Methanation of captured carbon dioxide in a solid oxide membrane reactor

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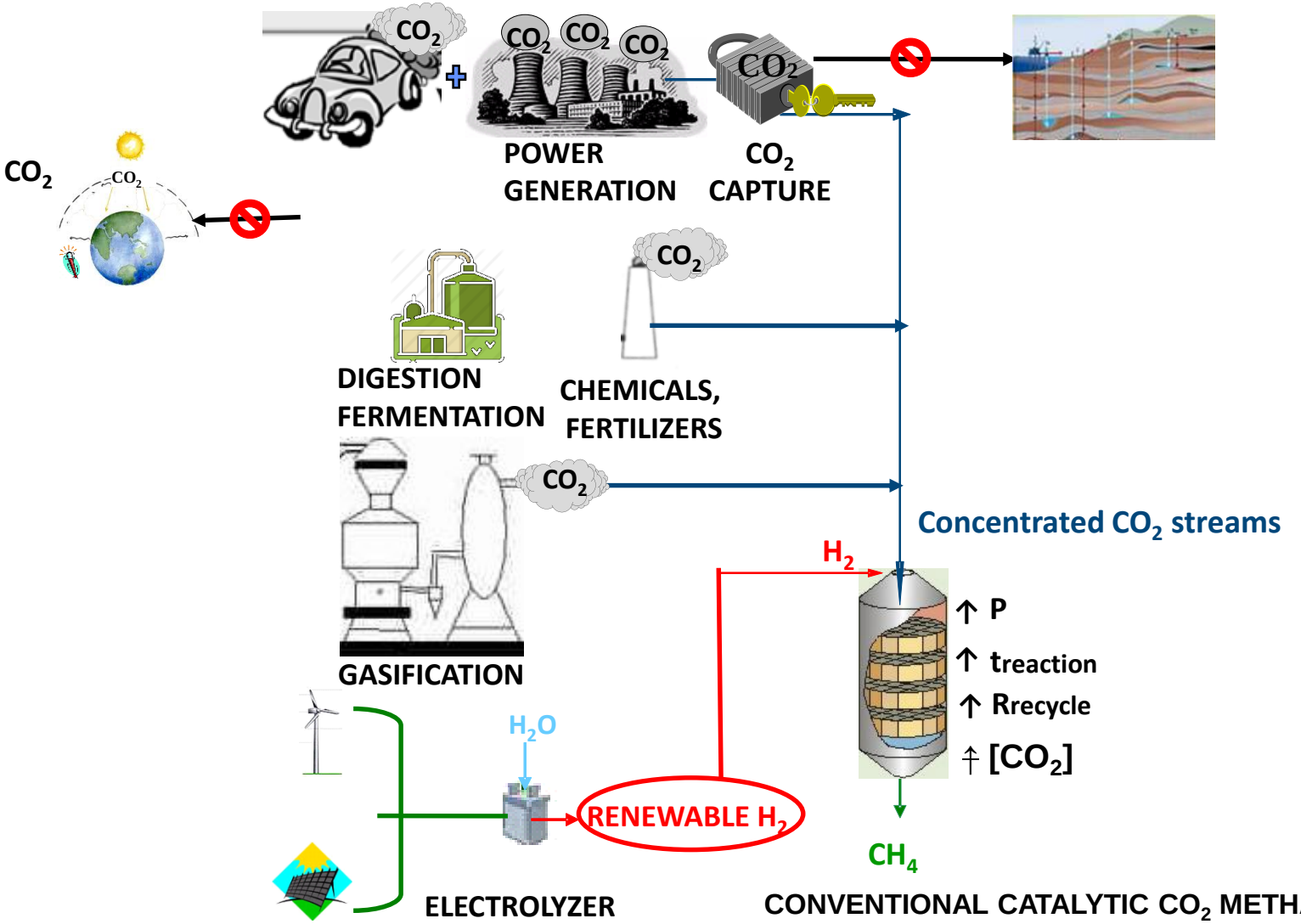
Catalytic CO_2 Methanation



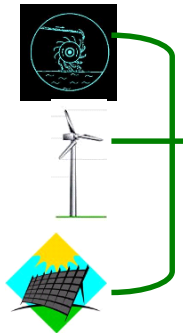
$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

Catalytic CO_2 Methanation: Challenges

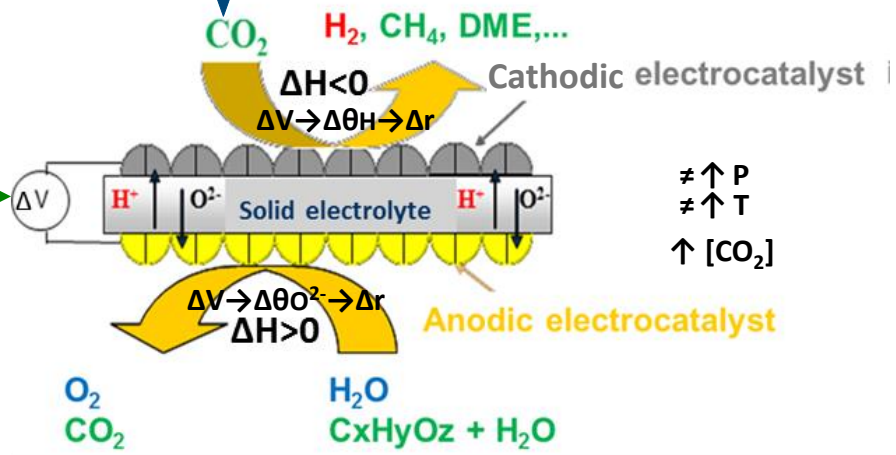
- ↑ Activity, selectivity & tolerance inhibitors and Poisons
- ↑ Lifetime ⇒ ↓ Deactivation (C, H_2O+ ↑ T) or regeneration methods
- Reactor design optimization: exothermicity control
- ↑ Energy efficiency (ηe)⇒↓ Energy required for CH_4 production
- ↓ CAPEX & OPEX
- Process intensification:
  - ✓ Selective activation (photo-electro/photo/electro-catalysis)
  - ✓ In-situ H_2 production

Electrochemically Enhanced Catalytic CO_2 Methanation with in-situ H_2 Production

Concentrated CO_2 streams



ELECTROCHEMICAL PROMOTION IN SOEMR



$\Delta r >> r_e$; $r_e = I/nF$ (electrocatalysis)

SOLID OXIDE ELECTROLYTE MEMBRANE REACTOR (DOUBLE CHAMBER)

- ✓ Different reaction gas: CO_2 (cathode) / H_2O, CxHyOz+H_2O.. (anode)
- ✓ Both electrodes catalytically active
- ✓ In-situ tuning activity/selectivity by ΔV/I (vs. ΔT):↓ P & T→↑ηe & ↓costs
- ✓ ↑ Lifetime (↓ poisoning, in-situ regeneration)→↓OPEX
- ✓ In-situ H_2 production from renewable energy & sources (H_2O, biomass residues: glycerol ($C_3H_8O_3$), ..)
- ✓ System integration (process intensification) →Compact design →↓ reactor size →↓ capital cost
- ✓ in-situ H_2 & co-O_2 production/CO_2 capture →↓operating costs
- ✓ Thermal control: electrolysis or reforming (endo.)/hydrogenation (exot.) →↑ηe & ↓costs

Methanation of captured CO_2 in a solid oxide electrolyte membrane reactor

Most previous studies

Lab-scale, 👎configurations (disks) and/or conditions (diluted gas) ➡ ***Fundamental aspects***

Challenges for viability (↑ energy efficiency,↓ costs & ↑ long term durability)

- ✓ ↑ Efficiency, selectivity, stability and durability of electro-catalysts: ↑ dispersion, ↓particle size, promoter or co-catalyst addition, etc.
- ✓ ↑ Chemical stability of solid electrolytes to CO_2, H_2O..
- ✓ ↓Ohmic losses: ↓electrode thickness, electrode supported thin electrolyte systems, ↑ ionic conductivity of electrolytes & e- conductivity of electrodes..
- ✓ ↓ $T_{operation}$ → ↑ Energy efficiency :→ ↑ ionic conductivity at low T→Intermediate T H^+ conductors
- ✓ ↓ Material cost: → cheap non noble metals
- ✓ ↑ Simplicity & scalability in material preparation

CIEMAT Research

- 👍 Bench-scale, ↑ flowrates, 1 atm., ↑ [CO_2] streams
- 👍 Easily adaptable tubular- double chamber configurations
- 👍 Cheap and widespread catalyst electrodes
- 👍 Appropriate & readily scalable deposition procedures

➡ ***Assessment of Potential Practical Application***

Methanation of captured CO_2 in a solid oxide electrolyte membrane reactor (CIEMAT research)

Aim: Development of integrated systems for in-situ H_2 production and CO_2 conversion to CH_4 and their study under realistic conditions

Approach: in-situ H_2 production (by steam electrolysis, hydrocarbon reforming, etc.) and CO_2 hydrogenation to CH_4 in intermediate-temperature solid oxide co-ionic (H^+ & O^{2-} conduction) electrolyte membrane reactors (double chamber)

Research activities:

✓ Development of easily scalable double-chamber reactor configurations of cheap, effective, selective, stable and durable electro-catalyst for both processes.

✓ Study under realistic conditions at bench scale for:

- Screening operating conditions and electrolytes/electro-catalysts
- Assessment of stability, durability and useful lifetime

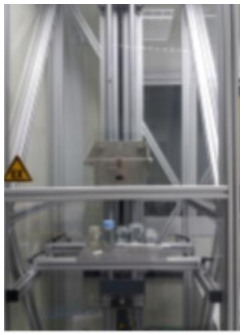
Methanation of captured CO_2 in a solid oxide electrolyte membrane reactor

Design & preparation of an easily scalable electro-catalyst configuration

Electrode supported tubular electrochemical cell:

- **Commercial tube** of anode supported co-ionic solid oxide electrolyte:
  Porous anode (Ni-perovskite) → internal chamber
  Co-ionic solid oxide electrolyte (perovskite) →intermediate film
- **Cu cathode**→ external chamber

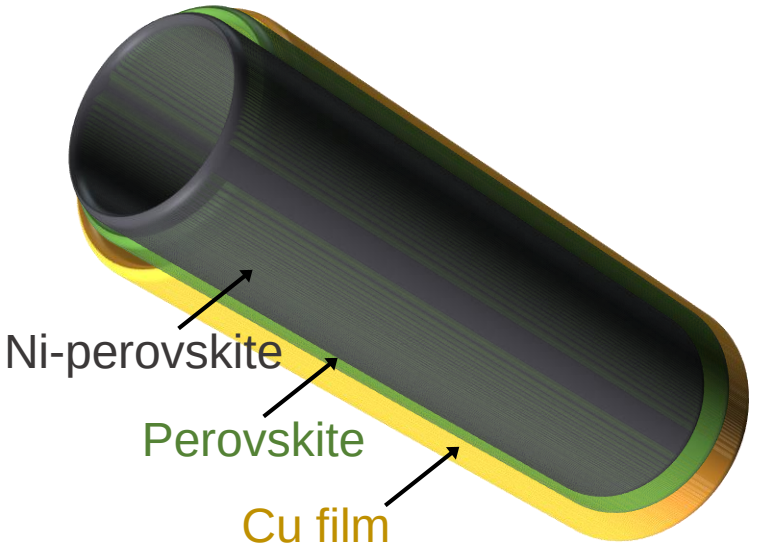
"Dip-coating": Pt thin film (Cu electroless activation)



PATENTED

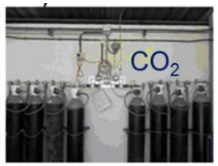
"Electroless": (Cu catalyst film)

PATENTED



Methanation of captured CO_2 in a solid oxide electrolyte membrane reactor

- Flow rate: up to 20 Nm^3/h, Temperature: up to 900 ° C, atmospheric pressure

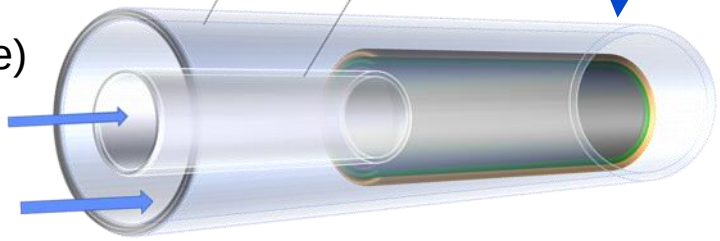


Quartz reactor

Quartz tube

10 % H_2 v/v in N_2 (H^+ source)
(ANODE)

Mix H_2/CO_2 = 4
(CATHODE)



Methanation of captured CO_2 in a solid oxide electrolyte membrane reactor

Screening of operating conditions:

Criteria: ↑ Energy Efficiency + ↓ Costs

- ✓ Maximize target fuel yield: CO_2 conversion (XCO_2) & selectivity (S_{CH4})
- ✓ Minimize energy input: maximize faradaic efficiency (η_c) & minimize energy cost (C_E)

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ (ΔHr<0)

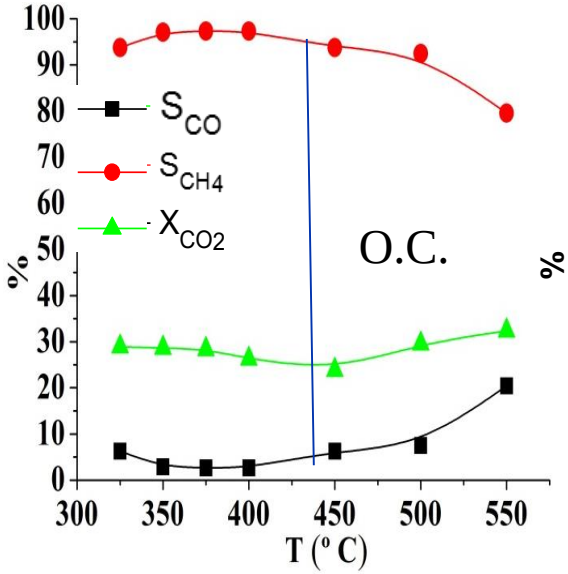
$CO_2 + H_2 \rightarrow CO + H_2O$ (ΔHr>0)

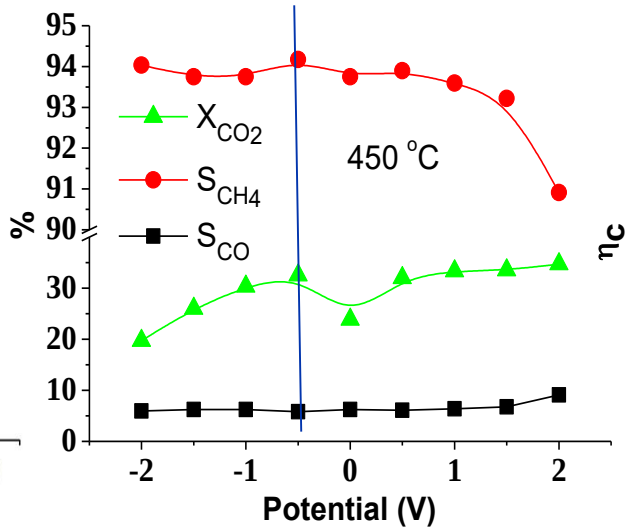
↑ Faradaic efficiency

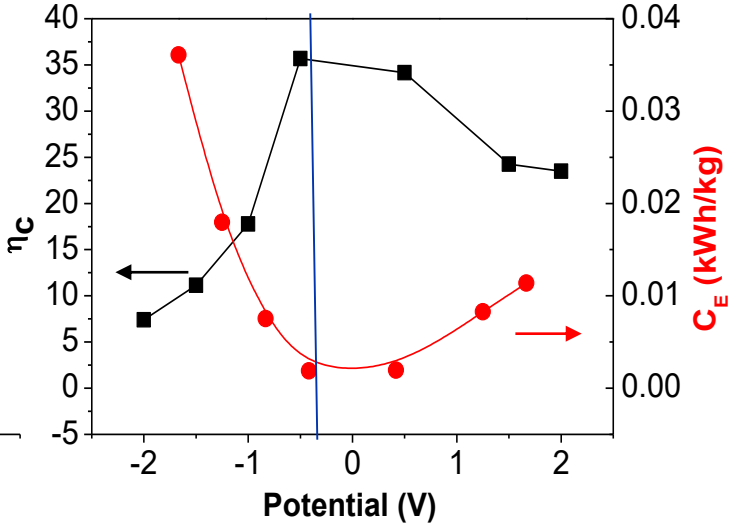
$$\eta_c = \frac{\left(\frac{m_p}{M_p}\right) * \left(\frac{\nu_e}{\nu_p}\right) * F}{I * t}$$

↓ Energy Cost (kWh/kg CH_4)

$$C_E = V * F * \frac{\left(\frac{\nu_e}{\nu_p}\right)}{(\eta_c * M_p)}$$







↑ Electropromotion

↑T ⇒↑ ionic/e- conductivy

↓ CH_4 purification cost

↑XCO_2. ↑ Sel_{CH4} ↓Sel_{CO}

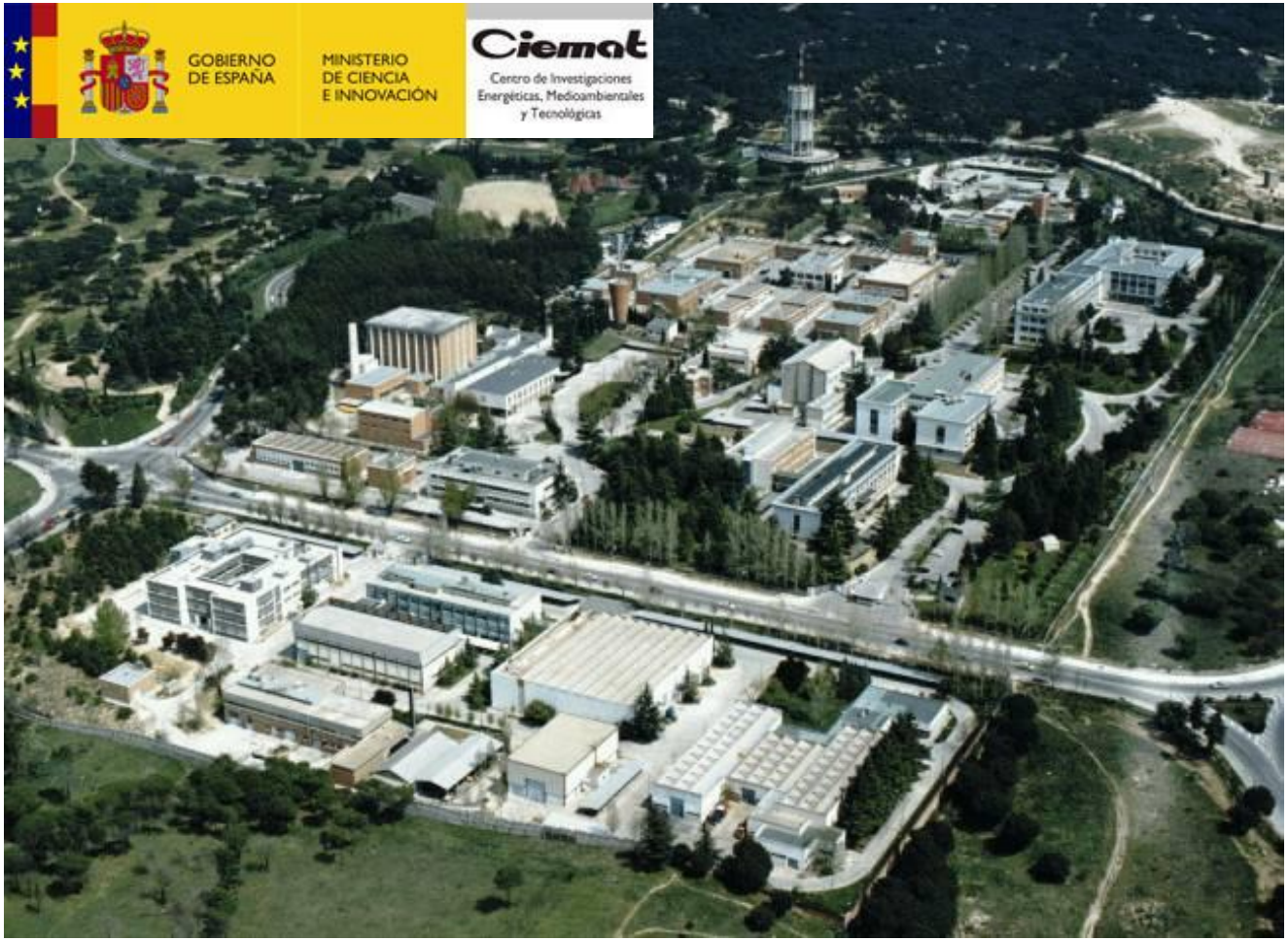
↑ Energy Efficiency.

η_c Max. & C_E Min.

Conclusions

- ✓ The development of viable solid oxide electrolyte based technologies for power to gas applications requires new and optimized advanced materials and testing under realistic conditions of potential practical application

- ✓ Material research opportunities for improving the activity, selectivity, stability, durability and scalability of electro-catalysts, as well as for increasing energy efficiency and reducing the cost of the process



Thank you for your attention!