the theoretical potentials are negative.
Thus, CO_2 reduction requires electrical energy input

➲ In **kinetics**, the **electrochemical reduction of CO_2 normally require certain overpotentials** (>1.0 V), i.e. **application of higher potential than thermodynamic potential**, to get reasonable amounts of reduced products.

In an aqueous electrolyte, the H_2O also undergoes reduction and releases H_2 as a major by-product. Thus, **water reduction is always in competition with CO_2 reduction reaction in electrochemical cells**.

Factors affecting on electrochemical reduction of CO_2

- Various factors will influence the eCO_2R process, including the **rate of formation**, **selectivity of target products** and **faradaic efficiency**.



Factors affecting CO_2R

Operating conditions
- Potential
- Electrolyte solution
- Temperature
- Flow rate
- Pressure
- pH

Cell design
- Catalyst/electrode material
- Type of working electrode
- Type of cell
- Membrane

Factors affecting on electrochemical reduction of CO_2

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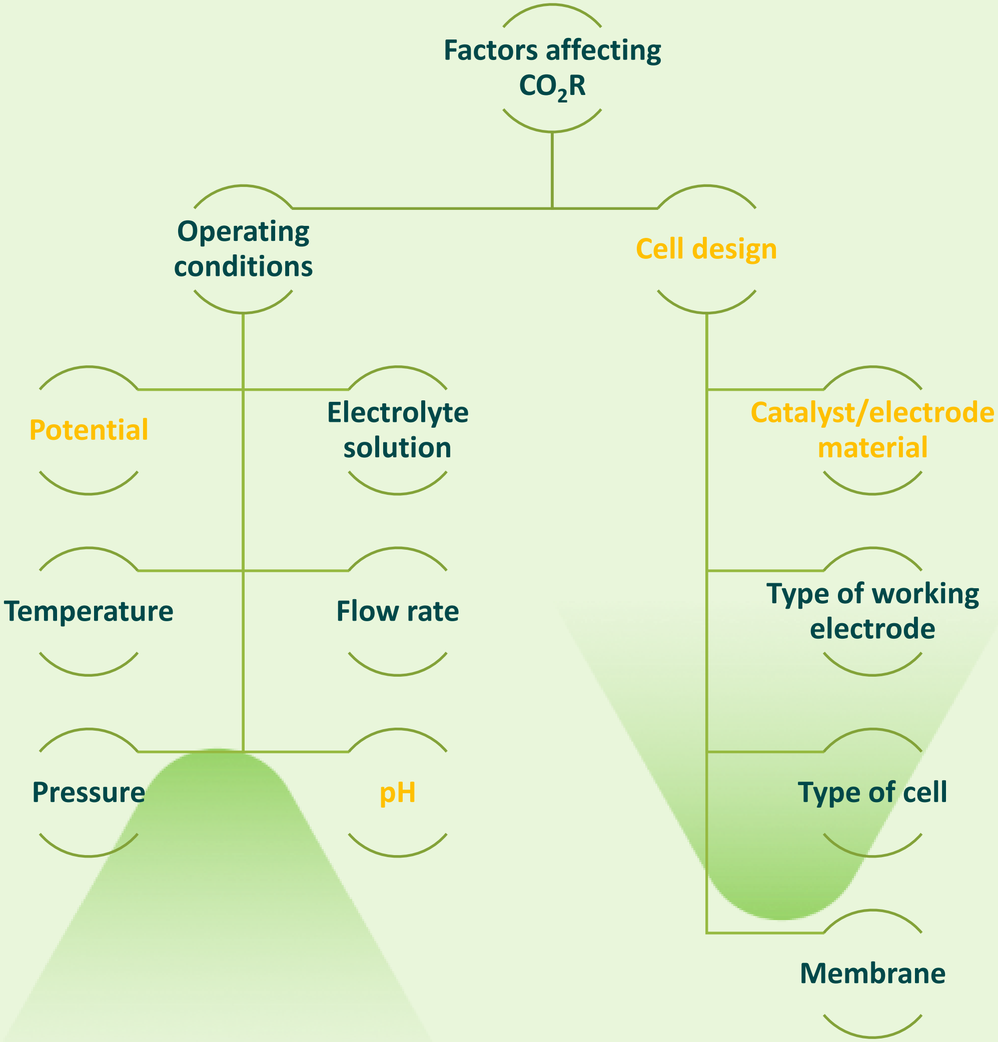


Factors affecting CO_2R

Operating conditions

Potential

Electrolyte solution

Temperature

Flow rate

Pressure

pH

Cell design

Catalyst/electrode material

Type of working electrode

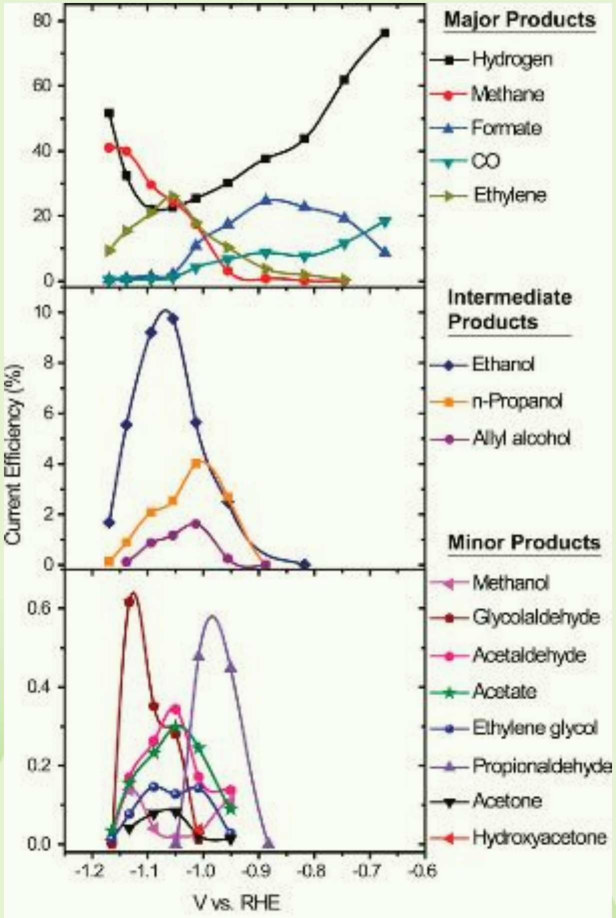
Type of cell

Membrane

Effect of potential on electrochemical reduction of CO_2

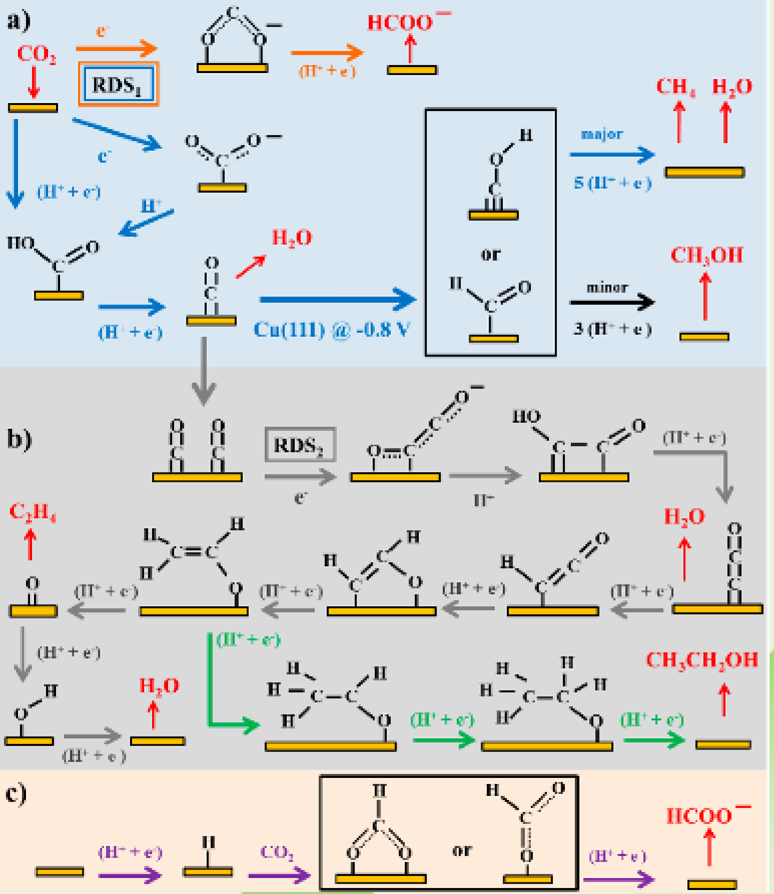
Possible products of CO_2 reduction as a function of potential

selectivity



R. Kortlever et. al, *J Phys Chem Lett.*, **2015,** 6, 4073

Possible reaction pathways for the electrocatalytic reduction of CO_2



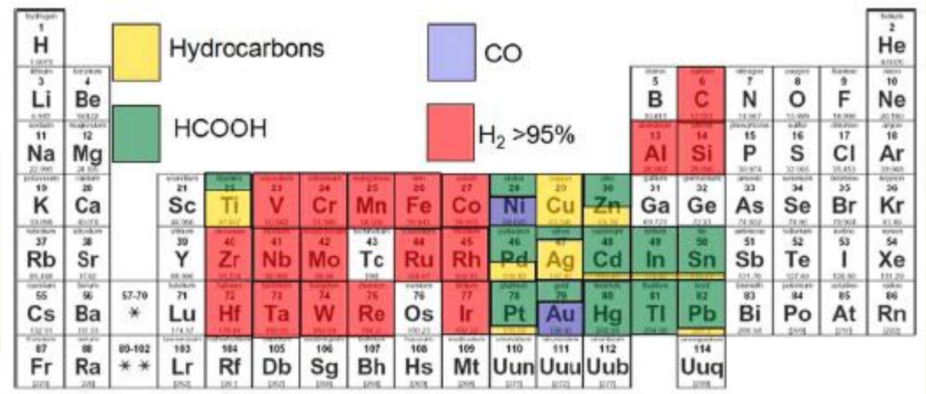
Effect of catalysts on electrochemical reduction of CO_2

- **Electrocatalysts** are needed to **bind and activate CO_2** in order to **reduce the high overpotentials** typically encountered
- Also, catalysts can drive **selective formation** of desired products

Four (4) distinct classes of metal catalysts have been identified, regarding the reduction product:

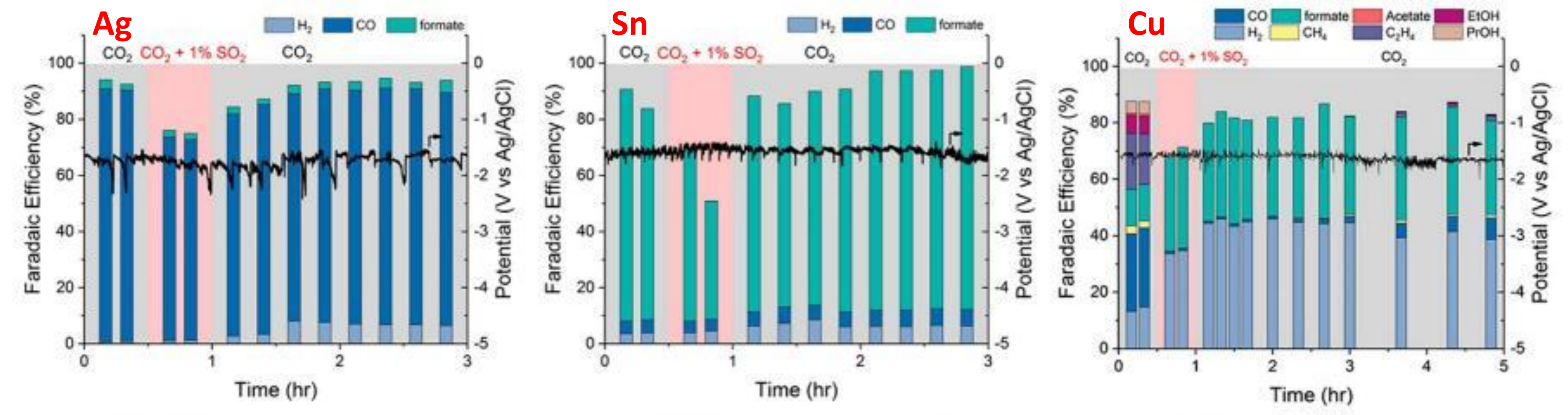
1. **formic acid**, **HCOOH,** formation metals (**Pb, Hg, In, Sn, Cd, Tl, Ir**)
2. **carbon monoxide**, **CO,** formation metals (**Au, Ag, Zn, Pd, Ga**)
3. **hydrocarbons**, e.g. methane and ethylene, formation metals (**Cu, Ti, Ag)**
4. **hydrogen**, **H_2,** formation metals (**Pt, Ni, Fe, Ti, Ir**)

Grouping of metals based on CO_2 reduction products in potassium bicarbonate ($KHCO_3$) based media



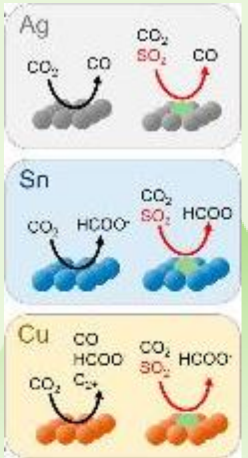
Effect of catalysts on electrochemical reduction of CO_2

Faradaic efficiency for possible products of CO_2 reduction over different catalysts



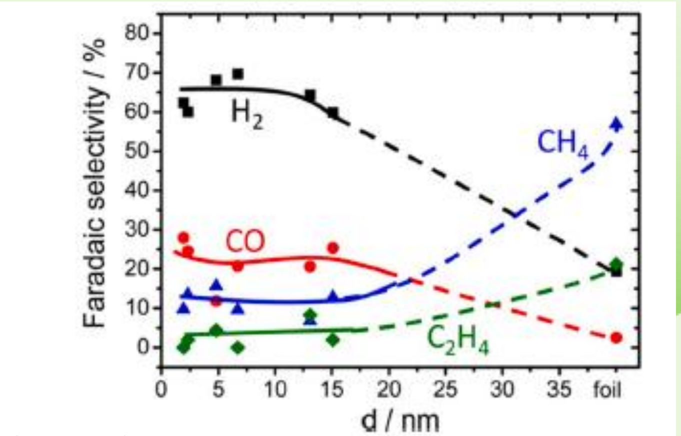
@100 mA·cm^{-2} in 1 M $KHCO_3$

W. Luc et al, J. Am. Chem. Soc. 2019, 141, 25, 9902-9909



- The surface morphology and roughness of catalysts significantly influence the catalytic activity and selectivity in the CO_2 electroreduction
- More undercoordinated sites provided by smaller NPs, have strong binding strength for key intermediates such as H and COOH

Catalytic selectivity of eCO_2R products on Cu nanoparticles

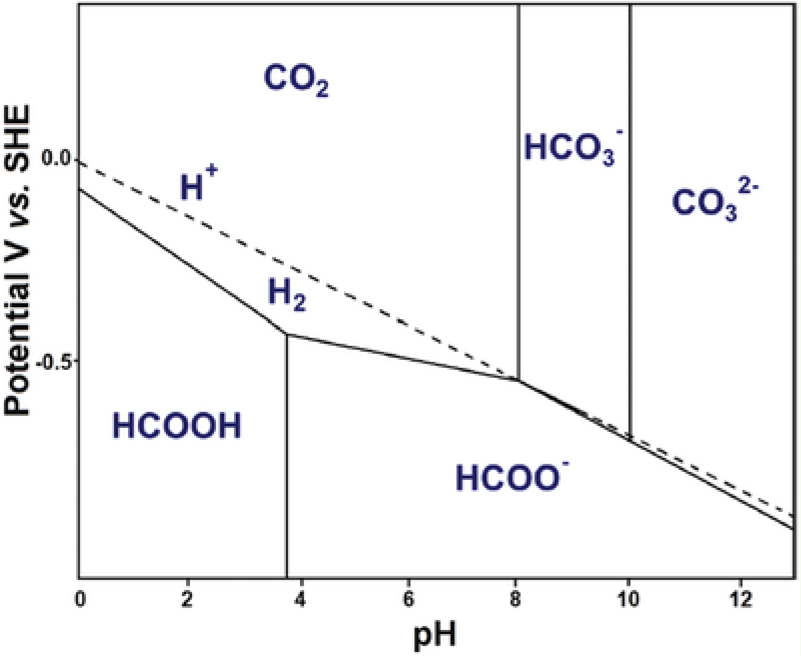


@ -1.1 V in 0.1 M $KHCO_3$

R. Reske et al. J Am Chem Soc 2014;136:6978-86

Effect of pH on electrochemical reduction of CO_2

- The **electrocatalytic selectivity** for target compounds is significantly influenced by pH.
- pH values close to the electrode surface will **differ** from the bulk electrolyte pH due to the generation of OH^- by both the competing hydrogen evolution reaction and CO_2 reduction



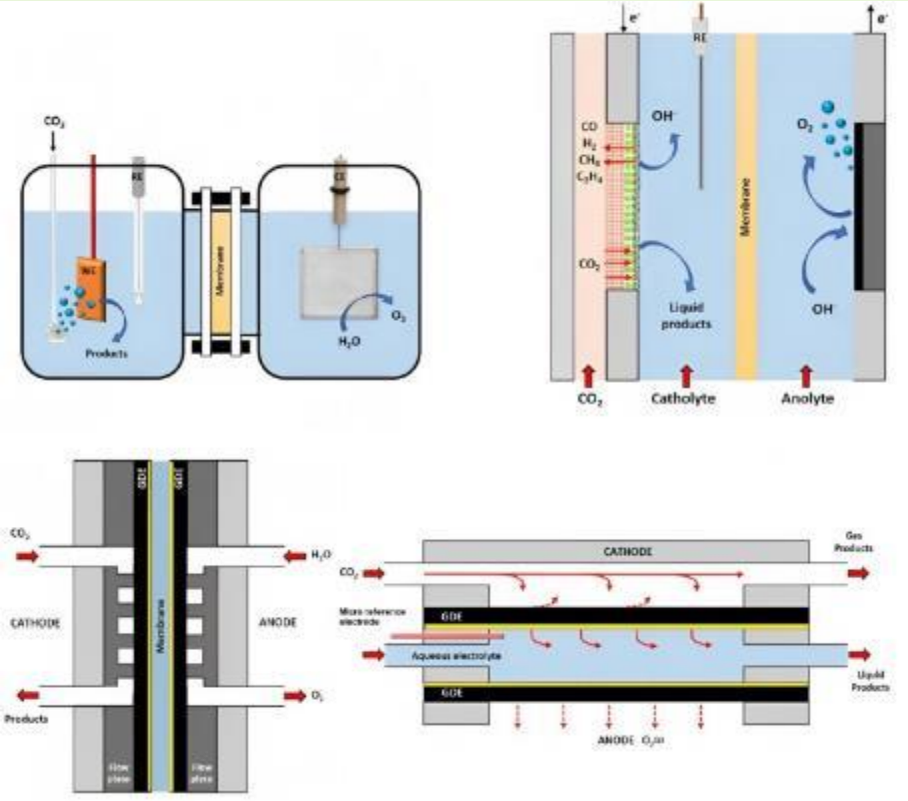
Pourbaix diagram illustrating the effect of pH on the phase stability of CO_2 in aqueous electrolytes

- Dominant carbon sources:
  - low pH (<6.5): Carboxylic acid (HCOOH)
  - medium pH (6.5-10.3), bicarbonate (HCO_3^-)
  - higher pH (>10.3): carbonate (CO_3^{2-})
- To suppress HER, the pH of aqueous electrolytes is usually maintained around 9 because the availability of H^+ is reduced
- Due to the catalytic reactions and diffusion limitations, the pH of the electrolyte and the cathode surface are different
- As long as the pH difference is smaller, mass transfer is enhanced, affecting the selectivity and the activity of the cathodic reaction

Effect of cell design on electrochemical reduction of CO_2

- eCO_2R cells are classified in **batch** or **continuous** operation.

H-type electrolytic cell | **gas feed flow cell**



PEM electrolyser cell | **microfluid electrolyser**

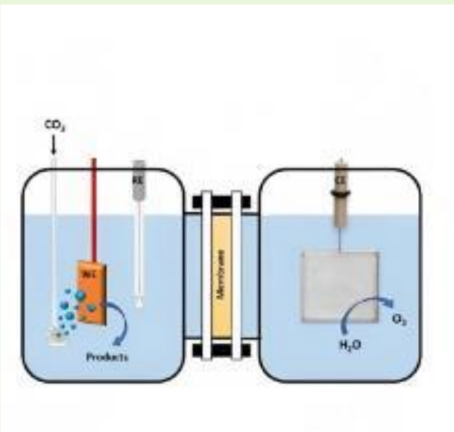
Effect of cell design on electrochemical reduction of CO_2

➡ **Two chambers separated by an ion-exchange membrane, with a reference, working and counter electrode.**

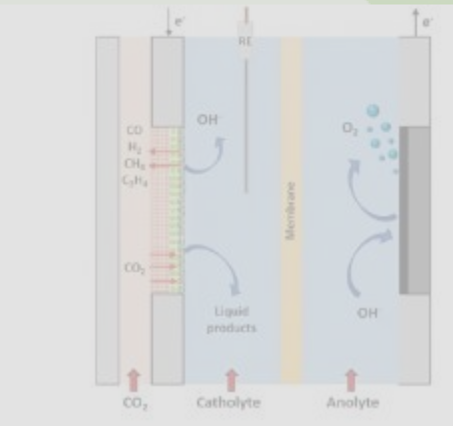
Advantages
- Convenient in lab-scale experiments
- Suitable for the study of half-cell reactions
- Possibility screening of electrocatalysts
- Commercially available
- Easy of assembly and reproducibility
- Low costs

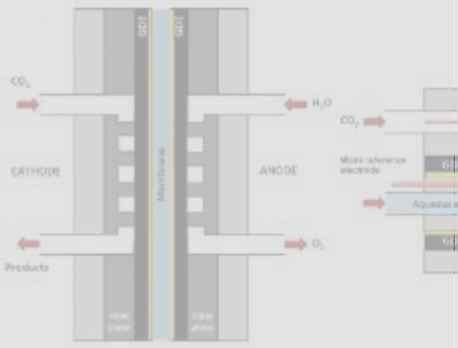
Drawbacks
- Poor mass transfer and mixing
- High cell resistance
- Low CO_2 conversion and current density
- Metallic contamination from electrolytes
- Not easy identification of liquid products
- Difficulty to use in large-scale application (limited electrode surface area and large distance between electrodes)
- High cell voltage and low energy efficiency

H-type electrolytic cell

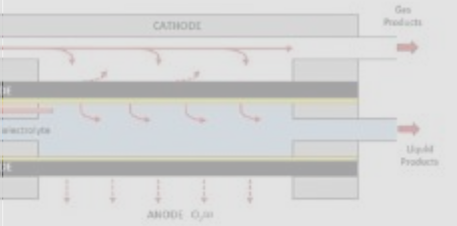


gas feed flow cell





PEM electrolyser cell



microfluid electrolyser

Effect of cell design on electrochemical reduction of CO_2

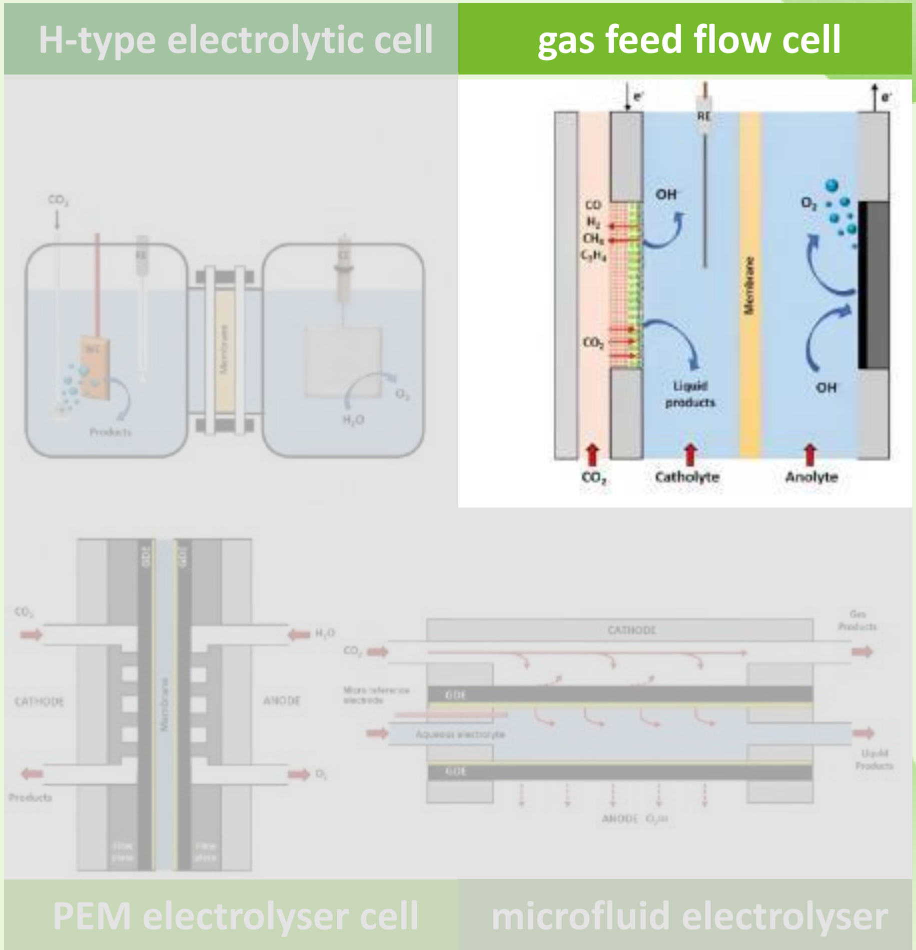
- ➡ **A compartment for the CO_2 gas flow, anolyte and catholyte**
- ➡ **Anode and cathode sides are separated by an ion-exchange membrane**
- ➡ **A gas diffusion electrode in the cathode**
- ➡ **A reference electrode in the cathode side**

Advantages

- Mass transport and mixing better compared to the H-cells
- Current density and Faradaic efficiency higher compared to the H-cells
- Potential for industrial applications
- Diffusion path shorter than that of H-cells

Drawbacks

- The way to supply CO_2 to the catalyst is critical
- Cell design is critical
- High ohmic drop and low energy efficiency



Effect of cell design on electrochemical reduction of CO_2

- ➡ **A gas diffusion electrode for anode and cathode sites separated by an ion-exchange membrane**
- ➡ **No liquid electrolyte and separation between gas diffusion electrodes and membrane**
- ➡ **No reference electrode (a working and counter electrodes are used)**

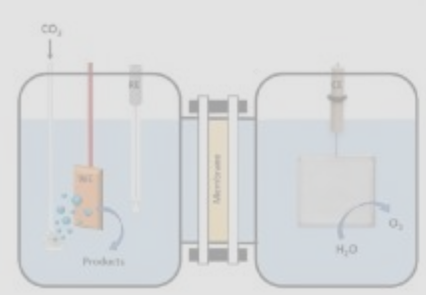
Advantages

- Relatively easy scale-up and pressurization
- Existing know-how (similarity to water electrolysers)
- Mass transport and mixing better than the H-cells
- Potential for industrial applications
- Cell resistance and ohmic loss lower compared to the basic cell (higher energy efficiency)
- Compact structure
- Reduced risk of catalyst poisoning due to impurities in the electrolyte

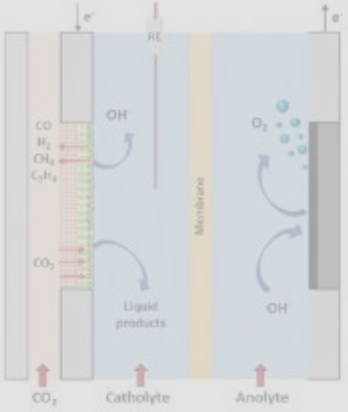
Drawbacks

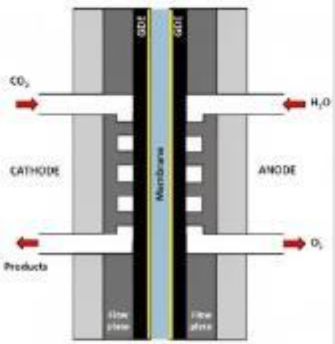
- pH imbalance between anode and cathode favoring the HER
- Cost and stability of membranes
- Resistance or product crossover due to membrane
- Strong corrosion at high overpotential

H-type electrolytic cell

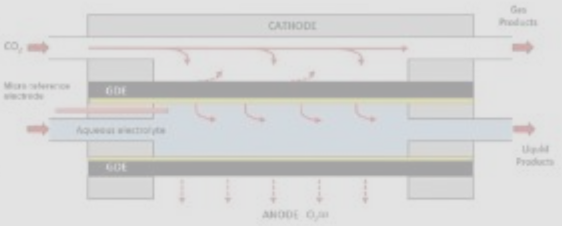


gas feed flow cell





PEM electrolyser cell



microfluid electrolyser

Effect of cell design on electrochemical reduction of CO_2

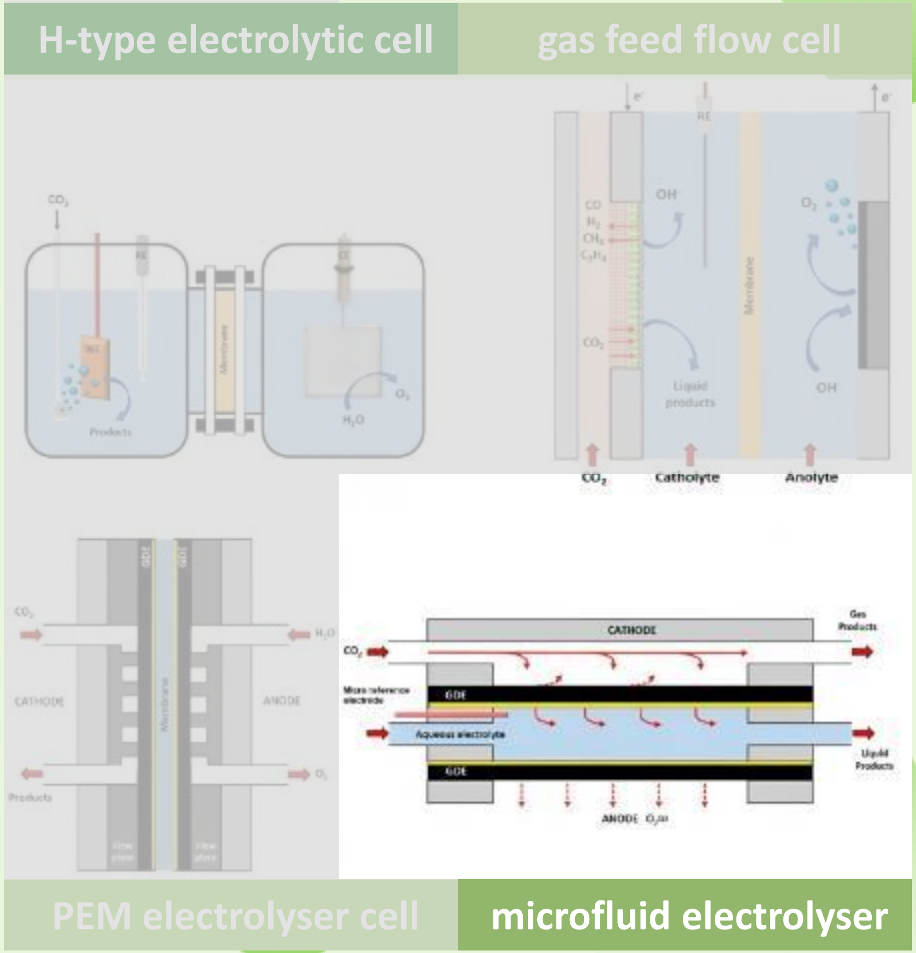
➡ **Two gas diffusion electrodes separated by a thin layer of electrolyte with a micro-reference electrode**

Advantages

- Current density and mass transport higher than PEM electrolyser cell
- Fast screening of catalysts
- Better control of flooding at electrodes
- Decrease of ohmic losses
- Avoidance of high membrane cost
- Flexibility in operating conditions
- Less decrease of pH

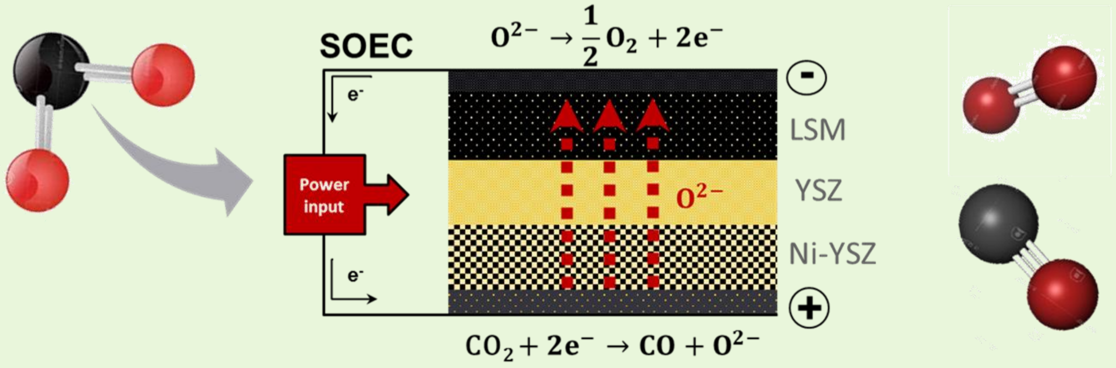
Drawbacks

- Less effective separation of products from electrodes
- Lower liquid product concentration
- Not easy pressurization
- Possibility of product re-oxidation



Solid Oxide Electrolysis Cells (SOECs)

CO_2 electrolysis



➡ **A cathode, an anode and a solid-oxide electrolyte**

Temperature in the range of 600-900°C

Advantages:

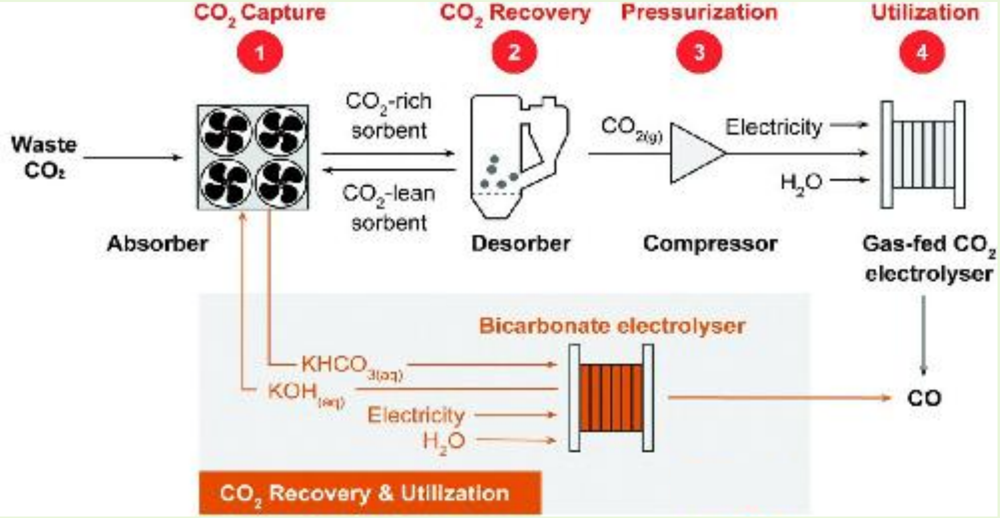
- Feed of gaseous CO_2 directly from source
- Both reversible potential and electrode polarization resistances decrease substantially with increasing temperature
- Efficiencies exceeding 95% (using higher heating value) are realistic
- Possibility of co-electrolysis of H_2O and CO_2 yielding syngas

Drawbacks:

- Specific electrodes are needed
- Impurities of gas feed cause the electrode passivation
- Carbon deposition
- Metal particles oxidation
- Cell degradation

Direct conversion of capture liquids

Process flow schematics for CO_2 electrolysis through purifying CO_2 streams compared with reactive capture.



J.H. Kim et al., Energy Environ. Sci. 2022, 15 (10), 4301

- The conventional upstream process for eCO_2R is carbon capture, producing a pure stream of CO_2 for subsequent conversion in the electrolyzer
- However, the purification of CO_2 is costly due to inefficient thermal/pressure swing
- Integrating CO_2 capture and conversion steps – a process called **reactive capture** – can offer improved system efficiencies

Reactive capture with capture liquids presents the opportunity to generate gaseous products at high concentration that are phase-separated from the liquid reactant.

Direct conversion of capture liquids

Amines

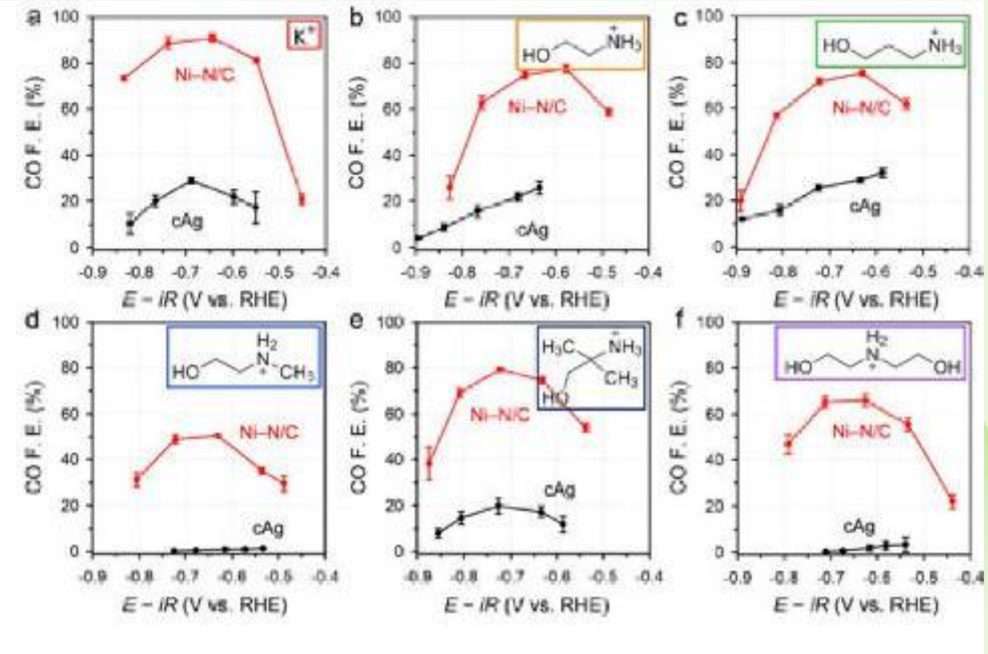
- Amine-based chemicals capture CO_2 and convert CO_2 into a chemisorbed form.
- Amine molecules capture CO_2 via the following reaction to form **carbamate ions**:

$$CO_2\,(g) + 2RNH_2\,(l) \rightarrow RNCOO^-\,(aq) + RNH_3^+\,(aq)$$

System configuration of amine capture liquid-fed electrolyzer with a BPM

- **Metal-based catalysts** (e.g. Ag, Cu, Ni, In and Pb) have been reported as electrocatalysts under amine-based electrolyte conditions to produce **CO** and **$HCOO^-$**
- Although reactive capture approaches to date show promise, these systems have not reached **industrial levels** of current density (**200 - 500 mA/cm²**)
- **Stability** remains a challenge

Faradaic efficiency for CO of amine-CO_2 electrolysis for various amine-based capture liquids



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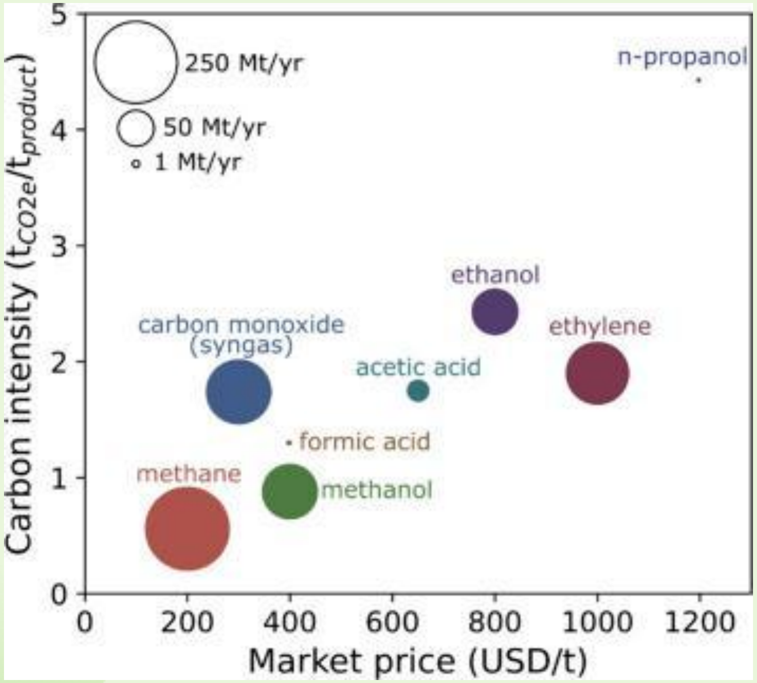
Economic prospects of electrochemical CO_2 conversion

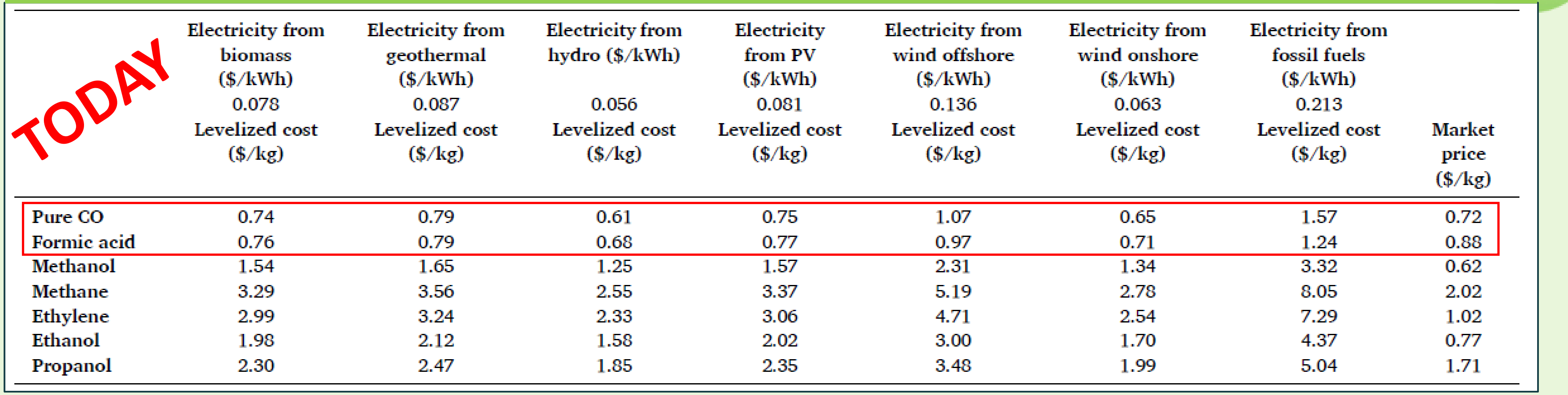


The market size, market price, and carbon intensity of the most common eCO_2R products

- **N-propanol**, a specialty chemical, offers a route to near-term economic and greenhouse gas reduction success. However, its small market size (0.2 Mt/yr) limits the overall carbon emission abatement impact to the Mt scale, a very small fraction of global CO_2 anthropogenic emissions at ~37 Gt/yr.
- In the pursuit of CO_2 impacts on the Gt scale, **ethylene** (140 Mt/yr) and **ethanol** (77 Mt/yr) are attractive targets, presenting a combination of high product value and large carbon intensity.

Economic prospects of electrochemical CO_2 conversion

Levelized costs of products obtained via eCO_2R at different electricity costs and comparison with the market price*
(current density 0.3 A/cm^2, Faradaic efficiency 90 %, CO_2 conversion 50 %)



TODAY

	Electricity from biomass ($/kWh) 0.078 Levelized cost ($/kg)	Electricity from geothermal ($/kWh) 0.087 Levelized cost ($/kg)	Electricity from hydro ($/kWh) 0.056 Levelized cost ($/kg)	Electricity from PV ($/kWh) 0.081 Levelized cost ($/kg)	Electricity from wind offshore ($/kWh) 0.136 Levelized cost ($/kg)	Electricity from wind onshore ($/kWh) 0.063 Levelized cost ($/kg)	Electricity from fossil fuels ($/kWh) 0.213 Levelized cost ($/kg)	Market price ($/kg)
Pure CO	0.74	0.79	0.61	0.75	1.07	0.65	1.57	0.72
Formic acid	0.76	0.79	0.68	0.77	0.97	0.71	1.24	0.88
Methanol	1.54	1.65	1.25	1.57	2.31	1.34	3.32	0.62
Methane	3.29	3.56	2.55	3.37	5.19	2.78	8.05	2.02
Ethylene	2.99	3.24	2.33	3.06	4.71	2.54	7.29	1.02
Ethanol	1.98	2.12	1.58	2.02	3.00	1.70	4.37	0.77
Propanol	2.30	2.47	1.85	2.35	3.48	1.99	5.04	1.71

- **CO and formic acid** show some **promising** conditions through their electrochemical production at the current operating conditions: the production cost is lower than that of the market
- **Methanol, methane, ethylene, ethanol, and propanol** productions via eCO_2R are **not economically favorable** compared to the market in all investigated cases

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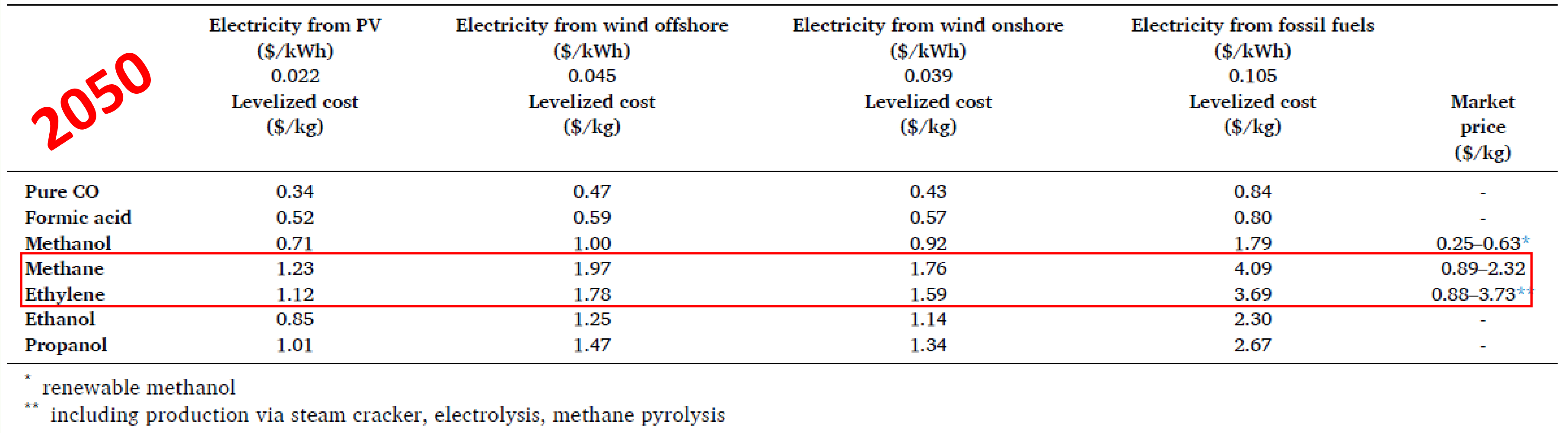
* *The economic analysis was conducted (G. Leonzio et al. Chem. Eng. Res. Des 208 (2024) 934–955) for a system producing **100 ton/day** of a product as in large-scale chemical production, with a process scheme consisting of an **electrolyser unit**, a **gas separation unit (PSA)** and a **distillation unit** when CO_2 liquid products are considered.*

Economic prospects of electrochemical CO_2 conversion

Reuse

Levelized costs of products obtained via eCO_2R for 2050 at different electricity costs and comparison with the market price* (current density 2 A/cm^2, Faradaic efficiency 90 %, CO_2 conversion 70 %)



2050

	Electricity from PV ($/kWh) 0.022 Levelized cost ($/kg)	Electricity from wind offshore ($/kWh) 0.045 Levelized cost ($/kg)	Electricity from wind onshore ($/kWh) 0.039 Levelized cost ($/kg)	Electricity from fossil fuels ($/kWh) 0.105 Levelized cost ($/kg)	Market price ($/kg)
Pure CO	0.34	0.47	0.43	0.84	-
Formic acid	0.52	0.59	0.57	0.80	-
Methanol	0.71	1.00	0.92	1.79	0.25–0.63*
Methane	1.23	1.97	1.76	4.09	0.89–2.32
Ethylene	1.12	1.78	1.59	3.69	0.88–3.73**
Ethanol	0.85	1.25	1.14	2.30	-
Propanol	1.01	1.47	1.34	2.67	-

* renewable methanol

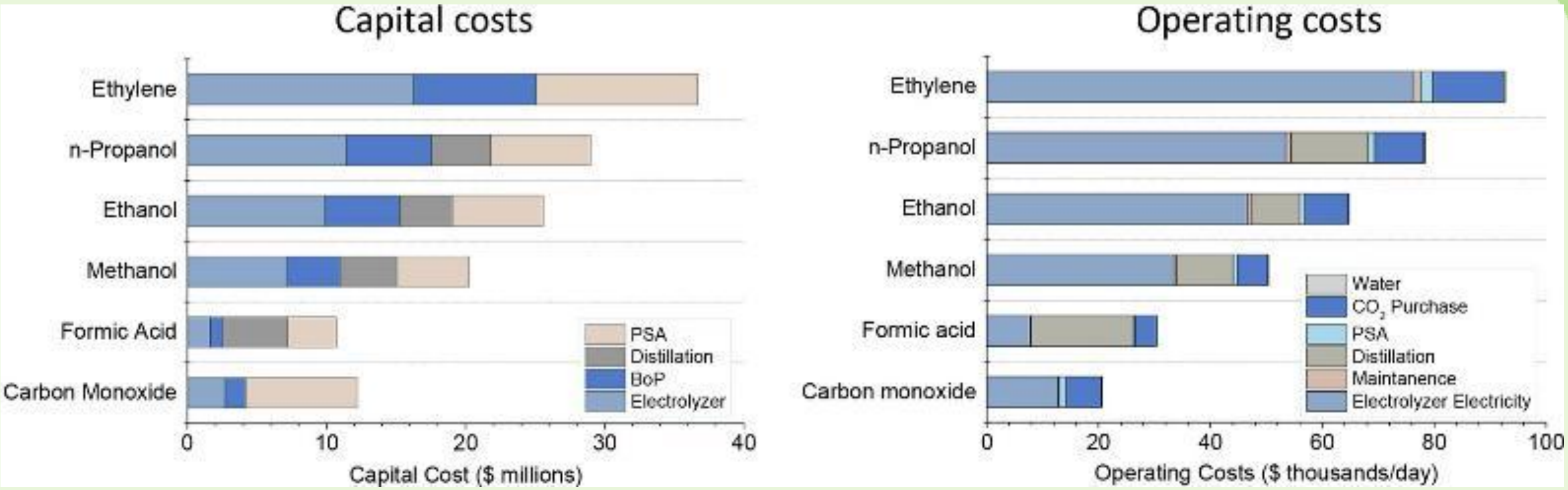
** including production via steam cracker, electrolysis, methane pyrolysis

- The input CO_2 price was reduced to 11 $/ton from the current 25 $/ton
- The **production cost** of compounds from eCO_2R **decreases**
- **Methane** and **ethylene** could be also **competitive** with the market due to a lower cost compared to the expected range

** The economic analysis was conducted (G. Leonzio et al. Chem. Eng. Res. Des 208 (2024) 934–955) for a system producing **100 ton/day** of a product as in large-scale chemical production, with a process scheme consisting of an **electrolyser unit**, a **gas separation unit (PSA)** and a **distillation unit** when CO_2 liquid products are considered.*

Economic prospects of electrochemical CO_2 conversion

Capital and operating costs for various products under optimistic case assumptions*



M. Jouny et al. Ind. Eng. Chem. Res. 2018, 57, 2165-2177

- **Ethylene** had the highest capital and operating costs due to the large amount of current (electricity) needed per kg of product. These high costs, along with a large CO_2 feedstock requirement, contributes to the **low profitability** of ethylene relative to other products
- In contrast, **formic acid** and **CO** benefited from a small power requirement, which reduces the cost of electricity and electrolyzer size
- **Formic acid distillation** is expensive, though PSA offers lower operating costs. However, gaseous products may need **compression** for storage or transport, potentially increasing overall costs despite cheaper separation methods

** production rate: **100 ton/day**, lifetime: 20 years, operating time: 350 days/year, **electricity price: 0.03 $/kWh**, **current density: 300 mA/cm^2**, **cell voltage: 2 V**, product selectivity: 90%, conversion: 50%, **CO_2 price: 40 $/ton**, interest rate: 10%, electrolyzer cost: 920 $/m^2*

Advantages of electrochemical CO_2 conversion

1. The process is completed through reactants gaining or losing electrons at an electrode (usually electrocatalyst), and **neither oxidizing agent nor reducing agent is needed**
2. Without adding an oxidizing or a reducing agent into the solution, the consumption of substances can be reduced, and the **side reactions can be greatly reduced**
3. **Products can be controlled accurately** via controlling the metal electrodes, current, voltage, and electrolytes
4. The separation process can be simplified, and **high-purity products** can be obtained
5. The reaction that may **not occur under usual conditions can be carried out through electrochemical reaction**
6. The reactions usually run under **ordinary temperature and pressure**, and the **energy consumption can decrease significantly**
7. The electricity used to drive the process can be provided by the **excess energy from intermittent renewable sources** instead of large-scale energy storage
8. The electrochemical **reaction systems are compact, modular, on-demand and easy for scale-up applications**

Challenges of electrochemical CO_2 conversion

- The **slow kinetics** of CO_2 electro-reduction, even when electrocatalysts and high electrode reduction potential are applied
- The **products selectivity** is one of the significant points to be investigated when evaluating the properties of catalysts
- The **high energy consumption**. The biggest challenge in CO_2 electro-reduction is **low performance of the electrocatalysts** (i.e., low catalytic activity and insufficient stability)
- The **low energy efficiency of the process**, due to the **parasitic or decomposition reaction of the solvent** at high reduction potential

Economic feasibility

Reuse

- What combination of **optimized figures of merit** will be sufficient for economic feasibility?
- How fast do the component **materials** (particularly catalysts) **degrade** over long periods of time?
- What are the **sources of CO_2** and how will potential **contaminants** such as sulfur-containing compounds impact electrolyzer design, as well as cell performance and catalyst durability?

- The cost to produce a given amount of CO is substantial and dependent on the current density at which the electrolyzer is being operated, leveling off at high current densities
- The current SoA performance (100 mA/cm^2) is still far from a performance level where the cost to produce CO starts to level off

Reuse

Thank you!

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