CO_2 electrolysis- CCU developments @vito

Santander, Spain

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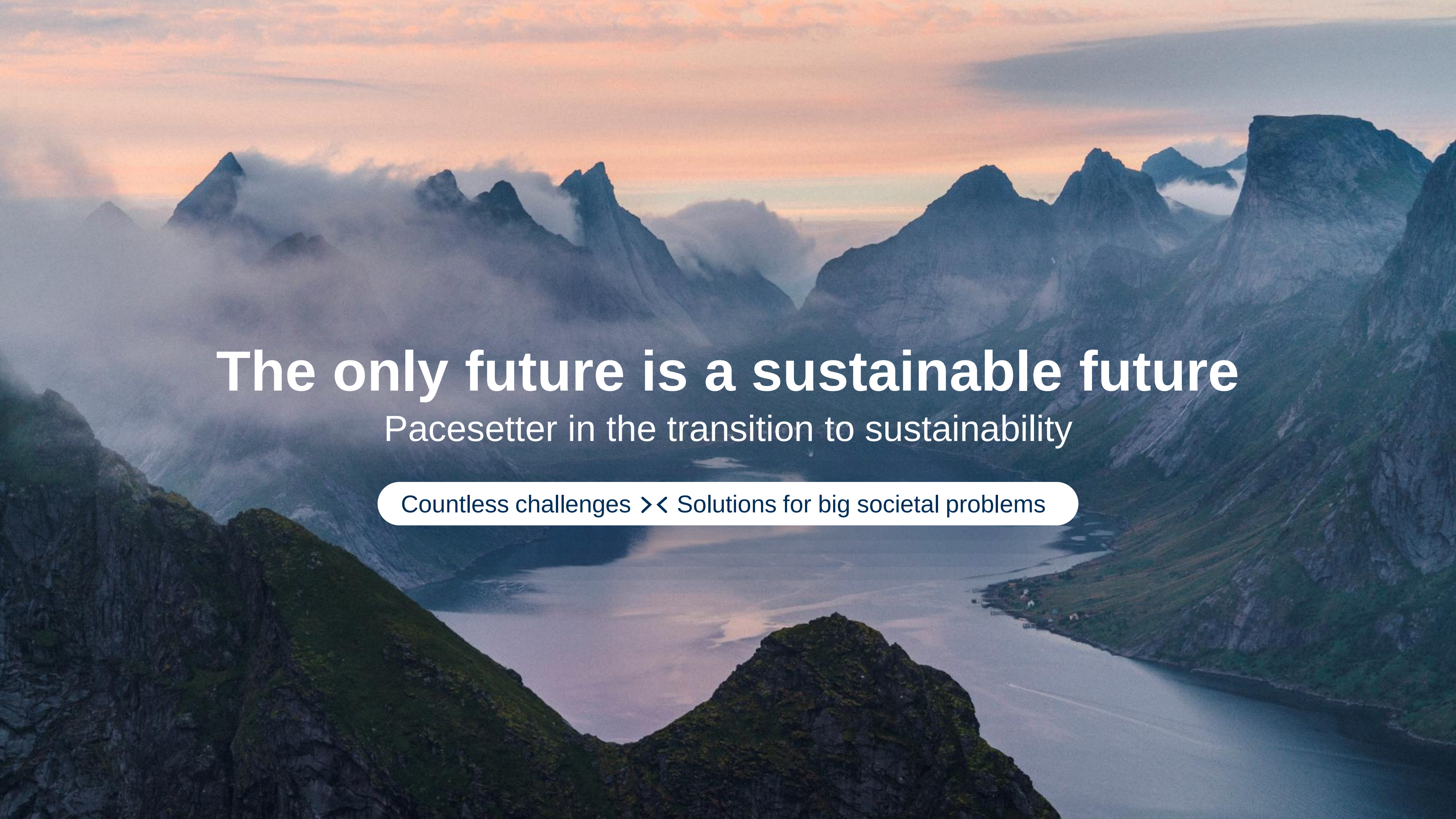

The only future is a sustainable future

Pacesetter in the transition to sustainability

Countless challenges >< Solutions for big societal problems




An independent research institute

Operating in today's economic and societal reality

- Multidisciplinary
- Science-based
- Demand-driven and beyond state-of-the-art
- Collaborative

That is how we create **impact**

Turning fundamental research into solutions

Creating value and increased competitiveness for companies and governments

Fundamental research

Research and education

Universities

Joint research projects,
Phds and postdocs

Applied research

Research in the economic reality

Research & Technology Organisations

Contract research
Techtransfer
Research projects, labs, pilots

Companies

Governments

Citizens

Technology Readiness Level

|1 |2 |3 |4 |5 |6 |7 |8 |9

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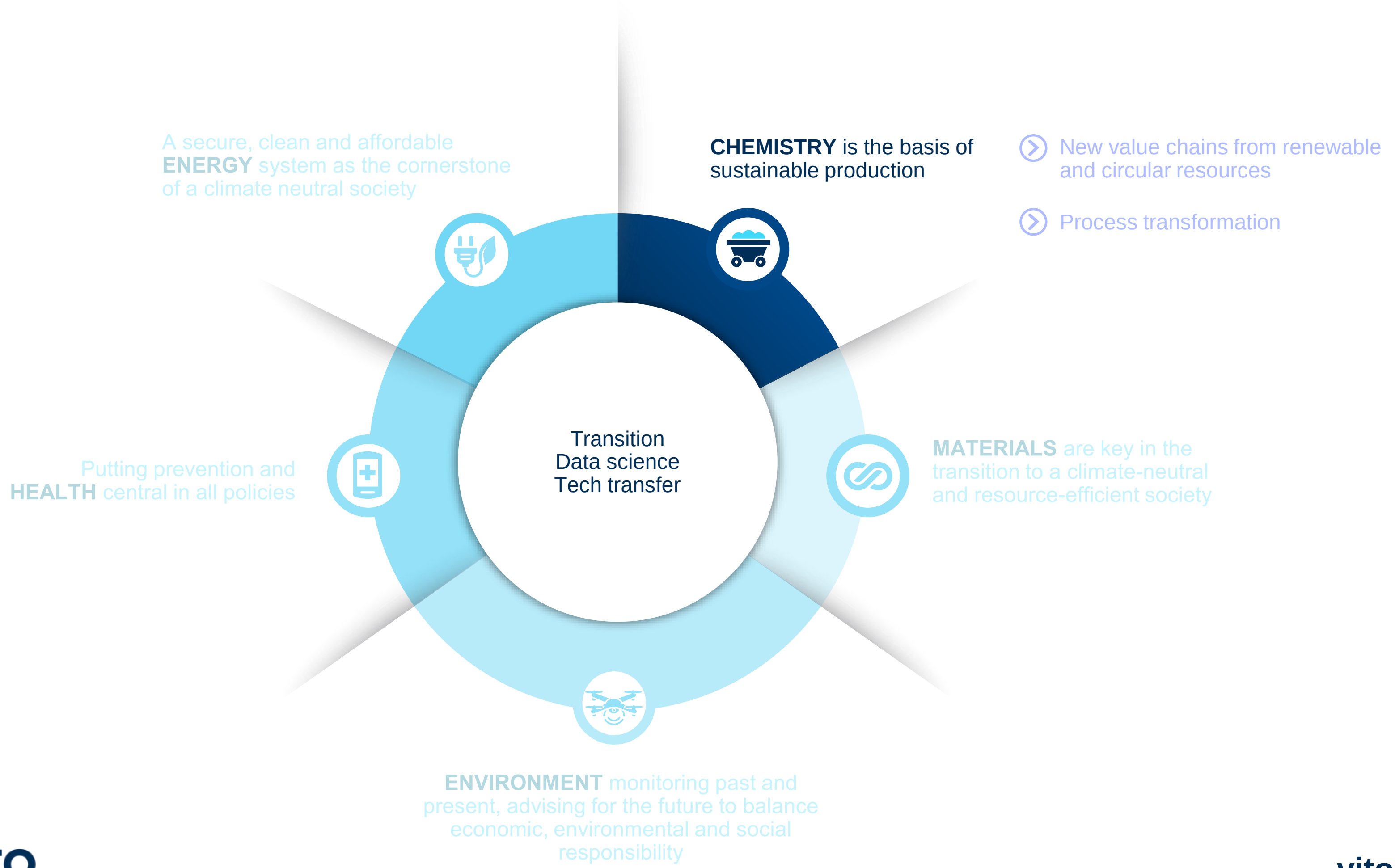

A secure, clean and affordable ENERGY system as the cornerstone of a climate neutral society
CHEMISTRY is the basis of sustainable production
New value chains from renewable and circular resources
Process transformation
Transition
Data science
Tech transfer
Putting prevention and HEALTH central in all policies
MATERIALS are key in the transition to a climate-neutral and resource-efficient society
ENVIRONMENT monitoring past and present, advising for the future to balance economic, environmental and social responsibility

Vision and strategy for a sustainable chemical industry

Focus on renewable and recycled feedstock

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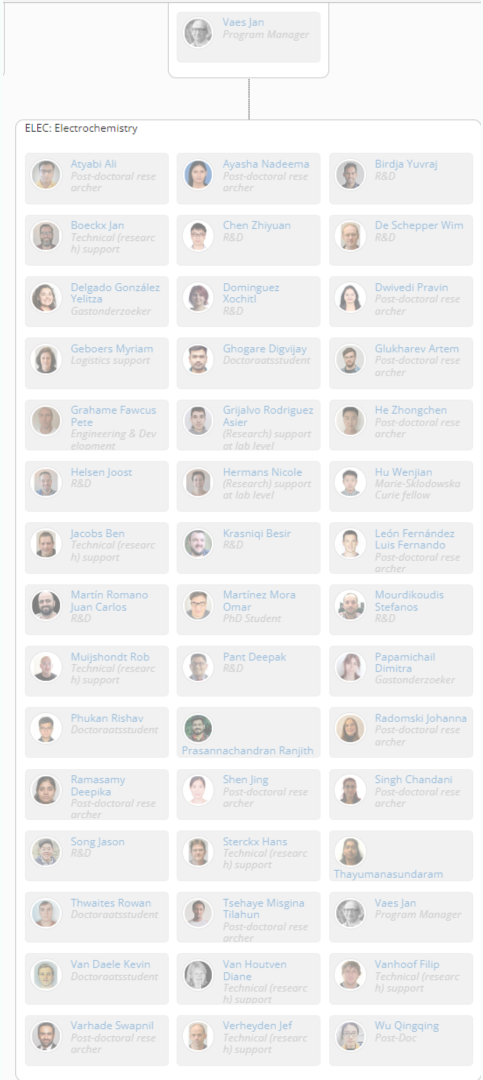
ELEC TEAM

- R&D project lead : 8
- Supporting staff: 10
- Postdoc/Jr. researchers: 22
- Phd students: 5

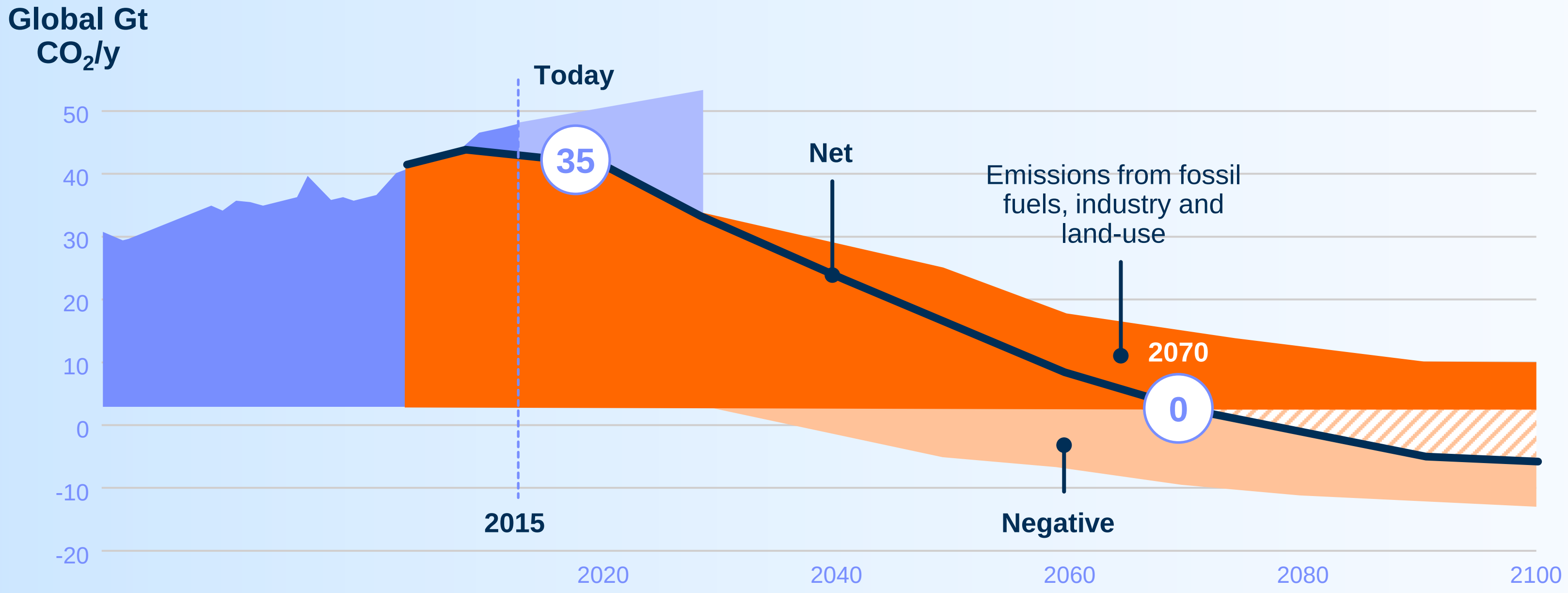
ELEC Topics

I. H_2 generation
II. CO_2 electroreduction
III. Electro-synthesis
  - Recycling/mining
  - Organic feedstock



CO_2 emission reduction

Global average temperature increase well below 2°C and limit to 1.5°C, above pre-industrial levels



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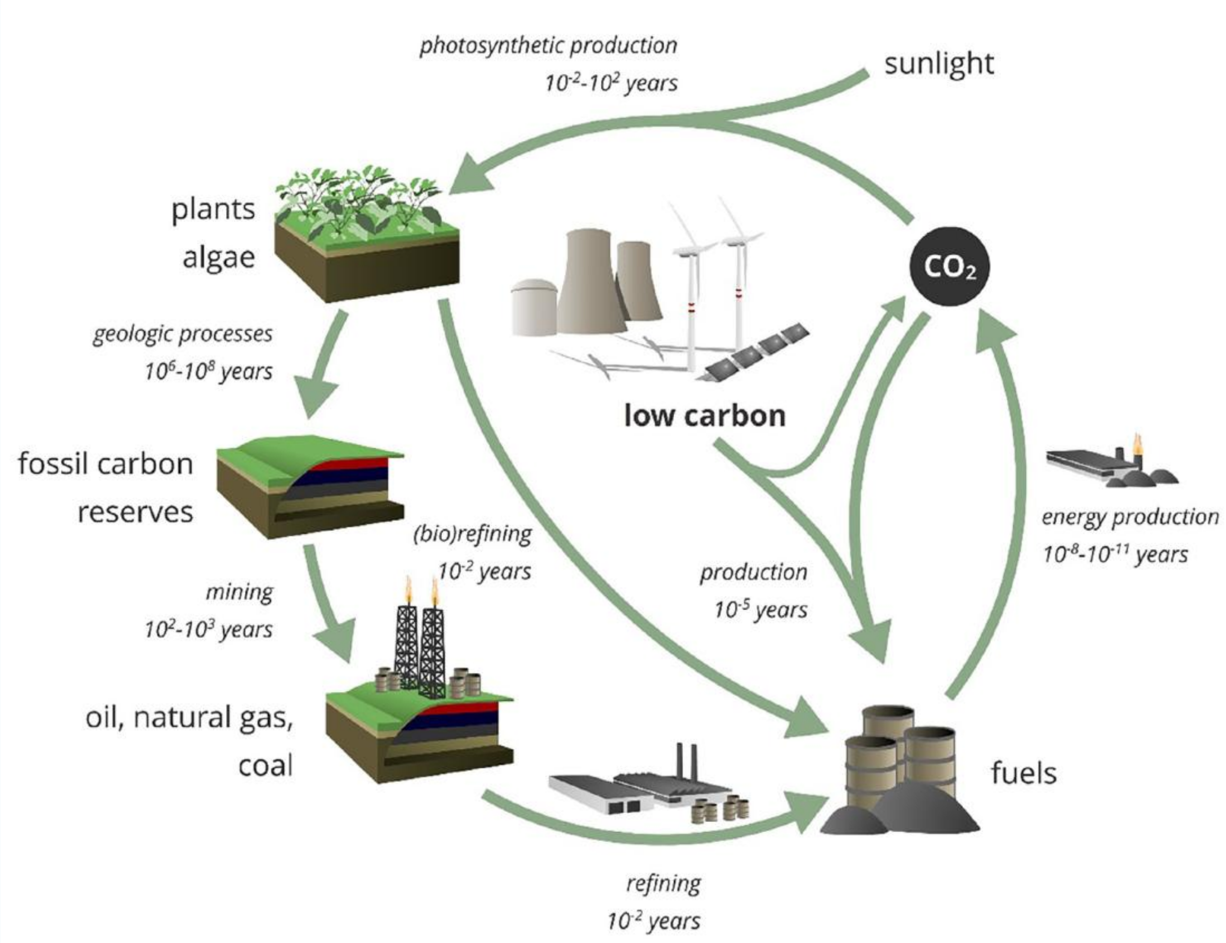
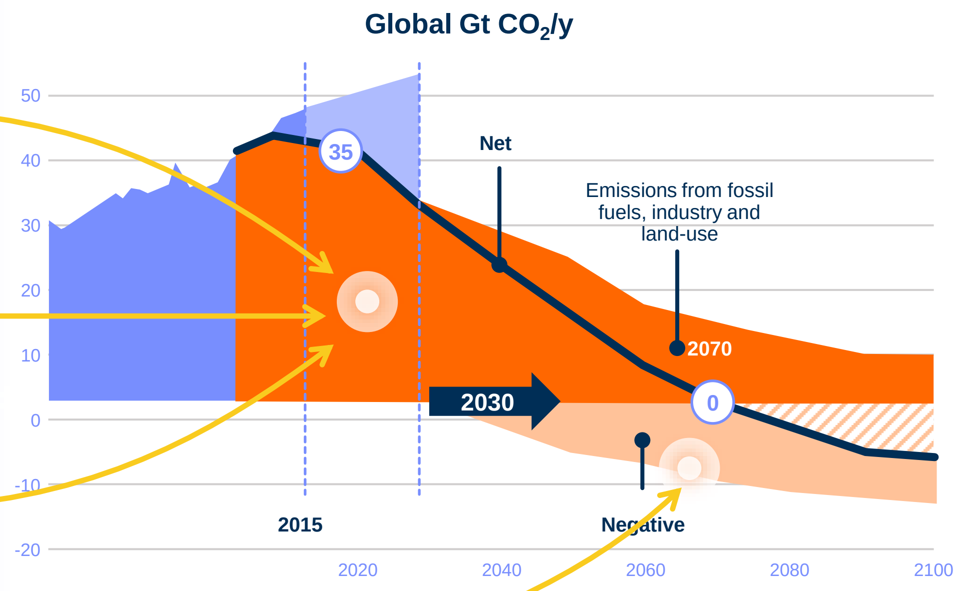


https://doi.org/10.1002/cssc.201601051

	Use case	Type CO_2 reduction
Fossil CO_2	E-Fuels E-Chemicals	**Avoiding** by replacement of fossil-based products
	Mineralization Storage	**Avoiding** by zero emission
Biogenic or DAC CO_2	Fuels Chemicals	**Avoiding** by cyclic re-use of emitted CO_2 and replacement of fossil-based products
	Mineralization Storage	**Negative**



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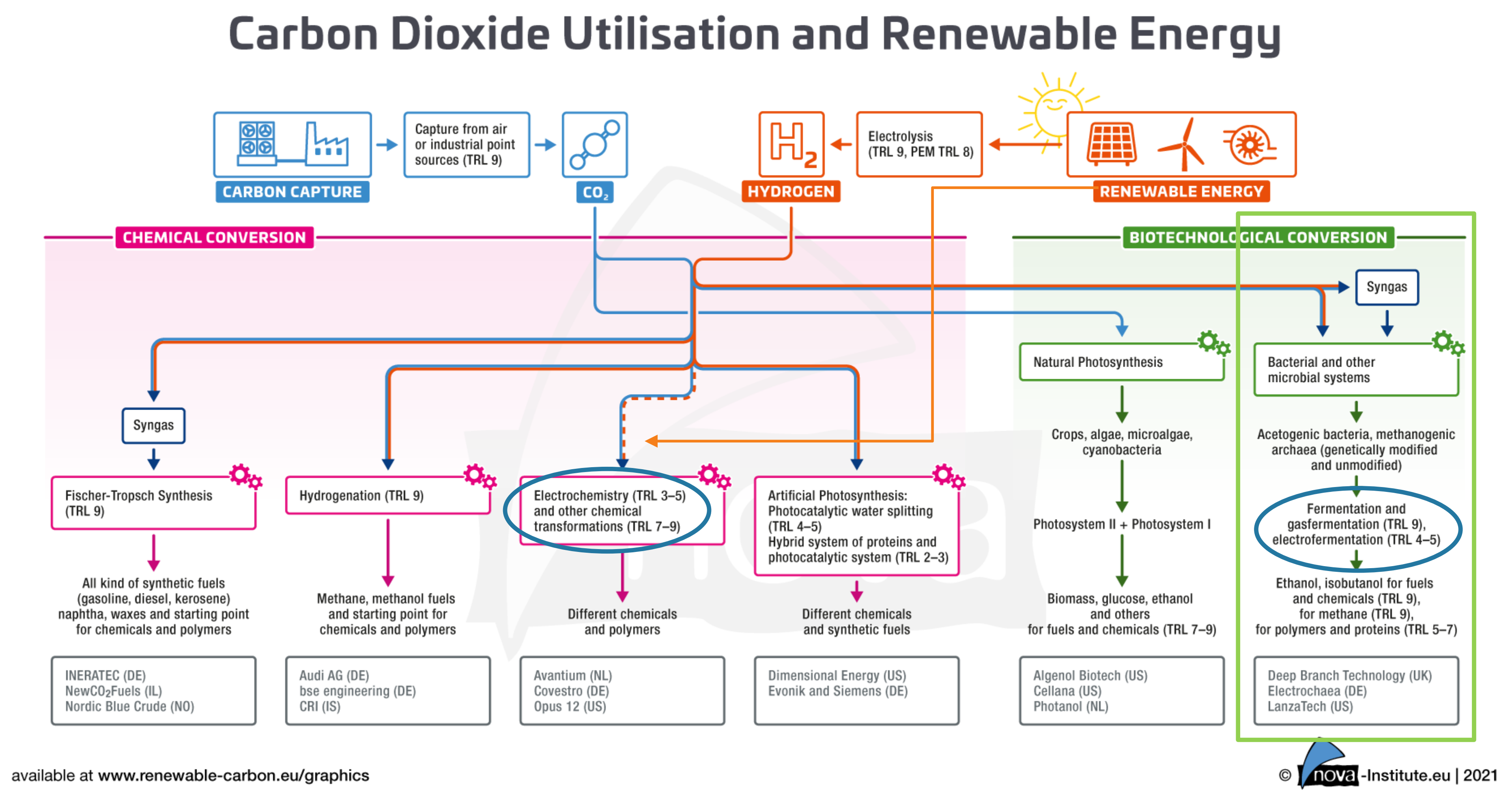
Carbon Dioxide Utilisation and Renewable Energy
CARBON CAPTURE
Capture from air or industrial point sources (TRL 9)
CO_2
HYDROGEN
Electrolysis (TRL 9, PEM TRL 8)
RENEWABLE ENERGY
CHEMICAL CONVERSION
BIOTECHNOLOGICAL CONVERSION
Syngas
Fischer-Tropsch Synthesis (TRL 9)
All kind of synthetic fuels (gasoline, diesel, kerosene) naphtha, waxes and starting point for chemicals and polymers
INERATEC (DE)
NewCO2Fuels (IL)
Nordic Blue Crude (NO)
Hydrogenation (TRL 9)
Methane, methanol fuels and starting point for chemicals and polymers
Audi AG (DE)
bse engineering (DE)
CRI (IS)
Electrochemistry (TRL 3–5) and other chemical transformations (TRL 7–9)
Different chemicals and polymers
Avantium (NL)
Covestro (DE)
Opus 12 (US)
Artificial Photosynthesis: Photocatalytic water splitting (TRL 4–5)
Hybrid system of proteins and photocatalytic system (TRL 2–3)
Different chemicals and synthetic fuels
Dimensional Energy (US)
Evonik and Siemens (DE)
Natural Photosynthesis
Crops, algae, microalgae, cyanobacteria
Photosystem II + Photosystem I
Biomass, glucose, ethanol and others for fuels and chemicals (TRL 7–9)
Algenol Biotech (US)
Cellana (US)
Photanol (NL)
Syngas
Bacterial and other microbial systems
Acetogenic bacteria, methanogenic archaea (genetically modified and unmodified)
Fermentation and gasfermentation (TRL 9), electrofermentation (TRL 4–5)
Ethanol, isobutanol for fuels and chemicals (TRL 9), for methane (TRL 9), for polymers and proteins (TRL 5–7)
Deep Branch Technology (UK)
Electrochaea (DE)
LanzaTech (US)
available at www.renewable-carbon.eu/graphics
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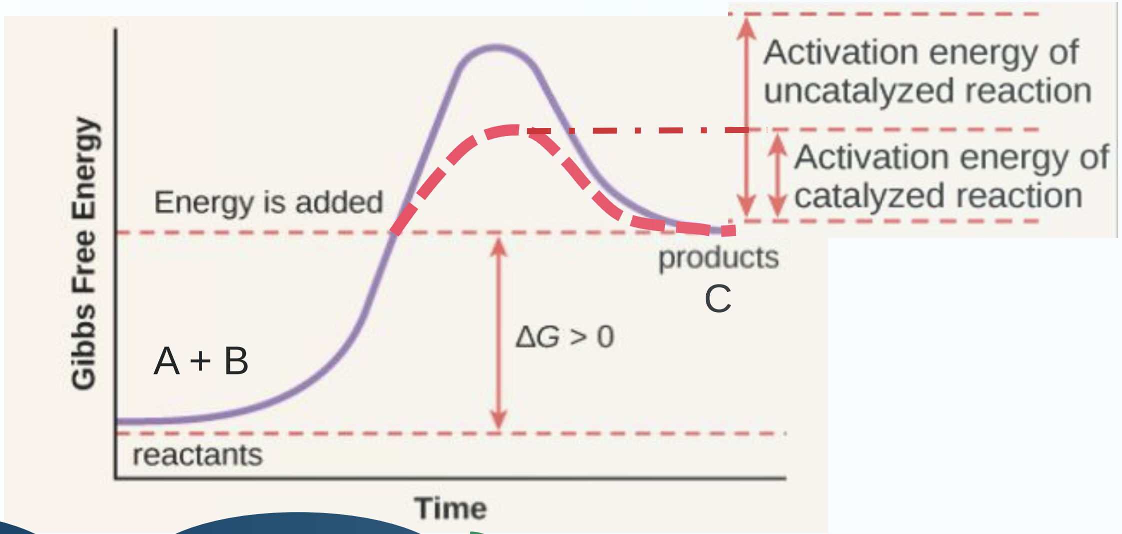
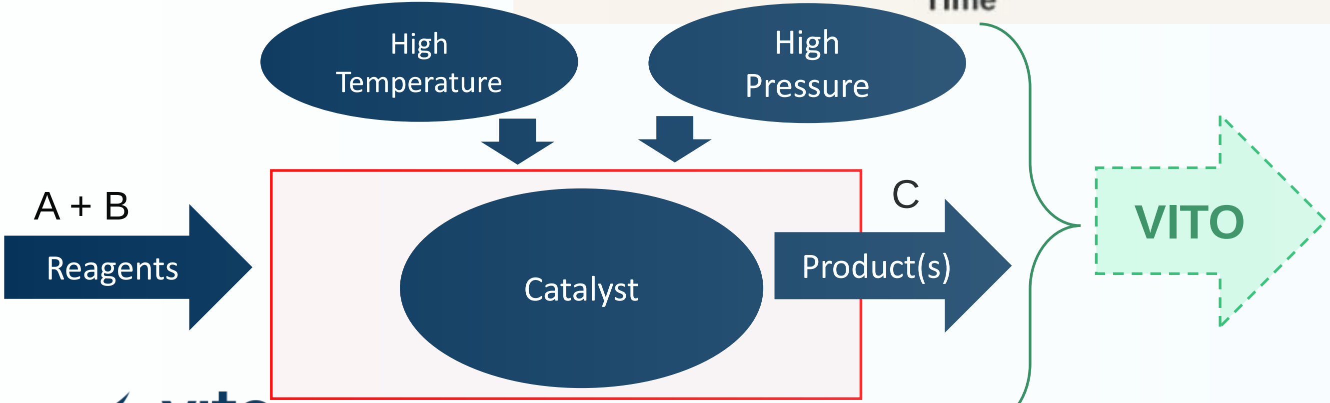




Mild conditions by
- electrochemical
- enzymatic

pathways

Electrochemistry ≡

1. Reduction
2. Oxidation
3. Electronic transport
4. Ionic transport

+8 electrons

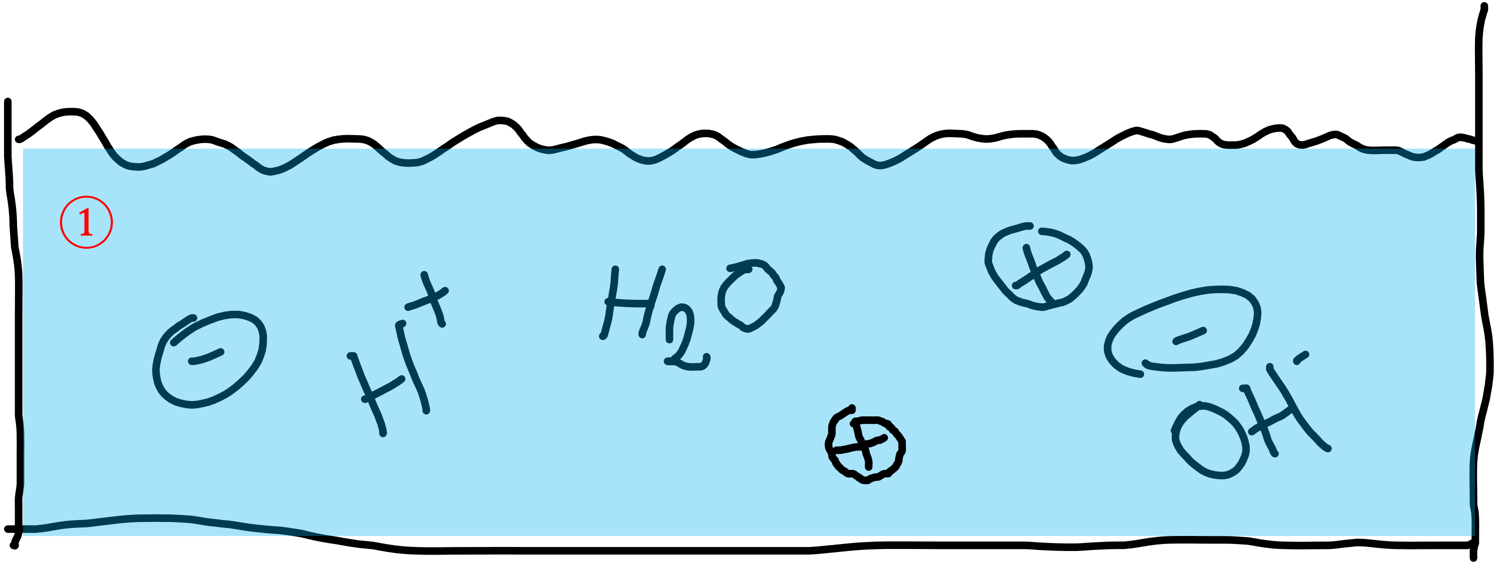
-8 electrons

$$CO_2(g) + \mathbf{2}H_2O \rightarrow CH_4(g) + \mathbf{2}O_2(g)$$

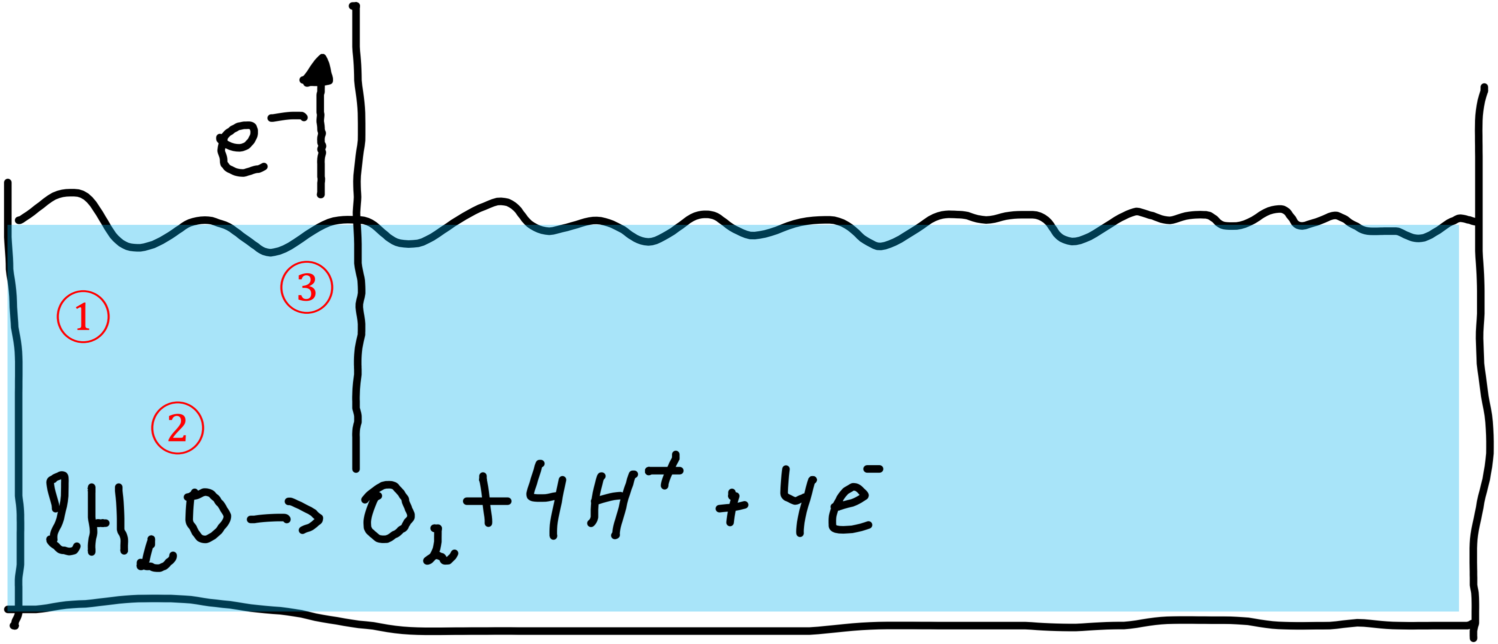
(+IV) (-II) (-II) (-IV) (0)

$$\mathbf{4}H_2O \rightarrow \mathbf{2}O_2(g) + \mathbf{8}H^+ + 8e^- \quad [\mathbf{1,23}\ \mathrm{V}]$$

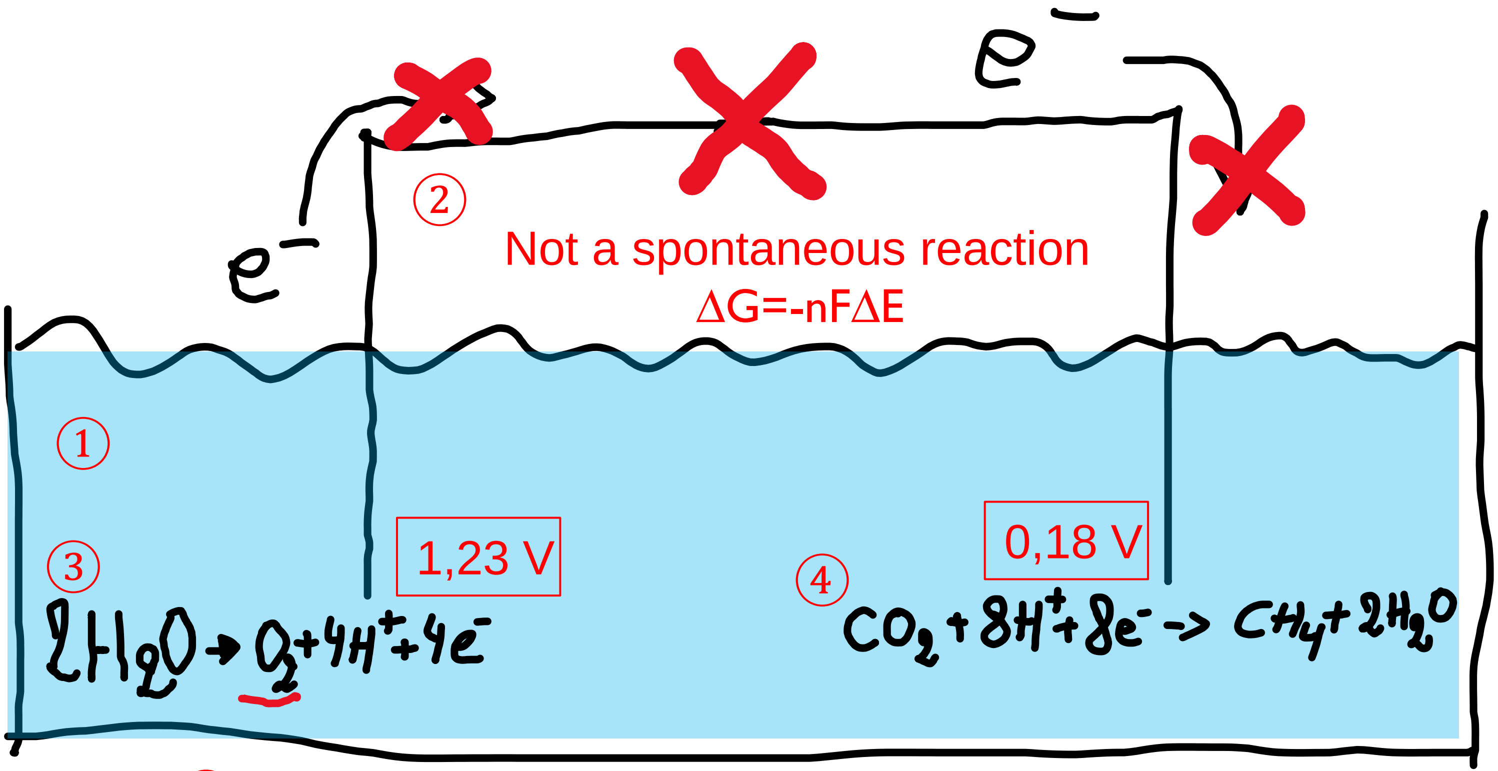
$$\mathbf{2}CO_2(g) + \mathbf{8}H^+ + \mathbf{8}e^- \rightarrow CH_4 + \mathbf{2}H_2O \quad [\mathbf{0,18}\ \mathrm{V}]$$



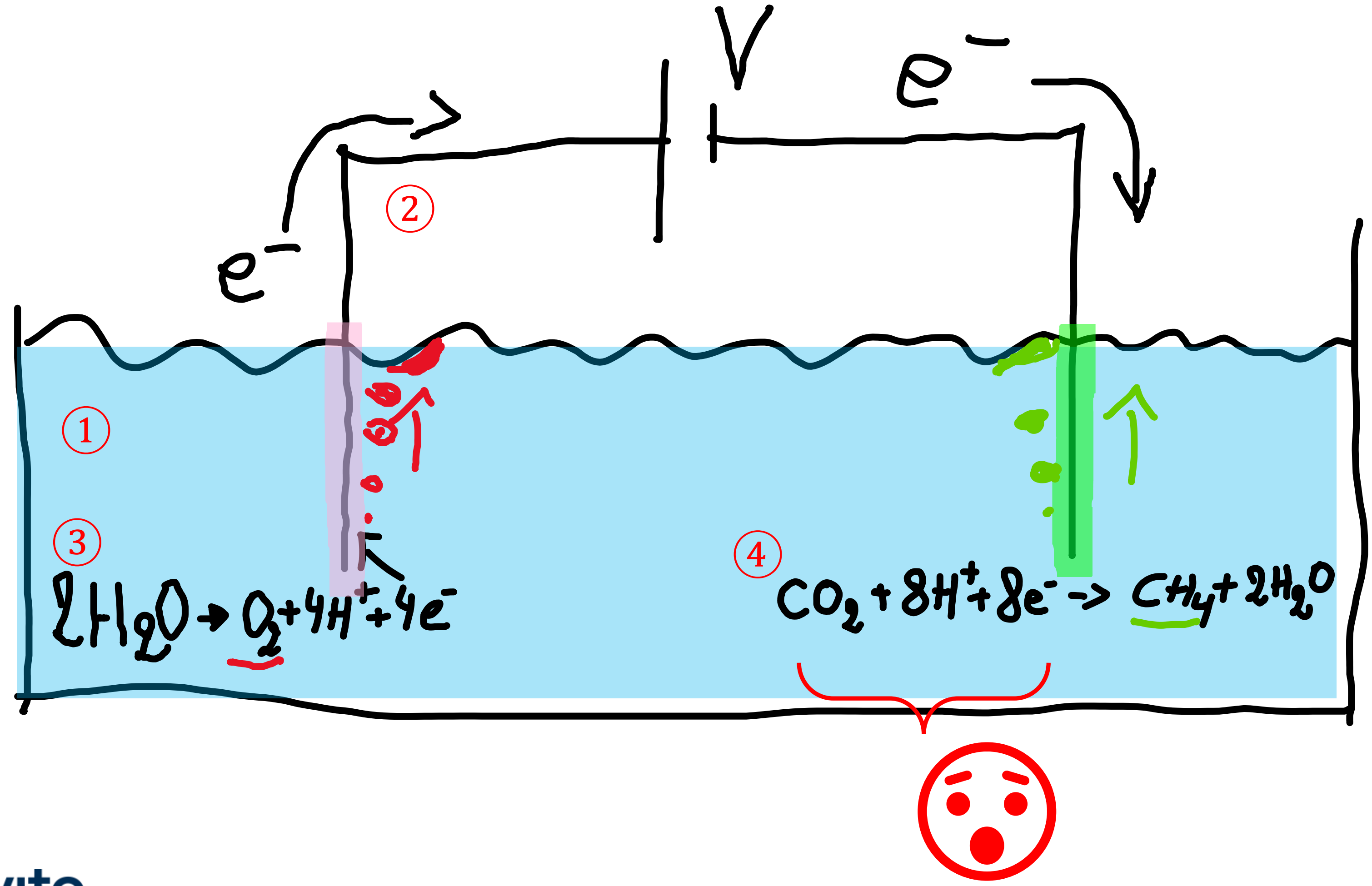
1 Electrolyte solution – ionic conductor



① Electrolyte solution – ionic conductor
② Oxidation reaction
③ Electronic conductor

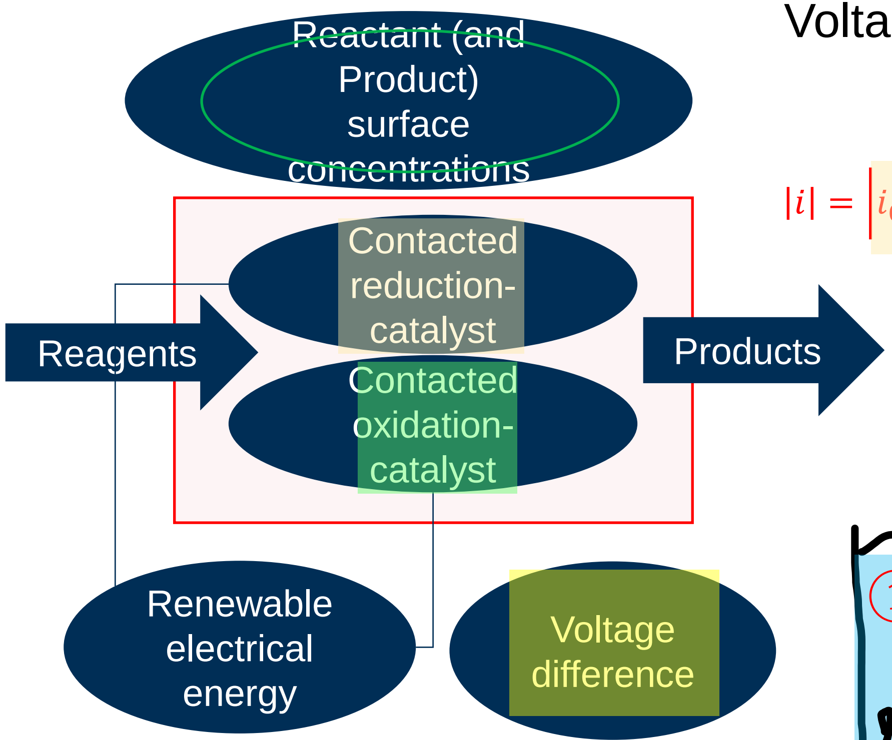


1. Electrolyte solution - ionic conductor
2. Electronic conductor - (electrons don't swim)
3. Oxidation half-reaction
4. Reduction half-reaction

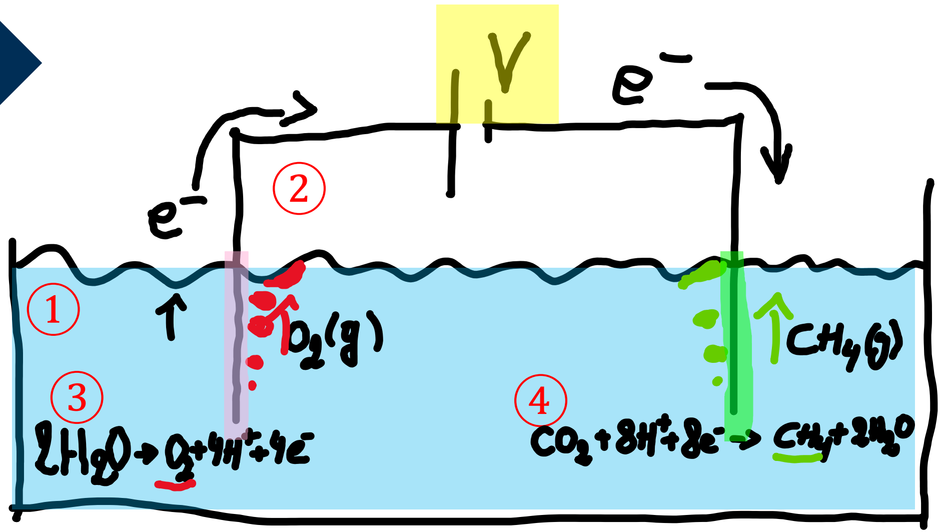

V
e⁻
e⁻
2
1
3
2H2O → O2 + 4H+ + 4e⁻
4
CO2 + 8H+ + 8e⁻ -> CH4 + 2H2O

Current = (electrons/time) ~ *productivity*

Voltage = energy barrier for electrons ~ *efficiency*



$$|i| = \left| i_{0,c}[Ox_2]_s \exp\left(-\frac{E_{red}-E_{0,red}}{RT}\right)\right| = \left| i_{0,a}[Red_1]_s \exp\left(\frac{E_{an}-E_{0,an}}{RT}\right)\right|$$



Why **electrosynthesis ?**

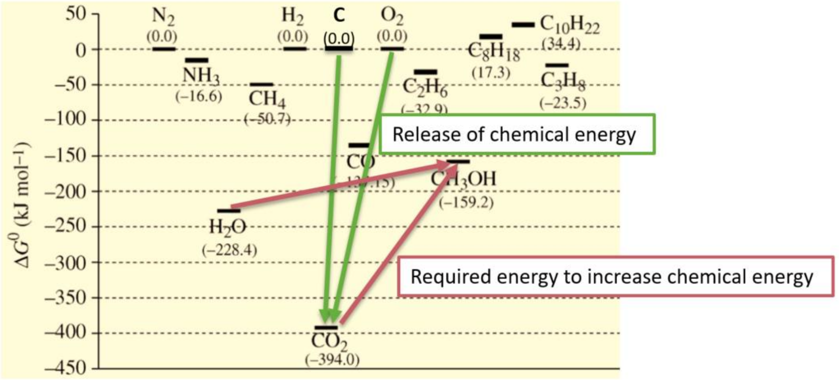
- **Mild conditions** in terms of reactor pressure and temperature
- Separation of **oxidation** and **reduction** parts, coupling possible
- Direct use of **renewable electricity** for the required reaction energy

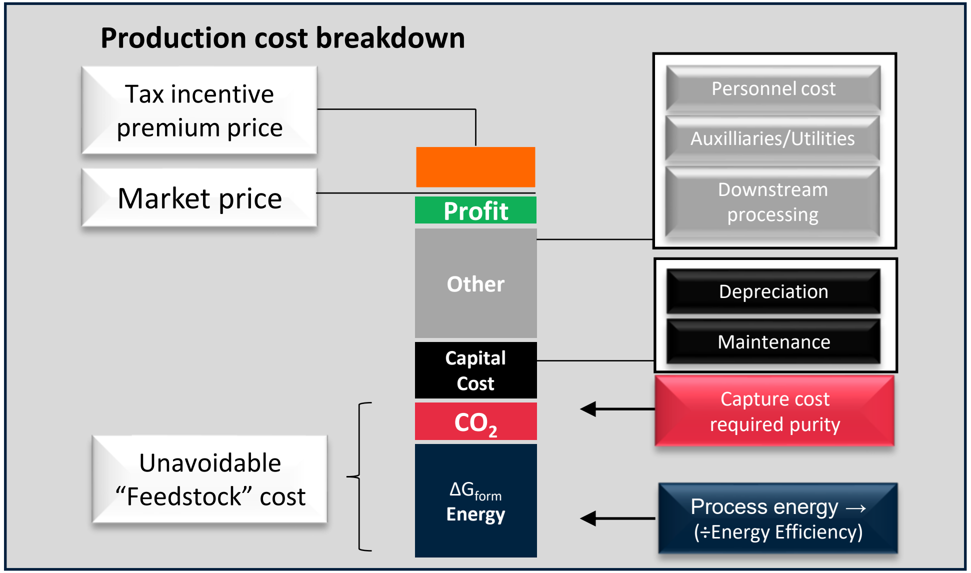
But boundary conditions:

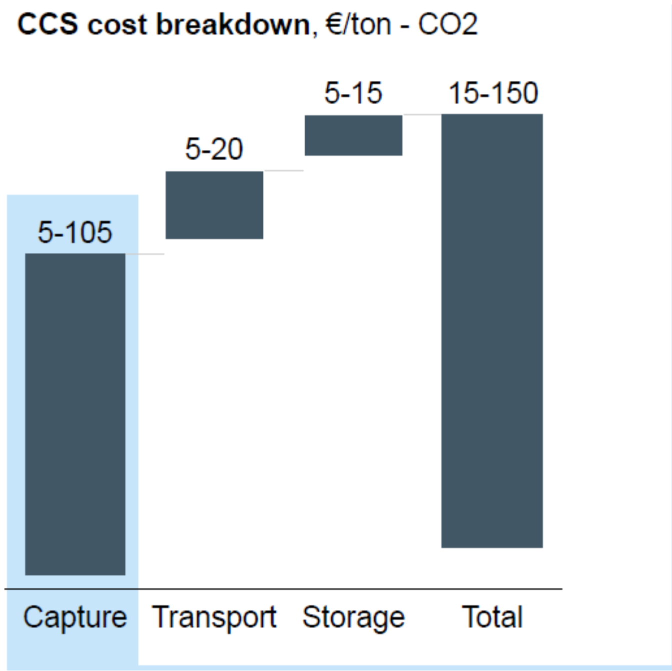
- You always need the **four ingredients**
- It happens at **the heterogeneous interphase**: mechanism should not be too complex

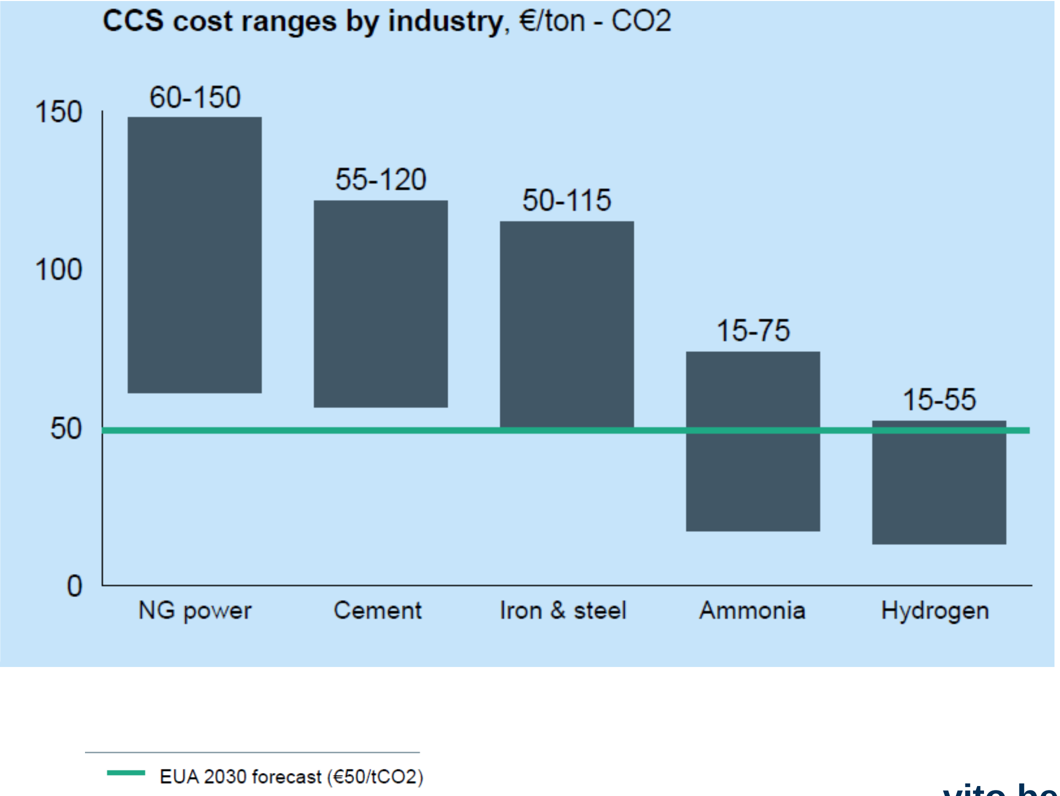
What does it take to convert CO_2

1) thermal. chemical. electrical. plasma. photons
2) Asssumed 100% Carbon efficiency CO_2 → product

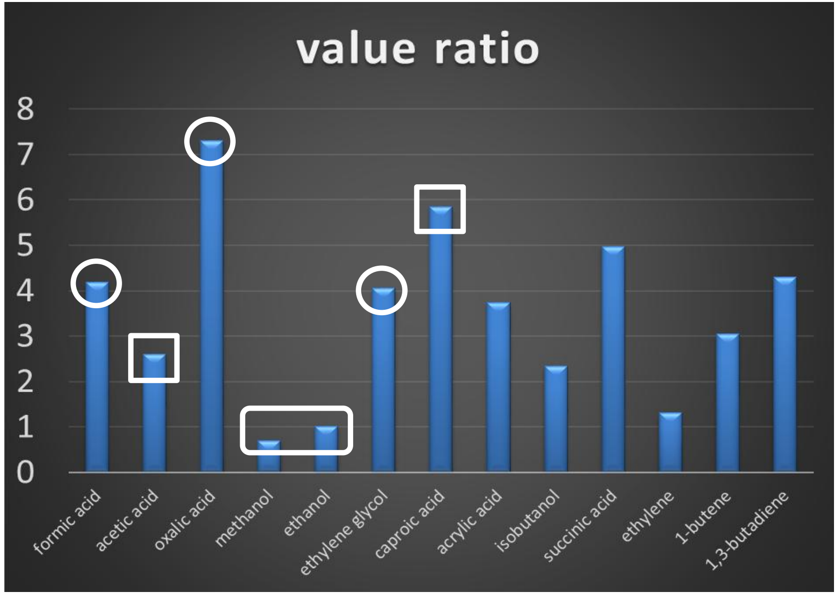


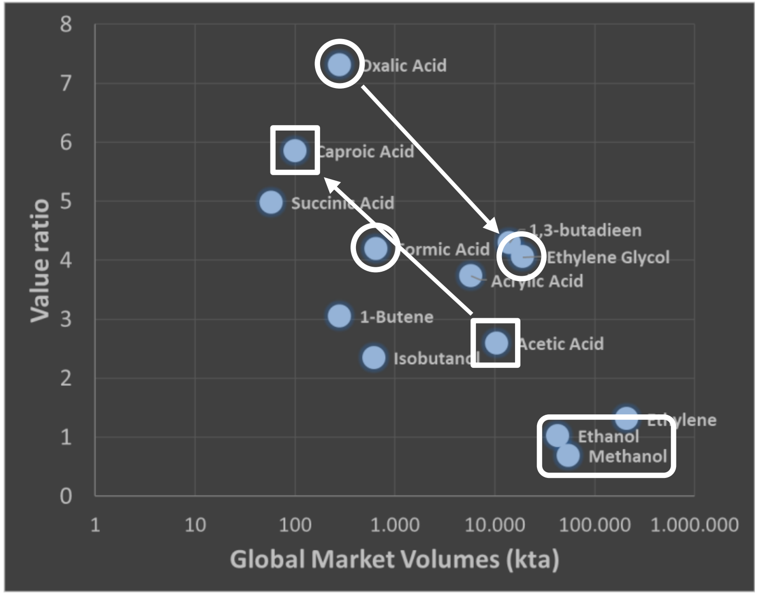



CCS cost breakdown, €/ton - CO2
5-105
5-20
5-15
15-150
Capture
Transport
Storage
Total


CCS cost ranges by industry, €/ton - CO2
150
100
50
0
60-150
55-120
50-115
15-75
15-55
NG power
Cement
Iron & steel
Ammonia
Hydrogen
EUA 2030 forecast (€50/tCO2)

NETL (DOE)





Profit potential relates to:

Value Ratio = $\frac{\text{Market price}}{\text{Unavoidable cost}}$

Determined by use/demand today

Formic acid: small market, high value

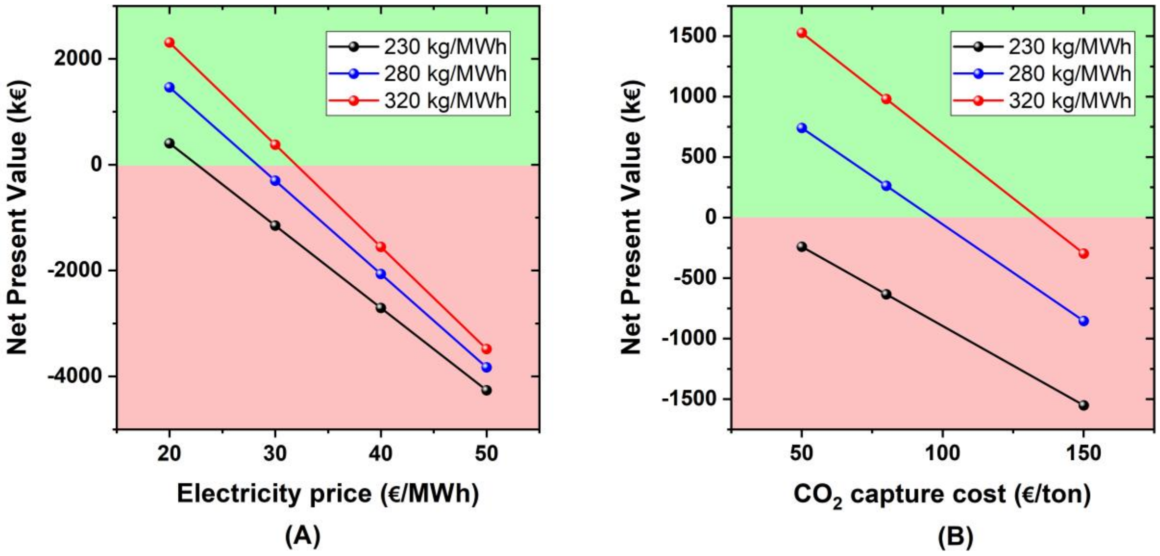
Oxalic acid: small market, but high value/volume derivatives

Fuels: electric power cost is build on top of this

Chain elongation strategies

Potential profitability of Formic acid production

- Capex:
  - Installation hardware
- Opex:
  - CO_2 , power, maintenance, personnel
- Assumptions: overall productivity (faraday & energy & downstream efficiencies)

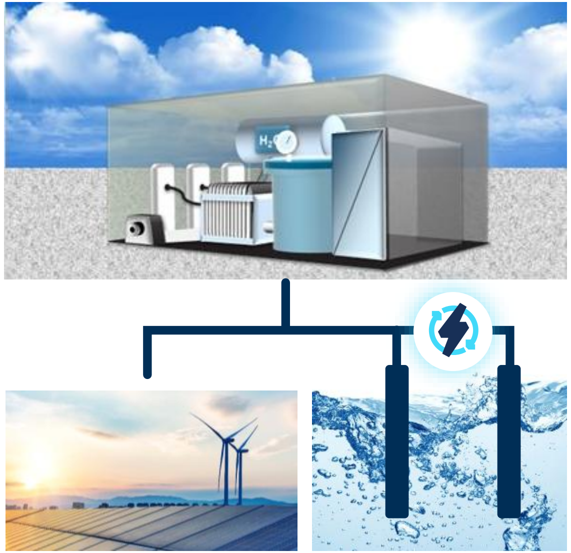


VITO’s activities

Point source

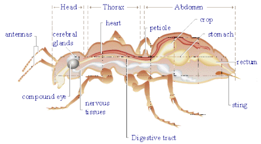
Direct Air Capture

Integrated capture & conversion



Syngas
Aviation fuel

Methanol
Marine fuel



Formic acid
CHOOH

Ethylene
Plastics

Electrochemical technology

Product IP

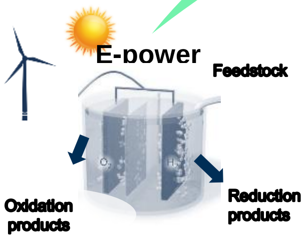
Industrialization

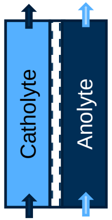
Demonstration/pilot

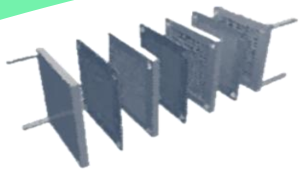
Process Intensification
- reactor design
- stacking

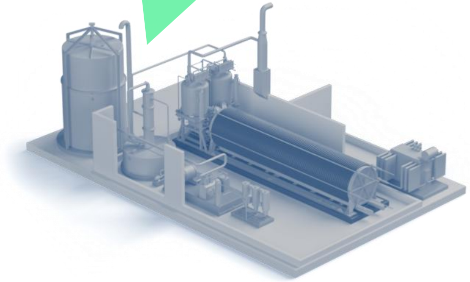
Reaction coupling
- anode +cathode
- electrolyte

Enabling tech
- e- catalyst
- half reaction









Creating impact

De-risk by clarifying the techno-economical picture
Understand the boundary conditions of
- *Component integration*
- *Cell design*
- *Process development*
- *Scalability*

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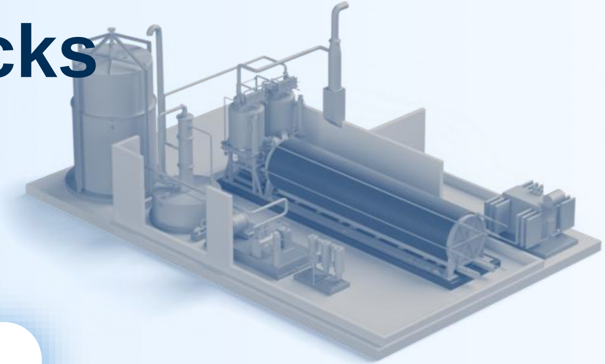
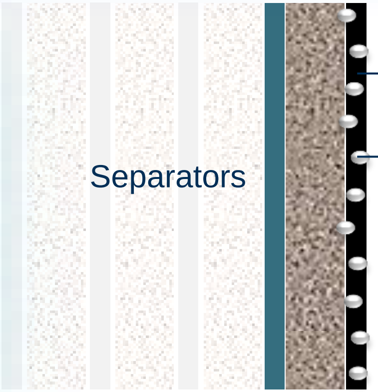
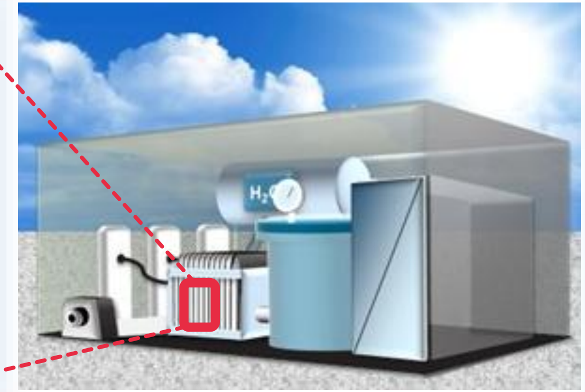
Focus on building blocks



Products

- Integrated process
- Stacks
- Components
- Enabling materials





Impact

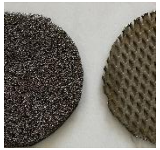
- Demo
- IP transfer licensing

Portfolio items - 2023

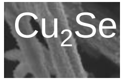
enabling components

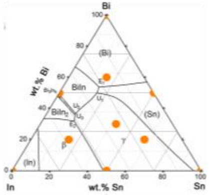
Separators

Electrode



Electro catalysts



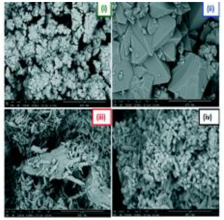


processes

Process development

PGM for recovery

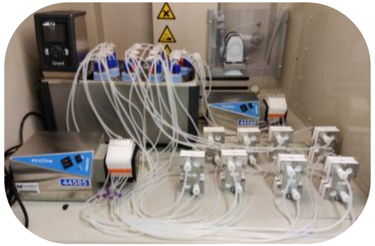
Nano shaping



- *IP on components & processes*
- *License model*
- *Contract Research*

process demo

Derisking



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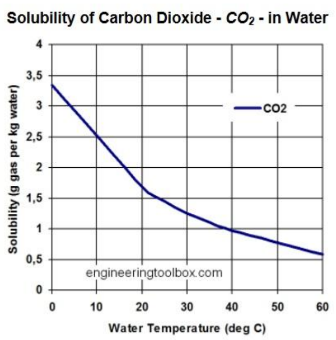
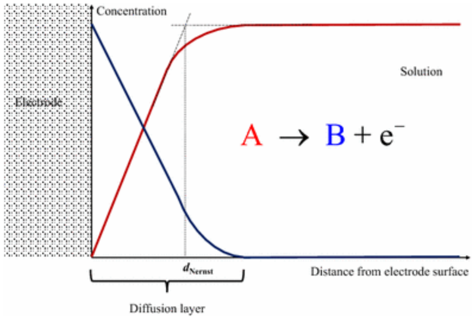
CO_2 is poorly soluble in aqueous environment





$j_{lim} \approx n.F.D_{CO2}(C_{bulk}/d_{Nernst})$

$\approx 2.96487.1{,}95.10^{-5.}.35.10^{-3}/(0{,}1.10^{-3})$

[(C/mol)(cm²/s)(mol/l)/m]

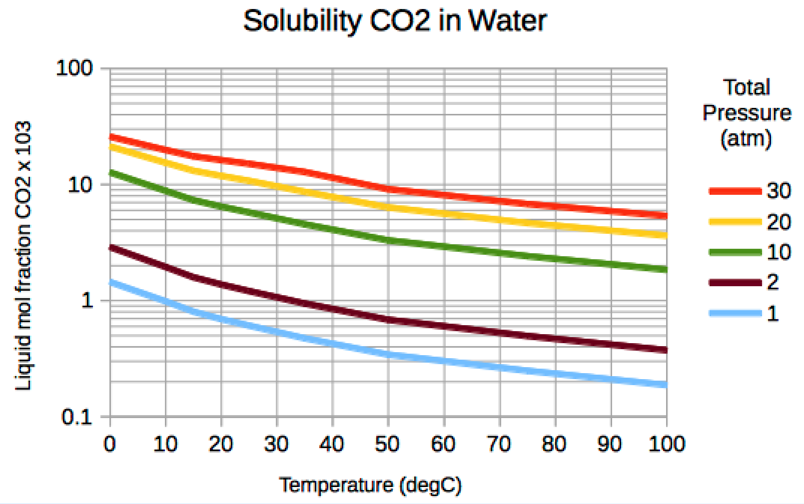
≈ 1317 A[(0,0001m²/0,001m³)/m]

≈ 132 A/m²

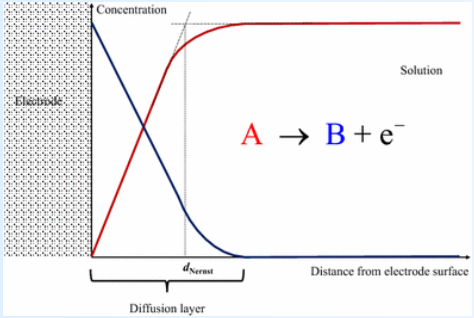
≈ 13 mA/cm²

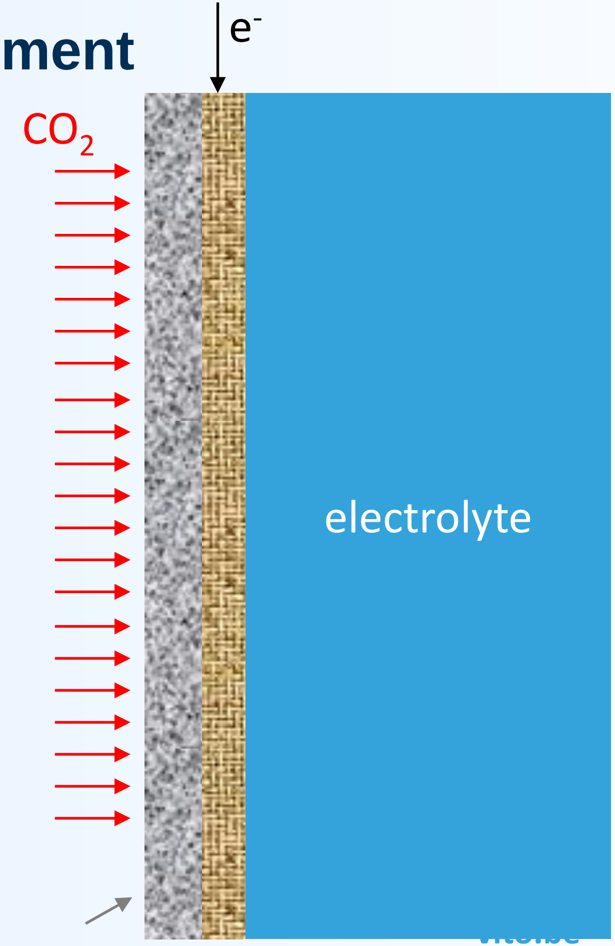
=> 100µm > *d* > 1 µm (highly turbulent)

CO_2 is poorly soluble in aqueous environment



1 bar => j_{lim} ≅ 13 mA/cm²
10 bar => j_{lim} ≅ 130 mA/cm²





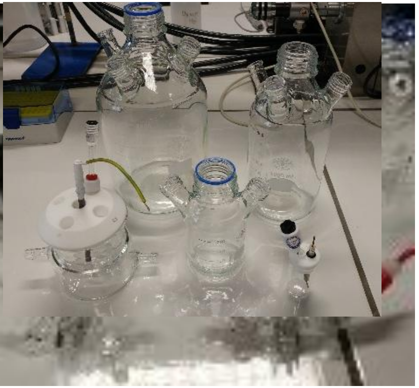
Hydrophobic layer

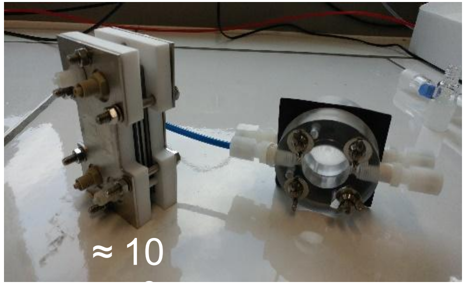
Labo to demonstrator

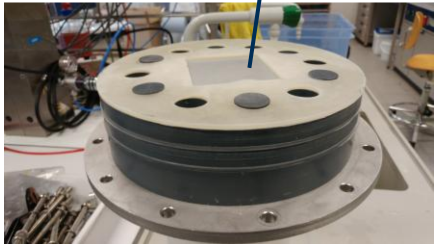
Electrochemical experiments

- Batch-type and flow reactors
- 1-, 2- and 3 compartment reactors (anodic, cathodic and gas chambers)
- Different volumes, possibilities for electrocatalysts/electrodes/products

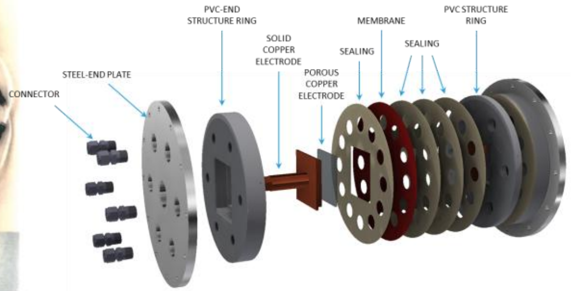
≈ 100-400 cm^2 electrode area







VITO GDE
≈ 300 cm^2



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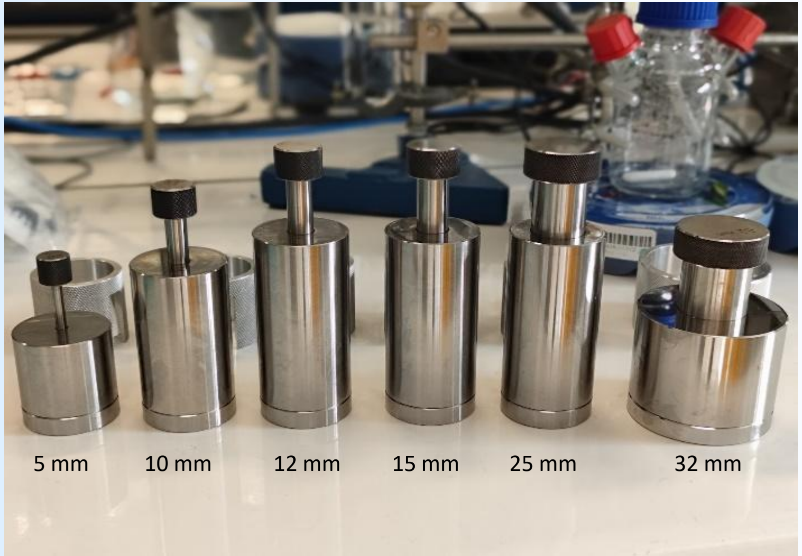
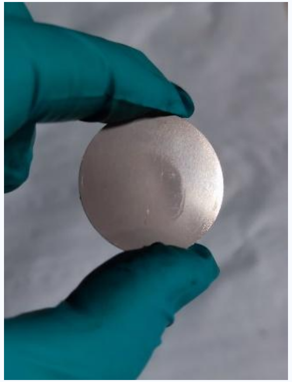
Small scale GDE manufacturing – pressing die

- A set of pressing dies with size of 5 to 32 mm diameter
  - Able to produce GDE with smaller size (less material consumption)
  - Can create dense/porous electrode from powder
  - Morphology can be tailored



For example

15 tons



Electrode production

- Particle synthesis, mixing, size selection
- (Hydraulic) (Hot) Press for electrodes, gas diffusion electrodes, catalyst coated membranes

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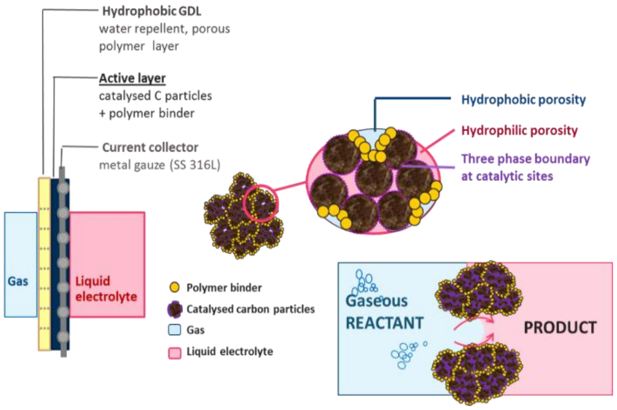
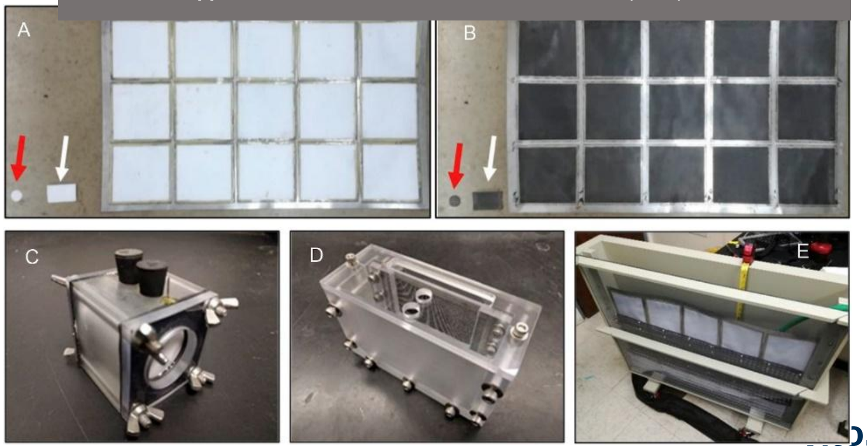
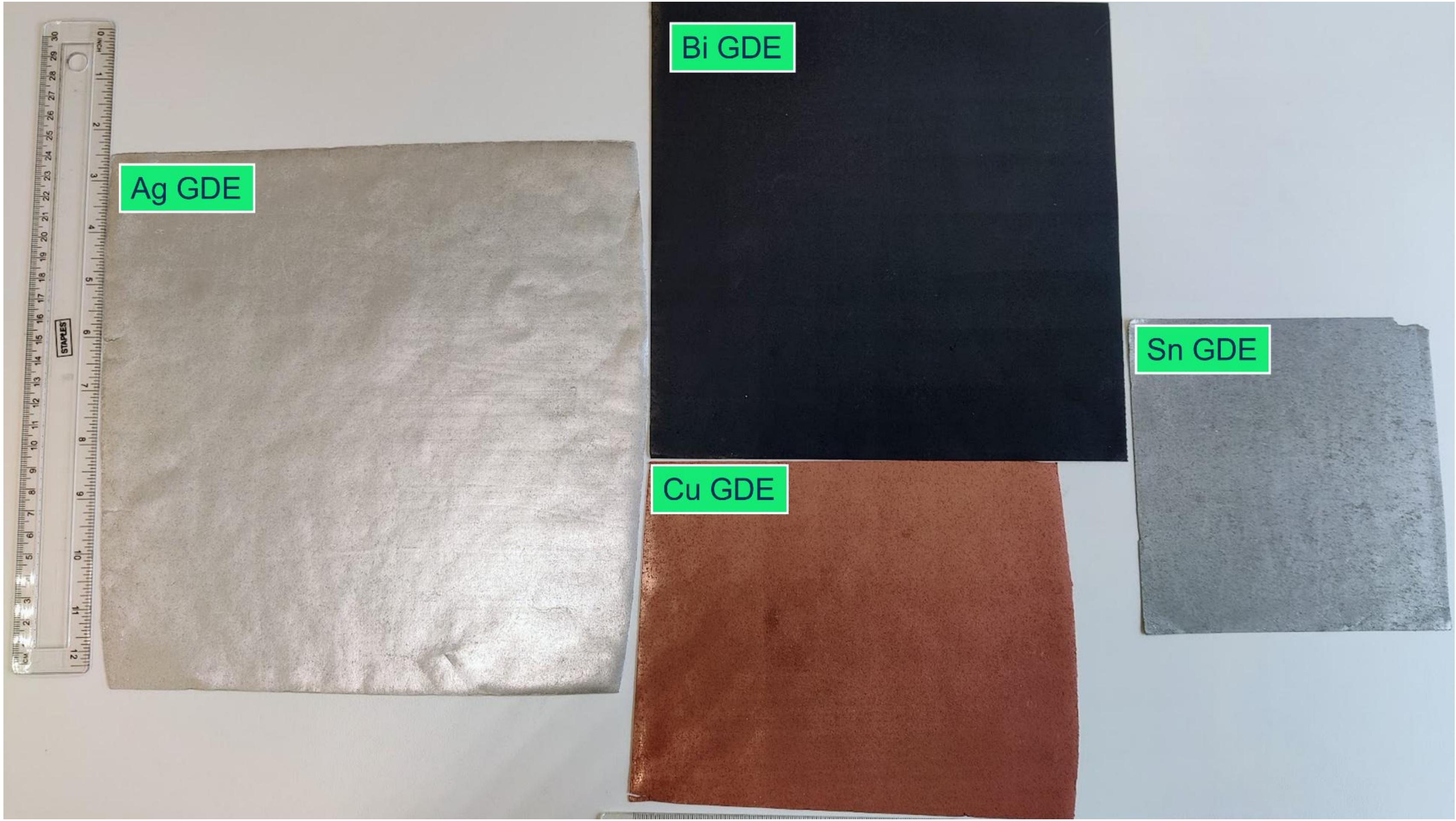
Vito gas diffusion electrode

- 10x smaller average pore size than commercial GDLs **(0.1 µm)**
- 10^3-10^4 x lower water permeability than commercial GDLs **(10 L/hm² bar)**
- **Superior** mechanical robustness
- Possibility of **tailored properties**



GDE in a 85 L Microbial fuel cell:
Patent application WO/2019/068,488; Water Research (2019), 148, 51-59

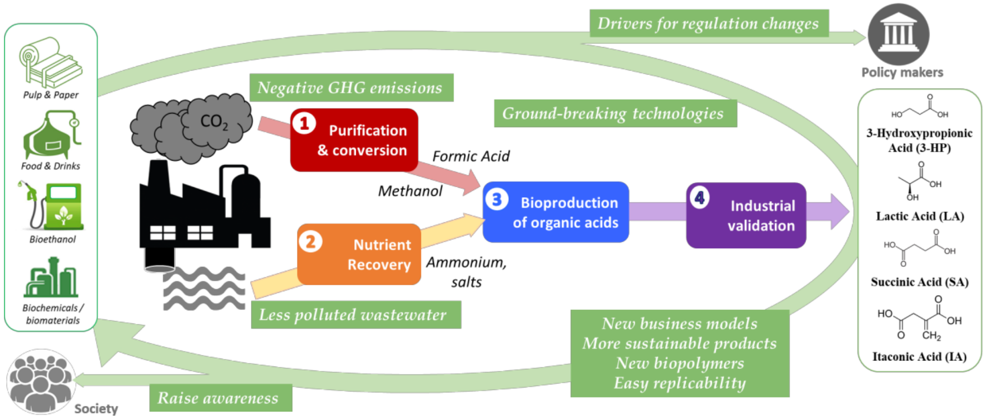



Bi GDE
Ag GDE
Sn GDE
Cu GDE
STAPLES

VIVALDI

vivaldi

Turns CO_2 emissions into sustainable bioproducts



- **InnoVative bIo-based chains for CO2 VALorisation as aDded-value organIc acids**

- The overall objective of the project is to stimulate investment in and implementation of Power-to-X technologies by developing innovative direct and indirect conversion processes for the chemical industry towards higher TRLs, while making use of renewable electricity and lowering the carbon footprint

- VITO is responsible for development and upscaling of electrodes (incorporating in-house catalyst or commercial one) for electrochemical conversion of CO_2 into Formate and Methanol.

- Duration: 2021 - 2025

- Total budget: € 6,969,968

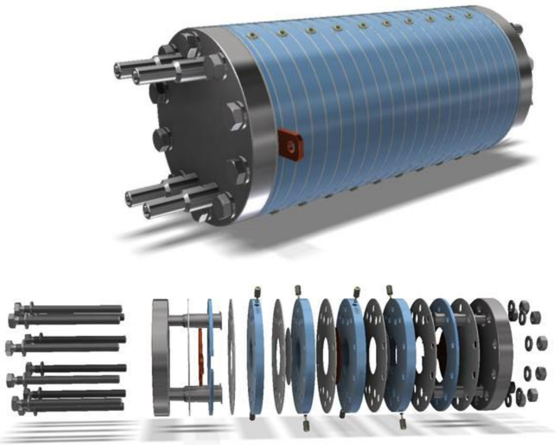
Partners:

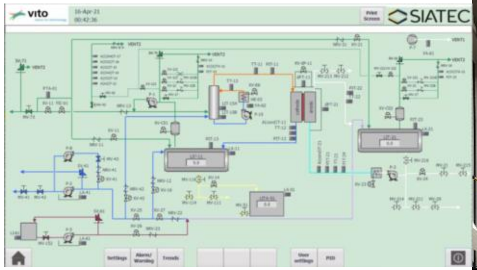
UAB Universitat Autònoma de Barcelona · BOKU · Luleå University of Technology · vito · LEITAT Technological Center · UFZ Helmholtz Zentrum für Umweltforschung · processium · Vertech Group · CO₂ Value Europe · isle · nutrition sciences · avantium · sunpine · Damm · BIOAGRA · NOVAMONT

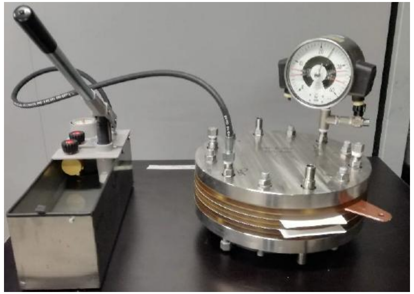
Funded by the Horizon 2020 Framework Programme of the European Union

CO2 electrolyzers

- H2020 **LOTER.CO2M** and ETF **PROCURA** projects TRL 6 - 5 kW pilot in progress today
- **ECO2FUEL** Green Deal project: 50 kW electrolyzer in 2023
- Towards renewable fuels – ranges (e.g., methanol, C_1-$C_{4,}$ …), also gasses: H_2, CO, …
  - 50 kW (5000 h/y): 20 t methanol/y (100 % select., 50 % η^{energy}), 30 t CO_2/y (100 % C η)
  - On-site demo

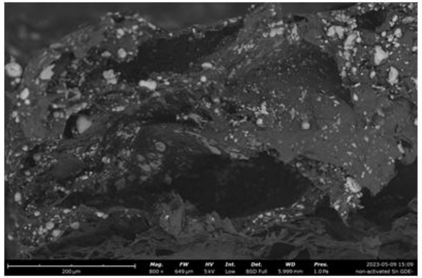




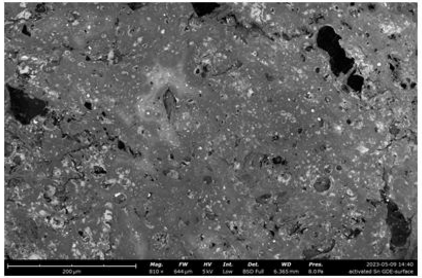


Sn-GDE- “Production” & "Activation"

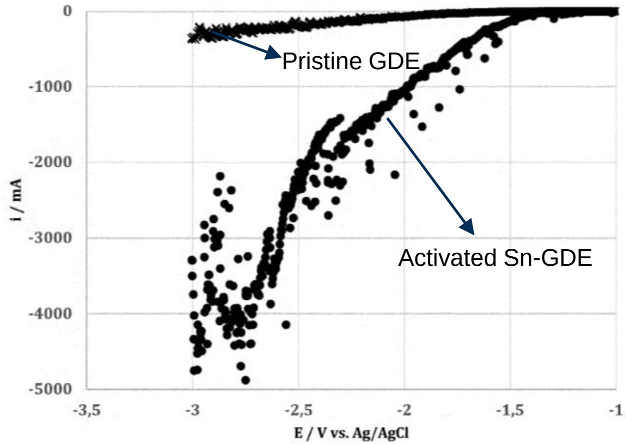
Ref: International patent no. WO2022013042A1, 2022

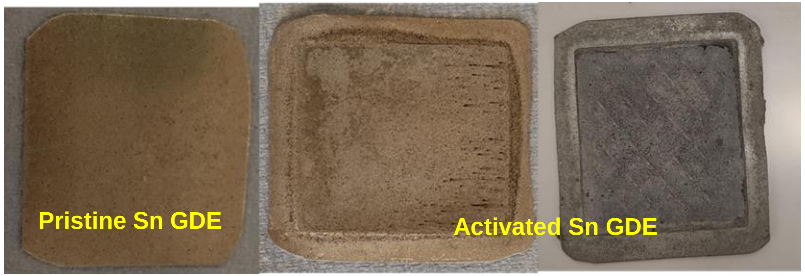


Sn-GDE Pristine



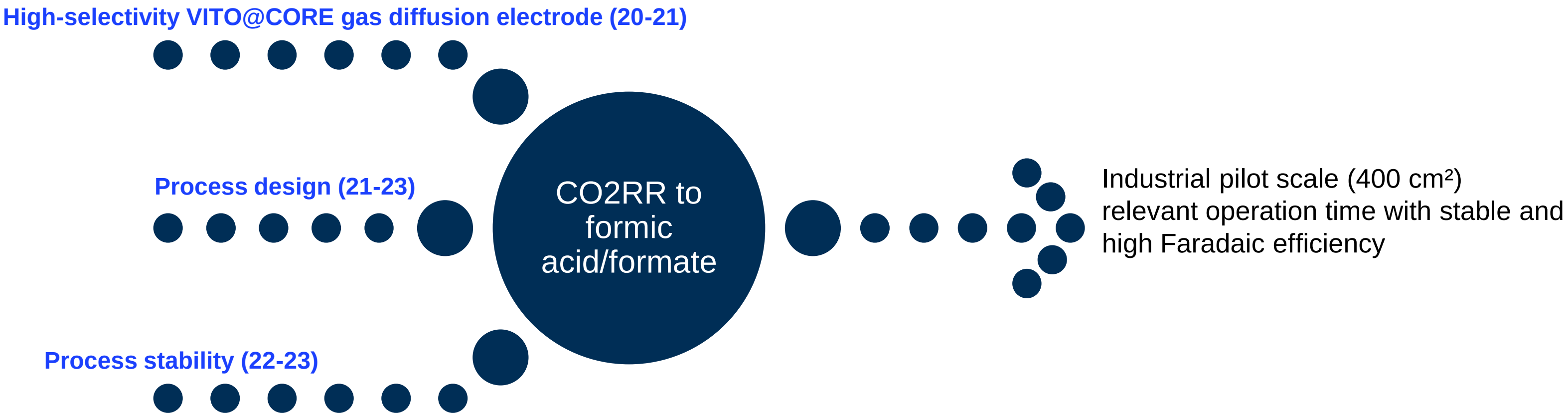
Sn-GDE freshly activated



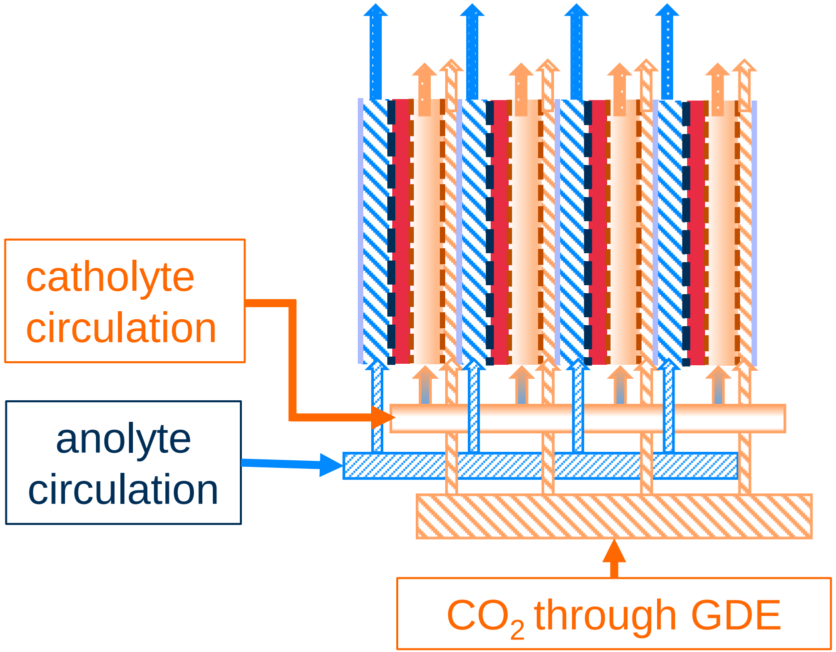


Electrochemical conversion of CO2 to formate

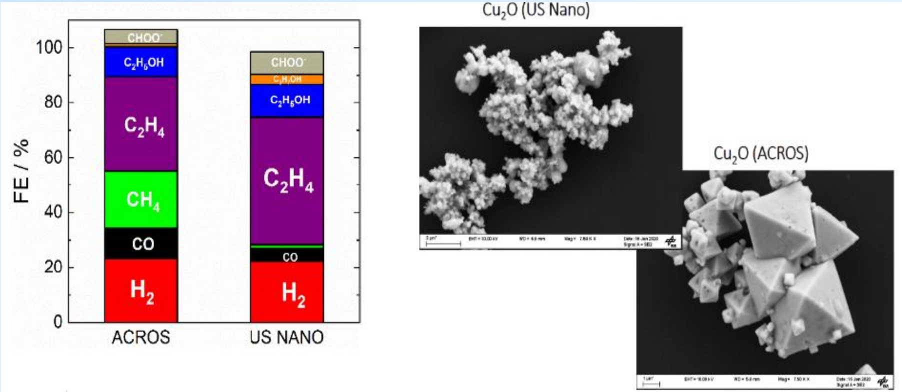
Industrial-scale relevant operation



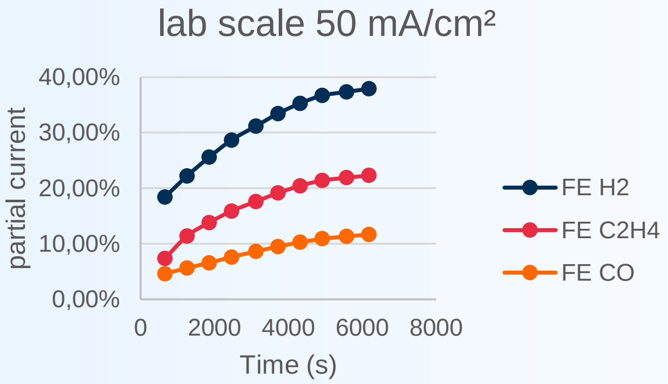
Next step: reactor with stackable GDE



Fuel production from CO2



DLR results

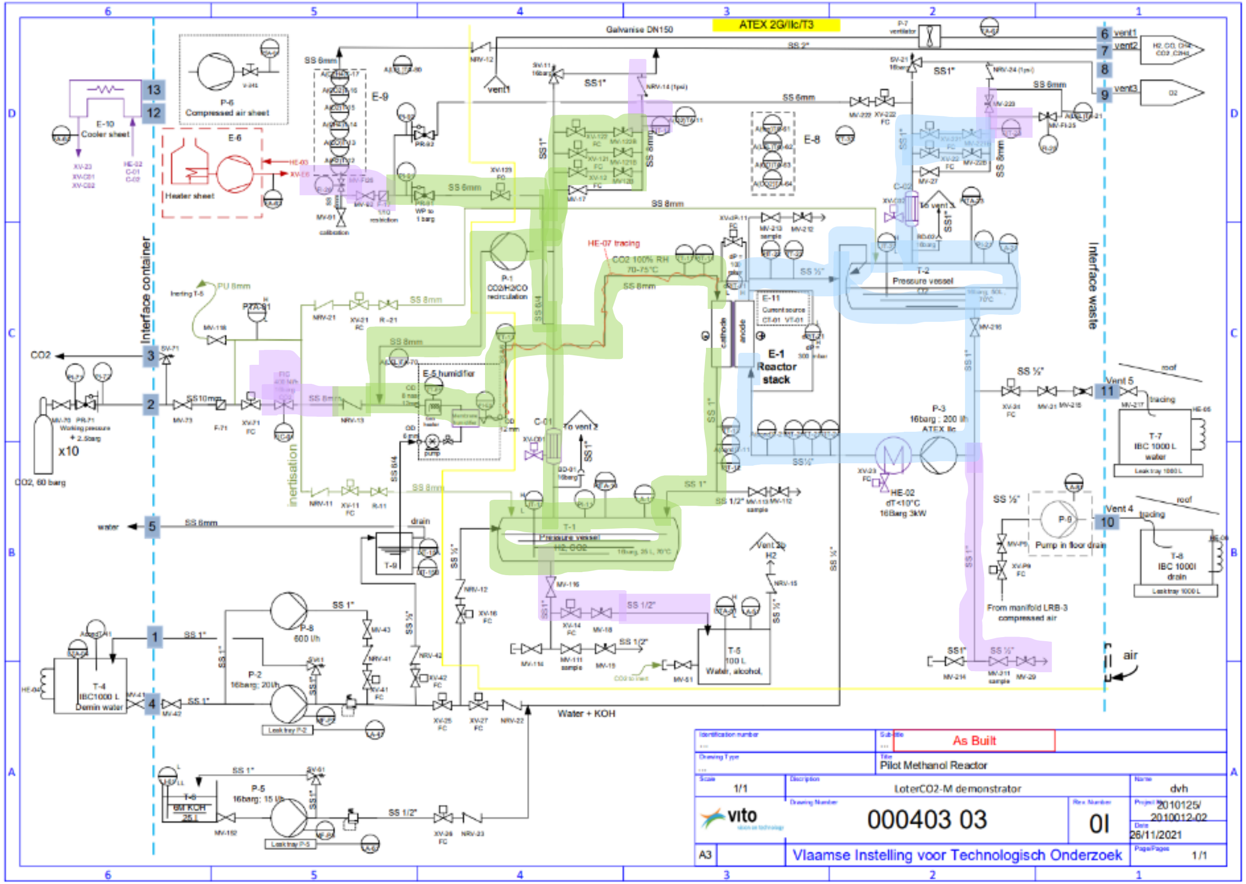


Vito results

5 kW process plant

based on H_2 generation equipment experience

- Control volume cathode:
  - CO_2 feed flow
  - Venting off-gas
  - Continuous gas flow to analyzer
  - Sample points for product
- Control volume anode:
  - Venting off-gas T2
  - Filling T2 (H_2O/KOH)
  - Sample point T2



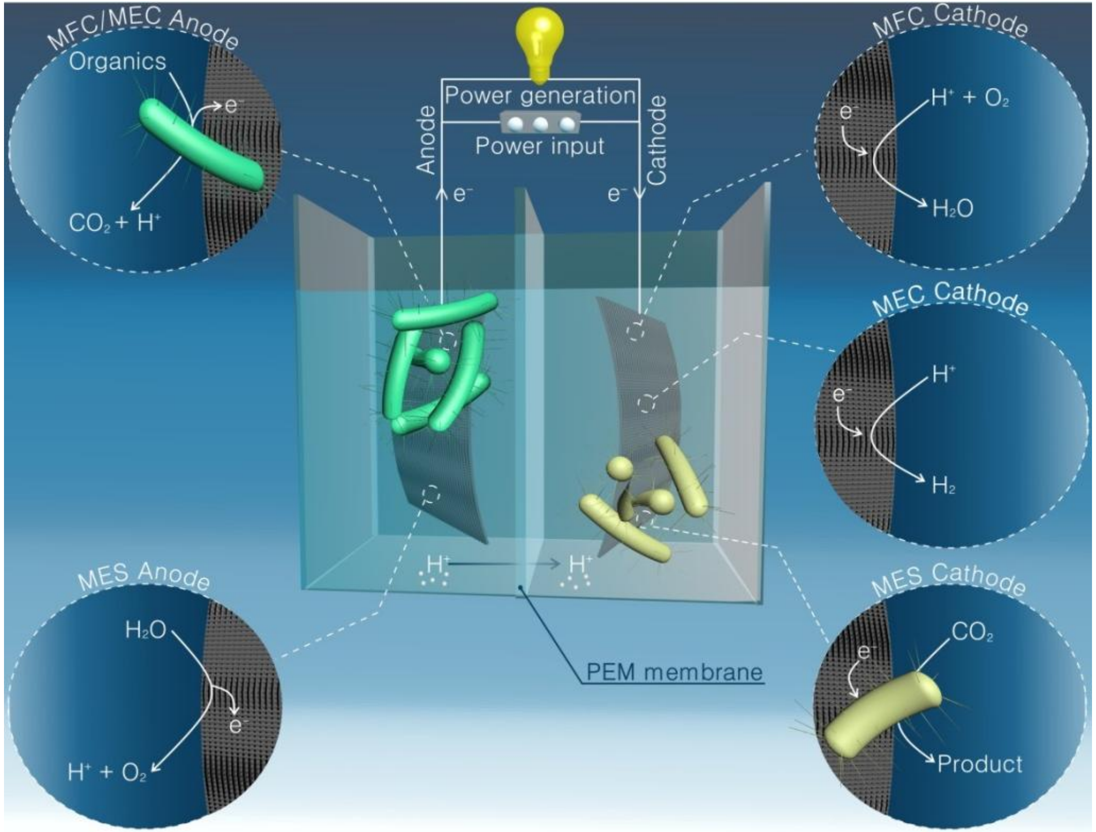

AH


Critical Raw Material free Low Temperature Electrochemical Reduction of CO2 to Methanol
vito
JM Johnson Matthey
RWE
BEKAERT
IRD
DTU
Funded by

Pilot@RWE

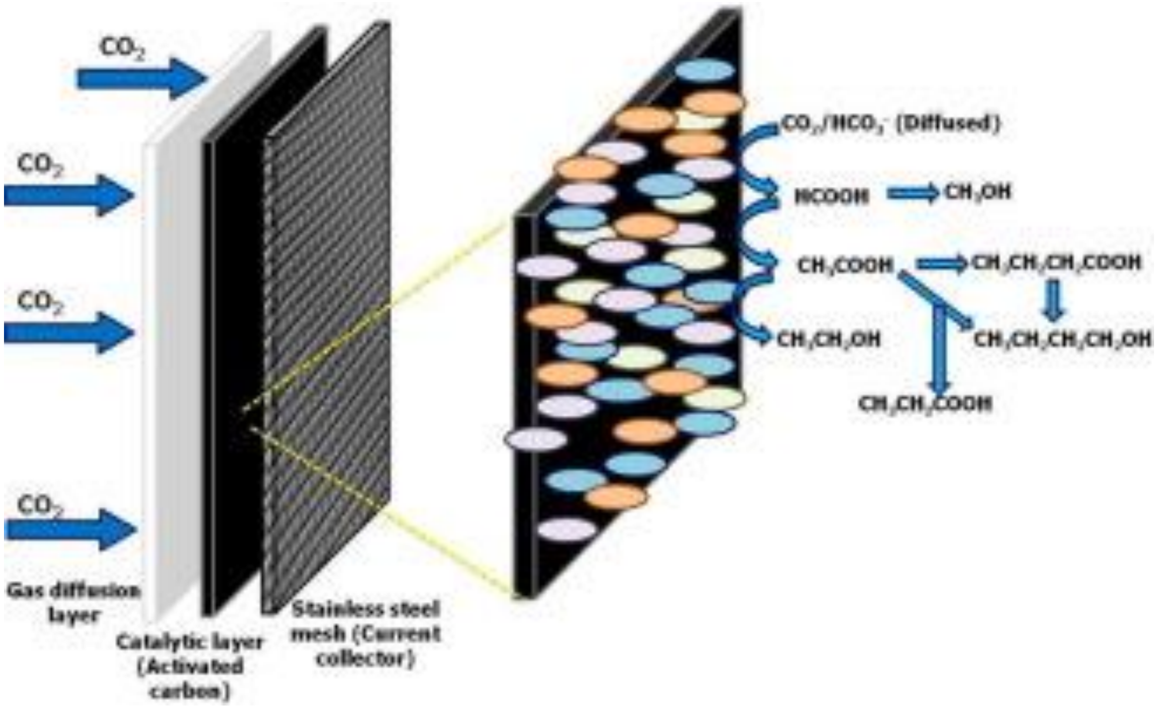
MICROBIAL ELECTROSYNTHESIS (MES)

BES for Biological and enzymatic conversions

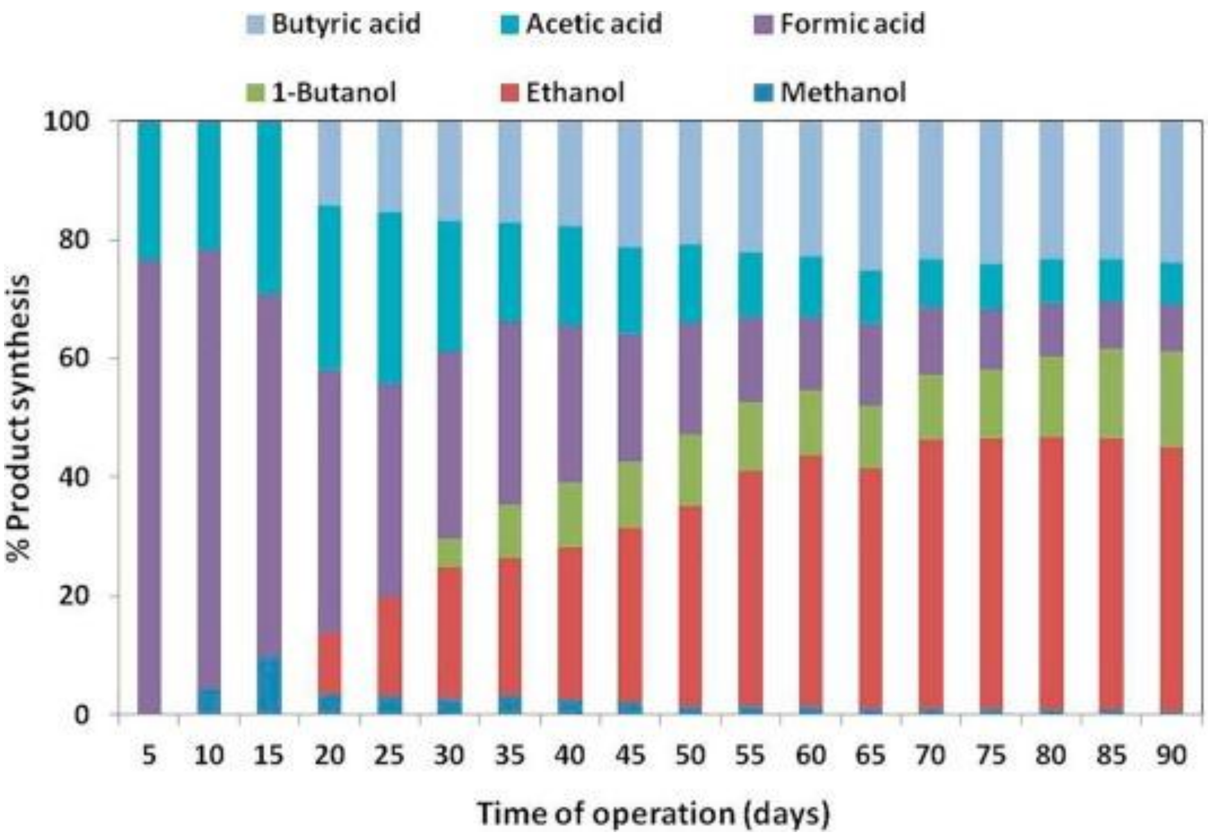


Katuri et al. 2018, Adv. Mat. 30 (1707072), 1-18

Electro-biocatalytic conversion of carbon dioxide to alcohols using GDE



Srikanth et al., 2018, Electro-biocatalytic conversion of carbon dioxide to alcohols using gas diffusion electrode, Bioresource Technology 265, 45-51



Percentage occupancy of different products in total product against operation time

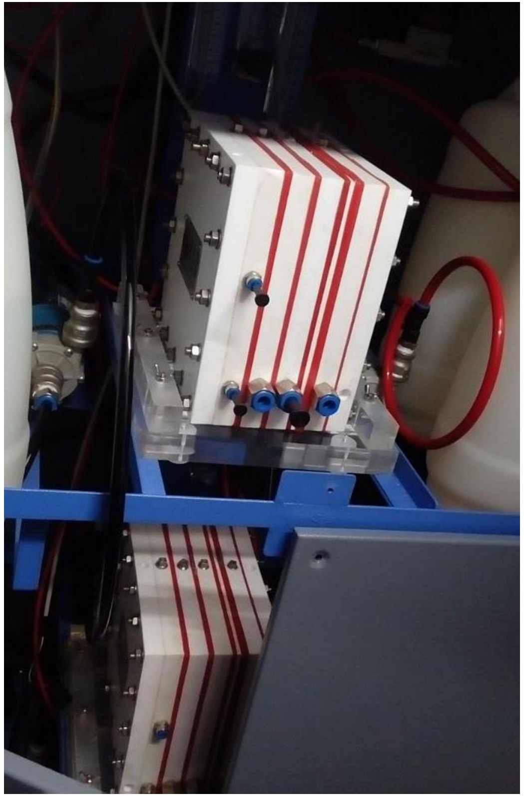
Srikanth et al., 2018, Bioresource Technology 265, 45-51

Biochemicals and biofuels obtained from CO2 in MES

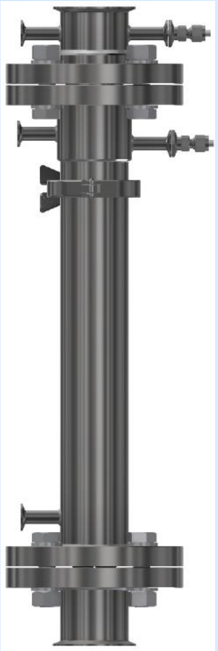
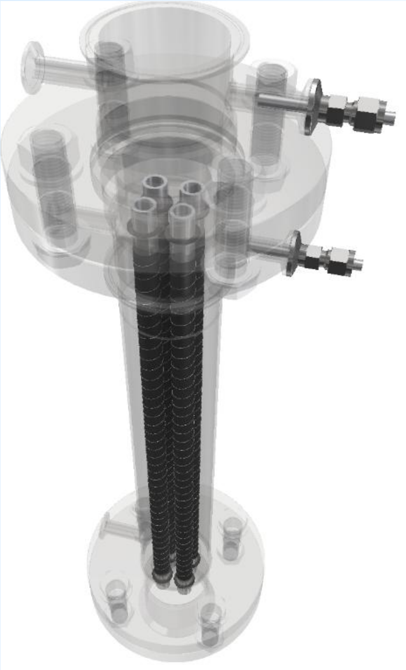
Product	Highest production rate (g/(L·d))	Main carbon sources	pH	T (°C)	Potentiostatic control (V *vs.* SHE)	Galvanostatic control (mA/cm²)	Cathode	Reference
Acetate	77	$NaHCO_3$	5.2	35	-1.10	n.a	3D-reticulated vitreous carbon	Jourdin et al. (2016)
Butyrate	5.70	CO_2:N_2 30:70 %	5.8	32	-0.85	-5 to -12	Carbon felt	Jourdin et al. (2019)
Caproate	2.41	Ethanol, CO_2 and $NaHCO_3$	7.0	30	n.a.	-1.0	Carbon felt	Jiang et al. (2020)
Butanol	0.06	CO_2	8.0	29	-0.80	n.a.	Gas diffusion electrode	Srikanth et al. (2018b)
Ethanol	0.18	CO_2	8.0	29	-0.80	n.a.	Gas diffusion electrode	Srikanth et al. (2018b)
	0.05	CO_2	5.4	25	-0.80	n.a.	Granular graphite	Blasco-Gómez et al. (2019)
Isopropanol	0.06	CO_2:N_2 10:90 %	5.0	30	n.a.	-0.5	Carbon felt	Arends et al. (2017)
Methane	12.5[b]	$NaHCO_3$	7	30	n.a.	-1.0 to -3.5	Graphite felt	Geppert et al. (2019)

Dessi et al., 2021. Microbial electrosynthesis: Towards sustainable biorefineries for production of green chemicals from CO2 emissions. Biotechnology Advances, 46, p.107675.

Pilot scale Bioelectrochemical systems



NOVEL DESIGN WITH 4 ELECTRODE TUBES

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