Sunlight-to-methane conversion via a hybrid photo(bio)electrochemical system

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Background

ALGAESOL conversion route for methane production

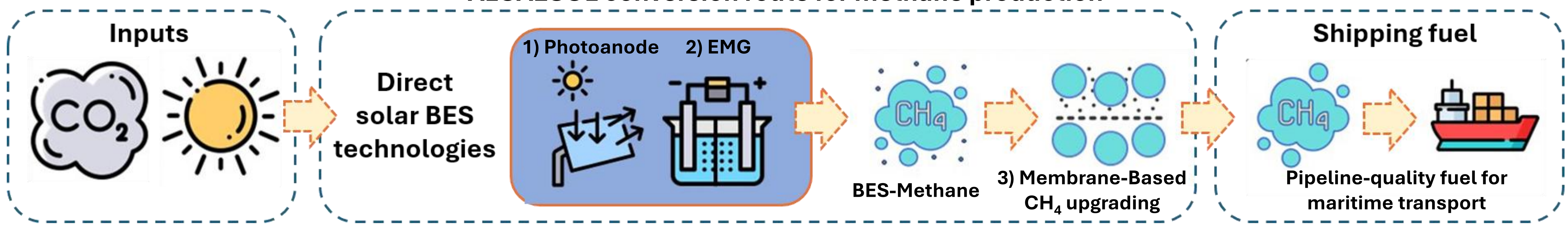

Figure 1: Maritime transport fuel production route for methane.

Motivation

- **Electromethanogenesis (EMG)** converts CO_2 into CH_4 using renewable electricity and a self-regenerating methanogenic biofilm.
- Coupling EMG process with a **photoanode** enables **direct-solar-driven CH_4 production**, reducing external electricity demand.
- Membrane technology is a sustainable alternative for final **upgrading to pipeline fuel's quality** standard.

Objectives

- **Development** and **optimization** of the **photoanode** and the **biocathode** independently.
- **Integration** of both electrodes in a novel **photo-bioelectrochemical reactor**.
- **Upgrading** produced synthetic methane using **sustainable membrane technology**.

Target KPIs

Photoanode:
- 10 mA/cm² photocurrent
- >85% Faradaic efficiency (FE)

EMG biocathode:
- 2 m³-CH_4/m³/day
- 10 A/m² current density
- > 90% FE

Materials & Methods

1) Photoanode development

- **Hematite (α-Fe_2O_3) photoanodes** were fabricated using a scalable screen-printing method on Fluorine-doped Tin Oxide (FTO) coated glass.
- A **sequential surface engineering approach** (Ti doping and GeO_2 passivation) was applied to overcome hematite's intrinsic charge-transport and kinetic limitations.

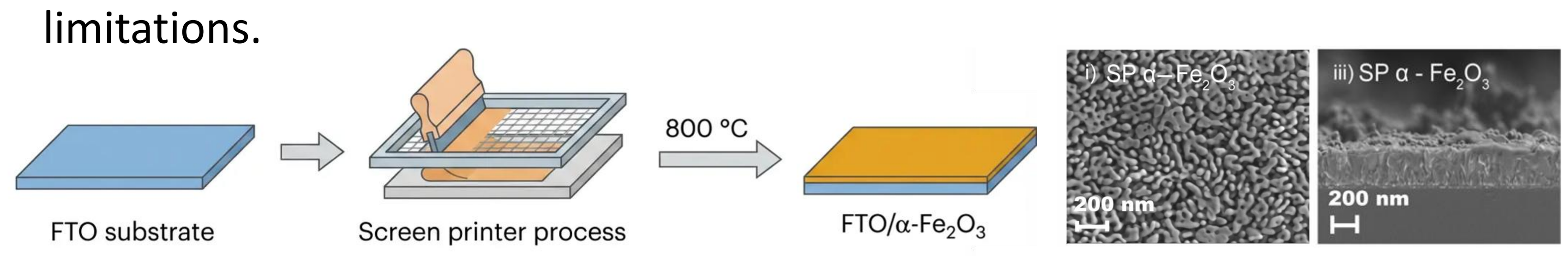

Figure 2: Schema of the synthetic procedure and top-view and cross-section FE-SEM images of the α-Fe_2O_3 photoanodes.

3) Membrane fabrication

- **Matrimid®** flat-sheet **membranes** were prepared using conventional solvent: **N-Methyl-2-pyrrolidone (NMP)** and **Tetrahydro-furan (THF)** as solvents.
- **Various polymeric concentrations** tested to optimize **morphology** and **gas-transport**.

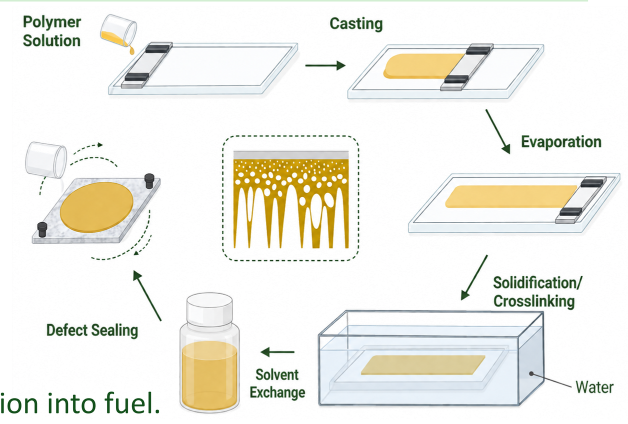

Figure 4: Schema of membrane fabrication for methane purification into fuel.

2) EMG biocathode development

Parallel stack of 3 double-chamber EMG cells (12 A/m²):

- **Anode** of Ti coated with MMO, 12 g Ir/ m² (total specific surface; 27 cm²) → water splitting.
- **Biocathode** of stainless-steel wool (total specific surface; 255 cm²) → **reduction of CO_2 to CH_4**, operating at 35±1°C and 150±6 mbarg.

Automated CO_2 injection controlled using a closed-loop PID strategy, with [CO_2] dissolved as input variable (10, 30 and 50%) to enhance purity of the methane produced.

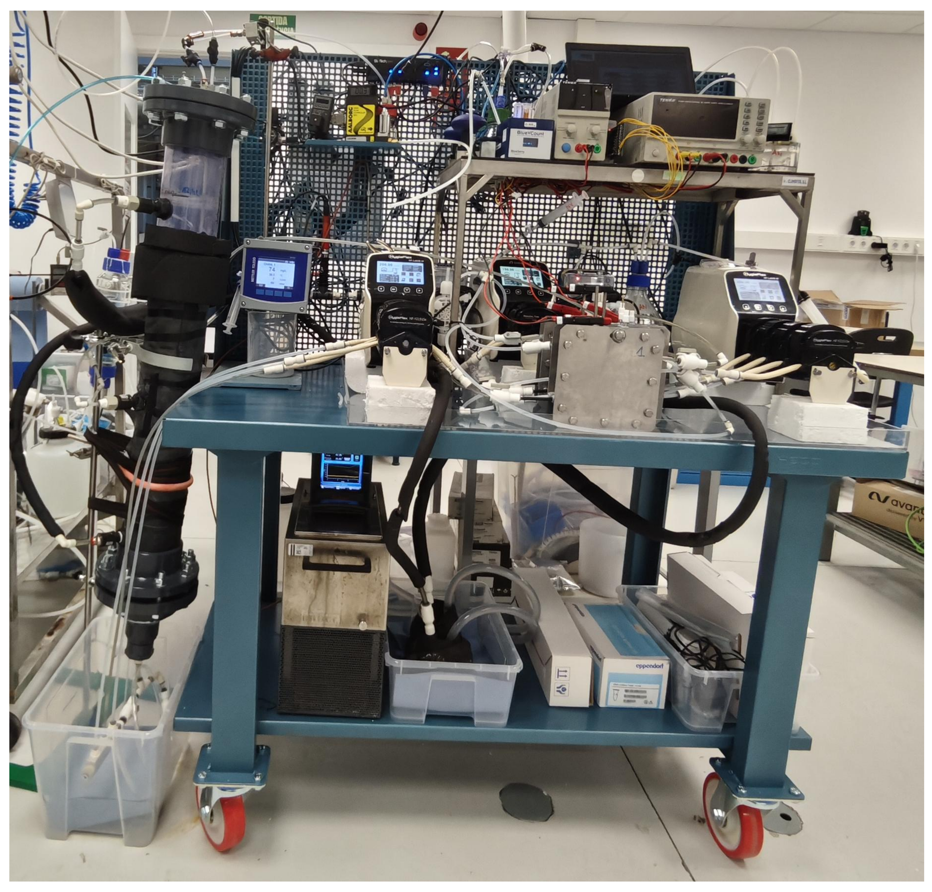

Figure 3: photograph of the BES-methane laboratory setup.

Results & Discussion

1) High performing photoanodes

- **State-of-the-art performance, high stability**
- **Complementary working conditions**, to be coupled with the EMG biocathode
- **Clear pathway towards targeted 10 mA/cm²** through tailoring of **oxidation substrate** and **light intensity**.

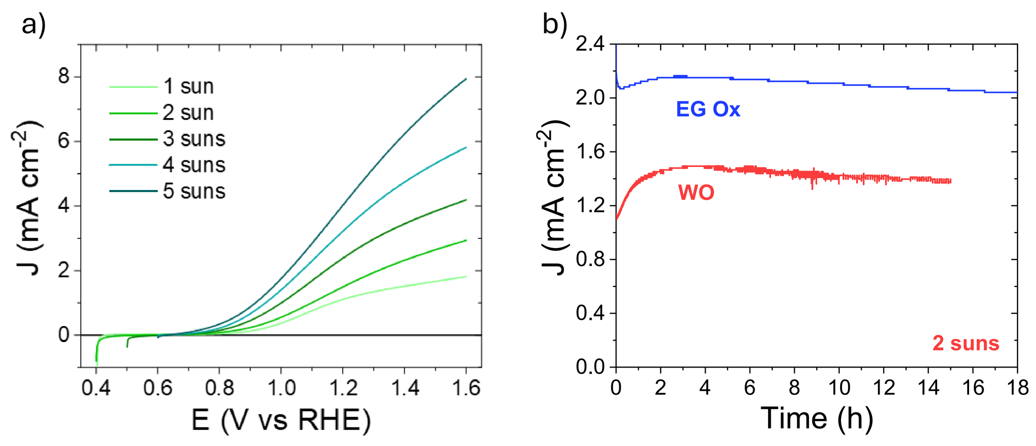

Figure 5: (a) Linear sweep voltammetry from 1 to 5 suns for ethylene glycol oxidation (EGOx). (b) Chronoamperometry at 1.4 V vs. RHE under 2 suns for WO and EGOx.

3) Membrane-based CH_4 upgrading into fuel

- A **trade-off** between **permeance** and **selectivity** was observed; **increasing** the **Matrimid®** concentration **improved ideal selectivity** but **reduced gas permeance**.
- **Further optimization** of membrane composition and fabrication parameters is required to **achieve target KPIs**.

Table 1: Pure gas permeation conditions: Steady-state operation, driving force 2 bar, room temperature. *GPU = 10^{-6} cm³(STP)/cm²/s/cmHg.

Matrimid® (Wt.%)	NMP : THF (Wt.%)	Permeance (GPU)*		Ideal Selectivity (CO_2/CH_4)
		CH_4	CO_2	
17	83:0	0.32	3.6	11.7
19	81:0	0.27	3.8	13.9
20	**80:0**	**0.12**	**1.8**	**15.1**
Target KPIs			>20-100	>20

2) Effect of dissolved CO_2 on EMG performance:

- **Lower [CO_2] dissolved** in the electrolyte lead to **less unreacted CO_2 in the outlet stream.**
- **No significant effect on CH_4 production rate, Faradaic, or CO_2 conversion efficiencies.**

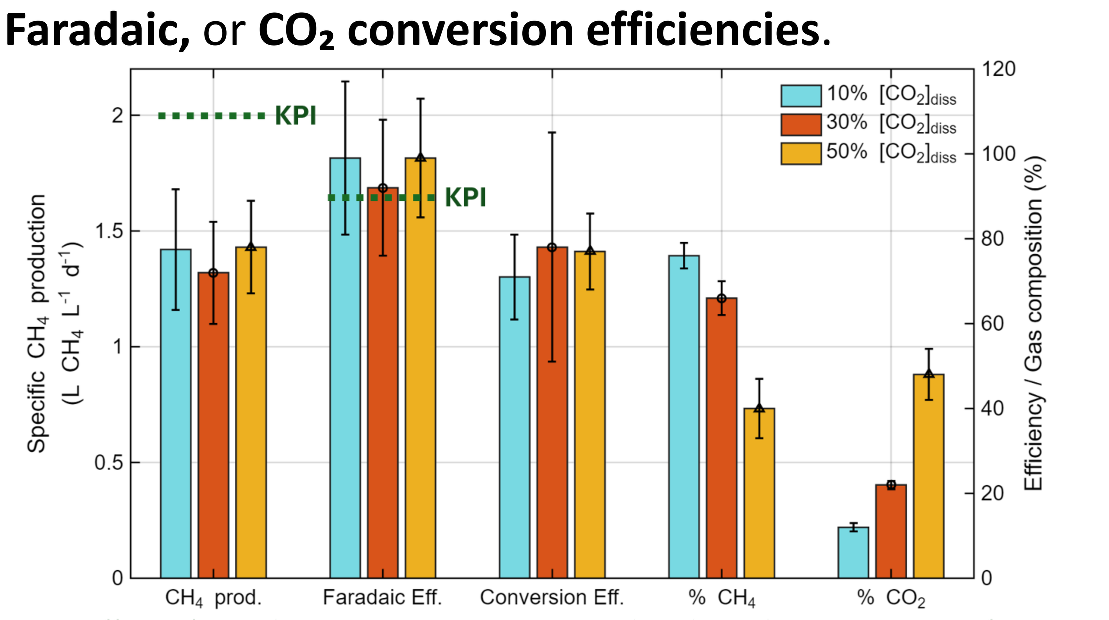

Figure 6: Effect of dissolved CO_2 concentration in the electrolyte on EMG performance. Bars represent specific CH_4 production, Faradaic efficiency, CO_2 conversion efficiency, and outlet gas composition (% CH_4 and CO_2), while error bars indicate standard deviation. Dashed green lines indicate the project KPIs.

Conclusions

All components independently validated:

- ✓ **High-performance hematite photoanodes** achieved.
- ✓ **Stable EMG biocathodes** demonstrated.
- ✓ **Membrane-based methane upgrading** successfully developed but **further optimization** is needed to achieve **pipeline-quality fuel**.

Next Steps

- → **Long-term stability testing** of the photoanode under varying sunlight conditions.
- → Integration of **photoanode** and **biocathode** into a novel **photo-bioelectrochemical reactor** (*patent under submission*).
- → Replacement of conventional solvents with **greener alternatives for membranes development**.

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