EERA AMPEA 16th JPSC meeting &
Workshop on "Carbon Capture, Storage & Utilization"

March 10 - 11, 2021

ALMA MATER STUDIORUM
UNIVERSITÀ DI BOLOGNA

Advanced materials for CCUS (at UniBo)

From nano-membranes to electrodes for CO_2 reduction

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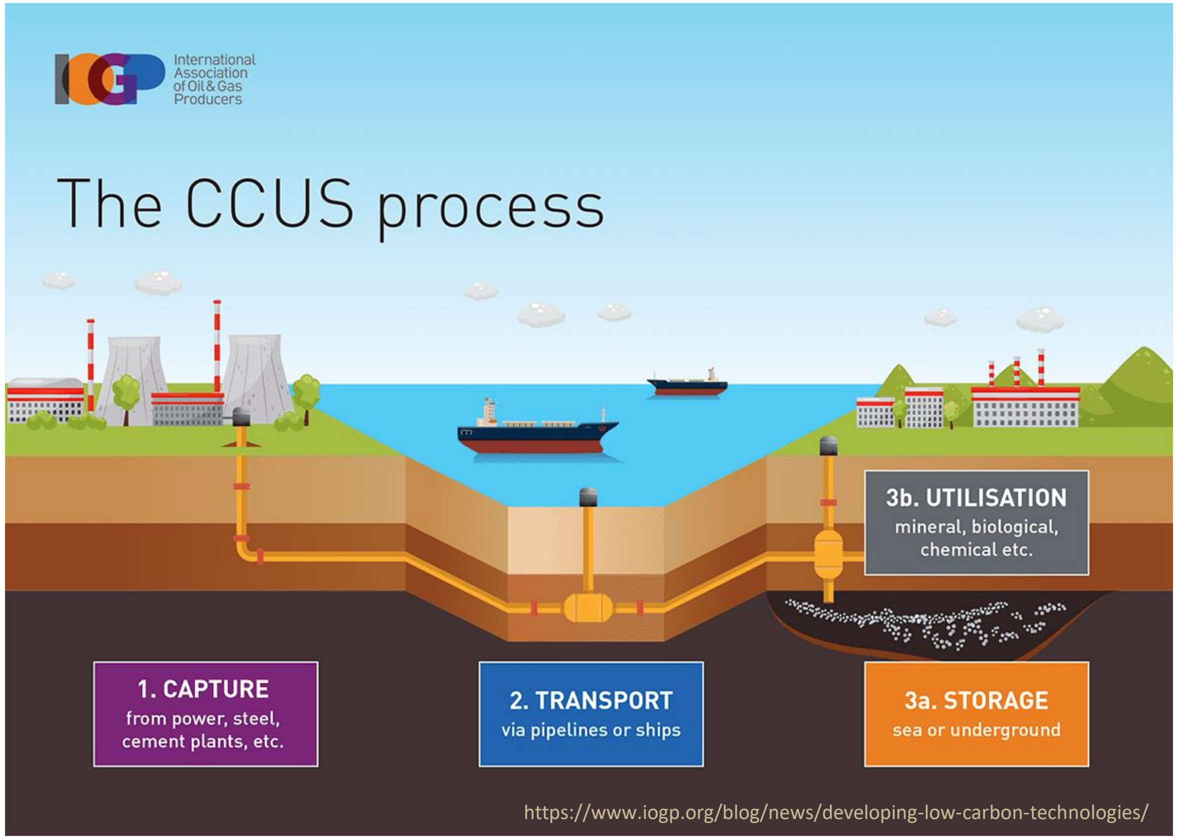
CCUS at UNIBO

- *Innovative Membranes for Carbon* ***Capture****:*
  - *Facilitated Trasport membranes for post-combustion Carbon Capture*
  - *Molecular sieves for pre-combution Capture.*
- *Modeling CO_2 - polymers interaction in* ***Transport*** *pipelines*
- *Coupled wellbore-reservoir flow simulations for CO_2 Geological* ***Storage***
- *CO_2* ***Utilization*** *strategies:*
  - *Photo-electrochemical reduction*
  - *Catalytic reduction*
  - …
  - …



Background on membrane separation

Membranes are material barriers that allow the passage of chemical species at different speed, thus allowing their separation .

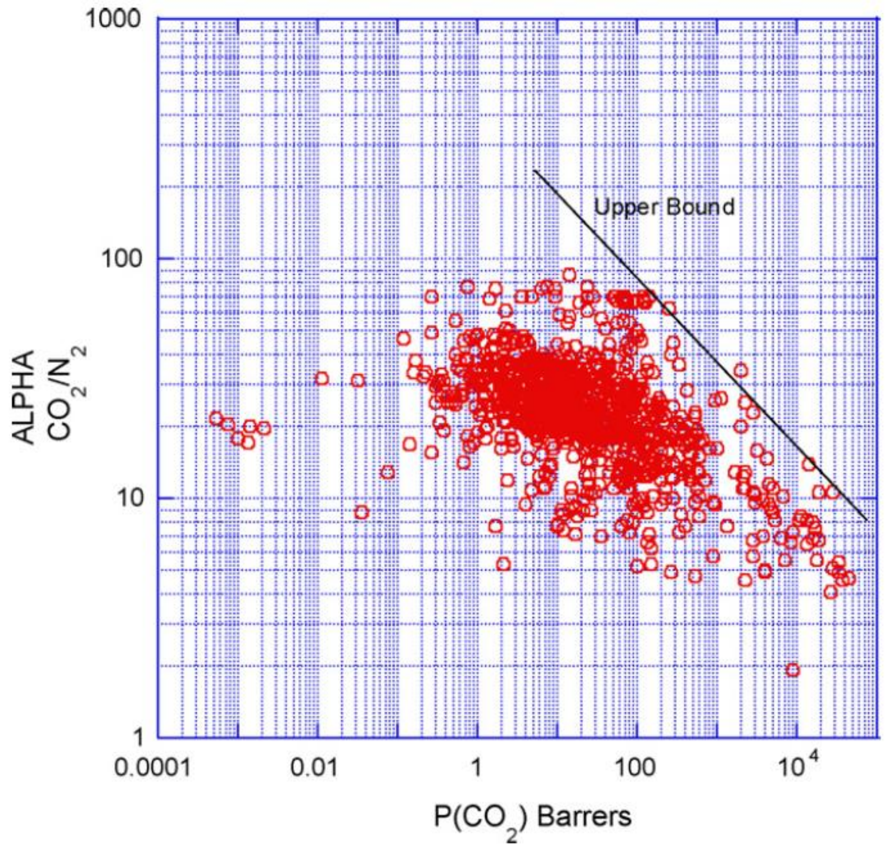
Their performances are related to their

- ***Permeability** related to the flow they can sustain:*

$$J_i = \frac{P_i}{\delta}\left(p_{i-up} - p_{i-down}\right)$$

- ***Selectivity** which define the separation ability:*

$$\alpha_{ij} \equiv \frac{y_i^d \big/ y_j^d}{y_i^u \big/ y_j^u} \underset{p_d \to 0}{\cong} \frac{P_i}{P_j}$$

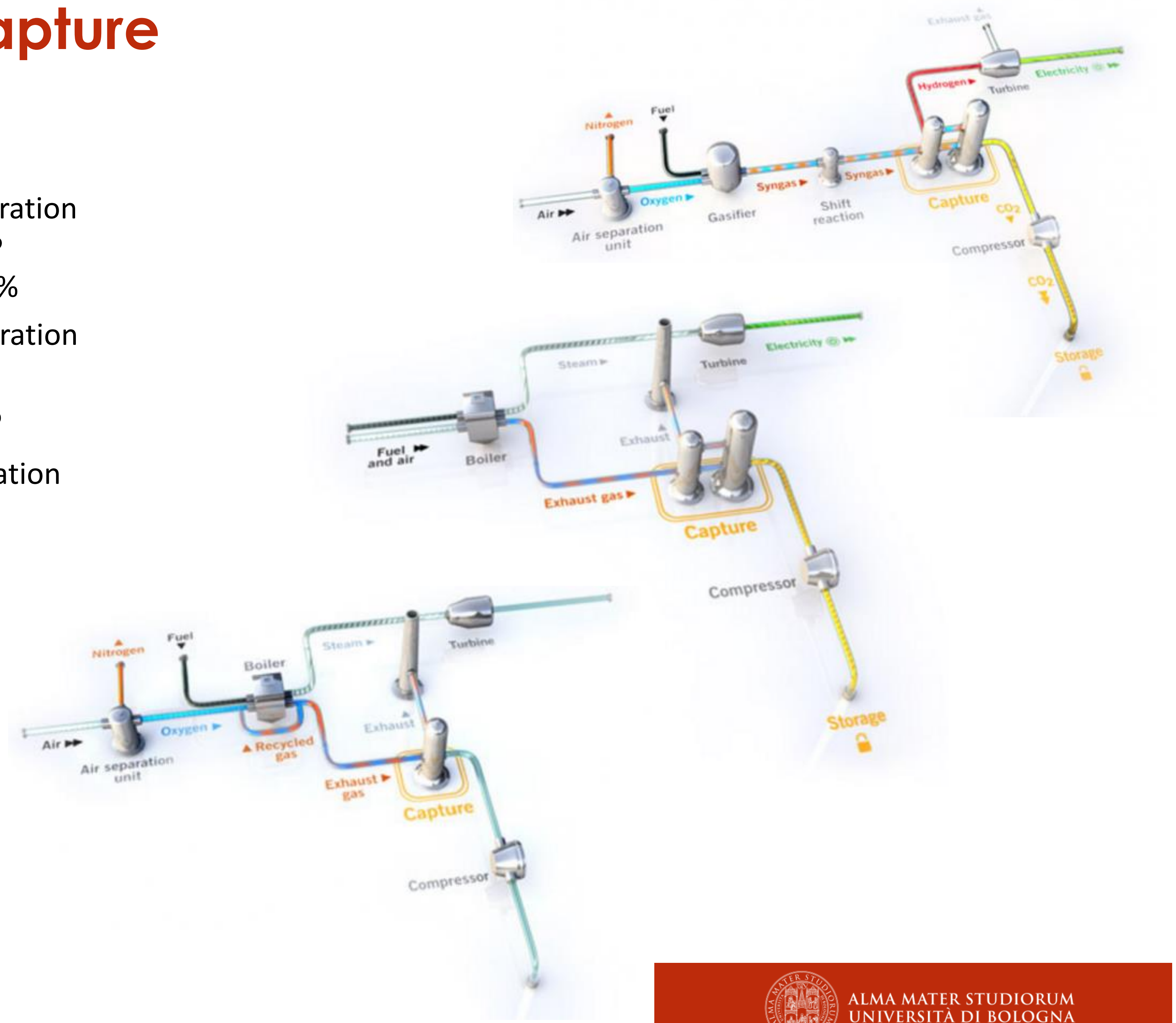


*Unfortunately in polymeric membranes a **trade off** exists between these two parameters, that makes difficult the development od highly permeable yet selective membranes.*

Membranes and CO_2 Capture

Different approaches to CO_2 Capture

Pre-Combustion →	H_2-CO_2 Separation High T and P $CO_2 \approx$ 15-50%
Post-Combustion →	N_2-CO_2 Separation low T and P $CO_2 \approx$ 5-10%
Oxyfuel →	N_2-O_2 Separation low T, and P, $O_2 \approx$ 21%



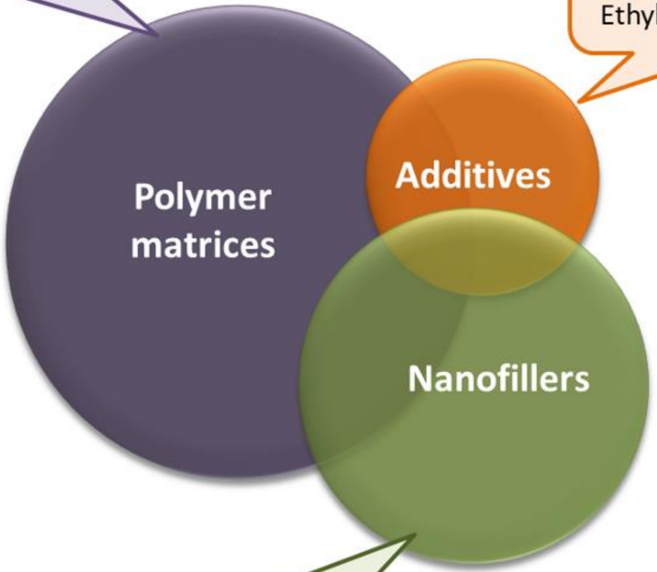
The nanomemc² Project

NanoMaterials Enhanced Membranes for Carbon Capture

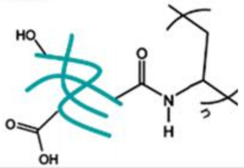
Grant Agreement no. 727734

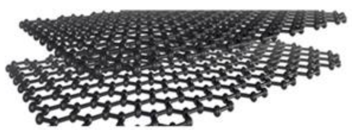
PVAm, PVA, PAA,PPO, PTMSP, PEBAX, Mod-PEBAX, SHPAA(A), SHPAA(B), $BmimNO_3$, PDMS

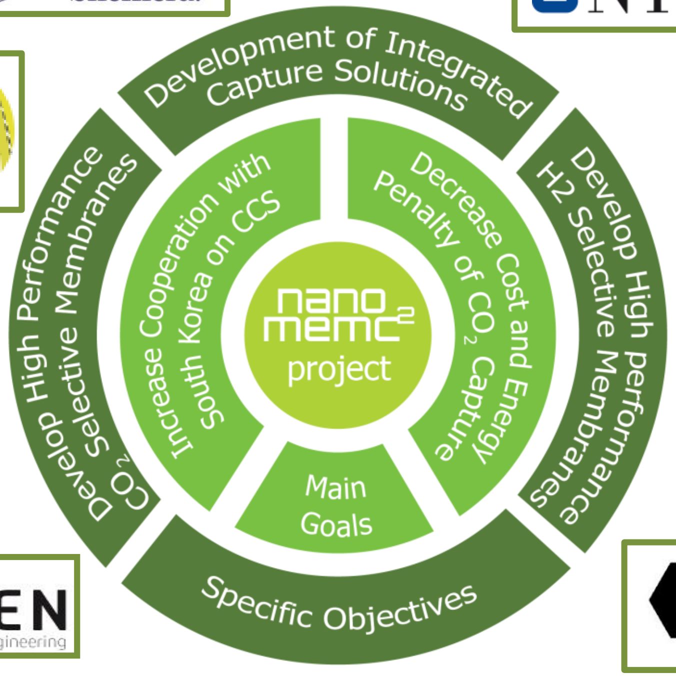
Emim Ac, ProK, L-Arginine, Glycine K, Cysteine K, Ethylamine Sarcosinate



Graphene, GO, pGO, GO-PVAm, MFC, CMC, MFC-PEG4, MFC-PPG, MFC-B-Alanine

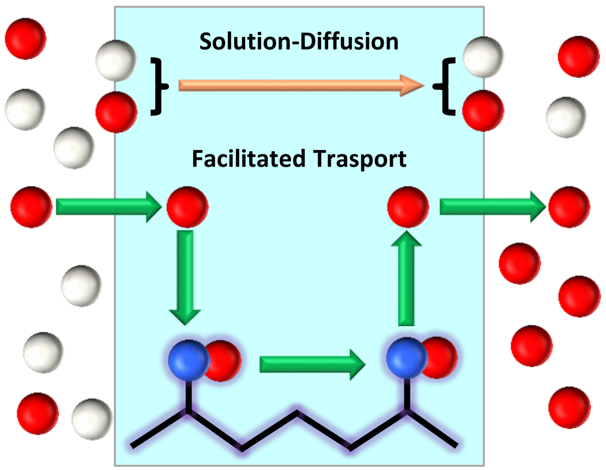


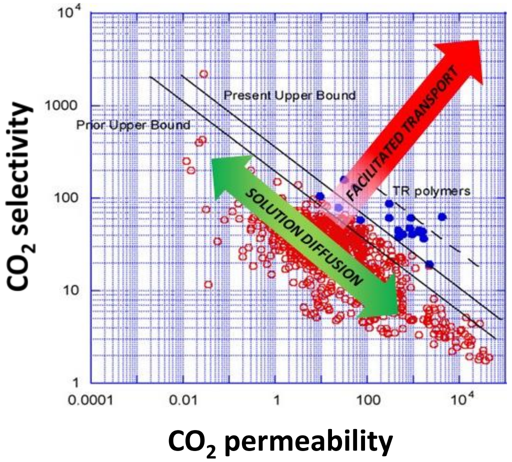




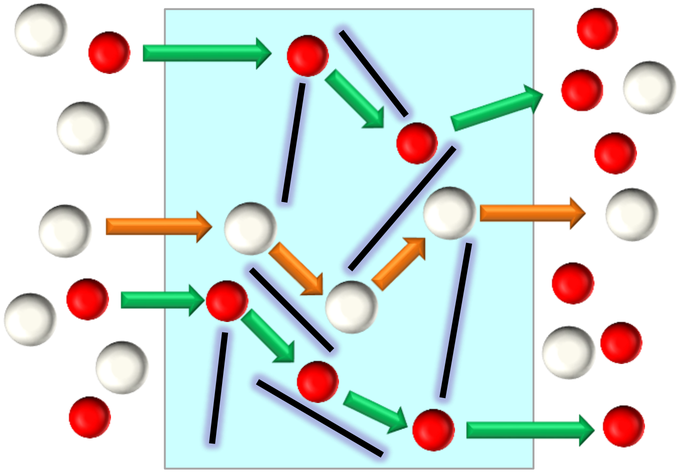
The nano memc² Project

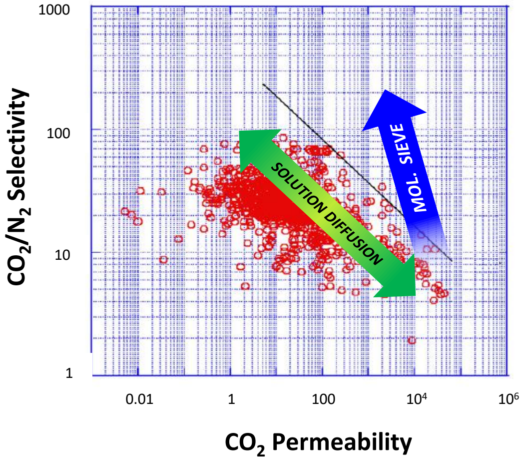
Facilitated Transport Hybrid Membranes

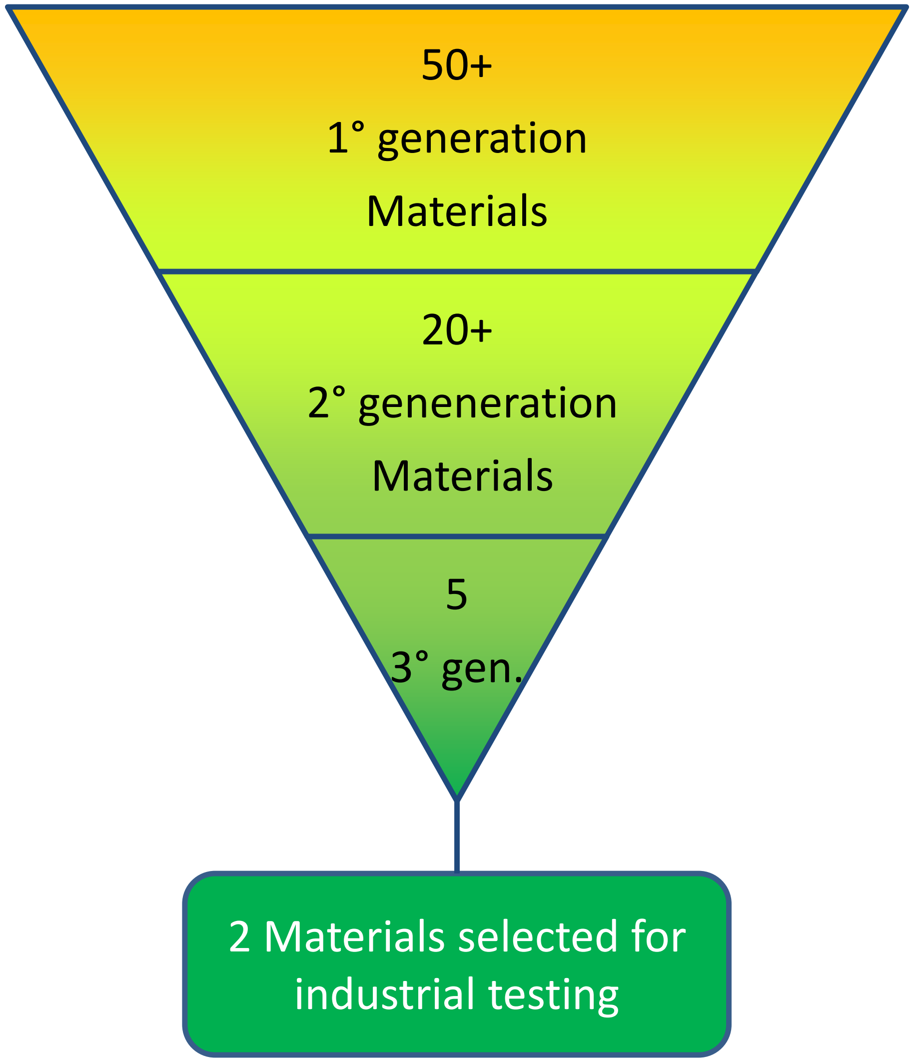




Molecular Sieves Hybrid Membranes







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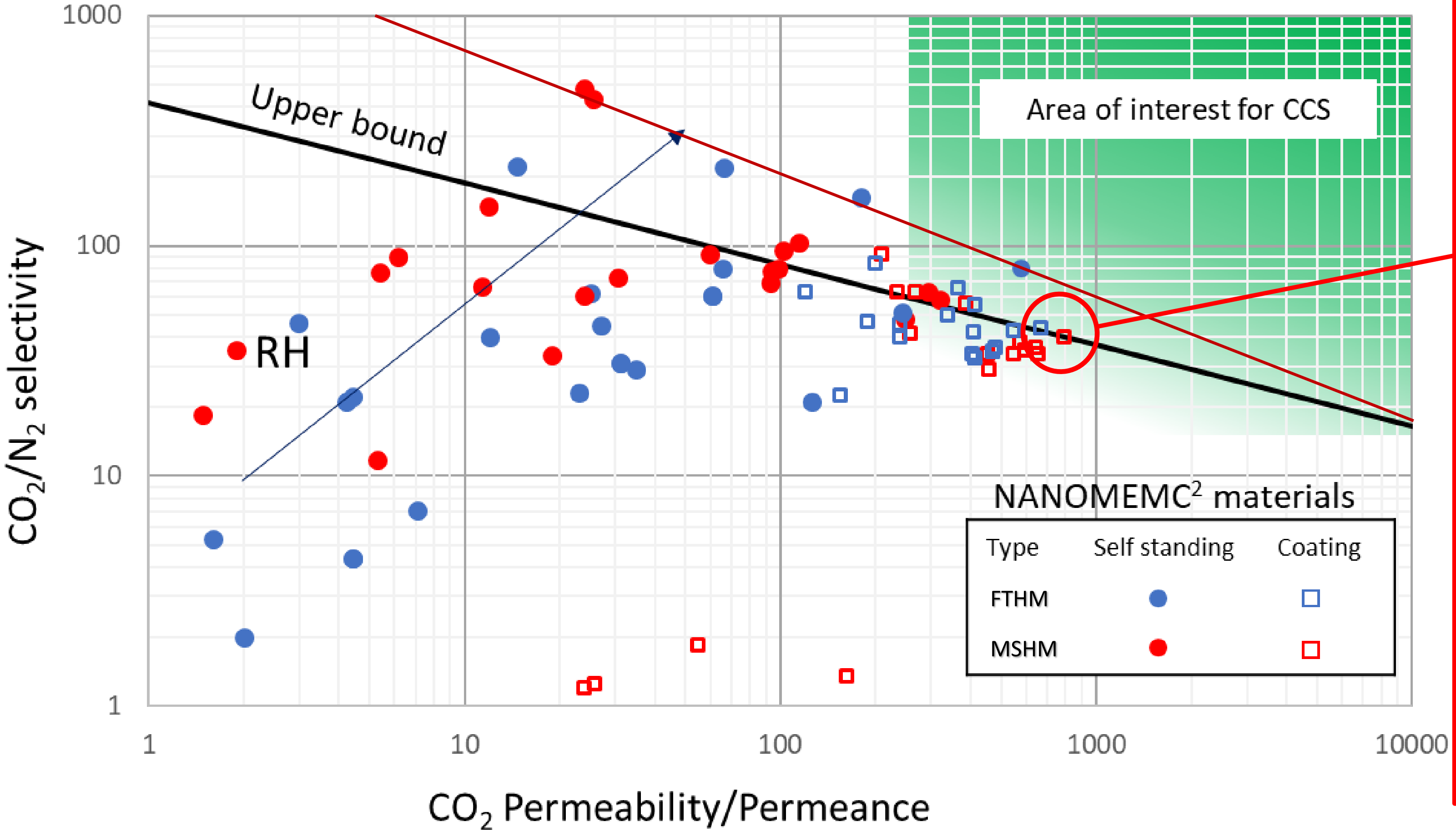
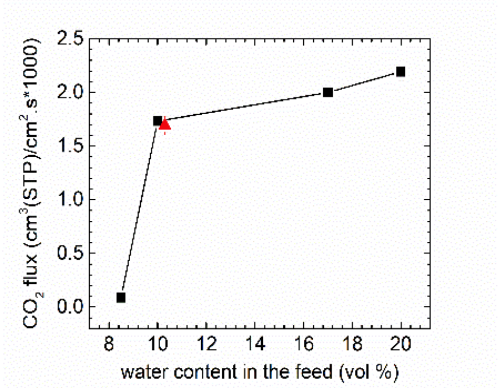
The nanomemc^2 Project

NANOMEMC^2 upper bound





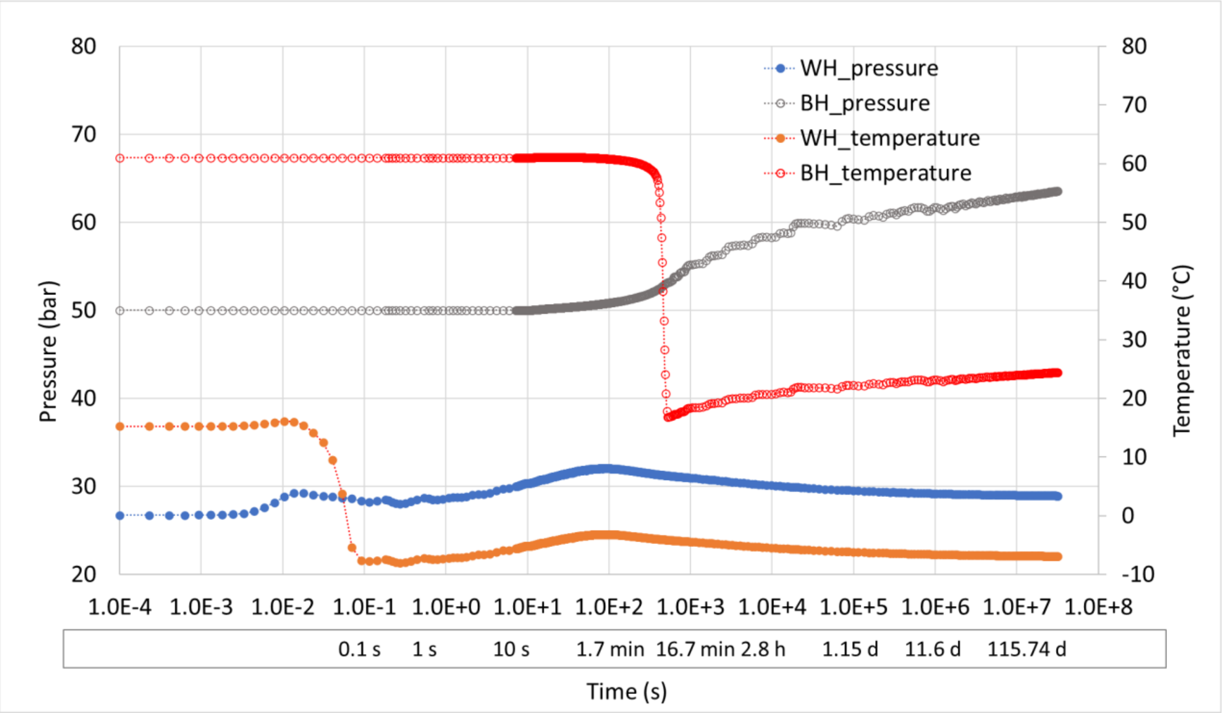
Casadei R.; Giacinti Baschetti M. et. Al. *Pebax® 2533/graphene oxide nanocomposite membranes for carbon capture*, «MEMBRANES», 2020, 10
Venturi D.; Chrysanthou A. et Al., *Arginine/Nanocellulose membranes for carbon capture applications*, «NANOMATERIALS», 2019, 9,

Geological CO_2 storage

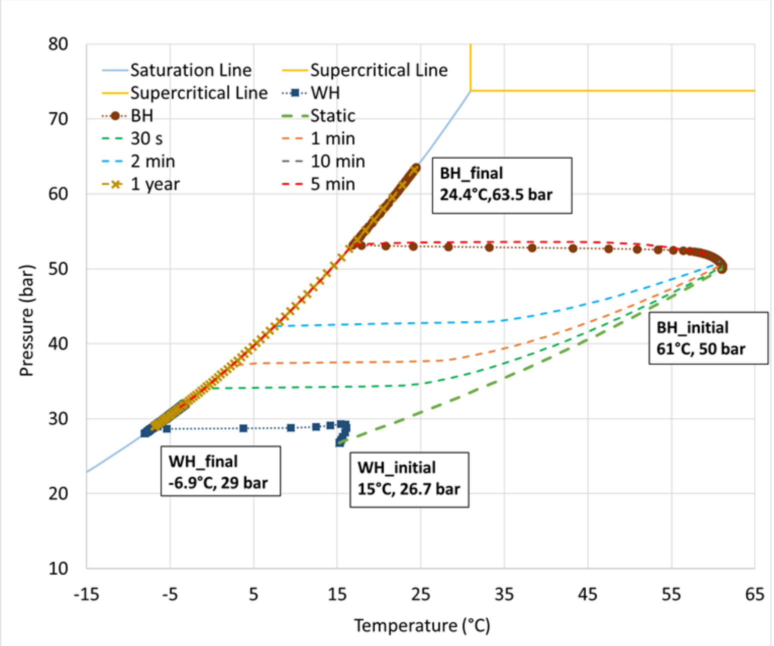
CO_2 injection entails sudden changes in CO_2 pressure and temperature with possible phase transitions that have severe effects on the integrity of wells and on the multiphase flow in the reservoir .

T2Well-ECO2M (LBNL, Berkeley, USA) is an integrated wellbore-reservoir numerical simulator for non-isothermal, multiphase, multicomponent flows that handles CO_2 injection in depleted reservoirs.

The geothermal research group at DICAM is involved in the improvements of the T2Well-ECO2M code.



CO_2 injection Well Head (WH) pressure, Bottom Hole (BH) pressure, WH temperature and BH temperature evolution.

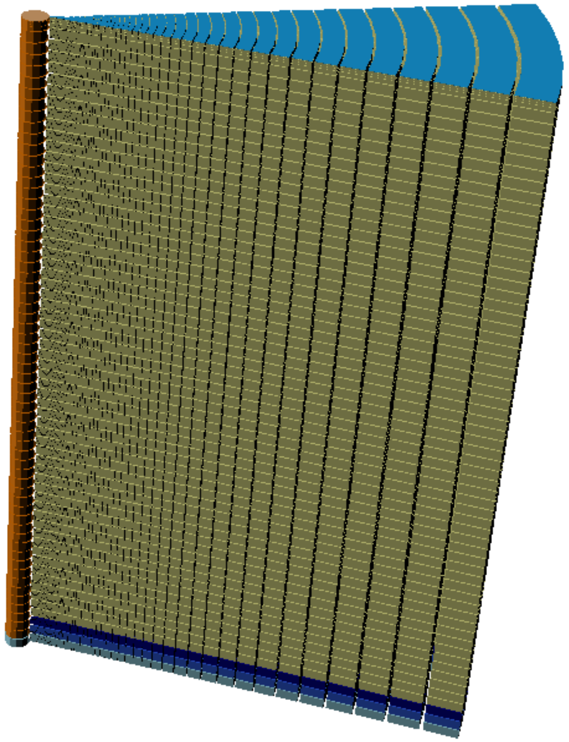


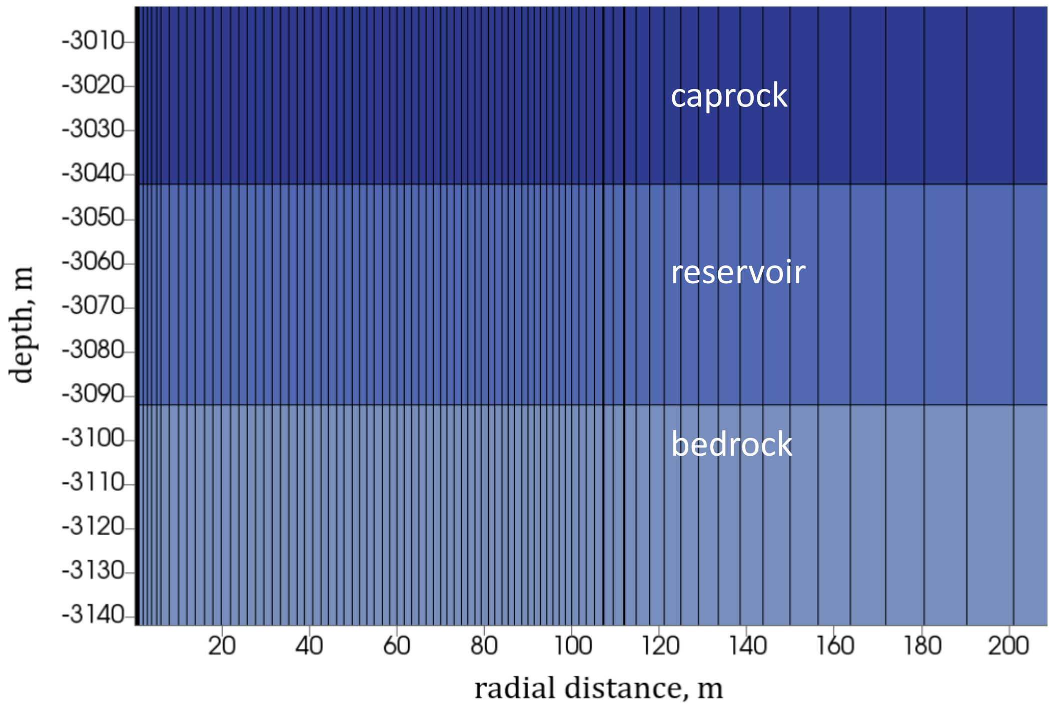
Phase diagram with the CO_2 saturation line, time evolution of WH and BH conditions and P-T profiles along the wellbore.

Numerical modeling entails pre-postprocess tools

Mesh visualisation with **TOUGH2Viewer** (developed at DICAM)

Conceptual model can consist of several domains defined by different petrophysical properties, wellbore and completion zone, surrounding rock, caprock reservoir and bedrock domain and also atmosphere.





CCS injection site 2D radially symmetric grid 8,160 block: left - 3D projection,
right - Horizontal mesh resolution

CO_2 Utilization strategies

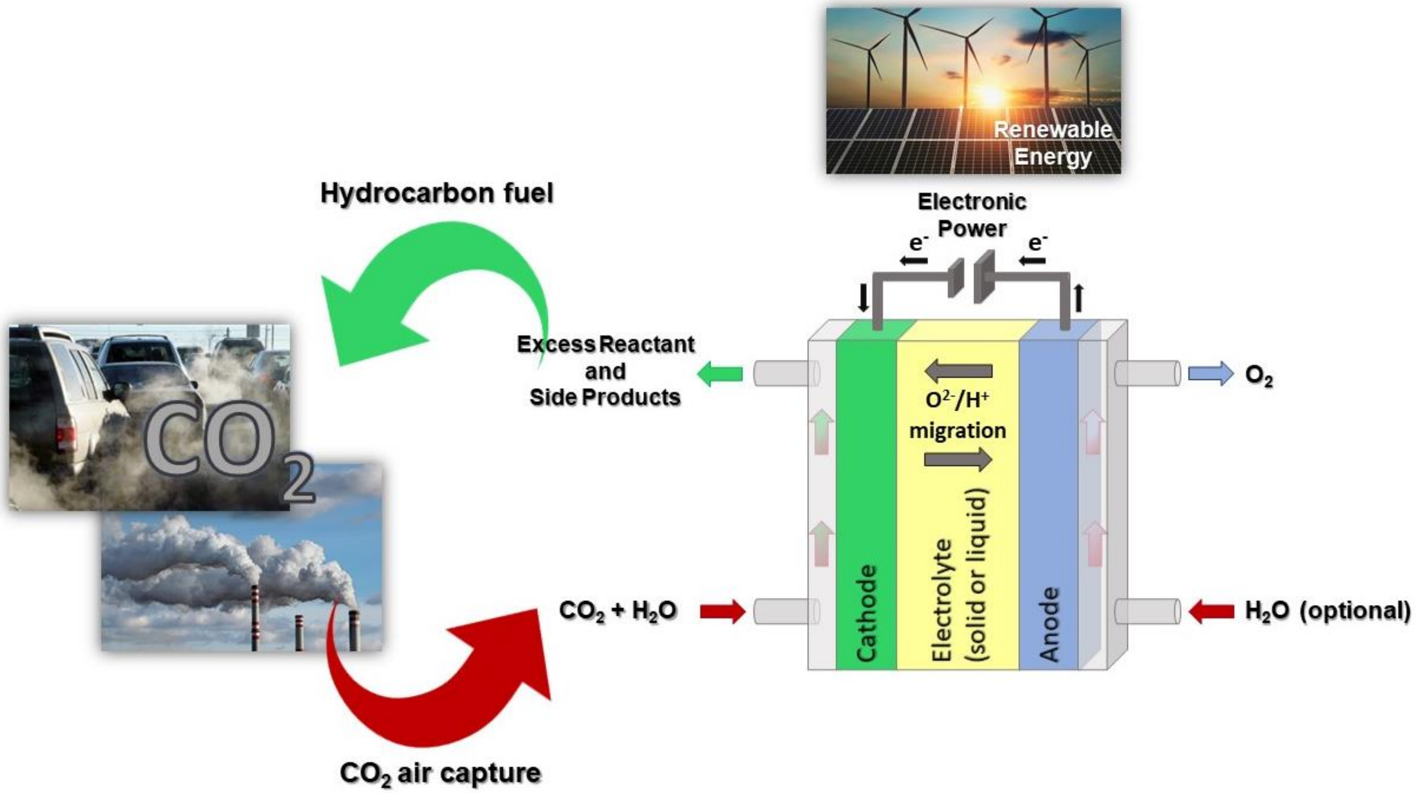
CO_2 Conversion: (photo) electrochemical Reduction

- The **(photo)electrochemical reduction reaction of CO_2 (CO2RR)** is very appealing for storing the excess of renewable energy into chemical bonds

- CO_2RR requires electrocatalysts to stabilize the $CO_2^{\bullet -}$ radical and intermediates

- Multiple electron-proton transfer reaction leads up to 16 different products some of the most valuable are: ethanol (C_2H_5OH), methane (CH_4) and ethylene (C_2H_4)

CO_2 electrolysis

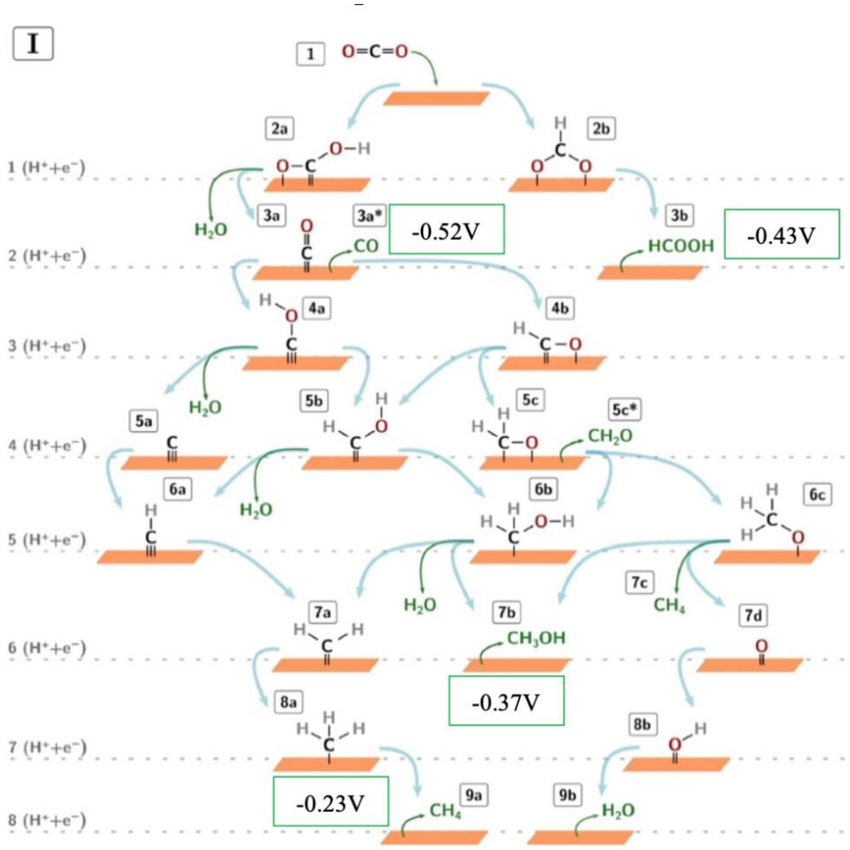


CO_2 Utilization strategies

CO_2 Conversion: Electrochemical Reduction

- It can be performed at **room temperature** and **ambient pressure**
- Low energy requirements (close to thermodynamic threshold)
- Electric power compatible with **renewable sources**
- Highly **controllable**
- High conversion **efficiency**
- Control over **reaction products**

Electrochemical conversion is advantageous for its **feasibility** and **industrial perspective**

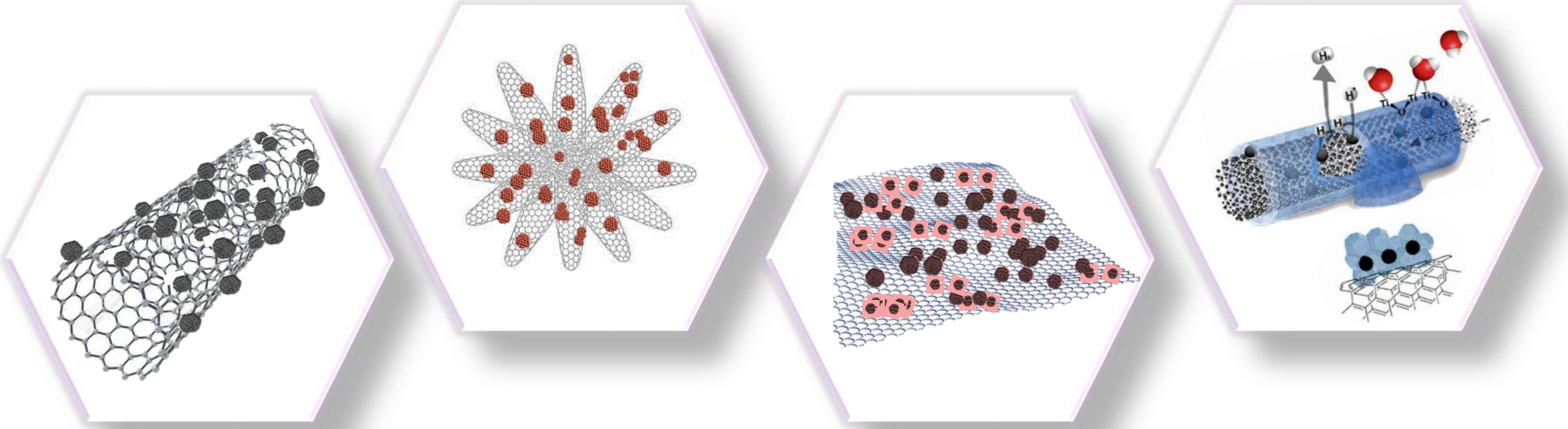


CO_2 Utilization strategies

Heterogenous Electrocatalysis

- Nanocomposite materials with innovative design:
  - ⇨ – Increasing the number of active sites
  - ⇨ – Increasing intrinsic activity

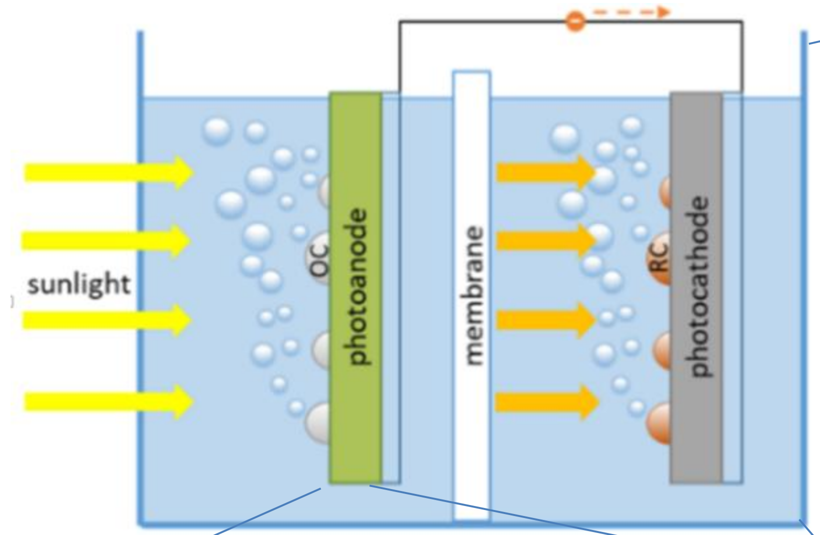
- High surface area
- High chemical stability
- Improve the selectivity and efficiency
- High currents with lower overpotentials

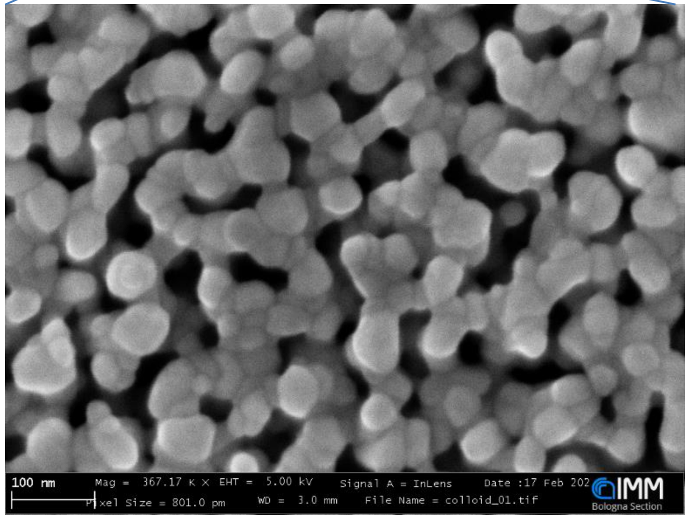


@Ni/NiO @Cu/CuO @Sn/SnO @CeO2

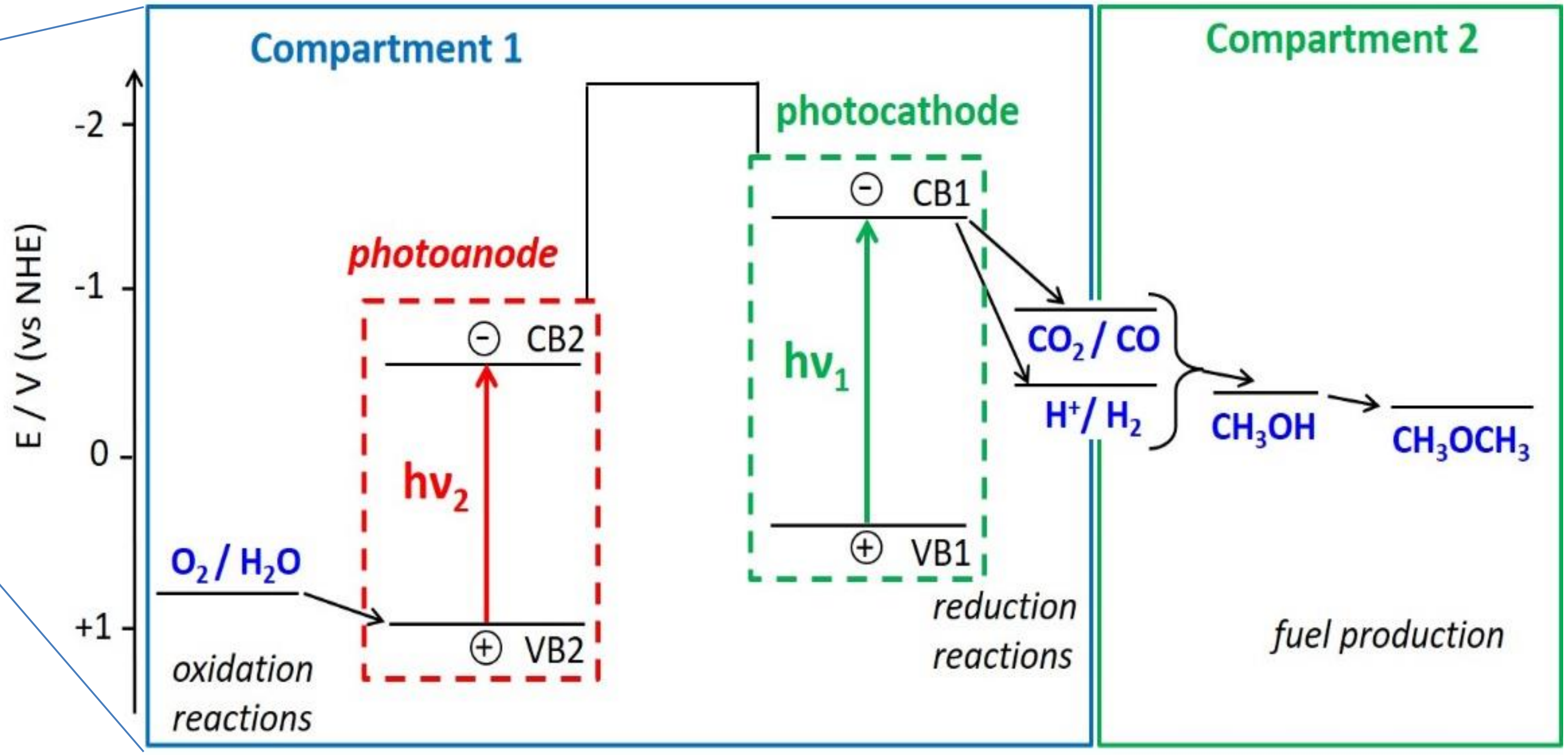
The CO2NDOR H2020 project

COmbined suN-Driven Oxidation and CO_2 Reduction for renewable energy storage





Nanostructured $WO_3/BiVO_4$ photoelectrode



https://condor-h2020.eu/

Coordinated by UNIBO

(Paola Ceroni, Luca Pasquini)

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CO_2 Utilization strategies

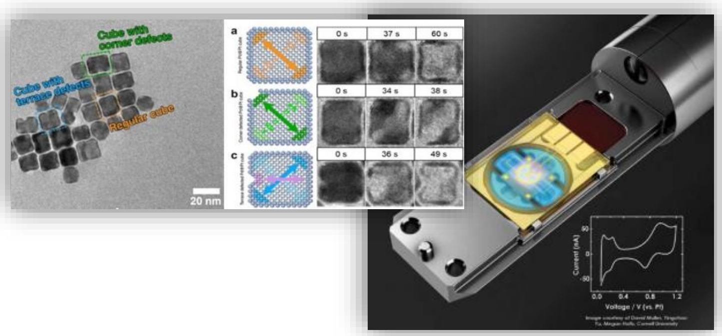
Our instrumentation

Potentiostats
Application of current or potential

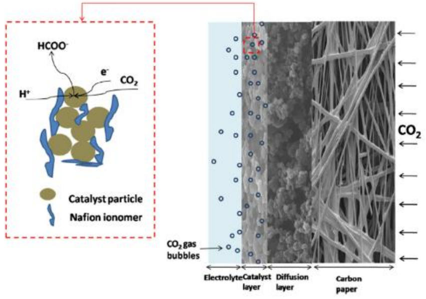
Gas Chromatographs
Analysis of gaseous products (H_2; O_2; CH_4; CO_2; CO)

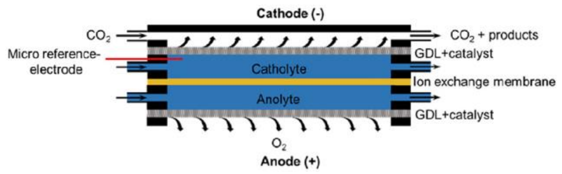
Ionic Chromatographs
Analysis of liquid products

Electrochemical In Situ TEM
Imaging during electrochemical measurements



Gas Diffusion Layer
To applicate the electrocatalyst in the electrolyser cell





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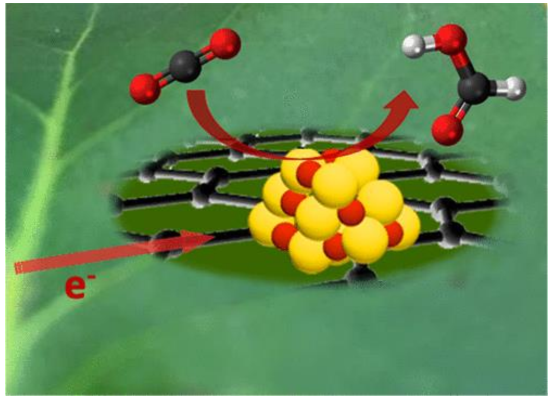
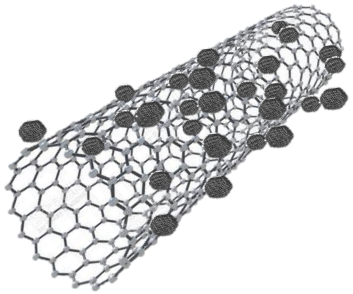
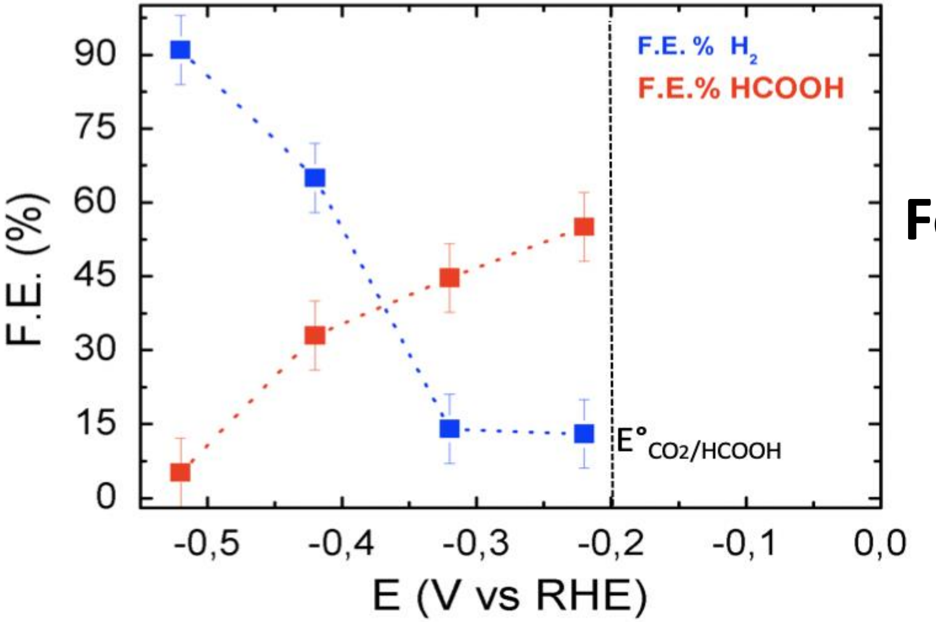
CO_2 Utilization strategies

Nanocomposite material: CNT@CeO_2



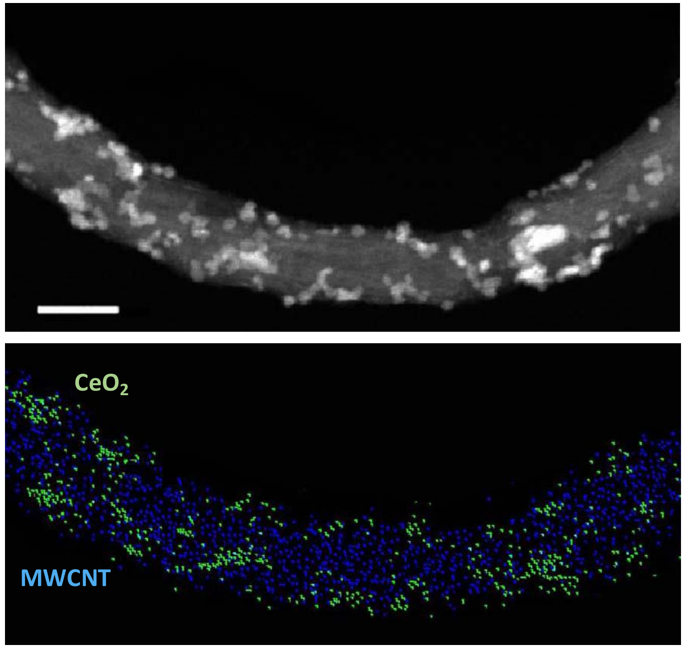




ACS APPLIED ENERGY MATERIALS
www.acsaem.org Article

Water-Mediated ElectroHydrogenation of CO_2 at Near-Equilibrium Potential by Carbon Nanotubes/Cerium Dioxide Nanohybrids

High FE for CO_2 conversion to Formic acid (50%)



CO_2 Utilization strategies

Nanocomposite material: Boron Doped Diamond @CeO_2

Very stable material with high FE for CO_2 conversion to Formic acid

Journal of Materials Chemistry A

ROYAL SOCIETY OF CHEMISTRY

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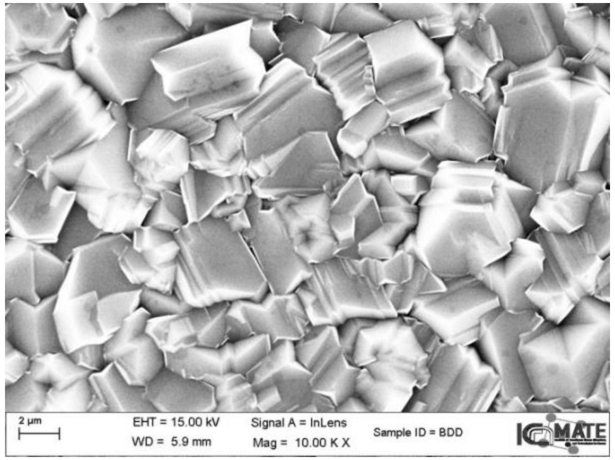
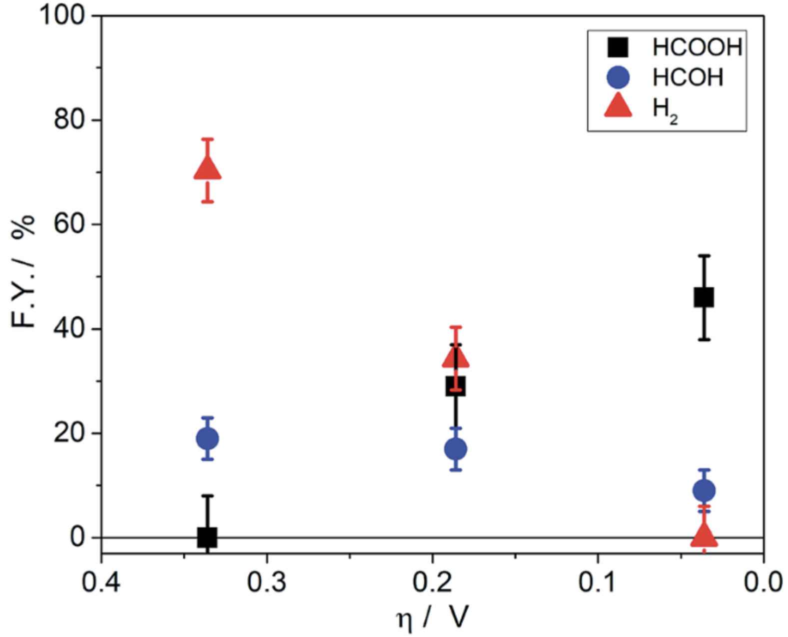
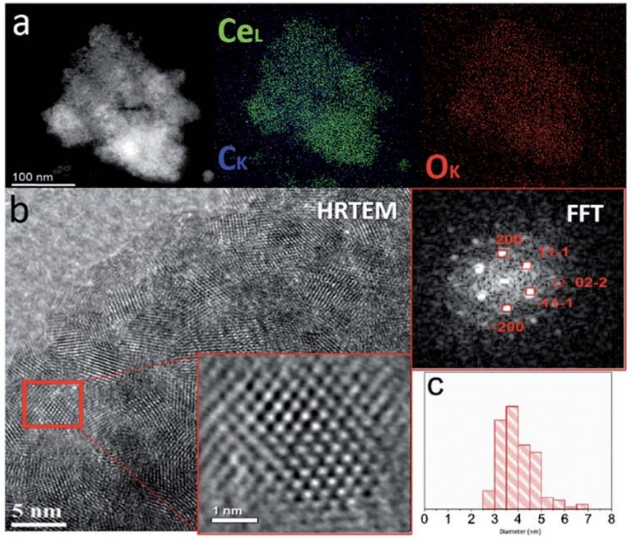
Cite this: *J. Mater. Chem. A*, 2019, 7, 17896

CO_2 reduction to formic acid at low overpotential on BDD electrodes modified with nanostructured CeO_2†







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Thank you!!

Questions

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