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Review

Bioelectrochemical Systems (BES) for Biomethane Production—Review

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Abstract: Bioelectrochemical systems (BESs) have great potential in renewable energy production technologies. BES can generate electricity via Microbial Fuel Cell (MFC) or use electric current to synthesize valuable commodities in Microbial Electrolysis Cells (MECs). Various reactor configurations and operational protocols are increasing rapidly, although industrial-scale operation still faces difficulties. This article reviews the recent BES related to literature, with special attention to electrosynthesis and the most promising reactor configurations. We also attempted to clarify the numerous definitions proposed for BESs. The main components of BES are highlighted. Although the comparison of the various fermentation systems is, we collected useful and generally applicable operational parameters to be used for comparative studies. A brief overview links the appropriate microbes to the optimal reactor design.

Keywords: bioelectrochemical system (BES); microbial electrolysis cell (MEC); reactor configurations; electro-fermentation; biomethane; direct interspecies electron transfer (DIET)

1. Introduction

The expanding human population increases proportionally the energy demand of mankind required to maintain living standards [1]. Fossil energy resources, e.g., coal, oil and natural gas, are running out, and their excessive exploitation leads to catastrophic environmental destruction in the foreseeable future [2]. Therefore, replacing fossil fuels with renewable energy carriers is more urgent than ever.

Bioelectrochemical systems (BESs) are relatively new technological developments. In these devices, substrates are transformed either to electricity (via using a microbial fuel cell (MFC)) [3] or to valuable chemical molecules (in a microbial electrolysis cell (MEC)) [4]. The typical BES reactor (both MFC and MEC) consists of two electrodes, the anode and cathode, which are connected via an external power source (MEC) or a resistance (MFC). The reactor body design concept reflects the need to separate anodic and cathodic spaces, which can be separated with the specific membrane(s) or not [5]. The MEC reactors have gained increasing interest recently (Figure 1).

It is apparent from Figure 1 that MFC enjoys wider interest among BES researchers, who published almost six times as many publications as those dealing with MEC. A very recent exhaustive review compiled the knowledge gathered about MFC during the past 20–25 years [6]; therefore, we will focus our interest on the less mature MEC aspects in this review. The MEC concept comprises the production of various chemicals using electricity [7]. The proportion of renewable but fluctuating "green electricity" production increases worldwide, e.g., from photovoltaic and wind technologies. The MEC technology offers a promising way to redirect the excess "green" electricity from the grid. Numerous engineering, microbial and molecular difficulties hinder the development of a robust,

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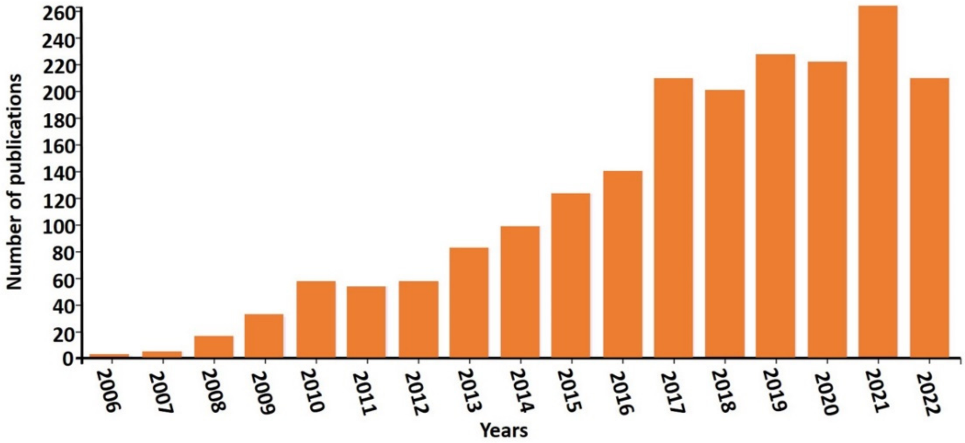
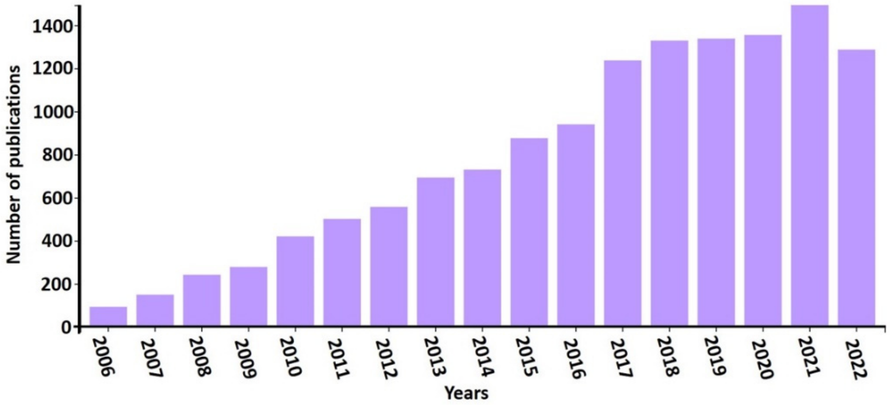
industrial MEC technology. This review aims to update the current trends, particularly from the point of view of new designs, used materials.



(**A**)



(**B**)

Figure 1. The number of relevant publications in the last 1.5 decades indicates the increasing interest in MEC (**A**) and MFC (**B**) technologies. Data was taken from the Web of Science (https://www.webofscience.com, accessed on 3 February 2023) using the keywords "microbial electrolysis cell" and "microbial fuel cell".

2. How It Started?

One of the first MEC prototypes was assembled in 1994 [8]. One year later, the same design was used to achieve electromethanogenesis [9]. Nevertheless, as MEC technology received wide attention in the early 21st century, hydrogen was the main target product [10–12]. Liu et al. suggested using MFC with external voltage to produce H_2 via water electrolysis [13]. Soon membrane-less systems were designed to reduce the costs [10,12,14,15]. The first proof-of-concept experiments of direct interspecies electron transfer (DIET) were performed in 2010 by Summers et al. The development of technological background started in the 90s [16]. In the early reports, methane appeared as a parasitic by-product of the electrohydrogenezis. Methane was gradually recognized as a potential main MEC product in the middle of the 2010s [17–20]. The electrosynthesis processes became more complex, and valuable commodities, i.e., biohytane [21–23], acetate [24], alcohols, volatile fatty acids and terpenoids [25] production, have been demonstrated in laboratory scale studies. In the following sections, we will focus on MEC-based bioelectromethanation.

3. Which Is What?

In searching the relevant BES/MEC scientific literature, one cannot escape taking note of the diversity of nomenclature as well as designs and performance measures, which make the various reports challenging to compare. Over the years, numerous definitions and designs have been proposed, sometimes confusing. To clarify the vocabulary, a collection of the most relevant designations and synonyms are listed as follows.

Bioelectrochemical system (BES): BES consists of an anode, where oxidation takes place, and a cathode, where reduction occurs and at least one of the electrodes utilizes microorganisms to catalyse the redox reaction via interaction with the electrode directly or through mediators. The electrode and surrounding microbiota, usually organized in biofilm, is called bioelectrode. The anode and the cathode can be separated by a membrane, but the membrane is not an indispensable component of BES. Frequently used synonyms: microbial electrochemical technology (MET) or microbial electrochemical system (MES) [26–33].

Biogas cleaning removes impurities, like water, hydrogen sulphides, etc., from the raw biogas by physicochemical means, such as adsorption, differential solubility, or membrane separation. Biogas cleaning can be divided into specific processes according to the target, for example, biogas desulphurization (removal of H_2S) or biogas drying (removal of water moisture) [34,35].

Biogas upgrading: Raw biogas contains predominantly methane (CH_4), CO_2, and other gasses, such as H_2S. The non-CH_4 gas components decrease the calorific value of biogas, can be harmful to live organisms, and some of them (for example, H_2S) are extremely corrosive, so they have to be removed before injection into the natural gas grids or used as alternative engine/vehicle fuel. As per the definition, biogas upgrading refers to removing CO_2 via transformation by catalytic conversion or separation of this major biogas component [34,35].

Biohythane: Hythane is a balanced mixture of hydrogen (10–30 *v*/*v*%) and methane (70–90 *v*/*v*%), a promising alternative to the conventional fossil gaseous energy carriers. Hythane has a higher fuel and heat efficiency. It can reduce carbon emission, increases burning speed, extends flammability range, and enhances combustion efficiency. Biohytane is produced from renewable biomass [21,36,37].

Direct interspecies electron transfer (DIET) is a syntrophic microbial interaction where free electrons are transferred/exchanged between microorganisms [38].

Electroactive microorganisms: Electroactive microorganisms can transfer electrons to the environment from the intracellular space or vice versa through the cell membrane [39,40]. Electroactive microorganisms and the electrodes used in BES participate in DIET.

Electrohydrogenesis: During electrohydrogenesis, the protons and electrons generated on the anode are transferred to the cathode. The microbial catalyst components, driven by the applied potential, combine electrons and protons to H_2, released from the cathode compartment [41].

Electromethanogenesis: Electromethanogenesis produces methane via electroactive microbes using CO_2 as the sole carbon source in an engineered system (biocathode) powered by electric current. Electromethanogenesis is a specific form of BES/MES when only CH_4 is produced from CO_2 with the additional input from electricity to provide the extra energy needed to recombine CO_2 with electrons and protons [42]. Electromethanogenesis is thus a subset of BES/MES, the microbial electrosynthesis of various chemicals.

Electrotrophic microorganisms: Electrotrophic microorganisms act as electron acceptors in electrogenic reactions. They are capable of taking up electrons from the environment and utilize in their metabolic reactions [43].

Exoelectrogenic microorganisms: Exoelectrogenic microorganisms are capable of generating electrical energy via the transfer the electrons, produced by substrate oxidation, to extracellular electron acceptors [44].

Microbial electrolysis cell (MEC): MECs are a distinct BES construction in which an external power source supplements the energy generated at the bioanode via biomass fermentation. Valuable commodities are formed at the cathode by overcoming the thermodynamically unfavourable reduction reactions. MECs may also operate with abiotically evolved H_2 in the cathodic chamber. Alternatively, the electrons are harvested from the cathode by electroactive microorganisms or soluble electron acceptors to produce H_2, CH_4, or other chemicals [15,45–48].

Microbial electrosynthesis (MES): Microbial electrosynthesis (MES) is a cathode-related process when electroactive microorganisms convert electricity to chemicals through CO_2 reduction. MES is a promising technology for renewable electricity storage, CO_2 capture and valuable commodities production. Methane, various alcohols, volatile fatty acids, terpenoids, bioplastics etc., can be produced in an MES reactor [5,24,25,31,48–51]. "Electro-fermentation" (EF) is used as a synonym for MES in some literature reports [5,52].

Microbial fuel cell (MFC): MFC is a type of BES where organic matter is decomposed via exoelectrogenic microbes near the anode, which serves as a terminal electron acceptor. The spontaneous electron movement from the electronegative bioanodes to the electropositive cathode in a circuit generates electric current [14,26,27,53–56].

Power-to-gas (P2G): Power-to-gas (P2G) refers to a technology that converts electrical energy to gas fuels, like H_2 or CH_4. The technology can be chemical (i.e., the Sabatier process) or biological (i.e., bioelectrochemical P2G) according to the source of power [28,30,57].

4. The BES Drivers

Extracellular electron transfer (EET) is an electron exchange process between microorganisms in a mixed microbial community [58]. (Figure 2) There are two mechanisms to perform EET, i.e., the indirect (IEET) and direct (DEET) processes.

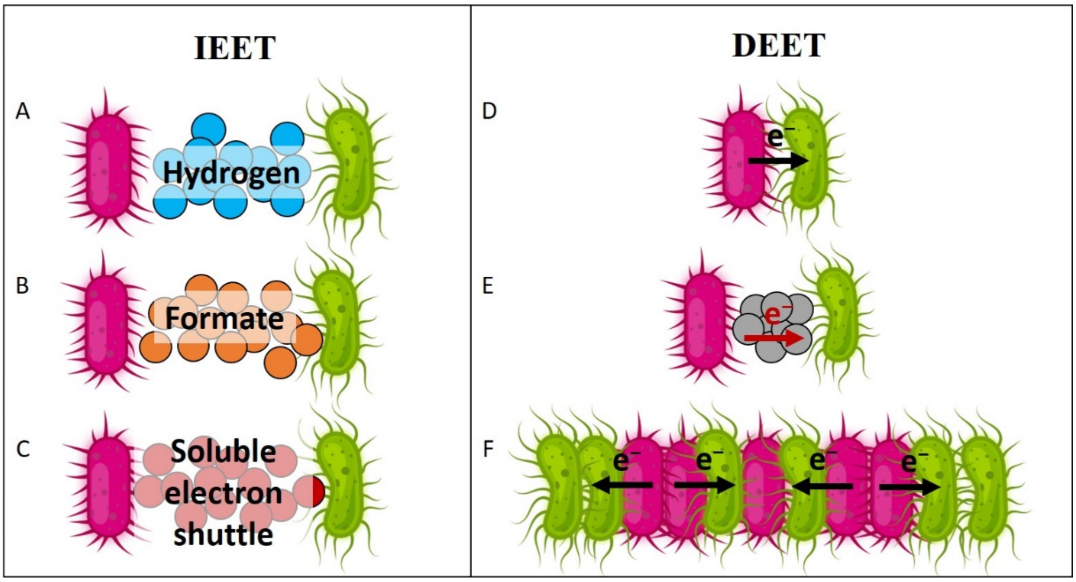


Figure 2. Extracellular electron transfer can occur as indirect (IEET) and direct extracellular electron transfer (DEET). For IEET, there is no need for a direct connection between the microorganisms because molecules, for example, (**A**) hydrogen, (**B**) formate, or (**C**) soluble electron shuttles, serve as electron carriers. On the contrary, DEET requires direct contact, such as (**D**) cytochromes and e-pili, (**E**) conductive material, or (**F**) conductive biofilm formation.

EET is established between microorganisms and their environment. If the exchange occurs between two microorganisms, it is also called interspecies electron transfer (IET), which could be indirect (IIET) or direct (DIET) [59].

Indirect or mediated extracellular electron transfer (IEET) was first recognized as the only route for EET in anaerobic microbial communities. Direct extracellular electron transfer (DEET) was described as an alternative mechanism between syntrophic microorganisms involving physical contact between the partners [60].

In IEET, there is no need for a direct connection between the donor and the acceptor [61] because a carrier, or mediator, such as hydrogen, formate, or soluble electron shuttles, reduced or oxidized by the cell is used to transfer the electrons between the redox partners [62]. In DEET, direct physical contact is needed between electron donors and electron acceptor microbes [61]. The direct contact is maintained frequently by pili, conductive biofilm formation, or flavins and cytochromes [63], although in many cases, the exact molecular mechanism is not clear [64]. Electroactive microorganisms possess these molecular structures. Hence they are capable of DEET [43].

DEET has several advantages over IEET, like faster electron transfer [65] and the more efficient reduction of CO_2 [4,59]. A complex enzyme system to produce mediators or carriers is not required for efficient DEET [60], but special conductive structures are needed on the surface of the microbes.

Electrofermentation, i.e., the generation of reducing equivalents by the electric current-assisted fermentative process, was reported [66]. Daniels and co-workers reported the reduction of CO_2 to CH_4 by the electrons from elemental iron [67]. The first electro-fermentation of CH_4 in a self-designed BES was demonstrated by Kuroda [9], although the term "electromethanogenesis" was born only in 2009 [41]. The classical DIET between *Geobacter sulfurreducens* and *Geobacter metallireducens* was first reported [16]. In 2014 Rotaru et al. observed and proved the DIET mechanism in a methanogenic culture, following the fate of (^{14}C)-bicarbonate [68]. Since then, more and more microorganisms have been recognized as capable of electron exchange, import and export, confirming that DIET could be a frequent pathway of syntrophic metabolism in the microbial world [43].

5. Bioelectrochemical System (BES) Concepts

Microbial Fuel Cells (MFCs) (Figure 3) are a type of Fuel Cells (FCs) where the chemical energy stored in organic substrates is transformed into electrical energy via microbial catalysis [69]. Conventional MFCs have two chambers, anodic and cathodic ones, separated by a proton exchange membrane (PEM) or salt bridge [70].

After the oxidation of organic matter, the electrons are transferred to the anode, which acts as a terminal electron acceptor, and the protons are released in the electrolyte [71]. The protons diffuse through the PEM to the cathode, while electrons travel through an external circuit, generating electric current [72]. In the aerobic cathode chamber, oxygen is reduced by electrons and protons and produces water [63]. In practice, there are several problems with the aerobic cathode chamber, like oxygen leakage through the PEM and low electric potential [13]. To solve these problems, the cathode chamber of MFC is usually made anaerobic. In this case, an external power source may be inserted into the circuit to overcome the theoretical thermodynamic barrier to produce H_2, the storable green fuel [13].

Theoretically, the potential needed for the reduction of protons to hydrogen is $E^0 = -0.410$ mV vs. Standard Hydrogen Electrode (SHE), while the reduction of CO_2 to methane via direct electron transfer, requires only $E^0 = -0.244$ mV vs. SHE [52]. The following equations show clearly why DEET (Equation (1)) is more energetically efficient than IEET (Equations (2) and (3)) during electromethanogenesis [48].

$$CO_2 + 8\,H^+ + 8\,e^- \rightarrow CH_4 + 2\,H_2O\ E^0 = -0.244\ \text{V vs. SHE} \tag{1}$$

$$2\,H^+ + 8\,e^- \rightarrow H_2\ E^0 = -0.421\ \text{V vs. SHE} \tag{2}$$

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O\ \Delta G0 = -131\ \text{kJ/mol} \tag{3}$$

In MEC (Figure 4), the electrons are generated from the decomposition of organic substrates at the anodic side via oxidation, so the external power supply does not act as the electron source of the system, but the potential difference between the electrodes increases [53]. Therefore the overall reaction of electromethanogenesis is not favourable in MEC [73].

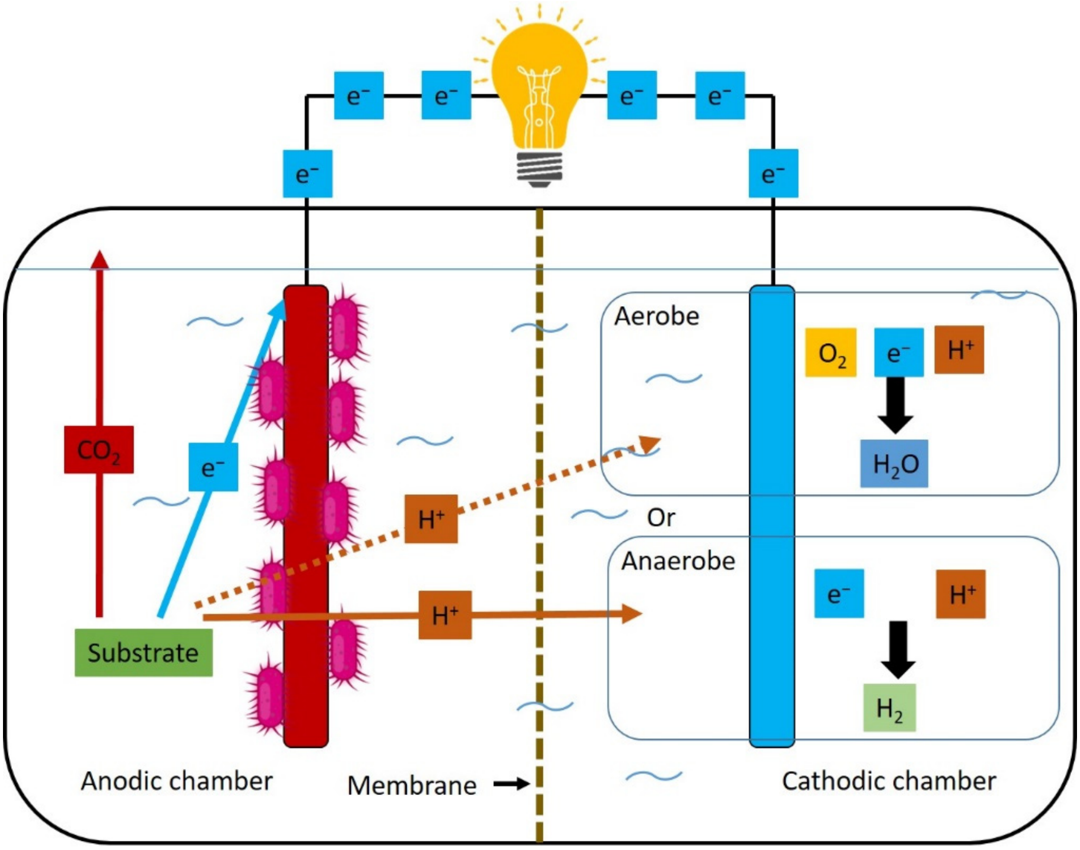


Figure 3. In microbial fuel cells (MFC), the organic substrates are oxidised by microorganisms. The anode serves as a terminal electron acceptor. The protons are released into the solution. The reactor contains a resistance, or consumer and a membrane. Protons diffuse through the selective membrane and recombine with the electrons again at the cathode. If the cathodic chamber is aerobic, the product is water. The product is hydrogen if anaerobic, though it is thermodynamically not favourable.

Due to the energy losses, overpotentials, like internal resistance caused by the PEM membrane [32], low conductivity of the electrolyte [74] and the activation energy of the imperfect catalyst [74], the theoretical electrode potential is not sufficient in real systems [75],. To lower the energy losses in the reactor, the membrane could be eliminated [32], the conductivity could be increased [76], and a more efficient catalyst could be applied to reduce the overpotential [18]. Precious metals, like platinum, seem to be the best catalyst, but the use of such catalysts at an industrial scale is deterred by their high price [18,36]. An alternative possibility to reduce the overpotential is the application of a special microbial community as a biocatalyst, in which the electrographic microbes are enriched by the environmental stress caused by the voltage [32]. The enriched microbial community can self-regenerate, so long-term application is possible even under industrial-scale operational conditions if regular evaluation and microbial community management are provided [75]. The appropriate microorganisms can reduce the system resistance, lower the activation energy barrier and increase current density by taking up the electrons for their metabolism or mediating with the other microorganism via DIET [77]. To achieve the best performance, the optimum external potential is one of the pivotal parts, and the enriched microbiome drives substrate oxidation and CO_2 reduction [32]. In an elegant series of experiments, Zhen and co-workers demonstrated that more negative cathode potential caused higher methane yields [78,79]. However, the exceedingly high negative potential may be accompanied by by-product generation, like acetate [32], within the domain of MES. An essential contribution to electro-biochemistry also comes from the electrode material and electrode geometry, which are vital parameters determining the formation of the electroactive biofilm (Tables 1–4). The related issues are discussed in detail in the section “Electrodes”.

Table 1. One chamber reactor configurations with carbon-based cathodes and their efficiency. Some articles provided the methane production rate in mol/L/d. To convert this unit to L/L/d, the Ideal Gas Law was used.

One Chamber Reactors Carbon Based Cathode									
Methane Production Rate (L/L/d)	**Voltage (V)**	**Cathode**	**Anode**	**Anode Surface (cm^2)**	**Cathode Surface (cm^2)**	**Membrane**	**Temperature**	**Reactor Volume**	**Reference**
29.7	0.7	Carbon cloth	Carbon cloth	40.0	40.0	No	55 °C	250 mL	[80]
1.6	0.75	Carbon felt	Carbon felt	40.0	40.0	No	55 °C	250 mL	[27]
1	−0.8–−1.2 vs. Ag/AgCl	Carbon felt	Graphite electrode	11.9	132.0	No	55 °C	350 mL	[81]
0.7	1	Coated carbon paper	Carbon paper	3.0	3.0	No	60 °C	10 mL	[17]
0.1	0.6	Carbon cloth	Carbon fiber brush			No	30 °C	40 mL	[82]
0.1	0.9	Graphite felt	Graphite felt	36.0	36.0	No	25 °C	500 mL	[29]
0.1	0.8	Graphite felt	Graphite felt	36.0	36.0	No	25 °C	500 mL	[29]
0.1	0.7	Thermally activated carbon felt	Thermally activated carbon felt	77.0	77.0	No	32 °C	32 L	[30]
0.1	2.0 vs. Ag/AgCl	Carbon felt	Carbon felt	388.0	388.0	No	22 °C	2.8 L	[83]
0.1	0.7	Graphite felt	Graphite felt	36.0	36.0	No	25 °C	500 mL	[29]
0.01	0.6	Graphite rod + graphite granules bed (10 g)	Graphite rod	2.1	4.0	No	41 °C	50 mL	[84]

Table 2. One chamber reactor configurations with metal-based and composite cathodes and their efficiency. Some articles provided the methane production rate in mol/L/d. To convert this unit to L/L/d, the Ideal Gas Law was used.

One Chamber Reactors Metal-Based and Composite Cathode									
Methane Production Rate (L/L/d)	**Voltage (V)**	**Cathode**	**Anode**	**Anode Surface (cm^2)**	**Cathode Surface (cm^2)**	**Membrane**	**Temperature**	**Reactor Volume**	**Reference**
1.8	0.24	Stainless steel pipe	Graphite felt sandwiched between cylindrical Ti collector	800.0	220.0	No	40 °C	6 L	[76]
0.9	1.0	Stainless steel	Carbon felt	25.0	76.0	No	25 °C	250 mL	[77]
0.9	0.3	Graphite carbon mesh coated with Ni, Cu, Fe	Graphite carbon mesh coated with Ni	2700.0	2700.0	No, nonwoven fabric separator	35 °C	20 L	[85]

Table 2. *Cont.*

One Chamber Reactors Metal-Based and Composite Cathode									
Methane Production Rate (L/L/d)	**Voltage (V)**	**Cathode**	**Anode**	**Anode Surface (cm^2)**	**Cathode Surface (cm^2)**	**Membrane**	**Temperature**	**Reactor Volume**	**Reference**
0.8	3–3.5	Stainless steel mesh	Ti mesh + Ir mixed metal oxides coating	20.0	20.0	No	35 °C	500 mL	[86]
0.6	−1.0 vs. Ag/AgCl	Stainless steel	Carbon felt	10.0	183.7	No	31 °C	180 mL	[87]
0.5	−0.4 vs. Ag/AgCl	Stainless steel	Carbon felt	10.0	183.7	No	30 °C	180 mL	[87]
0.3	1.2	Stainless steel cylinder	11 graphite plates inserted into a Stainless-steel cylinder	247.5	294.0	No	16 °C–35 °C	153 mL	[55]
0.2	0.9	Stainless steel	Graphite fiber brush			No	31 °C	1000 L	[88]

Table 3. Two or more chamber reactor configurations with carbon-based cathodes and their efficiency. Some articles provided the methane production rate in mol/L/d. To convert this unit to L/L/d, the Ideal Gas Law was used.

Two or More Chamber Reactors Carbon-Based Cathode									
Methane Production Rate (L/L/d)	**Voltage (V)**	**Cathode**	**Anode**	**Anode Surface (cm^2)**	**Cathode Surface (cm^2)**	**Membrane**	**Temperature**	**Reactor Volume**	**Reference**
12.5	0.85	Graphite felt	Ti mesh, Ir oxide coated (12 g Ir/m^2)	0.1	0.4 m^2/g	Nafion 117 proton exchange	30 °C	2 × 85 mL	[57]
5.2	−0.7 vs. SHE	Graphite felt	Ti mesh, Pt coated (50 g/m^2)	250.0	250.0	Fumasep FKB cathion exchange	31 °C	2 × 250 mL	[33]
2.4	−0.7 vs. SHE	Graphite felt	Graphite felt	290.0	290.0	Fumasep FKB cahtion exchange	30 °C	2 × 620 mL	[89]
1.8	−0.5	Carbon cloth	Carbon cloth	40.0	40.0	Nafion 117 proton exchange	55 °C	2 × 250 mL	[80]
1.4	−0.6 V	Graphite felt	Graphite felt	290.0	290.0	Fumasep FKB cathion exchange	30 °C	2 × 620 mL	[89]
1	−0.8–−1.2 vs. Ag/AgCl	Carbon felt	Graphite electrode	11.9	132.0	AS2S Cathion exchange	55 °C	2 × 350 mL	[81]

Table 3. *Cont.*

Two or More Chamber Reactors Carbon-Based Cathode									
Methane Production Rate (L/L/d)	**Voltage (V)**	**Cathode**	**Anode**	**Anode Surface (cm^2)**	**Cathode Surface (cm^2)**	**Membrane**	**Temperature**	**Reactor Volume**	**Reference**
0.8	1	Carbon fiber felt	Carbon nanotubes			PEM	25 °C	2 × 290 mL	[23]
0.5	−0.85–−1.15	Carbon felt	Carbon felt	49.0	49.0	AMI 7001 cathion exchange	30 °C	2 × 245 mL	[20]
0.5	0.8	Carbon cloth coated with activated carbon (5 mg/cm^2) + Pt (0.1 mg/cm^2)	Carbon brush		1705.0	AEM anion exchange tubes	room tp	A: 18 L C: 1 L	[37]
0.2	0.1	Graphite granule bed (2–6 mm)	Graphite granule bed (2–6 mm)			Fumasep FAD anion exchange + Fumasep FKE cathion exchange	25 °C	3 × 860 mL	[90]
0.2	−0.5 vs. Ag/AgCl	Carbon brush	Graphite rod	4.8	13,700.0	CMI 7000 cathion exchange	37 °C	800 mL	[91]
0.1	−0.5 vs. Ag/AgCl	Graphite plate	Graphite rod	4.8	40.3	CMI 7000 cathion exchange	37 °C	800 mL	[91]
0.1	−0.5 vs. SHE	Graphite plate	Graphite rod	15.6	15.0	CMI 7000 cathion exchange	37 °C	850 mL	[92]
0.1	0,7	Carbon paper	Carbon paper	10.0	10.0	Nafion 117 proton exchange	37 °C	2 × 150 mL	[93]
0.1	−1.4 vs. Ag/AgCl	Carbon stick with graphite felt layer	Pt	23 cm	11.0	Nafion 117 proton exchange	35 °C	200 mL	[79]
0.1	−0.4 vs. Ag/AgCl	Activated carbon fabric	Carbon fabric	150.0	138.0	Nafion 117 proton exchange	30 °C	C:1 L	[54]
0.1	−0.8 vs. Ag/AgCl	Granular graphite bed	Carbon felt	168.0		CMI 7000 cathion exchange	23 °C	2 × 500 mL	[42]
0.1	−0.9 vs. Ag/AgCl	Graphite rod	Carbon fabric	150.0	69.0	Nafion 117 proton exchange	35 °C	C: 1 L	[54]
0.03	−1.04 vs. Ag/AgCl	Carbon cloth + carbon black	Graphite fiber brush	1.0	7.0	Nafion 117 proton exchange	30 °C	2 × 152 mL	[94]
0.01	−1.02 vs. Ag/AgCl	Graphite fiber brush	Graphite fiber brush	1.0	6.3	Nafion 117 proton exchange	30 °C	2 × 152	[94]

Table 3. *Cont.*

Two or More Chamber Reactors
Carbon-Based Cathode

Methane Production Rate (L/L/d)	Voltage (V)	Cathode	Anode	Anode Surface (cm^2)	Cathode Surface (cm^2)	Membrane	Temperature	Reactor Volume	Reference
0.01	0.7	Carbon felt	Carbon felt + Pt	49.0	49.0	CMI 7000 cathion exchange	30 °C	2 × 240 mL	[19]
0.01	0.55	Graphite felt	Ti mesh, Pt coated (50 g/m^2)	250.0	250.0	Ralex CM cathion exchange	30 °C	2 × 280 mL	[73]
0.01	−1.1 vs. Ag/AgCl	Carbon laying	Carbon fabric	15,900.0	30,000.0	FKS-PET-130 cathion exchange	35 °C	A:145 L C: 50 L	[25]
0.003	−0.55––0.65 vs. Ag/AgCl	Carbon fiber brush	Carbon fiber brush	7,400,000.0	7,400,000.0	Nafion	34 °C	2 × 100 mL	[18]

Table 4. Two- or more chamber reactor configurations with metal-based and composite cathodes and their efficiency. Some articles provided the methane production rate in mol/L/d. To convert this unit to L/L/d, the Ideal Gas Law was used.

Two or More Chamber reactors
Metal-Based and Composite Chatode

Methane Production Rate (L/L/d)	Voltage (V)	Cathode	Anode	Anode Surface (cm^2)	Cathode Surface (cm^2)	Membrane	Temperature	Reactor Volume	Reference
1.4	1	Stainless steel mesh	Ti mesh, IrO_2 coated	72.0	450.0	CEM	37 °C	A: 1 L C: 4.5 L	[50]
0.01	0.8	Wet proof carbon cloth + Pt (0.5 g/cm^2)	Non-wet-proof carbon brush (pretreated)			2 CEM	21 °C	A:150 mL C: 80 mL	[52]
0.1	−0.86 vs. Ag/AgCl	Stainless steel mesh + Pt	Graphite fiber brush	1.0	7.0	Nafion 117 proton exchange	30 °C	2 × 152 mL	[94]
0.02	−0.7 vs. Ag/AgCl	Pt sheet	TiO_2/CdS photoanode	3.0	4.0	Ultrex CMI 7000 cathion exchange membrane	31 °C	2 × 350 mL	[95]
0.01	−0.55––0.65	Graphite bloch + carbon black + metals (Pt, Ni, Stainless steel)	Carbon fiber brush	7,400,000.0	10.6	Nafion	32 °C	2 × 100 mL	[18]

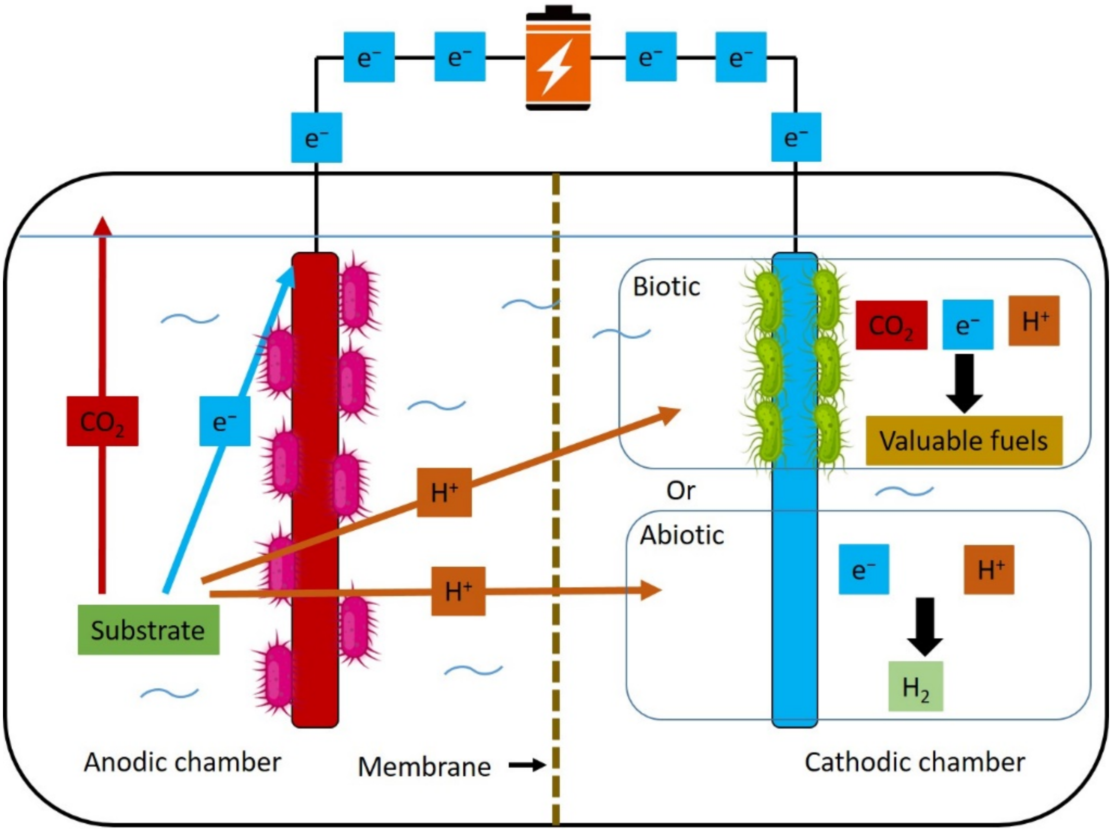


Figure 4. In a microbial electrolysis cell (MEC), the substrate is oxidised in the same way as in MFC. The electrons are transferred to the anode, while the protons are released into the electrolyte solution. The reactor contains a power source and sometimes a PEM membrane. The power source increases the potential difference between the electrodes, so hydrogen generation is favourable on the cathode. If the cathodic chamber contains electroactive microorganisms besides hydrogen, other valuable chemicals are produced depending on the microbial community developed on the biocathode.

When the published data for the optimum potential are compared, the results are difficult to relate because of the varying experimental conditions, e.g., electrode, electrolyte, temperature, membrane, inoculum, etc. Standardized experimental conditions to make the various parameters comparable would be needed. The difficulties associated with the complex and interrelated set of parameters can partially be resolved by calculations (see section "Calculations"). Nevertheless, the intricate relationships of the contributions of the individual parameters make the system difficult to describe and control precisely. According to Martín and co-workers, the overall energy (E) needed for the reactions can be described as the sum of the thermodynamically required energy for the desired reaction (E^n) and the overpotentials (η):

$$E = E^n + \eta^{act} + \eta^{ohm} + \eta^{mt} \tag{4}$$

where η^{act} is the overpotential of the electrodes' kinetic activations, η^{ohm} shows the energy loss due to ohmic resistance, and η^{mt} represents the overpotential because of the limited mass transport at the electrodes [96].

6. Trends in Reactor Design

In early developmental stages, reactors incorporating selective membranes were primarily studied [13,97,98]. The reactor design trends diverged towards simple, membraneless, cost-effective systems [15,27,99] on the one hand and sophisticated constructs equipped with the membrane(s) on the other hand [20,42,57,80,100]. The variety of BESs schemes fulfil the requirements for multifunctional tasks, e.g., NH_4 recovery [42], CO_2 removal [101], biohythane production [52]. Most systems contain at least one or two membranes. Membrane-containing and membrane-less setups have their advantages and disadvantages. In the next section some of the reactor designs are discussed.

6.1. Single Chamber Systems

In single-chamber reactors, the anode and the cathode are located in a single container, and the various ions and molecules can be exchanged unimpeded [48]. These arrangements have several advantages, such as lowering the construction and operation costs and simplifying the reactor design [102]. In certain applications, separating the biofilms formed on the anode and cathode offers improvements in system operation and sustainability. Reactors in which a separator, e.g., nonwoven fabric, is used to prevent short circuit is considered single-chamber reactor because the different molecules developed via the electrodes and the biofilm can exchange through the separator.

Glass vessel-type reactors are the simplest constructs at the laboratory scale. This reactor configuration requires only typical laboratory items like sealable serum bottles for the reactor body. The electrodes are inserted from the top of the glass vessel, and a separator or inert insulation are usually applied to avoid short circuit. As small as 5–10 mL vials have been converted to MEC systems [17,99]. Theoretically, roughly 6000 reactors can be assembled in one block using a single power supply in the right arrangement [99].

The first electromethanogenesis experiments were performed in a cylindrical reactor [9]. In these designs, one of the electrodes is located in the center of the reactor, while the other electrode is arranged around the central electrode in barrel shape arrangement (Figure 5). The anode [9] or the cathode [76] can be designated in the central position. In cylindrical reactors, the electrodes may have a relatively high surface area. The distance between the electrodes is critical. The "distant" electrode and the "adjacent" electrode arrangements differ in the gap width between the central and the barrel-shaped electrodes. Sometimes the barrel-shaped electrode is placed next to the inner wall of the reactor [55].

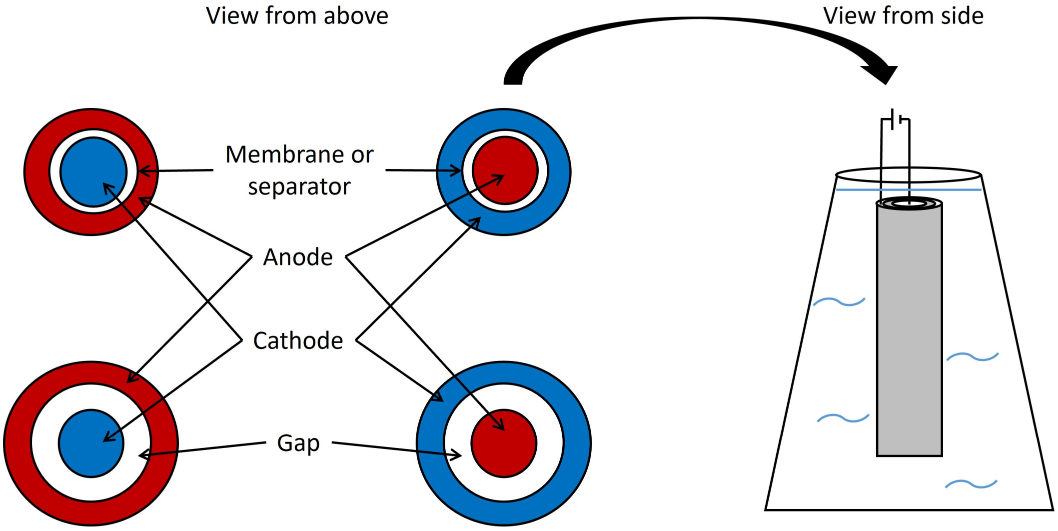


Figure 5. In cylindrical reactors, one electrode is inside the centre, while the other is placed around it. In the "distant" design, there is a gap between the electrodes filled with electrolytes or the solution, while in the "adjacent" design, there is only a membrane separation between the electrodes. Both the anode and the cathode can be the central electrode.

On the contrary, in the "adjacent" configuration, the electrodes are close. Hence a membrane or separator is placed between them to prevent short circuits. The small distance between the electrodes decreases the internal resistance of the system [37]. Hou et al. made a special version of the cylindric reactor, where a spiral wound electrode was used. This design resulted in a large specific surface area and potential scalability [103].

Following the BES reactor concept without membrane, a rectangular box-type reactor was introduced to increase the current density via increasing the electrode surface, and an economically more attractive device was constructed [14,88]. In this simple equipment, the electrodes face each other in a vertical assembly (Figure 6). This design is also suitable for scaling up because the specific surface area of the electrodes is easily changeable by increasing the number of electrode stacks. For example, a pilot scale continuous reactor configuration consisted of 24 modules and 144 electrode pairs in a 1000 L volume [88]. The rectangular box-type reactor has been built in versions containing membranes as well, the membranes inserted in between the electrodes [104].

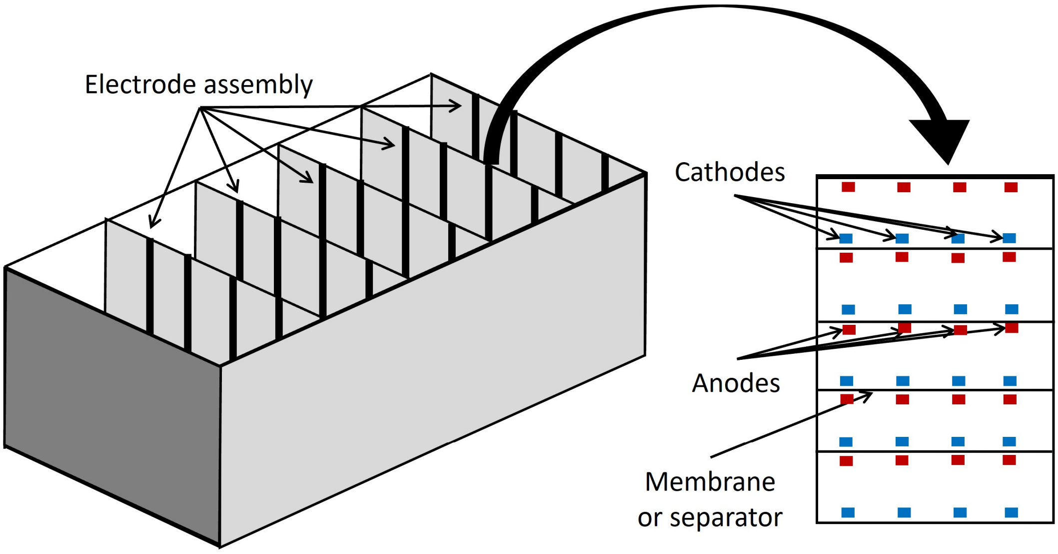


Figure 6. Rectangular box-type reactors are suitable for scale-up experiments. The electrodes are placed opposite each other, increasing the electrode surface and current density.

A more sophisticated design is the column-type reactor model. In column-type reactors, one electrode is positioned at the bottom, and the other is near the top of the reactor. “Cathode-on-top” and “anode-on-top” configurations have been tested for special applications. The advantage is separating the products to a certain degree without involving membrane. For instance, the cathode-on-top configuration prevents the product generated at the cathode from the biofilm on the anode. Guo et al. constructed an innovative column-type cathode-on-top reactor with a fixed graphite granules bed. In this arrangement, the anode is at the bottom of the reactor. H_2 gas, formed at the cathode, is separated from the microorganisms at the anode, which could consume it [105]. In the opposite configuration, i.e., “anode-on-the top”, a higher voltage (over 1.23 V) could be applied, and the oxygen formed at the cathode from water electrolysis exited the system without damaging the strict anaerobe methanogenic biofilm on the cathode [49,106].

6.2. Two Chamber Systems

In these designs, the chambers are separated by an ion-selective membrane. The use of membranes facilitates the production of pure product(s) [73]. The membrane can protect the obligate anaerobic methanogens from inhibitory products like oxygen [94]. Although a membrane increases the internal resistance, generates a pH gradient and increases the price and complexity of the system, some applications may be worth employing for maintaining a selective BES operating sustainably over an extended period [84].

H-cell reactors consist of two vessels, usually made of glass and separated by a membrane (Figure 7). This configuration is convenient for laboratory-scale experimentation, although the geometry of H-shape devices limits the gassing and stirring of the liquids around the electrodes. The distance between the electrodes and the relatively low surface of the membrane increases the internal resistance [54]. Allen and co-workers designed the H-cell arrangements in electrochemistry [107]. Later this design was used by Hongo et al. for microbial electrosynthesis (MES) of L-glutamic acid [108]. H-cell shaped reactors are one of the most commonly used two-chamber setups. The H-cell reactor acted as a microbial electrolysis device (MEC) when Liu et al. added extra voltage to an MFC and produced electrolytic hydrogen [13]. The process was reported as electrohydrogenesis for the first time [13]. Further development yielded the first microbial electrosynthesis (MES) systems producing acetate and other multicarbon organic compounds from CO_2 [109].

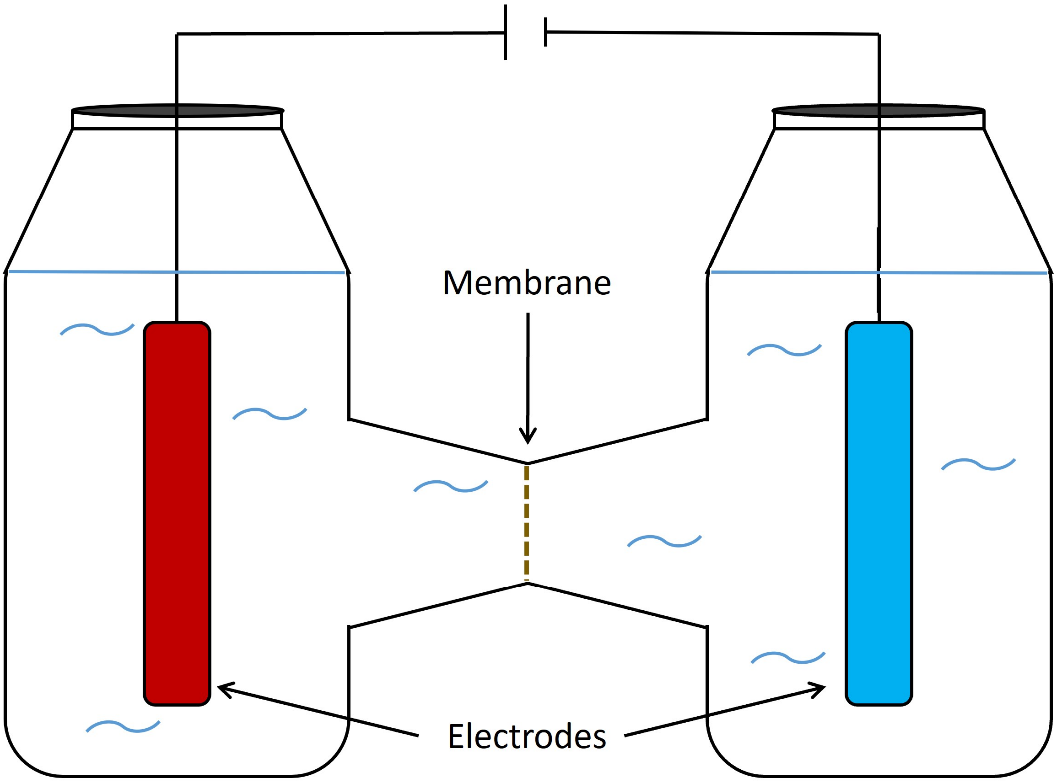


Figure 7. H-cell reactors are one of the most popular laboratory test designs for BES. It is easy to set up, though the size of the membrane and the possibility of stirring is limited.

While the two chambers are arranged in juxtaposition in the H-cell reactors, separated by the membrane assembly, in the concentric tubular reactors, the chambers are asymmetric, i.e., a larger chamber contains a smaller one (Figures 8 and 9). The larger "container" chamber can be the one housing either the anode [54] or the cathode [92]. Concentric tubular reactors have certain benefits relative to the H-cells, being more flexible than H-cells to assemble and alter the electrode chambers' geometry. The internal resistance can be adjusted by changing the electrode distances, and the membrane surface area can be easily modified. Enzmann et al. constructed a reactor in which the membranes were inserted in windows on the cylindrical wall of the cathode chamber [54], whereas, in the system designed by Liu and co-workers, the anodic chamber was separated with a membrane bag [92].

In a more complex cylindrical-tubular hybrid system, (Figure 9) the cathode chamber was made of 5 connected tubes, while the outer surface was covered with a membrane and carbon brush to serve as an anode [37].

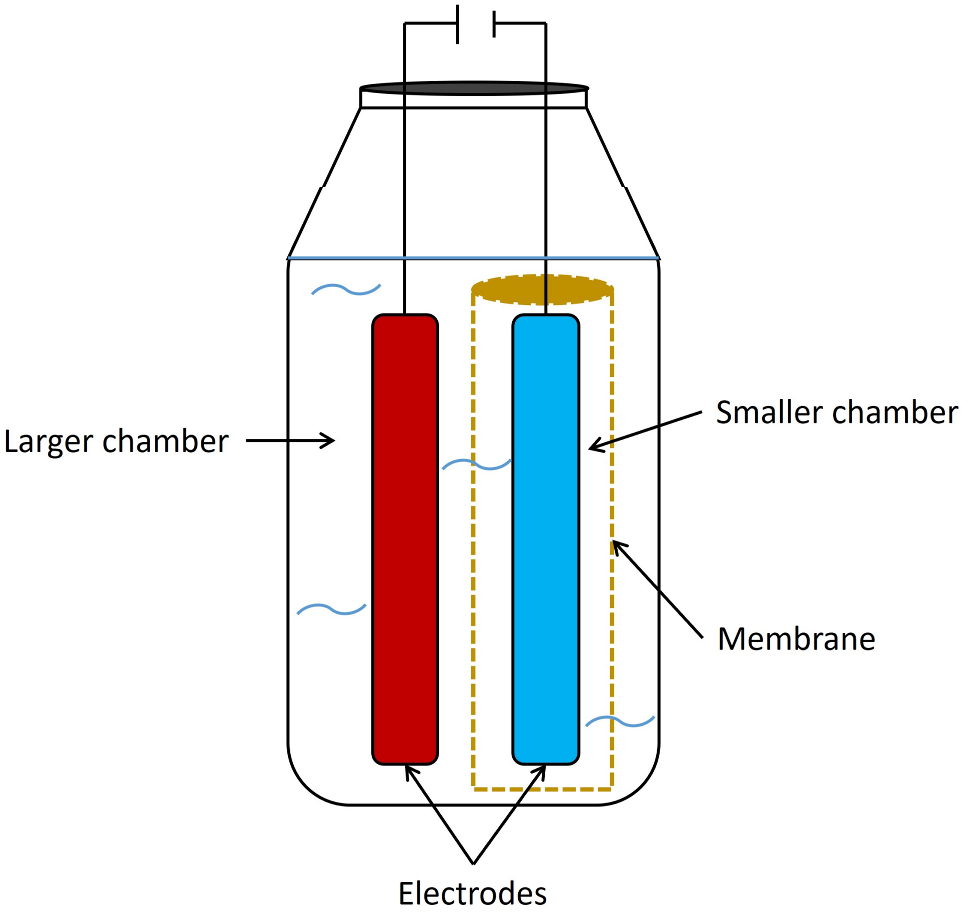


Figure 8. Concentric tubular reactors contain a smaller chamber inside a larger one. The two chambers are separated via a separator, or membrane, to increase the membrane surface. Either the anode or the cathode can be placed in the smaller chamber.

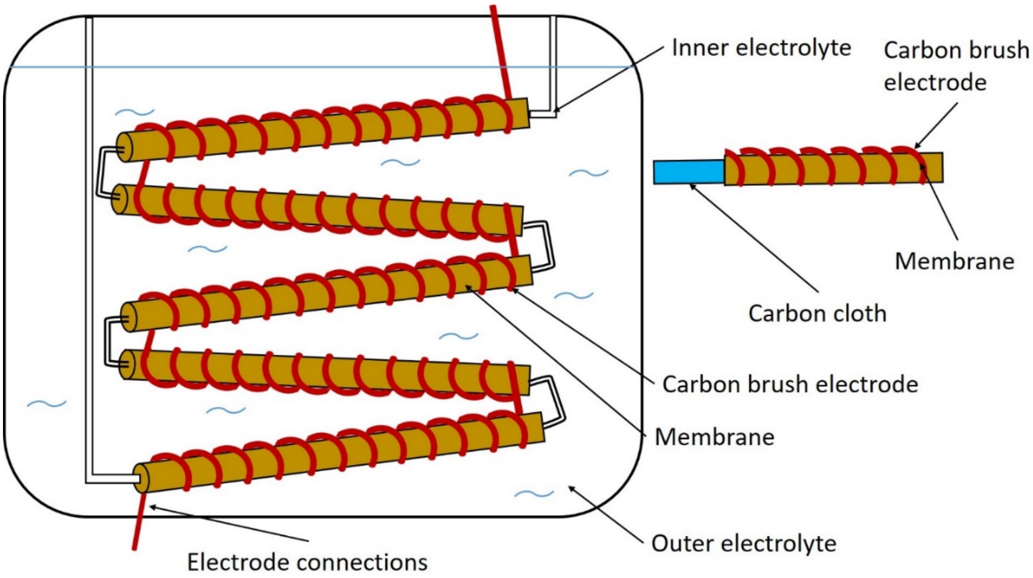


Figure 9. Schematic figure of a cylindrical tubular hybrid system constructed by Luo et al. [37]. It contains five tubes with titanium wire—carbon cloth—stainless steel mesh inner electrode (cathode) and carbon brush outer electrode (anode), separated with membrane. There is a continuous electrolyte (catholyte) flow in the internal space of the tubes.

In flat plate reactors, the electrodes are placed close to each other, which reduces the internal resistance (Figure 10). In this arrangement, the specific surface area can be exceptionally large. For example, using graphite granules bed as an electrode, a dramatic 1290 m^2 m^{-3} surface [98] has been achieved. The high surface favored the formation of a dense biofilm, hence improved performance [110]. The mass transfer was facilitated via serpentine flow in both chambers [26]. Nevertheless, flat plate reactors are not widely used, even in small-scale operations. They are too complicated for routine laboratory studies, and scaling up seems costly due to the energy consumption of the continuous recirculation of the liquid phase [111].

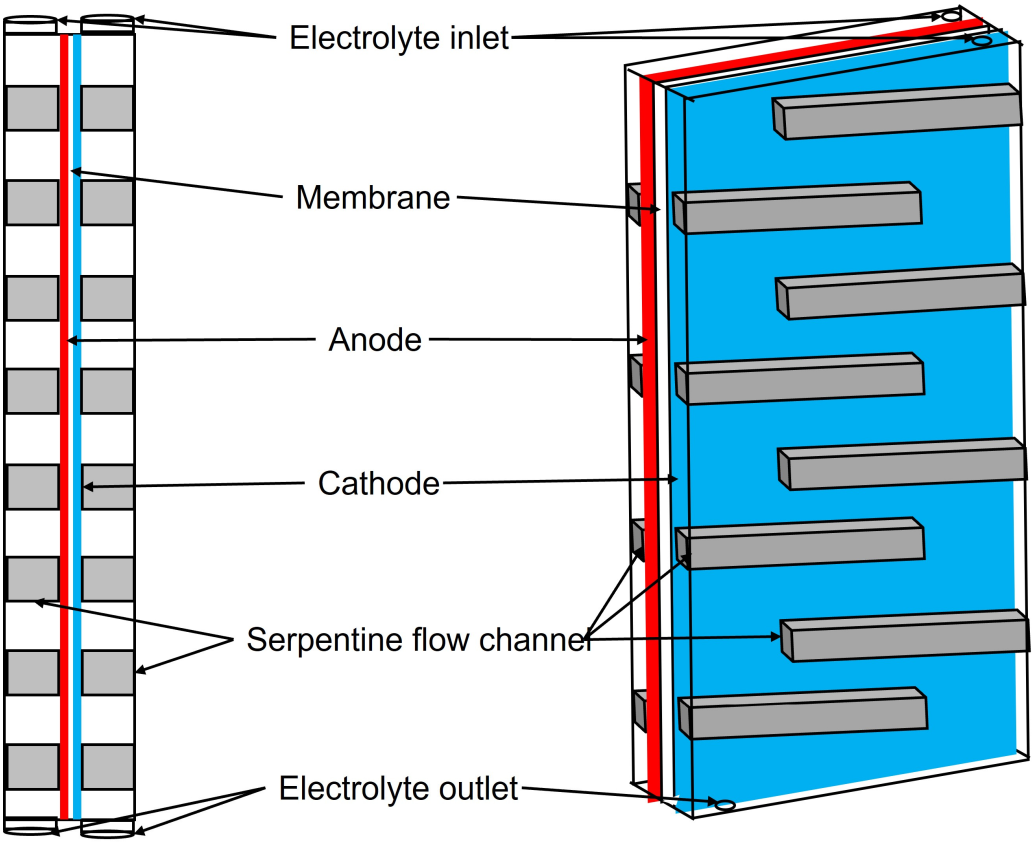


Figure 10. In flat plate reactors, the anode and the cathode are separated by a membrane. The specific surfaces are extraordinarily large thanks to the serpentine flow channels, which granules can further increase. Needs continuous flow of the liquid phase.

6.3. Advanced Designs

The first of the ingenious alternative BES concepts is the rotating bioelectrochemical reactor systems (BESs) [45]. The novel components of this reactor type include rotating disk electrodes and a control engine to change the position of the disks from time to time. One half of the disk is submerged in the electrolyte, while the other half is exposed to the gaseous phase. The half-disk in the liquid phase serves as an anode and the other half functions as a cathode in the gaseous phase. The anode and the cathode functions are thus altered in time. Unique, uniform, but distinct biofilms are built up on the surface of the two half disks. The number of electrode arrays can be increased, creating batteries for the basic units. Scaling-up is limited by the energy requirement of the rotating engine and the sustainability of the biofilm on the electrode surfaces.

In a different design concept, more than two reactor chambers are coupled together. The multiple chambers BESs usually serve specific tasks. As an example, the microbial desalination reactor system deserves special attention. In this reactor system, an accumulation chamber is inserted between the anodic and cathodic chambers [6,101]. The anodic chamber is separated from the accumulation chamber via a proton exchange membrane, while the cathodic chamber is separated via an anion exchange membrane. This arrangement allows the accumulation chamber to recover the simultaneous ammonium and bicarbonate ions and a high methane production rate. In a different version of the three-chamber construct, a two-sided cathode BES/MEC was tested for municipal waste water purification [90]. The device consisted of two cathodic chambers and one anodic chamber inserted in between them. The two cathodic chambers were connected in parallel by a titanium wire. The anodic chamber was separated from the cathodes by an anion exchange membrane (AEM) on one side and a cation exchange membrane (CEM) on the other. In the CEM cathode compartment, biogas and ammonia-nitrogen were produced by the microbial biofilm formed from activated wastewater sludge, which was fed into the reactor. Biogas was recirculated to the AEM cathode compartment, where biomethane was produced via biogas upgrading by reducing HCO_3^- to CH_4.

A further improvement of bioelectrochemical cells (BES) was achieved with microbial electrochemical separation cells (MESC), also referred to as microbial electrolytic capture, separation and regeneration cells (MECS) [112,113]. The MESC consists of four chambers, i.e., anodic, regeneration, absorption, and cathodic chambers, separated by anion exchange membrane and bipolar membrane. The multiple-chamber reactors, like MESC, offer a great opportunity for simultaneous wastewater treatment, biogas production, upgrading, and carbon and nitrogen recovery. However, their complexity limits their application in scale-up systems [112].

Other multifunctional and sophisticated BES reactor systems include systems like MFC-MEC coupled systems [19] or microbial photoelectrochemical systems (MPES), which utilize solar energy six times more efficiently than natural microbial systems [95]. Luo et al. described a microbial reverse-electrodialysis methanogenesis cell (MRMC), which did not require an external power supply because energy was generated from the salinity gradient in the dialysis system [94]. An advanced anaerobic osmotic membrane bioreactor-microbial electrolysis cell (AnOMBR-MEC) system achieved a simultaneous biogas upgrading, enhancing CH_4 yield and wastewater treatment [114].

7. The Components of the BES Systems

7.1. Membranes

Research and development on ion exchange membranes (IEMs) date back to the work of Oswald in 1890, who discovered that semipermeable membranes have impermeable properties to certain cations or anions present in the electrolytes [115]. The "Donnan exclusion potential" was delineated in 1911, and extensive experimental work on IEMs was started by Michelis and Fujita in 1925. Shöller and co-workers presented the idea of amphoteric and mosaic membranes, which generated interest in industrial applications [115]. Electrodialysis via membranes became an industrial process, and simultaneously the bipolar membrane was introduced [116]. The first large-scale desalination of seawater using membranes was carried out in the 1960s [115]. A significant step forward was the development of Nafion, the chemically stable cation exchange membrane based on sulfonated polytetra-fluorethylene by Dupont [115].

The use of membranes offers pros and contras. On the one hand, one can list among the benefits that membranes are essential to produce chemically pure products [73]. The presence of the membrane protects the methanogens from inhibitory compounds [94] or keeps the cathodic H_2 gas clean [102] and prevents the mixing of undesired molecular species, such as oxygen [84]. On the other hand, in a system incorporating a membrane, the pH gradient [113] and ohmic loss lower the efficiency of the product formation, while the complexity increases the investment and operational costs of the BES reactors [84].

The membranes used in BES can be classified into two groups, i.e., proton exchange membranes (PEMs) and ion exchange membranes (IEMs). IEMs include cation exchange membranes (CEMs) and anion exchange membranes (AEMs). A variety of IEMs, including inorganic–organic (hybrid), amphoteric, mosaic, and bipolar membranes (ion exchange composite membranes), have been introduced in the IEM market [115].

7.1.1. Proton Exchange Membranes (PEMs)

Proton exchange membranes (PEMs) were introduced in the 1970s by DuPont. The sulfonated polytetra-fluorethylene-based polymers, called Nafion membranes, showed not only high conductivity but also had long lifetimes [117]. PEMs can be categorized into five main groups according to the materials used in synthesis, such as [118]:

- Perfluorinated
- Partially fluorinated
- Non-fluorinated
- Acid-base blend
- Others

There are two mechanisms for transporting protons across the membrane, while electrons are repelled. The "proton hopping" or "Grotthus mechanism" and the "diffusion mechanism" or "vehicular mechanism" [119]. In the Grotthhus mechanism, a molecular vehicle is not required because protons are moving via breaking and forming hydrogen bonds. Protons are hopping from one hydrolyzed ionic site to another through the membrane. According to the vehicular mechanism, the protons are transferred via a hydrated proton (H_3O^+) [120]. The most important properties of PEMs are proton conductivity, water uptake, ion exchange capacity, gas permeability and physical stability [121]. These properties can be improved or modified by thinning the membrane [122] or blending with minor components, such as inorganic oxides, zeolites, proton conductive materials, etc. [120].

7.1.2. Ion Exchange Membranes (IEMs)

Ion Exchange Membranes (IEMs) control the traffic of charged molecules/ions within the electrolyte. These are semipermeable chemical structures consisting of a polymeric backbone and functionalized ionic groups attached to this scaffold [123].

The physicochemical properties of membranes are determined by the material of the basic "backbone" polymer chemistry, which provides mechanical, thermal, and chemical stability. The membrane backbone is frequently made of organic polymers, but there have been several other available proposed backbone materials, such as cellulose, metallic, and ceramic compounds [123,124]. The membrane backbone should possess properties for industrial applications [118,125].

- High permselectivity
- Low electrical resistance
- Good mechanical plasticity
- High chemical stability
- Easy and cheap production

The selectivity and specificity of IEMs are bestowed by the type, concentration and pattern of the attached functionalized groups, which define the permselectivity and electrical resistance [125]. According to the functionalized groups, the membranes can serve as cation exchange membranes (CEMs), anion exchange membranes (AEMs) and bipolar membranes (BPMs) [123]. AEMs are equipped with positively charged groups, like: $–NH_3{}^+$, $–NRH_2{}^+$, $–NR_2H^+$, $–NR_3{}^+$, $–PR_3{}^+$, $–SR_2{}^+$, etc., which do not let cations pass through but make the membrane permeable to anions. CEMs contain negatively charged ions like: $–SO_3{}^-$, $–COO^-$, $–PO_3{}^{2-}$, $–PO_3H^-$, $–C_6H_4O^-$, etc. Hence they are not permeable to anions [115]. BPM is a special construction which contains a CEM and an AEM layers, respectively [123].

The ionic groups are attached to the membrane polymeric core by chemical bonds to form a homogenous membrane or by weaker physical contact to form a heterogeneous membrane [118]. In general, homogenous IEMs have good electrochemical properties but weak mechanical strength. In contrast, heterogeneous IEMs have great mechanical strength, dimensional stability, and poor electrochemical performance [120].

Cation exchange membranes (CEMs)

CEMs contain negatively charged groups attached to diverse polymer backbones [126]. The pattern of the charged moieties alters the character of membranes. Their low conductivity is the main obstacle in industrial applications [126]. To improve the conductivity, the functionalized membrane surface can be interrupted repeatedly with non-functionalized segments. This leads to a well-defined nanoscale separation, which increases the conductivity to create block CEM [126]. Alternatively, the functionalized groups can be attached closely to make aggregates, resulting in densely functionalized CEMs [127]. There are several other modifications to alter the properties of the membrane [126].

Anion exchange membranes (AEMs)

In contrast to CEMs, AEMs contain positively charged groups to attract the anions and repel cations or neutral molecules [128,129]. There are concerns about using AEMs in the industry because of their poor conductivity and weak chemical stability. To improve these properties, new types of ionic groups and designs of polymeric architecture have been developed [126,127,130,131].

Bipolar membranes (BPMs) and other composite membranes

Bipolar membranes are made by the incorporation of at least one cation exchange layer (CEL), and an anion exchange layer (AEL) laminated together [116] or an interfacial layer inserted between the CEL and AEL [115,126]. Since their introduction, industrial applications have been interested in using BPMs in water electrolysers, CO_2 fuel cells, and flow batteries. The required features of BPM for an industrial application [132] include the following:

- fast chemical kinetics at the interface
- high conductivity of the individual bulk layers
- high water permeability
- low parasitic (ion) crossover
- long lifetime under operational current densities

Amphoteric ion exchange membranes (AIEMs) contain both weak acidic (negative charge) and weak basic (positive charge) groups that are randomly distributed within the membrane matrix [115]. This makes the AIEMs easily controllable because both charges can be found on the surface. The change of the pH can regulate precisely the separation of the samples by altering the overall charge of the membrane surface [126,133,134].

Mosaic membranes (MMs) are a version of AIEM technology [115]. In MMs, the positive and negative ions are not randomly inserted into the membrane core polymer. The various ions are arranged in ordered positions relative to each other [123]. The “ion-exchange mosaic membrane” and “charged mosaic membrane” are synonyms of this approach. MMs can be used to separate electrolytes from nonelectrolytes [135].

Monovalent ion perm-selective membranes (MIPMs) can select monovalent ions and block the passage of multivalent ions [136]. Several factors can influence the perm-selectivity of monovalent ions, such as [136]:

- distinct hydrated ionic radii
- different migration rate within the membrane
- the affinity of the ions to the membrane

There are monovalent anion perm-selective membranes (MAPMs), which are selective to monovalent anions and monovalent cation perm-selective membranes (MCPMs), which transport only monovalent cation through the membrane.

7.2. Electrodes

Choosing the suitable electrodes is a pivotal part of the design. The electrode and the microorganisms form a bioelectrode together to achieve high efficiency [90]. Generally, there are three types of electrode materials: carbon-based, metal-based and metal-carbon composite [134].

7.2.1. Carbon-Based Electrodes

A simple carbon rod was used in the first MEC by Kuroda et al. [9]. In the following research and development works, various forms of graphite and carbon were used, such as carbon cloth [41,82], glassy carbon rod [26], carbon paper [17], graphite brush [12], graphite plate [99], graphite granules bed [90], etc. Carbon-based materials are commonly used as anode or cathode electrodes or current collectors [111]. They usually have a high specific surface area to be offered for the microorganisms [113]. Furthermore, good adhesion properties [18] and remarkable biocompatibility [64] promote biofilm formation on the electrode surfaces, which is required for the functional bioelectrode [90].

Graphite is a well-known and the most stable allotrope of carbon commonly applied in BES systems [137,138]. The unique structure of the bonds between the carbon atoms offers special benefits for graphite. It is essentially formed of graphene layers where each carbon atom is bonded to three other carbon atoms with strong sigma bonds, creating continuous hexagons. The layers are connected with weaker van der Waals bonds [139]. This particular layered structure empowers the graphite with unique benefits, like chemical and physical stability and great thermal and electrical conductivity [137,139]. Graphite electrodes are the preferred ones among carbon-based BES materials. They are relatively cheap [56] and reusable [64]. There are several commercially available forms of graphite, for instance, rod [11], block [18], brush [91], plate [140] or sheet [141].

Other well-studied form of carbon is carbon nanotube. Carbon nanotubes (CNTs) can be divided into multi-walled (MW-CNT) and single-walled structures (SW-CNT). These are two-dimensional layers in cylindrical or planar shape [142]. CNTs have unique chemical, electronic, mechanical, and optical properties [143]. They are one of the most promising materials in BES and MFC electrode construction. Because of their excellent biocompatibility, great conductivity, extraordinarily huge specific surface (up to 1315 m^2/g) and adsorbent properties, the CNTs are used in biosensors, MFC systems and other BES applications. However, CNT is still a relatively expensive commodity with potential cytotoxic effects [64,142,144,145]. Carbon nanotube hollow-fibre was tested with mixed microbial cultures, and 34% higher CH_4 production was achieved relative to the non-electro conductive polymeric hollow-fiber media. A shift in the microbiome was observed as well [146].

Nevertheless, carbon-based materials have their own Achilles' heel in electrochemistry. For instance, graphene is a hydrophobic material. Therefore it has relatively low biocompatibility and is potentially toxic to fabricate [147]. Although stability is one of the benefits of carbon materials, like graphite, Siegert et al. achieved a remarkably high Coulombic recovery, over 1100% [18]. Coulombic recovery of over 100% indicates that the product was delivered from external sources, not only the electrical circuit. In this case, overpotential and methanogenic corrosion of the carbon electrode caused the extra methane production simultaneously with hydrogen formation; $2CO + 3H_2O \rightarrow CH_4 + HCO_3^- + H^+$, $\Delta G_0 = 17$ kJ/mol. The generated H_2 is consumed by the surface colonizer methanogens, which cause further cathode corrosion [18,79]. Finally, carbon materials have higher internal resistance compared to metal-based electrodes, which cause a significant energy loss during scaling-up [111].

7.2.2. Metal-Based Electrodes

Overpotential is one of the significant problems in BES. To reduce its deleterious effects, the surface of the electrode should be expanded and/or the resistance of the electrode should be reduced by choosing a suitable electrode material [18]. Metal-based electrodes are widely used, due to their enhanced conductivity and lower internal resistance, relative to carbon-based electrodes. They come in various forms, i.e., mesh [148], sheet [95], plate [149], wire [99], etc. (Table 5) Platinum (Pt) is one of the best noble metals for electrochemical systems because it is inert and has a low overpotential [150]. In the early times of MEC technology development, Pt was commonly used as a catalyst for hydrogen production [10,13,15,41]. Unfortunately, Pt is expensive and has a harmful impact on the environment upon disposal. Therefore current research intends to lower the usage of Pt or replace it with other metals [150]. Promising alternatives are nickel (Ni) [103], titanium (Ti) [151] and stainless steel (SS) [55] as electrode materials. Other metals, like gold, silver, copper, and iron, are great conductors (e.g., SS: 1.45 MS/m, copper: 59 MS/m) [152], but during the long-term application, their operational stability is low [138]. Relative to carbon-based electrodes, metal electrodes have a lower specific surface area, low biocompatibility and high corrosion risk [153]. Manufacturing them in 3-dimensional form is fairly complicated, so most of the metal electrodes work in a 2-dimensional fashion. The conventional 2-dimensional electrodes have some disadvantages. Their specific surface area is small. Hence they have low electrocatalytic activity, high internal resistance, high overpotential and quick formation of a deactivating layer on the surface [64]. Nevertheless, the high mechanical strength and conductivity are advantageous in large-scale systems [154].

Table 5. The electrical conductivity of various electrode materials. Data are taken from ThoughtCo. (New York, NY, USA). (https://www.thoughtco.com/ accessed on 26 June 2019).

Material	Conductivity (S/m) at 20 °C
Silver	6.30×10^7
Copper	5.96×10^7
Gold	4.10×10^7
Nickle	1.43×10^7
Platinum	9.43×10^6
Titanium	2.38×10^6
Stainless steel	1.45×10^6
Carbon (graphite)	$2–3 \times 10^5$

7.2.3. Composite Electrodes and Surface Modifications

To achieve the best efficiency, the electrode should possess the following abilities: good conductivity, non-toxicity, high corrosion resistance, high specific surface area and excellent biocompatibility [36,48]. Most pure materials (carbon or metal) have only a few preferred properties, but their effectiveness can be improved via surface modification.

Composite materials are made by surface modification, i.e., blending two electrode materials (carbon-carbon, carbon-metal, metal-metal composite) to exploit their benefits. Typically, carbon-based materials form the basis, and metals are the modifiers. The electrocatalytic properties of biocompatible carbon are improved via the metal modifier [48]. For instance, Park et al. prepared a complex metal mixture to be fixed on a graphite carbon mesh. This increased the Chemical Oxygen Demand (COD) removal efficacy, and the methane production rate increased by 1.7 times relative to the controls [85].

Similarly, a graphite fiber sheet with multiwall carbon nanotubes improved the electrical conductivity upon Ni addition [141]. Pt has several negative features, like cost or impact on the environment. Nevertheless, it is still a popular choice to modify carbon or metal electrode surfaces [37,47]. In contrast, modification of metal-based electrodes with carbon deposits is rare, although carbon electrodes are often used with a metal collector to improve conductivity [18,76].

Other surface modifications, such as coating [148], oxidation [155] or heating [22], have been tested with mixed results [48,52,57,155,156]. One of the aims of altering the surface of the electrode by coating is to change the electrostatic charge distribution and thereby facilitate the appropriate microbial biofilm formation. Most Gram-negative microorganisms have a negative surface charge [157]. Therefore positively charged groups on the electrode surface improves the microbial adhesion to the electrode [64]. Accordingly, Zhang et al. modified carbon cloths with several compounds, i.e., melamine, ammonia, chitosan, cyanuric chloride, 3-aminopropyltriethoxysilane and polyaniline [158,159], with mostly positive results.

The other aim of the modification with the coating is to increase the conductivity. The N-groups in the NH_4Cl interfered with the electrode surface by changing the porosity of the graphite, and the conductivity increased [160].

8. BES Operational Parameters

Numerous factors and parameters are variable in BES reactors, as discussed above. In addition, the introduction of various sludge, substrates, and electron donors makes comparing the systems [111] very difficult. In 2016 Rosa et al. recommended a design for general use, but it did not receive widespread acceptance [161]. Several models have been developed, and the experimental data are fitted to rationalize the observations. In this chapter, the frequently used models are briefly summarized.

8.1. Modified Gompertz Model

The Gompertz model was originally developed in 1825 to analyze the relationship between age and death rate in biological systems. The formula describes processes that begin and end relatively slowly, like growth [159]. The modified Gompertz and first-order kinetic models predict biomethane production precisely [162]. The modified Gompertz and first-order kinetic models describe the process with an error of 1.2–3.4% and 4.6–18.1%, respectively.

$$M = P \times exp\left\{-exp\left[\frac{R_{max} \times e}{P}(\lambda - t) + 1\right]\right\} \tag{5}$$

M is the cumulative methane production (mL/g COD), P is methane production potential (mL/g COD), R_{max} is maximum methane production rate (mL/g COD·day), λ is lag phase (day), t is time (day), e = 2.7183 [162,163].

8.2. Coulombic Efficiency

Coulombic efficiency is often calculated in scientific reports, and the formula can change according to the authors' definition of coulombic efficiency. Although η indicates the coulombic efficiency in physics [164], in many cases, "CE" is used instead of η. CE represents the efficiency of electron utilization for product conversion, considering the various losses in a BES system, e.g., thermodynamics, side reactions, recombination of the products, etc. Faraday efficiency (FE), faradaic efficiency, faradaic yield or current efficiency are the frequently mentioned synonyms [95]. To calculate CE, there are variations of the basic formula according to the available data sets. A very simple equation [78] is as follows

$$CE(\%) = \frac{mnF}{\int_0^t Idt} \tag{6}$$

where m is the number of moles of products harvested, n is the number of electrons required to form the products, F is the Faraday constant (96,486 C/mol of electrons), and I is the circuit current (A).

Siegert et al. used the following [18] version:

$$CE(\%) = \frac{\left[m_{CH_4} \times n_{CH_4} + m_{H_2} \times n_{H_2}\right] \times F}{\int_0^t Idt} \tag{7}$$

m is the number of moles of CH_4 or H_2 formed, respectively, n is the number of electrons required for the formation of the products [79].

If the CE represents the electrons utilized to produce a specific product, then the current-to-product name is in use as well [110]. For example, current-to-methane calculation:

$$CE(\%) = \frac{n_{CH_4} \times z_{CH_4} \times F}{\int_0^t Idt} \tag{8}$$

n_{CH4} (mol) is total moles of CH_4 produced; z_{CH4} is moles of electrons per mole of CH_4 [165].

Optimally, CE = 100%, though there are examples in the literature of higher numbers [25,79,166,167]. The common mistake in these CE calculations is disregarding the Faraday loss, i.e., a certain amount of current (=electrons) are diverted towards unwanted side reactions in real systems. To take into account this loss, the CE equation is scaled to COD removal [141]:

$$CE(\%) = \frac{\int_0^t Idt}{n \times F \times \Delta COD \times V} \tag{9}$$

where n is the stoichiometric number of electrons produced per mole of the substrate (24 for glucose),), V (L) is the liquid volume of the reactor, and ΔCOD is the removed COD (mol glucose/L) [141]. Other parameters are the same as above.

8.3. Current Density

Current density (j) is the amount of charge per unit of time that flows through a unit area of a chosen cross-section [168]. The production rate of the BES reactor is tightly connected to the current density, i.e., low current density prevents scaling up due to the insufficient current density caused by low conductivity [50,76]. There are several methods to resolve this situation, such as increasing the conductivity of the catholyte [76], leaving the membrane out from the reactor [18], enrichment of electroactive microorganisms and modification of electrode materials [50].

$$j = \frac{I}{A} \tag{10}$$

I (A) is current, and A (m^2) is the projected surface area of the electrode [169]. Alternatively, the current density of the whole system can be calculated. In this case, A (m^3) is the liquid volume [52].

8.4. Methane Production Rate

Methane production rate (MPR) gives information about the methane-producing capacity of reactors. The formula is used in BES [5,90] and conventional AD reactors [170,171]. So MPR can be considered a bridge across the gap between the BES and conventional AD system.

$$\gamma_{CH_4} = \frac{V_{CH_4}}{V_{liquid} \times t} \tag{11}$$

V_{CH4} is the amount of methane in the gas phase (L), V_{liquid} is the working volume (L or m^3), t is the experimental time between headspace measurement (d) [5,171]. The formula is expressed considering the projected surface area ratio.

$$\gamma_{CH_4} = \frac{V_{CH_4}}{A_{proj} \times t} \tag{12}$$

Here A_{proj} refers to the projected surface area, which could be the membrane, anode, cathode, electrodes, or all three together [165].

8.5. CO_2 Conversion Rate

The CO_2 conversion rate represents the efficiency of the conversion of bicarbonates into methane. The formula is the following:

$$\eta_C = \frac{m_{C/CH_4}}{TIC_0 - TIC_{end}} \tag{13}$$

where $m_{C/CH4}$ is the mass of carbon in the methane produced in one batch (mg); TIC_0 is the total mass of inorganic carbon in the initial substrate (mg); and TIC_{end} is the total mass of inorganic carbon at the end of the batch (mg) [110].

8.6. Other Indicative Parameters

Additional parameters are usually considered less important for the thorough characterization of the BES electrobiomethanation systems, although they could be important for comparing the various constructs [54]. For example, Reynold number (Re) is used to predict the flow regimes since it combines viscous and internal forces [172], while Bond (Bd) and Weber (We) numbers can predict the stable bubble size in bubble column reactors [25]. Power number, or Newton number (Ne), is a dimensionless number which describes the relationship between the resistance force and inertia force [173]. In reactors, it is commonly used to describe the power requirements for stirring purposes [111].

9. Microbial Background

The fuel production rates of the BES systems are strictly related to the microbiota in the form of biofilm at the electrodes and in bulk. The efficiency of the biotechnological process depends on the composition and biological activity of the microbial community in the vicinity of the electrodes [94]. To achieve electrosynthesis, the microorganisms have to pick up electrons to use them to reduce CO_2 to CH_4 or another commodity. This can be achieved through extracellular electron transfer or EET. There are two known mechanisms of EET, i.e., direct (DEET) and indirect (IEET) extracellular electron transfer. In IEET, the electrons are transferred via electron carriers like H_2, i.e., interspecies hydrogen transfer or IHT, or formate, i.e., interspecies formate transfer or IFT [60]. The direct route (DEET) should be distinguished from microbial respiration, where the microorganisms take up the electron carrier molecule and utilize the reducing power inside the cell [174]. To achieve DEET, electroactive microorganisms, called electrogens or electrotrotrophs, are needed in the system [175]. DEET is achieved via soluble electron shuttles, conductive particles, or direct contact by a cellular structures between the electron donor and electron acceptor partners [60]. If DEET occurs between two microorganisms without any external conductor, the phenomenon is called direct interspecies electron transfer (DIET) [59]. Complex enzyme structures are not required for DEET/DIET, so the speed of the electron transfer is 10^6 times faster than in IEET [65]. Hence the reduction of CO_2 is more efficient, resulting in higher product yield [4], lower CO_2 content [59] and a more stable reaction [176]. The electroactive microorganisms need special structures for electron conduction, like electroactive pili, c-type cytochromes or archaellum [141,177]

Both mixed [42,83,151,156] and pure cultures [17,25,54,161,178] have been employed in BES applications. The first conclusive evidences for DEET and DIET was made with well-defined co-cultures [16,68]. Since then, *Geobacter sulfurreducens* strain PCA and KN 400, and *Shewanella oneidensis* strain MR-1 became the preferred model organisms of microbial electrochemistry [179]. The experimental potential in sterile cultures is straightforward. There are less unknown biochemical events, while the different microbial metabolism pathways involved in the process are decreased. In contrast, mixed cultures have benefits, such as better tolerance against stress and fluctuation, higher production rate, and better biofilm-forming ability, which make mixed cultures more attractive in scaling up for industrial applications [31,64]. Up to now, more than 100 microorganisms have been described as electroactive [56], the majority (about 80%) of them are gram-negative [179], and 91% possess biofilm-building ability [179]. Biofilm formation was observed after 24 h on the electrode surface [75]. Certain microorganisms act as an anchor to help the attachment of methanogens, while the electroactive microorganisms [163]., for example, *Shewanella* secretes redox shuttles to improve the electron transfer [56]. In mixed cultures, many microorganisms can accomplish various tasks. Table 6 summarizes a few typical members involved in BES and their potential role in the process.

Table 6. Typical members in BES reactors and their potential roles.

Taxon	Chamber/Electrode	Possible Role	References
Desulfovibrio sp.	cathode	Catalyses BES H^2 production at cathode potentials ≤ -0.44 V versus NHE	[89]
Acetobacterium spp.	cathode	Most prevalent and active bacteria on the electrode in acetate production	[24]
Clostridium sp.	Bulk solution	Transferred electrons directly to an outside electron acceptor	[141]
Geobacter sp.	cathode	Well-known DIET partner	[82,163]
Hydrogenophaga sp.	cathode	Electroactive bacterium. Its role in electromethanogenesis is unclear	[163]
Azoarcus sp.	cathode	The facultative electroactive, role in BES needs further investigation	[148]
Tangfeifania sp.	cathode	It is detected frequently in BES reactors. They probably facilitate methanogenesis	[91]
Aminomonas sp.	cathode	Syntrophic methanogen partner electron transfer has not been documented	[91]
Desulfuromonas sp.	anode	Electroactive microbe	[77]
Bacteroidia sp.	Bulk solution	Hydrolyzes proteins and transforms the amino acids generated in the process into acetate	[85]
Azonexus sp.	cathode	Acetate oxidising bacterium, capable of DIET and DEET, it can be found frequently on anode as well	[92]

Since electroactive microorganisms have an impact on CO_2 reduction [48], their enrichment of them enhances the production of valuable commodities [92]. Several approaches have been tested to improve the microbial community in BES reactors, such as applying fixed potential [56], bioaugmentation with pure electroactive cultures, and *Geobacter* species [77]. Inocula taken from already running reactors [36], or genetically modified microbes have proven promising results [50]. Table 7 lists the Archaea that colonized the electrodes effectively and, therefore, probably possess electroactive abilities, though in several cases, the mechanism is still not proven. The most frequently found Archaea participating in cathode biofilms are *Methanobacterium* sp., *Methanobrevibacter* sp., *Methanosaeta* sp., *Methanosarcina* sp., *Methanotrix* sp. [24,50,85,92,110,114,140,148,163].

Table 7. Most frequently detected archea in BES reactors.

Archea	References
Methanobacterium palustre	[89]
Methanobacterium aarhusense	[89]
Methanothermobacter thermoautotrophicus	[80,180]
Methanothrix concillii	[29,91,92,181]
Methanospirillum hungatei	[29]
Methanosarcina flavescens	[29]
Methanoculleus bourgensis	[29]
Methanosphaera cuniculi	[29]
Methanobacterium formicicum	[83,85]
Methanobacterium petrolearium	[181]
Methanobacterium subterraneum	[35,181]
Methanosarcina thermophile	[85]

10. Conclusions

1. In this review, we compiled a cross-section of the ongoing research on bioelectrochemical systems (BES), emphasising electrochemical biomethane formation. In this endeavor, the first observation has been the large number and exponential growth of relevant scientific publications. This is not surprising in light of the recommenced interest towards renewable energy research and development.
2. We note that the various BES systems developed in numerous laboratories worldwide comprise a very distinct and diverse collection of the infrastructure, i.e., reaction vessels and parts thereof. This reflects the inventive approaches of the scientists working in the field, and the pioneering efforts should be welcomed by the scientific community. This can also be rationalized when a multitude of reactor designs, electrodes, and membranes are selected to perform optimally in specific applications. Unfortunately, the almost chaotic infrastructural assortments make comparing the various BES systems difficult. Therefore, it is advised to specify a few "general or basic BES reactor systems" to be included in the related studies as built controls to compare to the new or novel system designs.
3. This kind of standardization may help the development of BES systems beyond the curiosity-driven laboratory scale studies towards industrial applications, which is now hindered by the variety of diverse laboratory studies using several reactor designs and components' selection.
4. A consensus is needed regarding the indicator parameters in evaluating the various BES performances.
5. An equally important aspect is the need to consider that all BES systems employ biological components, i.e., pure strains of specific microbes or mixed microbial communities. These microbes make fundamental contributions to the job accomplished and thus have a great share in the success of the BES electrobiomethanization systems. The complexity of the physiology and biochemistry of these microbial participants significantly alters the success of the electrochemical process. The associated tasks to optimize electrochemistry with microbial fermentation/conversion are largely beyond the scope of this review. Only a short sketch of this viewpoint is outlined here. The amalgamation of the electrochemistry and biotechnology issues will be the subject of an upcoming report and much-related research.

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