Supplementary Information

Developing Sustainable Single Stage Reactors for Electrifying Bio-methanation: Perspective from Bio-Electrochemistry

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S1. Key performance metrics

To facilitate comparison between different electro-bioreactor systems, we recommend standardization of testing conditions and reporting several key performance metrics, which we define here. Kracke, et al. provided a comparison of key performance parameters in major literature studies of electro-bio-methanation using pure and mixed cultures.[1] However, direct comparison of the performance of various electrified bioreactors reported in the literature is complicated due to differences in the reactor type (e.g., H cell or flow cell), cathode/anode separator, reaction at the counter-electrode, and reported productivity units.[2–5]. An Excel tool for the calculations of key production parameters and reporting research data uniformly from bioelectrochemical systems is introduced by Patil, et al.[5]

Establishing standard testing conditions and relevant performance metrics is needed in future studies for accurate comparison to rapidly advance the field.

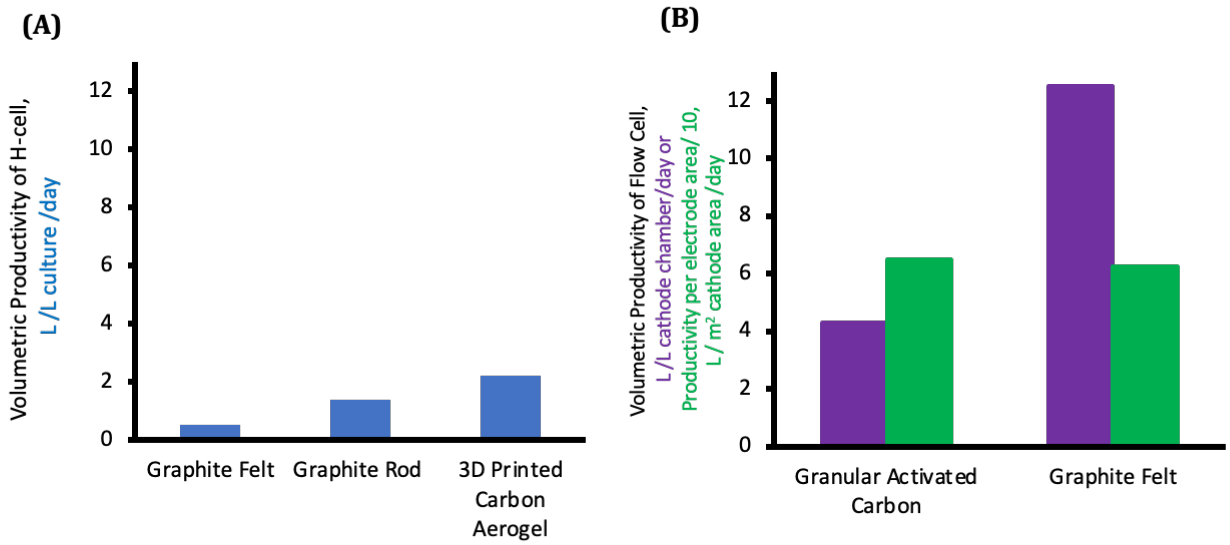

Figure S1: Productivity of electro-biomethanation normalized to culture volume in H-cell reactors (A) and normalized to cathode chamber volume or cathode area in Flow Cell reactors (B) with different carbon materials (Graphite Felt in H cell,[6] Graphite Rod,[1] 3D Printed Carbon Aerogel,[7] Granular Activated Carbon,[8] Graphite Felt in Flow Cell[9])

Volumetric Productivity (η_{VP})

Volumetric productivity is the rate of product evolution ($\mathbf{v_{CH4}}$) normalized by the reactor volume ($\mathbf{V_R}$) (Equation 1). It is central to decide the reactor size in industrial applications.[5] Higher volumetric productivity indicates more successful utilization of the reactor volume, and as will be shown in the next section, results in lower cost for methane production. The volumetric productivity is dependent on many parameters such as microbial cell density, microbial turnover rate, and electrolysis rate, which all need to be simultaneously optimized.[10]

$$\eta_{VP} = \nu_{CH4}/V_R \qquad \text{Equation 1}$$

We identified three different methods for productivity calculations in literature and the actual contribution of each representation for commercial development mainly depends on the relationship with the cost of methane production. Reactor type, critical material utilization and operational conditions are some key features for such an evaluation. In batch fed or continuous H-cells and column reactor-based studies, volumetric productivity is normalized to microbial culture volume, Figure S1(A).[1,6,7] Among H-cell studies, 3D printed electrodes show better volumetric productivity due to higher volume-normalized surface area of electrodes, leading to better utilization of the reactor volume.[1,6,7] Typically, in these reactors, microbial culture containing electrolyte is stored in the cathodic chamber of the reactor and magnetically stirred or recirculated using extremal pumps. In contrast, flow cell type reactors store microbial media in electrolyte tanks externally and recirculate through the electrodes containing flow cell unit. Some researchers have reported productivity in such reactors per cathodic chamber volume (Figure S1(B), purple bars) or by normalizing to the membrane area (Figure S1(B), green bars).[8,9]

However, we recommend system optimizations (e.g. ratios of microbial culture media optical density and volume to electrode surface area, cost) to get the optimal biocompatible productivity results from cost effective systems.

Faradaic Efficiency (η_F)

Faradaic efficiency is the ratio of charge ultimately utilized for the final product generation ($\mathbf{Q_{utilized}}$) to the total charge loaded ($\mathbf{Q_{total}}$) (Equation 2). In bio-catalyzed and mediated charge transfer processes, it indicates how efficiently the electrons are being converted into intermediate reactants by electrocatalysts and then into the desired product by the microbes. The Faradaic efficiency is also affected by cross-over of products and intermediates between anode and cathode during operation.

$$\eta_F = [Q_{utilized}]/[Q_{total}] \qquad \text{Equation 2}$$

In electro-bio-methanation reactors, the charge supplied to the system is initially consumed for water splitting (generating hydrogen) followed by CO_2 reduction at the biocatalyst mediated by hydrogen. Usually, an average of less than 5% of evolved hydrogen is lost due to consumption of hydrogen by microbes for non-methane producing needs.[11] Our previous work shows that Faradaic efficiency of electro-bio-methanation reactors can be sustained at >98% for over 4 weeks of continuous operation.[1]

Energy Efficiency (η_E)

Improvements that enhance the volumetric productivity need to be done in concert with increase in energy efficiency (Equation 3). The energy efficiency of bioreactors is predominantly controlled by voltaic efficiency which is the ratio of cell voltage ($\mathbf{E_{cell}}$) and reversible cell voltage ($\mathbf{E°_{cell}}$). Cell voltage of electro-bio-methanation reactor is a combination of overpotential and Nernst potentials of the water splitting reactions which are individually pH dependent. Energy efficiency is also dependent on η_F, however contribution from η_F is less than 2%.[12] Even though published literature has not reported energy efficiency values for the full system, from the reported cathodic half-cell potential values (630 mV vs SHE) [1] at 1 mA/cm^2 current density, we can estimate that the energy efficiency of single stage electro-bio methanation technology is still lower than 50%.

$$\eta_E = \eta_F * [E°_{cell}/ E_{cell}] \qquad \text{Equation 3}$$

Single-pass CO_2 conversion efficiency (η_C)

The ratio of CO_2 converted ($\mathbf{CO_{2\,converted}}$) to CH_4 to the total input carbon dioxide ($\mathbf{CO_{2\,input}}$) gives the single pass CO_2 conversion of the system (Equation 4) which can be optimized by engineering flow rates, steady state electrolysis rates, and microbial CO_2 uptake to achieve the maximum efficiency of microbial reaction and improving the selectivity to methane.

$$\eta_C = [CO_{2\ converted}]/[CO_{2\ input}] \qquad \text{Equation 4}$$

Stoichiometric conversion of one mole of CO_2 into methane requires four moles of hydrogen. Therefore, sufficient current must be passed to generate enough hydrogen to ensure this stoichiometry is met and CO_2 conversion is maximized. For example, at an input CO_2 flow rate of 10 sccm, not lower than 5.7 A of total current for HER is needed to enable full CO_2 conversion to CH_4. Note that generating enough hydrogen does not guarantee that all the CO_2 will be converted into methane—the microbial cell density and microbial turnover rate, as well as the residence time and mixing of the gases, are all important for maximizing single-pass conversion.

Outlet purity (η_P)

The quality of outlet gas is determined by the purity (Equation 5) which is the ratio of methane in the output (**$CH_{4\ measured}$**) compared to the total output gas composition. The main impurities in output gas are dependent on the CO_2 source, but typically are unreacted hydrogen (**$H_{2\ measured}$**) and carbon dioxide (**$CO_{2\ measured}$**). Sulfur, nitrogen, and other heteroatom-containing species may also be present in small quantities depending on the source of the CO_2.

$$\eta_P = [CH_{4\ measured}]/[CH_{4\ measured} + H_{2\ measured} + CO_{2\ measured}] \qquad \text{Equation 5}$$

Carbon selectivity (η_S)

In electro-bio-methanation, methane selectivity is the ratio of CO_2 converted (**$CO_{2\ converted}$**) to CH_4 to the total utilized CO_2 (**$CO_{2\ utilized}$**) (Equation 6).

$$\eta_S = [CO_{2\ converted}]/[CO_{2\ utilized}] \qquad \text{Equation 6}$$

Even at 100% purity of methane the overall carbon selectivity towards methane can be lower than 100% due to the carbon intake by microbes for their growth. However, most hydrogen-utilizing methanogens used in these systems produce only a small amount of cell mass as a side product-typical cell yields at optimum growth conditions range from 1.2–3 g dry cell mass per mole of CH_4 produced, which corresponds to 5–10% of the input CO_2.[11] At slower growth rates and sub-optimal growth conditions (commonly found in bio-electrochemical systems), the fraction of CO_2 converted to cell mass is typically even lower.[11]

A solid understanding of these performance metrics is important for determining the cost of producing methane using the electro-bioreactor technology. Technoeconomic analysis can be employed to help understand the relative importance of each of these factors and highlight key components of the system that require improvement.

S2. Process Flow Diagram and System Boundary of Studied Electro-Biomethanation Processes

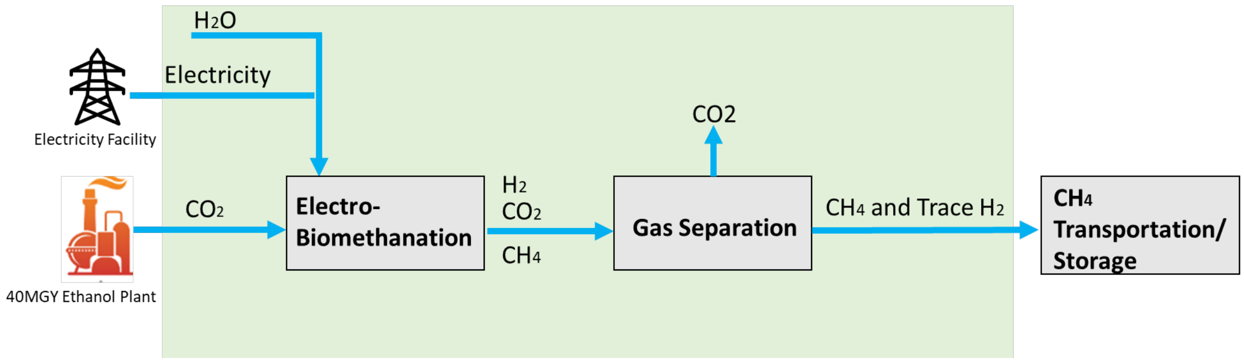

Figure S2. Process flow diagram of the electro-bio-methanation processes. The system boundary in this study is shown by shaded area including the CO_2-to-CH_4 reduction and gas separation stages.

S3. Major Economic Assumptions

Table S1: Major economic assumptions for discounted cash flow analysis.[13]

Economic parameters	Assumed basis
Basis year for analysis	2016
Debt/equity for plant financing	60%/40%
Interest rate and term for debt financing	8%/10 years
Internal rate of return for equity financing	10%
Total income tax rate	21%
Plant life	20 years
Construction period	3 years
Fixed capital expenditure schedule	32% in year 1
	60% in year 2
	8% in year 3
Start-up time	0.5 year
Revenues during start-up	50%
Variable costs during start-up	75%
Fixed costs during start-up	100%
Site development cost	9% of ISBL, total installed cost
Warehouse	1.5% of ISBL
Working capital	5% of fixed capital investment
Indirect costs	% of total direct costs
Prorated expenses	10
Home office and construction fees	20
Field expenses	10
Project contingency	10
Other costs (start-up and permitting)	10
Fixed operating cost	Assumed Basis
O&M	2.5% of ISBL
Manpower	3% of total direct costs
ISBL=inside battery limits (of the plant)	

S4. Capital and Operating Parameter Assumptions

Table S2: Key electro-bio-methanation process parameters for Modeled scenario and High and Low performance parameters for sensitivity analysis.

	High Performance	Modeled*	Low Performance
Electrolysis cell voltage	2.0 V	2.5 V	3.0 V
Electrolysis current density	75 mA/cm^2	50 mA/cm^2	37 mA/cm^2
Single-pass CO_2 conversion	97%	90%	85%
Methane productivity	12 g/L/h	8 g/L/h	6 g/L/h
Methane selectivity	98%	98%	90%
Electrode capital cost[14,15]	$700/m^2	$1400/m^2	$2100/m^2
Cost of electricity[16]	$0.00/kWh	$0.025/kWh	$0.06 kWh
CO_2 price[17]	$0/tonne	$25/tonne	$40/tonne

*Process parameters of modeled scenario are optimized values provided by R&D team.

Following the recent literature published on TEA on electrolyzer capital cost estimation,[6,7] we have analyzed the cost of electrolyzer in 3 different situations such as modeled case, and low and high-performance cases (Table S2). Based on reported current density and aqueous environments, alkaline water electrolyzers is selected as the most similar configuration to constraints dictated by biocatalyst.

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