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

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Electromethanogenesis enables the bioelectrochemical conversion of CO_2 to CH_4, using a self-regenerating microbial consortium operating under ambient conditions, supporting renewable electricity storage and carbon valorization.[1] Coupling the process to a photoanode allows solar-driven water oxidation to supply electrons to the biocathode, reducing energy demand and enabling direct sunlight-to-methane conversion.[2] Within the European project ALGAESOL, dedicated photo(bio)electrochemical (PBE) reactors were developed to integrate both electrodes, which were optimized independently before evaluating the coupled configuration. Also, a solar concentrator based on Fresnel lens was designed to accelerate the reaction kinetics in the photoanode and obtain larger photocurrents.

Hematite (α-Fe_2O_3) photoanodes were fabricated using a scalable Large Bath Coating (LBC) method on Fluorine doped Tin Oxide (FTO) coated glass, yielding uniform ~200 nm films upon annealing at 800 °C, with enhanced electronic conductivity due to Sn-doping at the FTO|photoabsorber interface. A sequential surface engineering approach (Ti doping, GeO_2 passivation, and Ni decoration) was applied to overcome hematite's intrinsic charge-transport and kinetic limitations.

In parallel, the biocathode was optimized within a parallel stack of 3 double-chamber bioelectrochemical cells, equipped with stainless-steel-wool cathodes (121 cm^2) and Iridium Midex Oxide anodes (9 cm^2), separated by a cation exchange membrane. A common electrolyte was used in both chambers, consisting of a mineral solution for hydrogenotrophic methanogens.[1] The cathode chambers were inoculated with methanogenic biomass, previously enriched from anaerobic sludge. The catholyte was recirculated at 200 mL min^{-1} to a bubble column, where CO_2 was continuously supplied to maintain stable dissolved CO_2. The anolyte was recirculated at the same flow rate to a buffer tank. The pHs of anolyte and catholyte, the anode and cathode gas production rates and their composition were continuously monitored.

The optimized photoanode reached 11 A m^{-2} at +0.4 V vs Ag/AgCl in 1 M NaOH (pH 13.5) in a 3electrode configurations under 1 sun illumination, comparable to state-of-the-art α-Fe_2O_3 electrodes. On the other hand, the biocathode reached 12 A m^{-2} at -1.2 V vs Ag/AgCl and the onset of the Hydrogen Evolution Reaction (HER) was observed at -0.8 V vs Ag/AgCl. The biocathode for electromethanogenesis showed stable operation at different dissolved CO_2 ranges as shown in Table 1.

Table 1: Effect of dissolved CO_2 and current density on CH_4 production and Coulombic efficiency.

Current density	Dissolved [CO_2]	CH4 production rate (L $L_{cat}^{-1}day^{-1}$)	Coulombic efficiency (%)
12	10-20	0.88 ± 0.30	51 ± 20
12	20-40	1.10 ± 0.08	67 ± 5
12	40-60	1.00 ± 0.14	60 ± 10
18	10-20	1.40 ± 0.47	57 ± 13

For the downstream purification of the biomethane stream, Matrimid® flat-sheet membranes were prepared using DMI (dimethyl isosorbide) and methyl-THF as sustainable and green solvents. Membranes were then fabricated at various polymeric concentrations to optimize morphology and gas-transport properties. They are expected to exhibit high CO_2/CH_4 separation performance, enabling efficient upgrading of the biocathode-derived methane to pipeline-quality CH_4.

The next phase of the project involves testing a novel PBE reactor, that will enable coupling the developed photoanode and biocathode. Both components performed efficiently and stably when tested independently. The work now focuses on optimizing interfacial charge transfer to enhance solar-to-fuel conversion efficiency. Long-term stability tests will be conducted under different sunlight conditions.

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1. Vega-Paredes, M. *et al.* (2025). Stabilising methane production in a series-stack of bioelectrochemical systems. *Journal of Power Sources* 656, 238119.
2. Xiao, S. *et al.* (2020). Hybrid microbial photoelectrochemical system reduces CO2 to CH4 with 1.28% solar energy conversion efficiency. *Chemical Engineering Journal* 390, 124530.