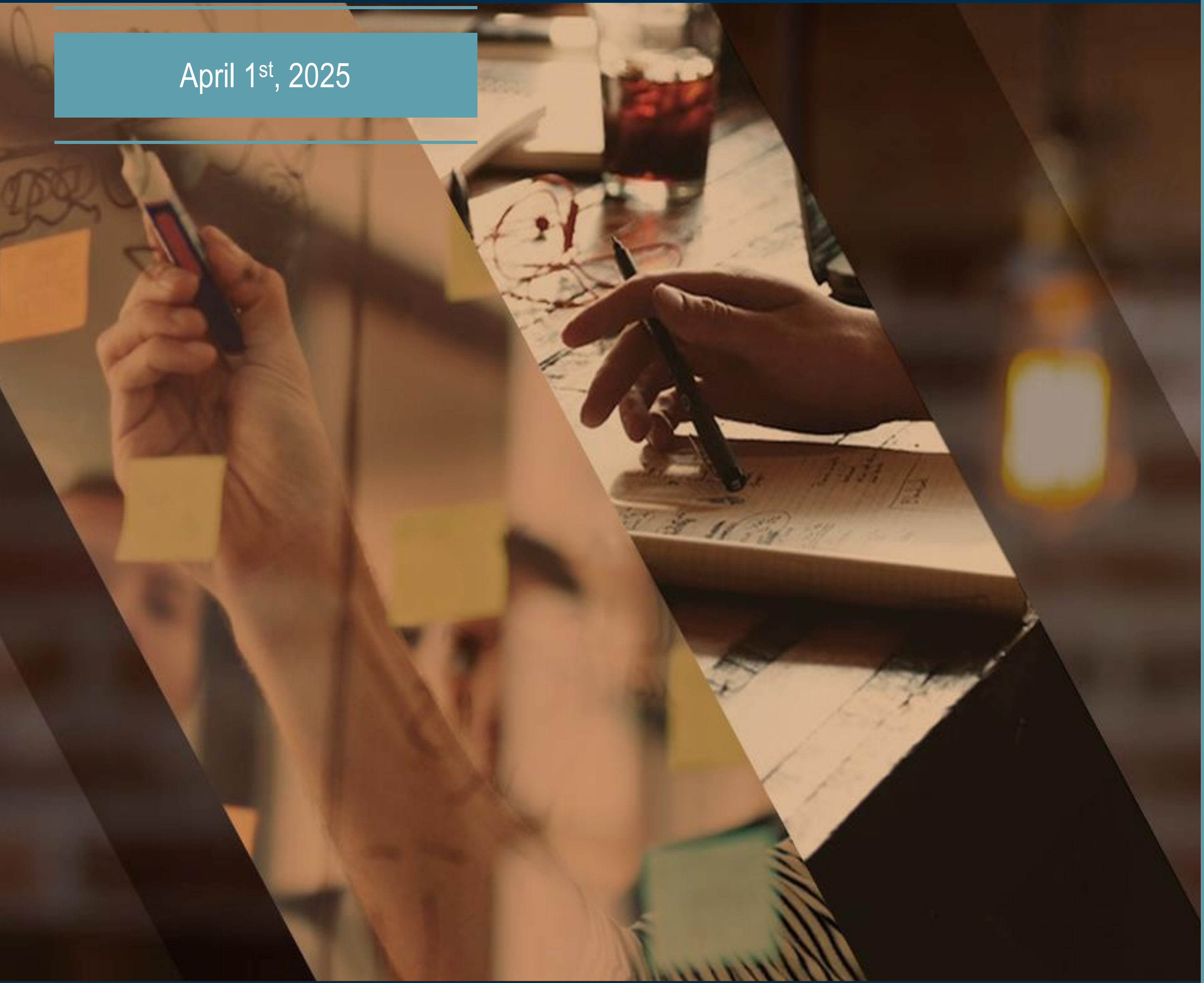
Norwegian research school
on hydrogen and hydrogen-based fuels

HySchool.no



April 1st, 2025

Electrochemical and thermochemical-based processes for production of chemicals

Prof. Massimo Santarelli
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Italian Institute of Technology (IT)
SISSA
HYSYLAB Torino
CO2 Circe Lab Torino

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H_2 and CO_2 laboratory

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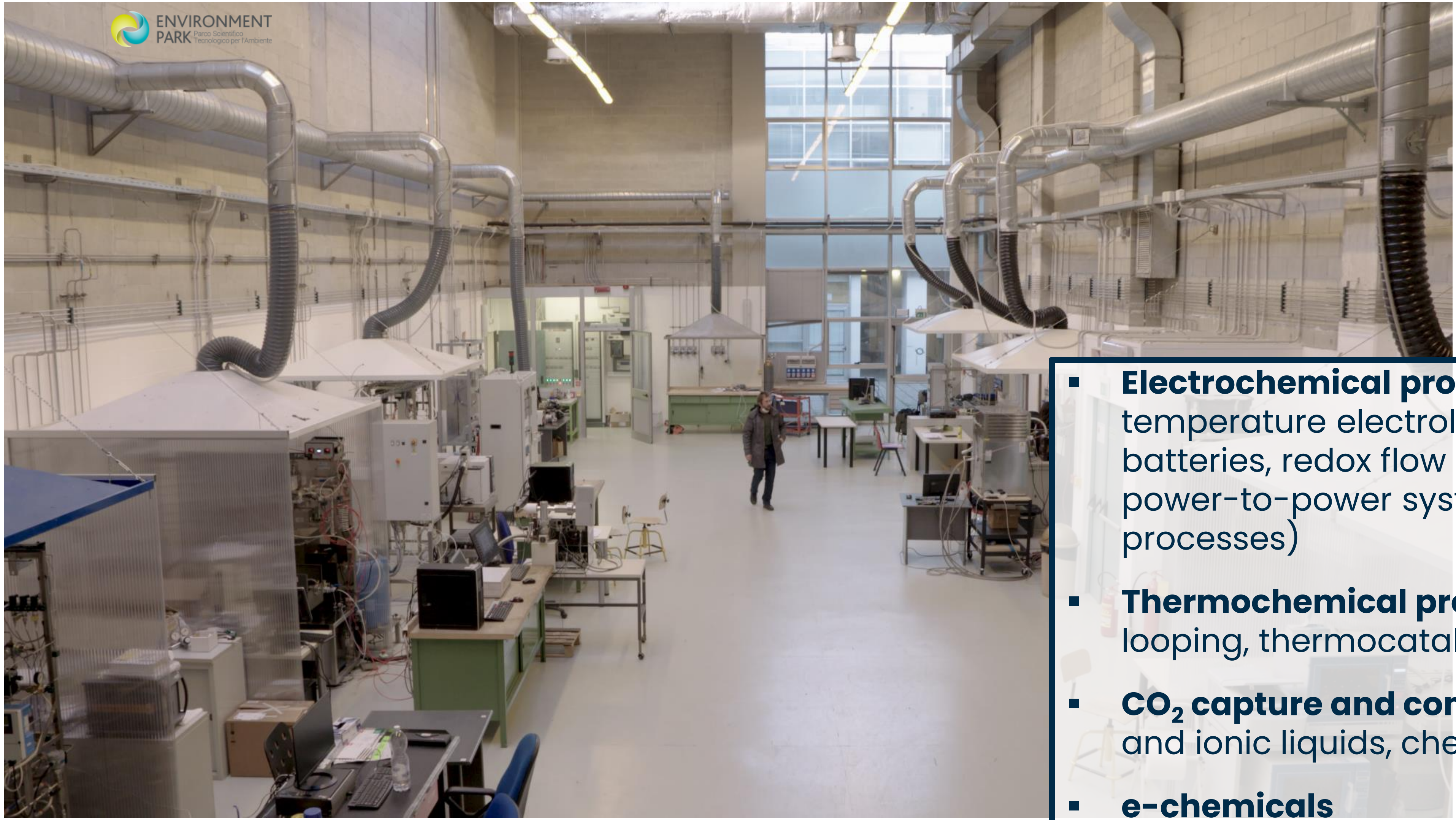
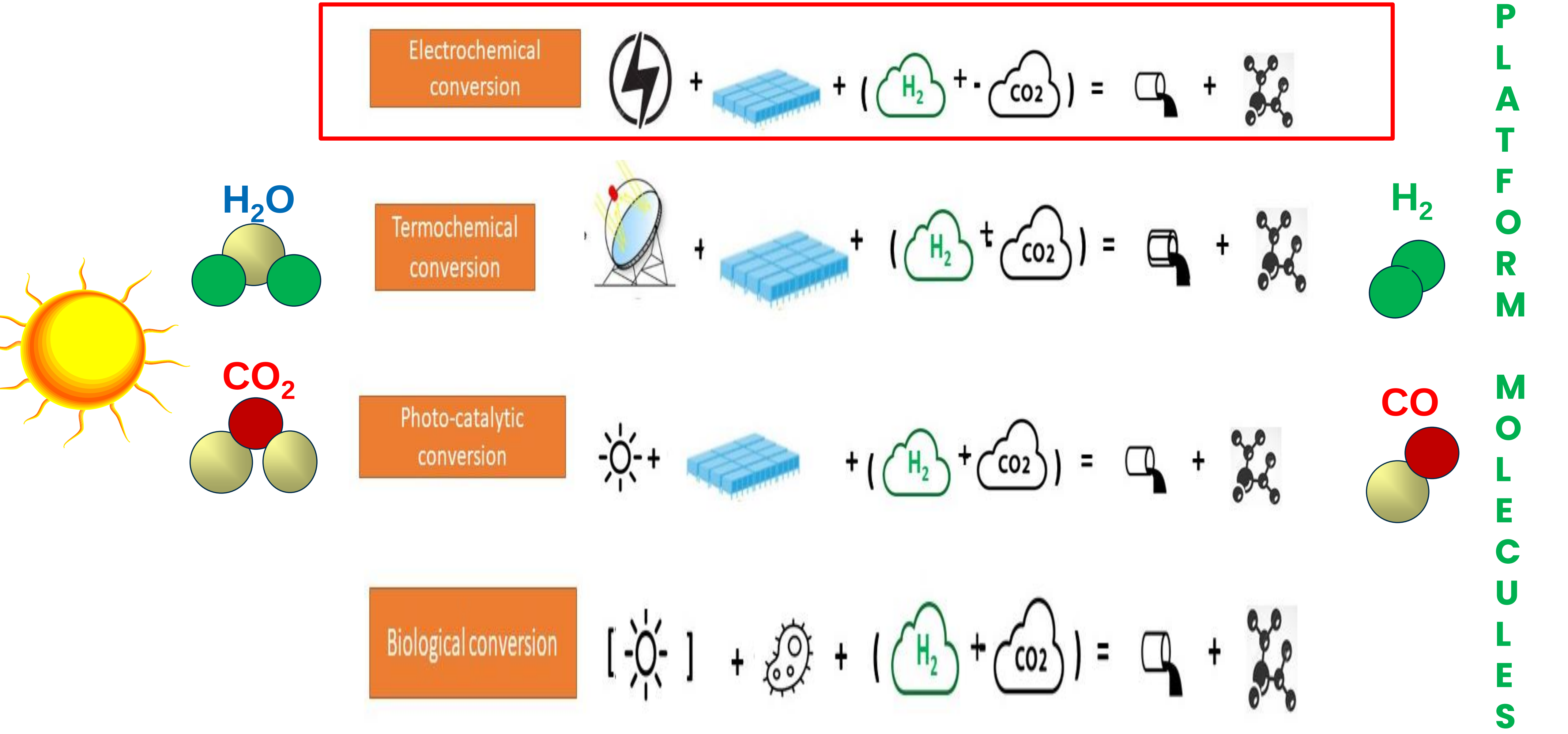


https://youtu.be/qUxnzP2J4yk

CO_2 Circle Lab

- **Electrochemical processes** (high and low temperature electrolysis, fuel cells, closed batteries, redox flow batteries, e-metals, power-to-power systems, plasma processes)
- **Thermochemical processes** (chemical looping, thermocatalysis, solar chemicals)
- **CO_2 capture and conversion** (membranes and ionic liquids, chemical looping)
- **e-chemicals**
- **solar chemicals**

e-pathway towards platform molecules



Co-ionic (H^+ + O^{--}) ceramic membranes

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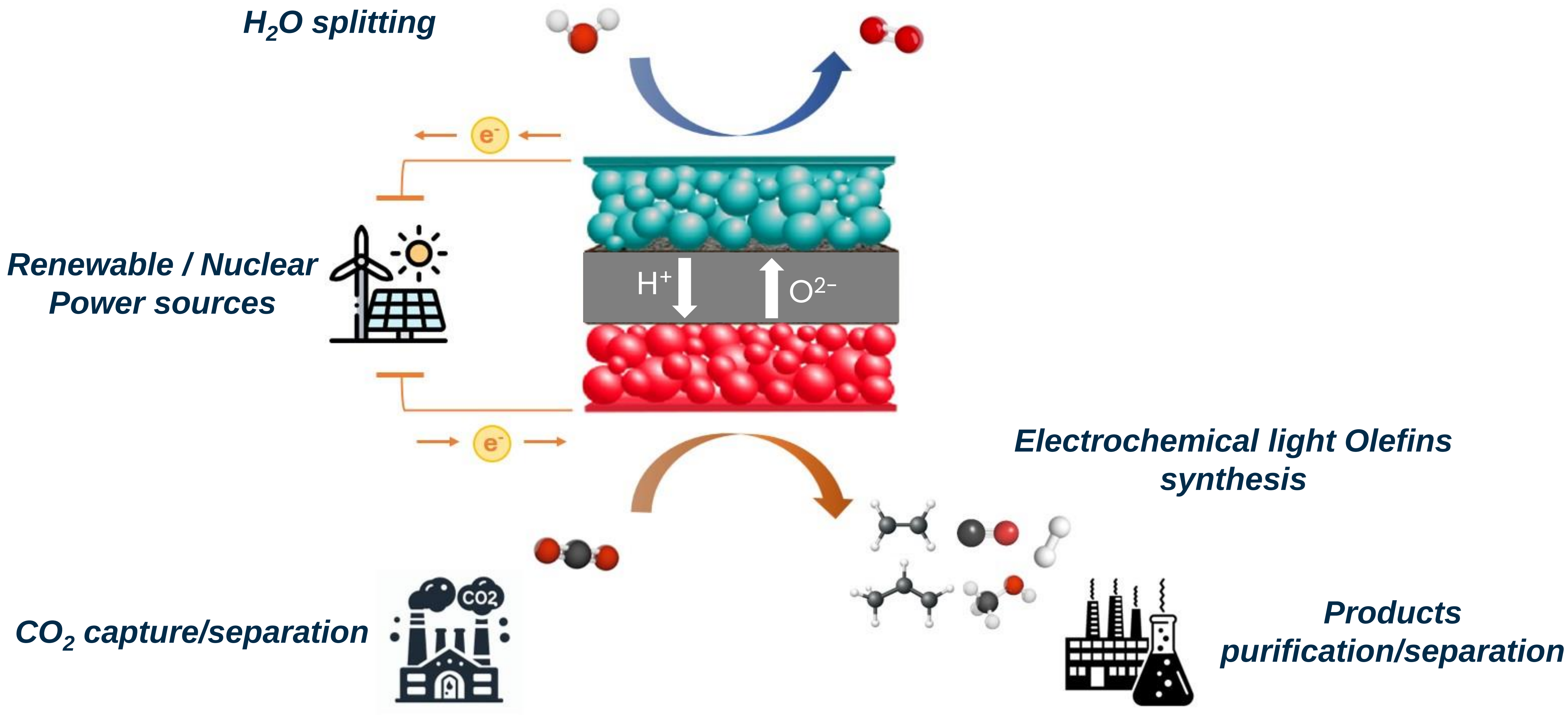
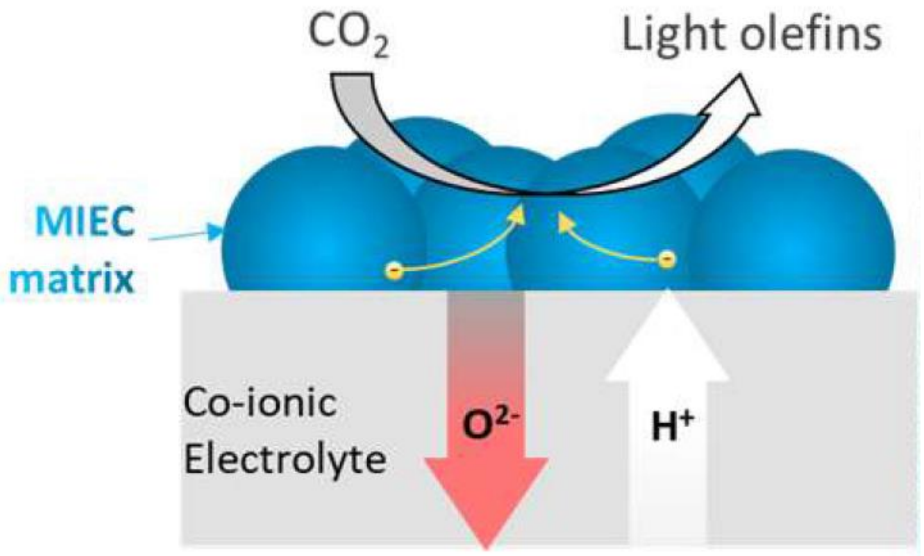
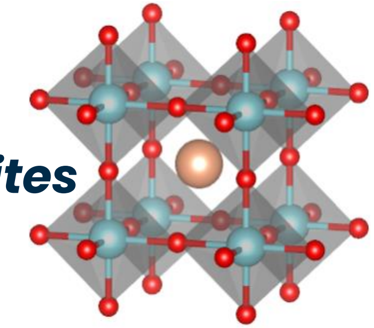
Nano-Engineered Co-Ionic Ceramic Reactors for CO_2/H_2O Electro-conversion to Light Olefins



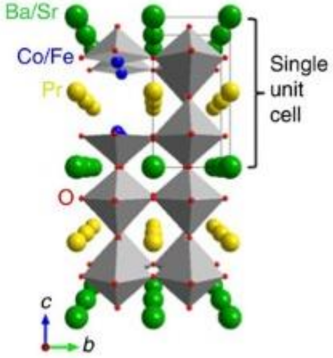
Development of Cathode Materials: *Triple conducting (H^+, O^{2-}, e^-) oxides matrices*



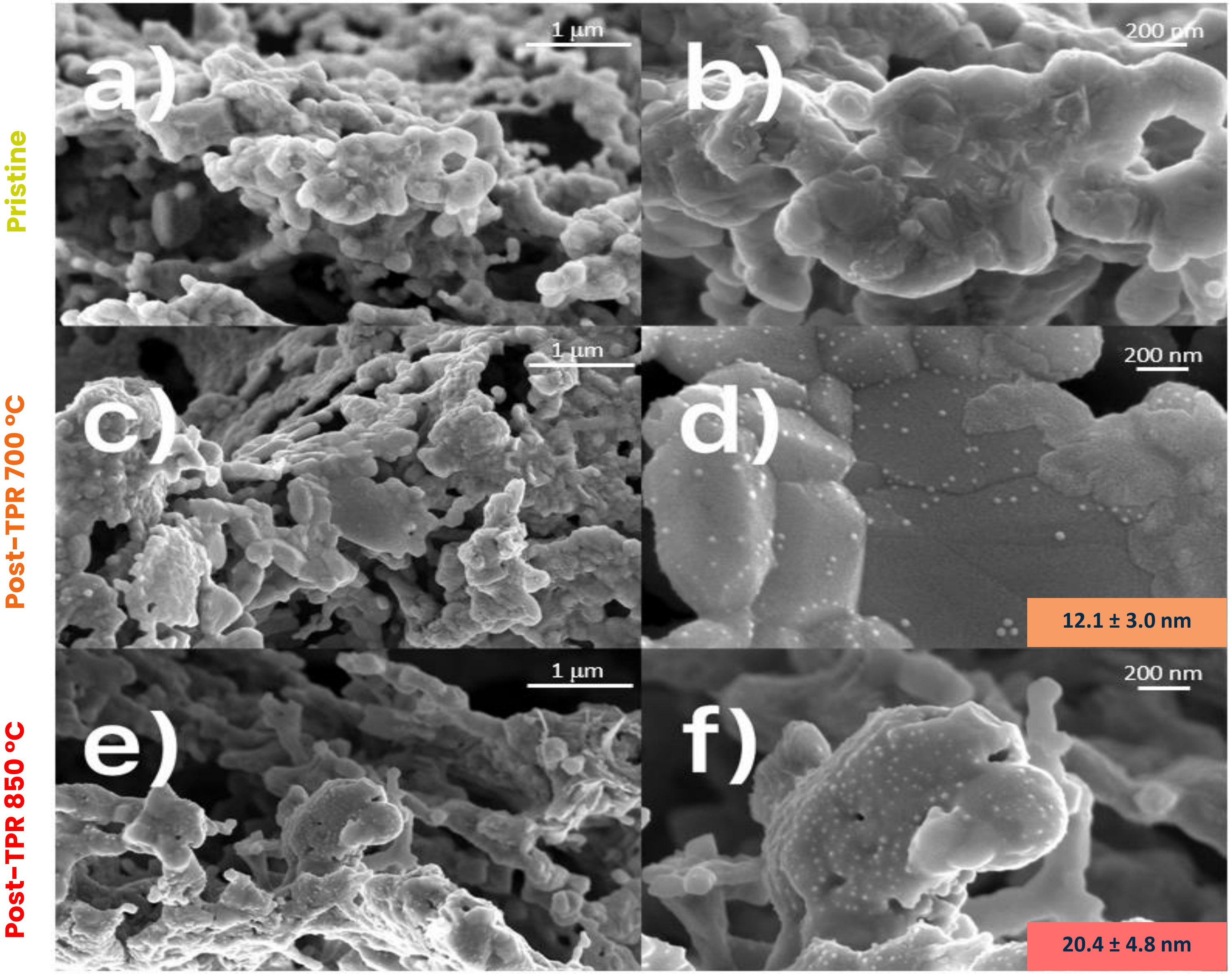
Perovskites



Double perovskites



Material | double-perovkite pre-reduced



SFNM $Sr_2FeNi_{0.4}Mo_{0.6}O_6$

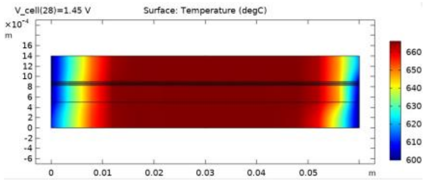
- Reduction with H_2 → **exsolved particles**
- **12 nm** @700 °C vs **20 nm** @850 °C

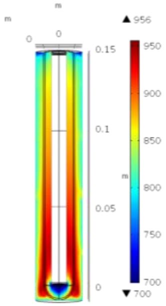
SFNM turns into a perovskite-like phase $Sr_3MoO_{6-\delta}$, along with the exsolution of a Ni-Fe-rich alloy
Strong catalytic effect on CO_2 reduction

Cell modeling: co-ionic (H^+ - O^{2-}) transport

Cell model

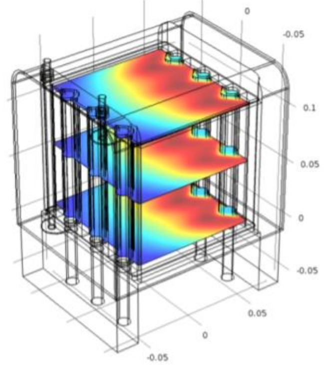
2D
planar+tubular

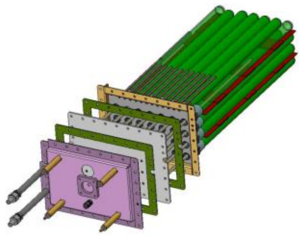




SRU/Stack model

3D
planar+tubular





Ionic transport in the membrane (Nernst-Planck-Poisson governing equations)

Defect conservation equation

$$\frac{\partial [X_k]}{\partial t} + \nabla \cdot J_k = \dot{\omega}_k$$

Defect transport flux (Nernst-Planck)

$$J_k = -D_k\left(\nabla[X_k] + \frac{z_k F}{RT}[X_k]\nabla\phi_e\right)$$

Gauss Law

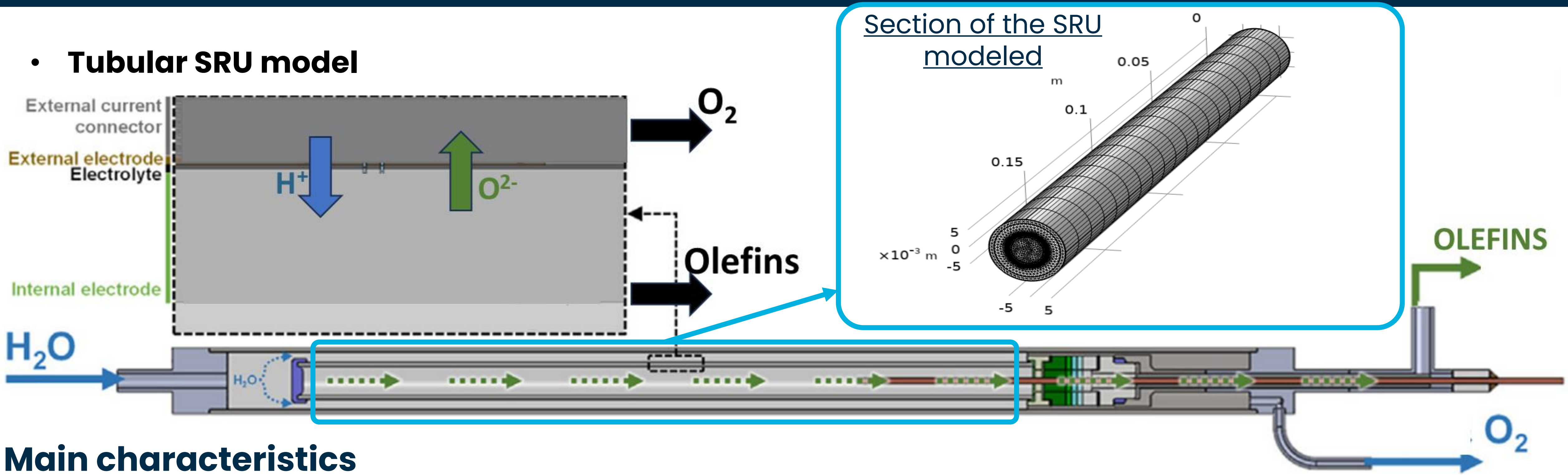
$$\nabla \cdot (\varepsilon_r \varepsilon_o \nabla\phi) = -\rho = -F\sum z_k[X_k]$$

Conductivity (Nernst-Einstein)

$$\sigma = \frac{F^2}{RT}\sum_{k=1}^{K} z_k^2 [X_k] D_k$$

CFD model development and simulations of the ci-EMR cells/stacks

- **Tubular SRU model**



Main characteristics

- Tube in shell configuration leading to sealed chambers:
  - Internal chamber with olefins production (avoids olefins dilution and allows recirculation)
  - External chamber with by-product (oxygen recovery with economic valorization)
- Porous conductive medium between electrode and external shell (lower losses and higher area)
- Self-contained modular sub-assembly for easier scaling and integration into larger systems

CFD model development and simulations of the ci-EMR cells/stacks

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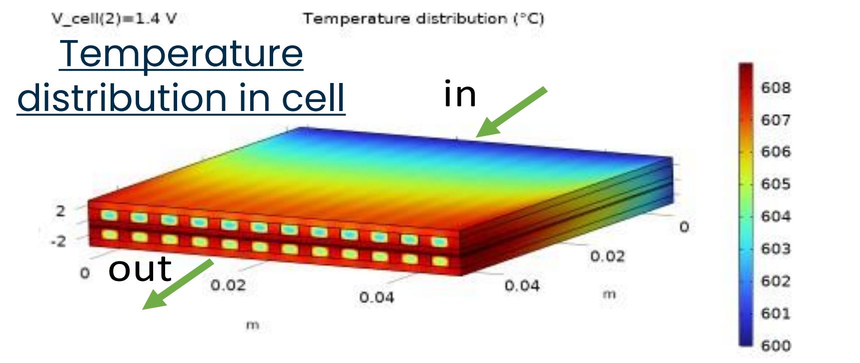
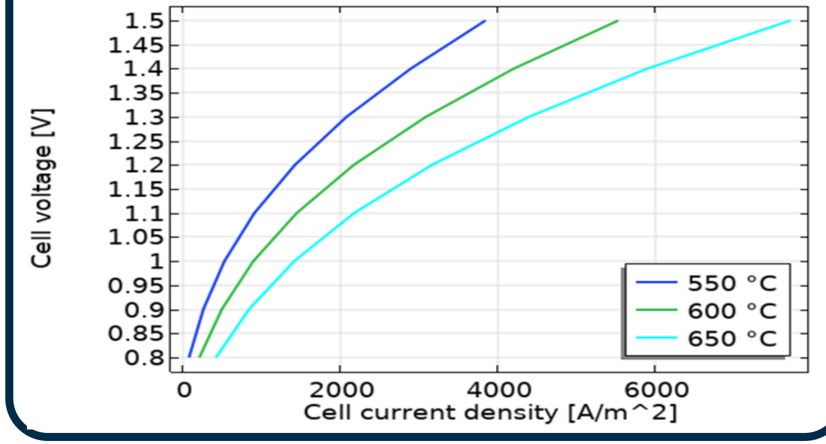
- **Planar SRU modelling**
  - 3D geometries
  - Implementation of thermal model

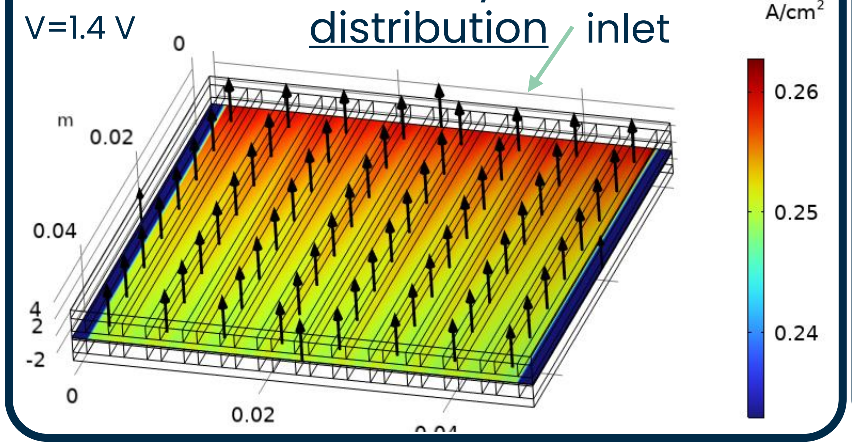


Results

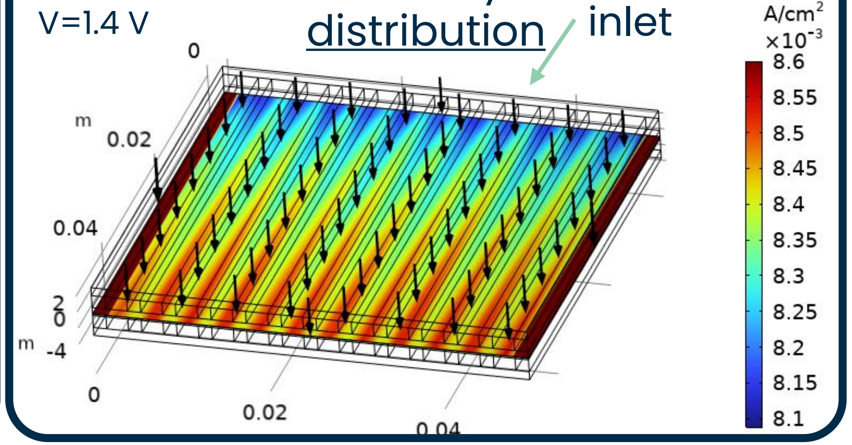
Polarization curves



H^+ current density volumetric distribution



O^{2-} current density volumetric distribution



Boundary Conditions			
	• Cell size = 5x5 cm^2 • $T_{inlet,gas}$ = T_{cell} • p=p_{atm} • Imposed potential	*Cathode* - $i_{0,HER} = 1.39 \cdot 10^7\ A/m^2 \cdot e^{\frac{-48.12\cdot 10^3 \frac{J}{mol}}{R\cdot T}}$	*Anode* - $i_{0,OER} = 5.38 \cdot 10^{11}\ A/m^2 \cdot e^{\frac{-180\cdot 10^3 \frac{J}{mol}}{R\cdot T}}$

Lei L. et al. "Energy storage and hydrogen production by proton conducting solid oxide electrolysis cells with a novel heterogeneous design" (https://doi.org/10.1016/j.enconman.2020.113044)

CFD model development and simulations of the ci-EMR cells/stacks

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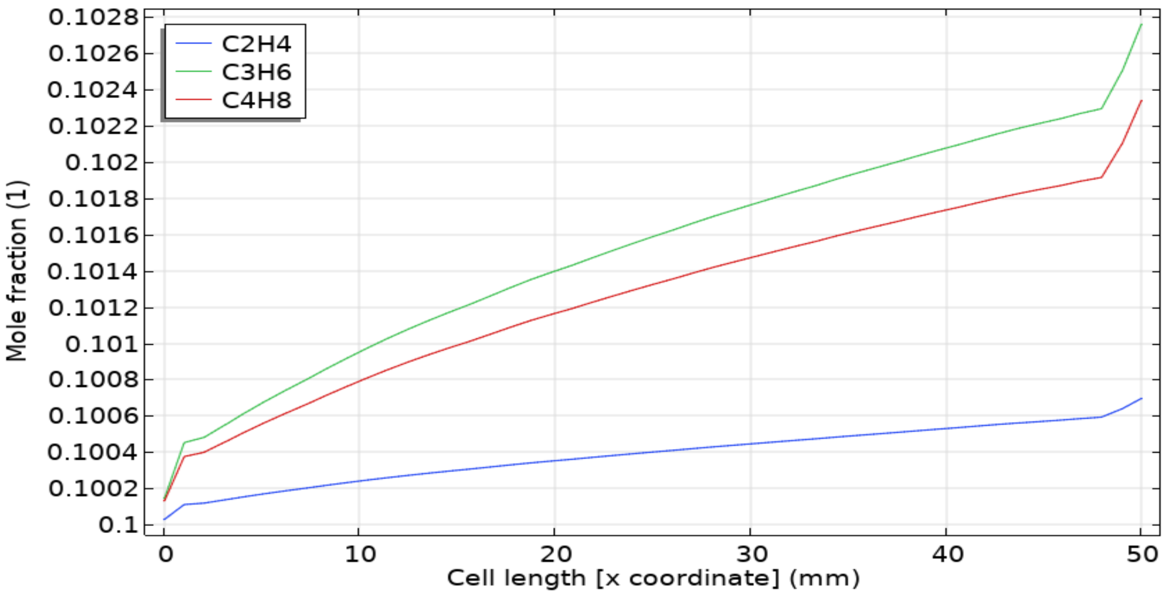
Electrochemical olefins production

- **CO_2 electro-hydrogenation to light-olefins** enhanced by co-ionic membranes

$$2CO_2 + 4H^+ + 12e^- \Leftrightarrow C_2H_4 + 4O^{2-}$$
$$3CO_2 + 6H^+ + 18e^- \Leftrightarrow C_3H_6 + 6O^{2-}$$
$$4CO_2 + 8H^+ + 24e^- \Leftrightarrow C_4H_8 + 8O^{2-}$$

Olefins molar fraction over cell length (V=1.9V)



- **Co-ionic reactions** at the electrodes only linked to the overall conductivity

- **Improvements currently evaluated:**

- Relation between partial current density of single defect and Butler-Volmer

$$i_{loc} = i_0\left(\exp\left(\frac{\alpha_a F\eta}{RT}\right) - exp\left(\frac{-\alpha_c F\eta}{RT}\right)\right)$$

- Variable pre exponential term of the Butler-Volmer

thermal-pathway towards platform molecules

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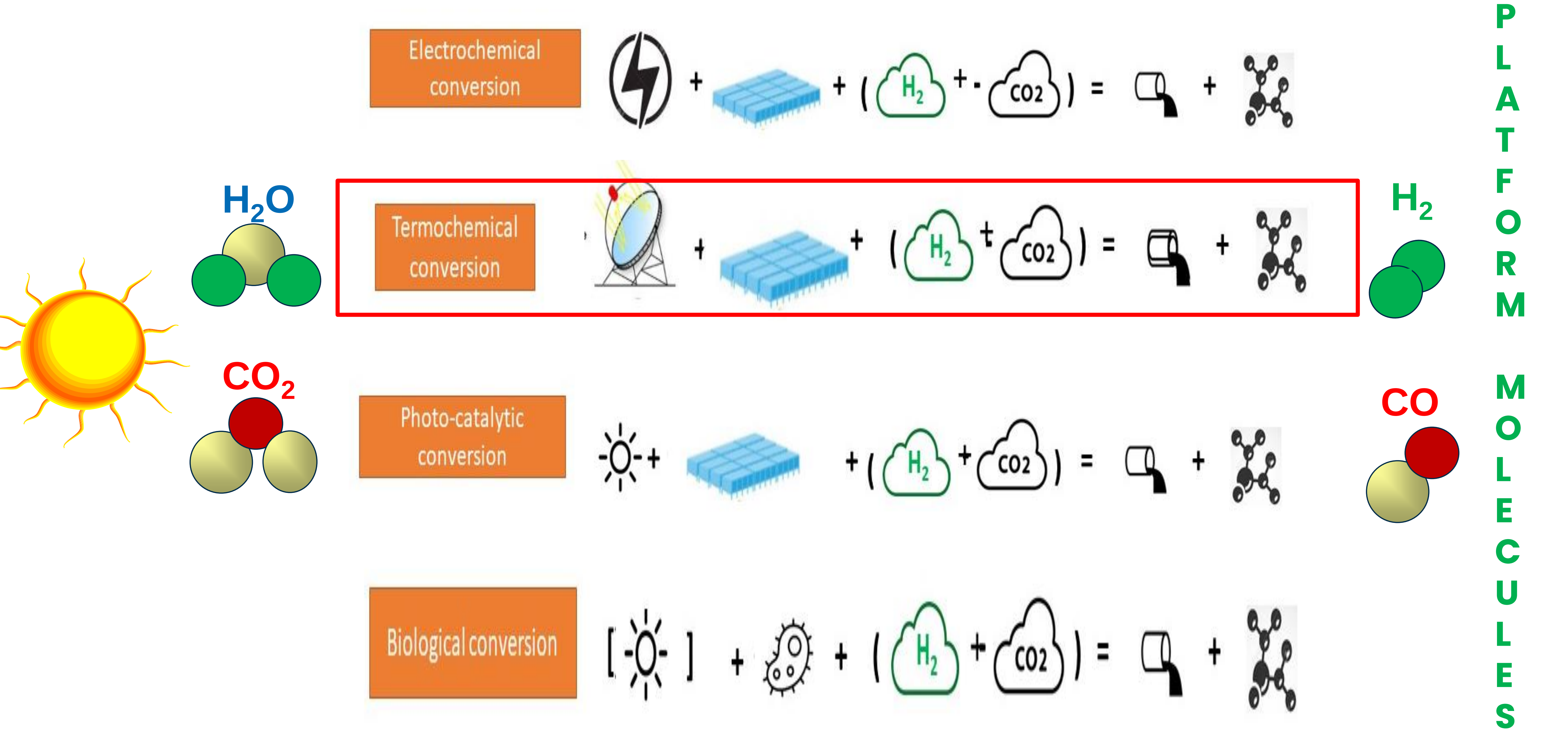

Thermochemical pathway: solid oxides for chemical looping

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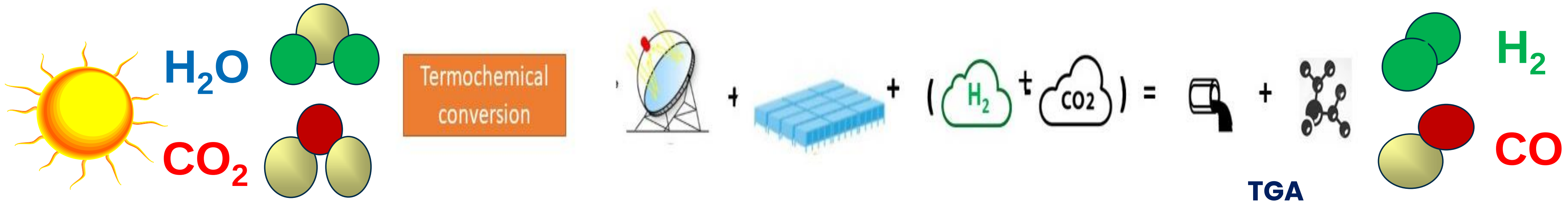
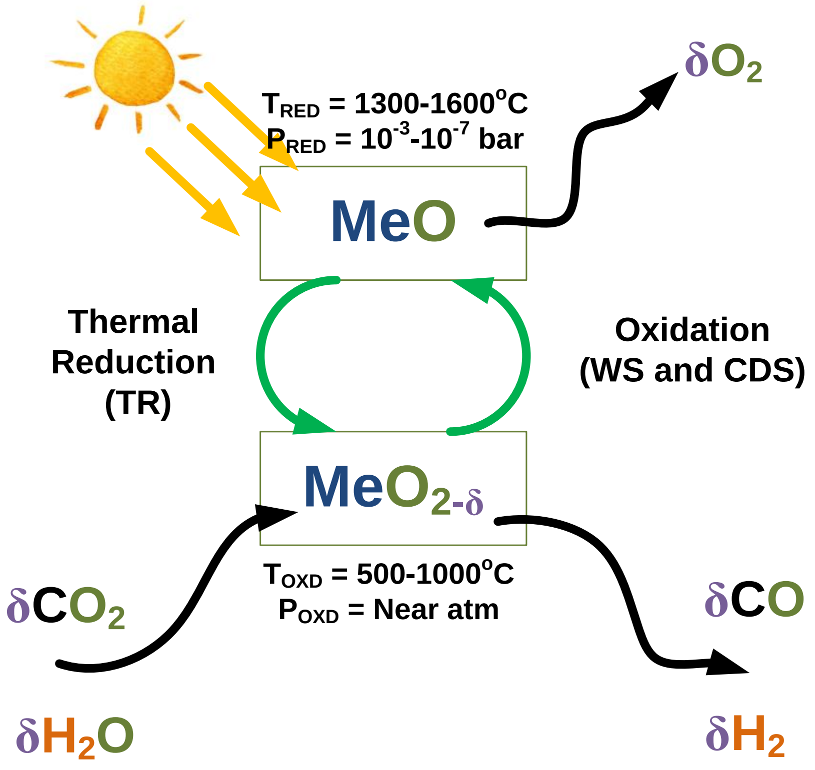
Chemical Looping based H_2O/CO_2 conversion



PLATFORM MOLECULES



Materials explored for Chemical Loopir

20%CeO_2-80%Fe_2O_3
$La_{0.75}Sr_{0.25}CoO_3$
$La_{0.75}Sr_{0.25}FeO_3$
70% Fe_2O_3-30% Al_2O_3
80% Fe_2O_3-$Ce_{0.5}Zr_{0.5}O_2$
25%LSF-SiO_2
50%LSF/SBA-15
$La_{0.5}Ca_{0.5}Fe_{0.25}Mn_{0.75}O_3$
$LaCo_{0.25}Fe_{0.50}Mn_{0.25}O_3$
$Gd_{0.3}Ce_{1.7}O_{2-\delta}$ (GDC)/Fe_2O_3
$La_{0.75}Sr_{0.25}FeO_3$-encapsulated Co_3O_4-NiO
$La_{0.8}Sr_{0.2}FeO_3$
$Sr_2FeNi_{0.4}Mo_{0.6}O_6$

TGA

REACTOR

SOLAR CONCENTRATOR

❖ $Sr_2FeNi_{0.4}Mo_{0.6}O_6$ (SFNM) for Chemical Looping

Experimental activity: structural evolution *vs* T

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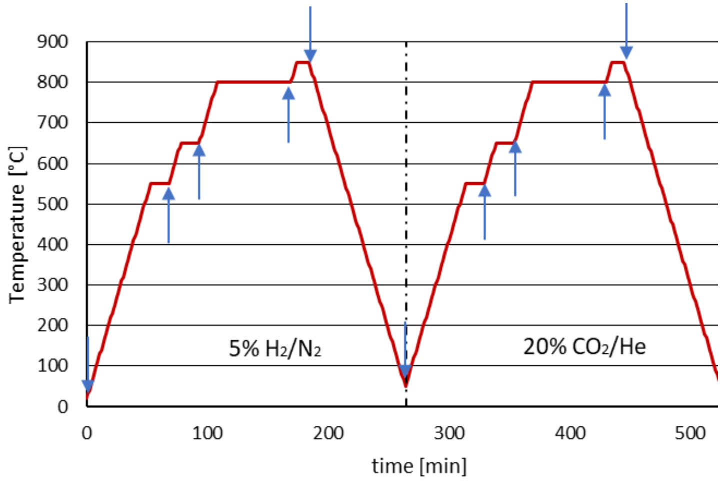
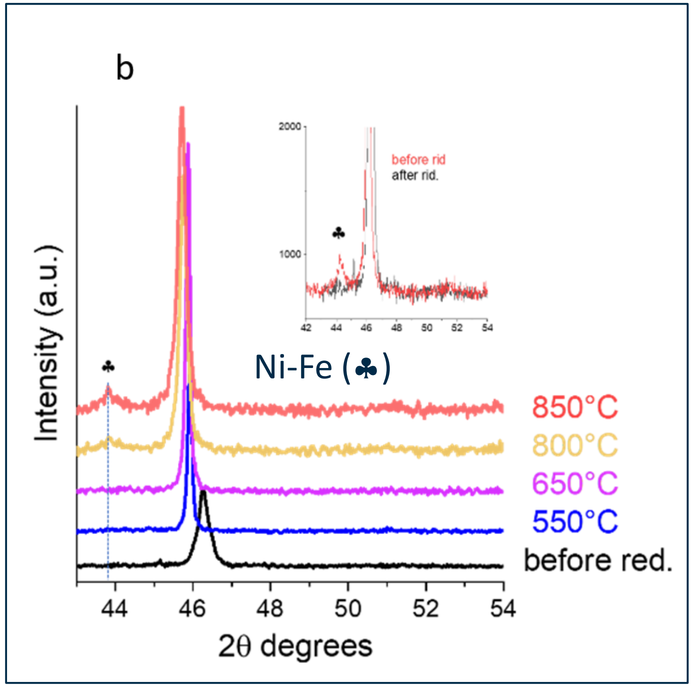
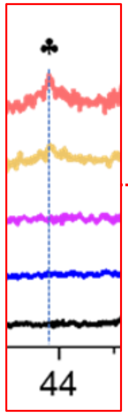
✓ Investigating the **structural evolution *vs* temperature**

- Temperature Programmed Reduction (**TPR**)
- *In situ* X-Ray Diffraction (**HC-XRD**)
- Diffractograms at 50, 550, 650, 800, 850 °C (*blue arrows*)
- Reduction: 5% H_2/N_2





TPR – Metal alloy exsolution



Ni-Fe alloy (♣) detected for T > 800 °C (*downstream, observed deriving from an exsolution process*)

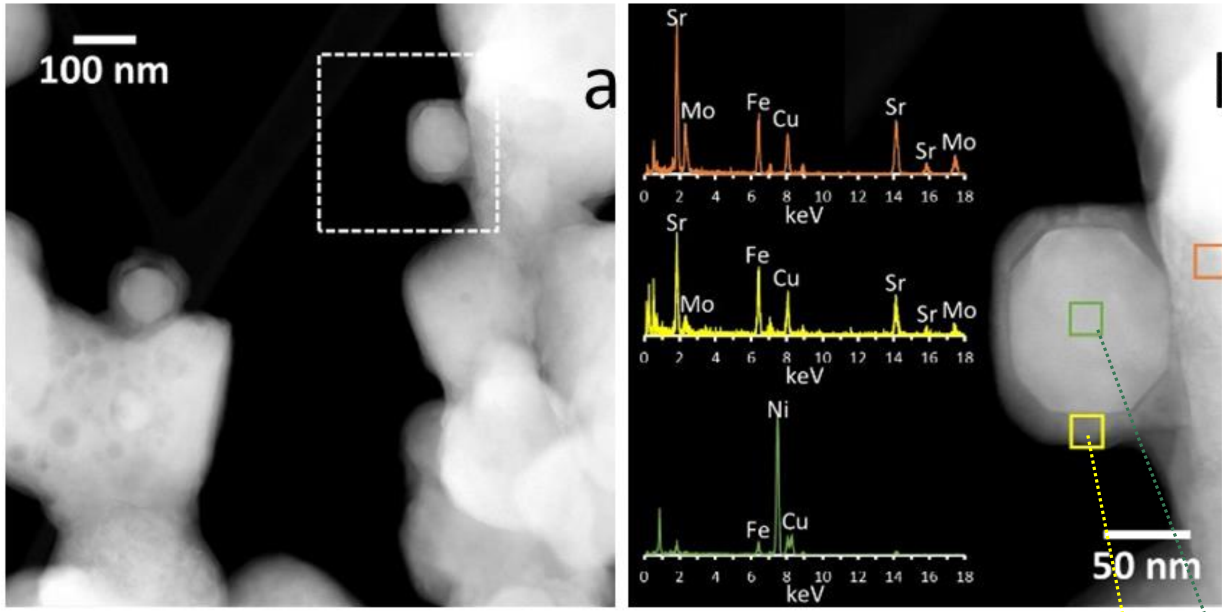
Experimental activity: long tested samples

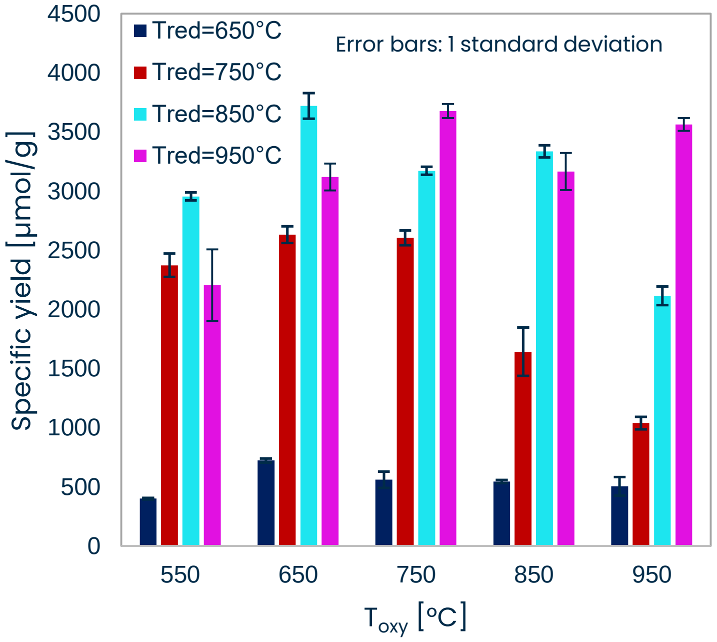
- Long-tested sample was analysed via HAADF-STEM, HRTEM and EDX

Exsolution-enhanced reverse water-gas shift chemical looping activity of $Sr_2FeMo_{0.6}Ni_{0.4}O_{6-\delta}$ double perovskite

Francesco Orsini, Domenico Ferrero, Salvatore F. Cannone, Massimo Santarelli, Andrea Felli, Marta Boaro, Carla de Leitenburg, Alessandro Trovarelli, Jordi Llorca, Georgios Dimitrakopoulos, Ahmed F. Ghoniem

Chemical Engineering Journal, Volume 475, 1 November 2023, 146083





Ni-Fe core

Perovskite-like shell

- Exsolution leads to the formation of **core-shell structures**
- The core contains **Ni-Fe**, while the matrix and the shell contain **Sr, Mo (some Fe)**
- The **exsolved core-shell structure appears to be very redox-active**

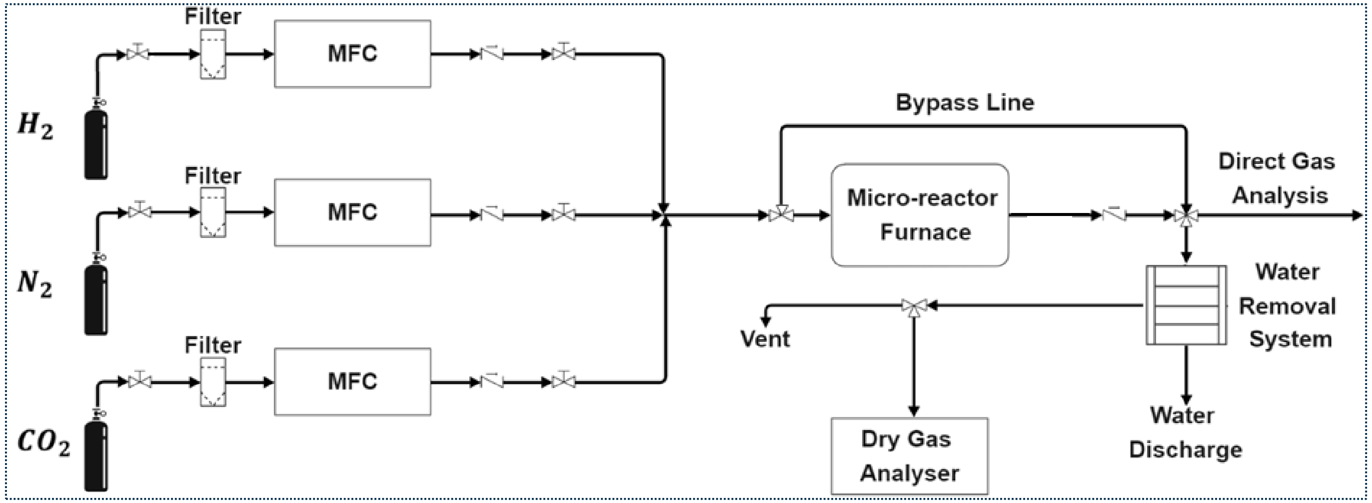
Optimal temperatures for maximizing the CO yield:

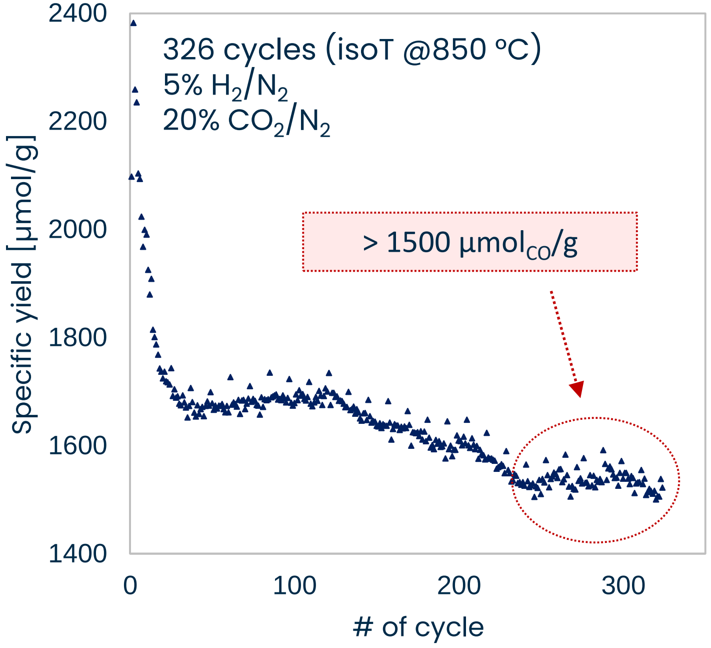
- $T_{red,opt} \approx 850$ °C
- $T_{oxy,opt} \approx 650$ °C

Experimental activity: SFNM redox stability (I)

✓ Assessing the material **stability** and CO yield **repeatability**

- Long-duration stability was explored through **320+ isothermal cycles** at **850 °C** (optimal T from previous tests)
- 5% H_2/N_2 – 20% CO_2/N_2
- Fixed-bed reactor coupled with online gas analysis (scheme below)

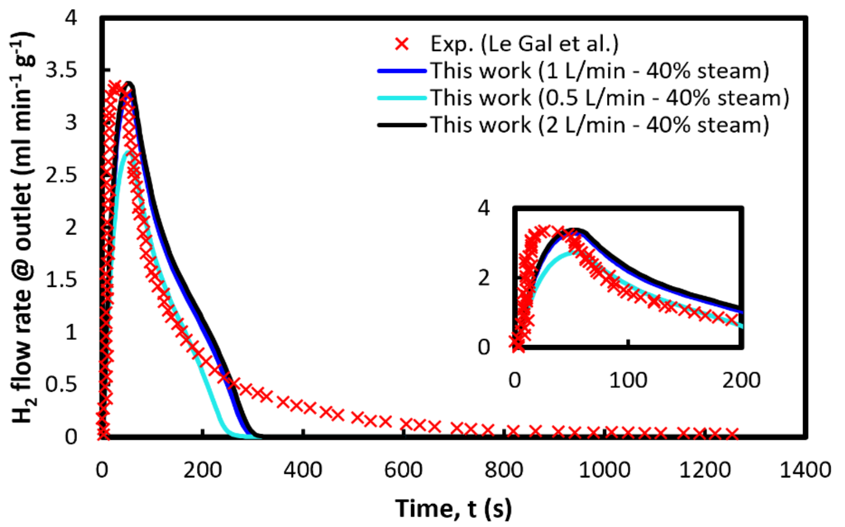




- Yield flattens out at > 1500 $\mu mol_{CO}/g$
- Long-tested SFNM thus seems to ensure good redox performances

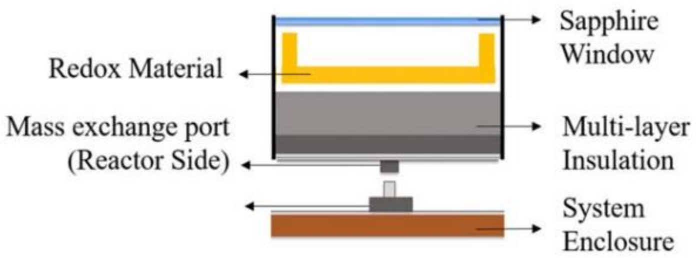
Scale-up and future concept

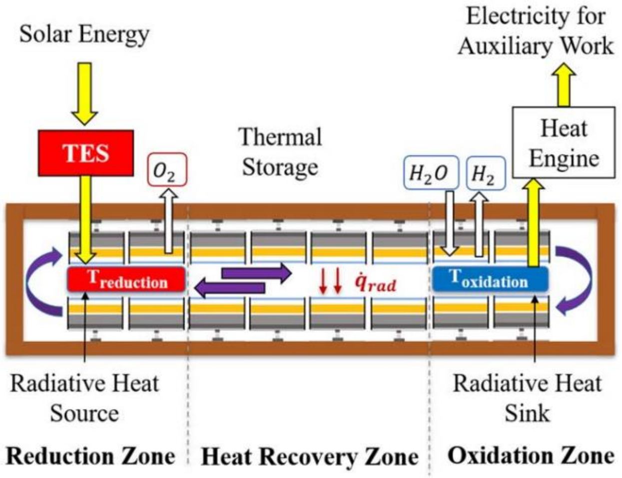
- Testing receiver/reactor in solar concentrator



Tubular fixed-bed

«Train Reactor» configuration





Collaboration with MIT

Multiphysics modeling – Reduction

Mass and momentum conservation (Brinkman)

$$\frac{\partial}{\partial t}(\epsilon_p \rho) + \nabla \cdot (\rho \mathbf{u}) = Q_m$$

$$\frac{\rho}{\epsilon_p}\left(\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u}\cdot\nabla)\frac{\mathbf{u}}{\epsilon_p}\right) = -\nabla p + \nabla \cdot \left[\frac{1}{\epsilon_p}\left\{\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}\mu(\nabla\cdot\mathbf{u})I\right\}\right] - \left(\frac{\mu}{\kappa} + \frac{Q_m}{\epsilon_p^2}\right)\mathbf{u}$$

Chemical species transport (Chapman-Enskog)

$$D_i^f = \left(\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{x_j}{D_{ij}}\right)^{-1} \qquad D_{ij} = \frac{0.00266\, T^{\frac{3}{2}}}{p M_{ij}^{\frac{1}{2}} \sigma_{ij}^2 \Omega_D} \qquad M_{ij} \coloneqq 2\left[\left(\frac{1}{M_i}\right) + \left(\frac{1}{M_j}\right)\right]^{-1} \qquad \{i, j = Ar, O_2\}$$

Local Thermal Non-Equilibrium

$$(1-\epsilon_p)\rho_s C_{p,s}\frac{\partial T_s}{\partial t} + \nabla\cdot \mathbf{q}_s = q_{sf}(T_f - T_s) + (1-\epsilon_p)Q_s$$

$$\epsilon_p \rho_f C_{p,f}\frac{\partial T_f}{\partial t} + \rho_f C_{p,f}\mathbf{u}\cdot\nabla T_f + \nabla\cdot\mathbf{q}_f = q_{sf}(T_s - T_f) + \epsilon_p Q_f$$

$q_{sf} = h_{sf} A_{sf}$
(literature correlations
for dual scale RPC)

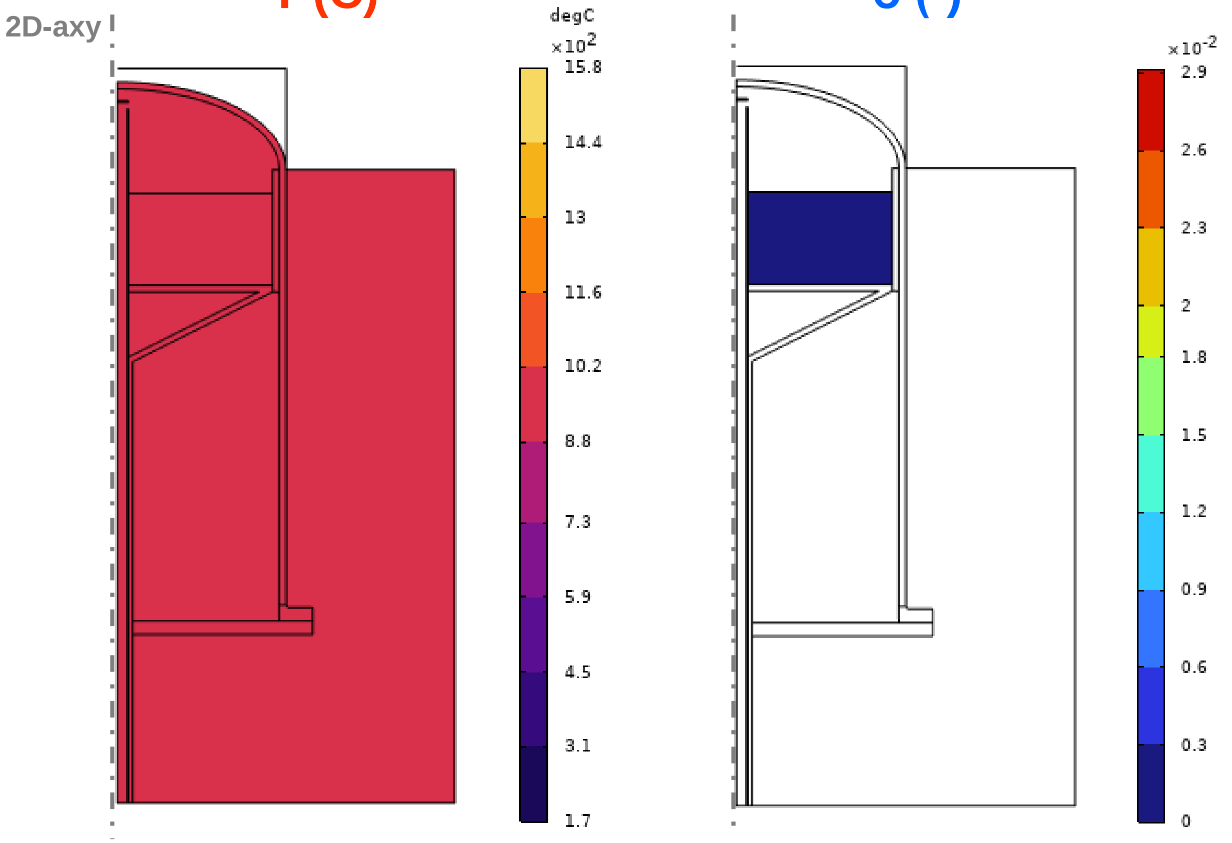
Internal radiative heat transfer (P1 approx.)

$$\nabla \cdot (-D_{P1}\nabla G) = -\kappa(G - 4\pi I_b)$$

$$G = \int_{4\pi} I(\Omega)\, d\Omega \ , \qquad D_{P1} = \frac{1}{3\kappa + \sigma_s(3 - a_1)}$$

Redox thermodynamics

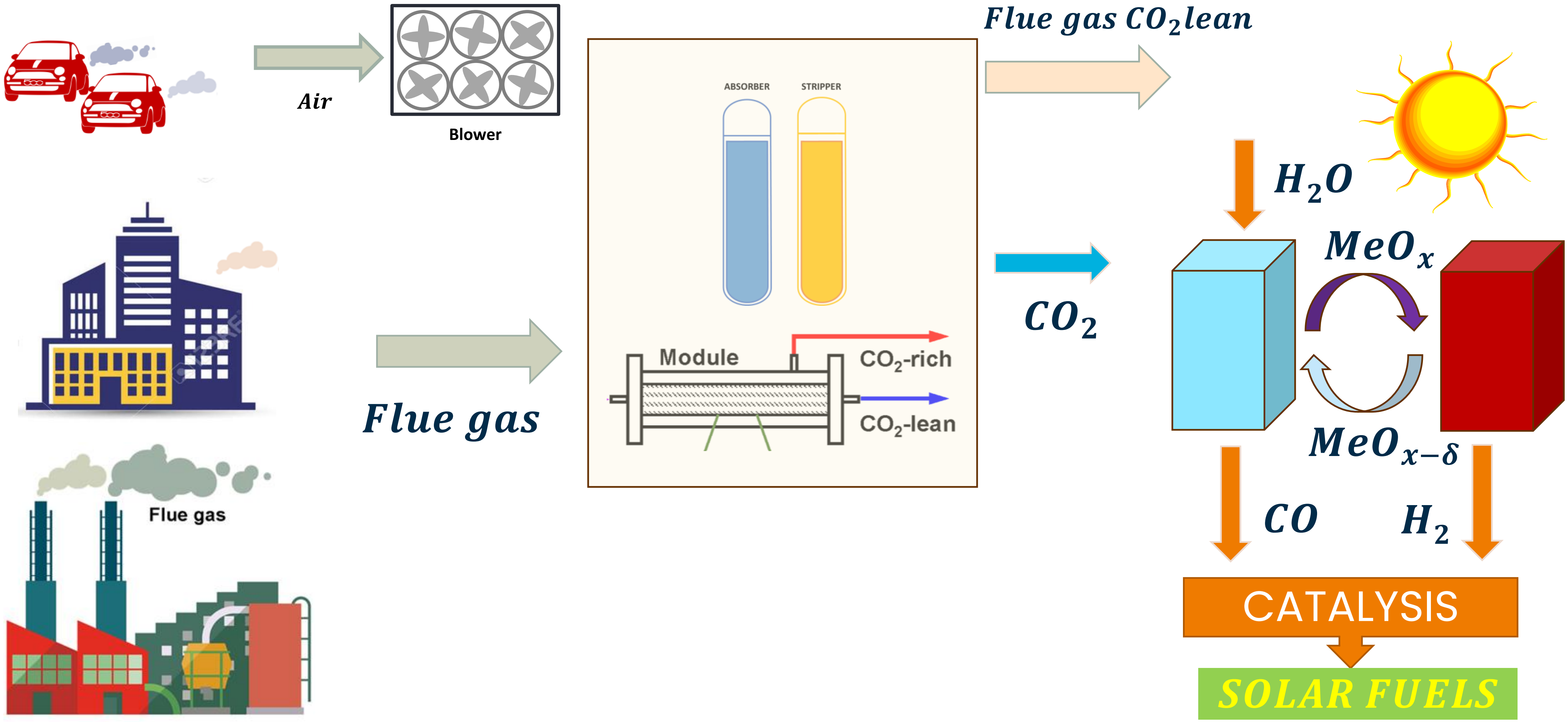
$$\delta_\infty(T, p_{O_2}) = \delta_{max}\frac{8700\, p_{O_2}^{n_{O_2}}\, e^{-\frac{195.6\,[kJ\,mol^{-1}]}{R_g T}}}{1 + 8700\, p_{O_2}^{n_{O_2}}\, e^{-\frac{195.6\,[kJ\,mol^{-1}]}{R_g T}}} \ , \qquad \delta(t=0) = 0$$



1 hour simulation results.

- The model will be used to:
  a. Compare different operational regimes (e.g., sweep *vs* vacuum)
  b. Explore the effect of the porous medium morphology
  c. Couple reduction and oxidation models via consistent initial conditions in the fluid domains

Scale-up and future concept



Plasma-assisted Chemical Looping

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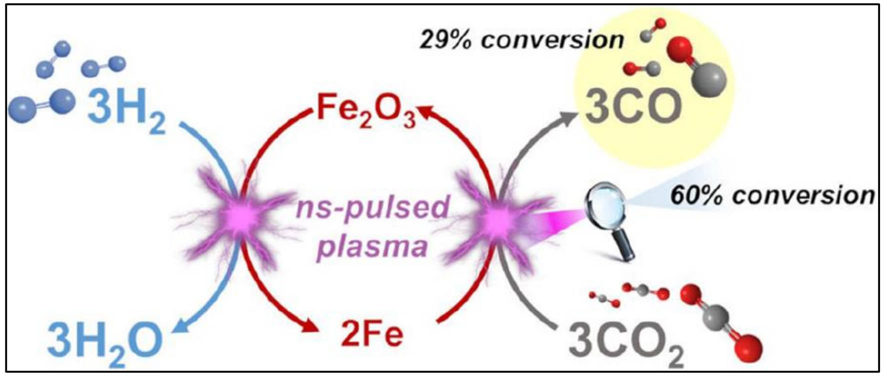
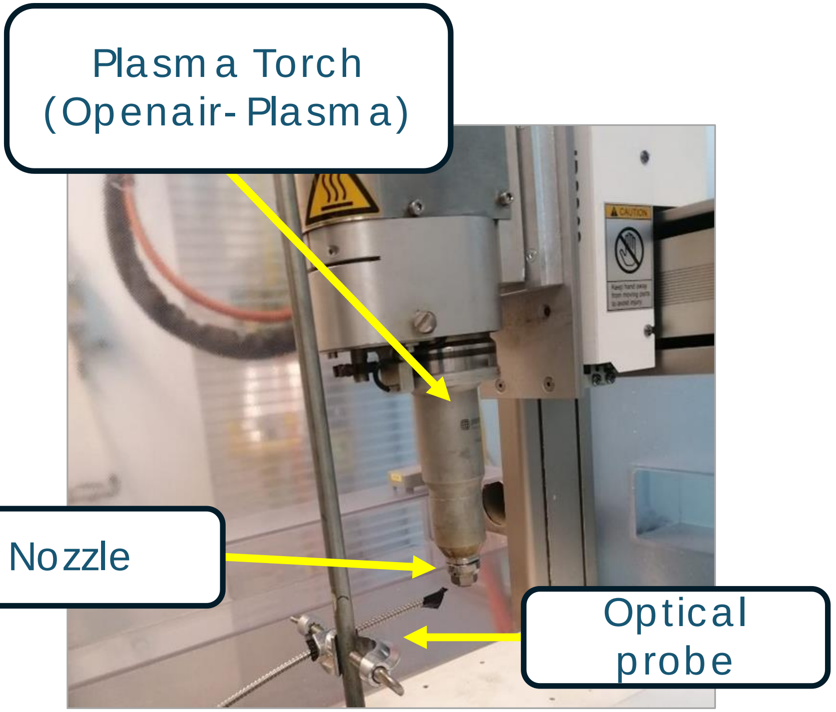
Improving CO_2 Conversion by Plasma-Assisted Chemical Looping

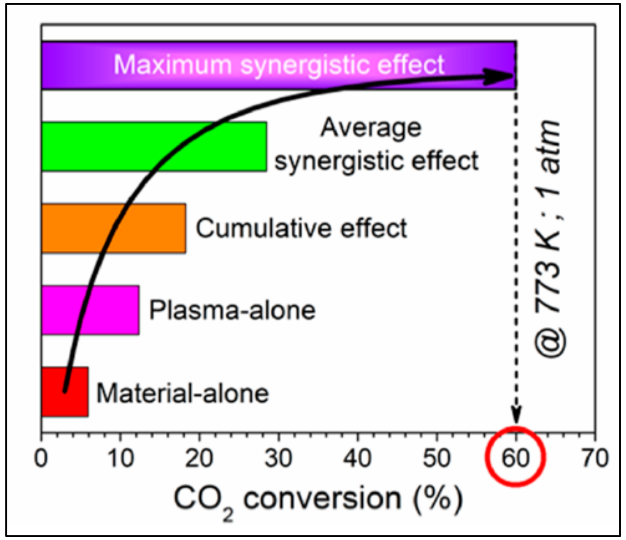


Plasma-based set-ups can be combined with a **packing material**, usually referred to as **plasma-catalysis**

Experimental setup: cold plasma is used to **dissociate CO_2.** Reduced SFNM material, placed downstream of the plasma, is expected to capture oxygen to **prevent CO recombination**



Main expectations: achieved up to 60% instantaneous CO_2 conversion in plasma: the process exhibited a 2-4-fold increase in CO_2 conversion compared to plasma or material alone*



[3] https://doi.org/10.1021/acsenergylett.2c00632

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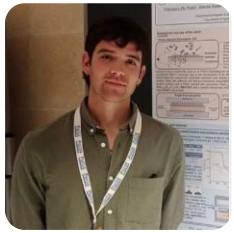

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Thank you for the attention!

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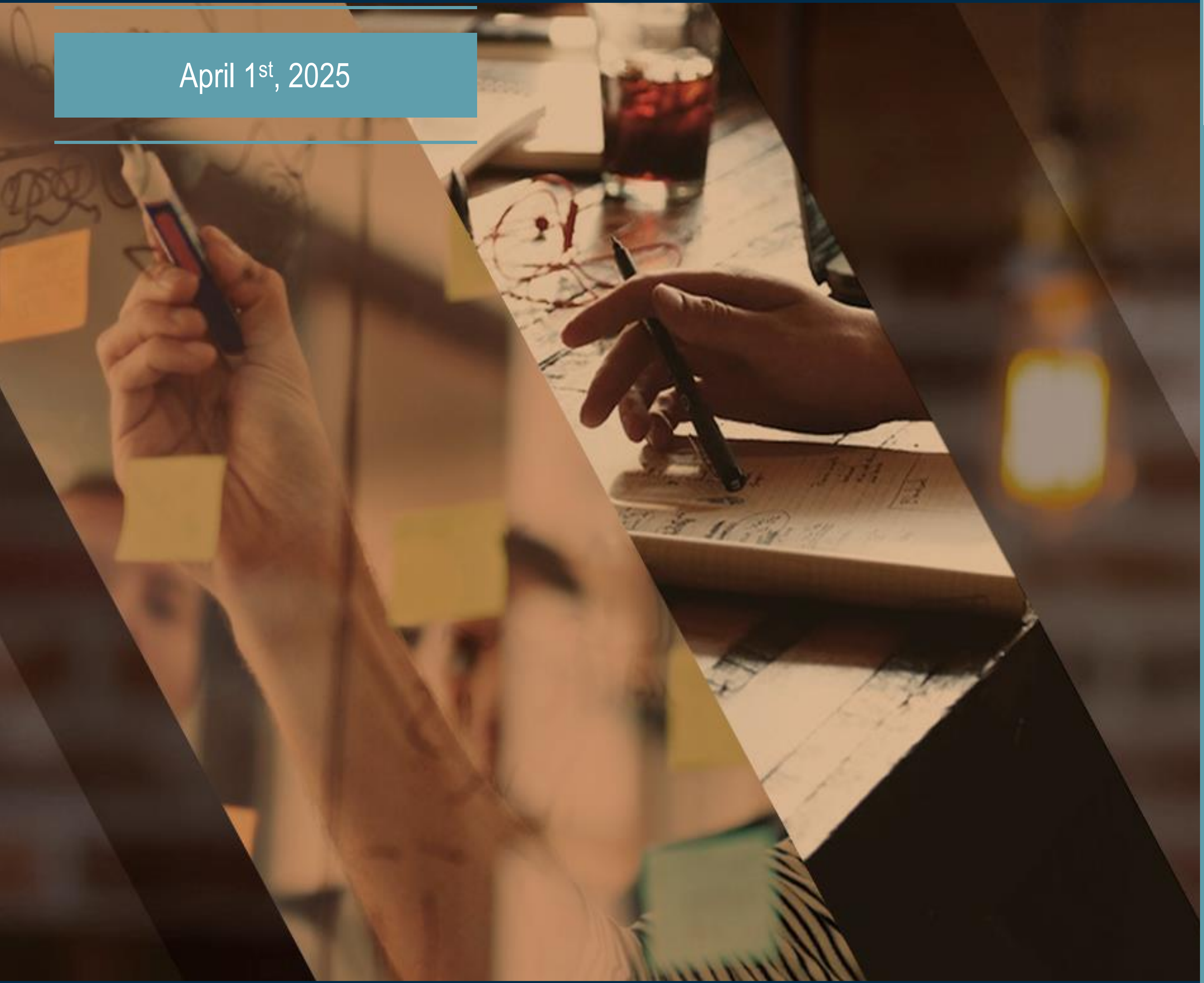
1859



April 1st, 2025

Electrochemical and thermochemical-based processes for production of chemicals

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