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

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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

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·m^{-2} (Table 1). For comparison, it may be recalled that commercial alkaline water electrolysis reactors usually work at several hundreds of A·m^{-2},

and proton exchange membrane (PEM) electrolysis cells can reach 20,000 A·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·m^{-1})	U (V)	Current density (A·m^{-2})	Gas production (L·d^{-1}·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 vinegar, PBS	0.07–0.18	0.9	0.25	13.8	0	–	552	550	7.5	9.1	[41]
					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]

Table 2

Different possible ways of writing acetate oxidation and related thermodynamic equations. By convention, reactions are written in the reduction direction. E_A is the equilibrium potential (V/SHE), $E_A{}^0$ is the standard potential (V/SHE), $E_A{}^{0\prime}$ is the formal potential at pH 7.0 (V/SHE), p_{CO2} is the CO_2 partial pressure (atm), which was assumed to be equal to the fugacity, C_i are the concentrations of the i species (mol·L^{-1}), which were assumed to be equal to activities, R (8.314 J mol^{-1} K^{-1}) is the universal gas constant, T (K) is the temperature, and F (96 485 C·mol^{-1}) is the Faraday constant. The standard potentials were calculated by using the standard molar Gibbs energy of formation of each compound as detailed in the Supporting Information.

Reaction and equilibrium potential	$E_A{}^0$ (V/SHE)	$E_A{}^{0\prime}$ (V/SHE) pH 7.0	Standard conditions
1 $\quad 2CO_2 + 7H^+ + 8e^- \rightarrow CH_3COO^- + 2H_2O$ $E_A = E_{A1}{}^0 - \frac{2.3RT}{8F}7pH + \frac{2.3RT}{8F}\log\left(\frac{p_{CO_2}^2}{c_{CH_3COO^-}}\right)$	0.071	-0.291	$T = 298.5$ K pH = 0 $p_{CO2} = 1$ atm $C_{CH3COO-} = 1$ M
2 $\quad 2CO_{2,aq} + 7H^+ + 8e^- \rightarrow CH_3COO^- + 2H_2O$ $E_A = E_{A2}{}^0 - \frac{2.3RT}{8F}7pH + \frac{2.3RT}{8F}\log\left(\frac{c_{CO_2,aq}^2}{c_{CH_3COO^-}}\right)$	0.093	-0.269	$T = 298.5$ K pH = 0 $C_{CO2,aq} = 1$ M $C_{CH3COO-} = 1$ M
3 $\quad 2HCO_3^- + 9H^+ + 8e^- \rightarrow CH_3COO^- + 4H_2O$ $E_A = E_{A3}{}^0 - \frac{2.3RT}{8F}9pH + \frac{2.3RT}{8F}\log\left(\frac{c_{HCO_3^-}^2}{c_{CH_3COO^-}}\right)$	0.187	-0.278	$T = 298.5$ K pH = 0 $C_{HCO3-} = 1$ M $C_{CH3COO-} = 1$ M

(Reaction 3) as the product. Each form leads to a different expression for the equilibrium potential of the reaction (Table 2).

The three equations lead to significantly different values of the standard potentials ($E_A{}^0$). These differences are due to the different standard conditions assumed for each equation (Table 2). It may be noted that the standard conditions assumed for Eqs. (2) and (3) are far from conditions that are usually met in MECs. For Eq. (2), according to the Henry law, the condition $C_{CO2,aq} = 1$ M assumes a CO_2 partial pressure of the order of 29 atm. For Eq. (3), according to the acid dissociation equilibrium, the standard condition $C_{HCO_3^-} = 1$ M at pH 0 leads to an unrealistic concentration of dissolved CO_2 of 2.24 10^6 M and to CO_2 partial pressure of 6.6 10^7 atm. These standard conditions are far from usual operating conditions. Eqs. (2) and (3) lead to inappropriate standard potential values ($E_A{}^0$) because of the unrealistic standard conditions they are based on. Moreover, if the concentration term is neglected in Eq. (3), an incorrect variation of E_A as a function of pH is obtained. Actually, a part of the pH impact is included in the third term of the equation because pH influences the HCO_3^- concentration (see Supporting Information). Eqs. (2) and (3) should consequently be avoided, except for specific purposes.

With regard to the formal potential values ($E_A{}^{0\prime}$), the errors induced by Eqs. (2) and (3) are minimized. Obviously, the three expressions lead to identical equilibrium potential (E_A) when the full equations are used with the right values of concentrations and pressure (see Supporting Information).

In conclusion, Eq. (1) should be preferred. This equation is established with standard conditions not so far from conditions that can be met in actual MECs. Moreover, practically, it is quite easy to find the value of the CO_2 partial pressure that must be used to calculate E_A accurately. For instance, in a single-compartment MEC working at atmospheric pressure, p_{CO2} should be equal to 0.33 atm and p_{CO2} should be 1 atm with separated compartments (see below).

Hydrogen evolution at the cathode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{4}$$

has an equilibrium potential E_C:

$$E_C = 0.0 - \frac{2.3RT}{F}pH - \frac{2.3RT}{2F}\log(p_{H_2}) \tag{5}$$

where p_{H2} is the hydrogen partial pressure. From this equation, the formal potential $E_C{}^{0\prime}$ at pH 7.0 and standard temperature is -0.414 V/SHE.

Coupling the oxidation of acetate at the anode (Reaction 1) with the reduction of water at the cathode (Reaction 4) leads to the overall reaction:

$$CH_3COO^- + H^+ + 2H_2O \rightarrow 2CO_2 + 4H_2 \tag{6}$$
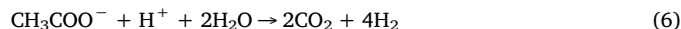
with the cell voltage (U)

$$U = E_A - E_C = 0.071 + \frac{2.3RT}{8F}pH + \frac{2.3RT}{8F}\log\left(\frac{p_{CO_2}^2 p_{H_2}^4}{C_{CH_3COO^-}}\right) \tag{7}$$

At pH 7.0, the equilibrium cell voltage is 0.123 V, which means that hydrogen evolution starts to be possible at a cell voltage as low as 0.123 V with an MEC that oxidizes acetate. Comparison with the equilibrium cell voltage of 1.23 V for water electrolysis shows the considerable benefit that could be expected from the MEC.

Eq. (7) shows a very low dependency of the equilibrium cell voltage on pH, only 7.4 mV per pH unit at 25 °C. Actually, the thermodynamics of both the anode and cathode reactions are significantly affected by the pH (52 mV/pH unit in Eq. (1) and 59 mV/pH unit in Eq. (5), respectively), but the global MEC thermodynamics is not highly dependent on pH, provided that the anode acidification and the cathode alkalinisation could be used to mitigate each other.

The evolution of the cell voltage as a function of the acetate concentration is illustrated in Fig. 1 for three different cases:

(a) MEC with separated anode and cathode compartments: CO_2 and H_2
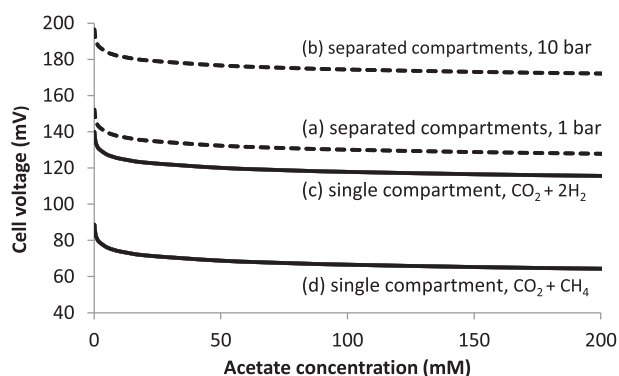
Fig. 1. Equilibrium cell voltages calculated with Eq. (7) versus acetate concentration. Calculations were performed at pH 7.0 and a temperature of 298.15 K. Dashed lines: two-compartment MEC under 10 (b) or 1 atm (a) pressure in each compartment. Continuous lines: single-compartment MEC under 1 atm total pressure for the production of pure hydrogen (c) noted $CO_2 + 2H_2$, or the complete conversion of hydrogen to methane (d) noted $CO_2 + CH_4$. In the case of methane production, the calculation was done with p_{CO2} and p_{H2} equal to 0.5 and 0.01 atm, respectively.

partial pressures were equal to 1 atm in the anode and cathode compartments, respectively;

(b) the same two-compartment MEC configuration operated under 10 atm pressure: p_{CO2} and p_{H2} were both equal to 10 atm;

(c) a single-compartment MEC: according to Reaction 6, the partial pressures of H_2 and CO_2 were 0.67 and 0.33 atm, respectively.

The cell voltage is weakly dependent on acetate concentration, except for very low concentrations of a few millimolars (Fig. 1). It is consequently not very useful to increase the substrate concentration with the objective of favouring the thermodynamics. Implementing a single-compartment or a double-compartment reactor is pretty similar from a thermodynamic point of view.

Interestingly, Fig. 1 points out that operating the reactor under pressure increases the equilibrium cell voltage only slightly. Only around 40 mV are lost when the pressure is increased from 1 to 10 atm. It can consequently be very beneficial to operate an MEC under pressure so as to produce pressurized gas directly at the reactor outlet. The power lost in the MEC is much less than the power that would be required for mechanical compression of the gas downstream. Moreover, microorganisms are generally not significantly sensitive to pressure up to very high values. For instance, high pressure processing, which is used for food preservation [52], must use pressures above 100 MPa – i.e. 1000 atm – in order to affect microbial populations [53]. It seems that there is no theoretical barrier to operating an MEC under pressure of several atm, although it has never been attempted so far to our knowledge. This may be a worthwhile research path for future MEC development.

2.2. Other advantages of MEC vs. water electrolysis

Microbial electrolysis has several well-known advantages. The electroactive biofilms develop spontaneously on the anode surface from the microbial species contained in the electrolyte. Consequently, forming microbial anodes does not require sophisticated electrode preparation steps as for most abiotic catalytic layers. Low cost electrode materials can be used such as some carbon-based materials. Microbial biofilms self-assemble and also self-sustain, allowing long-term MEC operation without maintenance [43]. They catalyse the electrochemical oxidation of a large variety of organic compounds [11–13].

An MEC that operates under appropriate control procedure (see Section 3.10) does not produce oxygen. This advantage has rarely been emphasized so far, but it is a great advantage in terms of process safety with respect to water electrolysis. Actually, the concomitant production of hydrogen and oxygen is an important issue in water electrolysis that is no longer present in an MEC. This safety asset becomes even more important if the objective is to produce pressurized hydrogen, because high internal pressure in water electrolysis considerably increases the risk of hydrogen cross-over to the anode compartment [54,55]. In an MEC, hydrogen transport to the anode only decreases the energy yield but does not exacerbate safety issues.

Similarly, the anode of an MEC operates at too low a potential for the production of chlorine to become a risk. This is also an advantage, because the electrolyte does not need to be freed from the chlorine ions, as is required for conventional water electrolysis.

The pH of the MEC electrolyte must be around neutrality because microbial anodes rarely accept extreme conditions [56]. Acidic electrolytes are prohibited because electroactive biofilms are inhibited at pH values one or two units below 7 [57–59]. On the other hand, the pH of the bulk electrolyte rarely reaches values above 10 in microbial electrochemical systems. The restricted range of pH around neutrality is clearly an advantage in terms of safety because the electrolyte can be handled easily without drastic precautions. It is, for instance, very much easier to replace and dispose of a phosphate solution at pH 7 rather than the KOH solution at pH 14 that is commonly used in alkaline water electrolysis cells.

2.3. MEC for methanation and microbial electrosynthesis

MECs for hydrogen production can also be the basis of electrosynthesis reactors for the production of a great variety of compounds. For example, hydrogenotrophic methanogenic *Archaea* can be set in the cathode compartment where they will use the hydrogen produced to reduce CO_2 to CH_4 [60,61]:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (8)$$

In a single compartment MEC, CO_2 produced at the bioanode can combine with hydrogen produced at the cathode [62] leading to the overall reaction:

$$CH_3COO^- + H^+ \rightarrow CO_2 + CH_4 \qquad (9)$$

Actually, methane may be considered as a side-product that pollutes hydrogen production [19,49] and must consequently be avoided [63,64,21,65] or, in contrast, MECs can be designed with the deliberate objective of producing methane [19,61,62].

The equilibrium cell voltage is plotted in Fig. 1 for a single-compartment MEC working in methanation (Reaction 9) under 1 atm total pressure, i.e. with CO_2 and CH_4 partial pressures of 0.5 atm each. In this case, the equilibrium cell voltage depends on the residual H_2 partial pressure present in the MEC. Logically, the more efficient methanogens are at consuming H_2, the lower the H_2 partial pressure becomes and the more the thermodynamics of hydrogen evolution is favoured. The curve was plotted for a hydrogen partial pressure equal to 0.01 atm. The equilibrium cell voltage becomes equal to zero for H_2 partial pressure of 10^{-4} atm (P_{CO2} = 0.5 atm, $C_{CH3COO-}$ = 1 M, pH = 7.0, T = 298.15 K), which means that the process would become spontaneous if the hydrogenotrophic methanogens were efficient enough to consume hydrogen very fast and maintain very low hydrogen partial pressure in the MEC.

Actually, the overall reaction (9) is identical to the acetoclastic pathway of methane production in anaerobic digestion. It is known that extremely low hydrogen partial pressure is required for this conversion to occur [66]. Here, the thermodynamics of the MEC shows that this conversion becomes spontaneous at very low H_2 partial pressure, as is known in the context of anaerobic digestion.

The interest of implementing an MEC to produce methane as often been presented as a complement to anaerobic digestion (AD). It is generally claimed that MECs can operate with lower concentrations of substrate than AD so, for instance, effluents from a digester could be an appropriate inlet stream for an MEC [17,62,67,68]. Coupling MEC to AD has been shown to accelerate the degradation of some recalcitrant compounds and alter the AD microbial community thus increasing biogas production [16]. It can also be hoped that a two-compartment MEC would produce a biogas richer in methane than that obtained through anaerobic digestion and could also protect the methanogenic consortia against inhibitory compounds that may be present in the wastes used as feedstock [61].

Acetate, butyrate, caproate and other compounds can also be synthesized at the cathode by coupling the electrochemical production of hydrogen with a microbially catalysed reaction that uses hydrogen as electron donor. So-called microbial electrosynthesis cells have been shown to be able to convert CO_2 into various products [69–73]. Some microbial electrosynthesis pathways are assumed to involve direct electron transfer from the cathode to the microorganisms [74] but mediation by hydrogen is often the main route [71,75].

The interest of coupling the electrochemical production of hydrogen with its microbially-catalysed utilization in the same reactor can be debated (see section 4.4). It has been argued that large-scale microbial electrosyntheses that involve hydrogen mediation would be better implemented via two separate reactors: an electrolyser for hydrogen production and, downstream, a gas-liquid contactor for the microbially-catalysed hydrogenation [75,76]. Here, the purpose is not to develop

this debate but only to illustrate the versatility of MECs, pointing out that consuming hydrogen in situ in the cathode compartment is beneficial to the thermodynamics.

2.4. Energy and thermal energy yields

The energy yield (γ_G) of an electrolyser that produces hydrogen is generally expressed as the ratio of the energy that could be recovered from the hydrogen produced to the electric energy consumed to generate it [77]:

$$\gamma_G = \frac{N_{H2}}{U} \frac{\Delta G^0_{c,H2}}{J} \tag{10}$$

where N_{H2} ($mol \cdot s^{-1} \cdot m^{-2}$) is the molar flux of hydrogen per unit cathode surface area, U (V) is the cell voltage, J ($A \cdot m^{-2}$) is the current density and $\Delta G^0_{c,H2}$ ($J \cdot mol^{-1}$) is the absolute value of the standard Gibbs free energy change for hydrogen combustion (237.1 $kJ \cdot mol^{-1}$)

In the context of pure hydrogen production, the objective is generally to further use the hydrogen in fuel cells, which means that only the Gibbs free energy can be exploited. In this case, methane, which is often produced in MECs due to Reaction 8, is considered as a side-product that must be avoided or separated and is not considered in the energy balance.

In contrast, if hydrogen is intended to be burned, the thermal energy yield (γ_H) can be assessed by using the standard enthalpy change of hydrogen combustion. Moreover, in this case, it may be useful to produce a mix of hydrogen and methane, for instance to be introduced into the gas distribution network. Both methane and hydrogen are used for their heat of combustion. The thermal energy yield γ_H is consequently calculated by taking the enthalpies of combustion of both hydrogen and methane into account:

$$\gamma_H = \frac{N_{H2}\Delta H^0_{c,H_2} + N_{CH4}\Delta H^0_{c,CH_4}}{U \quad J} \tag{11}$$

where $\Delta H^0_{c,H2}$ is the absolute value of the standard enthalpy change of hydrogen combustion (286 $kJ \cdot mol^{-1}$), $\Delta H^0_{c,CH4}$ is the absolute value of the standard enthalpy change of methane combustion (891 $kJ \cdot mol^{-1}$), N_{H2} and N_{CH4} ($mol \cdot s^{-1} \cdot m^{-2}$) are the molar fluxes of hydrogen and methane per unit cathode surface area.

The maximum limit values of the two energy yields can be assessed by using the equilibrium cell voltage in Eqs. (10) and (11). It should be noted that this assumption, which is usually made in order to assess the maximum limits of energy yields, is completely theoretical because an electrolyser cannot produce anything under equilibrium conditions.

In order to calculate the theoretical, maximum limit values of the energy yields, the molar fluxes of H_2 and CH_4 were extracted from the electron balance assuming that the Faradaic yields were equal to 100% at both anode and cathode. When 1 mol of electrons moves though the electrical circuit from the bioanode to the cathode:

– 0.25 mol of CO_2 is produced at the bioanode (Reaction 1), and x mole can be transformed to CH_4 (Reaction 8)
– 0.5 mol of H_2 is produced at the cathode (Reaction 4), and 4x mole can be transformed to CH_4 (Reaction 8)
– x mol of CH_4 can be produced by the combination of H_2 with CO_2 (Reaction 8).

This simple mass balance leads to the expression of the molar flux given in Table 3.

In a 2-compartment MEC, it was assumed that no methane was produced, so $x = 0$ and the molar flux of hydrogen, equal to $\frac{J}{F}$0.5, was input into Eqs. (10) and (11). The values of the pressure of CO_2 and H_2, equal to 1 atm in each compartment, were used to calculate the equilibrium cell voltage (Eq. (7)), which led to the maximum values of the energy yield γ_G and the thermal energy yield γ_H (Eqs. (10) and (11))

Table 3
Theoretical molar fluxes calculated with 100% Faradaic yields at both bioanode and cathode.

Gas molar flux N ($mol \cdot s^{-1} \cdot m^{-2}$)			
H_2	CO_2	CH_4	Total
$\frac{J}{F}(0.5 - 4x)$	$\frac{J}{F}(0.25 - x)$	$\frac{J}{F}x$	$\frac{J}{F}(0.75 - 4x)$

Table 4
Maximum energy and thermal energy yields for MECs and water electrolysis cell. The CO_2 and H_2 partial pressures were used to calculate the equilibrium cell voltage U_{eq} with Eq. (7). Calculations were performed with T = 298.15 K, pH = 7.0 and acetate concentration = 1 M. For the MEC with complete conversion of H_2 to CH_4, the partial pressure of hydrogen (p_{H2}) was assumed equal to 10^{-4} atm.

| Operating conditions	Gas composition (atm)			U_{eq} (V)	Max. limit values	
	p_{CH4}	p_{CO2}	p_{H2}		γ_G	γ_H
2-Compartment MEC without CH_4 production	0	1	1	0.123	10.0	12.1
1-Compartment MEC with production of various ratios of CH_4	0	0.5	0.5	0.109	11.3	13.6
	0.05	0.35	0.60	0.109	8.4	12.8
	0.20	0.40	0.40	0.105	3.9	12.0
	0.40	0.47	0.13	0.092	1.0	12.9
	0.49	0.50	0.01	0.059	0.14	19.5
	0.5	0.5	10^{-4}	0	0	7223
Water electrolysis	–	–	1	1.23	1.00	1.21

reported in Table 4.

For a single-compartment MEC, calculations were made for various CH_4 partial pressures, from no production of methane ($p_{CH4} = 0$) to the total conversion of hydrogen to methane ($p_{CH4} = 0.5$ atm). For each value of CH_4 partial pressure, the value of x and the partial pressures of H_2 and CO_2 were calculated by using Table 5. The values of the H_2 and CO_2 partial pressures were then used to calculate the equilibrium cell voltage (Eq. (7)), which led to the maximum values of the energy yield γ_G and the thermal energy yield γ_H (Eqs. (10) and (11)) reported in Table 4.

2.5. Comparison of MEC and water electrolysis in terms of theoretical energy yields

In a conventional water electrolysis cell, assuming 100% Faradaic yield at the cathode, the molar flux of hydrogen is equal to J/2F, so:

$$\gamma_G = \frac{\Delta G^0_c}{2FU} \tag{12}$$

Obviously, $\gamma_G = 1$ when U is set equal to the equilibrium cell voltage of 1.23 V ($\Delta G_c{}^0$ = -237.1 $kJ \cdot mol^{-1}$). For water electrolysis, the maximum value of γ_G is equal to unity because the reaction of water electrolysis

$$2H_2O \rightarrow O_2 + 2H_2 \tag{13}$$
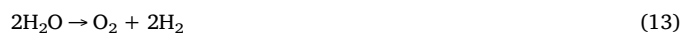
Table 5
Theoretical partial pressures calculated with 100% Faradaic yields at both bioanode and cathode using the mass balance described in Table 3.

Partial pressures in a single compartment MEC (atm)			
H_2	CO_2	CH_4	Total
$\frac{0.5 - 4x}{0.75 - 4x}$	$\frac{0.25 - x}{0.75 - 4x}$	$\frac{x}{0.75 - 4x}$	1

is exactly the reverse of hydrogen combustion.

The maximum limit values are assessed by assuming that electrolysers operate at the equilibrium cell voltage. Close to equilibrium, water electrolysis is an endothermic reaction. Water electrolysis should consequently be provided with heat so as to occur close to the equilibrium cell voltage. Nevertheless, the power that should be provided in the form of heat for water electrolysis to occur close to the thermodynamic equilibrium is not taken into account in the calculation of the thermal energy yield. For this reason the thermal energy yield can theoretically be greater than unity, as reported in Table 4 (γ_H = 1.21).

In an MEC, hydrogen is produced by Reaction 6, which is not the reverse of hydrogen combustion. This reaction requires considerably less electrical energy than water electrolysis, so the energy yields can be significantly higher than unity, up to 10 or 11.3 for γ_G depending on the MEC design (Table 4). Another way to explain the yields higher than unity is to say that an MEC takes advantage of two sources of energy, the energetic power and the chemical energy contained in the compounds that are oxidized at the bioanode. Only the electric energy is taken into account when assessing the energy yield. This approach is justified when the compounds oxidized at the bioanode are waste organic matter that must be treated. The yield equations would have to be modified if more valuable compounds were oxidized at the bioanode.

When the side-production of methane is enhanced, the energy yield, γ_G, which is related to hydrogen only, logically decreases (Table 4). In contrast, the thermal energy yield, γ_H, which takes the contributions of both hydrogen and methane into account, remains close to 12. This stability is the result of two antagonistic effects. On the one hand, the increase in methane ratio decreases γ_H because 4 molecules of hydrogen are required to form one molecule of methane (Reaction 8) but the standard enthalpy of methane combustion (891 kJ·mol^{-1}) is less than four times that of hydrogen combustion (286 kJ·mol^{-1}). On the other hand, by decreasing the partial pressure of hydrogen, the production of methane decreases the equilibrium cell voltage.

Finally, if the production of methane is very fast with respect to hydrogen evolution, the hydrogen partial pressure would tend to zero. In theory, the thermal energy yield would therefore tend to infinity (in Table 4 it is equal to 7223, when using a hydrogen partial pressure of 10^{-4} atm). This limiting case has a fundamental interest because it tends towards spontaneous anaerobic digestion. This is beyond the scope of a MEC. It might be speculated that this limiting case may be close to the field of electro-fermentation, in which electrical power intervenes by non-Faradaic pathways [78], which would result in considerable energy yields, although the meaning of electrical energy yield may be debate in this case.

The great values of the energy yields illustrate the interest of MEC technology. Energy yields up to 10 or 11 may theoretically be hoped for when considering only the production of hydrogen. This means that more than 10 times the electric power that is provided to the MEC is stored in hydrogen in the form of Gibbs free energy. This energy yield decreases significantly when the side-production of methane is not avoided but, in this case, the production of a hydrogen-methane mix keeps the thermal energy yield close to 12 for applications based on gas combustion.

3. The engineering challenges that must be tackled if the thermodynamics is to fulfil its promises.

3.1. An antagonism linked to the very essence of MEC

A large gap exists between the theoretical hopes and the experimental realizations. A glance at Table 1, which relates MEC pilots with volumes of at least several litres, confirms that hydrogen can be produced with cell voltages lower than that required for water electrolysis. Nevertheless, current densities remain dramatically low, often less than 1 A·m^{-2}.

One of the reasons for such poor performance has been the usual choice to try to apply MECs to wastewater treatment. Domestics wastewaters, which are the most commonly targeted for MEC feeding, have very low ionic conductivity, commonly of the order of 0.2 S·m^{-1}, sometimes less [79], and scaling up an electrochemical process with such poorly conductive electrolytes is an extremely tough challenge [80,81]. Actually, an "abiotic" electrochemical engineer would consider it heresy to put wastewater into an electrolyser.

More generally, sustaining microbial growth in a culture medium and implementing an electrolyser for large-scale hydrogen production are two antagonistic objectives. The electrochemical processes developed so far at industrial scale require the cleanest possible electrolytes, with the simplest possible chemical composition, in order to avoid deposit on the electrode surfaces and inhibition of the electrode catalysts. Abiotic electrocatalysts are generally very sensitive to any form of inhibition by adsorption of chemical compounds and would quickly lose their effectiveness in a culture medium. Moreover, electrolytes for water electrolysis are strongly acid or alkaline. At the opposite extreme, sustaining microbial growth requires neutral pH and chemically rich media. Culture media must contain a large number of ions, including Ca^{2+} and Mg^{2+}, which can result in hydroxide deposits and many chemical compounds that may adsorb on electrode surfaces. Here is the stumbling block of the whole enterprise: the two objectives are completely antagonistic.

3.2. Current density or volumetric production rate?

When reading the literature on MECs, an electrochemical engineer is surprised at not always finding the values of current density, while values of volumetric hydrogen production rates are generally reported. Physically, current and hydrogen production are not extensive variables relating to the reactor volume. Increasing the electrolyser volume does not increase the hydrogen production if the electrode surface area is not increased. For this reason, using the volumetric hydrogen production rate may lead to wrong conclusions. For example, a bioanode of 1 cm^2 surface area working at 100 A·m^{-2} in a reactor of 200 mL gives a volumetric hydrogen production rate of 0.5 N L$_{H2}$ L^{-1} d^{-1} (assuming 100% Faradaic yield). In comparison, a bioanode of 100 cm^2 working at only 1 A·m^{-2} in a reactor of 100 mL, produces 1 N L$_{H2}$ L^{-1} d^{-1}. Comparing these two systems by using the volumetric production rates would lead to the erroneous conclusion that the second bioanode performs better and may incite a designer to abandon the most promising bioanode able to provide 100 A·m^{-2}. In the case of electrochemical processes, the volumetric production rate is dependent on the reactor configuration, so it can completely skew the assessment of the electrode efficiency.

Current density must be used to characterize any electrochemical process. A glance at one of the pillars of electrochemical engineering literature can convince the reader of this [77]. In this book, the different industrial electrochemical processes are always described and compared in terms of current density. Other major parameters are also indicated, such as voltage, energy consumption, inter-electrode distance, and electrode surface area, but there is no mention of volumetric production rates.

It should still be kept in mind that volumetric production rates can be useful for specific purposes, mainly if the objective is to improve the compactness of reactors or to compare the area footprint of two systems. Similarly, for instance, the production rate per unit reactor weight becomes a major parameter for transportation and spatial applications. Nevertheless, such parameters address only specific targets, linked to given application. To contribute to the general development of MECs, the multidisciplinary research community should be advised to use current density systematically as the main parameter for characterizing and comparing MECs.

3.3. Why should increasing current density be a major goal?

In the general context of chemical engineering, heterogeneous processes using a solid catalyst are known to be one level more complex than homogeneous processes. Considering that an electrochemical process is based on two different heterogeneous catalytic reactions, which are interdependent, shows that its complexity is at least two levels higher than that of a homogeneous process. Consequently, replacing a homogeneous process by an electrochemical process can only be planned if considerable benefits are expected.

An electrochemical reactor is sophisticated piece of equipment, which is delicate to design and to implement. It requires two electrodes to be designed, generally set face to face, with an inter-electrode distance as small as possible to reduce the ionic resistance of the electrolyte. Maintaining uniform hydrodynamics within the narrow compartment(s) is difficult and costly in terms of pumping energy. The reactor must include several electrical connections and possibly large current collectors when the intrinsic conductivity of the electrodes is not high enough. Sometimes a separator is needed. Technically, such an arrangement needs many seals and rigid frames held by strong presses or a multitude of screws. Dismantling them is a labour-intensive operation, which may be quite frequent because electrodes wear out or are damaged by deposits. The maintenance is time-consuming and requires a high level of technical training. In addition, passing electricity through solutions is always a sensitive safety issue. Ohmic losses due to electrical connexions and the peripheral electrical set-up can be significant.

All these issues are exacerbated when the electrode surface becomes larger. Larger electrode surface area means greater likelihood of clogging or leakages, greater difficulty in maintaining flatness, higher number of connexions, more delicate and longer disassembly/reassembly operations, higher risk of stray currents… These are the reasons why ensuring high current density is the main objective that is targeted when designing electrolysers. Reducing the surface area of electrolysers is essential to allow their industrial development for the production of chemicals.

The case of water electrolysis can illustrate this situation. Actually, it would be possible to design low-cost water electrolysis reactors working at low current density. Alkaline electrolysers could work perfectly at low current density with cheap electrodes made of low grade steel. Furthermore, operating at low current would decrease the ohmic losses and could compensate the overpotential losses due to the absence of catalyst on the electrodes. Hydrogen produced at low current density in low-cost water electrolysers would not be more expensive than that produced in reversed PEM fuel cells, which can work at more than $10,000 \, A \cdot m^{-2}$. Nevertheless, low-cost water electrolysers working at low current density have never been contemplated for large-scale industrial development. On the contrary, researchers are still trying to improve electrocatalysts in order to increase current densities. This is not because of an irrational desire for high technology, but because ensuring high current density is an imperative for scaling-up industrial electrolysers to be used for large-scale hydrogen production, even for a reaction as simple as water electrolysis.

Obviously, this essential rule, established for large-scale production electrolysers, should be qualified, particularly in the context of microbial electrochemical technologies. One of the fascinating aspects of microbial electrochemical technologies is their capacity to generate ground breaking concepts. Microbial electrochemical technologies can thus be the source of new electrochemical processes that do not have ensuring high current density as a prerequisite for their development. For instance, microbial electrochemical snorkels [82,83] can be developed at large scale on the basis of low current, because they can be designed according to an extremely simple configuration. They can be considered as simple conductive biofilters [84], which do require neither a sophisticated arrangement nor specific care. Another example is electro-fermentation, a non-Faradaic microbial electrochemical

process, in which the potential is used to control the redox state of the microbial cells [78]. In this case, the current does not provide the charge necessary for conversion but it indirectly orients the catalytic pathway. Will it be possible to find such an innovative process for hydrogen production, for which maximising current density may not be the main requirement?

To sum up, two different research strategies must be explored to develop MEC. On the one hand, ground breaking concepts may be discovered, which might overcome the need to maximize the current density. This path remains open. On the other hand, if the objective is to adapt conventional electrolyser architectures to microbial catalysis, increasing current density must be considered as the main purpose.

3.4. Faradaic yields are useful tools for identifying operating issues in MECs

At the anode, the Faradaic yield expresses the ratio of the amount of electrons that are provided to the electric circuit to the total amount of electrons that could be extracted from the substrate oxidation. A glance at Table 1 shows a few anode Faradaic yields that are considerably higher than 100%. This phenomenon has been attributed to hydrogen cycling [39,45,85,86]. Hydrogen produced at the cathode reaches the anode, where it is oxidized:

$$H_2 \rightarrow 2H^+ + 2e^- \tag{14}$$

Although never evoked in the context of MEC yet, a similar scheme can also be postulated with methane. Methane results from the combination of H_2 produced at the cathode with CO_2 produced at the bioanode (Reaction 8), and could be oxidized at the bioanode [87,88]:

$$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^- \tag{15}$$

Anode Faradic yields above 100% reveals MEC dysfunction. This is an important issue which can cause significant hydrogen/methane loss.

At the cathode, the Faradaic yield is generally related to hydrogen production. It expresses the ratio of the amount of electrons that could be recovered from the hydrogen produced to the electrons that circulated in the electrical circuit. It can be anticipated that cathode Faradaic yields will be close to 100%, because it is difficult to see that any reaction other than the reduction of water/proton could occur at the cathode. Actually, the electrochemical reduction of CO_2, to formate for instance, would be possible [89,90] but has not been evoked in the case of MECs and is unlikely because of low partial pressure of CO_2.

Table 1 shows that cathode Faradaic yields most often ranging from 50 to 80%. These low values are due to the consumption of hydrogen either in the bulk (Reaction 8) or at the anode (Reaction 14), because cathode Faradaic yields are calculated using the hydrogen flow out of the reactor and not the hydrogen flow that is produced at the electrode surface. The low values of the cathode Faradaic yield essentially indicate the extent of the hydrogen consumption by side-reactions, or even hydrogen leaks, rather than being related to the electrochemical process of hydrogen evolution.

An extremely high value of the H_2 Faradaic yield (552%) is also reported in Table 1. It corresponded to the spontaneous production of hydrogen by sugar fermentation [41]. In this case the electrochemical process may play a minority role in hydrogen production. Substrates that contain fermentable compounds, such as sugars, may lead to strong overestimation of the contribution of the electrochemical process to hydrogen production. This issue should be systematically addressed when implementing substrates that include a fermentable part or when the composition of the substrate is not well mastered. It points out the necessity to perform control experiments at open circuit in order to assess the possible production of hydrogen and methane by microbial processes in the absence of electrochemical assistance. This is an important difference with water electrolysis, for which control experiments at open circuit are obviously useless. In contrast, such control experiments should be systematically performed for MECs that use

complex substrates, which may contain fermentable compounds.

In the absence of such control experiments, evaluations of the energy and thermal yields should be considered with caution, because a part of the hydrogen and/or methane production may result from microbial processes that have nothing to do with electrochemistry. To detect this type of situation, we suggest calculating the overall cathode Faradaic yield (Φ_{cath}), defined as the ratio of the electrons that could be recovered from the hydrogen and methane produced to the electrons circulating in the electrical circuit:

$$\Phi_{cath} = \frac{2FN_{H2} + 8FN_{CH4}}{J} \qquad (16)$$

where F (96,485 C·mol^{-1}) is the Faraday constant, N_{H2} and N_{CH4} (mol·s^{-1}·m^{-2}) are the molar fluxes of hydrogen and methane per unit cathode surface area, and J is the current density (A·m^{-2}).

Values of Φ_{cath} above 100% indicate the side-production of hydrogen and/or methane by non-electrochemical pathways, as was the case for several MEC pilots reported in Table 1. In such cases the energy and thermal yield values keep some practical meaning, because any source of production is obviously welcome, but the contribution of electrochemistry, if any, cannot be evaluated. In a few extreme cases, where Φ_{cath} exceeds 200%, electrochemistry makes a minority contribution (unless there is an electro-fermentation effect [78]).

On the other hand, it should be noted that a Φ_{cath} value lower than 100% does not prove definitively that no microbial hydrogen and/or methane side-production occurs, because of the possible conversion of hydrogen to other compounds. Calculating Φ_{cath} cannot replace open-circuit control experiments.

In conclusion, the anode Faradaic yield and the overall H$_2$ Faradaic yield are easy-to-calculate parameters that allow the direct detection of possible dysfunctions such as H$_2$ re-cycling at the anode, H$_2$ consumption in the bulk, and H$_2$ side-production by fermentation. Apparently, these dysfunctions often occur in MEC pilots (Table 1). On the other hand, the overall cathode Faradaic yield should be used systematically to detect possible side-productions of hydrogen and/or methane.

3.5. Electrolyte: a key issue

As explained in Section 3.1, polluting the electrolyte with so dirty medium as one suitable for microbial growth appears a very curious idea to an "abiotic" electrochemical engineer. It seems even more surprising that the majority of MEC pilots have been applied to the treatment of effluents and wastewater (Table 1) [28,36]. These media have very low ionic conductivity, commonly of the order of 0.2 S·m^{-1}, sometimes less [79], which makes the design of efficient electrochemical cells extremely difficult [80,81]. Higher current densities, of 1.35 A·m^{-2}, have been obtained with MEC pilots by adding phosphate buffer into the effluent [41], and using a synthetic medium supplemented with acetate as the substrate has given up to 10 A·m^{-2} [91]. To the best of our knowledge, the highest current density reached with an MEC several litres in volume, of 42.5 A·m^{-2}, was obtained by using a high concentration of salt (35 g/L NaCl) to attain a fair ionic conductivity of 9 S·m^{-1} [48].

Low conductivity of the electrolytes is a major reason for the poor performance reported so far with large-sized MECs [80,92]. At low ionic conductivity, it is very important to optimize the MEC architecture in order to permit the electrodes to work in conditions that are the least detrimental possible [93] and increasing size inevitably leads to a rapid decrease in performance [81].

To overcome this major obstacle, many attempts have been made to develop microbial anodes able to operate in saline and hypersaline media [48,94–97]. According to a recent review [98], the most efficient halotolerant microbial anodes have been prepared with inocula coming from salt marshes [99–101]. These microbial anodes produced up to 85 A·m^{-2} under polarization at 0.1 V/SCE with acetate 40 mM. They

Table 6

Transport numbers in the bulk of the electrolyte for a saline electrolyte composed of NaCl 45 g·L^{-1}, CH$_3$COONa 40 mM, NH$_4$Cl 37 mM and phosphates 3 mM, pH 7.5 [101]. The molar ionic conductivities are taken from the Handbook of Chemistry and Physics [102]. Transport numbers were calculated according to: $t_i = \frac{\lambda_i C_i}{\sum_k \lambda_k C_k}$ as described in [79], where $\sigma = \sum_k \lambda_k C_k = 10.7$ S·m^{-1} is the theoretical ionic conductivity of the medium.

Ion	Concentration C_i (mM)	Molar ionic conductivity λ^0_i (10^{-4} m^2·S·mol^{-1})	Transport number t_i (%)
Na$^+$	810	50.1	37.9
NH$_4^+$	37	73.5	2.5
K$^+$	4.2	73.5	0.3
Cl$^-$	807	76.3	57.5
CH$_3$COO$^-$	40	40.9	1.5
H$_2$PO$_4^-$	1.8	36	0.06
HPO$_4^{2-}$	1.2	114	0.13

operated in media containing NaCl at 45 g·L^{-1} with an ionic conductivity of 10.4 S·m^{-1}, i.e. a value of the same order as those used in water electrolysis. For instance, the ionic conductivity of a thin PEM is around 10 S·m^{-1} and the 20–30% KOH electrolytes commonly used in alkaline water electrolysis can reach 60 S·m^{-1} [5].
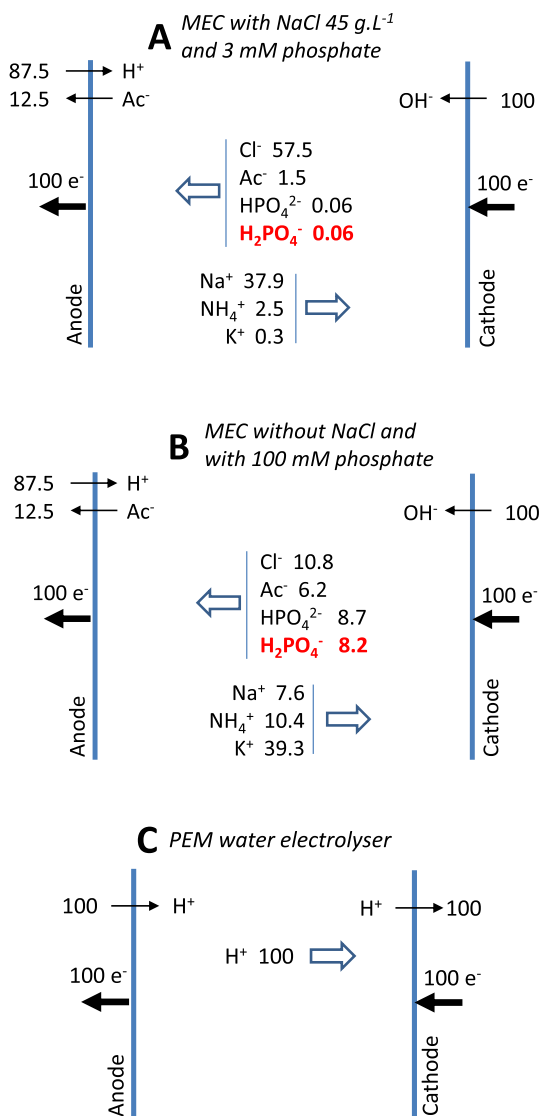
The major components of the electrolyte used to develop this halotolerant microbial anode were NaCl 45 g·L^{-1} (770 mM), CH$_3$COONa (40 mM), NH$_4$Cl (37 mM) and phosphates (3 mM) [101]. The transport numbers (Table 6) indicated that, in the solution bulk, far from the concentration gradients occurring in the vicinity of the electrode surfaces, 95% of the current was carried through the electrolyte by the motion of Na$^+$ to the cathode (37.9%) and of Cl$^-$ to the anode (57.5%). NaCl played its role of current carrier through the electrolyte perfectly.

It may be recalled that, as observed in Table 6, neither H$^+$ nor OH$^-$ help to carry electricity through the electrolyte. Their concentrations are too low around neutral pH to have any effect on the ionic transport of electricity [79]. Rigorously speaking, the salt marsh inoculum added at 5 to 10% v/v into the medium should modify the accurate distribution of the transport numbers, mainly with the addition of small concentrations of sulphate, magnesium and calcium ions. Nevertheless, these small disturbances should not modify the general situation described here.

The ionic transport through the electrolyte can be outlined by means of the ion fluxes expressed on the basis of 100 electrons exchanged at the electrodes. When 100 electrons are transferred to the anode, 12.5 molecules of acetate are consumed and 87.5 protons are produced at the bioanode (Reaction 1), while 100 hydroxide ions are produced at the cathode (Reaction 4). To compensate for the ion imbalance thus created, 57.5 Cl$^-$ and 1.5 CH$_3$COO$^-$ ions move to the anode, while 37.9 Na$^+$ and 2.5 NH$_4^+$ ions move to the cathode (Fig. 2A). This emphasizes a crucial problem: migration does not contribute to pH balance at the electrodes. The phosphate species, which were present in this medium at only 3 mM, played no significant role in ionic transport through the bulk of the electrolyte.

The protons produced at the anode are not driven away from the anode zone by migration and they are not neutralized by the migration of buffering species to the anode. The flux of H$_2$PO$_4^-$ ions, the only species which could mitigate the anode acidification is only of 0.06 ion for 100 electrons exchanged. Similarly, the OH$^-$ ions produced at the cathode are not driven away by migration. The anode vicinity acidifies and the cathode vicinity alkalinizes, and only diffusion due to the concentration gradients can mitigate anode acidification and cathode alkalinization.

From a thermodynamic standpoint, cathode alkalinization is detrimental to the hydrogen evolution reaction rate (Reaction 4). In addition, alkalinization of the cathode vicinity is a specific problem for MECs, because cations such as Ca^{2+} and Mg^{2+}, which are required to sustain the bioanode, deposit in the form of hydroxides on the cathode

A *MEC with NaCl 45 g.L⁻¹ and 3 mM phosphate*

87.5 → H^+
12.5 ← Ac^-

OH^- ← 100

100 e^- (Anode) → 100 e^- (Cathode)

← Cl^- 57.5 / Ac^- 1.5 / HPO_4^{2-} 0.06 / **$H_2PO_4^-$ 0.06**

→ Na^+ 37.9 / NH_4^+ 2.5 / K^+ 0.3

B *MEC without NaCl and with 100 mM phosphate*

87.5 → H^+
12.5 ← Ac^-

OH^- ← 100

100 e^- (Anode) → 100 e^- (Cathode)

← Cl^- 10.8 / Ac^- 6.2 / HPO_4^{2-} 8.7 / **$H_2PO_4^-$ 8.2**

→ Na^+ 7.6 / NH_4^+ 10.4 / K^+ 39.3

C *PEM water electrolyser*

100 → H^+ / H^+ → 100

H^+ 100 →

100 e^- (Anode) / 100 e^- (Cathode)

Fig. 2. Ion fluxes due to migration. The numbers of ions are calculated on the basis of 100 electrons passing through the electrical circuit. (A) Saline electrolyte composed of NaCl 45 g·L⁻¹, CH_3COONa 40 mM, NH_4Cl 37 mM and potassium phosphates 3 mM, pH 7.5 [101]; (B) same electrolyte without NaCl and with potassium phosphates 100 mM; (C) PEM electrolyser.

surface. Salt precipitation and chemical fouling of the cathode surface is known to be a severe drawback in microbial electrochemical processes [103–105,50].

In a microbial fuel cell, bubbling CO_2 inside the cathode compartment has been successfully used to reduce the pH and reducing the overpotential related to oxygen reduction [106]. In an MEC, the same process also succeeded in reducing the bulk pH but had a limited effect on the cathode overpotential [107]. It was suspected that the pH may have kept high local value near the cathode surface.

Anode acidification is an even more crucial issue because, in addition to the detrimental effect on the thermodynamics, microbial anodes are severely inhibited, or even deteriorated, at slightly acid pH values [57,59].

In the medium used in the previous works to form efficient halo-tolerant anodes, the low ability to mitigate anode acidification may be attributed to the low concentration of phosphates. Nevertheless, even if the phosphate concentration was increased to 100 mM, or more, the situation would be only slightly improved. For instance, with 100 mM of phosphate species, 1.7 $H_2PO_4^-$ ions migrate towards the anode for

100 electrons exchanged (Table S3 in supporting information). Actually, the problem is exacerbated by the heavy addition of NaCl. Using high salt concentration in the supporting electrolyte is a usual practice in order to increase the electrolyte ionic conductivity, which was equal to 10.7 S·m⁻¹ here (Table 6), but, in return, it decreases the migration flux of the buffering species to the anode. In the absence of NaCl, the $H_2PO_4^-$ ion migration flux would increase to 8.2 (Fig. 2B), but the ionic conductivity of the medium would fall to 2.6 S·m⁻¹ (Table S3 in supporting information). The detrimental effect of high salt concentration has already been observed experimentally [108].

The usual practice of adding salts into the medium may consequently not be optimal in the MEC context. Of course, high salt concentration increases the ionic conductivity of the electrolyte but, in return, it decreases the capacity of the migration to mitigate anode acidification, and local pH decrease is a major rate-limiting step for microbial anodes. An interesting way to optimize the electrolyte for MEC may be to increase the buffer concentration to the maximum tolerated by microbial anodes, instead of adding massive amounts of non-buffering salts. Moreover, increasing phosphate concentration should have a double beneficial effect: migration of HPO_4^{2-} species would mitigate the bioanode acidification on the one hand, and the presence of hydrogenated phosphate species would enhance the homogeneous catalysis of hydrogen evolution at the cathode (Section 3.7) on the other.

Because of the variety of ions contained in the electrolytes used in MEC, the ion migration fluxes will remain far from the ideal case of PEM electrolysers (Fig. 2C). PEM fixes the anions in its structure, so that only protons migrate through the electrolyte and proton migration fully balances proton production at the anode and proton consumption at the cathode. The sensitivity of microbial anodes to local acidification is a major issue for MECs. Accordingly, mastering ion transport with the objective of mitigating the anode acidification will remain a major challenge in developing MECs able to work at high current density.

3.6. Anode material and morphology

3.6.1. Material

The question of anode material has been widely studied, which has led to many comprehensive review articles [109–113]. Carbon-based materials have undoubtedly been the most widely used and have commonly led to efficient microbial anodes [112,114,115]. Unfortunately, the modest electronic conductivity of these materials would make it necessary to use metallic current collectors if large surface areas were to be implemented. For this reason, metallic anodes are interesting alternatives [116,117]. Stainless steel has shown a promising capacity to form microbial anodes [116,118–120], particularly in the form of foam [121]. Nevertheless, if a high concentration of salt is used, chloride ions strongly increase the risk of pitting corrosion. If the potential of the anode is not accurately controlled (see Section 3.10) severe corrosion can occur. Copper does not seem really suitable although it has shown excellent ability to form microbial anodes [117], because, with a standard potential of dissolution of 0.34 V/SHE (0.1 V/SCE), the anode potential would have to be controlled very accurately and any accidental drift towards high values could cause the release of Cu^{2+} ions into solution. These ions are severely toxic for microbial cells. Copper-polymer hybrid compounds may be an interesting alternative [122].

Titanium is known to be unsuitable for anode applications because its passivation layer is poorly conductive. The problem has been solved by coating titanium with metal oxides such as ruthenium and tantalum oxides [123] to design so-called dimensionally stable anodes (DSA). A few studies have described DSA-supported microbial anodes [124–126] but the use of DSA to support microbial anodes remains poorly documented as yet.

3.6.2. 2-dimensional vs. 3-dimensional

The interest of using porous electrodes to form microbial anodes has been emphasized by numerous studies, as reviewed recently [110,113]. Nevertheless, some studies comparing 2-dimensional and 3-dimensional electrodes in identical conditions have cast some doubt on the actual benefit provided by the 3-dimensional structures, either with multi-species communities [127] or with pure cultures [128]. This important issue would deserve further research because it may be a key factor for increasing the performance of microbial anodes. For instance, a multilayer structure has allowed current density to be boosted to 390 A·m^{-2} [129]. Could multi-layered structures, with internal distances of the order of several millimetres, constitute a better option than porous structures with sub-millimetre pores? This will be a major question for future research, and work has started to establish relationships between the optimal 3-dimensional structure and the physicochemical and microbial characteristics of the system [130].

3.6.3. Surface topography

The performance of microbial anodes can also be improved by working on the topography of the surface [131]. Actually, surface topography has often been considered as an important parameter in the development of efficient electroactive biofilms [118,132–135] but its impact is generally embedded in more complex surface modifications. Studies specifically devoted to the electrode surface topography, identified as the main and, if possible, the sole parameter to be addressed, have been rare so far. Recent studies carried out with gold have shown that the current density can be multiplied by a factor close to 7 with random micro-roughness [136] and close to 10 by micro-structuring of the electrode surface [137]. These studies were performed with pure cultures of *Geobacter sulfurreducens* and addressed the early phase of biofilm formation. In contrast, aged multispecies biofilms have shown non-significant sensitivity to surface micro-roughness [138]. These various results illustrate the great interest of developing this research direction.

3.6.4. Chemical surface modification

Many studies have chemically modified the electrode surface in the aim of enhancing interfacial electron transfer from the biofilm to the anode material. This issue has been the subject of several reviews [139–141,110,142]. However; it can be feared that some chemical modifications may be difficult to scale up to large sized electrodes in an economically efficient way. This issue should be considered with some care when the objective is to propose industrially-oriented strategies.

### 3.6.5. Biofilm redox properties

Preparing the most efficient possible electrocatalytic layers has been a major field of research and development in electrochemical engineering. In contrast, in microbial electrochemical technologies, the catalytic layer is the electroactive biofilm that develops on the electrode surface spontaneously and the means of action to make the biofilm do what the engineer would like it to do are limited. How can the biofilm be made to select for the most efficient electroactive species from a multispecies medium [143,144]? How can it be forced to form the most electron conductive matrix [145–148]? The applied potential may be a tool that helps to achieve this objective [149,150] but may not always be effective [151,152]. This item is still under debate [153,154,101] (see a short review in [114]). The electron transfer capacity of a biofilm matrix may also be improved by developing it around ultra-microelectrodes [155]. Increasing the electron transfer capability of microbial anodes is currently a hot research topic, which is mainly turned towards understanding the basic processes, but guidelines are still lacking for the engineer who wants to drive the electroactive biofilm towards maximum performance.

3.7. Cathode material and homogeneous catalysis of hydrogen evolution

The choice of the cathode material of MECs has also been the subject of many studies [26,37,156,157]. Platinum is clearly expensive and loses a large proportion of its catalytic capacity for hydrogen evolution at the neutral pH values that are imposed by microbial anodes. Stainless steel, nickel and cobalt alloys have been detected as promising candidates [158–162] even though they, too, remain quite expensive.

Porous materials have sometimes been proposed as MEC cathodes, with the objective of increasing the surface area available for hydrogen evolution. This solution may be successful at the laboratory scale, but cannot be adopted for high current density. At high current density, the bubble coverage (the fraction of the electrode surface area covered by adhering bubbles [163]) would decrease the effective conductivity of the interstitial electrolyte [164] and finally coalesce in the porous structure, blocking the electrode. Using a porous electrode to evolve gas is generally not an industrial option, unless the electrolyte is forced through it [164].

A homogeneous catalysis of hydrogen evolution is possible, based on using weak acids [165,166]. Weak acids, such as phosphates [166], release hydrogen atoms by electrochemical deprotonation on some metallic surfaces:

$$H_2PO_4^- + e^- \rightarrow HPO_4^{2-} + \frac{1}{2} H_2 \tag{17}$$
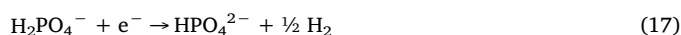
This reaction produces hydrogen and the fast acid-base equilibrium that follows:

$$HPO_4^{2-} + H_2O \rightarrow H_2PO_4^- + OH^- \tag{18}$$
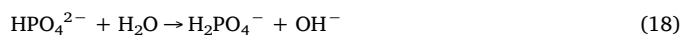
results in the overall reaction of water reduction:

$$H_2O + e^- \rightarrow \frac{1}{2} H_2 + OH^- \tag{19}$$

Carbonates have been shown to have the same capacity [167]. This reactional pathway, called cathodic deprotonation reaction [166], corresponds to a homogeneous catalyst for water reduction: the water molecule no longer interacts with the electrode but the weak acid molecule ensures electron transfer with the electrode material. Less energy is required to extract the hydrogen atom from the acid molecule than from the water molecule. This catalytic pathway is particularly effective on mild steel [168] and stainless steel [166,167] surfaces. It decreases the overpotential necessary for hydrogen evolution, working around neutral pH, using cathodes made of steel, which can be less expensive than nickel alloys. Stainless steel has been widely used as cathode material in large scale MECs. Of the eight different pilots reported in Table 1, seven used stainless steel cathodes [39,43–45,48,49,51]. Furthermore, phosphate is contained in many electrolytes used in the laboratory to develop microbial anodes, which makes this system highly suitable for MECs [169]. In fact, this kind of catalysis might already have happened in some MECS without being identified [170].

In the current state of the art, we would advise choosing a stainless steel cathode coupled to the homogeneous catalysis of hydrogen evolution by weak acids [171]. Nevertheless, the choice of steel grade is not easy. Using highly saline medium to decrease the ohmic drop induces a high risk of pitting corrosion because of the high concentration of chloride ions. Actually, the potential imposed on the cathode during MEC operation protects it against corrosion and a low grade stainless steel could be used. Nevertheless, any accidental interruption of the applied potential may lead to fast corrosion of low grade stainless steels. To avoid the risk of accidental corrosion, a high-grade stainless steel may be preferred, e.g. 254 SMO (EN 1.4547; ASTM UNS S31254), which can resist corrosion in marine environments thanks to its molybdenum content, but at higher price. The choice may be some kind of wager on the confidence that can be placed on the operating procedure.

3.8. Temperature and substrate concentration

Temperature is known to have a considerable effect on the performance of microbial anodes. This may seem surprising for an electrochemist who works with abiotic electrochemical reactions. Temperature intervenes in the kinetics of abiotic electron transfer only through the ratio $\frac{RT}{nF}$, which results in an electrochemical reaction that is generally not extremely sensitive to temperature, particularly in the 15–40 °C range, in which most MECs operate. In contrast, the electroactive biofilm introduces an additional overpotential into the kinetics, which is highly sensitive to the temperature, because of the involvement of enzyme-catalysed reactions in the microbial catalysis. The impact of temperature on microbial anodes has been widely investigated in the context of microbial fuel cells (see [172] for a short review). It has often been observed that an optimum temperature exists for MFCs, generally in the 35–45 °C range [173–176], even though the use of thermophile species has started to be proposed [14].

Industrial electrolysers generally work at high current density and the energy lost in ohmic drop increases their operating temperature. It may be hoped that the same situation will be possible with MEC, so that the ohmic energy losses will be sufficient to maintain the temperature to the optimum without the need to heat the reactor.

It is generally accepted that the current provided by microbial anodes fed with acetate varies with the substrate concentration according to a Michaelis-Menten type law:

$$j = j_{max} \frac{[acetate]}{K_S + [acetate]} \tag{19}$$

where K_S is an affinity constant of the order of a few mM [145,177]. On the other hand, substrate inhibition is generally found to occur for concentrations above about 50 mM [177]. This means that acetate concentration should not have a significant effect on the current in the 20–50 mM range. As a rule of thumb, the optimal range of acetate concentration can be taken in this range. This can be considered as a drawback of MECs with respect to water electrolysis, if one considers that water concentration is 55.6 M at 25 °C. Substrate depletion in the anodic biofilm can lead to mass transport rate limits in the MEC.

3.9. Reactor architecture

An important theoretical advantage of MECs over water electrolysis is that they can work in the absence of a separator between the anode and the cathode. In water electrolysis, it is mandatory to separate oxygen and hydrogen for obvious safety reasons. In MECs, separation is required only if the objective is to produce pure hydrogen, in order to separate it from CO_2 produced at the bioanode. CO_2 can either simply pollute the hydrogen or result in the production of methane (see Section 2.3).

Engineering text books are full of smart and sophisticated reactor architectures but it must be said that the great majority of industrial electrolysers have a plate-and-frame design, also known as sandwich or filter-press [178]. As evoked above, an electrochemical reactor is inherently complex, and it seems wise to extrapolate it to the simplest possible configuration.

Nevertheless, in the case of an MEC, it can be anticipated that the bioanode would be the rate-limiting electrode. In consequence, an anode surface area larger than that of the cathode may be a good choice. The simplest way to achieve such a configuration is to use two coaxial cylindrical electrodes with the cathode as the inner electrode [48,40]. The resistance of the electrolyte between the two cylinders can be calculated as (see supporting information):

$$R_{S,cylindrical} = \frac{\rho}{2\pi h} \ln\left(\frac{r_2}{r_1}\right) \tag{20}$$

where r_1 is the cathode radius, r_2 is the anode radius, h is the electrode height exposed to the electrolyte and ρ is the electrolyte resistivity. The co-axial design can be compared with a filter-press design on the basis of the same cathode surface area. The surface area of the cathode is $2\pi r_1$ multiplied by the height, h. In filter-press configuration, this planar cathode would be in front of a planar bioanode of the same surface area, leading to the electrolyte resistance:

$$R_{S,planar} = \rho \frac{l}{2\pi r_1 h} \tag{21}$$

where l is the inter-electrode distance. For comparison, here $l = r_2 - r_1$. The ratio of the electrolyte resistances in the coaxial vs. filter-press configuration is:

$$\frac{R_{S,cylindrical}}{R_{S,planar}} = \frac{\text{Ln}\left(1 + \frac{l}{r_1}\right)}{\frac{l}{r_1}} \tag{22}$$

This ratio is always higher than 1. Consequently, on the basis of the same cathode surface area, the cylindrical configuration always leads to a lower electrolyte resistance than the filter-press configuration. This configuration could consequently be advised for MEC, particularly when the application does not impose the use of a separator. Indeed, although no impossible, the insertion of a circular separator can be a rather prohibitive technical difficulty [48,40].

3.10. Control procedure

Industrial electrolysers are generally operated galvanostatically, i.e., by imposing a value of current. This control mode is the simplest from the electrical engineering standpoint. It is also appropriate for many electrochemical reactions because the reaction rate is thus directly controlled by the operator. Unfortunately, this control mode cannot be used for MECs. Under galvanostatic control, both electrodes must provide the imposed current (Fig. 3). If the microbially-catalysed reactions of the bioanode were not able to provide the imposed current for any reason, such as a decrease in the substrate concentration, decrease of the temperature, or disturbance of the microbial community, the potential of the anode would increase, possibly reaching that
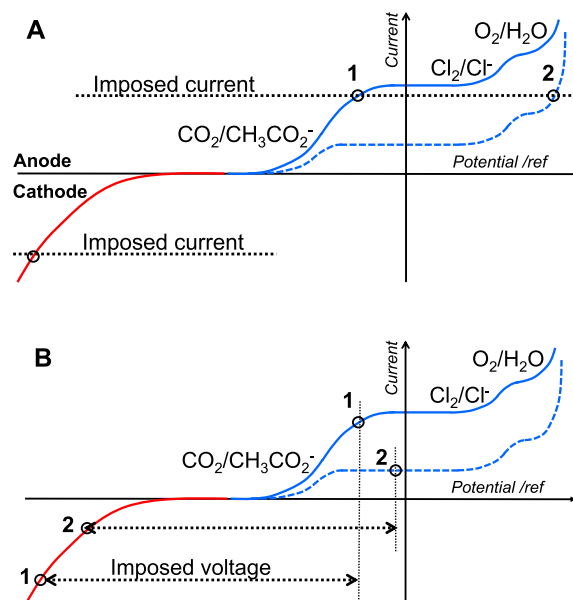

Fig. 3. MEC control strategies schematized on a current-potential diagram. (A) Galvanic control: the microbial anode operates at point 1; if the current accidentally drops (e.g. substrate depletion, temperature drop…) it can be pushed to point 2 where chlorine and oxygen are produced. (B) Constant voltage control: if the current decreases, the microbial anode is protected from drifting to excessively high potentials.

required for the oxidation of water or some dissolved species, e.g., chloride ions. The oxidation of water produces oxygen and the oxidation of chloride produces chlorine and hypochlorite. In any case, the compounds produced would be highly toxic for the electroactive biofilms and would be produced at the electrode surface, right in contact with the biofilm. This means that, under galvanic control, any deficiency of microbial catalysis would be severely punished by the destruction of the electroactive biofilm.

The sensitivity of microbial anodes to oxygen and chlorine makes it imperative to prevent the potential from drifting above the threshold value at which one of these compounds can be produced. Potentiostatic control, i.e. controlling the potential of the anode against a reference electrode, is not possible at industrial scale because it requires electrical equipment that is too expensive. Furthermore, the presence of a reference electrode in an industrial reactor is a source of technical problems. Microbial electrolysis cells should consequently be operated under constant voltage. This mode may allow the anode potential to be controlled provided that the kinetics of the cathode is sufficiently well-known and stable. The cathode could be used as a pseudo-reference electrode and, as long as care was taken to keep a sufficient security margin, controlling the voltage should avoid the anode reaching the potential threshold value of water or chloride oxidation (Fig. 3).

4. Needs in research and possible short-term perspectives

The formal cell equilibrium voltage of 0.123 V at pH 7.0 (Section 2.1) and the energy and thermal energy yields, which can exceed 10 (Section 2.4), provide the MEC technology with very attractive theoretical assets. Additional advantages have been discussed as summarized in Table 7.

Much remains to be done to bring these theoretical advantages to possible industrial development. Chiefly, the analysis in Section 3 points out a kind of negative feedback loop that hinders the MEC as current density increases: local pH decreases at the bioanode, local pH increases at the cathode, and migration fails to compensate for these pH gradients. These local pH changes have obvious detrimental thermodynamic effects. In addition, acidification of the bioanode inhibits, or even destroys, its electrocatalytic properties and, similarly, alkalinization of the cathode leads to cathode fouling. This negative feedback against increased current density should be kept in mind in any research that intends to develop large-scale MECs for industrial production.

4.1. Microbial anode

Improving the bioanode kinetics is a hot research topic (Section 3.6), which is making fast progress in understanding basic mechanisms.

MEC development will obviously take benefit of these advances, provided the methods can be applied at fair cost to electrodes of large surface area. Notably, the search for acidophilic electrogenic microbial species should be pursued [56,179] with the hope to develop acid-tolerant microbial anodes.

By comparison with the domain of abiotic electrochemical engineering, a few directions seem to have been poorly investigated so far and may be recommended. The electrode surface topography is a key parameter to improve abiotic electrodes. Modelling electrode micro-roughness has been the subject of a huge number of studies (see a short review section 3 of [131]). This basic knowledge has not been exploited in the field of microbial anodes yet, although it may help rapid strides to be made in optimizing surface topography. Actually, the situation is not very clear, because the impact of the electrode topography is not clearly obvious in the case of microbial anodes [131]. Some studies claim that this effect is no longer significant for mature biofilms [138]. It may be speculated that the impact of surface topography observed during the early phase of biofilm formation [136,137] may then be masked by the appearance of limiting steps in mature biofilms. This topic would deserve further research to reach clear conclusions.

Similarly, despite the huge number of studies using 3-dimensional porous anodes (Section 3.4), it is still difficult to know if there is a range of optimal pore sizes to avoid pore clogging by the biofilm and to benefit from all the porosity. Here again the theoretical tools developed in electrochemical engineering, particularly for modelling reactive transport inside pores [180], could be very helpful to guide reflection, as has started to be done to optimize surface micro-structuring (Fig. 4). A similar theoretical approach applied to 3-dimensional porous electrodes may help in designing optimal porous structures for the development of microbial anodes, particularly by taking into consideration the effect of local acidification inside the porous structure (Fig. 4).

Finally, more intensive research on metallic electrodes may be hoped in order to avoid the need of 2-dimensional current collector that is required with carbon-based electrodes. For instance, using DSA may be a lead to pursue. The great advantage of DSA is that they are fully appropriate for implementation in large electrochemical reactors because they were designed for this purpose. They would deserve further research in the field of MECs. A recent technique of titanium etching, which has shown excellent performance in PEM water electrolysis (10 000 A·m^{-2}, 100 h), may also be of great interest for supporting microbial anodes [181].

4.2. Hydrogen evolution cathode

Improving cathode kinetics seems to be as necessary as working on the bioanode kinetics. The usual metallic catalysts that work in acidic or alkaline conditions are no longer efficient at the close-to-neutral pH
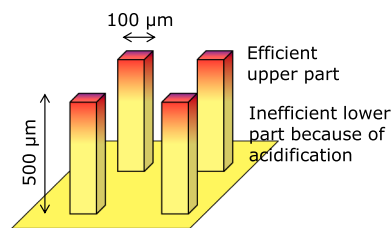
Table 7
Summary of the advantages and disadvantages of MEC evoked in the different sections of the present article.

	Section
Pro	
Low equilibrium cell voltage 0.123 V (1.23 V for water electrolysis)	2.1
Possibility to work at high pressure with low energy consumption	2.1
Anode: low cost material; self-assembled and self-sustained electrocatalyst; various organic compounds can be oxidized; does not require pure electrolyte	2.2
Safety: no O_2 production; eco-friendly electrolyte	2.2
Can produce methane, notably by using effluents from anaerobic digestion	2.3
High theoretical maximum energy yield 11.3 (1 for water electrolysis)	2.4
High theoretical maximum thermal yield around 12 (1.21 for water electrolysis)	2.4
Cons	
Hydrogen can be consumed at the bioanode	3.4
Bioanode is very sensitive to slightly acid pH	3.5
Adding salts in order to increase the electrolyte ionic conductivity reduces the capacity of migration of the buffering species to mitigate anode acidification	3.5
Ca^{2+}, Mg^{2+} and other ions, which are required to sustain the biofilm, make hydroxide deposits on the cathode due to local alkalinisation	3.5
Saline electrolyte increases the corrosion risk of materials (electrodes, frame…)	3.6 and 3.7
Bioanodes do not accept high temperature and high substrate concentration (for comparison $[H_2O] = 55.6$ M for water electrolysis)	3.8

Fig. 4. Scheme of surface micro-structured microbial anode formed with Geobacter sulfurreducens. Micro-pillars were 500 μm high, 100 μm wide and 200 μm apart. Biofilm coverage ensured high local current density of 14 A·m^{-2} on the top of the micro-pillars. An assessment of the reactive transport of the buffering species showed that local acidification prohibited biofilm-based catalysis in the lower part (from [136]).

imposed by the bioanodes. The search for acidophilic or alkaliphilic microbial anodes should be pursued but few efficient solutions can be anticipated so far [56]. It thus seems necessary to continue working on the cathode kinetics for hydrogen evolution around neutral pH.

Microbial catalysis of hydrogen evolution is an exciting research subject [182,183]. It may have interesting applications, notably in anaerobic biocorrosion [168,184,185], but it cannot provide an actual solution for the catalysis of hydrogen evolution at high current density. The high current density required for an electrolysis process to be economically efficient would drastically remove the biofilm from the electrode surface [75]. The search for catalysts efficient around neutral pH will no doubt be a long-term endeavour, considering that progress is still required concerning the catalysts used for conventional water electrolysis [7,6,186,187]. For MECs, the homogeneous catalysis option seems promising as it is appropriate for the pH range (Section 3.7). Its eco-friendly aspect is another significant advantage.

Alkalinization of the cathode vicinity is a severe problem because cations such as Ca^{2+} and Mg^{2+}, which are required to sustain the bioanode, deposit on the cathode surface [103–105,50]. It may be hoped that hydrogen bubbling may mitigate cathode fouling [162] and that this virtuous effect will be even more effective at high current density. The mechanisms of hydrogen bubble formation on electrodes have been a traditional research topic in electrochemical engineering for decades [188–190], and are still attracting interest [191–194], notably because bubble formation contributes significantly to the cathode overpotential. This theoretical knowledge has not yet been exploited in the field of MECs and should be helpful for designing the right cathode configurations to mitigate deposits.

The best way to avoid hydroxide deposit would be to limit cathode alkalinisation. With this objective, CO_2 has successfully been used to reduce the bulk pH but with a limited effect on the cathode overpotential [107]. Work in this direction should be pursued by focusing the local effect on the cathode surface. CO_2-diffusion electrodes, which have been developed for CO_2 reduction, may offer interesting leads [195]. Here, the purpose of using gas-diffusion cathodes would not be to reduce CO_2, but to diffuse CO_2 as close to the cathode surface as possible.

In addition, this direction is all the more interesting because bicarbonate may play the role of a homogeneous catalyst of hydrogen evolution (see Section 3.7). In addition, bicarbonate would migrate to the anode and thus help to mitigate anode acidification. For all these reasons, the supply of CO_2 to the cathode compartment is a worthwhile research direction [196]. Nevertheless, it contributes to CO_2 pollution of the hydrogen produced and would thus be fully appropriate only when hydrogen purity is not an important criterion, e.g. for the production of methane or other compounds (Sections 2.3 and 4.4).

4.3. Electrolyte composition to mitigate pH gradients

The insufficient ionic conductivity of the solution has been the main

stumbling block in developing large-sized, efficient MECs. Using (hyper-)saline electrolytes has been considered as a possible solution. This hope should be qualified by considering that high concentrations of salts hinder the buffering capacity of the electrolyte and, in particular, exacerbate the local acidification of the anodic biofilm (Section 3.5). Adapting microbial anodes to high concentrations of buffer, instead of NaCl, should be an important research direction worth pursuing for MEC improvement [197].

Furthermore, using a hypersaline electrolyte, particularly one containing chlorides, increases the risk of corrosion and consequently the cost of the materials to be used. Obviously, the electrodes are supposed to be protected against corrosion during operation because of the applied potential, but they are not protected during maintenance phases or if polarization is accidentally interrupted. Highly saline electrolyte imposes heavy constraints on the choice of materials. For all these reasons, working on the electrolyte composition remains a major objective [108]. The aim should be to optimize the electrolyte composition, particularly by increasing the concentration of buffering species while acclimatizing the bioanode to such a medium.

4.4. MEC design and control

As a preliminary remark in this section, it may be noticed that the capacity to implement high pressure MEC should be a promising pathway to investigate which, to the best of our knowledge, has not been approached so far.

An innovative system design decoupling the bioanode from the hydrogen evolution cathode could be of considerable interest. In this case, each electrode is set in a different electrochemical reactor. The link between the two reactors is made by a hydraulic loop that contains a redox mediator, which is reduced in the reactor equipped with the bioanode and oxidized in the reactor that ensures hydrogen evolution. This decoupled system has been successfully applied to water electrolysis [54,55], with the main advantage of separating hydrogen and oxygen production reactors. In the case of MECs, such a system allows completely different electrolytes to be used for the bioanode and the hydrogen evolving cathode. This could solve the problem of cathode deposit and may considerably help in controlling pH balances in the two separated reactors, but at the price of some loss in terms of thermodynamics. This system is just starting to be applied to MECs [198] and should deserve further great interest.

Concerning MEC control, it has been emphasized here that Faradaic yields can be used to detect dysfunctions such as hydrogen cycling, hydrogen consumption in the bulk, and hydrogen production by fermentation (Section 3.4). With the objective of building simple theoretical tools to control MEC operation, it should now be helpful to further develop the model by integrating local pH calculations and then combining the model with the experimental measurements of local pH [199,200]. It would thus be possible to pinpoint the actual operating conditions of each electrode and to establish some first guidelines for controlling MEC operation.

The severe limitation due to acidification of the microbial anodes may be tackled by an appropriate control procedure. Periodically reversing the polarity, so that the anode works as a cathode, can be a way to consume the protons accumulated within and around the biofilm [201–203]. This is an emerging area of research, and the duration and frequency of polarity inversion and their impact on MEC production remain to be assessed. The recent advances in reversible electrodes [201,202], or more appropriately bidirectional electrodes [204,205], could be an helpful source of new strategies for MEC control that would allow microbial acidification to be mitigated by periodic polarity reversal.

Finally, an MEC can be considered as a part of a more complex production unit. As evoked above (Section 2.3), MECs can be used with the aim of synthesizing methane and more complex compounds. In this case, hydrogen is used as an intermediate reactant [75]. As explained in

Section 3.3, an electrolyser dedicated to large-scale production must operate at high current density to be economically efficient. This means that hydrogen must evolve quickly, forming big bubbles with short residence times. In contrast, in the current state of the art, microbially-catalysed hydrogenation reactions have low reaction rates – partly due to gas-liquid mass transfer limitations, which require specific gas-liquid contactors to be used [206,207,76]. Seeking the optimum therefore implies separating the MEC and the synthesis reactor. The MEC would produce hydrogen, pure or mixed with CO_2 and possibly methane, and the MEC gas outlet would be used as the input of a gas-liquid contactor, where the microbially-catalysed synthesis would occur.

This two-steps system would allow optimising the gas-liquid transfer in the contactor while ensuring high hydrogen evolution rate in the MEC. It would thus no longer be necessary to seek to maximize the synthesis reaction rate within the MEC. MEC optimization is relieved of this constraint. In addition, the production of CO_2 as a side-product in the MEC is no longer a concern, particularly if the final goal is to hydrogenate CO_2 in the downstream synthesis reactor. This two-step system would also make it possible to take full advantage of the introduction of CO_2 into the cathode compartment for pH control (Section 4.2), without fear of polluting the output flow.

5. Conclusions

In designing an MEC we are trying to have it both ways. Basically, an MEC must achieve the association of two antagonistic processes. On the one hand, electrolysers for large scale production are ideally implemented with clean electrolytes, whose chemical composition is as simple as possible, with high ionic conductivity and extreme pH values. On the other hand, microbial processes require chemically rich culture media and neutral pH, and often do not accept highly conductive solutions. The ranges of optimal conditions of the two kinds of processes are disjoint. This is not a hindrance at the low current densities that are sufficient to support metabolic processes. In contrast, when the engineer tries to force the process towards industrial production at high current densities, the discrepancy in the optimal conditions wrecks the system. Some kind of negative feedback loop hinders the MEC as current density increases. Will MECs be able to become an industrial technology? This remains a tough question and an exciting challenge. This critical review proposes research lines to be explored in the hope of being able to answer this question.

Acknowledgements

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apenergy.2019.113938.

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