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Microbial electrolysis cell (MEC): Strengths, weaknesses and research needs from electrochemical engineering standpoint

Raphaël Rousseau, Luc Etcheverry, Emma Roubaud, Régine Basséguy, Marie-Line Délia, Alain Bergel*

Laboratoire de Genie Chimique, Université de Toulouse, CNRS, INP, UPS, Toulouse, France

HIGHLIGHTS

- Thermodynamic basics of MEC are revisited.
- Equilibrium cell voltage of 0.123 V and maximum energy yield of 10 are main advantages.
- Faradaic yields can help identifying various MEC malfunctioning.
- Adding salts to increase the electrolyte ionic conductivity exacerbates pH issues.
- Local pH gradients and ion migration form a negative feedback loop.

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ABSTRACT

Microbial electrolysis cells (MECs) produce hydrogen at the cathode associated with the oxidation of organic matter at the anode. This technology can produce hydrogen by consuming less electrical energy than water electrolysis does. However, it has been very difficult so far to scale up efficient MECs beyond the size of small laboratory cells.

This article firstly revisits the fundamentals of MECs to assert their theoretical advantages. The low formal equilibrium cell voltage of 0.123 V and electrical and thermal energy yields as high as 10 and 12, respectively, are major assets. Other theoretical strengths are discussed, including the possibility to produce methane, and some safety advantages.

The experimental achievements at pilot scale (several litres volume) are analysed through the prism of electrochemical engineering. This analysis leads to recommendations to modify some research efforts, notably by giving priority to increasing current density rather than working with volumetric parameters, using Faradaic yields to detect dysfunctions, and systematizing control experiments at open circuit. The critical analysis successively addresses electrolytes, electrode kinetics, temperature, substrate concentration, reactor architecture, and control procedures. It brings to light intrinsic weaknesses of the MEC concept and identifies improvements that can be made using current technology, for instance, by the catalysis of hydrogen evolution at neutral pH. The problem of the low electrolyte conductivity is pointed out and, in return, how increasing it can be detrimental to the key issue of anode acidification. Finally, research lines are proposed with the objective of moving ahead towards MEC development.

1. Introduction

The need to switch from fossil energies to carbon-neutral sources has received unanimous agreement in principle, but how the switch can actually be made is still not obvious. The production of electrical energy from renewable sources such as wind, sunlight, marine streams and tides are very appealing options. Nevertheless, all these sources are intermittent and require efficient storage methods to smooth their fluctuations. The production of hydrogen by water electrolysis holds great promise for the transformation of electrical energy to chemical energy that can be stored, transported, and finally consumed or transformed back into electricity on demand [1,2]. Although various types of water electrolysis technologies are mature [3–5], progress still needs to be made if they are to be integrated into large-scale, economically

* Corresponding author.
E-mail address: alain.bergel@toulouse-inp.fr (A. Bergel).

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efficient energy networks [5]. In particular, electrocatalysts should be improved and their cost reduced [6,7]. For instance, a recent techno-economic analysis has stated that water electrolysis using solar electricity is still not economically competitive compared to hydrogen production from fossil sources [8].

In this framework, microbial electrolysis has been thought to offer a worthwhile, innovative route. The concept of microbial electrolysis cells (MECs) was first proposed in 2005 [9,10]. The core of an MEC consists of a microbial anode and an "almost conventional" hydrogen evolution cathode. The electrolyte in the anodic compartment must contain microorganisms and the culture medium necessary for their growth. Some microorganisms spontaneously colonize the anode surface and form an electroactive biofilm, which acts as the electro-catalyst. Thanks to this biofilm, the microbial anode can oxidize a large variety of low-cost carbon compounds [11–13].

The main advantage of MEC versus abiotic water electrolysis is that the oxidation of water is replaced by the oxidation of organic compounds, which can occur at significantly lower redox potentials. The thermodynamic cell voltage of an MEC is thus considerably reduced with respect to the famous 1.23 V threshold of water electrolysis in standard conditions [10]. The power consumed by an electrolysis cell is proportional to the cell voltage. In consequence, looking at the thermodynamics, it has been speculated that the MECs could be the breakthrough that will push electrolysis towards economic efficiency for hydrogen production. This major asset and other theoretical advantages of MECs are discussed in the "Thermodynamic basics and theoretical advantages" section of the present article.

A huge amount of work has been done to develop MECs, as proved by the more than 20 review articles published in the last five years [14–35,12,36,37]. The most cited review article, written by the inventors of the MEC, has now been cited more than 550 times [38], which shows the extent of research activity on MECs.

In spite of such research efforts, all attempts to scale up to large-sized MECs have encountered great difficulties [39,40]. Most MEC pilots with volumes of at least several litres display very low hydrogen production, corresponding to the cathode working at less than 1 $A{\cdot}m^{-2}$ (Table 1). For comparison, it may be recalled that commercial alkaline water electrolysis reactors usually work at several hundreds of $A{\cdot}m^{-2}$, and proton exchange membrane (PEM) electrolysis cells can reach 20,000 $A{\cdot}m^{-2}$. Even with such high current densities, the water electrolysis technology is considered to need further improvement [5,8]; this shows the very long way left to go for MECs.

The purpose of the present study is to analyse the MEC concept and the advances reported in the literature from the standpoint of electrochemical engineering. Actually, designing an MEC is a strong multidisciplinary challenge and it may be useful to recall the basics of electrochemical engineering so as to take stock and stimulate renewal. For this purpose, basic concepts of thermodynamics adapted to MECs are recalled and used to assess the theoretical strengths of MECs. The literature is then reviewed, successively addressing inoculum, electrode material, temperature, substrate concentration, electrolyte, control procedure, and reactor architecture. For each step, the objective is not to propose a comprehensive review - such reviews are already available - but to find some answers to the questions that an electrochemical engineer with the objective of designing a MEC asks himself. Theory and literature data are analysed through the prism of electrochemical engineering. This approach leads to a non-current vision of the MEC technology, which suggests reorienting some research directions if the objective is to scale-up MECs to large-sized units.

2. Thermodynamic basics and theoretical advantages

2.1. Basics of MEC thermodynamics

The main advantage of the MEC over abiotic water electrolysis is that, at the anode, the oxidation of water is replaced by the oxidation of organic compounds. Thanks to the action of microorganisms, the oxidation of organic compounds consumes considerably less energy than oxidation of the strong water molecule. The oxidation of acetate to CO_2/HCO_3^- is the most widely used model reaction for bioanodes [38]. According to this model, from the thermodynamic standpoint, the bioanode compartment is a system that consumes acetate and produces CO_2 and HCO_3^-. The first basic question that an electrochemical engineer may ask himself, without entering into consideration on kinetics, is whether it is more relevant to write the oxidation reaction with gaseous CO_2 (Reaction 1), dissolved CO_2 (Reaction 2) or HCO_3^-

Table 1
Characteristics of MEC pilots with volumes of at least several litres. V is the total reactor volume, σ is the ionic conductivity of the electrolyte, U is the cell voltage, PBS phosphate buffer solution. Current densities and production rates are expressed with respect to the cathode projected surface area. The anode Faradaic yield (*An.*) is the ratio of the electrons circulating in the electrical circuit to the electrons that could be extracted from the amount of substrate oxidized. The cathode Faradaic yield (H_2) is the ratio of the electrons that could be recovered from the H_2 produced to the electrons circulating in the electrical circuit. The overall cathode Faradaic yield (ϕ_{cath}) is defined in Section 3.4. γ_G and γ_H are the energy and thermal yields defined in Section 2.4. The lines in italics give maximum values relating to different operating conditions that do not match together.

V (L)	Cathode surface area (cm^2)	Anolyte	σ ($S{\cdot}m^{-1}$)	U (V)	Current density ($A{\cdot}m^{-2}$)	Gas production ($L{\cdot}d^{-1}{\cdot}m^{-2}$)		Faradaic yields (%)			Energy yields (–)		Ref.
						H_2	CH_4	An.	Cath H_2	Φ_{cath}	γ_G	γ_H	
1000	72 288	Winery effluent	0.07–0.18	0.9	0.25	13.8	0	–	552	550	7.5	9.1	[41]
		vinegar, PBS			0.93	0	30.2	–	0	1295	0	16.6	
120	3 360	Wastewater acetate	0.17	*1.1*	*0.3 max*	*3.6*	*0.06*	*16*	*55*	–	*0.69*	–	[42]
				1.1	*0.10 max*	*3.6 max*	*0*	–	*52 max*	–	*0.69 max*	*0.83 max*	[43]
5 × 2	3 024	Wastewater	0.7	1.08	0.61	1.0	yes	19	23	16	0.19	0.22	[44]
2 × 2	840	Wastewater	0.05	1.0	0.22	2.1	0.4	11–807	96	168	1.2	2.3	[45]
				1.0	0.24	1.06	0.23	–	44	82	0.5	1.1	[46]
6.6 × 2	2 226	Wastewater	0.16	*0.7*	*0.53 max*	*0.166*	–	*97–460*	–	–	–	–	[39]
30	5 778	Synthetic wastewater	–	NA	0.78	–	–	27	–	–	–	–	[47]
16	3 852	Wastewater	–	NA	0.72	–	–	11	–	–	–	–	[47]
		Effluent, acetate	–	NA	1.09	–	–	8	–	–	–	–	[47]
4	188	Saline synthetic medium, acetate	9	1.56	42.5	201	Yes	–	47	> 47	0.37	–	[48]
130	16 300	Wastewater	0.75–1.3	1.0	0.3	2.52	< 5%	28	84	≥84	1.03	1.24	[49]
33	4 466	Sewage sludge	–	2.0	0.01	0	0.28	–	–	1117	0	6.45	[50]
18	1 705	Synthetic wastewater, sucrose	0.17–0.5	0.8	0.1	0.45	0.82	–	–	372	0.69	5.55	[40]
16	1 800	Pig slurry, acetate	2.6	1.0	1.75	17.8	< 2%	7–9	78	101	1.25	1.5	[51]