

CO₂ as a Raw Material

electrochemical processes to produce fuels and chemicals

CCUS in Action” – A Deep Dive
into the Future of Carbon
Capture and Utilization

Online Webinar-22/05/2025

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- **Introduction**
 - The role of CO₂ in mitigating challenges related to renewable energy deployment
 - Processes to convert CO₂ into chemicals/fuels
- **Electrochemical reduction of CO₂ process**
 - Essentials and technologies for electrochemical CO₂ conversion
- **Low temperature CO₂ reduction**
- **High temperature, Solid Oxide Electrolysis for CO₂ conversion**
- **Advantages, challenges and prospects of electrochemical CO₂ conversion**

CO₂ reduction to value-added products



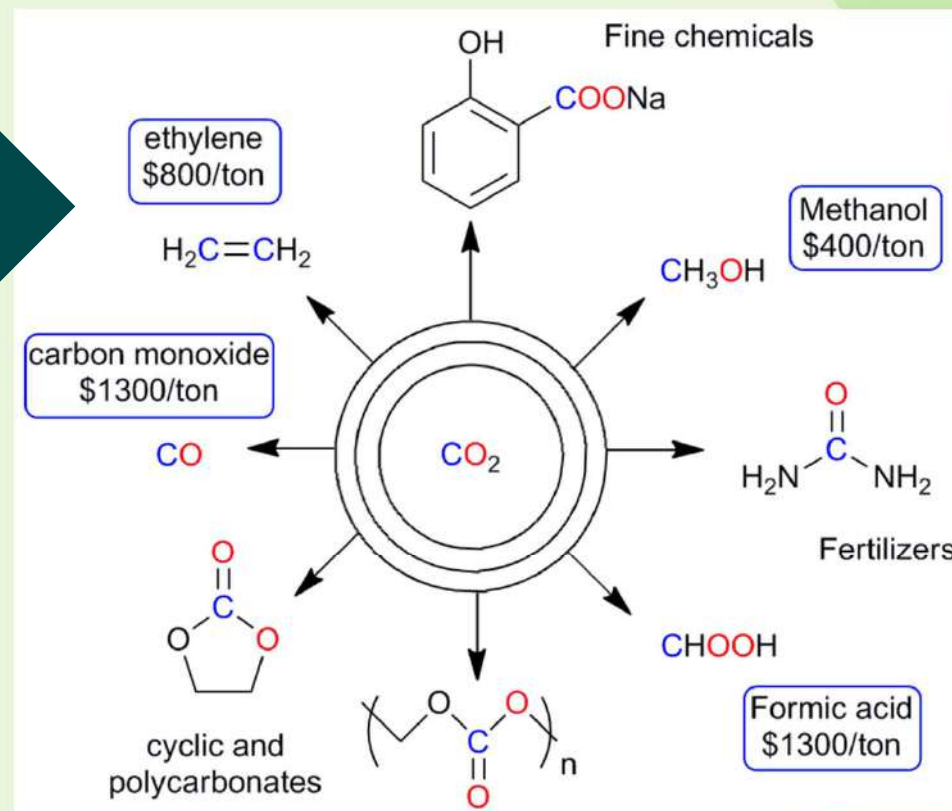
- Global annual demand: 200 Mt

- 110 Mt of CO₂ 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

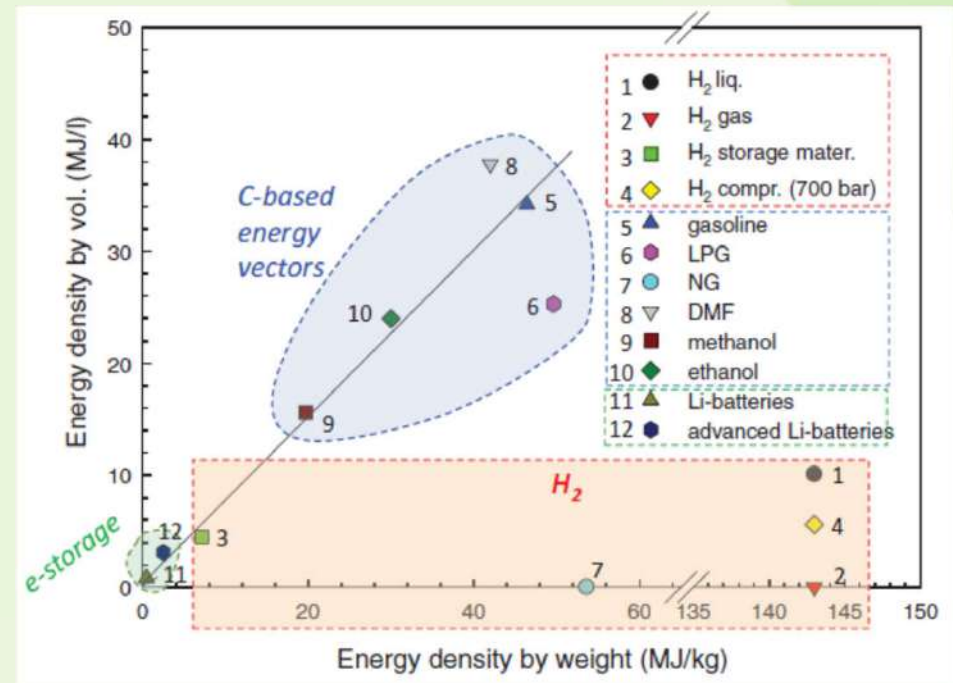
- Annual production: 24 Gt



Energy density of liquid and gaseous fuels

Requirements for suitable energy vectors:

- i. have both a high energy density by volume and by weight
- ii. be easy to store without a need for high pressure at room temperature
- iii. be of low toxicity and safe to handle, and show limited risks in their distributed (non-technical) use
- iv. show a good integration in the actual energy infrastructure without the need of new dedicated equipment
- v. have a low impact on the environment in both their production and their use



G. Centi, S. Perathoner, *Greenhouse Gas Sci Technol.*, **2011**, 1, 21

Energy density per weight vs per volume in a series of liquid and gaseous fuels, H₂, and electrical energy

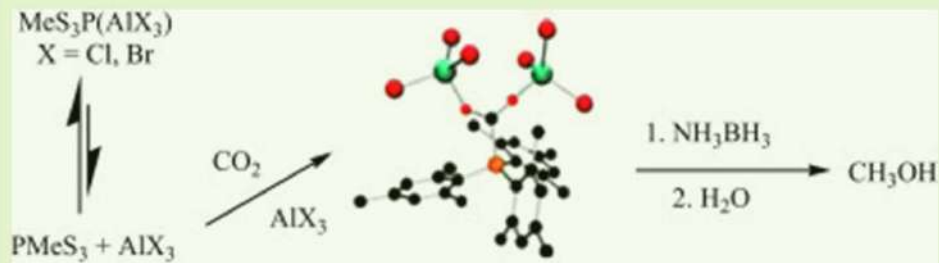
- Liquid fuels are fulfilling all the requirements, except of greenhouse gases emissions
- It is preferable and more sustainable to find an efficient solution to recycle the CO₂ to form fuels using renewable energy rather than develop new energy vectors

Processes to convert CO₂ into chemicals/fuels



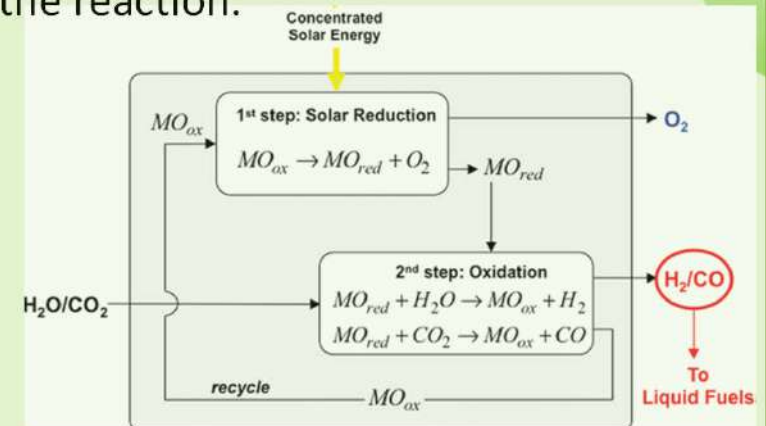
A. Stoichiometric reactions

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.



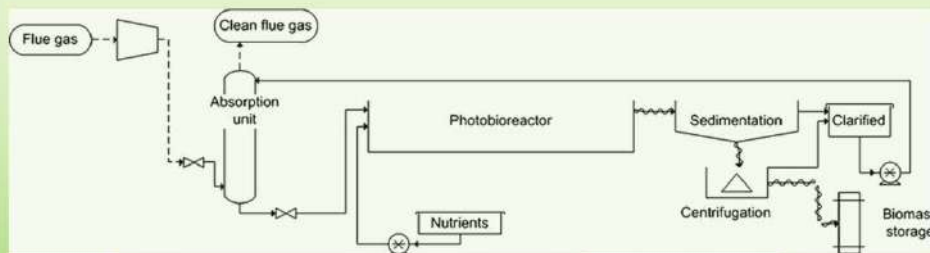
B. Thermo-chemical reactions

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



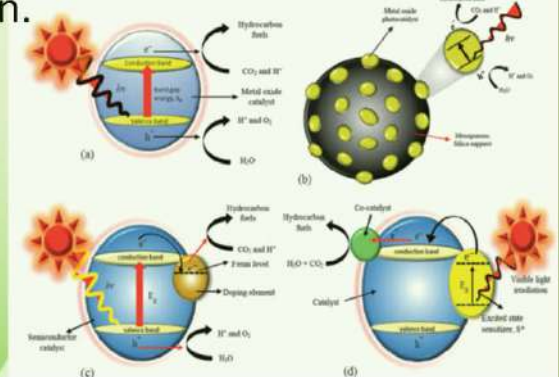
C. Biochemical processes

Use of microalgae for bio-fuels production.



D. Photocatalytic reactions

The transformation of CO₂ into fuel by using solar light irradiation.

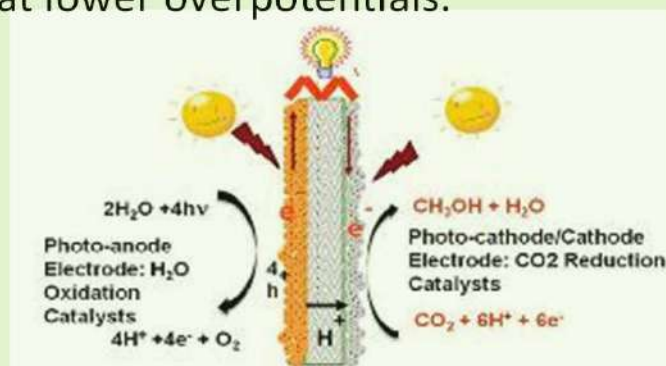


Processes to convert CO₂ into chemicals/fuels



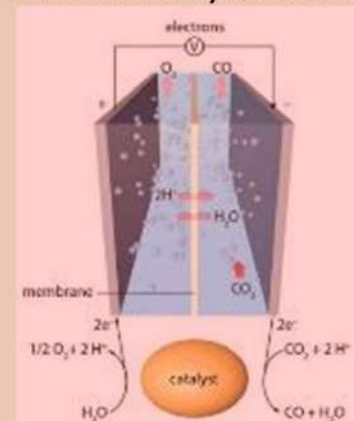
E. Photo-electrochemical (PEC) reactions

Use of semiconductors as anode/cathode electrodes. Yield highly reduced and selective CO₂ reduction products (methanol, ethanol, etc.), at lower overpotentials.

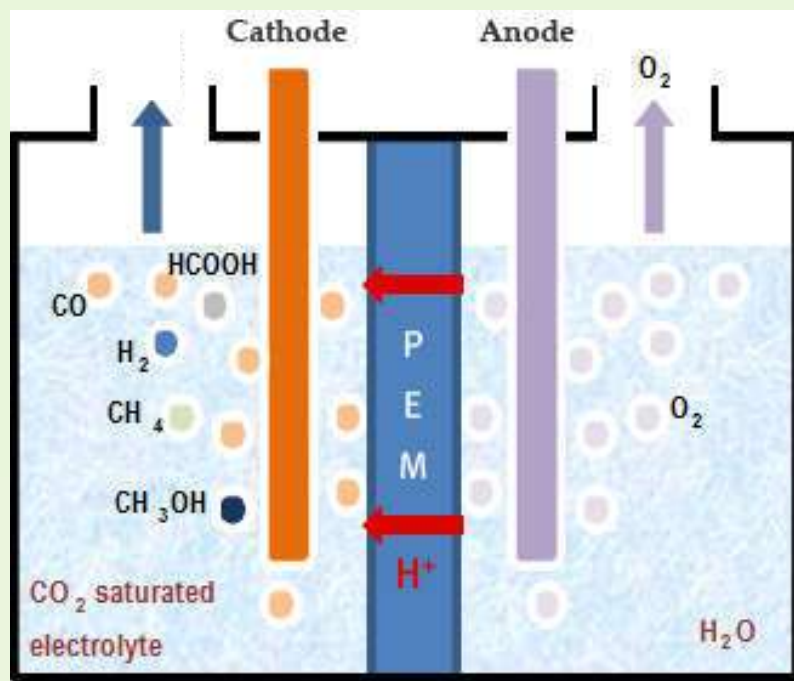


F. Electrochemical reductions

Use of electric energy (potential) to reduce CO₂ into chemical and/or fuels.



Essentials of electrochemical reduction of CO₂



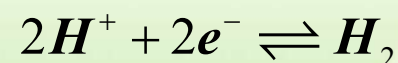
Electrochemical CO₂ conversion process:

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

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

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

The CO₂ reduction reaction usually competes with the hydrogen evolution reaction (HER):



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

Essentials of electrochemical reduction of CO₂

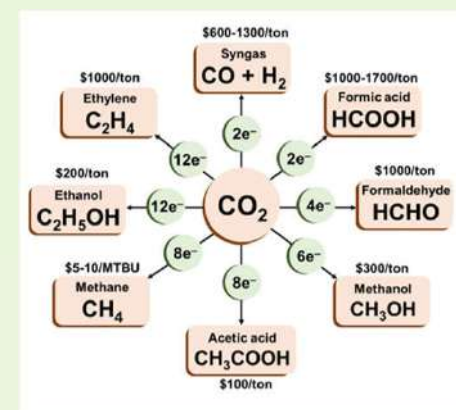
The half-cell reactions of cathode during electrochemical CO₂ reduction

Cathodic half-cell reaction (reduction process) $\Delta G^\circ_{\text{rxn}} = -nFE^\circ_{\text{cell}} \Rightarrow E^\circ_{\text{cell}} = -\Delta G^\circ/nF$
(V vs. NHE at pH=0)

$4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\uparrow$	-1.23	Hydrogen
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO}\uparrow + \text{H}_2\text{O}$	-1.33	CO
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-1.39	Formic acid
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + 1/2\text{O}_2$	-1.37	Formaldehyde
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-1.21	Methanol
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	-1.14	Ethanol
$3\text{CO}_2 + 18\text{H}^+ + 18\text{e}^- \rightarrow \text{C}_3\text{H}_7\text{OH} + 5\text{H}_2\text{O}$	-1.13	Propanol
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-1.06	Methane
$2\text{CO}_2 + 14\text{H}^+ + 14\text{e}^- \rightarrow \text{C}_2\text{H}_6 + 4\text{H}_2\text{O}$	-1.08	Ethane
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	-1.15	Ethylene

Potential products of CO₂ electroreduction:

Carbon monoxide (CO)
Formic acid (HCOOH) or formate (HCOO⁻)
Methanol (CH₃OH) or ethanol (C₂H₅OH)
Methane (CH₄) or Ethylene (C₂H₄)
Formaldehyde (CH₂O)
Oxalic acid (H₂C₂O₄) or oxalate (C₂O₄²⁻)



➡ In **thermodynamics**, the Gibbs free energy of CO₂ reduction ($\Delta G_{\text{rxn}} = -n \cdot F \cdot E_{\text{cell}}$) is always positive at medium and high pH range, hence, the theoretical potentials are negative.

Thus, CO₂ reduction requires electrical energy input

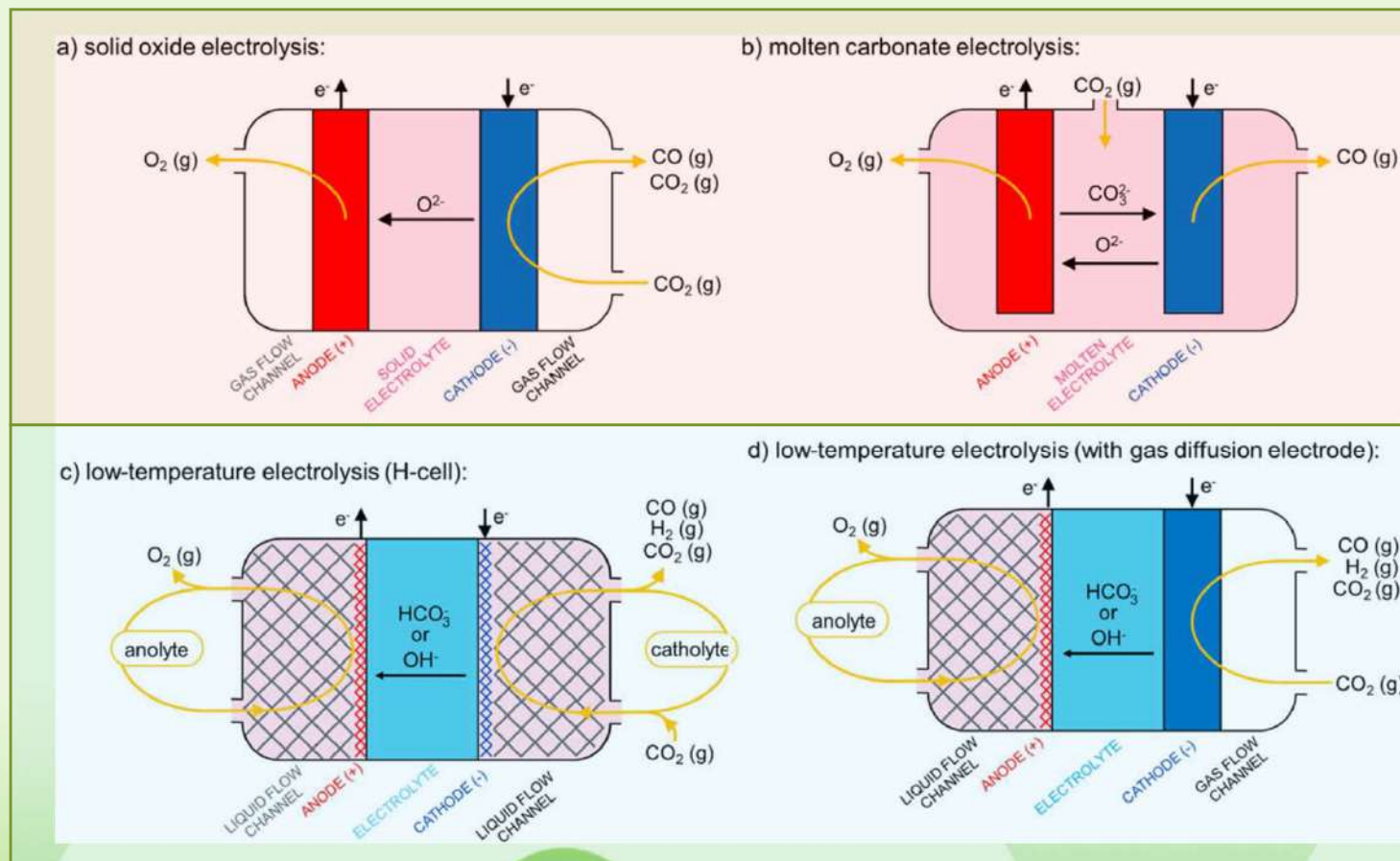
➡ In **kinetics**, the electrochemical reduction of CO₂ normally require certain overpotentials (>1.0 V), i.e. application of higher potential than thermodynamic potential, to get reasonable amounts of reduced products.

In an aqueous electrolyte, the H₂O also undergoes reduction and releases H₂ as a major by-product. Thus, **water reduction is always in competition with CO₂ reduction reaction in electrochemical cells.**



Technologies for CO₂ Electrolysis

Low vs. High temperature CO₂ electrolysis

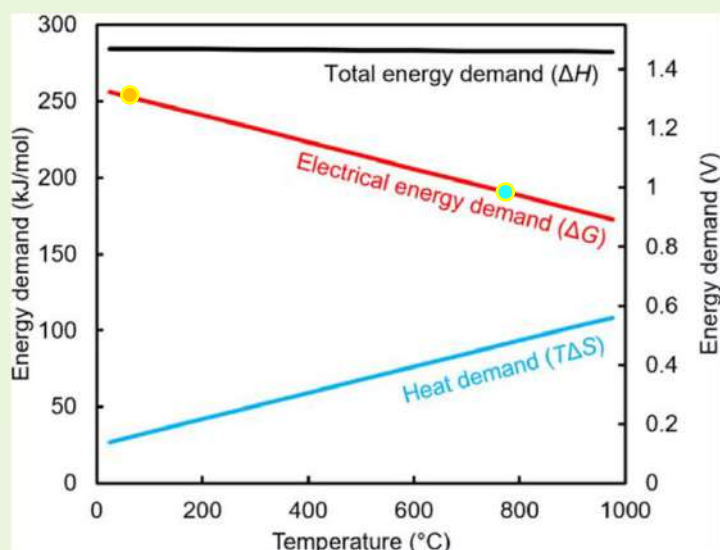


R. Kungas, *J. Electrochem. Soc.*, **2020**, 167, 044508



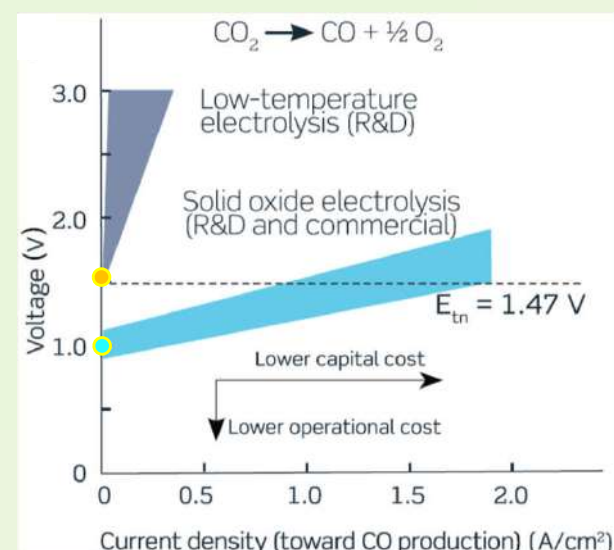
Low vs. High temperature CO₂ electrolysis

THERMODYNAMICS



Energy demand for CO₂ electrolysis

KINETICS



Performance for CO₂ splitting: potential vs current density

- **High temperature (SOEC) technology offers markedly higher thermodynamic performance:** an increasing fraction of the total energy demand can be provided in the form of **heat** ($T \cdot \Delta S_f$, entropy term)
- **At low temperatures, kinetics are slow and higher overpotentials (energy) are required to achieve high current densities (production rate)**



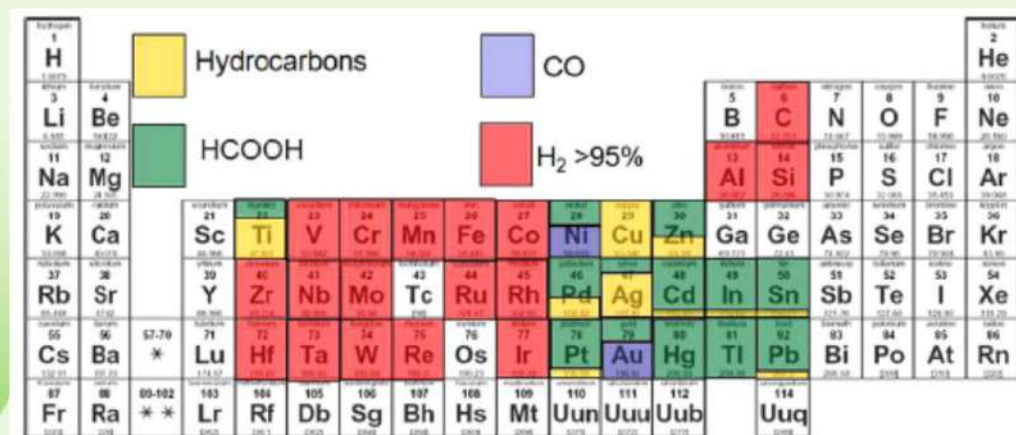
Electrocatalysts for CO₂ reduction

- ⏏ **Electrocatalysts** are needed to **bind and activate CO₂** 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:

- formic acid, HCOOH**, formation metals (**Pb, Hg, In, Sn, Cd, Tl, Ir**)
- carbon monoxide, CO**, formation metals (**Au, Ag, Zn, Pd, Ga**)
- hydrocarbons**, e.g. methane and ethylene, formation metals (**Cu, Ti, Ag**)
- hydrogen, H₂**, formation metals (**Pt, Ni, Fe, Ti, Ir**)

Grouping of metals based on CO₂ reduction products in potassium bicarbonate (KHCO₃) based media



Legend:

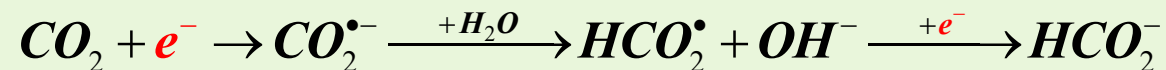
- Hydrocarbons (Yellow)
- CO (Purple)
- HCOOH (Green)
- H₂ >95% (Red)

Periodic table showing metal catalysts grouped by CO₂ reduction product in potassium bicarbonate (KHCO₃) based media. The table is color-coded according to the legend.

Example: electrocatalysts for formic acid production



- Electrochemical reduction of CO₂ in aqueous solution to **Formic acid (HCOOH)** and **Formate** ion (HCOO⁻) was reported as early as **1870**
- **Formic acid** can be produced with very high Faradaic efficiencies on metals with **high overpotential for H₂ production** (e.g. Hg, Pb, metal oxides, alloys and MOF catalysts)
- The electrochemical conversion of CO₂ to formic acid “HCOOH” (and formate “HCOO⁻”) is a **two-electron process**:



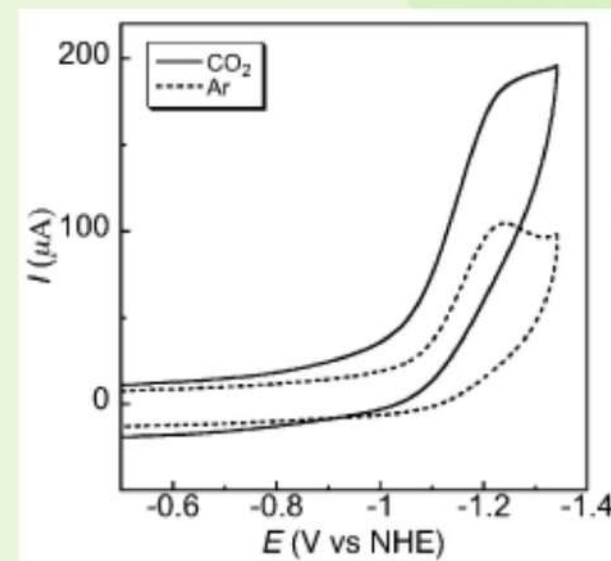
The **rate determining step** is the **formation of the CO₂^{•-} anion radical** at the high overpotential region and is the second electron transfer leading to the formation of formate at low overpotential.



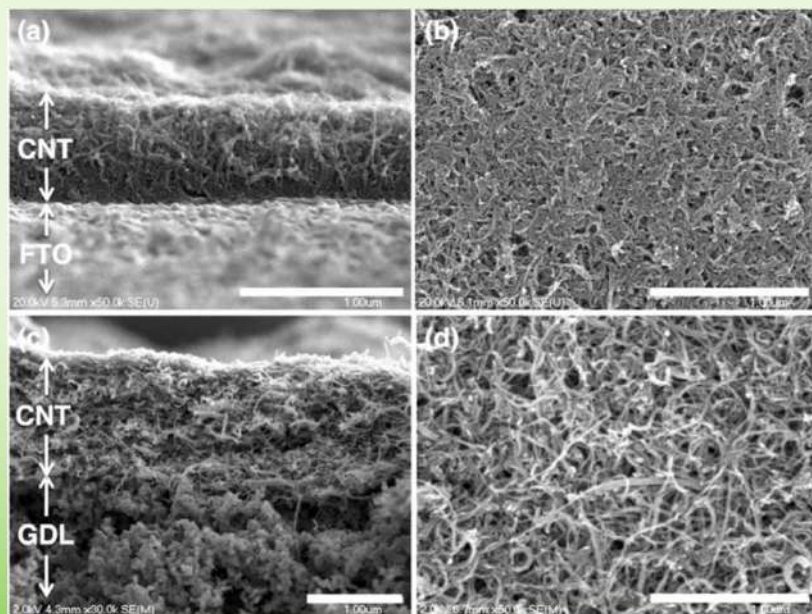
Example: electrocatalysts for formic acid production



Carbon nanotube-coated GDE with surface-bound
Ir pincer dihydride catalyst



Cyclic voltammograms in water, under Ar (dotted) and 1 atm CO₂ (solid) at 100 mVs⁻¹ scan rate



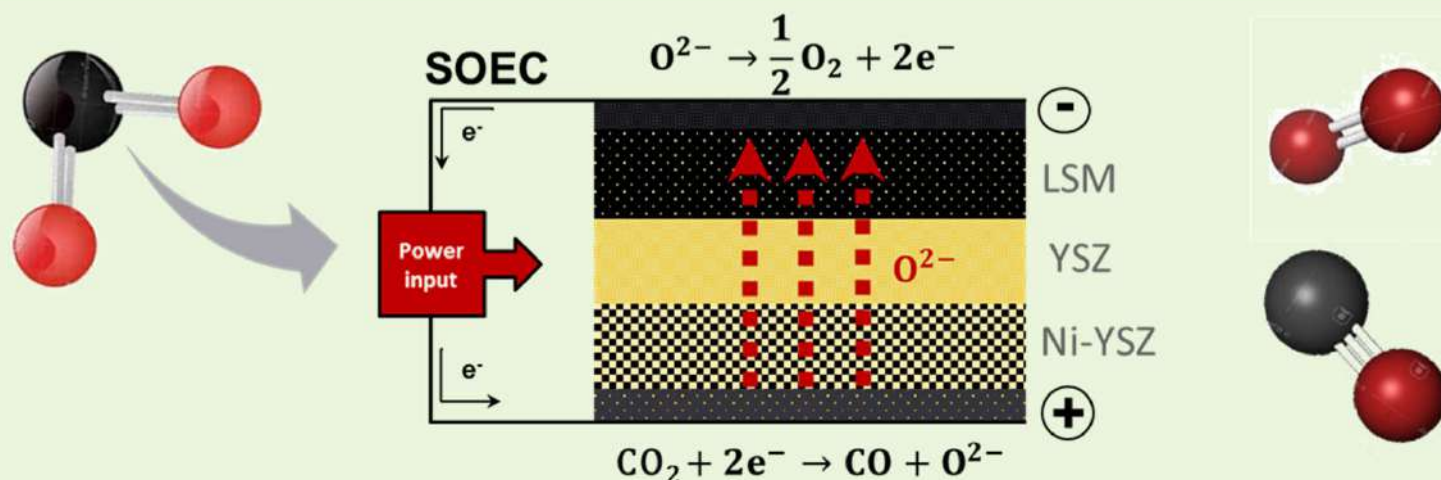
- The supported Ir catalyst exhibits notable efficiency (96%), selectivity (83%), and longevity for the production of formate
- Optimization with a gas diffusion electrode modified with the Ir catalyst gives current densities up to about 15 mA·cm⁻²

Kang P, Zhang S, Meyer TJ, Brookhart M. *Angew. Chem. Int. Ed.* 2014;53:1-6



Solid Oxide Electrolysis Cells (SOECs)

CO₂ electrolysis



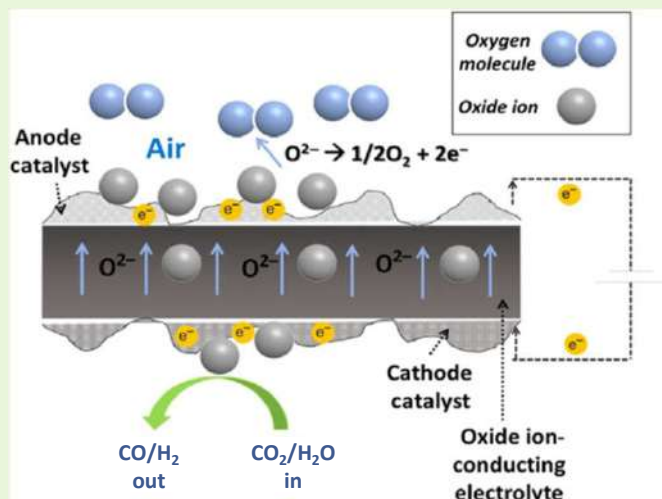
Temperature
in the range
of 600-900°C

Advantages of solid oxides electrolysis:

- Feed of gaseous CO₂ 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 H₂O and CO₂ yielding syngas

Solid Oxide Electrolysis Cells (SOECs)

H₂O and CO₂ co-electrolysis

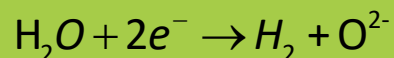


- Single step process to produce “white” syngas (CO/H₂)
- Tailoring of the syngas ratio (H₂:CO) by adjusting the operating parameters
- Syngas can be converted to a diverse range of chemical base products by subsequent catalytic reactions

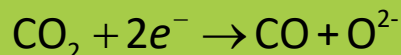
A highly promising CO₂ valorization technology in a ‘Power-to-Syngas’ or ‘Power-to-X’ scenario

During high-temperature co-electrolysis three reactions are possible at the fuel electrode:

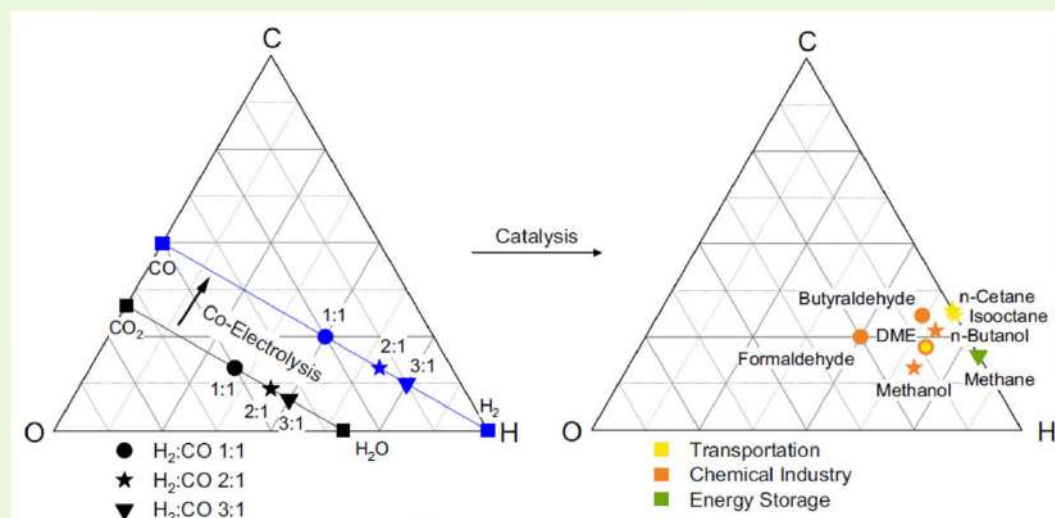
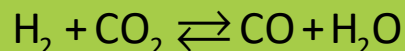
(i) electrochemical conversions of steam to H₂



(ii) electrochemical conversion of CO₂ to CO



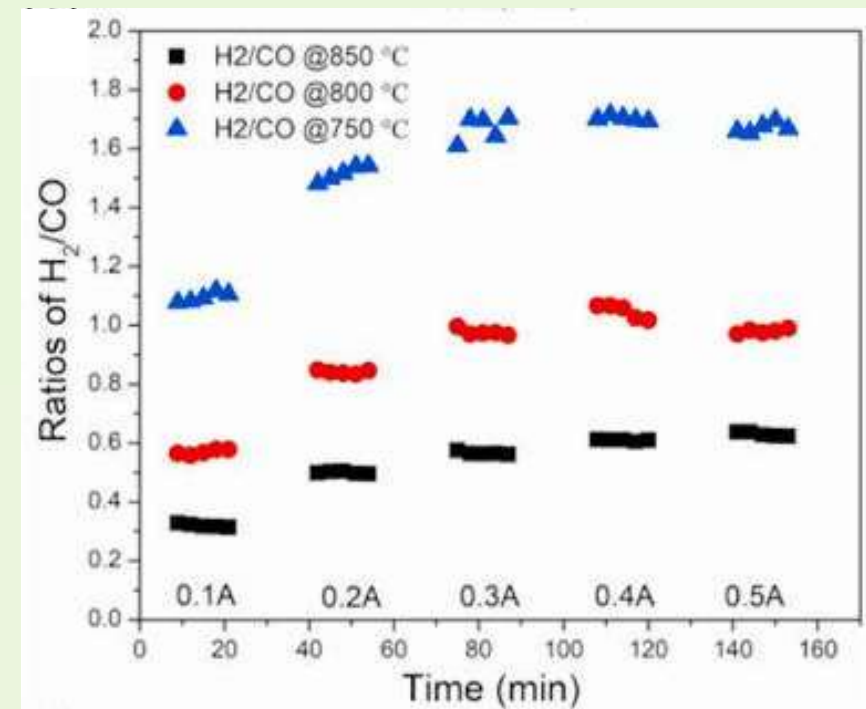
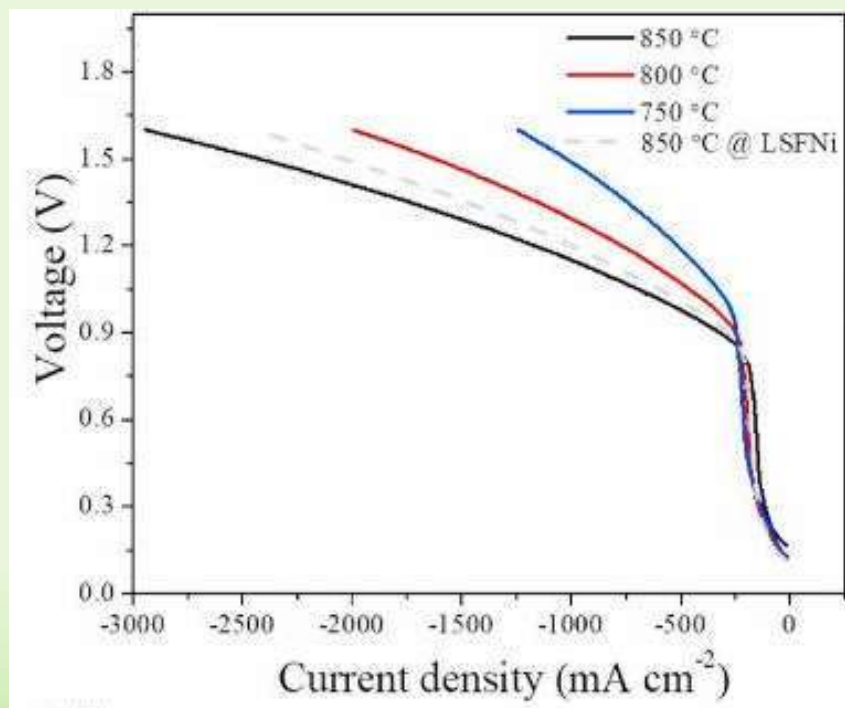
(iii) reverse water gas shift (RWGS) reaction:



Solid Oxide Electrolysis Cells (SOECs)

H₂O and CO₂ co-electrolysis

Syngas production with tunable H₂/CO yield via co-electrolysis of H₂O and CO₂



L. Bian et al., *Journal of Power Sources*, **2021**, 482, 228887



Solid Oxide Electrolysis Cells (SOECs)

H₂O and CO₂ co-electrolysis

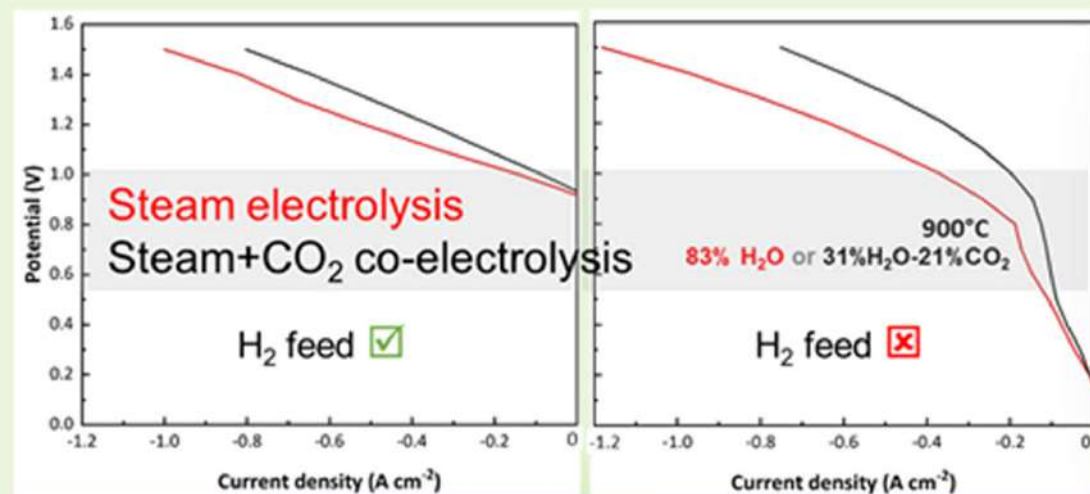
Syngas production with tunable H₂/CO yield via co-electrolysis of H₂O and CO₂

Ni-metal-free cathode electrodes

A class of substituted Lanthanum Chromites $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_x\text{M}_{1-x}\text{O}_{3-\delta}$ [M= Mn, Fe, Co, Ni] for Solid Oxide Water Electrolysis & CO₂+Water co-electrolysis

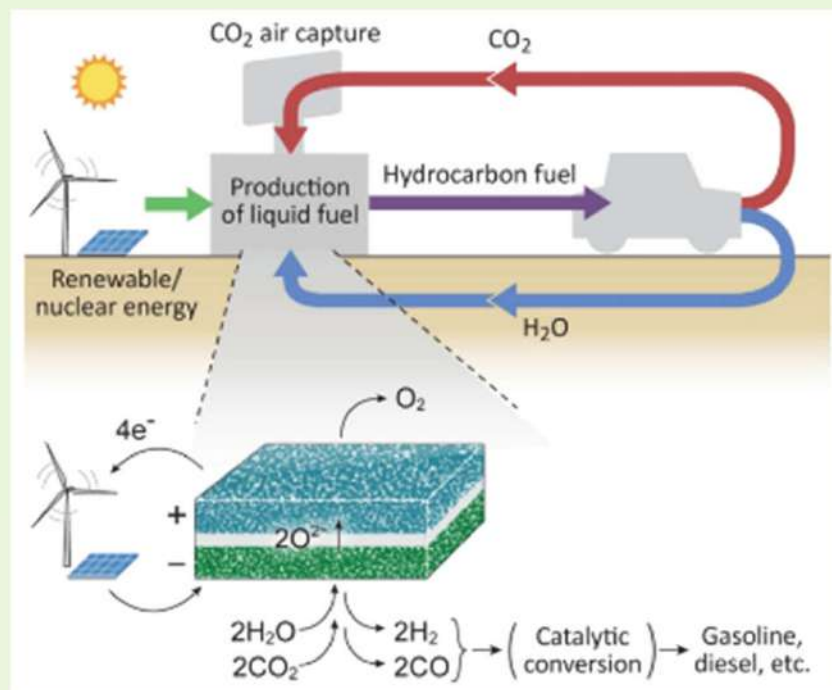
Mixed conducting materials

- ▶ allow the geometric extension of the electrochemical reaction zone, TPB in the entire volume of the electrode
- ▶ promote the electrochemical reaction in the SOEC fuel electrode

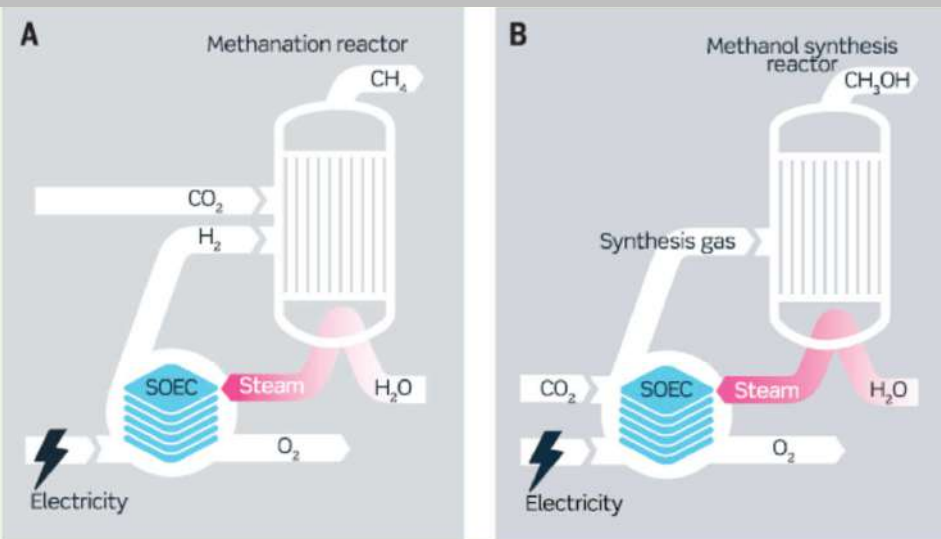


Solid Oxide Electrolysis Cells (SOECs)

H₂O and CO₂ co-electrolysis



Integration of solid oxide electrolysis systems with a synthesis process



A. Hauch et al., *Science*, **2020**, 370, eaba6118

Advantages of electrochemical CO₂ 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 CO₂ conversion



- The **slow kinetics** of CO₂ 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 CO₂ 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



Proposed optimizations & research directions



A. Optimization of activity, selectivity, and stability of catalysts

- ❖ high production faradaic efficiency and low hydrogen evolution reaction
- ❖ high active surface area which may provide more active sites
- ❖ synthesize materials with different advantages and the nanoscale catalysts with special 3D structures could be developed and investigated
- ❖ better understanding of the reaction process

B. Scaling up the reactors and reaction systems

- ❖ continuous system on a large scale should be designed and optimized
- ❖ use of gas diffusion electrodes (GDEs) to improve the mass transfer process
- ❖ use of waste waters or other carbon-capture solutions as the electrolyte
- ❖ development of high temperature (solid state) electrolyzers





Reuse

Thank you!

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Economic feasibility



- 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 CO₂** 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/cm²) is still far from a performance level where the cost to produce CO starts to level off

