Scaling-up a Photo-electrocatalytic System for CO_2 Capture and Conversion to Oxo-products: the SunCoChem approach.

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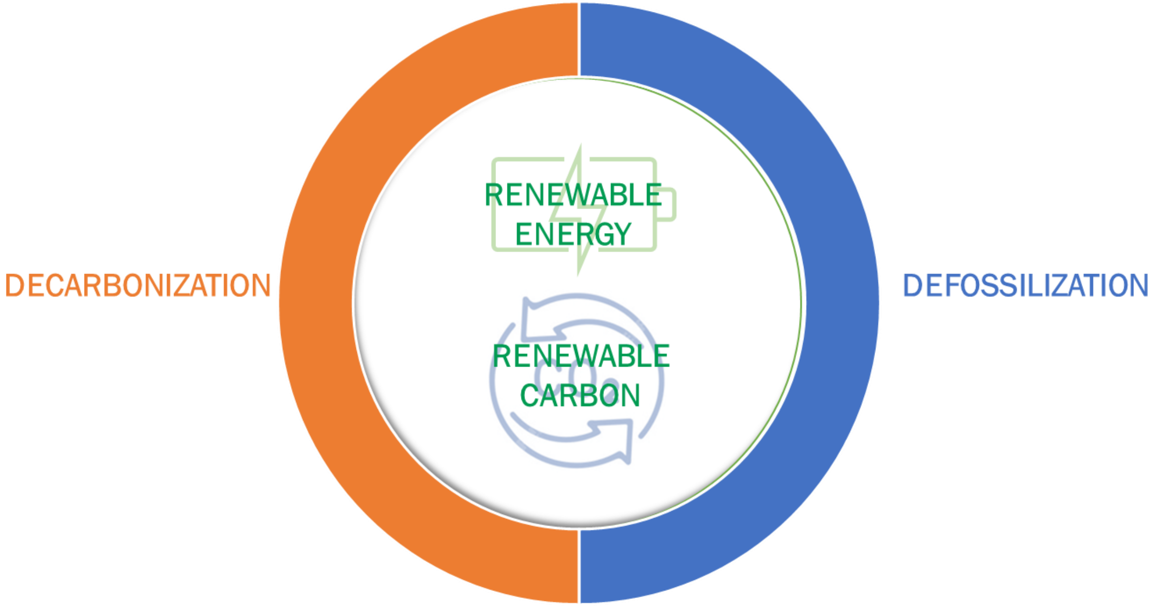
DECARBONIZATION & DEFOSSILIZATION

30
Gigatons of CO_2 emitted yearly

95%
Chemicals based on fossil fuels

The Chemical Industry is Europe's third largest greenhouse gas emitter, with over 30 Gt_{CO_2} yearly.



Why photo/*electrochemical conversion technology* for the sustainable production of chemicals and fuels?

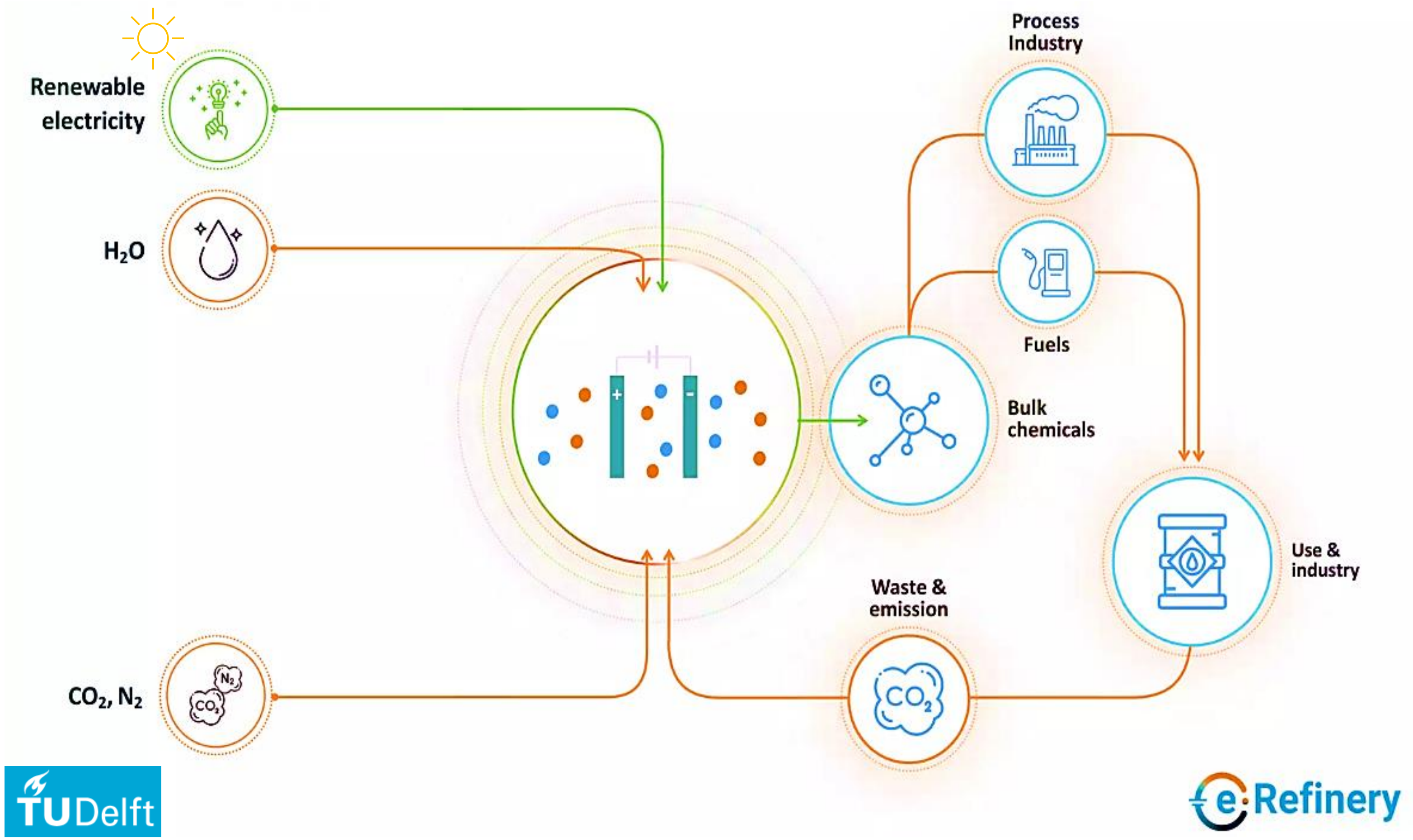


Figure taken from: https://www.tudelft.nl/en/e-refinery

COMPETITIVE ADVANTAGES OF PHOTO-ELECTROCHEMICAL CO_2 REDUCTION ($E-CO_2R$) OVER HYDROGENATION TECHNOLOGY

Direct exploitation of sunligh & Renewable electricity

The e-CO_2R is easily coupled to **renewable electricity sources** that can **directly feed the electrochemical cell for the CO_2 reduction** into value added products

Ambient pressure and temperature

The e-CO_2R happen under ambient temperature and pressure.
The electrochemical cell has great usability because of its **independence from high pressures and temperatures for the reaction to take place.**

No high value reactants needed

The e-CO_2R does not need the use of high-value reactant as H_2.
Water and low-cost electrolytes are commonly used.

Key critical aspects for Photo-Electrochemical CO_2 Conversion (e-CO_2R) and Industrialization

Increase active area of electrocatalyst

The former method is certainly the **necessary step for scale-up** and long-term reactor design **by defining industrial fabrication processes**

Engineering cost reduction

High engineering cost for the electrochemical cell development, both for the **manufacturing processes and raw materials** (e.g. catalyst)

Increase cell durability

The reaction stability of an EC is **critical to achieve a good device durability** and is mainly derived from the reactor configuration

Increase current density and selectivity

The current density depends on the combined effect of **catalyst activity and electrode/electrolyte engineering** that also impact selectivity

The engineering critical point to be developed to face the e-CO_2R key critical points

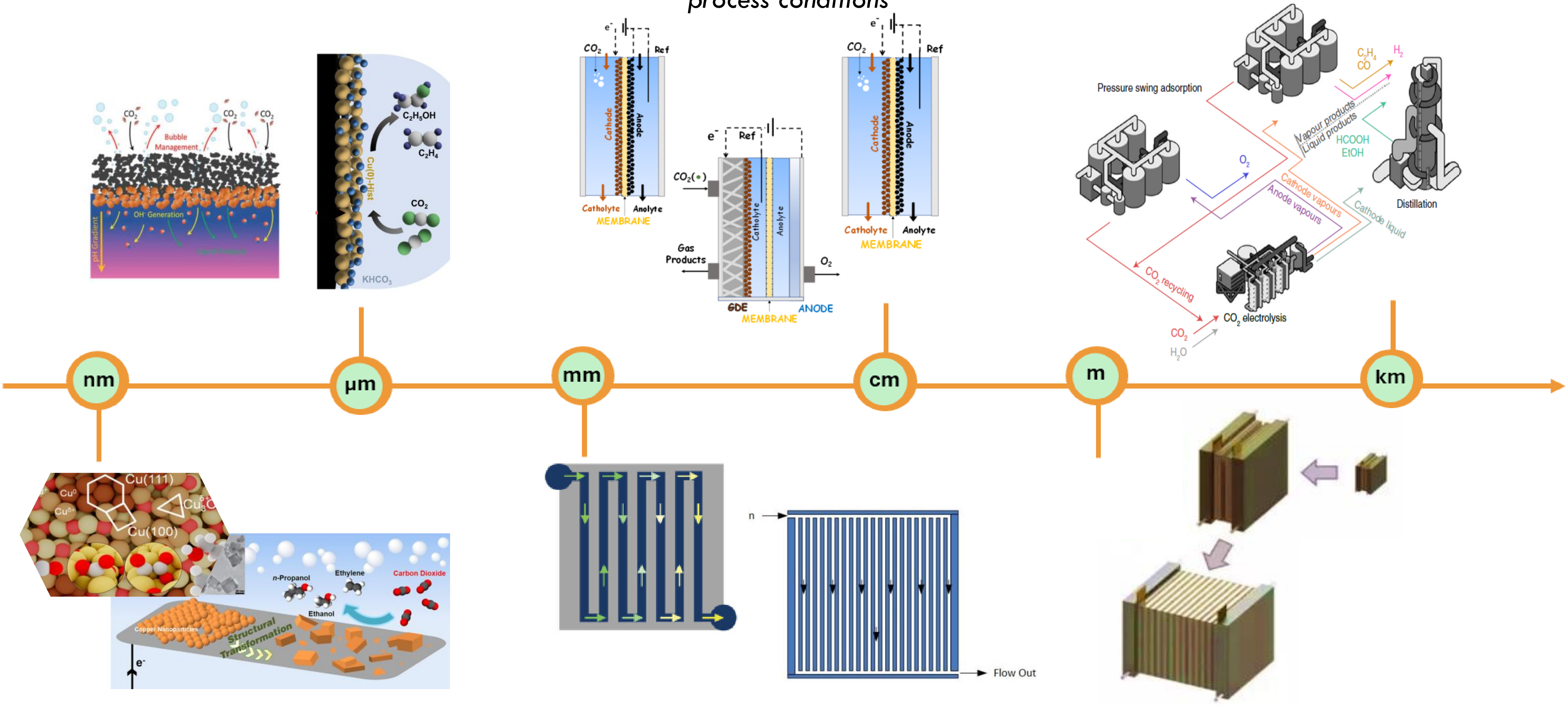
Catalyst material

Operative conditions

Electrochemical cell configuration

How to face the challenges of the e-CO_2R ?

Multidisciplinary approach for engineering of catalysts, reactors and process conditions



Figures taken from the literature

Our efforts to scale-up the e-CO_2R

Politecnico di Torino
IIT Istituto Italiano di Tecnologia @PoliTo
DISAT chimica fisica materiali scienza e ingegneria
CREST Catalytic Reaction Engineering for Sustainable Technologies
Fondazione Compagnia di San Paolo
TRAPEZIO Paving the way to research excellence and talent attraction
Fondazione CRT
ohmium
Baker Hughes
eni
Piano Nazionale di Ripresa e Resilienza
Finanziato dall'Unione europea NextGenerationEU

TRL5/6 Demonstrations of (photo)-electrocatalytic CO_2 reduction (E-CO_2R)

HORIZON 2020

Technical Coordination

SunCO2Chem: **(2020-2024) Photoelectrocatalytic device for SUN-driven CO_2 conversion into green CHEMicals.** Grant agreement 862192

ReCO2DE: **(2017 – 2022) Recycling carbon dioxide in the cement industry to produce added-value additives: a step towards a CO_2 circular economy.** Grant agreement 768583.

Coordination

Celbicon: **(2016 – 2019) Cost-effective CO_2 conversion into chemicals via combination of Capture, ELectrochemical and BI-ochemical CONversion technologies.** Grant agreement 679050.

Eco2CO2: **(2012 – 2016) Eco-friendly biorefinery fine chemicals from CO_2 photo-catalytic reduction.** Grant Agreement 309701

Partner

ocean: **(2017 – 2022) Oxalic acid from CO_2 using Eletrochemistry At demonstratioN scale.** Grant agreement 767798

SunCO2Chem

PhotoElectroCatalytic Device for Sun-Driven CO_2 conversion into Green Chemicals

- European project funded under the topic: *CE-NMBP-25-2019 – Photocatalytic synthesis (RIA)*
- **4,5 years** duration, from 1/05/2020 to 31/10/2024
- **Budget**: 6,7 M€, of which 6,6M€ funded by the EC
- Coordinated by **Eurecat and Politecnico di Torino**

SunCO₂Chem

PhotoElectroCatalytic Device for Sun-Driven CO_2 conversion into Green Chemicals

Consortium

14 partners from 8 European countries

6	3	1	3	1
Research institutions	R&D SMEs	Standardisation body	Chemical industries	EU International Cooperation partner

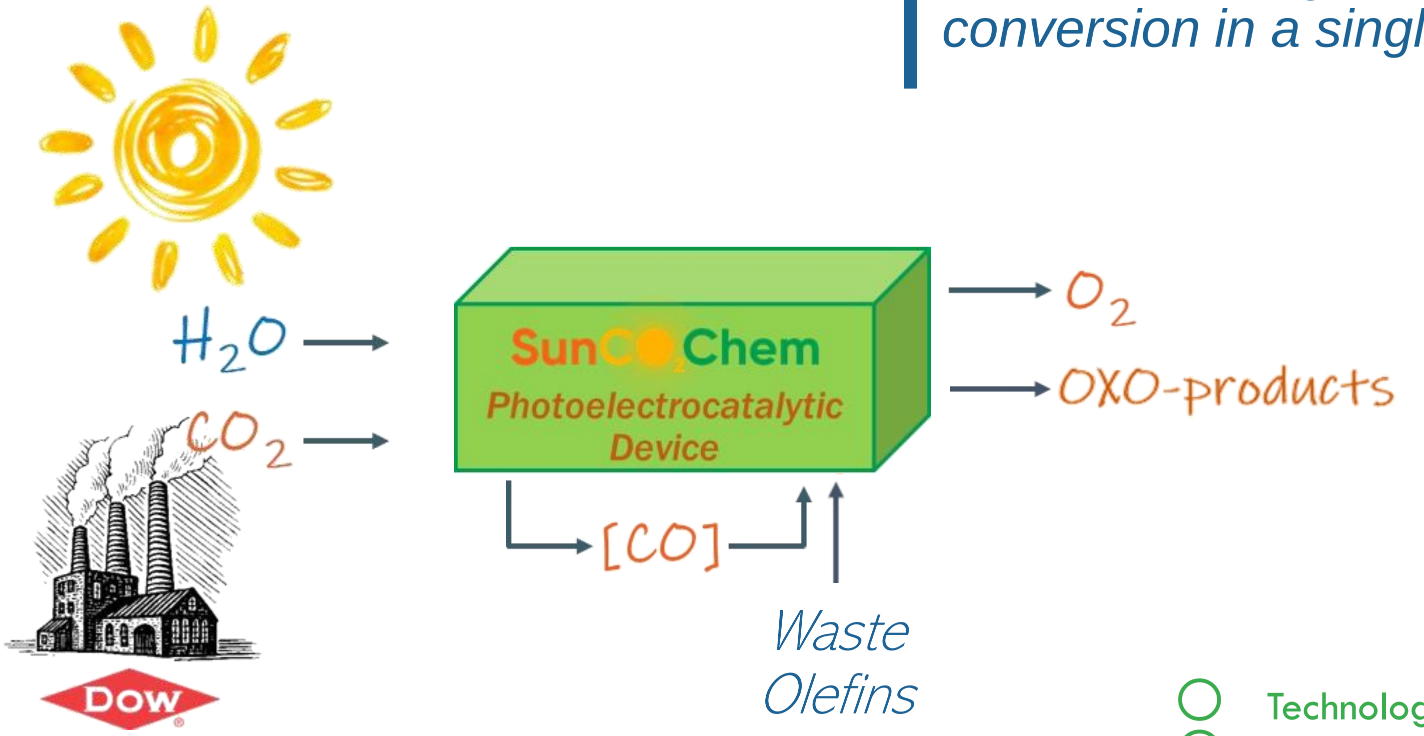
eurecat, avantium, DOW, HZB Helmholtz Zentrum Berlin, HYSYTECH, iff, iit ISTITUTO ITALIANO DI TECNOLOGIA, POLITECNICO DI TORINO, INTERNATIONAL HELLENIC UNIVERSITY, UNE Normalización Española, SOLARONIX, cnrs, io·li·tec Ionic Liquids Technologies, laurentia technologies

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 862192.

CONCEPT

SUN-driven production of high-value chemicals

Self-biased tandem photoelectrocatalytic reactor (TPER) to manufacture oxo-chemicals from CO_2, water and sunlight integrating CO_2 capture and conversion in a single unit.



- Technology class: Photo(electro)chemical CO_2 conversion
- Timeline: 2020 – 2024
- From TRL3 to TRL5

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CIRCULAR ECONOMY GOAL

Production of three sustainable oxo-products from CO_2

GLYCOLIC ACID Hydroformylation of formaldehyde	VALERALDHEYDE Hydroformylation of Butene (DOW waste by-product)	LIMOXAL ™ Hydroformylation of limonene
Building block applied in dying and tanning, flavouring preservative and emulsion additive.	*Building block applied as food flavouring, in resin and rubber products.*	*Building block applied as a perfuming agent, in personal care and house cleaning products.*

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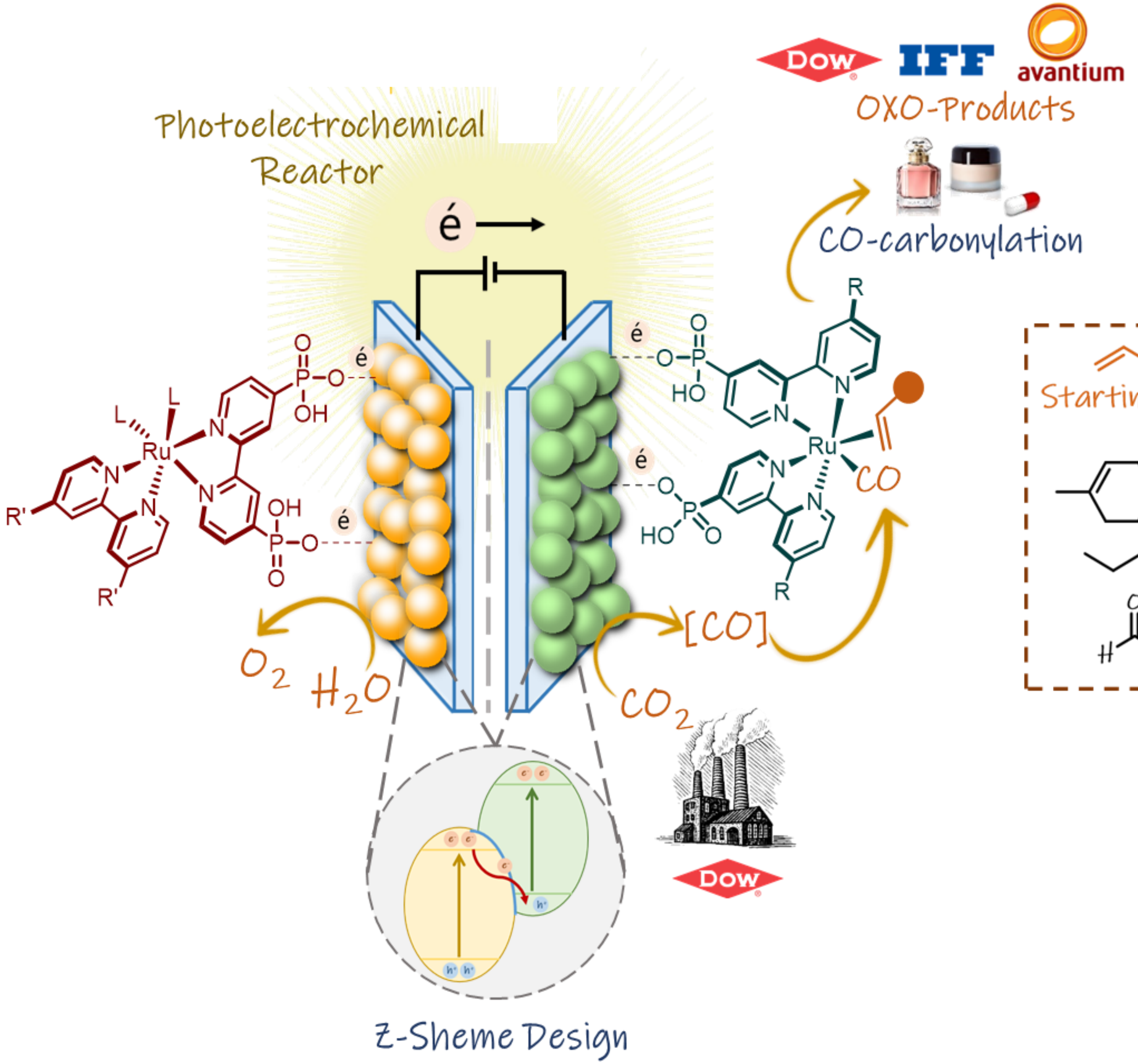
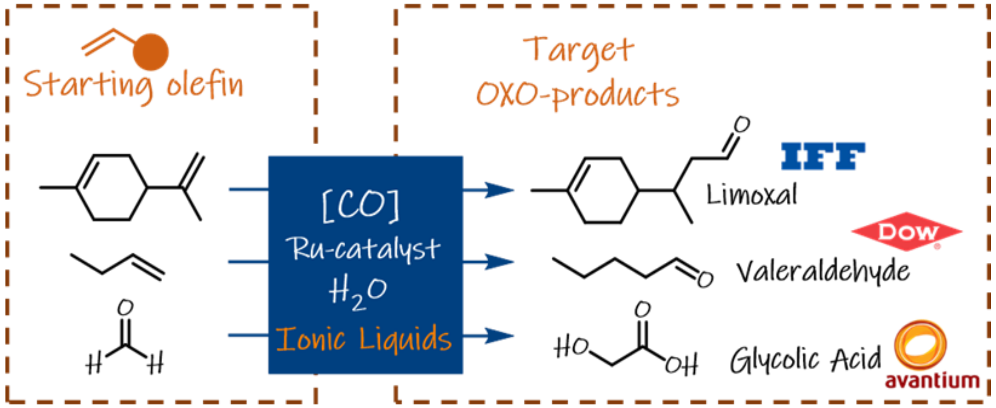
SUNCOCHEM APPROACH



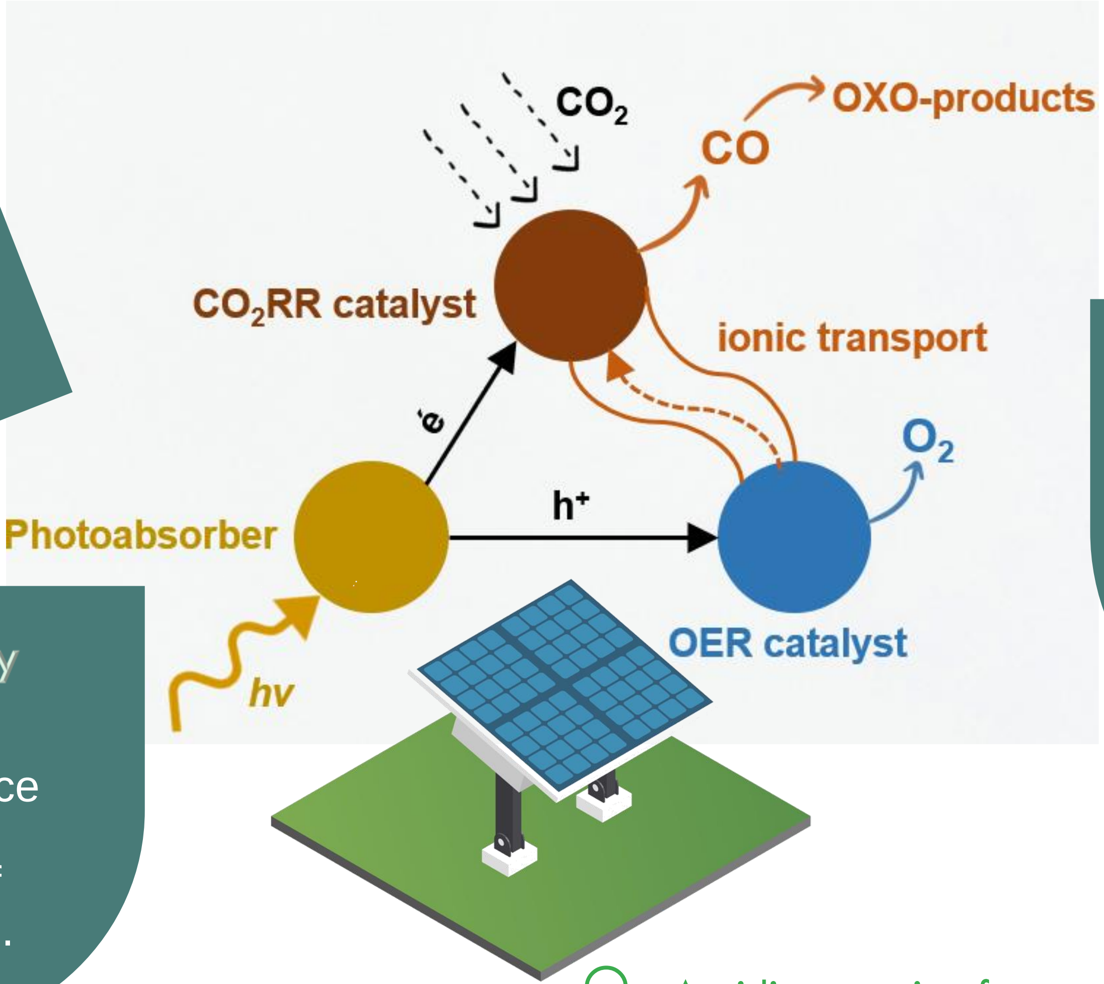


TECHNICAL CHALLENGES

Targets & Sustainability criteria

Efficiency

> 10% of Sunlight to CO conversion efficiency with a current density of 20 mA·cm^2



Sustainability

< 50% CO_2 emissions versus actual routes from fossil fuels

Stability

< 5% of performance loss in 1000h of operation.

- Avoiding or using few amounts of critical raw materials
- Valorizing industrial wastewater and CO_2 streams

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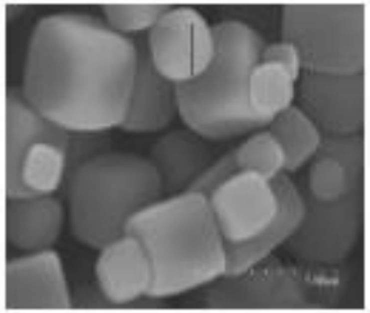
PROJECT PHASES

7 WPs in 54 months (2020 – 2024)

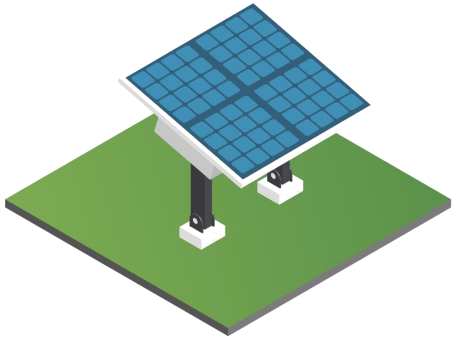
TRL3

1. Development of materials and components of the TPER cell
2. Upscaling, testing and validation of the TPER device
3. Integration and optimisation of materials and components
4. Socio-economic and environmental impact assessment

TRL5







TPER (2000 cm^2) validation

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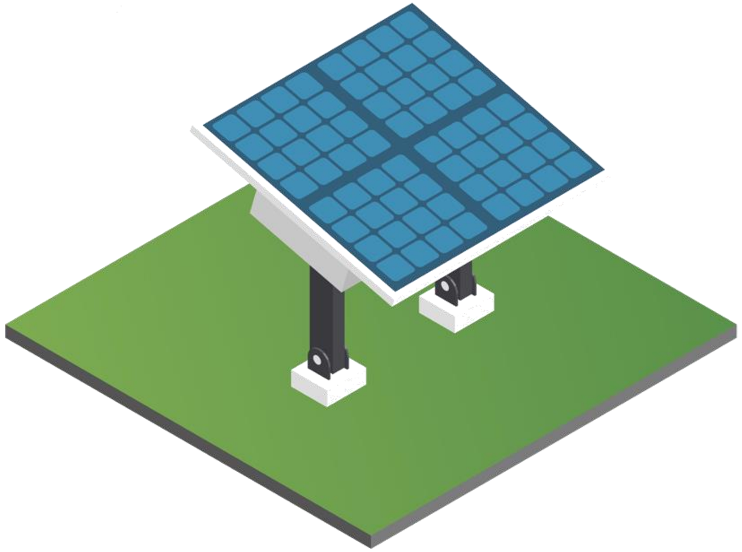
Politecnico di Torino

Novelty/Unique Selling point

SunCO2Chem

TPER device

Compact and easily scalable design to be used as artificial leaf



ANODIC CHAMBER

Smart photoelectrodes

- Water oxidation to O_2

CATHODIC CHAMBER

Photo- and *non*-photoassisted coupled reactions

- Selective PEC CO_2 reduction to CO
- CO-hydroformylation of OXO-products

High CO_2 conversion via *Ionic Liquids* electrolytes

Stable & efficient MEA *via* a *transparent bipolar membrane*

Integrated FLUE GAS Cleaning & CO_2 CAPTURE CHAMBER

CO_2 capture from flue gas stream with

- Asymmetric polysulfone membrane
- CO_2 concentration in *Ionic Liquids*

Low-cost **PEROVSKITE SOLAR CELLS** to boost internal photo-voltage

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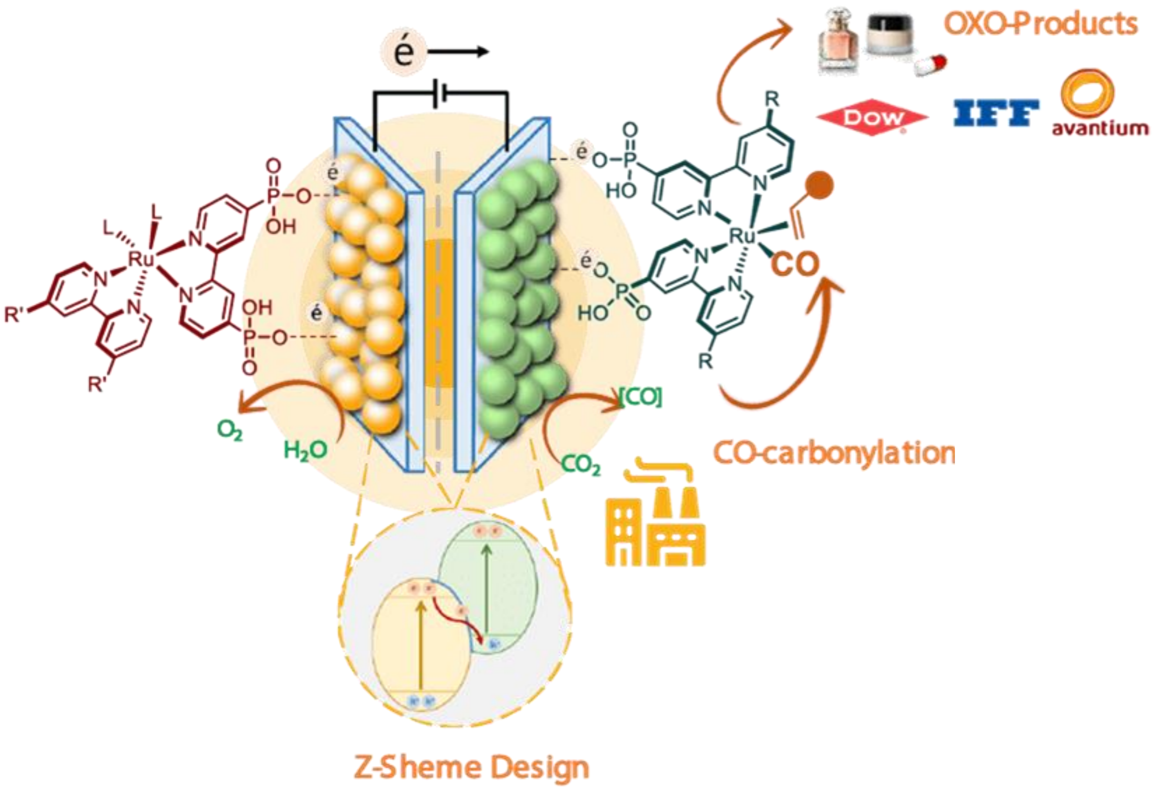
Novelty/Unique Selling point

TPER components



Multi-heterojunction photoelectrodes for Z-scheme mimicking:

- Metal oxide nanoparticles
- Molecular organometallic chromophores
- Molecular catalysts for water oxidation, CO_2 reduction and hydroformylation

Transparent Bipolar Membranes

Bipolar Membrane-Electrode Assembly to maximize catalyst performance:

- Constant pH and ionic gradients at both compartments
- Use of different electrolytes

Ionic Liquid's for CO_2 capture and conversion

- Good CO_2 absorption
- Low viscosity
- High CO_2 and organic reagents solubility
- High electrochemical stability
- High CO_2 conversion ability

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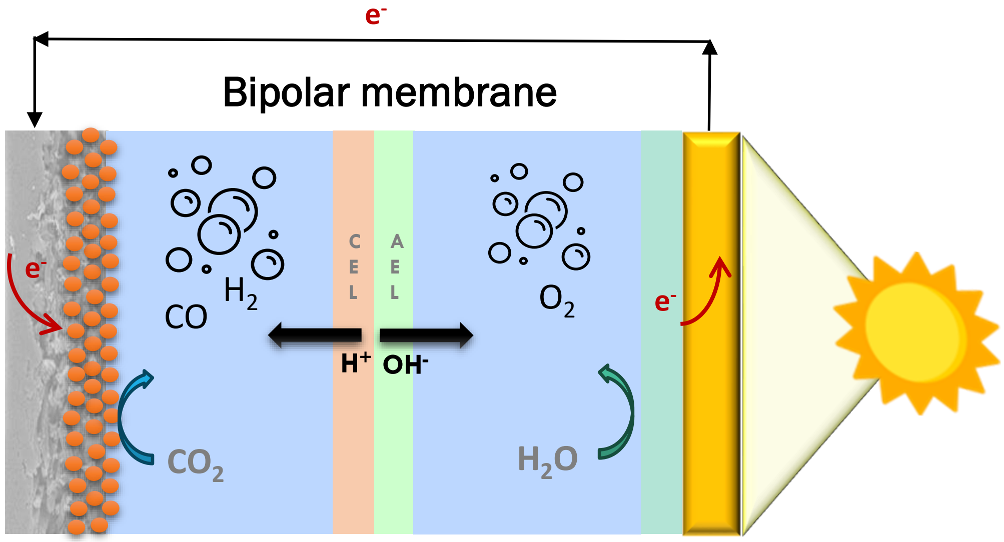
SUNCOCHEM TPER Driving-reactions



Cathode (CO_2RR/HER)

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

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

Photo-Anode (OER)

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

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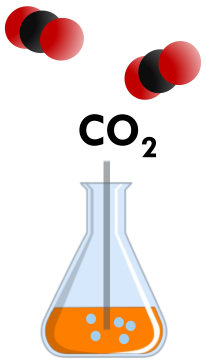
TPER Electrode Materials

- **Cu-based electrode as Cathode**
- **$BiVO_4$ electrode as Photo-Anode**

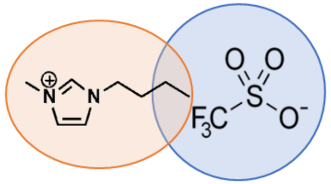
- **Electrolyte:**

Ionic Liquids to enhance CO_2 solubility & selectivity to CO

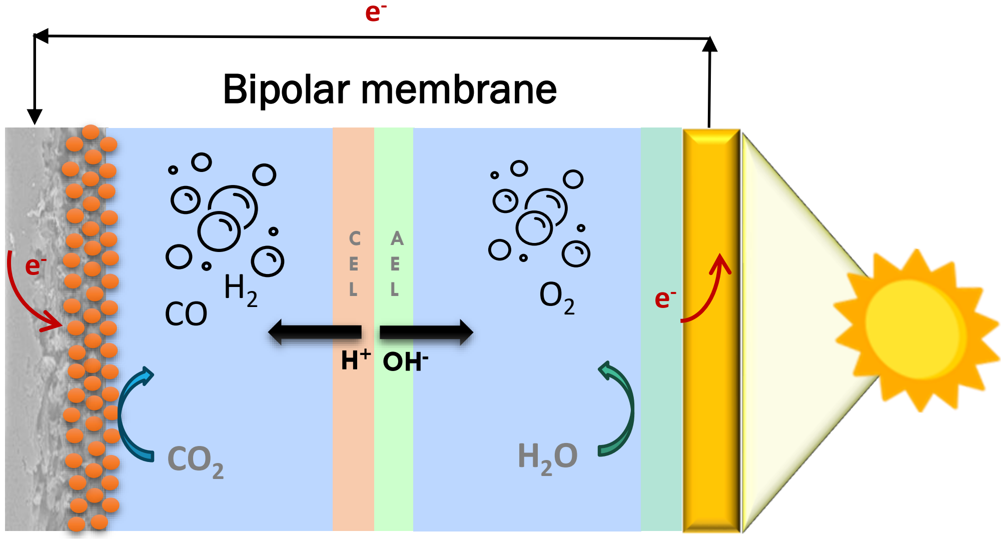


Acetonitrile (ACN)

IL- based Catholyte



0.3M [BMIM][SO_3CF_3]



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Ref. Hernández S. et. al. Communications Chemistry (2023) 6, 84.

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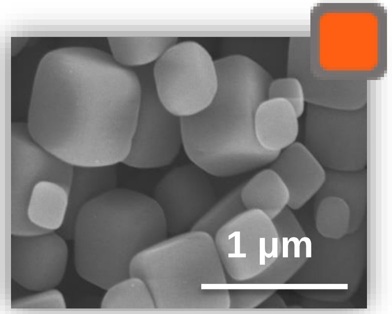
Politecnico di Torino

E-CO_2R catalyst & electrodes fabrication

SunCO2Chem

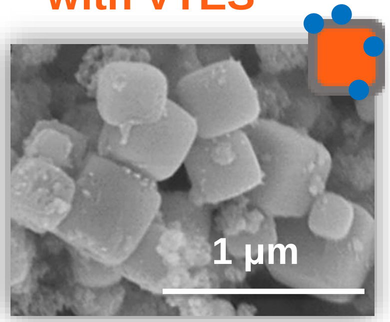
GDE preparation by **spray coating**

Cu_2O/SnO_2 Nps



- **Cu_2O cubes** covered by a **SnO_2 shell**

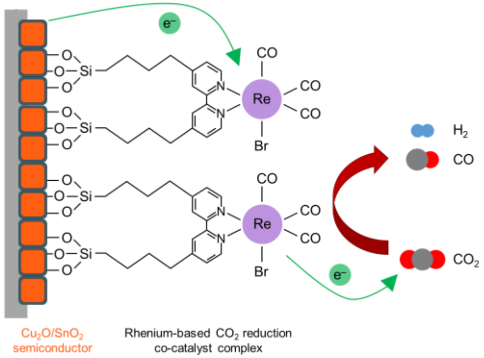
Functionalization with VTES



Coating of Cu_2O/SnO_2 in a VTES (VinylTriEthoxySilane) solution in IPA/H_2O.

Electropolymerization with Rhenium complex

Vinyl groups reduction to form radical couplings and subsequent C-C bond formation.



Molar Ratio		
Cu	Sn	Si
45-40	1	0.5

laurentia technologies

eurecat Technology Centre of Catalonia

Zammillo F., Guzmán H., De los Bernardos M., Pavan G., Hernández S., et. al. Chem. Eng. J. 2024, Submitted.

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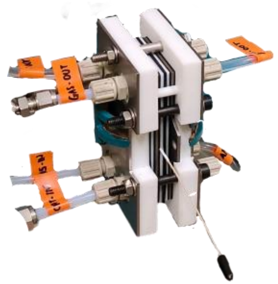
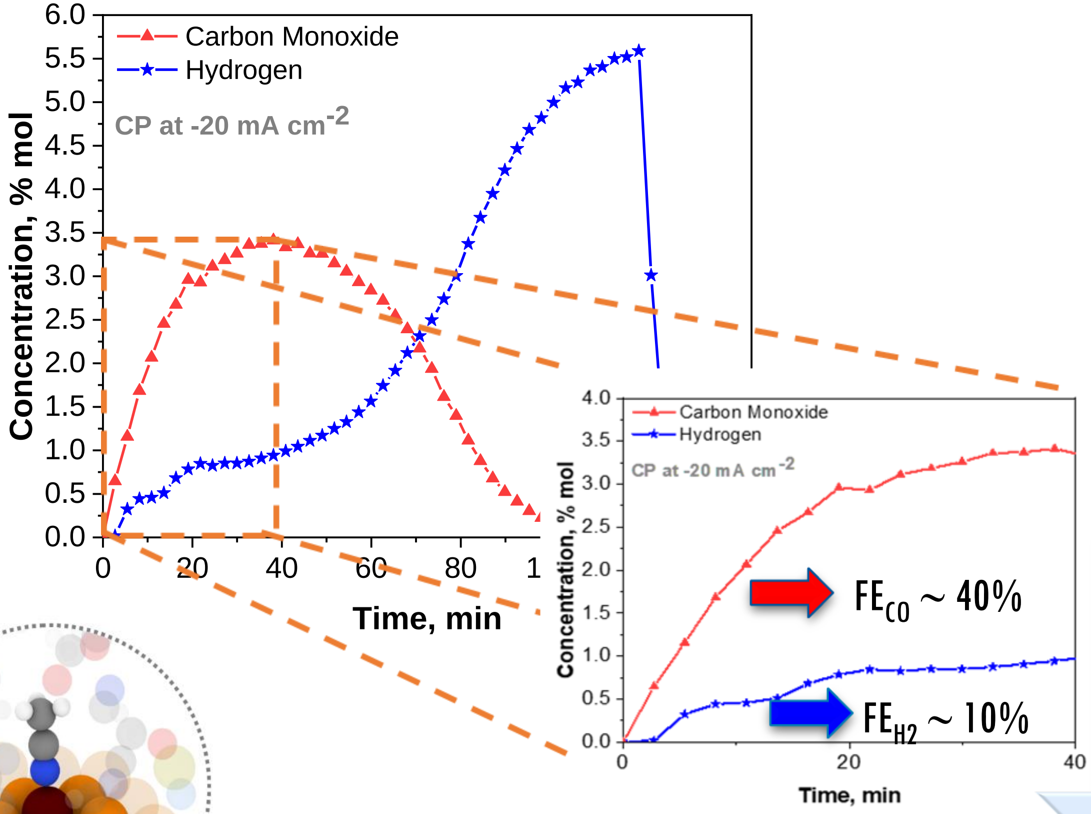
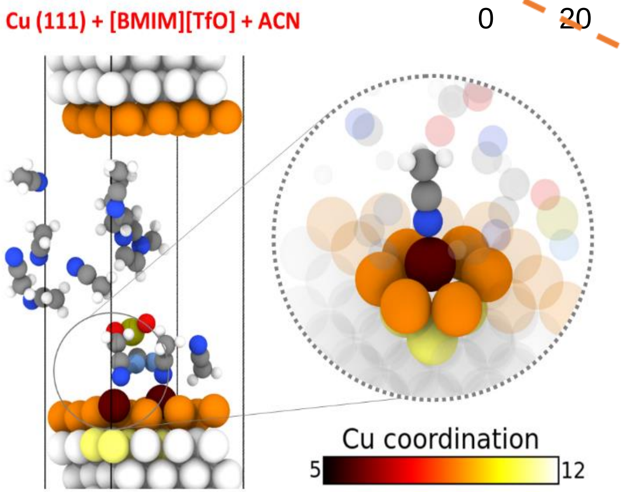
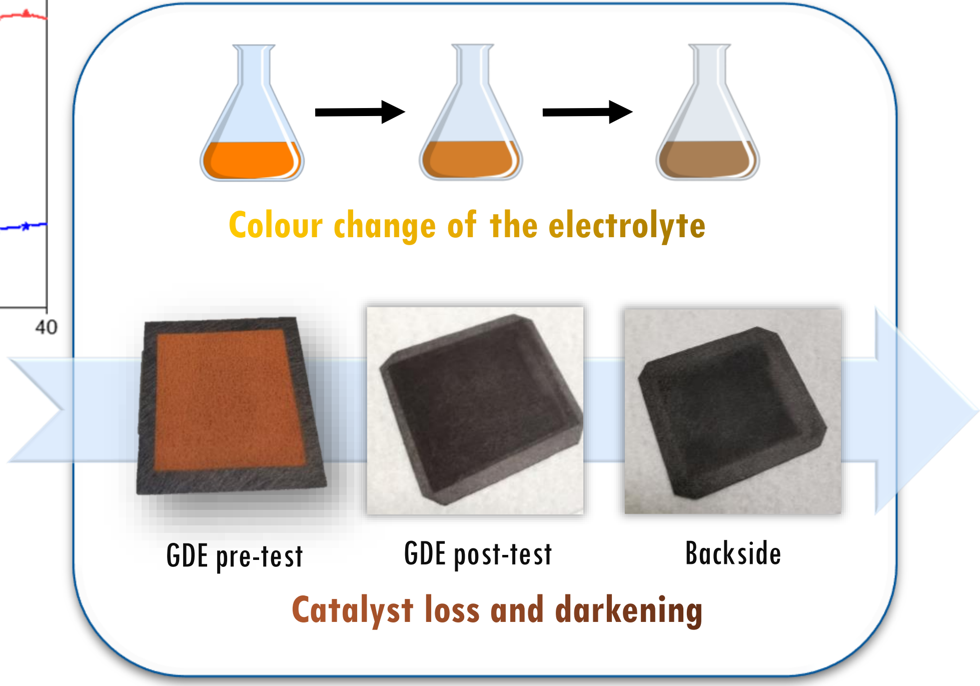
Issue of aprotic electrolytes for CO_2 concentration





- **The acetonitrile solvent displace the Cu atoms** from the electrode surface.
- The **IL molecules** (i.e. $[SO_3CF_3]$) **dissolve Cu ions**.
- The **electrode support is damaged** by the aprotic electrolyte (hydrophobicity loss & carbon amorphization).





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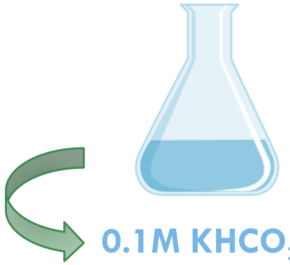
How to enhance stability and efficiency?

Let's employ

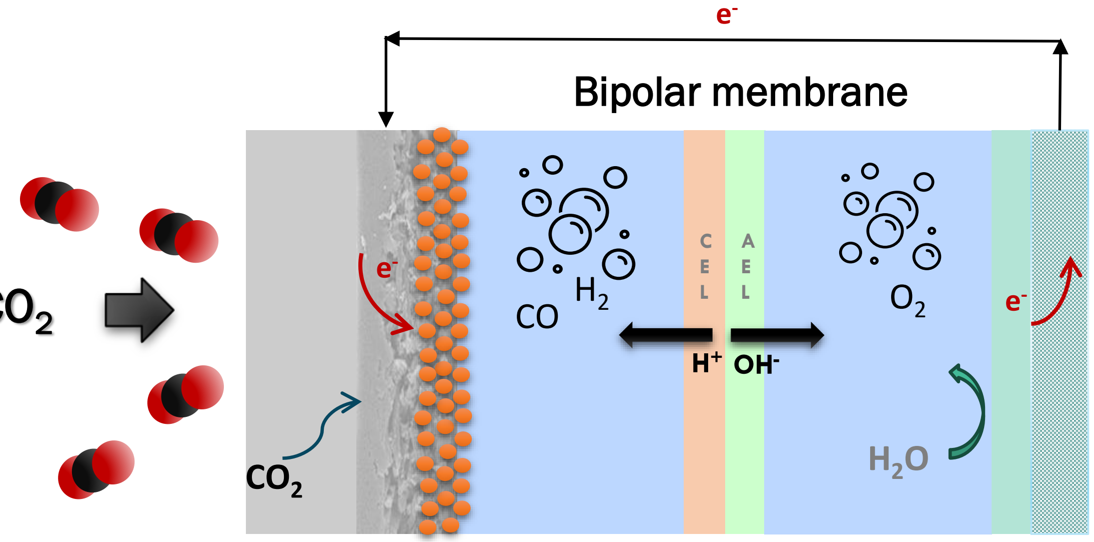
- Low-cost Cu-based electrode as Cathode in a flow cell
- **Gas Diffusion Electrode (GDE) configuration:**

→
- To boost **CO_2 mass transport rate**
- To increase the **energy efficiency**

Water- based Electrolyte



0.1M $KHCO_3$ in H_2O



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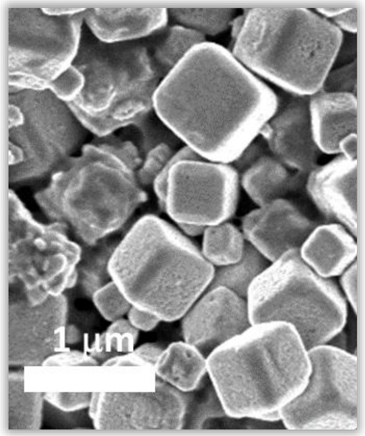
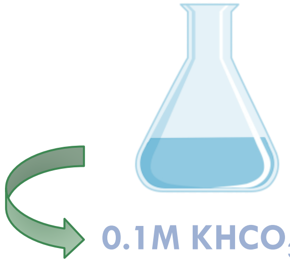
Cu-based GDE long-term stability in Aqueous Electrolyte

GDE operating in flow-through configuration



Pre-test GDE



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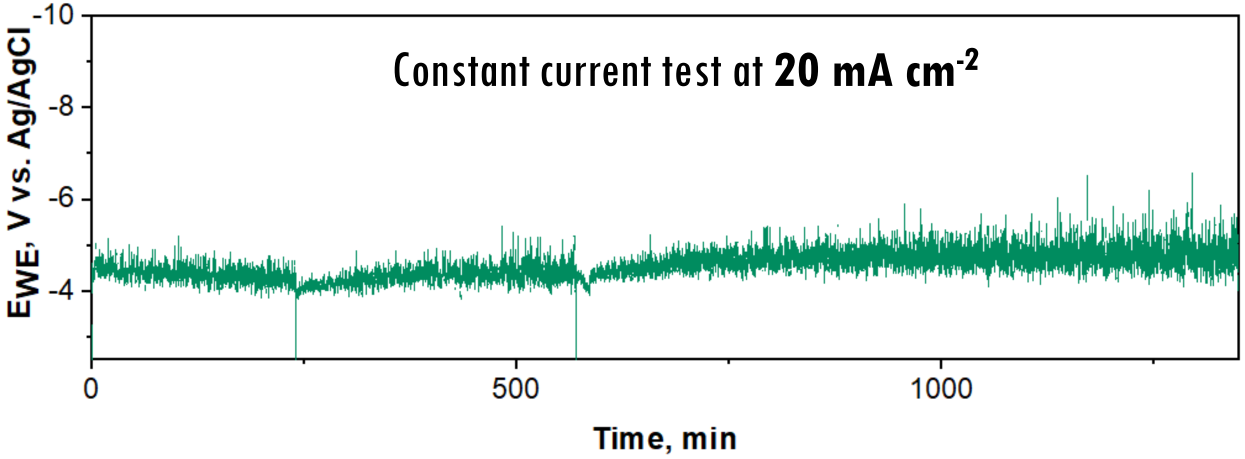

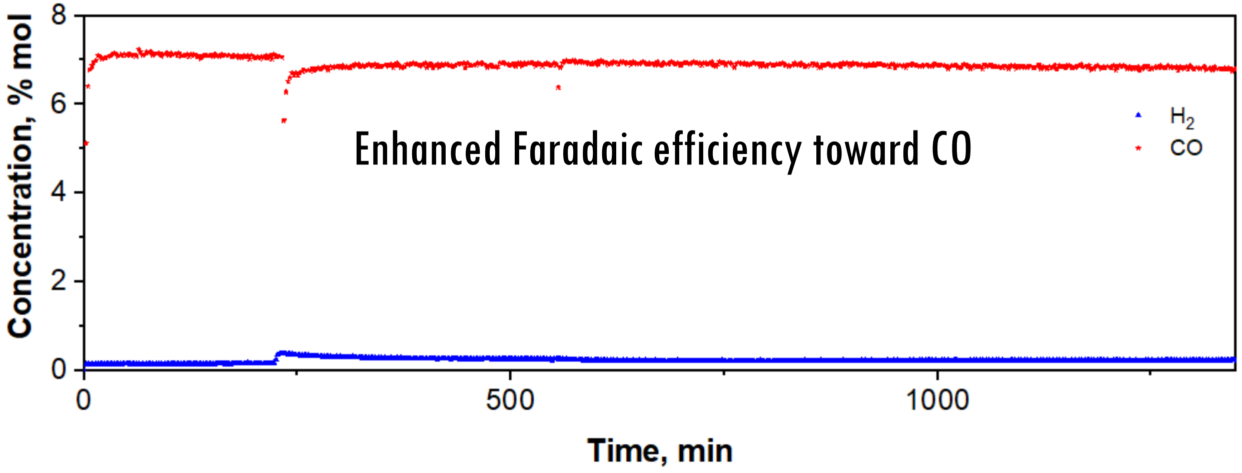

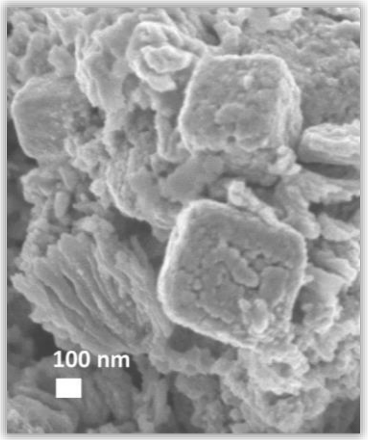

Post-test GDE

Steady CO production over the 24 hours

FE_{CO} = 90%

Flooding hindered (**stable H_2 production**)

Zammillo F., Guzmán H., De los Bernardos M., Pavan G., Hernández S., et. al. Chem. Eng. J. 2024, Submitted.

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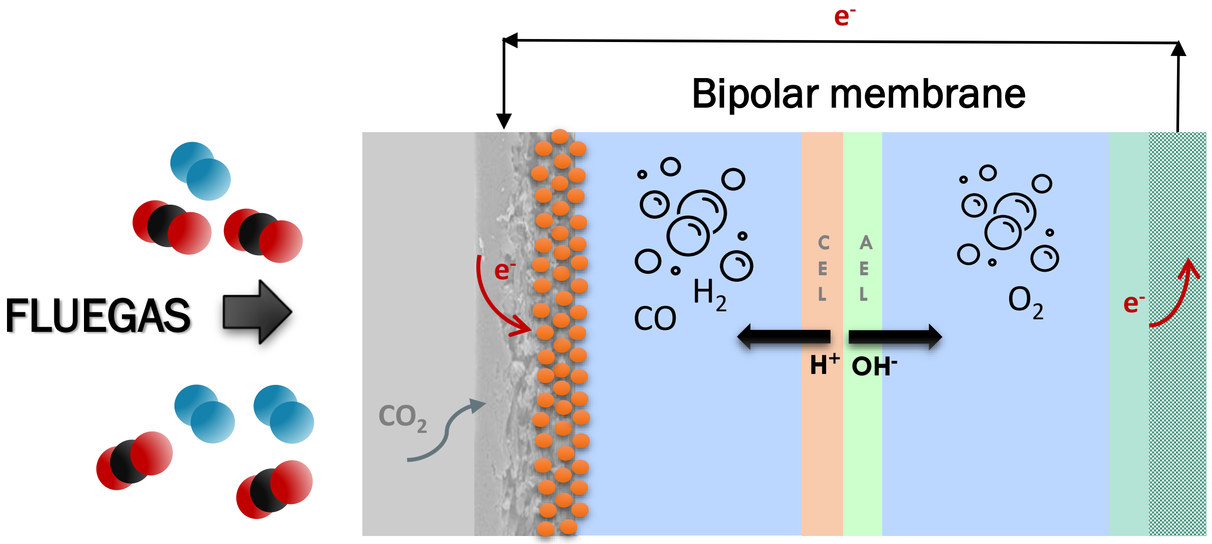
What happen if we operate with flue-gas instead of CO_2?



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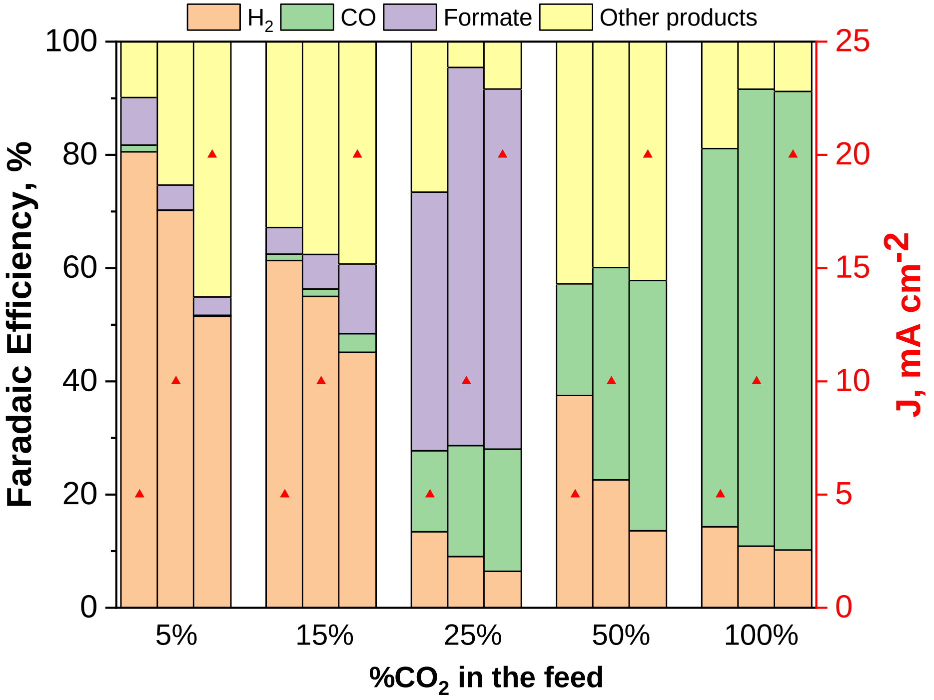
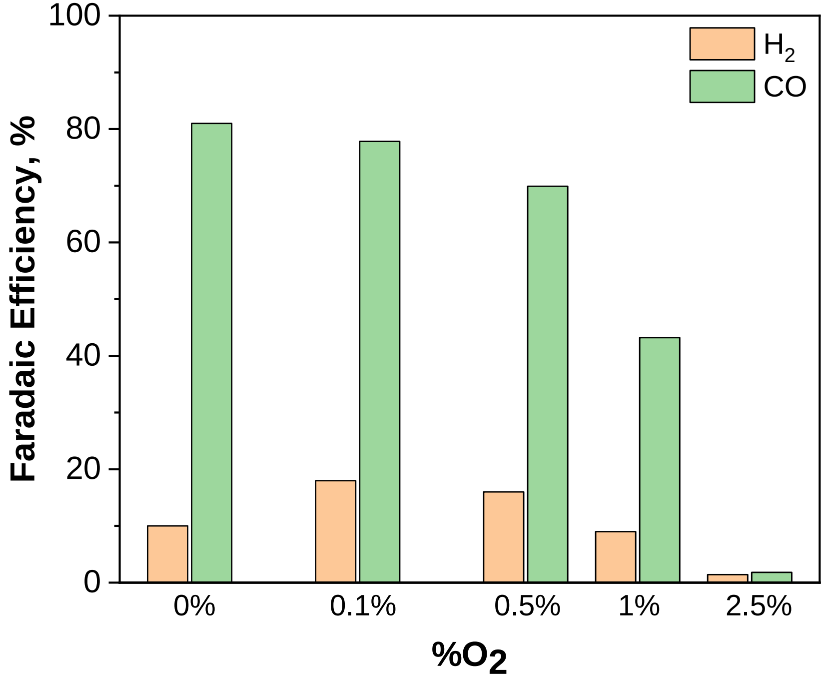
Effect on Cu-based GDE of CO_2 dilutants in Fluegas

N_2-diluted CO_2



O_2-containing CO_2



e-CO_2R Selectivity changes in presence of N_2

e-CO_2R conversion is hindered by the ORR in the presence of O_2

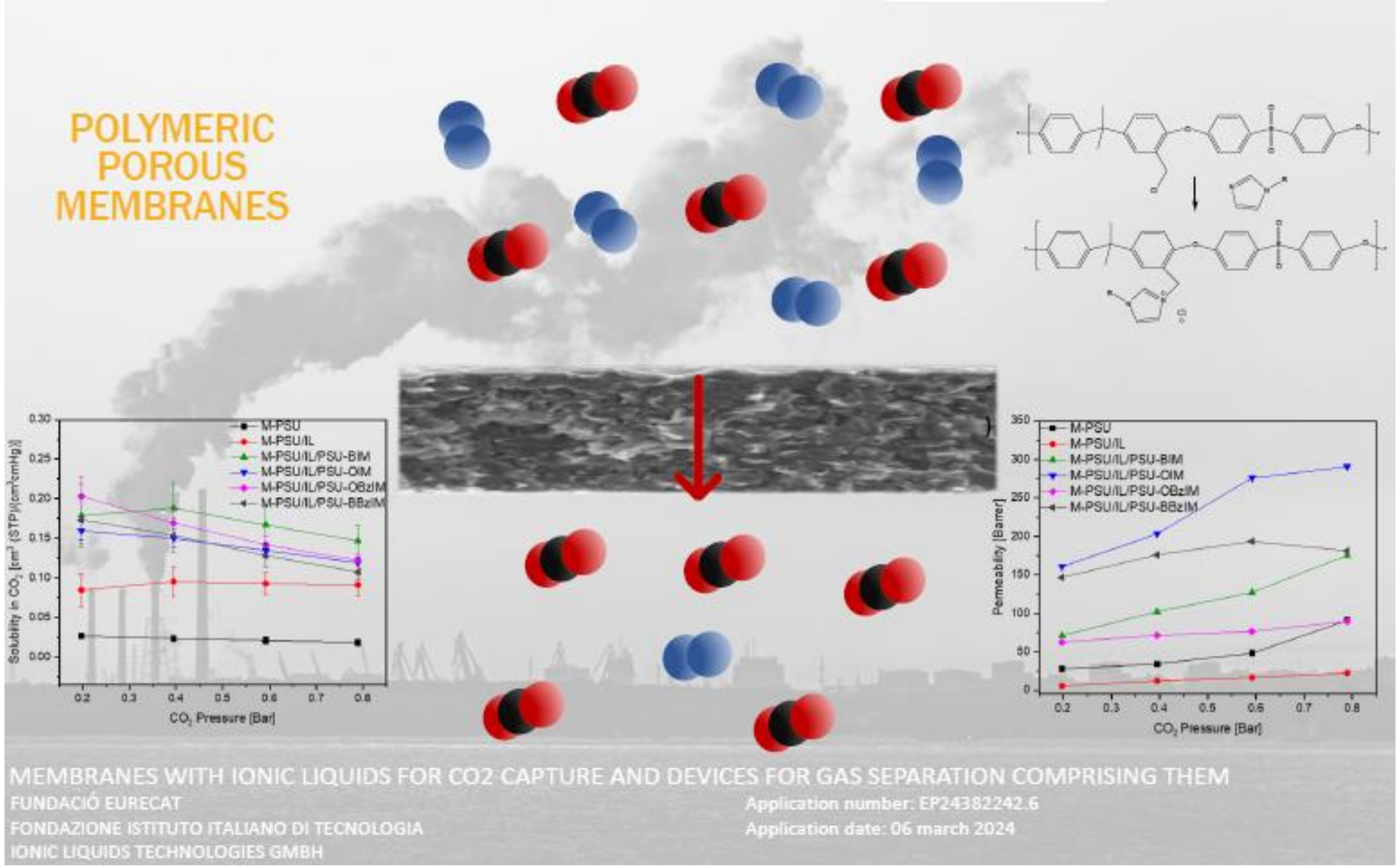
Zammillo F., Guzmán H., Turturici L., Hernández S., et. al. paper under preparation.

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No. 862192.

How to avoid contaminants/dilutants effect on CO_2 conversion efficiency?

Let's integrate:

CO_2 separation and concentration



MEMBRANES WITH IONIC LIQUIDS FOR CO2 CAPTURE AND DEVICES FOR GAS SEPARATION COMPRISING THEM

Patent application number: EP24382242.6, **2024**

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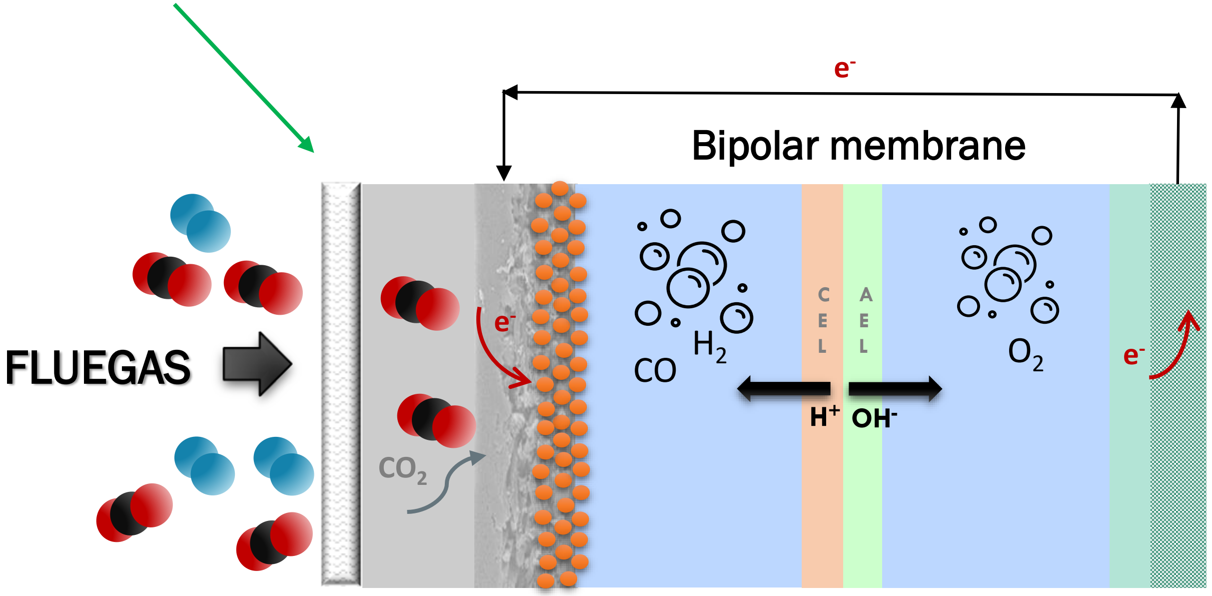
How to avoid contaminants effect on CO_2 conversion efficiency?

Let's employ

- Low-cost Cu-based GDE as Cathode
- Fluegas as a feedstock
- **Coupling of CO_2 separation with conversion**



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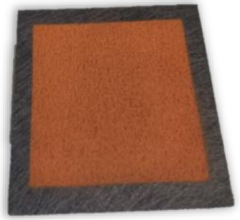
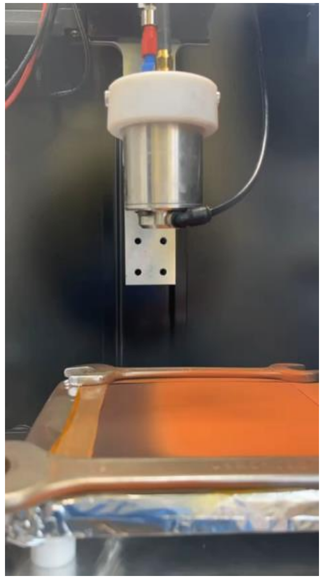
Scale-up of GDE Manufacturing

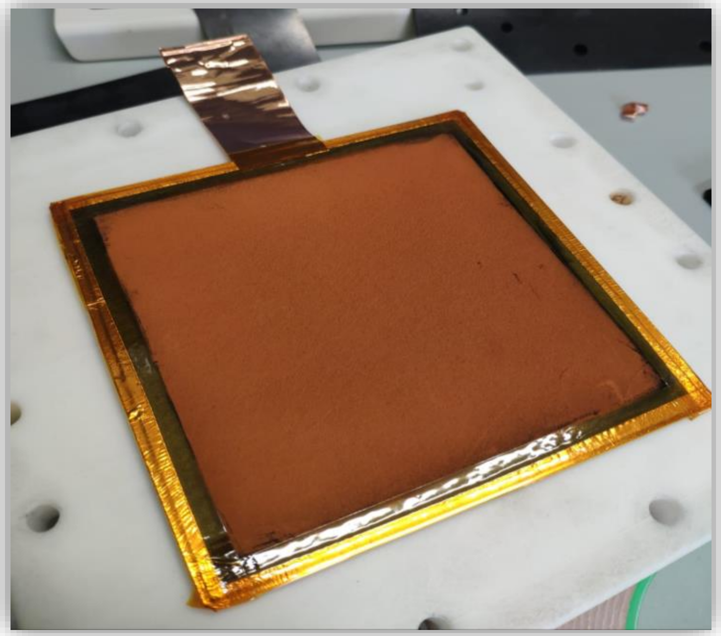
Let's employ

- Low-cost Cu-based GDE as Cathode
- Fluegas as a feedstock
- **Coupling of CO_2 separation with conversion**
- Scale-up the system to 100 cm^2

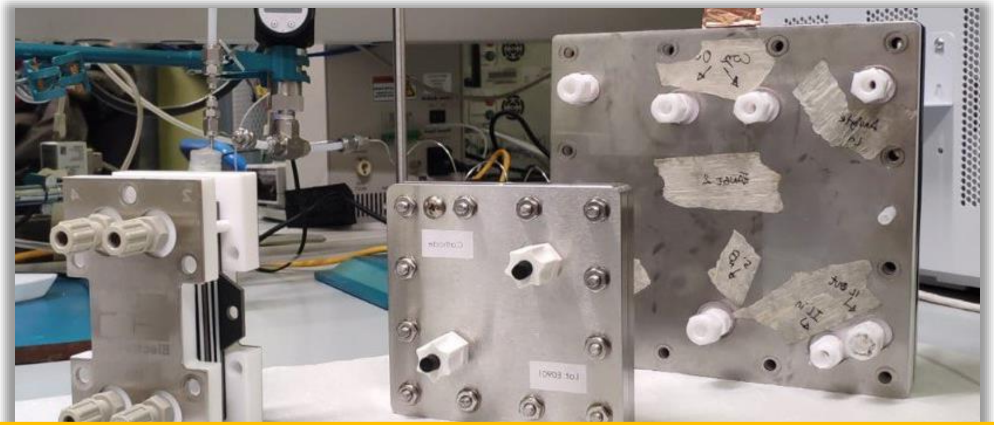


10 cm^2





100 cm^2



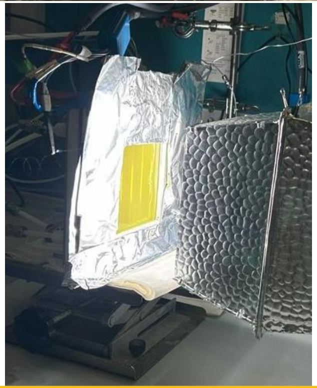
Zammillo F., Guzmán H., Hernández S., et. al.
Paper under preparation.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 862192.

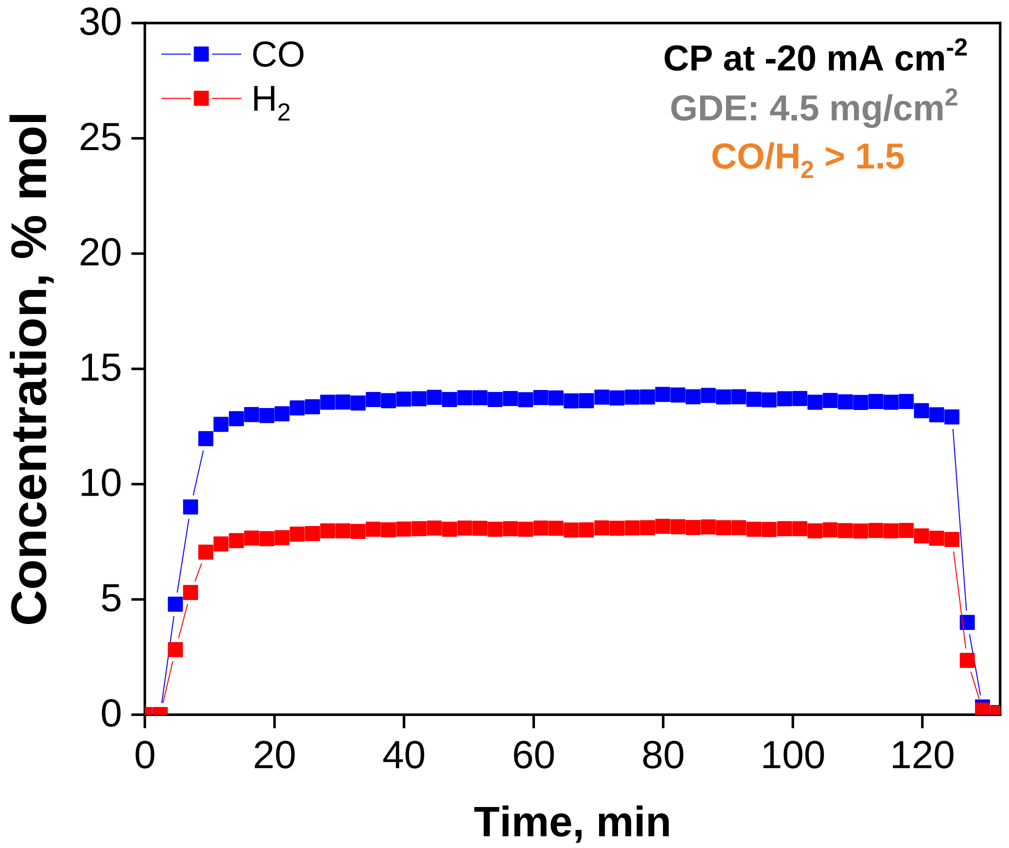
Sun-driven CO_2 capture and conversion

SunCO$_2$Chem

Scaling-up at 100 cm^2



Full TPER ($BiVO_4$ Photo-anode & dark Cathode)



CO_2 conversion: 30%

STF efficiency = 3.9% (without PV cells)

> 4.5% with PV cells providing 4.4V

Zammillo F., Guzmán H., Hernández S., et. al. Paper under preparation.

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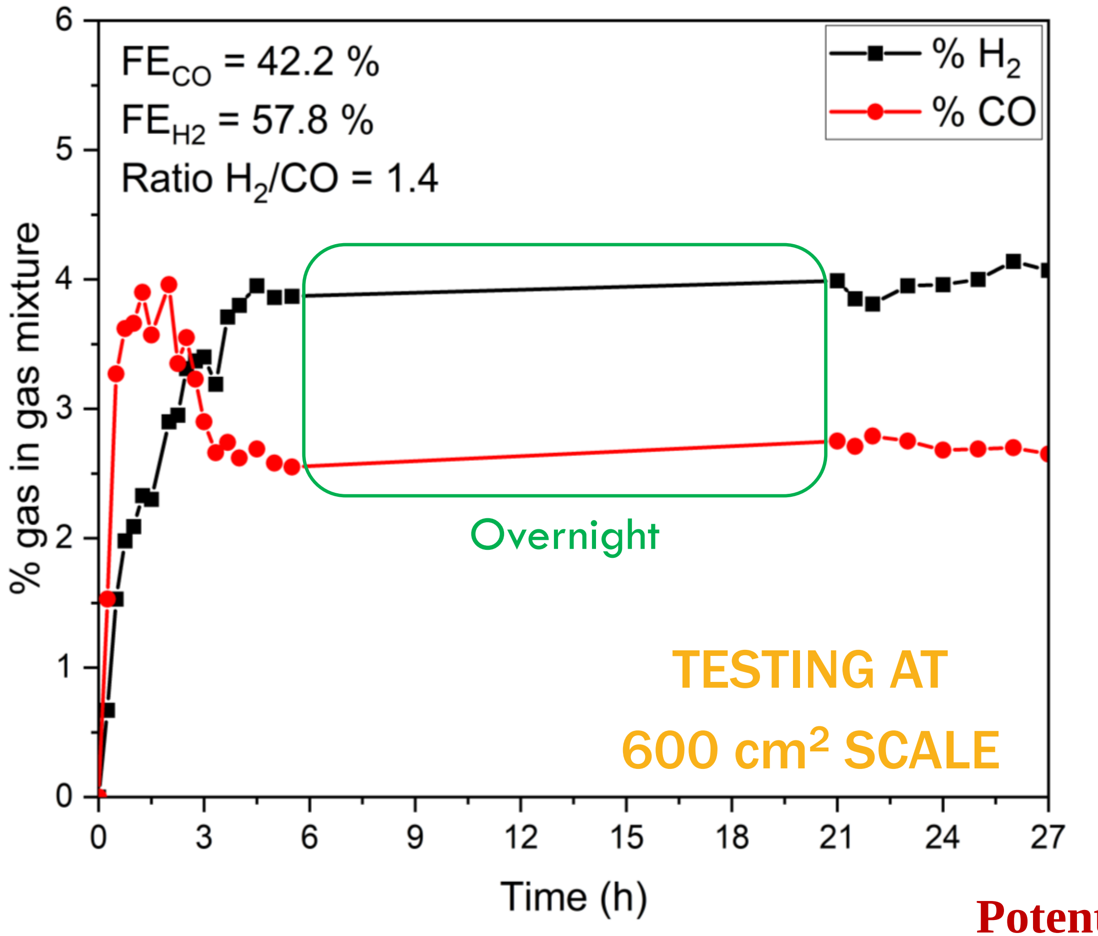
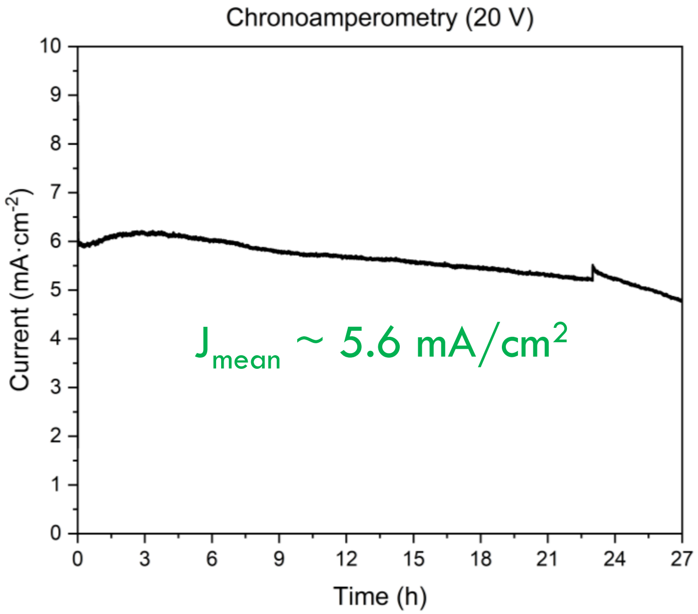
TRL4 validation campaign

Scaling-up at 500 cm^2

Stability test of 1 string of 5 cells at a constant **20 V (4V each cell)**



- **Stability demonstrated for 27 h** of continuous test under bias.
- After steady-state, **Syngas with FE ~100 % was stably generated.**
- **TRL5 prototype is being optimised** to enhance performance by reducing internal resistances and electrical losses.



Potential STF eff. 4 – 4.5 % (under simulated sunlight irradiation)

Zammillo F., Guzmán H., Hernández S., et. al. Paper under preparation.

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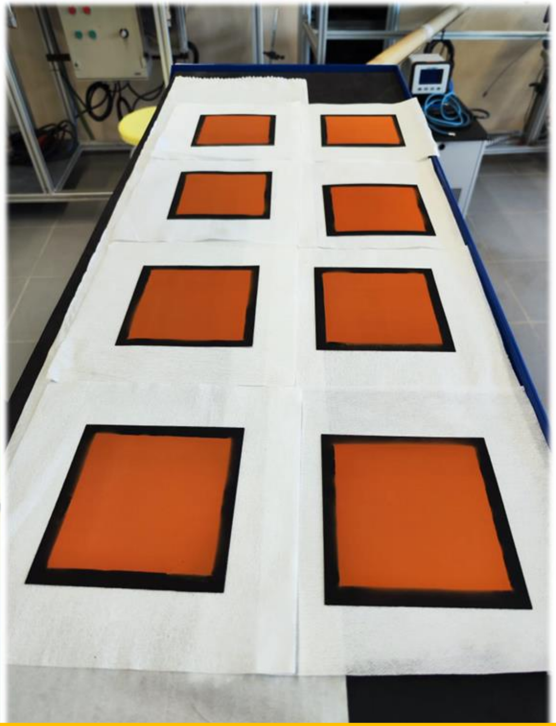
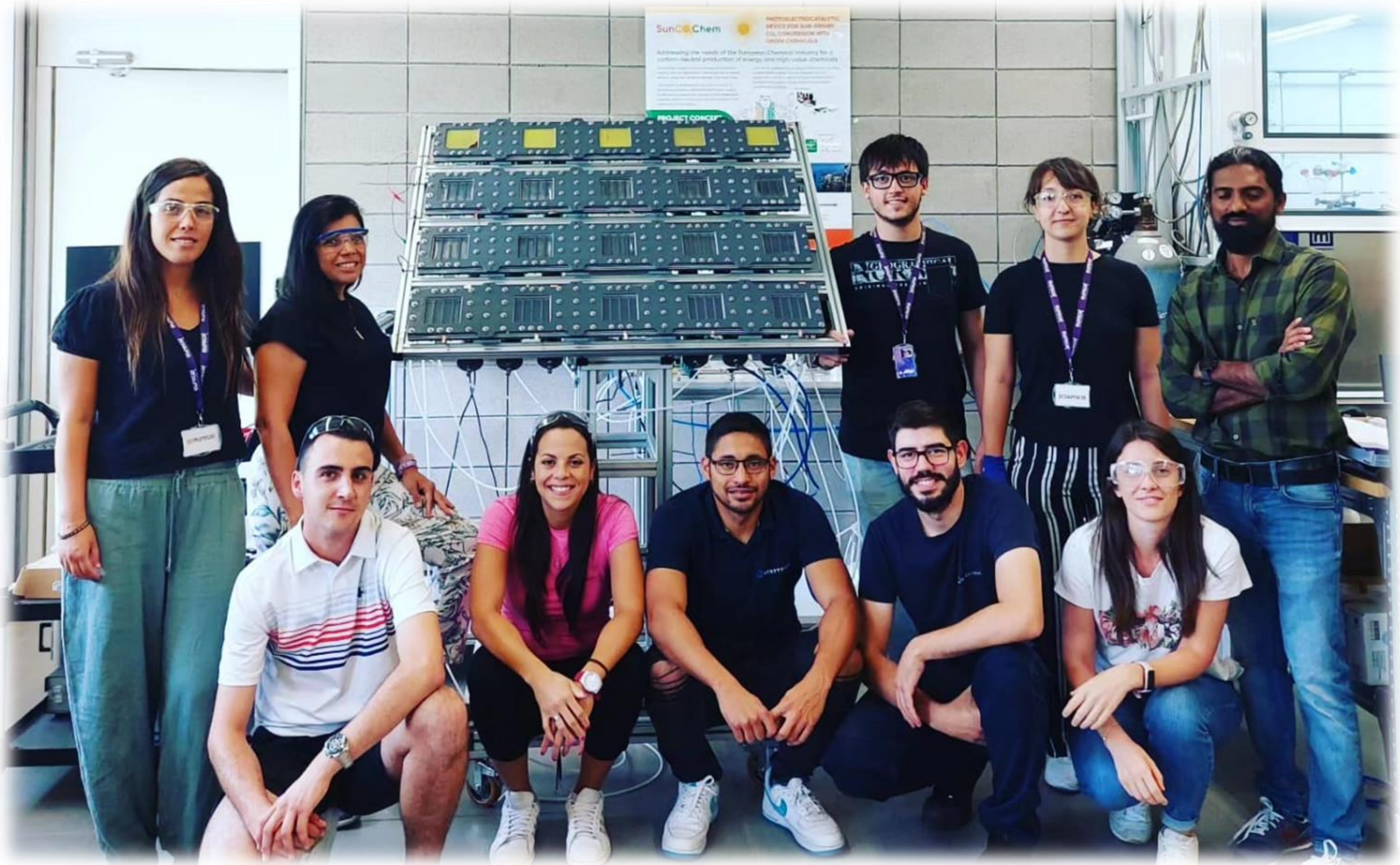
SunCoChem Test bench for TRL4 validation

SunCO2Chem

HORIZON 2020

Scaling-up at 0.24 m^2





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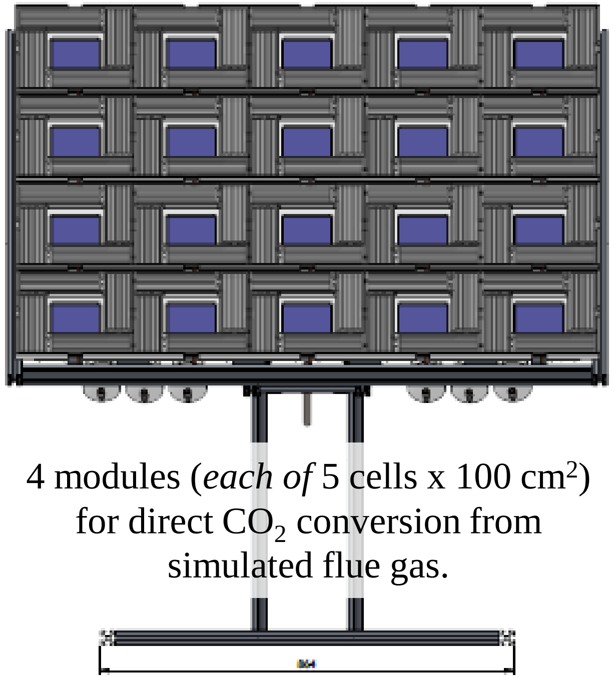
Politecnico di Torino

SunCoChem TRL4 Demonstration

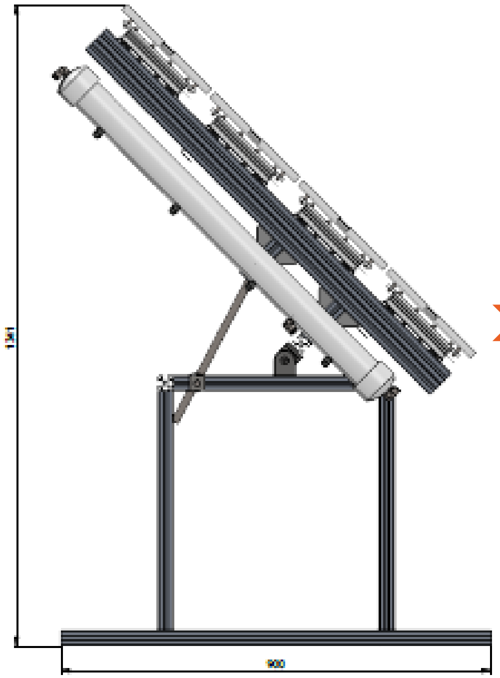
SunCO₂Chem

Scaling-up at 0.24 m^2

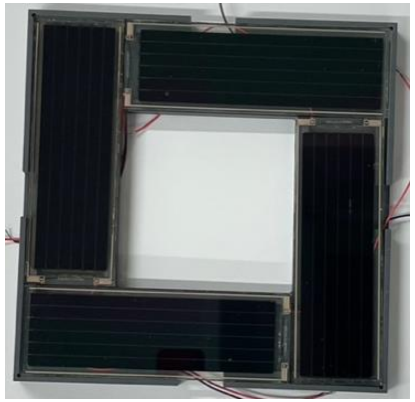
HySyTech

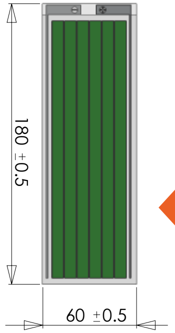


4 modules (*each of* 5 cells x 100 cm^2) for direct CO_2 conversion from simulated flue gas.



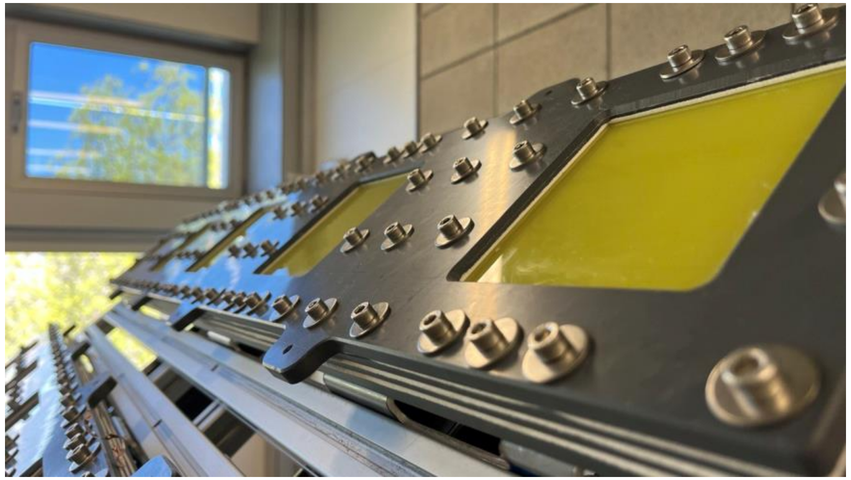
SOLARONIX





Sun simulator

4 Perovskite-based PV modules will be integrated on each PEC cell



- Photo-anode: **S-doped $BiVO_4$**
- Anolyte: Na-phosphate buffer (pH = 9) + Na_2SO_3
- Cathode: **Cu_2O/SnO_2-VTES_Re GDE**
- Catholyte: $KHCO_3$
- Membrane: **Bipolar membrane**

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SunCoChem TRL4 Demonstration

Scaling-up at 0.24 m^2

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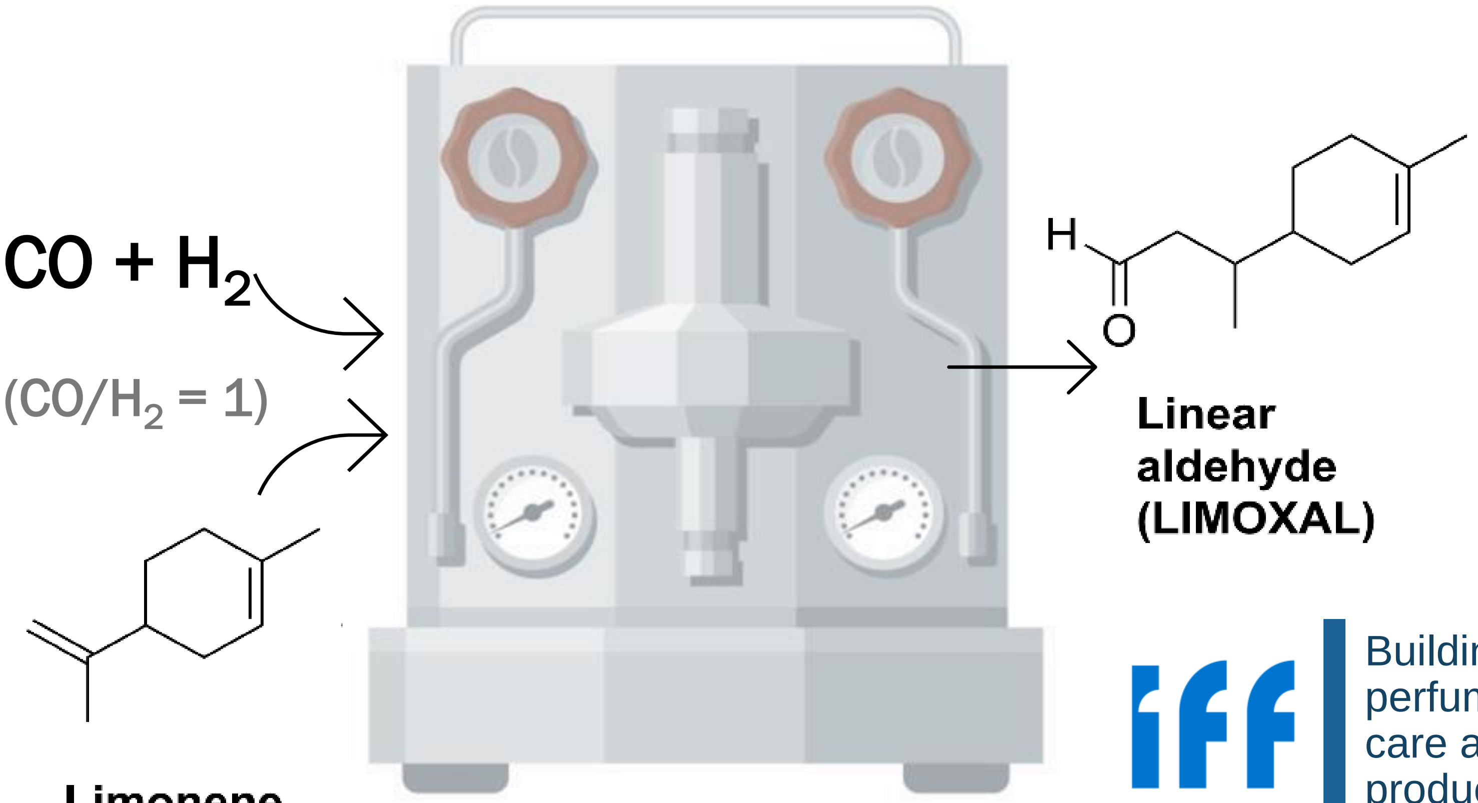
TRL4 Demonstration

Oxo-products synthesis from syngas

Limoxal ™

Hydroformylation of limonene



Limonene

Building block applied as a perfuming agent, in personal care and house cleaning products.

99% of Limonene conversion with CO_2 / CO / H_2 feedstock ($CO:H_2$ = 1:1) from TPER

> 89% of selectivity to linear aldehyde

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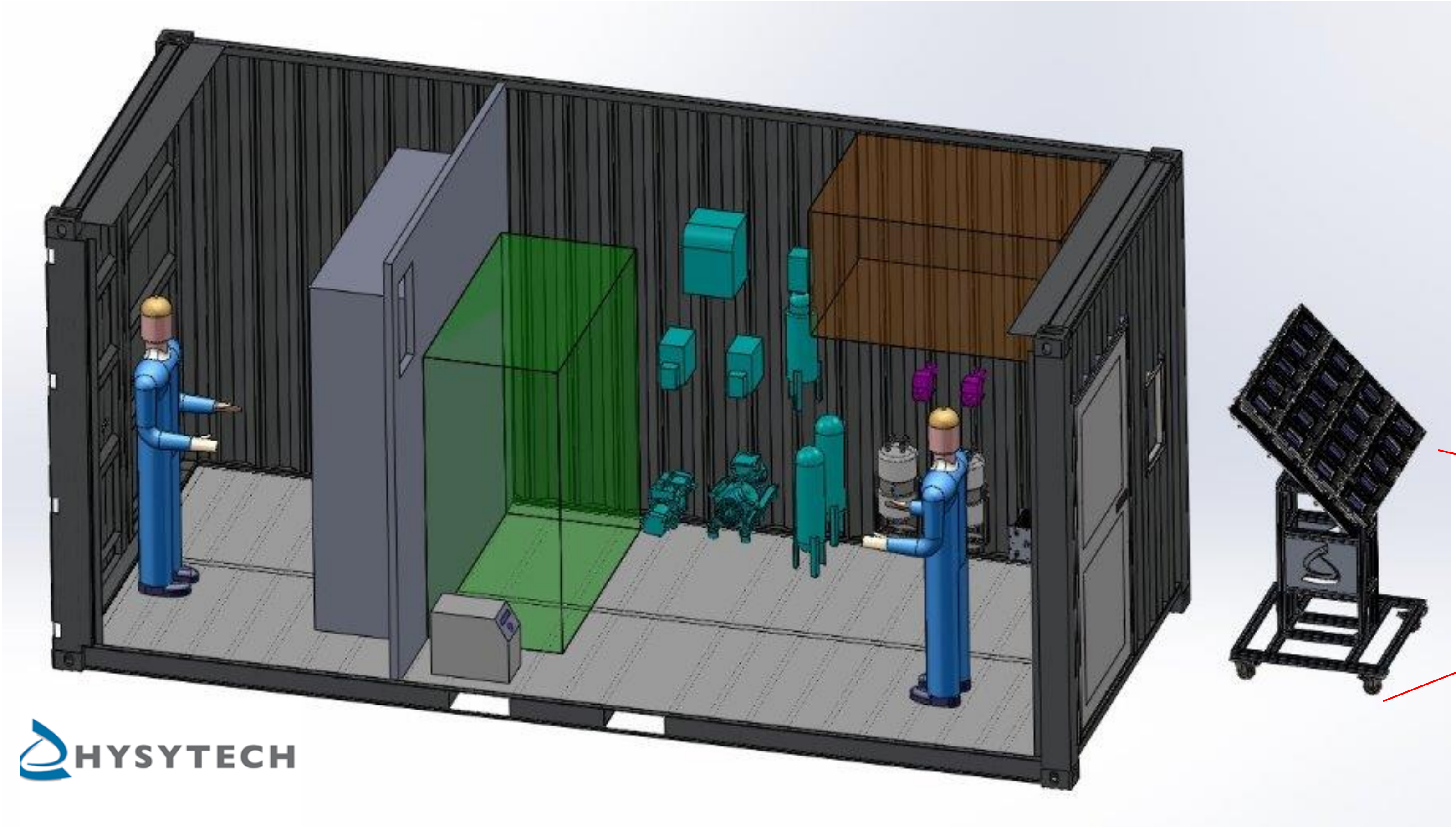
SunCO$_2$Chem

TRL5 Demonstration

Oxo-products synthesis from CO_2 water and sunlihgt



HYSYTECH

eurecat

Amposta, Spain

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Exploitation Outcomes

7 Prioritized results out of 15 SUNCOCHEM results (M22/M48)

- Selective polysulfide membrane for CO_2 Capturing
- High-voltage perovskite solar cells
- Scale-up of the synthesis of metal oxides nanoparticles
- Ionic liquids for CO_2 reduction, their synthesis and purification
- Scaled-up photoelectrodes for water splitting and O2 evolution
- Photo-electrochemical reactor for the sustainable production of syngas from CO_2
- Scalable solar fuel device design that allows for high solar energy conversion efficiency

✓ **End-users:**
Scientific community, chemical, goods and CO_2, Original Equipment Manufacturers (OEM's), among others

✓ **Time-to-market:**
4-15 years depending on the result

✓ **Exploitation routes:**
IPR Protection (Patents, trade secret, copyright), direct industrial use, further research and TRL increase

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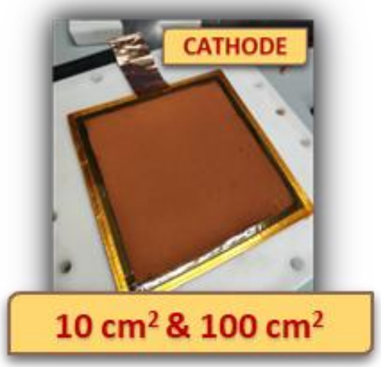
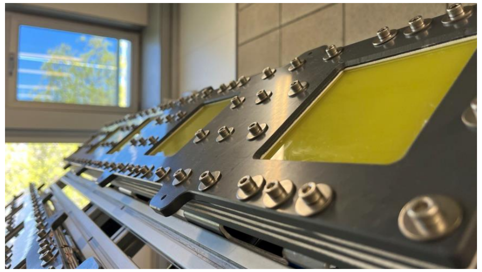
Conclusions

- We established a protocol for the **reproducible and scalable catalysts synthesis & preparation of $BiVO_4$ and Cu-based GDEs from 10 to 100cm^2**



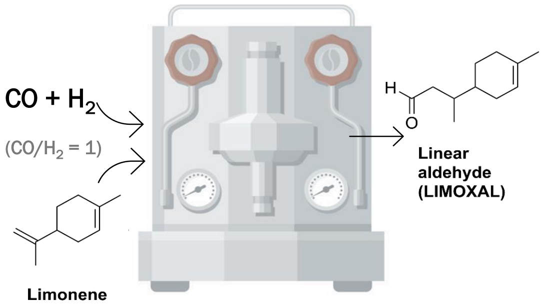
- A long-term test (24h) **at 10 cm^2** scale of the **Cu-based GDEs showed good stability** towards CO production (**FE = 90%**), **offering different market possibilities (CO/H_2 ratios)** depending on the operative condition.

- A **high CO_2 capture and conversion (25%) efficiency was achieved at 100 cm^2** scale.



- The **SunCoChem TPER demonstrated a STF efficiency close to 4%.** It was **scaled-up in a modular system of total 0.2 m^2** and is ready to be tested under simulated sunlight.

- NEXT STEP: **TRL5 demonstration in October 2024 for production of Limoxal from CO_2!**



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SunCO2Chem

Final Conference

Advancing towards a carbon-neutral and sustainable chemical production

OCTOBER 23rd 2024
9:30 – 16:15 CEST

HYBRID EVENT:
Eurecat's facilities in Tarragona
In streaming via Zoom

Register at:
https://cutt.ly/SunCoChem_Event

SunCO2Chem

SunCO2Chem

Thank you for your attention!
& Follow the TRL5 demonstration of SunCoChem

@SunCoChem_EU www.suncochem.eu info@suncochem.eu

The financial support of the SUNCOCHEM project (Grant Agreement No 862192) of the European Union's Horizon 2020 Research and Innovation Action programme is acknowledged.