# Reactors for Microbial Electrobiotechnology

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**Abstract**  From the first electromicrobial experiment to a sophisticated microbial electrochemical process – it all takes place in a reactor. Whereas the reactor design and materials used strongly influence the obtained results, there are no common platforms for MES reactors. This is a critical convention gap, as cross-comparison and benchmarking among MES as well as MES vs. conventional biotechnological processes is needed. Only knowledge driven engineering of MES reactors will pave the way to application and commercialization. In this chapter we first assess the requirements on reactors to be used for bioelectrochemical systems as well as potential losses caused by the reactor design. Subsequently, we compile the main types and designs of reactors used for MES so far, starting from simple H-cells to stirred tank reactors. We conclude with a discussion on the weaknesses and strengths of the existing types of reactors for bioelectrochemical systems that are scored on design criteria and draw conclusions for the future engineering of MES reactors.

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**Graphical Abstract**
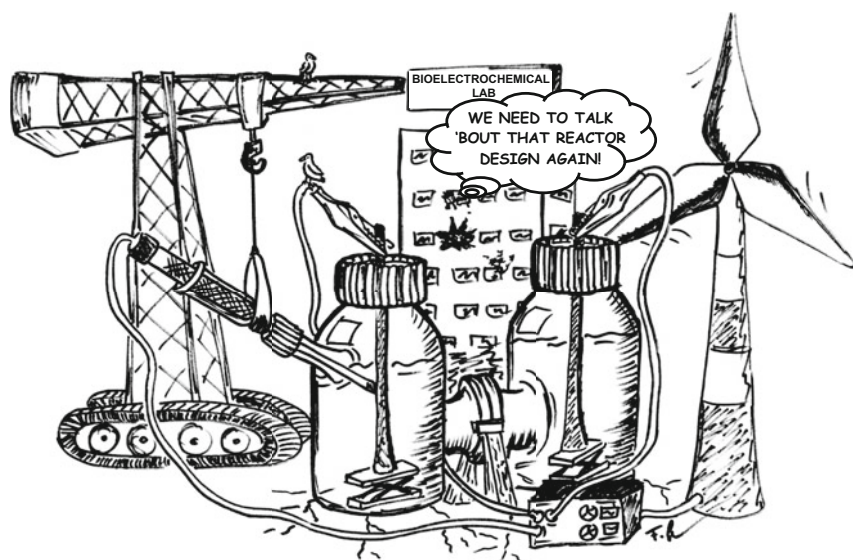


**Keywords** Bioelectrochemical systems, Bioelectrosynthesis, Microbial electrochemical technology (MET), Microbial electrolysis cells (MEC), Microbial electrosynthesis (MES), Reactor concepts, Scoring

**Contents**

# 1 Introduction

## 1.1 Reactors in Electrobiotechnology

The positive effects of electrical currents on glutamic acid fermentation have been described since the late 1970s [1]. Several electrochemically influenced biosyntheses and applications thereof followed in the literature, with an entire research field developing around these bioelectrochemical systems [2–4]. The early studies

developed and exploited basic experimental setups that can be regarded as the first bioelectrochemical systems [1, 2]. These reactors were made of two glass bottles, each forming an electrochemical half-cell hosting the anode and cathode, respectively. The bottles were merged with a glass connection in an H-shape, leading to the name "H-shaped cells" or "H-cells" [1]. In this connection, a membrane was often used to separate the electrolytes of the two electrochemical half cells while maintaining an ionic connection. This kind of reactor is still used in basic electrobiotechnology studies [5]. However, the field has advanced, with several different enzymatic and microbial processes for bioelectrosynthesis [6–8] having been developed. Consequently, generic and versatile reactors that can be used in the study and engineering of different processes, as well as reactors tailored toward a specific process, are needed. Importantly, these reactors have to fulfill both microbial and electrochemical demands at the same time, which means there will always be a trade-off. Among other parameters, the preferred reactor designs strongly depend on the used substrates (gaseous vs. dissolved compounds), products, and required downstream processing (gaseous vs. dissolved compounds, membrane separation vs. thermal or other processes) and include membrane and membraneless approaches [9]. Furthermore, many research groups are investigating bioelectrochemical systems with their own individual reactor designs, which often are constructed around the need for cheap, easy, and fast solutions. Thus, highly diverse and nonoptimized reactors can be found in the literature.

This chapter discusses the reactors used for microbial and enzymatic electrosynthesis and highlights basic considerations for their future engineering. Special electrode configurations and materials, such as fluidized bed reactors, are extensively discussed in Chap. 7 [10]. For microbial electrosynthesis (MES), the majority of reactors to date, especially microbial electrolysis cells (MECs), are based on designs derived from microbial fuel cells (MFCs) – a generally well-studied and well-reviewed research field, as discussed elsewhere [11, 12]. These designs, however, are derived from electrochemistry; thus, biotechnological requirements (e.g. working with pure cultures under sterile conditions) are usually not considered. In this chapter, we discuss reactor designs for MEC aiming at hydrogen or methane production, or MES [3, 13].

One of the biggest challenges in advancing the field of MES is the scalability and comparability of different studies [5, 14]. Important factors for the scale-up of MFCs and MECs, with special emphasis on considerations for cheap materials with good performance, were extensively reviewed elsewhere [11, 15–19]. In this chapter, a broad variety of reactor types is discussed and scored by design and performance, which can be assessed either from an engineering or scientific perspective. Indeed, some reactor types are ideally suited for laboratory-scale testing (e.g. of strict anaerobic bacteria) but are unsuited for engineered settings.

A quantitative comparison of the results of the studies and the reactor setups is often impossible. This can be attributed to differences in the studies, their objectives, reactor designs, missing parameters, and different calculations used, despite several seminal works being available that describe the required datasets [5, 12, 20]. In the next section of this chapter, we discuss reactor specifications and

parameters, which should be stated and discussed in any study of microbial electrochemical technologies.

## 1.2   General Characterization of the Systems

When characterizing industrial bioproduction processes, key parameters include yields and rates. Consequently, the reactors used for realizing these processes should allow the study and subsequent engineering of these parameters toward optimization. This also holds true for reactors in electrobiotechnology. Besides the substrates of carbon and nitrogen, among others, that are common for all bioprocesses, electrons are also key reactants in electrobiotechnology. Electrons are added to (via reduction at the cathode) or withdrawn from (via oxidation at the anode) the reactor broth; in this sense, parameters such as product yield per electron and/or cell yield per electron (see Table 1) should be considered [21]. The electron transfer can be achieved by several mechanisms (see [22, 23]), but it always depends on an electrode facing the reactor liquid. Consequently, this need to interface the electrode(s) and liquid, as well as separate the anode and cathode chamber, creates the hybrid character of bioelectrochemical systems. These systems have to combine the needs of conventional bioreactors with the qualities of an electrochemical reactor. Thereby, depending on the specific process (e.g. if electroactive planktonic cultures or electrodes for biofilms are used), electrode engineering (see [7]) and reactor engineering for MES are additional challenges. For microbial electrosyntheses based on mediated electron transfer, reactors with improved mass-transfer regimes are required. Hence, because no reactors for bioelectrochemical systems are currently available off the shelf and no gold standard yet exists, a plethora of different materials and geometries thereof have been used to build reactors for bioelectrochemical systems. To date, these reactors are usually used in one specific study and in one laboratory (see [8, 24]). As a consequence, only limited comparisons can be made between studies and reactors. This also holds true when one aims to benchmark MES with microbial synthesis, without involving electrons as reactants.

To overcome these obstacles, the standardization of data representation is emphasized in different publications [20, 25] and will pave the way for systematic assessment of MES. An overview on the important parameters for the fields of bioelectrochemistry, reactor engineering, electrochemistry, biotechnology, and biofilm characterization are given in Table 1. Reactor design parameters are especially underrepresented in the literature; they can be reported with dimensionless numbers, like the Reynolds number or Newton number, which are highly useful to describe the flow field or mixing environment.

Of all described parameters, we want to draw special attention to coulombic efficiency, which is often calculated in studies; however, its definition may vary depending on the perspective of the authors. Therefore, it is very important to thoroughly describe the math so that no doubts regarding comparisons between

**Table 1** Important parameters from different disciplines for the characterization of bioelectrochemical systems

| Parameters | Equation | Explanation | Relevance |
|---|---|---|---|
| *Reaction engineering* | | | |
| Reynolds number (*Re*) | $Re = \frac{\rho N D^2}{\mu}$ | $\rho$ – liquid density, kg m$^{-3}$; <br> $N$ – rotational speed, s$^{-1}$; <br> $D$ – stirrer diameter, m; <br> $\mu$ – dynamic viscosity, kg m$^{-1}$s$^{-1}$ | Used to predict flow regimes. Important for assessing diffusion limitations |
| Newton number (*Ne*) | $\frac{P}{\rho N^3 D^5}$ | $P$ – power, J s$^{-1}$; <br> $\rho$ – liquid density, kg m$^{-3}$; <br> $N$ – rotational speed, s$^{-1}$; <br> $D$ – stirrer diameter, m | Useful for analyzing power requirements for stirring purposes |
| Specific volumetric power input | $\frac{P}{V_L}$ | $P$ – power, J s$^{-1}$; <br> $V_L$ – Liquid volume, m$^3$ | Used for analyzing energy flow and energy balances |
| Vessel volumes per minute (vvm) | $\frac{Q_G}{V_L}$ | $Q_G$ – Gas flow rate, m$^3$ min$^{-1}$; <br> $V_L$ – Liquid volume, m$^3$ | Used for assessing effective gas flow through the system |
| Space-time-yield (*STY*) | $\frac{\dot{m}_p}{V_L}$ | $\dot{m}_p$ – mass flow rate, kg s$^{-1}$; <br> $V_L$ – Liquid volume, m$^3$ | Used for analyzing mass and energy flow and balances |
| Pressure (*p*) | *p* (measured) | *p* – pressure, Pa | |
| Damköhler number (*Da*) | $kC_0^{i-1}\tau$ | $k$ – reaction rate constant; <br> $C_0$ – initial concentration, kg m$^{-3}$; <br> $i$ – kinetic reaction rate order ; <br> $\tau$ – mean residence time, s | Quick estimate for the possible degree of conversion achievable in a system |
| *Electrochemistry* | | | |
| Coulombic efficiency (*CE*) | $\frac{n_{eff}}{\frac{Q}{zF}}$ | $n_{eff}$ – amount of product produced, mol; <br> $Q$ – charge spent, A s$^{-1}$; <br> $z$ – electron stoichiometry ; <br> $F$ – Faraday constant, As | Relates the number of electrons released/consumed by the substrate/educt in an ideal scenario to that achieved in practice. |

(continued)

**Table 1** (continued)

| Parameters | Equation | Explanation | Relevance |
|---|---|---|---|
| Specific electrode surface area (SSA) | $\frac{A_e}{V_e}$ | $A_e$ – surface area of the electrode, m$^2$; $V_e$ – volume of the electrode, m$^3$ | Measure of the "accessible"/"useful" surface area of the electrode (under debate how it is determined) |
| Surface to volume ratio (SVA) | $\frac{A_e}{V_R}$ | $A_e$ – surface area of the electrode, m$^2$; $V_R$ – volume of the reactor, m$^3$ | Used for process scaling and engineering |
| Wagner number ($Wa$) | $\frac{\kappa}{l}\frac{d\eta}{dj}$ | $\kappa$ – conductivity of the solution, S m$^{-1}$; $l$ – characteristic length, m; $\frac{d\eta}{dj}$ – slope of the overpotential current curve | Useful for assessing the uniformity of the current density distribution between two electrodes |
| Potential | $E$ | $E$ – vs. a reference electrode, V | Thermodynamic driving force |
| Current density | $j_{geo}$ or $j_{vol}$ | $j$ – Current per (specific) surface area, A m$^{-2}$ or reactor volume, A m$^{-3}$ | Used for comparing materials and designs as well as scaling and engineering |
| *Biotechnology* | | | |
| Cell number or biomass ($X$) | $X$ | $X$ – amount of biomass, g | Used for process description and benchmarking to "conventional" biotechnology |
| Product yield ($Y_{P/S}$) | $\frac{P}{S}$ | $P$ – amount of product, g; $S$ – amount of substrate, g | Used for process description and benchmarking to "conventional" biotechnology |
| Biomass yield ($Y_{X/S}$) | $\frac{X}{S}$ | $X$ – amount of biomass, g; $S$ – amount of substrate, g | Used for process description and benchmarking to "conventional" biotechnology |
| Growth rate | $\frac{d\ln X}{dt}$ | h$^{-1}$ | Used for process description and benchmarking to "conventional" biotechnology |
| *Biofilm characterization numbers* | | | |
| Thickness | $l_b$ | $l_b$ – thickness, μm | |
| Density | $\rho_b$ | $\rho_b$ – biofilm density, kg m$^{-3}$ | |
| Cell density | $X_b$ | $X_b$ – number of cells per volume, m$^{-3}$ | |
| Conductivity | $\kappa_b$ | $\kappa_b$ – conductivity of the biofilm, S m$^{-1}$ | |
| Cytochrome concentration | $C_{cyt}$ | $C_{cyt}$ – cytochrome concentration, mol L$^{-1}$ | |

| | | | |
|---|---|---|---|
| Rugosity ($f_r$) | $\frac{A_r}{A_g}$ | $A_r$ – effective surface area, m²; $A_g$ – geometric surface area, m² | |
| Porosity ($\phi$) | $\frac{V_V}{V_T}$ | $V_V$ – volume of void, m³; $V_T$ – total volume, m² | |
| *Electrobiotechnology (proposed)* | | | |
| Cell yield per electron ($Y_{X/e^-}$) | $\frac{\Delta X}{Q} F$ | $\Delta X$ – amount of grown biomass, g; $Q$ – charge spent, A s⁻¹; $F$ – Faraday constant | Used for process description and benchmarking |
| Product yield per electron ($Y_{P/e^-}$) | $\frac{P}{Q} F$ | $P$ – amount of product, g; $Q$ – charge spent, A s⁻¹; $F$ – Faraday constant | Used for process description and benchmarking |

studies arise. Furthermore, coulombic efficiency calculations can be biased by a simple and common experimental error: the addition of a chemically indeterminate compound (or mixtures of compounds), such as yeast extract or meat hydrolysate, to the defined growth medium, which can potentially serve as a carbon source. A simple way to overcome this problem is to use the measurement of chemical oxygen demand as the total carbon equivalent [12] for the coulombic efficiency calculation.

In knowledge-driven engineering, we believe that an advanced modelling of processes across scales ranging from liquid dynamics to microbial extracellular electron transfer is needed (see also [26]). Therefore, future studies proposing scale-up factors for electrobiotechnological processes are warranted [25].

## 1.3    What Drives Reactor Efficiency?

The reactors used in bioelectrochemical systems are hybrids. They encompass aspects of fluid-based reactions and surface reactions in addition to electrochemical constraints, such as the need to minimize the distance between reaction centers. In bioelectrochemistry, which typically relies on enzymatic electrode reactions, a complex interplay between biological moieties, electrodes, and the educts are needed for the success of a reaction. The interplay between electrodes and biology is described in [6, 7]. For example, the substrate availability at a certain location on electrodes is controlled by reactor design parameters; the likelihood that the reaction takes place there depends on where that location is relative to the counter electrode. Therefore, the closer a point is to the counter electrode, the lower the internal resistance is at that point.

Essentially, concerning the design parameters of a reactor, the deviation of a bioelectrochemical system from the ideal conditions is defined by three main aspects, which are determined by the reactor design:

1. Ohmic loss
2. Concentration polarization
3. Electrode overpotentials

In the following sections, we discuss these key aspects in detail.

### 1.3.1    Ohmic Losses

Because electrical current is generated or used in all bioelectrochemical systems, an effective reactor has to be designed to minimize ohmic losses. Therefore, three main aspects can be considered: current collection at the electrodes, high electrolyte conductivity, and a small distance between the anode and cathode.

The ohmic resistance of the electrodes and current collector is often neglected in small-scale setups. However, it becomes important when scaling-up and assessing the energetic efficiency of processes. Carbon and carbon-based materials are often used as electrode materials as well as current collectors. They are cheap materials with good electrode performance and biocompatibility. However, unlike metals, for example, carbon materials have a higher internal resistance, which can lead to significant losses in scaled-up systems compared to the theoretical cell voltage. Rozendal et al. found that fibrous graphite or granular graphite can lead to losses of several hundreds of millivolts in scaled-up systems compared to laboratory scale due to contact resistances [27]. However, even in laboratory-scale systems with only 1 cm$^2$ electrode surface, a current collector can significantly increase performance [28].

In addition to the ohmic resistance of the electrodes and current collectors, the ohmic resistance due to the ionic solution can be even more relevant. The solution-based ionic resistance of a bioelectrochemical system depends mainly on two parameters: (a) the specific ionic conductivity and (b) the electrode distance. Unfortunately, the selected electrolyte and its ionic conductivity will always depend on the application, with the addition of supporting electrolyte salts being undesirable and cost-intensive. However, because it directly affects reactor performance, applications with already inherently high-conductivity electrolytes, such as urine, are clearly advantageous from an energy perspective [29]. Similar to electrolyte conductivity, the distance between the anode and cathode determines the internal resistance of the cell [30, 31]. A smaller distance leads to decreased internal resistance and voltage drop. However, depending on the mixing in the reactor, distances that are too small can decrease performance due to the unwanted crossover of species, which can significantly decrease performance due to the (bioelectro)chemical short circuits and development of mixed potentials [32]. In bioelectrochemical production processes, the prime example for crossover is oxygen produced at the anode; this leads to a problem when it reaches the cathode, which may rely on the catalytic activity of strictly anaerobic bacteria. Generally, the insertion of a membrane is critical to enable short anode-cathode distances while maintaining the necessary chemical redox gradient between the two electrodes. Evidently, membrane resistances usually increase internal resistance as well [33]. Alternatively, unwanted crossover can be hindered without increasing internal resistance by clever control of the liquid flow. For instance, in an MFC with 1-cm spacing between the electrodes, one study showed no detectable dissolved oxygen near the anode by imposing an advective flow of the anolyte toward the cathode [34]. In contrast, the batch operation of the same reactor lead to dissolved oxygen concentrations of approximately 0.05–0.1 mg L$^{-1}$ at a 1-cm distance of the cathode.

Depending on the application and the focus, the design generally can be adapted and optimized to minimize internal resistance and/or crossover [33]. In experimental designs with three-electrode setups for basic investigation, the internal resistance will not play a significant role, especially when using chronoamperometry to characterize the system, for example. In this case, another resistance will be of

importance: the uncompensated resistance between the working and reference electrodes will highly influence the obtained data [35].

### 1.3.2 Concentration Polarization

As already mentioned, reactions in bioelectrochemical systems take place on electrode surfaces. There, mass transfer between the bulk liquid and the electrode surface as well as in the bulk liquid has to be addressed by the reactor design to decrease losses from concentration polarization. The reactant availability on the electrodes is of crucial importance. Simultaneously, reaction products (e.g. hydroxyl ions [36] or protons) have to be removed from the electrode surfaces. Because the ion concentration in typical electrolytes is much higher than the proton concentration, charge balance will be achieved through the migration of ions other than protons [37]. This can lead to drastic acidification of the anode and alkalization of the cathode, thermodynamically and microbially inhibiting the electrode reactions. The mass transport from and to the electrode surface can be achieved through diffusion, migration, and convection (discussed in detail in [26]). While diffusion will always be slow compared to convection and mainly controlled by the temperature, pressure, and the substrate concentration gradient, convection is proportional to the local velocity ($\mu$). The velocity field can be adjusted by the reactor design (see Table 1 for Reynolds and Newton numbers) and operation, substantially increasing current densities.

In a reactor by Sleutels et al., an advective flow away from the anion exchange membrane in an MEC increased the performance by twofold [38]. This substantial increase is related to a smaller diffusion layer on the membrane, leading to better ion transport through the membrane and thus buffer regeneration at the anode. Another example for an improved flow-field has been shown by Zhao et al., who introduced non-reactive activated carbon granules into the anode compartment, leading to increased current densities. A computational fluid dynamics simulation has proven that higher current densities were achieved due to better substrate distribution [39]. A similar approach used PVC foam and recirculation in the anode chamber [40] to improve the flow regime, reduce dead space, induce crossflow on the electrode, and thus increase performance. In other successful examples, the electrolyte flow was forced through the electrodes [41], maximizing substrate availability and proton efflux in three-dimensional electrodes.

### 1.3.3 Electrode Overpotentials

Electrode overpotentials emerge from non-ideal catalytic activity of the electrodes and are determined by the interplay of the electrode (and its morphology) with the electroactive biofilm. This subject area is described elsewhere (see [7, 22]). However, one aspect is directly related to the reactor design: increasing the

electrode surface-to-volume ratio (SVR) very likely increases currents as the active and reactive surface are increased. It has been shown for MFCs that only the cathode SVR is important [42, 43]. This might be correct for specific MFCs run with acetate, but it cannot be generalized and very much depends on which electrode is limiting. Self-evidently, increasing the SVR by increasing the surface of the electrode that does not limit the process will not increase the reactor's effectiveness.

## 2 Reactors for Microbial Electrolysis Cells and Microbial Electrosynthesis

MECs were originally developed from MFCs for the production of hydrogen gas using microorganisms, waste streams, and electric energy [44]. The hydrogen formation takes place at the (bio)cathode, where electrons are used to reduce protons that were produced at the (bio)anode. This anodic process includes either the decomposition of waste to electrons, protons, and small molecules such as $CO_2$ by microorganisms [44] or water electrolysis to oxygen, electrons, and protons [45, 46] by an abiotic catalyst. The voltage generated by a bioanode combined with a cathode aiming for hydrogen evolution is too low for the reduction of protons to hydrogen [47]. Therefore, even if electric power is produced at the anode via degradation of waste, external additional energy has to be provided to enable hydrogen formation. In particular, the voltage has to be leveraged because theoretically an applied circuit voltage of at least 110 mV [47] is needed in addition to the energy coming from the MFC.

The reaction at the cathode can be abiotic using electrodes made of, for example, platinum to catalyze the reaction [44] or biotic catalyzed by microorganisms [48]. In a wider definition, MECs can also be used to produce other fuels and chemicals [49]. If more complex compounds are formed, the process is typically referred to as microbial electrosynthesis (MES) although MES principally refers to all anodic and cathodic bioproduction processes, whether they start from $CO_2$ or from organic substrates [4].

Some of the reported MES and MEC processes for the production of chemicals are summarized in Table 2 from a reactor engineering perspective. Generally, the vast majority of MEC and MES are performed at the laboratory scale, with volumes ranging from the milliliter up to the liter scale. Hence, these experimental setups are mostly suitable for addressing a fundamental research question, but they are often poorly defined from an engineering perspective. To date, several reactor concepts have been developed and will be further described in this section.

**Table 2** Process performance of different bioelectrochemical systems for synthesis (*AEM* anion exchange membrane, *AV* applied voltage, *CE* coulombic efficiency *CEM* cation exchange membrane, *CC* carbon cloth, *CP* carbon paper, *L* liquid phase, *G* gas phase, *MEC* microbial electrolysis cell, *MFC* microbial fuel cell, *n.a.* not applicable, *n.d.* not determined, *PMM* poly(methyl methacrylate), *SS* stainless steel, *ww* wastewater, *Y* yield)

| Reference | Product | Cathode/anode | Reactor material | Membrane | Spec. cathode area [m²/m³ liquid] | Volume anode/cathode | Operation mode |
|---|---|---|---|---|---|---|---|
| **Two-chamber systems** | | | | | | | |
| *H-cell reactors* | | | | | | | |
| [50] | Hydrogen | CP with 0.5 mg Pt/cm², 12 cm²/CC, 12 cm² | Glass bottles | 3.5 cm², Nafion | 6 | Each 200 mL_L, 110 mL_G | Batch |
| [51] | Methane | Unpolished graphite, 58 cm²/ unpolished graphite, 58 cm² | Glass bottles | Nafion | 29 | Each 200 mL_L, 170 mL_G | Continuous gas inlet + Fed-Batch (media replacement) |
| [52] | Acetate | Unpolished graphite, 65 cm² (both electrodes) | Glass bottles | Nafion | 32.5 | 200 mL/ 200 mL | Continuous flow with recirculation |
| [53] | Methane | Woven graphite felt | Glass bottles | Nafion | n.d. | 40 mL/40 mL | Batch |
| [54] | Acetate | Unpolished graphite sticks (both electrodes) | Glass bottles | Nafion | n.a. | 200 mL/ 200 mL_L | Continuous with recirculation |
| [51] | Methane | Unpolished graphite, 58 cm²/ unpolished graphite, 58 cm² | Glass bottles | Nafion | 29 | Each 200 mL_L, 170 mL_G | Fed-Batch |
| *Concentric tubular reactors* | | | | | | | |
| [55] | Acetate | NanoWeb RVC, 4.1 cm²/platinum wire | Glass | Nafion | 1.41 | 12 mL/288 mL | Fed-batch |
| [56] | Ethanol | Glassy carbon, 2.5 cm²/Pt wire | Glass | Dialysis membrane | 22.7 | 11 mL/ undefined | Batch |
| [57] | Acetate, propionate | Platinum (both electrodes) | Glass | Diaphragm | n.a. | 5 mL/100 mL | Batch |
| [58] | Acetate, propionate and butyrate | Neutral red activated graphite felt/ platinum wire, adapted bioreactor | Glass | Cellulose Acetate modified glass filter | 144 | 250 mL/ 500 mL, 250 mL_G | Batch |
| [51] | Methane | Unpolished graphite, 58 cm²/ unpolished graphite, 58 cm² | Glass bottle | Nafion | 7.25 | 800 mL cathode chamber | Continuous |

*Cube reactors*

| Ref | Product | Electrode | Material | Membrane | Value | Volume | Mode |
|---|---|---|---|---|---|---|---|
| [50] | Hydrogen | CP, 7 cm²/CC, 7 cm² | Plexiglas | 7.1 cm² Nafion | 25 | 28 $mL_L$ each, 120 $mL_G$ | Batch |
| [59] | Hydrogen | CP with 0.5 mg Pt/cm², 26.5 cm²/CP (+graphite granules), 26.5 cm² | Plexiglas | 11.4 cm² Nafion | 9.8 | 192–256 $mL_L$, 292 mL in total | Batch |
| [60] | Acetic Acid | Carbon felt with Stainless steel collectors 100 cm²/Iridium oxide coated titanium mesh 100 cm² | Pespex | Fumatech FAB + FKB | n.d. | 1,050 mL | Batch with recirculation |
| [61] | Hydrogen | CC with 0.5 mg/cm² Pt, 1 cm²/Graphit granules with graphit rod, 184.8 cm² | n.a. | 0.07 cm² AEM | 16.7 | 6 $mL_L$, 8 mL granules/ 28 $mL_L$, 18 $mL_G$ | Batch |
| [62] | Hydrogen | Titanium mesh, 786 cm²/Graphite felt, 452 cm² | PMM | 256 cm² Nafion | 26.2 | Each 3 LL, 300 $mL_G$ | Batch |
| [63] | 1,3-Propanediol | Graphite plates, 100 cm² (both electrodes) | Pespex | 100 cm² CEM | 50 | 200 mL/ 200 mL | Continuous |

*Serpentine flow channel reactors*

| [64] | Hydrogen | Platinum coated titanium mesh, 425 cm²/graphite felt, 250 cm² | n.a. | 250 cm² CEM | 151.8 | Each 280 mL | Continuous |
| [64] | Hydrogen | Platinum coated titanium mesh, 425 cm²/graphite felt, 250 cm² | n.a. | 250 cm² AEM | 151.8 | Each 280 mL | Continuous |

*Electrodialysis/reverse electrodialysis reactors*

| [65] | Methane | Several cathodes tested, ca. 7 cm² | Lexan | 6x AEM, 6x CEM, each 8 cm² | 25 | 28 $mL_L$ each, 100 $mL_G$ | Batch |

*Stirred tank electroreactors (STER)*

| [66] | p-Hydroxybenzoic acid | Graphite/titanium gauze, adapted bioreactor | Glass/SS | 3.14 cm² CEM | 0.76 | 2.5 L/n.d. | Fed-batch |

**Single chamber systems**

*Cube type*

| [67] | Hydrogen | CC with 0.5 mg/cm² Pt, 7 cm²/Graphit brush, 0.22 m² | PC | None | 25 | 28 $mL_L$, 15 $mL_G$ | Batch |

(continued)

**Table 2** (continued)

| Reference | Product | Cathode/anode | Reactor material | Membrane | Spec. cathode area [m²/m³ liquid] | Volume anode/cathode | Operation mode |
|---|---|---|---|---|---|---|---|
| [68] | Hydrogen | CC with 0.5 mg/cm² Pt, 7 cm²/Graphit brush, 0.22 m². | PC | None | 24.6 | 28.5 mL$_L$, 14.5 mL$_G$ | Fed-Batch |
| [69] | Methane | SS, 0.15 m²/graphite fiber brush | PC | None | 60 | 2.5 L | Continuous |
| [70] | Methane | SS mesh, 16.5 m²/Graphite fiber brush | PE (Steel-reinforced) | None | 18.1 | 910 L | Continuous |
| *Bottle type* | | | | | | | |
| [71] | Hydrogen | CC with 0.5 mg/cm² Pt, 20 cm²/CC, 14 cm² | Glass | None | 6.7 | 300 mL$_L$, 200 mL$_G$ | Batch |
| [72] | Methane | SS, 62 cm²/Graphite fiber brush | Glass | None | 8.6 | 700 mL$_L$, 100 mL$_G$ | Batch |
| *Cathode on top* | | | | | | | |
| [73] | Hydrogen | Platinum um coated titanium/graphite granule | Glass | None | n.a. | 150 mL | Batch |
| [74] | Methane | Ni Hollow fiber membranes/Graphite fiber brush | Plexiglas | None | 4 | 350 mL | Fed-Batch |
| [75] | Hydrogen | SS mesh/granulated active carbon and graphite block | PVC | None | n.a. | 40 mL | Batch with recirculation |
| *Rotating disks* | | | | | | | |
| [76] | Methane | Carbon fiber sheets, 947 cm² each half | Perspex waterpipe | None | 54.1 | 1.75 L | Continuous |
| *Cylindrical* | | | | | | | |
| [77] | Methane | SS, 144.4 cm²/carbon felt, 10 cm² | SS | None | 80.2 | 180 mL | Batch |

| Reference | Inoculum | Substrate | $E_{cathode}$ [mV vs. SHE] | CE | $j_{geo}$ [A m$^{-2}$] | $Y$ [mol/mol substrate] | $Y$ [mol m$^{-3}$ d$^{-1}$] |
|---|---|---|---|---|---|---|---|
| **Two-chamber systems** | | | | | | | |
| *H-cell reactors* | | | | | | | |
| [50] | Domestic ww | Acetate | 250–850 (AV) | 60–78% | 0.15–0.88 | 2.9 | n.a. |
| [51] | Anaerobic digester sludge | $CO_2$ from Biogas, Glucose | −700 | 80–88% | 0.4 | n.a. | n.a. |
| [52] | Several organisms; e.g. *Sporomusa sphaeroides* | $CO_2$ | −400 | 84% | n.a. | n.a. | 0.012 |
| [53] | Pure cultures/mixed cultures | $CO_2$ | 1.5 V cell voltage | n.d. | n.d. | n.d. | n.d. |
| [54] | *Sporomusa ovata* | $CO_2$ | −400 | 86% | n.a. | n.a. | 0.141 |
| [51] | Anaerobic digester sludge | Glucose | −700 | 81–84% | 1 | n.a. | n.a. |
| *Concentric tubular reactors* | | | | | | | |
| [55] | Ponds and ww | $CO_2$ | −850 | Up to 88% | 37 | 0.48 | 1.3 |
| [56] | Engineered *Shewanella oneidensis* | Glycerol | 440 (AV) | n.a. | 0.138 | 0.745 | 13.3 |
| [57] | *Propionibacterium freudenreichii* | Glucose, lactate | −390 | 100 | 0.5 | n.a. | 12.7 |
| [58] | *Clostridium acetobutylicum* | $CO_2$ | 2,000 (AV) | n.a. | n.a. | n.d. | 2.6 |
| [51] | Anaerobic digester sludge | Ethanol, organic acids, acetate | −700 | 80–90% | 1.1–3.0 | n.a. | n.a. |
| *Cube reactors* | | | | | | | |
| [50] | Domestic ww | Acetate | 450–850 (AV) | 65–67% | 1.4–7.1 | n.a. | n.a. |
| [59] | ww | ww or Acetate | 230–590 (AV) | 10–26% | 0.563 | 0.0125 mg/mg | n.a. |
| [60] | Pre-enriched microbial community from anaerobic digester | $CO_2$, Bicarbonate | Galvanostatic, −50 mA | 72.6% | 5 | n.d. | 0.70 g/L/d |
| [61] | Soil and ww | e.g. acetic acid (several tested) | 200–800 (AV) | n.a. | n.a. | 3.65 | 49.1 |
| [62] | Other MEC | Acetate | 500 (AV) | 53% | 0.47 | 2.1 | 0.89 |

(continued)

**Table 2** (continued)

| Reference | Inoculum | Substrate | $E_{cathode}$ [mV vs. SHE] | CE | $j_{geo}$ [A m$^{-2}$] | Y [mol/mol substrate] | Y [mol m$^{-3}$ d$^{-1}$] |
|---|---|---|---|---|---|---|---|
| [63] | Microbial consortium | Glycerol | −0.39 | 48% | 0.6 | 0.5 | 24 |
| *Serpentine flow channel reactors* | | | | | | | |
| [64] | Other MEC | Artificial ww | 1,000 (AV) | 47% | 2.3 | n.a. | 17.9 |
| [64] | Other MEC | Artificial ww | 1,000 (AV) | 83% | 5.3 | n.a. | 93.8 |
| *Electrodialysis/reverse electrodialysis reactors* | | | | | | | |
| [65] | Other MEC | Acetate | −300 to −1,000 | 74–81% | 0.71–2.6 | 0.27–0.6 | 0.5–1.93 |
| *Stirred tank electroreactors (STER)* | | | | | | | |
| [66] | *Pseudomonas putida* | Citric acid | −500 | n.a. | 125 | 0.75 | 0.009 |
| **Single chamber systems** | | | | | | | |
| *Cube type* | | | | | | | |
| [67] | MFC | Acetate | 300–800 (AV) | 79–98% | n.a. | n.a. | 139.3 |
| [68] | ww | Acetate and $CO_2$ | 700 (AV) | 88.80% | 10.6 | n.a. | 1.45 |
| [69] | MFC | Acetate | 900 (AV) | >100% | 1.18 | n.a. | 5.27 |
| [70] | ww and sludge | ww | 900 (AV) | n.a. | 0.41 | n.a. | 6.64 |
| *Bottle type* | | | | | | | |
| [71] | Domestic ww | Acetate | 600 (AV) | 32–75% | 14 | 0.92–2.48 | 30.8 |
| [72] | Activated sludge | Acetate | 500–900 (AV) | 8–29% | 0.11–0.42 | 260 mL/mg | 6.25 |
| *Cathode on top* | | | | | | | |
| [73] | Activated sludge | Acetate | 200–1,000 (AV) | 92–96% | Up to 170 A/m$^3$ | n.a. | 6.8 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| [74] | Anaerobic digester sludge | Acetate | 0.5–0.9 V cell voltage | 81% | Up to 50 A/m² | 86.5 | 0.028 m³/m³/d |
| [75] | Geobacter sulfurreducens | Acetate | 800 (AV) | 188% | 1.37 | 0.82 | 1 |
| *Rotating disks* | | | | | | | |
| [76] | Domestic ww | Acetate | −1,100 to −1,300 | n.a. | n.a. | n.a. | up to 23.6 |
| *Cylindrical* | | | | | | | |
| [77] | Two-chamber MEC | Acetate | 400–1,000 (AV) | n.a. | n.a. | n.a. | Up to 39.1 |

## 2.1 Single-Chamber Systems

Although several reactors use membranes to separate the anode and cathode chambers, the membrane also creates extra resistance for proton diffusion to the cathode, increasing the internal resistance of the systems (see Sect. 1.3.2) [67]. To overcome this challenge, single-chamber reactor concepts have been developed. While producing hydrogen at the cathode, the anodic reaction is meant to produce $CO_2$ from the decomposition of organic material, which can be collected together with the hydrogen in the headspace of the reactor [48]. A major disadvantage is that the hydrogen produced at the cathode side can be consumed by microorganisms from the anode (e.g. methanogens). Therefore, most systems meant to produce hydrogen result in the production of methane if methanogens are not inhibited [78]. Fu et al. described the possibility of growing a methane-producing community in a single-chamber reactor and then transferring the cathode to a two-chamber system to increase product yield and purity [79]. Xafenias et al. also discovered that membrane and membraneless systems lead to different products – in their case, acetate or methane [80]. Especially in terms of scale-up, single-chamber systems can be the better choice because membranes are usually prone to biofouling, need maintenance, and are very cost-intensive as a consequence [15]. Single-chamber systems have only one electrolyte solution. In two-chamber systems, the electrolyte solution is separated into a catholyte and an anolyte. Electrodes may be physically separated from each other in single-chamber systems by separators for preventing electrical short circuits.

### 2.1.1 Single-Chamber Cube-Type Reactors

One of the first single-chamber reactors was developed from the cube-type system and is mainly the same as shown in Fig. 1, except for the fact that the membrane is left out [67]. This system is used to produce hydrogen [67] as well as methane [68, 81] (see Table 2). Because of its simple and membrane-free design, this design does not prevent chemical crossover; however, because they are easy to handle, cube-type reactors are often used for scale-up experiments. The electrode surface area can be easily varied by increasing the number of electrodes or using three-dimensional structures. Rader and Logan suggested introducing several pairs of electrodes into a single-chamber system because they found it easier to increase the number of electrodes for scale-up than to increase the electrode surface area [69]. This also may prevent ohmic losses due to internal resistance drops (see Sect. 1.3.1). Therefore, they created a system that was similar to several combined cube-type systems, with anodes and cathodes placed alternatingly. Separators between anodes and cathodes were used to avoid short circuits. With a continuous substrate flow, hydrogen and methane were produced [69]. A similar system was also used for a pilot-scale application by Cusick et al. to produce methane and hydrogen [70]. This system included 144 pairs of electrodes in a 1,000-L reactor.
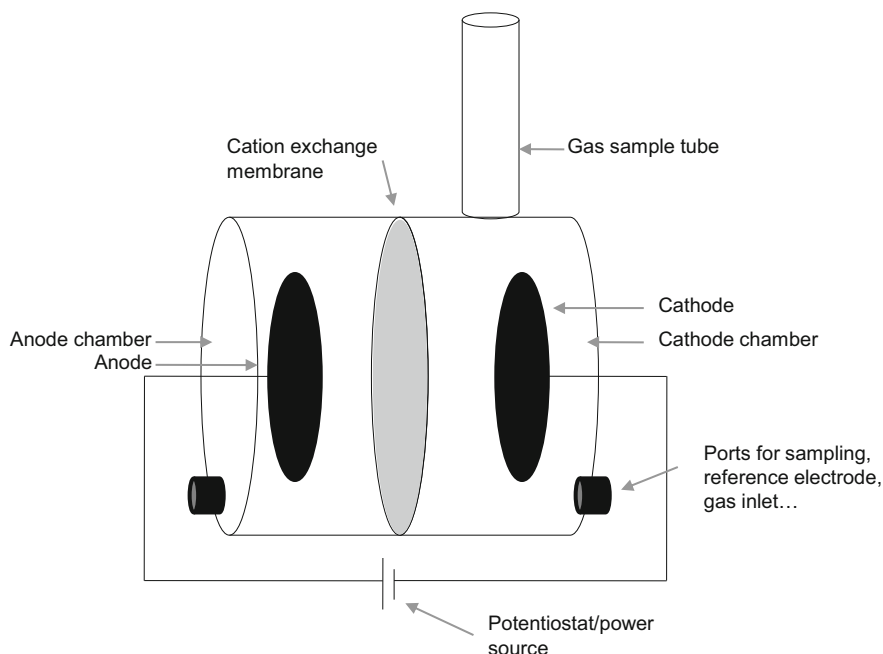
**Fig. 1** Cube-type reactors are easy to manufacture and are suitable for basic investigations as well as pilot-scale studies. Electrode types and electrode surface areas can be easily varied. These reactors are used from smaller scales to pilot scale, up to volumes of 1 m$^3$

### 2.1.2 Cylindrical Reactors

Similar to the two-chamber concentric cylindrical systems (discussed later), cylindrical single-chamber systems have been used. One example is a reactor designed by Bo et al., which consists of a steel cylinder that works as the cathode and a concentric anode placed within the cathode cylinder [77]. This enables a homogenous potential distribution within the reactor. However, the distance between anode and cathode is high compared to the electrode-membrane stacks often used in cube-type reactors. A disadvantage is that the cathode material, which is crucial for the product generation, cannot be varied easily for future investigations (Fig. 2) [82].

### 2.1.3 Bottle-Type Reactors

One system that is especially suitable for screening and preliminary laboratory-scale investigations is the bottle-type system (Fig. 3). Here, both electrodes are placed in a small bottle, such as a septum bottle [83, 84]; between the electrodes, an isolator can be used to avoid short circuiting [71]. Unfortunately, the placing of the
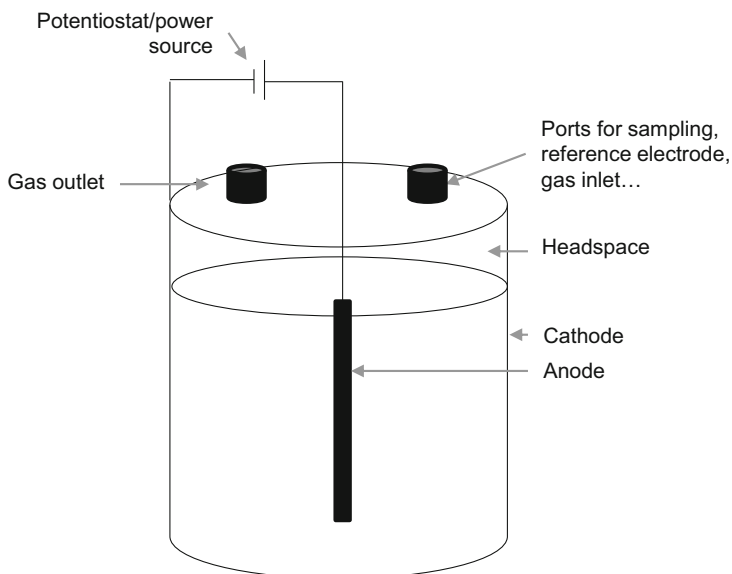
**Fig. 2** Single-chamber cylindrical reactors are comparable to cube-type reactors and are typically used on a laboratory scale, with volumes of up to 200 mL
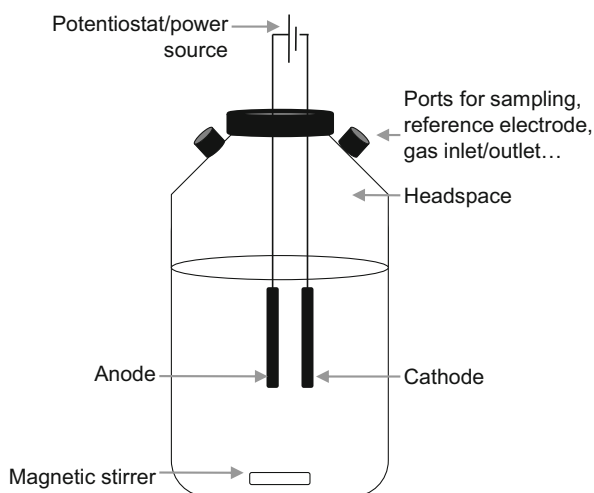


**Fig. 3** Single-chamber bottle type reactors are easy and cheap to manufacture. They can be used for preliminary investigations and screening experiments. This reactor type is typically used on a small scale with volumes up to 800 mL

electrodes is not fixed, decreasing the reproducibility and controllability of the experiments. However, because all required items are commonly used in laboratories, this system can be built up in a short time and without high costs. Screening

systems with these mini-reactors, which use just one power supply for several experiments at a time, have been introduced [84].

The performance of these systems is mainly driven by the high SVR of the used cathodes [72, 85]. This reactor type can also be operated with the cathode above the anode, so it is a mixture of the previously described bottle-type reactor and the later-described cathode-on-top system [72]. However, because the space inside the septum bottles is limited, experiments dealing with three-dimensional electrodes, for example, cannot be carried out on a sufficient scale. In general, the specific electrode area seems to be low compared to investigations with other reactor types (Table 2). Therefore, the same design can be carried out in a cylindrical reactor by replacing the septum bottle [86].

### 2.1.4 Column-Type Reactors

To avoid the contact of hydrogen with anodic microorganisms, which are capable of metabolizing the product, a cathode-on-top design has been developed [73]. The electrodes do not face each other horizontally; rather, the cathode is placed above the anode, so that hydrogen bubbles generated at the cathode leave the cultivation medium without passing the anode and the attached microorganisms, respectively (Fig. 4). However, the internal resistance of the reactors is high due to the large distance between the anode and cathode (see Sect. 1.3.1). The anode can be designed as a fixed bed, providing better support for microbial attachment [73]. Liu et al. developed a cathode-on-top system, including a fluidized bed anode instead of a fixed bed anode to produce hydrogen [75]. In this reactor, carbon granules are fluidized at the bottom part of the reactor to increase the anode surface and the biofilm support.

Katuri et al., on the other hand, suggested using hollow-fiber membranes as cathodes to combine filtration and electrosynthesis [74]. This special column-type reactor system can therefore be referred to as an electromicrobial membrane reactor. For this type of reactor design, mathematical models have already been suggested by Li et al. [87]. The cathode-on-top design aims to improve hydrogen production without using a membrane. However, it is not suitable if gases are produced at the anode (e.g. oxygen or carbon dioxide), which lead to a purity decrease of the product gas or, in case of methane production at the cathode, to an inhibition of microorganisms by oxygen. To avoid this, it is possible to create an anode-on-top design, where the anode is placed above the cathode. This is an interesting approach to prevent the contact of the produced oxygen at the anode to strictly anaerobic microorganisms for MES based on carbon dioxide [88], without introducing a membrane. This type of reactor has been used in the first generation of MFC studies but was replaced by systems with lower internal resistances.
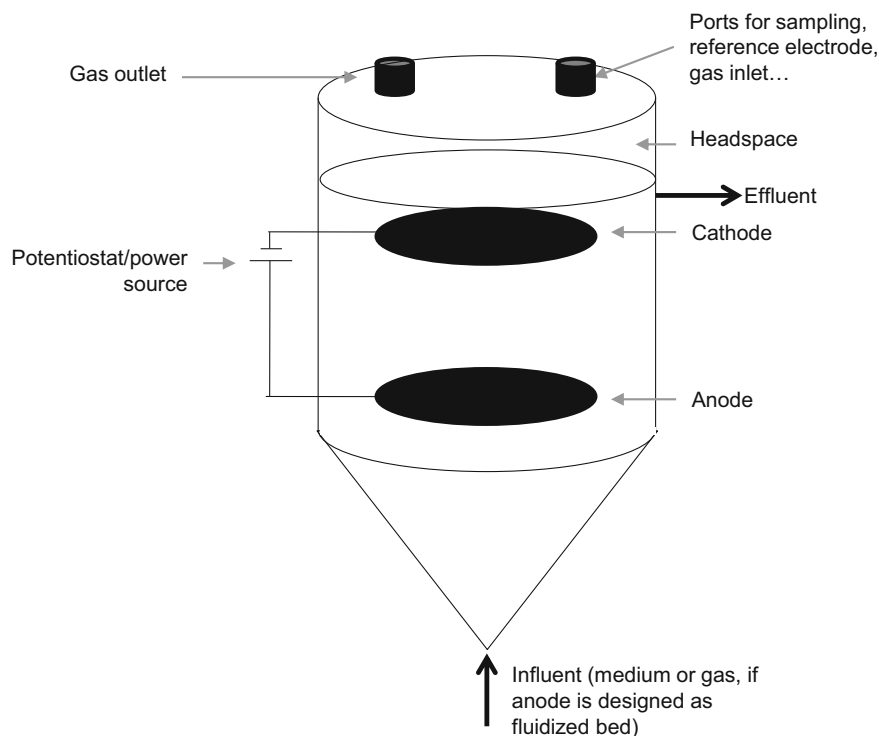
**Fig. 4** Cathode-on-top reactors can be used to prevent gasses from interfering with the reaction at the bottom electrode. They are currently used on the laboratory scale with volumes of up to 8 L

### 2.1.5 Rotating Disk Reactors

Another interesting reactor was designed by Cheng et al., who used a cylindrical single-chamber reactor with intermitted rotating half-disks as electrodes [76]. Both electrode half-disks are alternately submerged in the liquid phase and exposed to the gaseous phase (Fig. 5). Thus, each disk half alternately becomes an anode and a cathode: a cathode when exposed to the gaseous phase and an anode when submerged in the liquid phase. At every moment, there is always a bit of the gas-phase electrode that is submerged in the liquid phase, so there is an ionic connection between the electrodes. This approach results in the formation of a uniform biofilm all over the disk. The main product is methane, which is released directly to the gas phase. One advantage of this design is that no pH gradient can occur between the cathode and anode [76].

Although the number of electrodes can be increased, scale-up is limited because much energy is needed to rotate the electrodes in a potentially viscous medium. The design of the reactor is shown in Fig. 4. (For more detailed sketches and photographs see Cheng et al. 2011.)
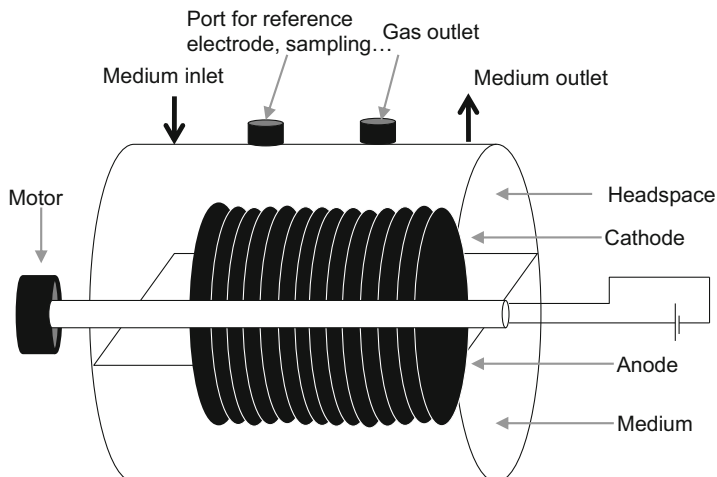
**Fig. 5** The rotating disk reactor is a sophisticated reactor design, which allows the use of high numbers of electrodes enabling highly specific electrode areas. The reactor is currently used on the laboratory scale with volumes of up to 2 L

## 2.2 Two-Chamber Systems

Many MEC/MES consist of two chambers – an anode chamber and a cathode chamber, separated by a membrane. Despite the fact that membranes may limit the performance of a system due to their electrical resistance and their resistance to ion flux itself (see Sects. 1.3.1 and 1.3.2), a membrane can be of importance, especially if high coulombic efficiencies are needed, because it prevents exchanges between the electrode (chambers) through the diffusion of reduced and/or oxidized chemicals (chemical short circuits). Membranes also prevent product diffusion between the chambers [67]. In case of cathodic methane production, for example, a membrane hinders oxygen diffusion from water electrolysis to the cathode chamber, which may inhibit the oxygen-sensitive microbial community [45]. Of course, this is only the case when the membrane materials are chosen according to the needed selectivity. Usually, reactors with membranes create products or off-gas streams with higher purities than reactors without membranes [67, 89].

### 2.2.1 H-Cell Reactors

As already introduced, one of the most common two-chamber reactor setups are the so-called H-cells. They consist of two chambers, usually a glass bottle each, separated by a membrane. Figure 6 shows the typical design of an H-cell, while Table 2 lists some investigations carried out in H-cells [53]. MES in H-cells starting from $CO_2$ was first reported by Nevin et al. in 2010; since then, many MES investigations have been carried out in H-cells [52, 54]. The majority of these
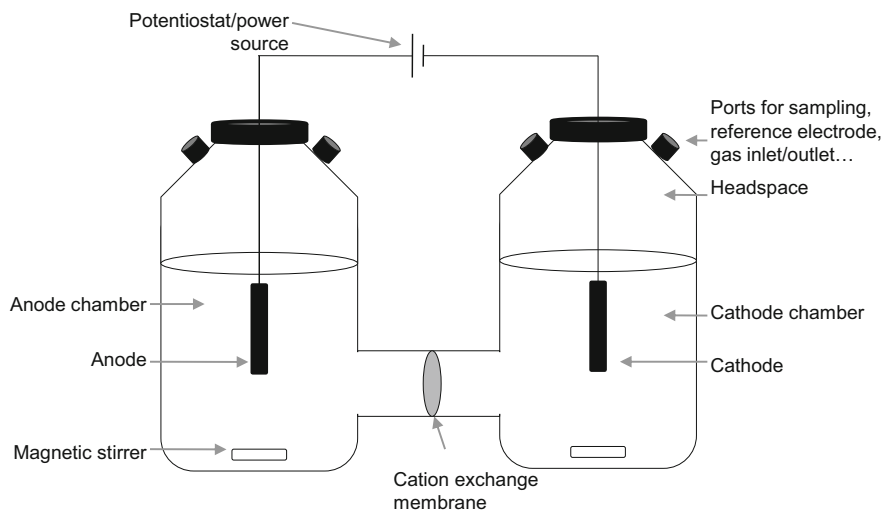
**Fig. 6** H-cell reactors are the workhorse of bioelectrochemical systems in studies where separation is needed. They are used on the laboratory scale in volumes of up to 200 mL

studies yielded acetic acid as the major or only product (Table 2); in some cases, other products, such as methane [90] or butyrate [58], were reported. H-cells have an existing wide distribution, relatively easy setup, the possibility to introduce a magnetic stirrer and gas inlet, and easy usage of various electrode materials. A typical setup uses two 200-mL flasks separated by a cation-exchange membrane and graphite sticks as both the anode and cathode. H-cells are ideal systems for preliminary investigations and comparative studies of membrane or cathode materials, although some disadvantages occur: limited means of gassing and stirring geometry, elevated internal resistance due to the comparably long electrode distance (and hence a voltage drop between the electrodes [91]) and, from a technical point of view, the inability to scale-up. The low space-time yields of the MES studies given in Table 2 also indicate that this reactor might not be ideal for reaching industrial relevance with MES. However, the yields may be limited by the microorganisms in several cases and not by the reactor system itself.

### 2.2.2 Concentric Tubular Reactors

Concentric tubular cells have been used in several investigations as laboratory-scale alternatives to H-cells. The two chambers are not next to each other; rather, the anode chamber is placed within the bigger cathode chamber, separated by a cylindrical glass tube with a membrane window, usually at the bottom of the anode chamber (Fig. 7) [92]. Some of the studies that used this type of laboratory-scale reactor are listed in Table 2. An interesting investigation about this type of reactor was done by Xu et al., who compared methane formation in a biogas-upgrading process in H-cells and in a concentric cylindrical MEC [51]. They
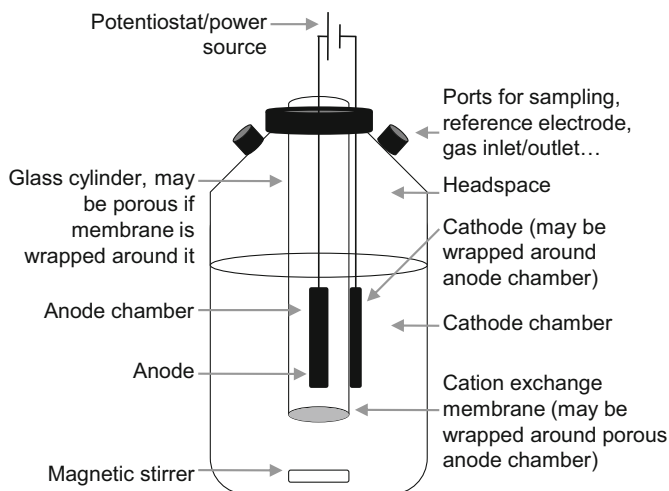
**Fig. 7** Concentric tubular reactors are further developed H-cells with improved specific surface areas. These reactors are currently used on the laboratory scale with volumes up to 1 L

concluded that the concentric cylindrical MEC performed better; however, the comparison is difficult to make because the membrane area, the substrate, and the process type were different. This publication also showed that continuous operation is possible for this reactor type [51]. Jourdin et al. demonstrated the operation of this reactor type in fed-batch mode, with the reactor being used as a testing system for new electrode materials in acetate-producing MES [55].

An advantage of this reactor compared to the H-cell is that the setup is easier and less space consuming; in addition, the membrane area can be varied easily when using a "membrane bag" instead of a membrane window in a glass cylinder [51]. The electrodes can be close together to decrease the internal resistance of the system by wrapping the membrane around a porous glass cylinder and thus constructing an electrode-membrane assembly. The electrode SVR appears to be smaller than in H-cells (see Table 2). Similar designs on a larger scale have been used by Sasaki et al., Carmona-Martinez et al., and Jeon et al. [58, 93, 94]. Sasaki produced methane on a 2–4 L scale in a concentric cylindrical reactor [93]. Carmona-Martinez also investigated the long-term performance and hydrogen production of the used system [94]. Jeon characterized a 1-L MES producing acetic acid, propionic acid, and butyric acid [58]. One interesting final outcome of this study is the similarity of the yields obtained when electrochemically producing hydrogen by an applied voltage, compared to a system growing with 2 atm of hydrogen overhead pressure. This outcome indicates that the hydrogen coming from hydrogen evolution at the cathode could be the reason for the improvement of the bioelectrocatalysis compared to a standard cultivation without electrochemistry [58]. The points discussed in this section illustrate that this kind of system is more scalable than the H-cell. However, because mixing is hindered by the inserted

chamber, low-velocity zones and concentration gradients, which depend on the diffusivity of the substrate, could appear in larger systems. Studies have addressed this challenge and increased mixing by applying an external loop [95]; continuous operation of the system has been reported [96].

### 2.2.3 Two-Chamber Cube-Type Reactors

Another relatively common reactor is the cube-type or cylindrical MEC. Basically, this reactor is similar to the H-cell. However, the two chambers are not two bottles; rather, they are two cylindrical, flat, disk-shaped chambers resulting from the carving of cubic plastic materials (see also Table 2), which are separated by a membrane. Therefore, the membrane area relative to the volume can be increased compared to the H-cell [50] or decreased using a small membrane window [59]. Furthermore, this type of reactor does not necessarily have a headspace for gas collection, necessitating a gas outlet (pipe or tube) on the top of the two chambers [61]. In a comparison between cube cells with larger headspace and cube cells with very little headspace, the cells with the larger headspace turned out to be more practical in terms of sampling [59]. A sketch is given in Fig. 1; Ditzig et al. and Wang et al. also provided more detailed design drawings [59, 68].

An investigation by Liu et al. in 2005 compared the performance of a cube MEC and an H-cell during hydrogen production. Interestingly, less hydrogen was found in the cube system, possibly because of product diffusion through a larger membrane area to the anode chamber [50]. A similar reactor design was used by Villano et al. to create a "fixed bed reactor," introducing graphite granules to the chambers. To ensure mixing, medium recirculation is applied in that approach [89]. Compared to the H-cell, this reactor has an advantage of decreased distance between the cathode and anode, which lowers the internal resistance [59]. Because the membrane area, gas inlet and outlet, substrate inlet, and electrode distance can be varied, this system is more flexible and also more scalable than an H-cell. Continuous operation modes for such cubic reactor types have also been reported [63].

Even direct concentration of the MES product acetate was realized in this system by applying a second membrane to create a three-chamber system [60]. Cubes should therefore be preferred only in experiments preparing pilot scale applications if a direct electron transfer is realized versus a mediated electron transfer due to their limited mixing. Disadvantages are difficulties in mixing and gassing due to the rounded bottom if a cylindrical or disk-shaped approach is used. Furthermore, there might be a dead zone at the very bottom of the reactor, where the application of a stirrer or a sparger is not possible due to their size. However, Rozendal et al. have used a similar reactor with at least 3 L of working volume [62].

### 2.2.4 Flat-Plate Reactors

Flat plate reactors with serpentine flow channels have been designed and applied to generate hydrogen [64, 97] and methane [49]. The electrodes are placed very close to each other by an electrode-membrane assembly, decreasing the ohmic losses within the electrolyte [64]. A sketch of the reactor is given in Fig. 8; a more detailed drawing, especially of the periphery and heating jacket, has been published elsewhere [97]. Examples of applications can be found in Table 2. By applying bipolar plates in a cube-type reactor, a stacking can be realized; they act as excellent current collectors, which also improves the uniform potential distribution [98]. This approach has only been applied in MFCs so far. However, due to its advantages, its use in MES seems very promising.

Due to a recirculation of the medium with the possibility of mixing outside the MEC, concentration gradients could occur in the electrolyte between the inlet and outlet of the reactor chamber. In any case, the contact time between the electrolyte and electrodes is improved due to the long flow path, which could lead to higher yields. The larger specific electrode surface also improves the production yields (see also Table 2). Because the design is rather complicated compared to H-cells and cube-type reactors, this system would not be the first choice to start screening experiments or proof-of-concept-investigations. However, because the process is mechanically divided up into at least two compartments, it can serve as a reactor for more in-depth mechanistic investigations. A scale-up of this concept does not seem
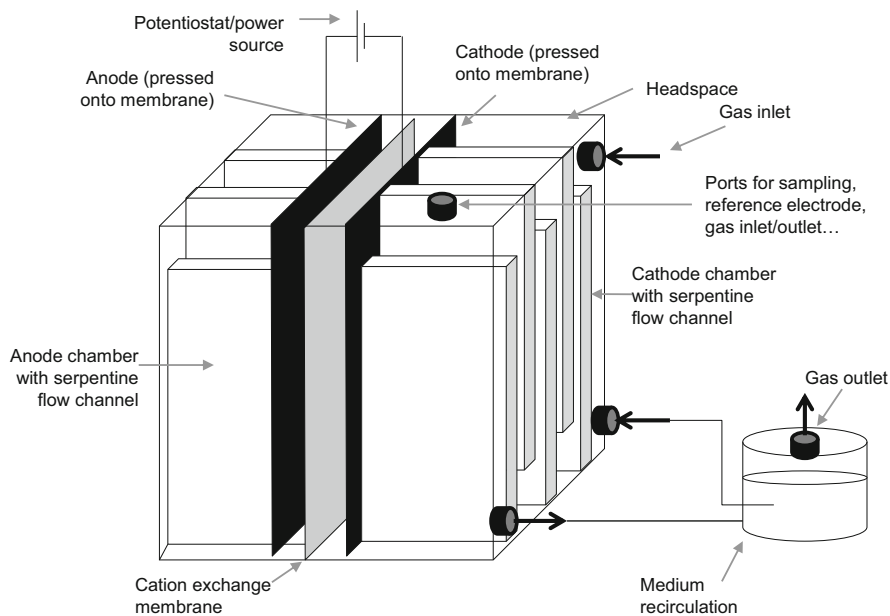


**Fig. 8** Serpentine flow channel reactors feature low ohmic losses due to narrow electrode spacings. These reactors are typically used on the laboratory scale with volumes of up to 300 mL

to be practical because permanent media recirculation is rather energy intensive and the application of larger or three-dimensional electrodes is limited.

Flat-plate reactors, which are considered to be conventional fuel cell designs, and lamellar flow systems also fall into this reactor category [99, 100]. Flat-plate reactors can serve as models for any kind of bioelectrochemical reactor. Key limitations are that the flat-plate approach can create mixing and clogging issues for fluids containing solids, requiring a decent dimensioning of the fluid chambers. In lamellar systems, relatively high performances ($>1$ kA m$^{-3}$ at the liter scale, $>250$ A m$^{-3}$ at the pilot scale) are reached compared to other systems.

### 2.2.5 Bioelectrochemical Systems with Reverse Dialysis Stack Reactors as a Process Variation

As mentioned previously, external voltage has to be provided to allow the formation of hydrogen at the cathode. One method to generate the needed voltage is to couple an MEC system with a biotic anode for reverse electrodialysis, which generates current by combining the flows of low-concentration salt solutions and high-concentration salt solutions, separated from each other by both cation- and anion-exchanging membranes. This leads to a potential difference across the membranes [65]. The resulting reverse-electrodialysis microbial-electrolysis system is comparable to the previously mentioned cube-type reactors, whereby the membrane is substituted with a reverse electrodialysis stack as shown in Fig. 9 (adapted from Luo et al. 2014). In this stack, cation-exchange membranes and anion-exchange membranes are placed alternately [65].

This system has been used for hydrogen production as well as for methane production; examples are given in Table 2. This reactor was designed to overcome the problem of external power addition to the MEC. The needed energy can be gained by converting salinity gradient energy to electrical energy, thus providing the added potential needed for evolution of the products [65]. However, a critical study is missing: how much power is consumed additionally by regeneration of the high/low salt concentration solutions and liquid transport within the reverse electrodialysis stack. Without this, the total energy savings cannot be calculated and there will probably be losses in efficiency because of the larger internal resistance of the system.

### 2.2.6 Stirred Tank Electroreactors

The standard workhorse in biotechnology is the stirred tank reactor. Therefore, it desirable to create stirred tank electroreactors (i.e. standard bioreactors) equipped with electrodes [14, 66]. These stirred tank electroreactors allow for benchmarking between bioelectrosynthesis and "conventional" biosynthesis; they also open the door for the implementation of bioelectrosynthesis into existing infrastructure and process lines. However, what sounds easy at first glance is a rather difficult task
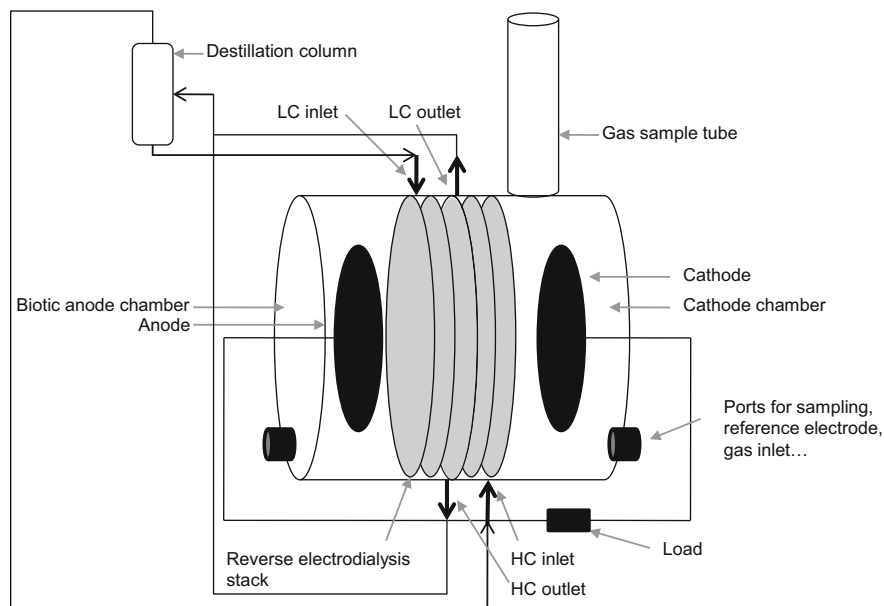
**Fig. 9** MES with a reverse electrodialysis stack is comparable to cube-type reactors gaining additional energy from salinity gradients. These reactors are typically used on the laboratory scale with volumes of up to 200 mL

from an engineering point of view. Because most bioreactor lids are made of stainless steel, electrical insulation of the electrodes has to be ensured for correct measurements. An installation has to be inserted into the reactor to generate two separate chambers. The space in a laboratory-scale bioreactor (0.5–3 L) is limited due to the standard reactor assemblies such as the stirrer, gas sparger, and baffles.

The necessary equipment for process control and automation can be included in the stirred tank electroreactors and give new insights into process behavior. An example is an investigation carried out by Hintermayer et al., who inserted a cathode chamber of glass into a standard bioreactor [66]. Apart from that, the lid was electrically isolated via a silicone ring and the stainless-steel stirrer was replaced by a non-conductive one. A crude sketch is given in Fig. 10 (see Hintermayer et al. 2016 for detailed drawings). Although the reactor design is well characterized in this study, low space-time yields were achieved.

Rosa et al. have devised upgrade kits for bioreactors, enabling different conventional bioreactor systems to be used for bioelectrotechnology [14]. These upgrade kits can be tailored to different reactor designs and scales, can be reversibly mounted, and are suitable for a plethora of application conditions (e.g. environmental and biotechnological operation modes). The resulting electrobioreactors were used to cultivate the electroactive model organism *Shewanella oneidenis* MR-1 [14]. Based on the demonstrated upgrade kit, it will be possible not only to study and engineer a specific bioelectrotechnological
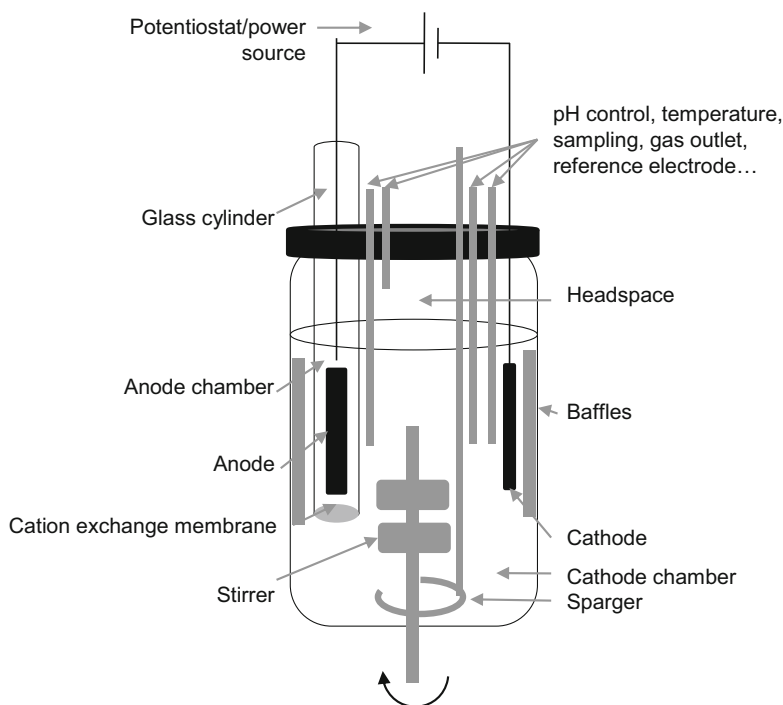
**Fig. 10** The stirred tank electroreactor is based on a conventional bioreactor with an upgrade kit to enable electrobiotechnology under more standardized conditions. This reactor type is used on the laboratory scale up to volumes of 2.5 L

application with high reproducibility and confidence in the process control, but comparisons also can be made across studies and laboratories (which have not been possible to date), thus enabling standardization, knowledge-driven engineering, and its benchmarking to conventional processes.

## 2.3   A Critical Assessment of MET Reactor Designs

Several reactor types have been described in Sect. 2, which are scored according to different performance and design parameters in the following section. As the implementation of particular reactors belonging to the same reactor type can significantly differ, the chosen designs are depicted with the relevant literature and exemplary rated. The chosen parameters were derived from the requirements for a successful design described in Sect. 1. As indicated in Table 3, the performance was assessed according to the anode/cathode distance and current collection, (which directly affect the performance by ohmic losses), electrolyte mixing (which can decrease mass transport limitation and concentration polarization), SVR (which

**Table 3** Ranking of the different reactor types for bioelectrochemical systems in terms of performance and design

| Reactor type | Performance | | | | | | Simplicity of design | | |
|---|---|---|---|---|---|---|---|---|---|
| | Anode/cathode distance | Electrolyte mixing | $A_{spec}$ | Current collection | Chemical crossover | Dealing with solids | Scalability | Cost | Complexity |
| Cube-type [67] | − | − | +/− | +/− | − | +/− | − | ++ | +/− |
| Cathode-on-top [101] | −− | +/− | − | − | − | − | +/− | + | + |
| Rotating disk [76] | − | + | + | +/− | − | +/− | + | +/− | +/− |
| H-cells [53] | −− | +/− | − | +/− | ++ | +/− | − | + | + |
| Tubular [102] | + | +/− | − | + | +/− | +/− | +/− | + | + |
| Serpentineflow [99] | ++ | + | ++ | + | + | +/− | + | − | − |
| Stirred-tank electroreactor [14] | − | ++ | − | +/− | ++ | +/− | +/− | − | +/− |

affects volumetric current densities and production yields), chemical short circuits, and how the design deals with solids. Furthermore, the scalability, expected costs, and complexity of the design were rated because those parameters determine applicability and practical implementation. In any case, considering the purpose of a reactor is necessary when deciding on the importance of the different rating parameters, especially when doing experimental laboratory work with fundamental research questions versus application-driven experiments. The anode/cathode distance, for example, is negligible in three-electrode setups for the investigation of microbe-electrode interactions, whereas it is crucial for a scale-up reactor. Along with the difficult comparability in terms of key performance indicators, it is impossible to provide a conclusive recommendation on the best reactor designs.

Many of the reactor systems discussed here do not adhere to several of the key requirements of well-functioning microbial electrochemical technology. Obviously, this is not always essential: for example, in research and development, simple designs that can be replicated easily in the laboratory are preferable over highly engineered systems. Some of the systems used thus far, such as reactors with sequential anode/cathode placements (cathode-on-top), have so many drawbacks that it seems best to phase these out. There are, after all, certain laws of nature that cannot be defeated. In terms of well-engineered systems, there is no reactor configuration that outcompetes all others due to the different requirements for different applications. Several reactors are quite suitable for applications, such as flat plate and lamellar systems, as shown via pilot trials.

Generally, when designing reactors, more attention should be given to the internal resistance and mixing issues (stirred tank vs. plug flow). Computational fluid dynamics can be very helpful here (see also [26] for some insights). The overall message around reactor design is perhaps that more attention has to be paid to existing knowledge (e.g. from the electrochemistry field). If microbial electrobiotechnologies such as MES want to gain credibility, unifying designs that adhere to the key physical laws are essential. The availability of commercial reactors can truly help in this context because they improve worldwide access to well-described technology. Finally, a good reactor also comes with a good set of descriptive parameters, such as SVR, electrode surfaces, anode-cathode distances, and so on [20]. The best-scoring reactor designs come with this dataset because these parameters formed the basis of their designs.

## 2.4 Further Considerations

Apart from the reactor design itself, at least two more things need to be considered when building new reactors for MEC and MES: (1) the electrode material and geometry and (2) the membrane material in a two-chamber system. The electrode has a huge impact on the process performance. Thus, the electrode material needs to be conductive, must give a support to biofilm formation (when needed) or be at least biocompatible, and have an appropriate SVR. Finally, (low) cost and scalability are

also desired characteristics for the electrode materials. Even if precious metal electrodes provide the best conductivity, they are not applicable in larger systems due to their high costs. Alternatives have been reported, with some using material compositions that influence the surface attachment of the microbes [45, 103–105]. Kerzenmacher [7] provides further information about electrode design and material.

Also interesting in terms of reactor design is the membrane material. The widely used Nafion membranes perform well, but they are still too expensive for technical applications. Already from the onset, lower cost membranes have been used that operated as well as Nafion [106]. Multiple types of membranes are available; usually they are differentiated as cation and anion exchange membranes. Instead of membranes, other materials such as ceramic or porous glass diaphragms/separators have also been used [107]; however, the selectivity and permeability of these materials are much less specific and different from ionic exchange membranes because they are basically porous barriers that create longer diffusion pathways. These characteristics have to be considered and compared when choosing a material. Comparisons of different membrane materials have been published elsewhere [64, 108–111].

Scaling-up reactors also may not be feasible due to constraints of the designed reactors and parts thereof. It has to be discussed whether numbering-up approaches are more likely to improve the performances of bioelectrochemical reactors on a pilot scale. Cusick et al. reported the use of 24 electrode modules, which were working successfully in parallel, in their microbial electrolysis cell pilot-scale study [70]. A smart reactor design takes all of the above into account. However, a well-engineered reactor is more than its scientific principles: it is guided by engineering constraints, for which we provide a non-exhaustive matrix in Fig. 11.

Applicability is mainly about four key aspects: reliability, scalability to the desired scale, cost-effectiveness for the purpose, and uniqueness relative to what
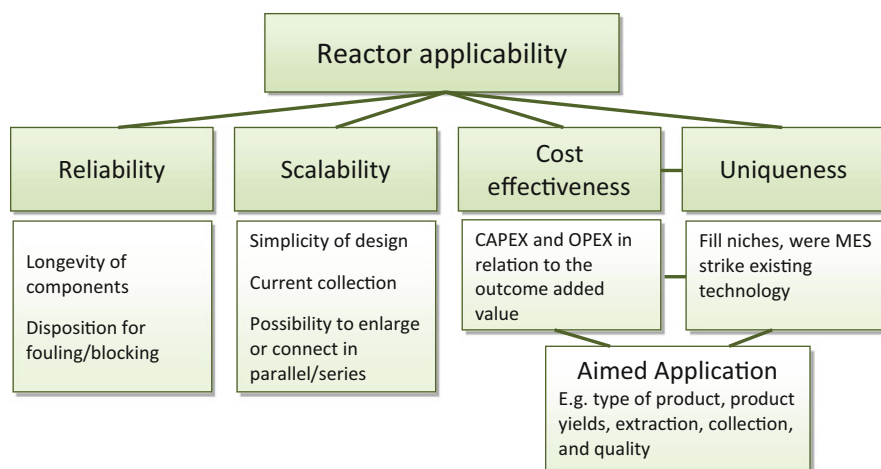


**Fig. 11** A matrix to determine the applicability of METs

exists. Scalability depends on the needs and should be matched with the well-established field of electrochemistry. In this field, electrodes are scaled up to the maximum (~2 m$^2$) to enable good current collection and mixing. This should be emulated in the field of METs. In our opinion, it is incorrect to strive for the miniaturization of systems to minimize problems such as ohmic loss. Adequate reactor design can ensure loss minimization, whereas a larger scale can drive down cost and maintenance. Cost-effectiveness speaks for itself: the combination of capital expenditures and operational expenditures needs to be competitive. For example, relative to anaerobic digesters, METs will be more expensive due to high materials usage; however, depending on the target outcome, added value is created. For example, to identify products that can theoretically benefit from electrical assistance in MES or electrofermentation, feasible and interesting metabolic pathways have been reviewed [112], and it has been demonstrated what is worth producing economically [113, 114]. Here, yield and product quality will also be critical. If the system is run with waste, an extra requirement has to be accomplished: treatment efficiency, including carbon dioxide, nitrogen, and phosphorus removal.

The hardest parameter to assess is uniqueness. For instance, when considering the prime example of MET, the MFC, lessons can also be learned for MES. MFCs that generate power from wastewater have not yet found applications because of one disadvantage: anaerobic digestion is very mature in this sector. Moreover, when a digester converts a loading of, say, 50 kg carbon dioxide m$^{-3}_{reactor}$ d$^{-1}$, this relates to a theoretical current flow of 6,979 A m$^{-3}$. It is highly unlikely that MFCs will obtain this. However, MFC have unique features: they work in an oxidative manner, thus delivering effluents devoid of sulfides; operate as a biofilm process; and enable power production at low temperatures [115], even at the seafloor. These unique features should drive applications and thus the system design. Similarly, MES poses the unique advantage of enabling selective production of multicarbon compounds from $CO_2$ in one step, coupled to electricity in a direct or indirect (e.g. $H_2$ generation) manner. This can be coupled with in situ extraction [60], which decreases the need for additional extraction steps.

# References

1. Hongo M, Iwahara M (1979) Application of electro-energizing method to L-glutamic acid fermentation. Agric Biol Chem 43(10):2075–2081. https://doi.org/10.1080/00021369.1979.10863776
2. Schievano A, Pepé Sciarria T, Vanbroekoven K et al (2016) Electro-fermentation – merging electrochemistry with fermentation in industrial applications. Trends Biotechnol 34(11):1–13. https://doi.org/10.1016/j.tibtech.2016.04.007
3. Schröder U, Harnisch F, Angenent LT (2015) Microbial electrochemistry and technology: terminology and classification. Energy Environ Sci 8(2):513–519. https://doi.org/10.1039/C4EE03359K

4. Rabaey K, Rozendal RA (2010) Microbial electrosynthesis – revisiting the electrical route for microbial production. Nat Rev Microbiol 8(10):706–716. https://doi.org/10.1038/nrmicro2422
5. Krieg T, Sydow A, Schröder U, Schrader J, Holtmann D (2014) Reactor concepts for bioelectrochemical syntheses and energy conversion. Trends Biotechnol 32(12):645–655. https://doi.org/10.1016/j.tibtech.2014.10.004
6. Schmitz LM, Rosenthal K, Lütz S (2017) Enzyme-based electrobiotechnological synthesis. Adv Biochem Eng Biotechnol. https://doi.org/10.1007/10_2017_33
7. Kerzenmacher S (2017) Engineering of microbial electrodes. Adv Biochem Eng Biotechnol. https://doi.org/10.1007/10_2017_16
8. Rosenbaum MA, Berger C, Schmitz S, Uhlig R (2017) Microbial electrosynthesis: pure and defined mixed culture engineering. Adv Biochem Eng Biotechnol. https://doi.org/10.1007/10_2017_17
9. Roy S, Schievano A, Pant D (2016) Electro-stimulated microbial factory for value added product synthesis. Bioresour Technol 213:129–139. https://doi.org/10.1016/j.biortech.2016.03.052
10. Deeke A, Sleutels THJA, Donkers TFW, Hamelers HVM, Buisman CJN, Ter Heijne A (2015) Fluidized capacitive bioanode as a novel reactor concept for the microbial fuel cell. Environ Sci Technol 49(3):1929–1935. https://doi.org/10.1021/es503063n
11. Janicek A, Fan Y, Liu H (2014) Design of microbial fuel cells for practical application: a review and analysis of scale-up studies. Biofuels 502:79–92
12. Verstraete W, Rabaey K, Logan BE et al (2006) Microbial fuel cells: methodology and technology. Environ Sci Technol 40(17):5181–5192. http://www.ncbi.nlm.nih.gov/pubmed/16999087
13. Moscoviz R, Toledo-Alarcón J, Trably E, Bernet N (2016) Electro-fermentation: how to drive fermentation using electrochemical systems. Trends Biotechnol 34(11):856–865. https://doi.org/10.1016/j.tibtech.2016.04.009
14. Rosa LFM, Hunger S, Gimkiewicz C, Zehnsdorf A, Harnisch F (2016) Paving the way for bioelectrotechnology: integrating electrochemistry into bioreactors. Eng Life Sci 53 (9):1689–1699. https://doi.org/10.1002/elsc.201600105
15. Logan BE (2009) Scaling up microbial fuel cells and other bioelectrochemical systems. Appl Microbiol Biotechnol 85(6):1665–1671. https://doi.org/10.1007/s00253-009-2378-9
16. Kipf E, Koch J, Geiger B et al (2013) Systematic screening of carbon-based anode materials for microbial fuel cells with Shewanella oneidensis MR-1. Bioresour Technol 146:386–392. https://doi.org/10.1016/j.biortech.2013.07.076
17. Baudler A, Schmidt I, Langner M, Greiner A, Schröder U (2015) Does it have to be carbon? Metal anodes in microbial fuel cells and related bioelectrochemical systems. Energy Environ Sci 8(7):2048–2055. https://doi.org/10.1039/C5EE00866B
18. Clauwaert P, Aelterman P, Pham TH et al (2008) Minimizing losses in bio-electrochemical systems: the road to applications. Appl Microbiol Biotechnol 79(6):901–913. https://doi.org/10.1007/s00253-008-1522-2
19. Zhou M, Chi M, Luo J, He H, Jin T (2011) An overview of electrode materials in microbial fuel cells. J Power Sources 196(10):4427–4435. https://doi.org/10.1016/j.jpowsour.2011.01.012
20. Patil SA, Gildemyn S, Pant D, Zengler K, Logan BE, Rabaey K (2015) A logical data representation framework for electricity-driven bioproduction processes. Biotechnol Adv 33(6:736–744. https://doi.org/10.1016/j.biotechadv.2015.03.002
21. Koch C, Harnisch F (2016) Is there a specific ecological niche for electroactive microorganisms? ChemElectroChem 3(9):1282–1295. https://doi.org/10.1002/celc.201600079
22. Simonte F, Sturm G, Gescher J, Sturm-Richter K (2017) Extracellular electron transfer and biosensors. Adv Biochem Eng Biotechnol. https://doi.org/10.1007/10_2017_34
23. Vidakovic-Koch T (2017) Electron transfer between enzymes and electrodes. Adv Biochem Eng Biotechnol. https://doi.org/10.1007/10_2017_42

24. ter Heijne A, Geppert F, Sleutels THJA, Batlle-Vilanova P, Liu D, Puig S (2017) Mixed culture biocathodes for production of hydrogen, methane, and carboxylates. Adv Biochem Eng Biotechnol. https://doi.org/10.1007/10_2017_15
25. Sharma M, Bajracharya S, Gildemyn S et al (2014) A critical revisit of the key parameters used to describe microbial electrochemical systems. Electrochim Acta 140:191–208. https://doi.org/10.1016/j.electacta.2014.02.111
26. Korth B, Harnisch F (2017) Modeling microbial electrosynthesis. Adv Biochem Eng Biotechnol. https://doi.org/10.1007/10_2017_35
27. Rozendal RA, Hamelers HVM, Rabaey K, Keller J, Buisman CJN (2008) Towards practical implementation of bioelectrochemical wastewater treatment. Trends Biotechnol 26(8):450–459. https://doi.org/10.1016/j.tibtech.2008.04.008
28. Xie X, Yu G, Liu N, Bao Z, Criddle CS, Cui Y (2012) Graphene–sponges as high-performance low-cost anodes for microbial fuel cells. Energy Environ Sci 5(5):6862. https://doi.org/10.1039/c2ee03583a
29. Luther AK, Desloover J, Fennell DE, Rabaey K (2015) Electrochemically driven extraction and recovery of ammonia from human urine. Water Res 87:367–377. https://doi.org/10.1016/j.watres.2015.09.041
30. Cheng S, Logan BE (2011) High hydrogen production rate of microbial electrolysis cell (MEC) with reduced electrode spacing. Bioresour Technol 102(3):3571–3574. https://doi.org/10.1016/j.biortech.2010.10.025
31. Fan Y, Hu H, Liu H (2007) Enhanced Coulombic efficiency and power density of air-cathode microbial fuel cells with an improved cell configuration. J Power Sources 171(2):348–354. https://doi.org/10.1016/j.jpowsour.2007.06.220
32. Harnisch F, Wirth S, Schröder U (2009) Electrochemistry communications effects of substrate and metabolite crossover on the cathodic oxygen reduction reaction in microbial fuel cells: platinum vs. iron (II) phthalocyanine based electrodes. Electrochem Commun 11(11):2253–2256. https://doi.org/10.1016/j.elecom.2009.10.002
33. Harnisch F, Schröder U (2009) Selectivity versus mobility: separation of anode and cathode in microbial bioelectrochemical systems. ChemSusChem 2(10):921–926. https://doi.org/10.1002/cssc.200900111
34. Cheng S, Liu H, Logan BE (2006) Increased power generation in a continuous flow MFC with advective flow through the porous anode and reduced electrode spacing. Environ Sci Technol 40(7):2426–2432. https://doi.org/10.1021/es051652w
35. Madjarov J, Popat SC, Erben J, Götze A, Zengerle R, Kerzenmacher S (2017) Revisiting methods to characterize bioelectrochemical systems: the influence of uncompensated resistance (iRu-drop), double layer capacitance, and junction potential. J Power Sources 356:408–418. https://doi.org/10.1016/j.jpowsour.2017.03.033
36. Popat SC, Ki D, Rittmann BE, Torres CI (2012) Importance of OH- transport from cathodes in microbial fuel cells. ChemSusChem 5(6):1071–1079. https://doi.org/10.1002/cssc.201100777
37. Oliot M, Galier S, Roux de Balmann H, Bergel A (2016) Ion transport in microbial fuel cells: key roles, theory and critical review. Appl Energy 183:1682–1704. https://doi.org/10.1016/j.apenergy.2016.09.043
38. Sleutels THJA, Hamelers HVM, Buisman CJN (2011) Effect of mass and charge transport speed and direction in porous anodes on microbial electrolysis cell performance. Bioresour Technol 102(1):399–403. https://doi.org/10.1016/j.biortech.2010.06.018
39. Zhao L, Li J, Battaglia F, He Z (2016) Computational investigation of the flow field contribution to improve electricity generation in granular activated carbon-assisted microbial fuel cells. J Power Sources 333:83–87. https://doi.org/10.1016/j.jpowsour.2016.09.113
40. Brown RK, Harnisch F, Wirth S et al (2014) Evaluating the effects of scaling up on the performance of bioelectrochemical systems using a technical scale microbial electrolysis cell. Bioresour Technol 163:206–213. https://doi.org/10.1016/j.biortech.2014.04.044

41. Sleutels THJA, Lodder R, Hamelers HVM, Buisman CJN (2009) Improved performance of porous bio-anodes in microbial electrolysis cells by enhancing mass and charge transport. Int J Hydrog Energy 34(24):9655–9661. https://doi.org/10.1016/j.ijhydene.2009.09.089
42. Liu H, Cheng S, Huang L, Logan BE (2008) Scale-up of membrane-free single-chamber microbial fuel cells. J Power Sources 179(1):274–279. https://doi.org/10.1016/j.jpowsour.2007.12.120
43. Cheng S, Logan BE (2011) Increasing power generation for scaling up single-chamber air cathode microbial fuel cells. Bioresour Technol 102(6):4468–4473. https://doi.org/10.1016/j.biortech.2010.12.104
44. Zhang Y, Angelidaki I (2014) Microbial electrolysis cells turning to be versatile technology: recent advances and future challenges. Water Res 56:11–25. https://doi.org/10.1016/j.watres.2014.02.031
45. Geppert F, Liu D, van Eerten-Jansen M, Weidner E, Buisman C, ter Heijne A (2016) Bioelectrochemical power-to-gas: state of the art and future perspectives. Trends Biotechnol 34(11). https://doi.org/10.1016/j.tibtech.2016.08.010
46. Lovley DR (2011) Powering microbes with electricity: direct electron transfer from electrodes to microbes. Environ Microbiol Rep 3(1):27–35. https://doi.org/10.1111/j.1758-2229.2010.00211.x
47. Liu H, Cheng S, Logan BE (2005) Production of electricity from acetate or butyrate using a single-chamber microbial fuel cell. Environ Sci Technol 39(2):658–662. http://www.ncbi.nlm.nih.gov/pubmed/15707069
48. Logan BE, Call D, Cheng S et al (2008) Microbial electrolysis cells for high yield hydrogen gas production from organic matter. Environ Sci Technol 42(23):8630–8640. https://doi.org/10.1021/es801553z
49. Van Eerten-Jansen MCAA, Heijne AT, Buisman CJN, Hamelers HVM (2012) Microbial electrolysis cells for production of methane from $CO_2$: long-term performance and perspectives. Int J Energy Res 36(6):809–819. https://doi.org/10.1002/er.1954
50. Liu H, Grot S, Logan BE (2005) Electrochemically assisted microbial production of hydrogen from acetate. Environ Sci Technol 39(11):4317–4320. https://doi.org/10.1021/ES050244P
51. Xu H, Wang K, Holmes DE (2014) Bioelectrochemical removal of carbon dioxide ($CO_2$): an innovative method for biogas upgrading. Bioresour Technol 173:392–398. https://doi.org/10.1016/j.biortech.2014.09.127
52. Nevin KP, Hensley SA, Franks AE et al (2011) Electrosynthesis of organic compounds from carbon dioxide is catalyzed by a diversity of acetogenic microorganisms. Appl Environ Microbiol 77(9):2882–2886. https://doi.org/10.1128/AEM.02642-10
53. Park DH, Laivenieks M, Guettler MV, Jain MK (1999) Microbial utilization of electrically reduced neutral red as the sole electron donor for growth and metabolite production. Appl Environ Microbiol 65(7):2912–2917
54. Nevin KP, Woodard TL, Franks AE (2010) Microbial electrosynthesis: feeding microbial electrosynthesis: feeding microbes electricity to convert carbon dioxide and water to multicarbon extracellular organic. MBio 1(2):e00103–e00110. https://doi.org/10.1128/mBio.00103-10. Editor
55. Jourdin L, Freguia S, Donose BC et al (2014) A novel carbon nanotube modified scaffold as an efficient biocathode material for improved microbial electrosynthesis. J Mater Chem A 2 (32):13093. https://doi.org/10.1039/C4TA03101F
56. Flynn JM, Ross DE, Hunt KA, Bond DR, Gralnick JA (2010) Enabling unbalanced fermentations by using engineered electrode-interfaced bacteria. MBio 1(5):1–8. https://doi.org/10.1128/mBio.00190-10.Editor
57. Emde R, Schink B (1990) Enhanced propionate formation by Propionibacterium freudenreichii subsp. freudenreichii in a three-electrode amperometric culture system. Appl Environ Microbiol 56(9):2771–2776

58. Young Jeon B, Lae Jung I, Hyun Park D (2012) Conversion of carbon dioxide to metabolites by Clostridium acetobutylicum KCTC1037 cultivated with electrochemical reducing power. Adv Microbiol 2(3):332–339. https://doi.org/10.4236/aim.2012.23040

59. Ditzig J, Liu H, Logan BE (2007) Production of hydrogen from domestic wastewater using a bioelectrochemically assisted microbial reactor (BEAMR). Int J Hydrog Energy 32 (13):2296–2304. https://doi.org/10.1016/j.ijhydene.2007.02.035

60. Gildemyn S, Verbeeck K, Slabbinck R, Andersen SJ, Prévoteau A, Rabaey K (2015) Integrated production, extraction, and concentration of acetic acid from CO2 through microbial electrosynthesis. Environ Sci Technol Lett 2(11):325–328. https://doi.org/10.1021/acs.estlett.5b00212

61. Cheng S, Logan BE (2007) Sustainable and efficient biohydrogen production via electrohydrogenesis. Proc Natl Acad Sci U S A 104(47):18871–18873. https://doi.org/10.1073/pnas.0706379104

62. Rozendal RA, Hamelers HVM, Euverink GJW, Metz SJ, Buisman CJN (2006) Principle and perspectives of hydrogen production through biocatalyzed electrolysis. Int J Hydrog Energy 31(12):1632–1640. https://doi.org/10.1016/j.ijhydene.2005.12.006

63. Zhou M, Chen J, Freguia S, Rabaey K, Keller J (2013) Carbon and electron fluxes during the electricity driven 1,3-propanediol biosynthesis from glycerol. Environ Sci Technol 47 (19):11199–11205. https://doi.org/10.1021/es402132r

64. Sleutels THJA, Hamelers HVM, Rozendal RA, Buisman CJN (2009) Ion transport resistance in microbial electrolysis cells with anion and cation exchange membranes. Int J Hydrog Energy 34(9):3612–3620. https://doi.org/10.1016/j.ijhydene.2009.03.004

65. Luo X, Zhang F, Liu J, Zhang X, Huang X, Logan BE (2014) Methane production in microbial reverse-electrodialysis methanogenesis cells (MRMCs) using thermolytic solutions. Environ Sci Technol 48(15):8911–8918. https://doi.org/10.1021/es501979z

66. Hintermayer S, Yu S, Krömer JO, Weuster-Botz D (2016) Anodic respiration of Pseudomonas putida KT2440 in a stirred-tank bioreactor. Biochem Eng J 115:1–13. https://doi.org/10.1016/j.bej.2016.07.020

67. Call D, Logan BE (2008) Hydrogen production in a single chamber microbial electrolysis cell lacking a membrane. Environ Sci Technol 42(9):3401–3406. https://doi.org/10.1021/es8001822

68. Wang A, Liu W, Cheng S, Xing D, Zhou J, Logan BE (2009) Source of methane and methods to control its formation in single chamber microbial electrolysis cells. Int J Hydrog Energy 34 (9):3653–3658. https://doi.org/10.1016/j.ijhydene.2009.03.005

69. Rader GK, Logan BE (2010) Multi-electrode continuous flow microbial electrolysis cell for biogas production from acetate. Int J Hydrog Energy 35(17):8848–8854. https://doi.org/10.1016/j.ijhydene.2010.06.033

70. Cusick RD, Bryan B, Parker DS et al (2011) Performance of a pilot-scale continuous flow microbial electrolysis cell fed winery wastewater. Appl Microbiol Biotechnol 89(6):2053–2063. https://doi.org/10.1007/s00253-011-3130-9

71. Hu H, Fan Y, Liu H (2008) Hydrogen production using single-chamber membrane-free microbial electrolysis cells. Water Res 42(15):4172–4178. https://doi.org/10.1016/j.watres.2008.06.015

72. Guo Z, Thangavel S, Wang L et al (2017) Efficient methane production from beer wastewater in a membraneless microbial electrolysis cell with a stacked cathode: the effect of the cathode/anode ratio on bioenergy recovery. Energy Fuel 31(1):615–620. https://doi.org/10.1021/acs.energyfuels.6b02375

73. Guo K, Tang X, Du Z, Li H (2010) Hydrogen production from acetate in a cathode-on-top single-chamber microbial electrolysis cell with a mipor cathode. Biochem Eng J 51(1):48–52. https://doi.org/10.1016/j.bej.2010.05.001

74. Katuri KP, Werner CM, Jimenez-Sandoval RJ et al (2014) A novel anaerobic electrochemical membrane bioreactor (AnEMBR) with conductive hollow-fiber membrane for treatment of

low-organic strength solutions. Environ Sci Technol 48(21):12833–12841. https://doi.org/10.1021/es504392n

75. Liu J, Zhang F, He W, Yang W, Feng Y, Logan BE (2014) A microbial fluidized electrode electrolysis Cell (MFEEC) for enhanced hydrogen production. J Power Sources 271:530–533. https://doi.org/10.1016/j.jpowsour.2014.08.042

76. Cheng KY, Ho G, Cord-Ruwisch R (2011) Novel methanogenic rotatable bioelectrochemical system operated with polarity inversion. Environ Sci Technol 45(2):796–802. https://doi.org/10.1021/es102482j

77. Bo T, Zhu X, Zhang L et al (2014) A new upgraded biogas production process: coupling microbial electrolysis cell and anaerobic digestion in single-chamber, barrel-shape stainless steel reactor. Electrochem Commun 45:67–70. https://doi.org/10.1016/j.elecom.2014.05.026

78. Clauwaert P, Verstraete W (2009) Methanogenesis in membraneless microbial electrolysis cells. Appl Microbiol Biotechnol 82(5):829–836. https://doi.org/10.1007/s00253-008-1796-4

79. Fu Q, Kuramochi Y, Fukushima N, Maeda H, Sato K, Kobayashi H (2015) Bioelectrochemical analyses of the development of a thermophilic biocathode catalyzing electromethanogenesis. Environ Sci Technol 49(2):1225–1232. https://doi.org/10.1021/es5052233

80. Xafenias N, Mapelli V (2014) Performance and bacterial enrichment of bioelectrochemical systems during methane and acetate production. Int J Hydrog Energy 39(36):21864–21875. https://doi.org/10.1016/j.ijhydene.2014.05.038

81. Cheng S, Xing D, Call DF, Logan BE (2009) Direct biological conversion of electrical current into methane by electromethanogenesis. Environ Sci Technol 43(10):3953–3958. https://doi.org/10.1021/es803531g

82. Yang W, Kim K-Y, Saikaly PE et al (2017) The impact of new cathode materials relative to baseline performance of microbial fuel cells all with the same architecture and solution chemistry. Energy Environ Sci 10(5):1025–1033. https://doi.org/10.1039/C7EE00910K

83. Kobayashi H, Saito N, Fu Q et al (2013) Bio-electrochemical property and phylogenetic diversity of microbial communities associated with bioelectrodes of an electromethanogenic reactor. J Biosci Bioeng 116:114–117. https://doi.org/10.1016/j.jbiosc.2013.01.001

84. Call DF, Logan BE (2011) A method for high throughput bioelectrochemical research based on small scale microbial electrolysis cells. Biosens Bioelectron 26(11):4526–4531. https://doi.org/10.1016/j.bios.2011.05.014

85. Hu H, Fan Y, Liu H (2009) Hydrogen production in single-chamber tubular microbial electrolysis cells using non-precious-metal catalysts. Int J Hydrog Energy 34(20):8535–8542. https://doi.org/10.1016/j.ijhydene.2009.08.011

86. Guo X, Liu J, Xiao B (2013) Bioelectrochemical enhancement of hydrogen and methane production from the anaerobic digestion of sewage sludge in single-chamber membrane-free microbial electrolysis cells. Int J Hydrog Energy 38(3):1342–1347. https://doi.org/10.1016/j.ijhydene.2012.11.087

87. Li J, He Z (2016) Development of a dynamic mathematical model for membrane bioelectrochemical reactors with different configurations. Environ Sci Pollut Res 23(4):3897–3906. https://doi.org/10.1007/s11356-015-5611-3

88. Giddings CGS, Nevin KP, Woodward T, Lovley DR, Butler CS (2015) Simplifying microbial electrosynthesis reactor design. Front Microbiol 6:1–6. https://doi.org/10.3389/fmicb.2015.00468

89. Villano M, Monaco G, Aulenta F, Majone M (2011) Electrochemically assisted methane production in a biofilm reactor. J Power Sources 196(22):9467–9472. https://doi.org/10.1016/j.jpowsour.2011.07.016

90. Marshall CW, Ross DE, Fichot EB, Norman RS, May HD (2012) Electrosynthesis of commodity chemicals by an autotrophic microbial community. Appl Environ Microbiol 78(23):8412–8420. https://doi.org/10.1128/AEM.02401-12

91. Liang P, Huang X, Fan M-Z, Cao X-X, Wang C (2007) Composition and distribution of internal resistance in three types of microbial fuel cells. Appl Microbiol Biotechnol 77 (3):551–558. https://doi.org/10.1007/s00253-007-1193-4

92. Pozo G, Jourdin L, Lu Y, Ledezma P, Keller J, Freguia S (2015) Methanobacterium enables high rate electricity-driven autotrophic sulfate reduction. RSC Adv 5(109):89368–89374. https://doi.org/10.1039/C5RA18444D

93. Sasaki D, Sasaki K, Watanabe A, Morita M, Igarashi Y, Ohmura N (2013) Efficient production of methane from artificial garbage waste by a cylindrical bioelectrochemical reactor containing carbon fiber textiles. AMB Express 3(1):17. https://doi.org/10.1186/2191-0855-3-17

94. Carmona-Martínez AA, Trably E, Milferstedt K, Lacroix R, Etcheverry L, Bernet N (2015) Long-term continuous production of H2 in a microbial electrolysis cell (MEC) treating saline wastewater. Water Res 81:149–156. https://doi.org/10.1016/j.watres.2015.05.041

95. Rabaey Clauwaert P, Aelterman P, Verstraete WK (2005) Tubular microbial fuel cell for efficient electricity generation. Environ Sci Technol 39(20):8077–8082

96. Danzer J, Kerzenmacher S (2016) Filtration-active. Fuel Cell

97. Rozendal RA, Jeremiasse AW, Hamelers HV, Buisman CJ (2007) Hydrogen production with a microbial biocathode. Environ Sci Technol 42(2):629–634

98. Shin S-H, Choi Y, Na S-H, Jung S, Kim S (2006) Development of bipolor plate stack type microbial fuel cells. Bull Kor Chem Soc 27(2):281–285

99. Min B, Logan B (2004) Continuous electricity generation from domestic wastewater and organic substrates in a flat plate microbial fuel cell. Environ Sci Technol 38(21):5809–5814. https://doi.org/10.1021/es0491026

100. Rabaey K, Bützer S, Brown S, Keller J, Rozendal RA (2010) High current generation coupled to caustic production using a lamellar bioelectrochemical system. Environ Sci Technol 44 (11):4315–4321. https://doi.org/10.1021/es9037963

101. Kim BH, Chang IS, Jang JK, Geun CG (2003) Membraneless and mediatorless microbial fuel cell. 1(12):0–4. doi:https://doi.org/10.1016/j.(73)

102. Gil-Carrera L, Escapa A, Moreno R, Morán A (2013) Reduced energy consumption during low strength domestic wastewater treatment in a semi-pilot tubular microbial electrolysis cell. J Environ Manag 122:1–7. https://doi.org/10.1016/j.jenvman.2013.03.001

103. Siegert M, Yates MD, Call DF, Zhu X, Spormann A, Logan BE (2014) Comparison of nonprecious metal cathode materials for methane production by electromethanogenesis. ACS Sustain Chem Eng 2(4):910–917. https://doi.org/10.1021/sc400520x

104. Zhang T, Nie H, Bain TS et al (2013) Improved cathode materials for microbial electrosynthesis. Energy Environ Sci 6(1):217. https://doi.org/10.1039/c2ee23350a

105. Zhen G, Lu X, Kobayashi T, Kumar G, Xu K (2016) Promoted electromethanosynthesis in a two-chamber microbial electrolysis cells (MECs) containing a hybrid biocathode covered with graphite felt (GF). Chem Eng J 284:1146–1155. https://doi.org/10.1016/j.cej.2015.09.071

106. Rabaey K, Lissens G, Siciliano SD, Verstraete W (2003) A microbial fuel cell capable of converting glucose to electricity at high rate and efficiency. Biotechnol Lett 25(18):1531–1535. https://doi.org/10.1023/A:1025484009367

107. Emde R, Swain A, Schink B (1989) Anaerobic oxidation of glycerol by Escherichia coli in an amperometric poised-potential culture system. Appl Microbiol Biotechnol 32(2):170–175. https://doi.org/10.1007/BF00165883

108. Ki D, Popat SC, Torres CI (2016) Reduced overpotentials in microbial electrolysis cells through improved design, operation, and electrochemical characterization. Chem Eng J 287:181–188. https://doi.org/10.1016/j.cej.2015.11.022

109. Chae KJ, Choi M, Ajayi FF, Park W, Chang IS, Kim IS (2008) Mass transport through a proton exchange membrane (Nafion) in microbial fuel cells. Energy Fuel 22(1):169–176. https://doi.org/10.1021/ef700308u

110. Babanova S, Carpenter K, Phadke S et al (2017) The effect of membrane type on the performance of microbial electrosynthesis cells for methane production. J Electrochem Soc 164(3):H3015–H3023. https://doi.org/10.1149/2.0051703jes
111. Zeppilli M, Lai A, Villano M, Majone M (2016) Anion vs cation exchange membrane strongly affect mechanisms and yield of CO2 fixation in a microbial electrolysis cell. Chem Eng J 304:10–19. https://doi.org/10.1016/j.cej.2016.06.020
112. Kracke F, Krömer JO (2014) Identifying target processes for microbial electrosynthesis by elementary mode analysis. BMC Bioinformatics 15:410. https://doi.org/10.1186/s12859-014-0410-2
113. Logan BE, Rabaey K (2012) Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. Science 337(6095):686–690. http://science.sciencemag.org/content/337/6095/686. Accessed 12 Apr 2017
114. Desloover J, Arends JBAA, Hennebel T, Rabay K, Rabaey K (2012) Operational and technical considerations for microbial electrosynthesis. Biochem Soc Trans 40(6):1233–1238. https://doi.org/10.1042/BST20120111
115. Pham TH, Rabaey K, Aelterman P et al (2006) Microbial fuel cells in relation to conventional anaerobic digestion technology. Eng Life Sci 6(3):285–292. https://doi.org/10.1002/elsc.200620121