Review

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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 the electric current for the synthesis of valuable commodities in Microbial Electrolysis Cells (MECs). The number of various reactor configurations and operational protocols increasing rapidly although, the industrial scale operation is still facing 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 to link the appropriate microbes to the optimal reactor design is given.

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

1. Introduction

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

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

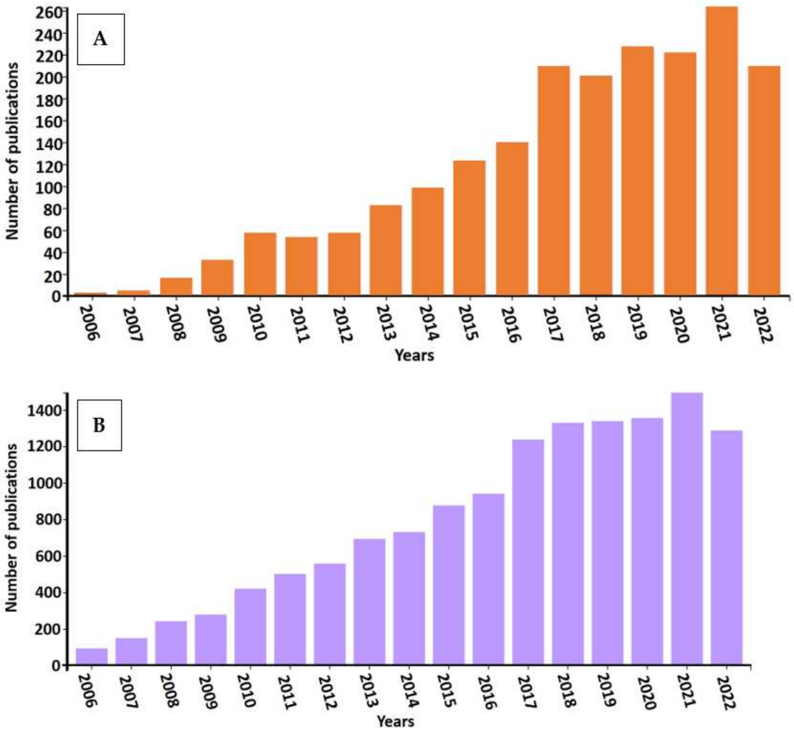

Figure 1. Number of relevant publications in the last 1.5 decadees indicate clearly the increasing interest in MEC (A) and MFC (B) technologies. Data taken from web of science (https://www.webofscience.com), using the key words “microbial electrolysis cell” and “microbial fuel cell”.

It is apparent from Figure 1 that MFC enjoys wider interest among BES researchers, who published almost 6 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, industrial MEC technology. This review aims to update the current trends, particularly from the point of view of new designs, used materials.

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 the MEC technology received wide attention in the early 21th century, hydrogen was the main target product [10–12]. Liu et al. suggested to use 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 parasitic by-product of the electrohydrogenezis. Methane was gradually recognized as a potential main MEC product in the middle of 2010s [17–20]. The electrosynthesis processes became more complex, 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 to take note of the diversity of nomenclature as well as designs and performance measures, which make the various reports difficult to compare. Through the years, numerous definitions and designs have been proposed, which are 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 the 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. Collectively the electrode and surrounding microbiota, usually organized in biofilm, is called **bioelectrode**. The anode and the cathode can be separated by membrane but the membrane is not indispensable component of BES. Frequently used synonyms: microbial electrochemical technology (MET) or microbial electrochemical system (MES) [26–33].

Biogas cleaning is the process to remove impurities, like water, hydrogen sulphides, etc. from the raw biogas by physico-chemical 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 mostly 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 the living organisms, and some of them (for example H_2S) are extremely corrosive, so they have to be removed before injection to the natural gas grids or use as alternative engine/vehicle fuel. As per definition, biogas upgrading refers to the removal of 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%), which is 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): DIET is a syntrophic microbial interaction, where free electrons are transferred/exchanged between microorganisms [38].

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

Electrohydrogenesis: During electrohydrogenesis the protons and the 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, which is released from the cathode compartment [41].

Electromethanogenesis: Electromethanogenesis is a process of producing methane via electroactive microbes using CO_2 as the sole carbon source in an engineered system (biocathode) powered with 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 carry out the recombination of CO_2 with electrons and protons [42]. Electromethanogenesis is thus a subset of BES/MES, the microbial electrosynthesis of a variety of chemicals.

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

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

Microbial electrolysis cell (MEC): MECs is 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 a MES reactor [24,25,31,48–52]. "Electrofermentation" (EF) is used as a synonym of MES in some literature reports [50,53].

Microbial fuel cell (MFC): MFC is a type of BES, where organic matter is decomposed via exoelectrogenic microbes near the anode, which serves as terminal electron acceptor. The spontaneous electron movement from the electronegative bioanodes to the electropositive cathode in a circuit generates electric current [14,26,27,54–57].

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 [28,30,58].

4. The BES drivers

Extracellular electron transfer (EET) is an electron exchange process between the microorganisms in a mixed microbial community [59]. (Figure 2.) There are two mechanisms to perform EET, i.e. the indirect (IEET), and direct (DEET) processes.

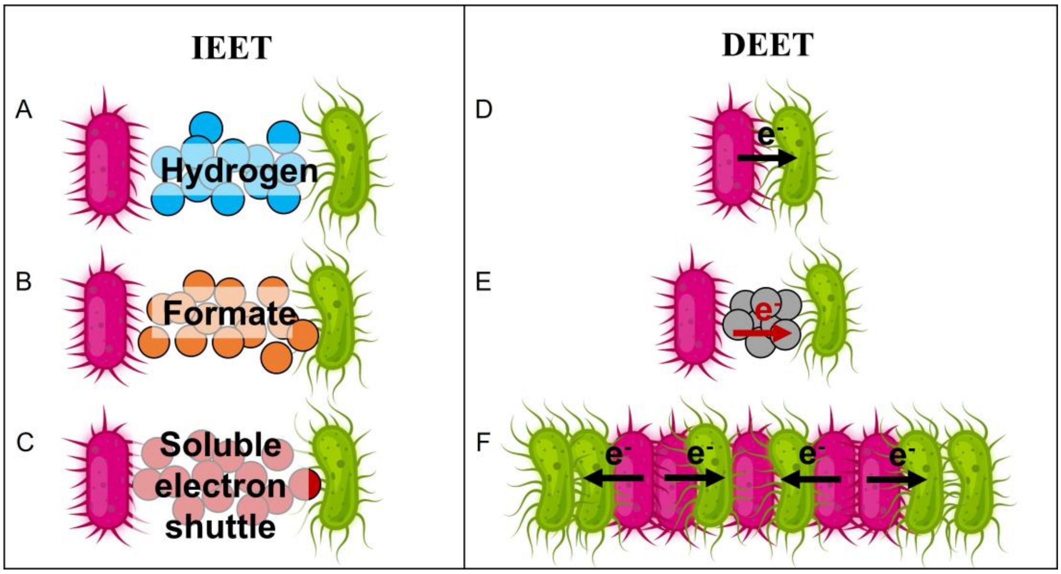

Figure 2. Extracellular electron transfer can take place as indirect (IEET) and direct extracellular electron transfer (DEET). For IEET there is no need for a direct connection between the microorganisms, because molecules, for example **(A)** hydrogen, **(B)** formate, or **(C)** soluble electron shuttles serve as electron carriers. On the contrary, DEET requires a 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) [60].

Indirect, or mediated extracellular electron transfer (IEET) has been first recognized as the only route for EET in anaerobic microbial communities. The direct extracellular electron transfer (DEET) was described as alternative mechanism between syntrophic microorganisms involving physical contact between the partners [61].

In IEET there is no need for direct connection between the donor and the acceptor [62], because a carrier, or mediator, such as hydrogen, formate, or soluble electron shuttles, reduced or oxidized by the cell are used to transfer the electrons between the redox partners [63]. In DEET a direct physical contact is needed between electron donor and electron acceptor microbes [62]. The direct contact is maintained frequently by pili, conductive biofilm formation, or flavins and cytochromes [64], although in many cases the exact molecular mechanism is not clear [65]. Electroactive microorganisms possess these molecular structures, hence they are capable of DEET [43].

DEET has several advantages over IEET, like faster electron transfer [66], the more efficient reduction of CO_2 [4,60]. A complex enzyme system to produce mediators, or carriers is not required for efficient DEET [61], but special, conductive structures are needed on the surface of the microbes.

Electrofermentation, i.e. generation of reducing equivalents by electric current assisted fermentative process was reported [67]. Daniels and co-workers reported the reduction of CO_2 to CH_4 by the electrons from elemental iron [68]. The first electrofermentation 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 [69]. Since then more and more microorganisms have been recognized as having the capability to 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 to electrical energy via microbial catalysis [70]. Conventional MFCs have two chambers, anodic and a cathodic ones, separated by a proton exchange membrane (PEM) or salt bridge [71].

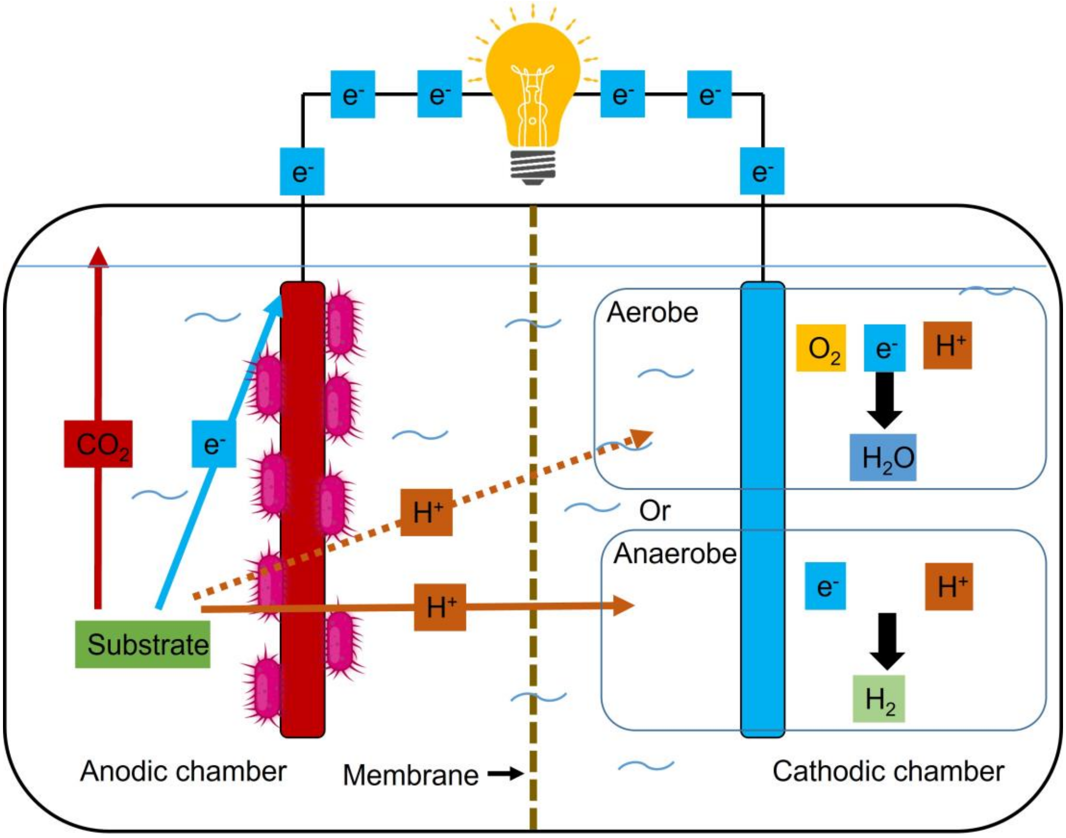

Figure 3. In *m*icrobial fuel cell (MFC) the organic substrates are oxidised by microorganisms. The anode serves as terminal electron acceptor, the protons are released to the solution. The reactor contains a resistance, or consumer and a membrane. Protons diffuse through the selective membrane and recombine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

After the oxidation of organic matter, the electrons are transferred to the anode, which acts as terminal electron acceptor, and the protons are released in the electrolyte [72]. The protons diffuse through the PEM to the cathode, while electrons travel through an external circuit, generating electric current [73]. In the aerobic cathode chamber oxygen is reduced by electrons and protons and produce water [64]. 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 reduction of CO_2 to methane via direct electron transfer, requires only E^0= -0.244 mV vs. SHE [53]. The following equations show clearly why DEET (Eq. 1.) is more energetically efficient, than IEET (Eq. 2, 3) during electromethanogenesis [48].

$CO_2 + 8\ H^+ + 8\ e^- \rightarrow CH_4 + 2\ H_2O\ E^0 = -0.244$ V vs. SHE (eq. 1)

$2\ H^+ + 8\ e^- \rightarrow H_2\ E^0 = -0.421$ V vs. SHE (eq. 2)

$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O\ \Delta G0 = -131$ kJ/mol (eq. 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 [54], therefore the overall reaction of electromethanogenesis is not favourable in MEC [74].

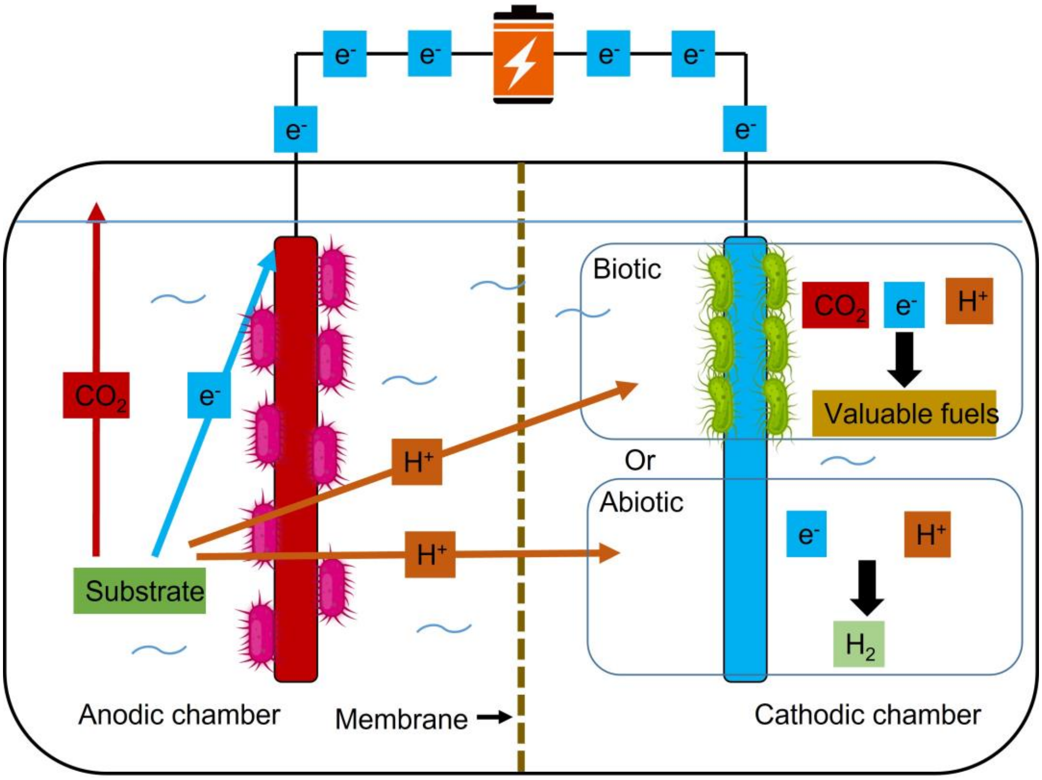

Figure 4. In a microbial electrolysis cell (MEC), the substrate is oxidised in the same way like in MFC. The electrons are transferred to the anode, while the protons are released into the electrolyte solution. The reactor contains a power source and sometimes a PEM membrane. The power source increases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

Due to the energy losses, overpotentials, like internal resistance caused by the PEM membrane [32], low conductivity of the electrolyte [75] and the activation energy of the imperfect catalyst [75], the theoretical electrode potential is not sufficient in real systems [76],. To lower the energy losses in the reactor, the membrane could be eliminated [32], the conductivity can be increased [77], and more efficient catalyst can be applied to reduce the overpotential [18]. Precious metals, like platinum, seem the best catalyst, but the use of such catalysts at 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 biocatalyst, in which the electrotrophic microbes are enriched by the environmental stress caused by the voltage [32]. The enriched microbial community is capable for self-regeneration so the long-term application is possible even under industrial scale operational conditions if regular evaluation and microbial community management is provided [76]. The appropriate microorganisms are able to reduce the system resistance, they lower the activation energy barrier and increase current density by taking up the electrons for use in their own metabolism, or mediate to the other microorganism via DIET [78]. To achieve the best performance, the optimum external potential is one of the pivotal parts, and the enriched microbiome drives the 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 [79,80], although exceedingly high negative potential may be accompanied by by-product generation, like acetate [32] within the domain of MES. An important contribution to electro-biochemistry also comes from the electrode material, and electrode geometry, which are vital parameters determining the formation of the electroactive biofilm. The related issues are discussed in detail in section “Electrodes”.

Table 1. One chamber reactor configurations with carbon-based cathodes and their efficiency. Some of the 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	[81]
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	[82]
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	[83]
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	[84]
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	[85]

Table 2. One chamber reactor configurations with metal-based and composite cathodes and their efficiency. Some of the 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 cylindral Ti collector	800.0	220.0	No	40 °C	6 L	[77]
0.9	1.0	Stainless steel	Carbon felt	25.0	76.0	No	25 °C	250 mL	[78]
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	[86]
0.8	3 - 3.5	Stainless steel mesh	Ti mesh + Ir mixed metal oxides coating	20.0	20.0	No	35 °C	500 mL	[87]
0.6	-1.0 vs Ag/AgCl	Stainless steel	Carbon felt	10.0	183.7	No	31 °C	180 mL	[88]
0.5	-0.4 vs Ag/AgCl	Stainless steel	Carbon felt	10.0	183.7	No	30 °C	180 mL	[88]
0.3	1.2	Stainless steel cylinder	11 graphite plate inserted to a Stainless steel cylinder	247.5	294.0	No	16 °C - 35 °C	153 mL	[56]
0.2	0.9	Stainless steel	Graphite fiber brush			No	31 °C	1000 L	[89]

Table 3. Two or more chamber reactor configurations with carbon-based cathodes and their efficiency. Some of the 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	[58]
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 cathion exchange	30 °C	2*620 mL	[90]
1.8	- 0.5	Carbon cloth	Carbon cloth	40.0	40.0	Nafion 117 proton exchange	55 °C	2*250 mL	[81]
1.4	-0.6 V	Graphite felt	Graphite felt	290.0	290.0	Fumasep FKB cathion exchange	30 °C	2*620	[90]
1	-0.8 - -1.2 vs Ag/AgCl	Carbon felt	Graphite electrode	11.9	132.0	AS2S Cathion exchange	55 °C	2*350 mL	[82]
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 cation exchange	30 °C	2*245 mL	[20]
0.5	0.8	Carbon cloth coated with activated carbon (5 mg/cm²) + Pt (0.1 mg/cm²)	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	[91]
0.2	-0.5 vs. Ag/AgCl	Carbon brush	Graphite rod	4.8	13700.0	CMI 7000 cathion exchange	37 °C	800 mL	[92]
0.1	-0.5 vs. Ag/AgCl	Graphite plate	Graphite rod	4.8	40.3	CMI 7000 cathion exchange	37 °C	800 mL	[92]
0.1	-0.5 vs SHE	Graphite plate	Graphite rod	15.6	15.0	CMI 7000 cathion exchange	37 °C	850 mL	[93]
0.1	0,7	Carbon paper	Carbon paper	10.0	10.0	Nafion 117 proton exchange	37 °C	2*150 mL	[94]
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	[80]
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	[55]
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	[55]
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	[95]
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	[95]
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 cation exchange	30 °C	2*280 mL	[74]
0.01	-1.1 vs Ag/AgCl	Carbon laying	Carbon fabric	15900.0	30000.0	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	7400000.0	7400000.0	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 of the 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	[51]
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	[53]
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	[95]
0.02	–0.7 vs. Ag/AgCl	Pt sheet	TiO_2/CdS photoanode	3.0	4.0	Ultrex CMI 7000 cation exchange membrane	31 °C	2*350 mL	[96]
0.01	-0.55 - -0.65	Graphite bloch + carbon black + metals (Pt, Ni, Stainless steel)	Carbon fiber brush	7400000.0	10.6	Nafion	32 °C	2*100 mL	[18]

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):

$$E = E^n + \eta^{act} + \eta^{ohm} + \eta^{mt} \quad \text{(eq. 4)}$$

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 [97].

6. Trends in reactor design

In early developmental stages reactors incorporating selective membranes were primarily studied [13,98,99]. The reactor design trends diverged towards simple, membrane-less, cost-effective systems [15,27,100] on the one hand and sophisticated constructs equipped with membrane(s) on the other hand [20,42,58,81,101]. The variety of BESs schemes fulfil the requirements for multifunctional tasks, e.g. NH_4 recovery [42], CO_2 removal [102], biohythane production [53]. Most systems contain at least one, or two membranes. Membrane containing, and membrane-less set-ups 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, 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 [103]. In certain applications the separation of the biofilms formed on the anode and cathode, respectively offers improvements in system operation and sustainability. Reactors, in which a separator, e.g., nonwoven fabric, is used to prevent short circuit is considered as single-chamber reactor because the different molecules developed via the electrodes and the biofilm are capable to exchange through the separator.

Glass vessel-type reactors are the simplest constructs at laboratory scale. This reactor configuration requires only typical laboratory items like sealable serum bottles for reactor body. The electrodes are inserted from the top of the glass vessel and a separator or an inert insulation are usually applied to avoid short circuit. As small as 5-10 mL vials have been converted to MEC systems [17,100]. Theoretically, roughly 6,000 reactors can be assembled in one block using a single power supply in the right arrangement [100].

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.). Either the anode [9] or the cathode [77] 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 [56]. To the contrary, in the "adjacent" configuration the electrodes are close to one another, hence a membrane or separator is placed between them to prevent short circuit. The small distance between the electrodes decreases the internal resistance of the system [37]. Hou et al. made a special version of cylindric reactor, where spiral wound electrode was used. This design resulted in large specific surface area and possible potential scalability [104].

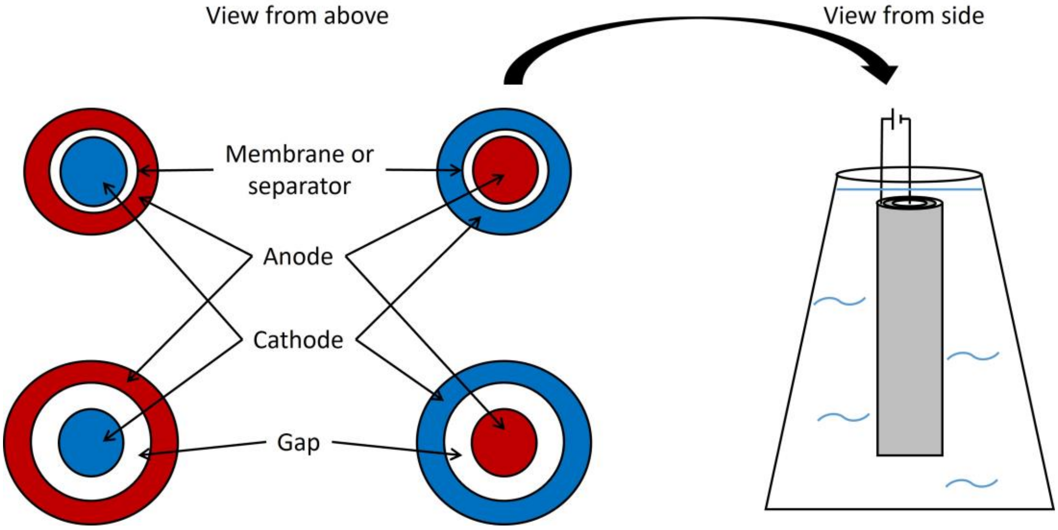

Figure 5. In cylindrical reactors, one electrode is inside the centre, while the other is placed around it. In "distant" design, there is a gap between the electrodes filled with electrolyte or the solution, while in "adjacent" design there is only a membrane separation between the electrodes. Both the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

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 [89,105]. In these simple equipments the electrodes face each other in a vertical assembly (Figure 6.). This design is suitable for scaling-up as well, because the specific surface area of the electrodes is easily changeable by increasing the number of the electrode stacks. For example, a pilot scale continuous reactor configuration consisted of 24 modules and in total 144 electrode pairs in 1,000 L volume [89]. The rectangular box type reactor has been built in versions containing membranes as well, the membranes inserted in between the electrodes [106].

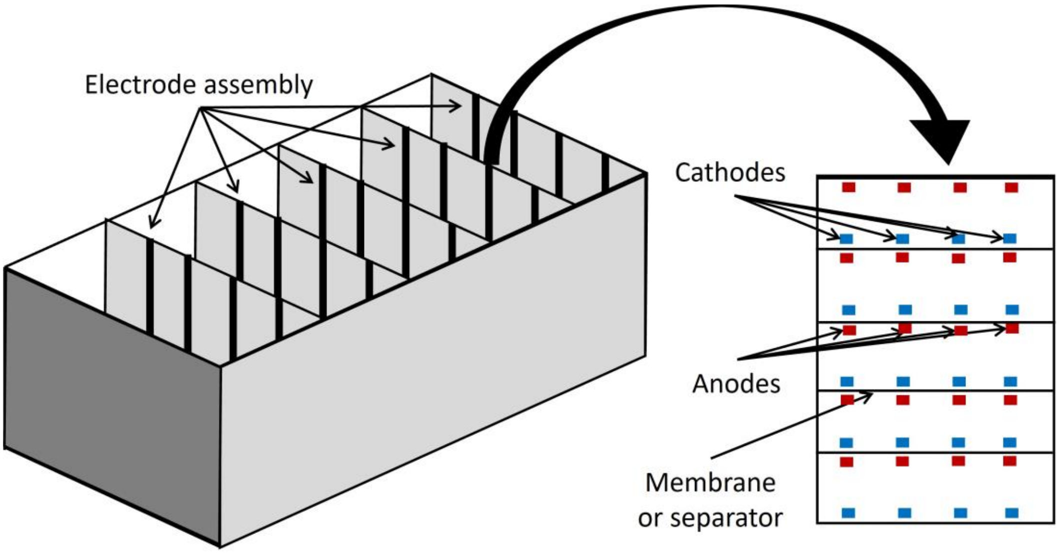

Figure 6. Rectangular box type reactors are suitable for scale-up experiments. The electrodes are placed opposite each other, the electrode surface and current density is increased.

A more sophisticated design is the **column-type reactor** model. In the column-type reactors one electrode is positioned at the bottom, the other is near the top of the reactor. Both "cathode-on-top" and "anode-on-top" configurations have been tested for special applications. The advantage is in separating the products to a certain degree even without involving membrane. For instance, cathode-on-top configuration prevents the product generated at the cathode, from the biofilm situated on the anode. Guo et al. constructed an innovative column-type cathode-on-top reactor with 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 [107]. 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 strictly anaerobe methanogenic biofilm on the cathode [49,108].

6.2. Two chamber systems

In these designs the chambers are separated by an ion-selective membrane. The use of membrane facilitates the production of pure product(s) [74]. The membrane can protect the obligate anaerobic methanogens from inhibitory products, like oxygen [95]. Although a membrane increases the internal resistance, generates pH gradient and increases the price and complexity of the system, in some applications may be worth to employ for maintaining a selective BES operating sustainably in extended time period [85].

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 relative low surface of the membrane increases the internal resistance [55]. Allen and co-workers designed the H-cell arrangements in electrochemistry [109], later this design was used by Hongo et al. to microbial electrosynthesis (MES) of L-glutamic acid [110]. H-cell shaped reactors are one of the most commonly used two chamber setups. The H-cell reactor acted as microbial electrolysis devices (MEC), when Liu at el added extra voltage to a MFC and achieved electrolytic hydrogen production [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 [111].

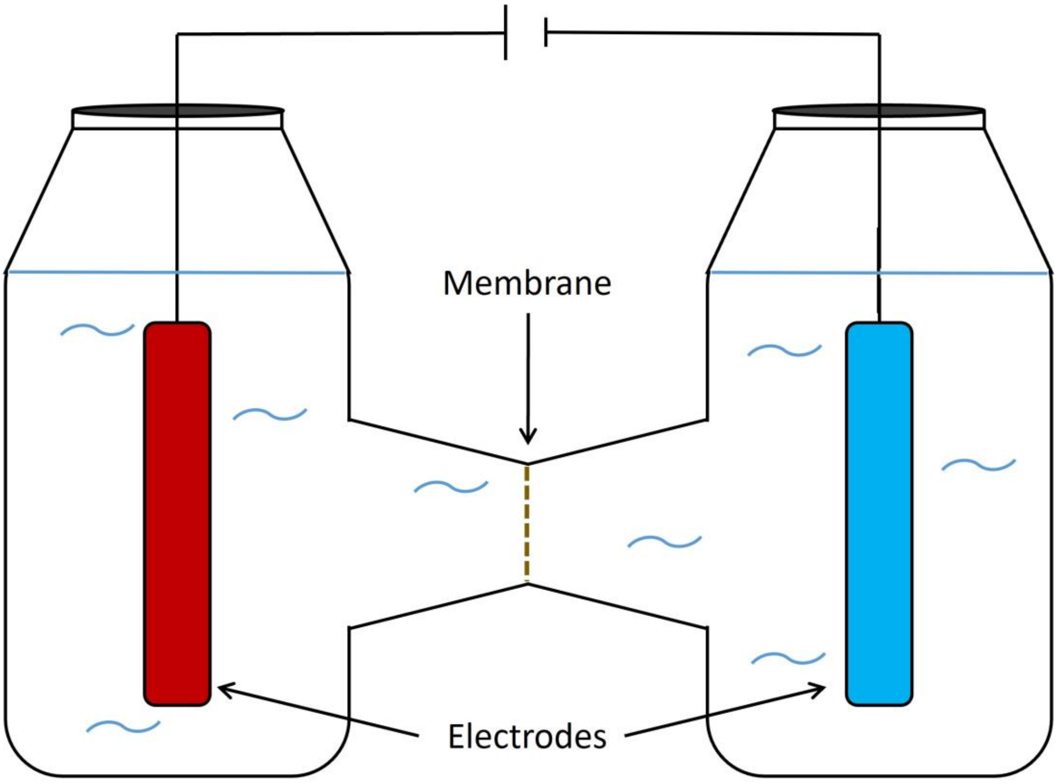

Figure 7. H-cell reactors are one of the most popular laboratory test designs for BES. It is easy to set up, though the size of the membrane and the possibility to stirring are limited.

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 (Figure 9.). The larger "container" chamber can be the one housing either the anode [55] or the cathode [93]. Concentric tubular reactors have certain benefits relative to the H-cells, being more flexible than H-cells to assemble and to alter the electrode chambers' geometry. The internal resistance can be adjusted by changing the electrodes 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 [55], whereas in the system designed by Liu and co-workers, the anodic chamber was separated with a membrane bag [93].

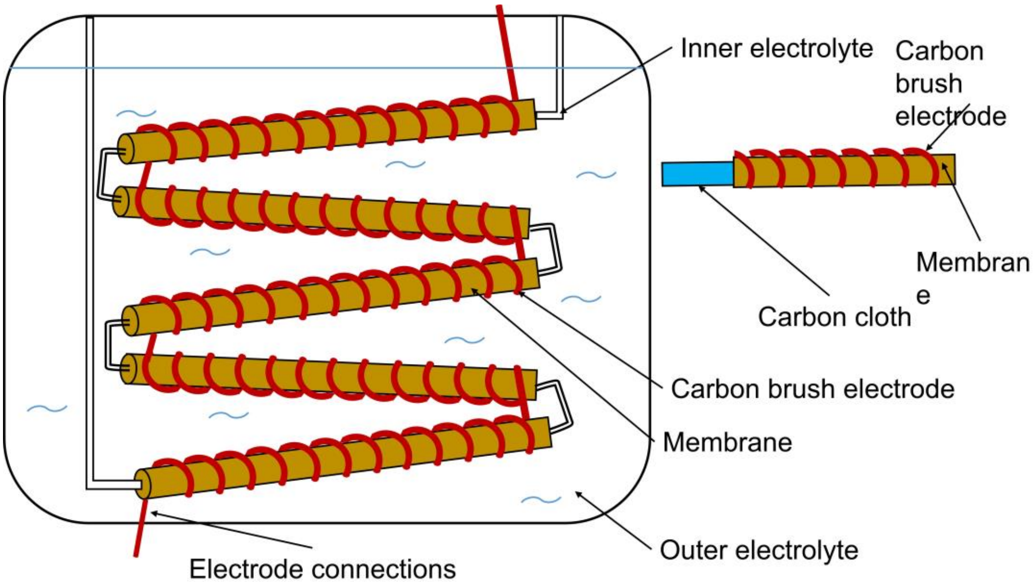

Figure 8. Schematic figure of cylindrical tubular hybrid system constructed by Luo et al. [37]. It contains five tubes with titanium wire - carbon cloth - stainless steel mesh inner electrode (cathode) and carbon brush outer electrode (anode), separated with membrane. There is a continuous electrolyte (catholyte) flow in the inner space of the tubes.

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

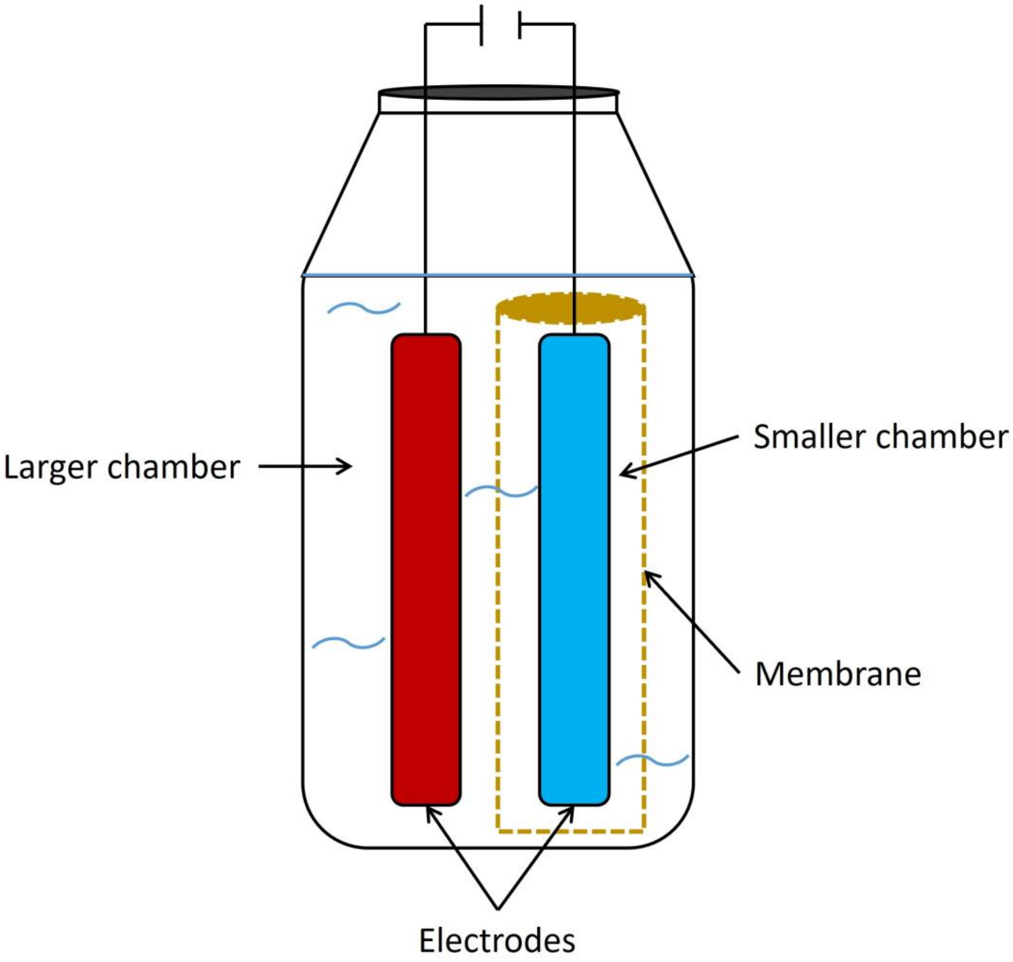

Figure 9. Concentric tubular reactors containing a smaller chamber inside a larger one. The two chambers are separated via separator, or membrane to increase the membrane surface. Either the anode or the cathode can be placed in the smaller chamber.

In **flat plate reactors** the electrodes are placed close to each other, which reduces the internal resistance. In this arrangement the specific surface area can be exceptionally large. For example, using graphite granules bed as electrode a dramatic 1,290 m^2 m^{-3} surface [99] has been achieved. The high surface favored the formation of a dense biofilm, hence improved performance [112]. The mass transfer was facilitated via serpentine flow in both chambers [113]. Nevertheless, flat plate reactors are not widely used even at 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 [114].

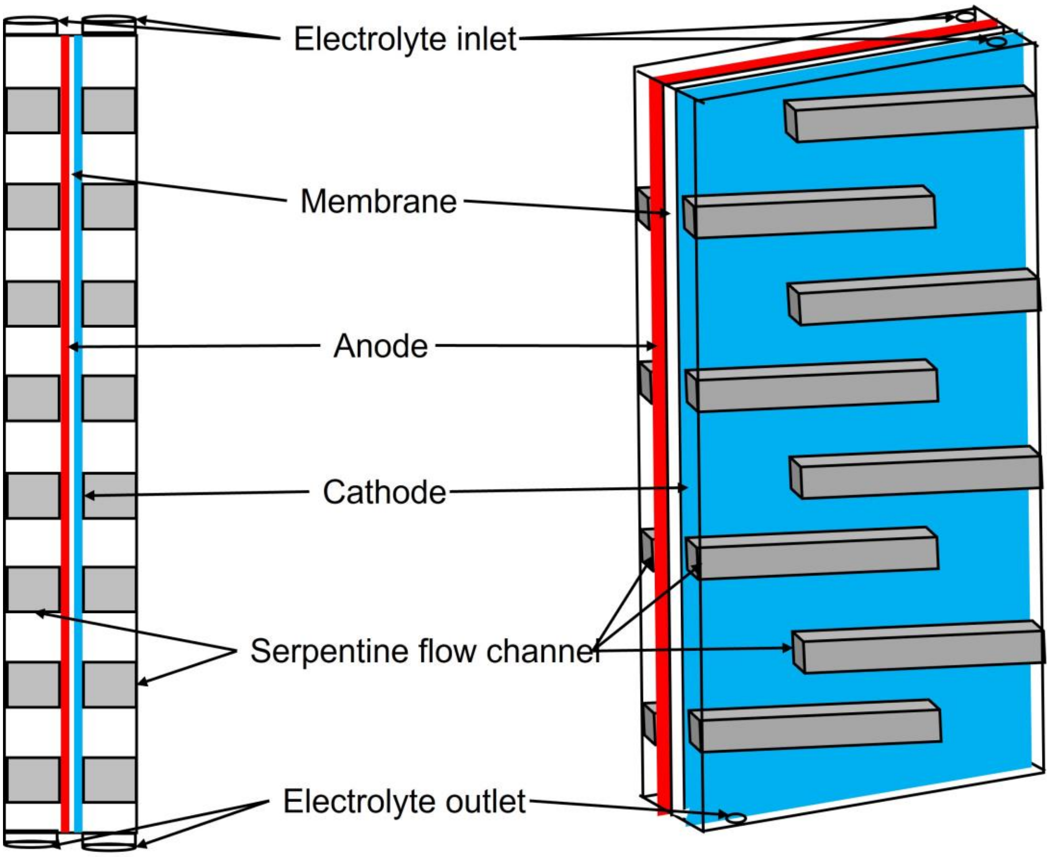

Figure 10. In flat plate reactors the anode and the cathode are separated with membrane. The specific surfaces are extraordinary large thanks to the serpentine flow channels, which can be further increased by granules. Needs continuous flow of the liquid phase.

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 anode and the other half functions as 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 the electrode arrays can be increased creating batteries of the basic units, scaling-up is limited by the energy requirement of the rotating engine and sustainability of the biofilm on the electrode surfaces.

In a different design concept more than two reactor chambers are coupled together. The **multiple chamber 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 [6,102] . The anodic chamber is separated from the accumulation chamber via 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 along with 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 [91]. 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 side. In the CEM cathode compartment biogas, as well as ammonia-nitrogen was produced by the microbial biofilm formed from activated wastewater sludge, which was fed into the reactor. The produced 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 cell (MESC), also referred to as microbial electrolytic capture, separation and regeneration cell (MECS) [115,116]. The MESC consists of four different chambers, i.e., anodic, regeneration, absorption and cathodic chambers, separated with anion exchange membrane and bipolar membrane. The multiple-chamber reactors, like MESC offer a great opportunity to simultaneous wastewater treatment, biogas production, biogas upgrading, and carbon and nitrogen recovery, though their complexity limits their application in scale-up systems [115].

Other multifunctional and sophisticated BES reactor systems include systems, like MFC-MEC coupled system [19], or microbial photoelectrochemical system (MPES), which utilize the solar energy 6 times more efficiently than the natural microbial systems [96]. 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 [95]. An advanced anaerobic osmotic membrane bioreactor-microbial electrolysis cell (AnOMBR-MEC) system achieved a simultaneous biogas upgrading, enhancing CH_4 yield and wastewater treatment [117].

7. The components of the BES systems

7.1. Membranes

Research and development on ion exchange membranes (IEMs) dates back to the work of Oswald in 1890, who discovered that the semipermeable membranes have impermeable properties to certain cations or anions present in the electrolytes [118]. The "Donnan exclusion potential" was delineated in 1911 and the extensive experimental work on IEMs 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 [118]. Electrodialysis via membranes became an industrial process and simultaneously the bipolar membrane was introduced [119]. The first large scale desalination of sea water using membranes was carried out in the 1960s [118]. A major step forward was the development of Nafion, the chemically stable cation exchange membrane based on sulfonated polytetra-fluorethylene by Dupont [118].

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 [74]. The presence of the membrane protects the methanogens from inhibitory compounds [95] or keeps the cathodic H_2 gas clean [103] and prevents the mixing of undesired molecular species, such as oxygen [85]. On the other hand, in a system incorporating membrane the pH gradient [116] and ohmic-loss lowers the efficiency of the product formation, while the complexity increases the investment and operational costs of the BES reactors [85].

The membranes used in BES can be classified in two groups, i.e., proton exchange membranes (PEMs) and ion exchange membranes (IEMs). IEMs include the cation exchange membranes (CEMs) and anion exchange membranes (AEMs). A variety of IEMs, including inorganic–organic (hybrid), amphoteric, mosaic, bipolar membranes (ion exchange composite membranes) have been introduced in the IEM market [118].

7.1.1. Proton exchange membranes (PEMs)

Proton exchange membranes (PEMs) were introduced in 1970s by DuPont. The sulfonated polytetra-fluorethylene based polymers, called Nafion membrane showed not only high conductivity, but also had long lifetime [120]. PEMs can be categorized into five main groups according to the materials used in synthesis such as [121]:

- Perfluorinated
- Partially fluorinated
- Non-fluorinated

- Acid-base blend
- Others

In general, there are two mechanisms for transport of the protons across the membrane, while electrons are repelled. The "proton hopping" or "Grotthus mechanism" and the "diffusion mechanism" or "vehicular mechanism" [122]. 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 hydrolysed ionic site to another through the membrane. According to the vehicular mechanism, the protons are transferred via hydrated proton (H_3O^+) [123]. The most important properties of PEMs are the proton conductivity, water uptake, ion exchange capacity, gas permeability and physical stability [124]. These properties can be improved or modified, via thinning the membrane [125], or via blending with various minor components, such as inorganic oxides, zeolites, proton conductive materials, etc [123].

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 [126].

The physico-chemical properties of membranes are determined by the material of the basic "backbone" polymer chemistry, which provides the 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, ceramic compounds [126,127]. The membrane backbone should possess properties for the industrial application like [121,128].

- 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 functionalised groups, which define the permselectivity and electrical resistance [128]. According to the functionalised groups, the membranes can serve as cation exchange membranes (CEMs), anion exchange membranes (AEMs) and bipolar membranes (BPMs) [126]. 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 to 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 for anions [118]. BPM is a special construction, which contains a CEM and an AEM layers, respectively [126].

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 [121]. In general, homogenous IEMs have good electrochemical properties, but weak mechanical strength. In contrast, heterogeneous IEMs have great mechanical strength and dimensional stability, poor electrochemical performance [123].

Cation exchange membranes (CEMs)

CEMs contain negatively charged groups, attached to diverse polymer backbones [129]. The pattern of the charged moieties alters the character of membranes. Their low conductivity is the main obstacle in industrial application [129]. 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 increase the conductivity to create block CEM [129]. Alternatively, the functionalized groups can be attached to each other closely, to make aggregates and result in densely functionalized CEMs [130] There are several other modifications to alter the properties of the membrane [129].

Anion exchange membranes (AEMs)

In contrast to CEMs, AEMs contain positively charged groups to attract the anions and repel cations or neutral molecules [131]. There are concerns about the utilization of AEMs in industry, because of the poor conductivity and weak chemical stability. To improve these properties, new types of ionic groups and designs of the polymeric architecture has been developed [129,132–134].

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 [119], or an interfacial layer inserted between the CEL and AEL [118,129]. Since their introduction, the industrial applications are interested in the use of BPMs in the fields of water electrolysers, and CO_2 fuel cells, and flow batteries. The required features of BPM for an industrial application [135] include:

- 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 [118]. This makes the AIEMs easily controllable, because both of the 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], [136].

Mosaic membranes (MMs) are a version of AIEM technology [118]. 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 [126]. The "ion-exchange mosaic membrane" and "charged mosaic membrane" are synonyms of this approach. MMs can be used for separation of electrolytes from nonelectrolytes [137].

Monovalent ion perm-selective membranes (MIPMs) can select monovalent ions and block the passage of multivalent ions [138]. Several factors can influence the perm-selectivity of monovalent ions, such as [138]:

- distinct hydrated ionic radii
- different migration rate within the membrane
- 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 [91]. In general, there are three types of electrode materials: carbon-based, metal-based and metal-carbon composite [139].

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 like such as carbon cloth [41,83], glassy carbon rod [113], carbon paper [17], graphite brush [12], graphite plate [100], graphite granules bed [91], etc. Carbon based materials are commonly used as either anode or cathode electrodes or as current collector [114]. They usually have high specific surface area to be offered for the microorganisms [116]. Furthermore, good adhesion properties [18] and remarkably biocompatibility [65] promote the biofilm formation on the electrode surfaces, which is required for the functional bioelectrode [91].

Graphite is a well-known and the most stable allotrope of carbon, which is commonly applied in BES systems [140,141]. The unique structure of the bonds between the carbon atoms offers special benefits for the 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 to each other with weaker van der Waals bonds [142]. This particular layered structure empowers the graphite with unique benefits, like chemical and physical stability, great thermal and electrical conductivity [140,142]. **Graphite electrodes** are the preferred ones among carbon-based BES materials. They are relatively cheap [57] and reusable [65]. There are several commercially available forms of the graphite, for instance; rod [11], block [18], brush [92], plate [143] or sheet [144].

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 [145]. CNTs have unique chemical, electronic, mechanical, and optical properties [146]. They are one of the most promising materials in BES and MFC electrode construction. Because of the excellent biocompatibility, great conductivity, extraordinary huge specific surface (up to 1,315 m^2/g) and adsorbent properties, the CNTs are used in biosensors, MFC systems and other BES applications, although CNT is still a relatively expensive commodity and has potential cytotoxic effect [65,145,147,148]. **Carbon nanotube hollow-fiber** was tested with mixed microbial cultures and 34% higher CH_4 production was achieved relative to the non-electro conductive polymeric hollow-fiber media and a shift in the microbiome was observed as well [149].

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 potentially toxic to fabricate [150]. Although, stability is one of the benefits of carbon-materials, like graphite, Siegert et al. achieved an extraordinary high Coulombic recovery, over 1,100 % [18]. Coulombic recovery over 100% indicate that the product was delivered from external sources, not only from 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 [18,80]. Finally, carbon materials have higher internal resistance compared to metal-based electrodes, which cause a significant energy loss during scaling-up [114].

7.2.2. Metal-based electrodes

Overpotential is one of the major 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 the carbon-based electrodes. They come in various forms, i.e., mesh [151], sheet [96], plate [152], wire [100], etc. Platinum (Pt) is one of the best noble metals for the electrochemical systems, because it is inert and has a low overpotential [153]. At the early times of the MEC technology development, Pt was used commonly as 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 totally replace it with other metals [153]. Promising alternatives are nickel (Ni) [104], titanium (Ti) [154] and stainless steel (SS) [56] 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) [155], but during long-term application their operational stability is low [141]. Relative to the carbon-based electrodes, metal electrodes have a lower specific surface area, low biocompatibility and the risk of corrosion is high [156]. It is fairly complicated to manufacture them in 3-dimensional form, 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 deactivating layer on the surface [65]. Nevertheless, the high mechanical strength and conductivity, are advantageous in large-scale systems [157].

Table 5. The electrical conductivity of various electrode materials. Data are taken from ThoughtCo. (https://www.thoughtco.com/).

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)	$2\text{-}3*10^5$

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 of the pure materials (carbon or metal) have only a few of these 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, the carbon-based materials form the basis and metals are the modifiers, thereby 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 1.7 times relative to the controls [86]. Similarly, a graphite fiber sheet with multiwall carbon nanotubes improved the electrical conductivity upon Ni addition [144]. 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 electrode with carbon deposits is rare, although carbon electrodes are used often with a metal collector, to improve the conductivity [18,77].

Other surface modifications, such as coating [151], oxidation [158] or heating [22] have been tested with mixed results [48,53,58,158,159]. One of the aims in altering the surface of the electrode by coating is to change the electrostatic charge distribution and thereby facilitating the appropriate microbial biofilm formation. Most of the Gram-negative microorganisms have negative surface charge [160], therefore positively charged groups on the electrode surface improves the microbial adhesion to the electrode [65]. Accordingly, Zhang et al. modified carbon cloths with several compounds, i.e. melamine, ammonia, chitosan, cyanuric chloride, 3-aminopropyltriethoxysilane and polyaniline [161] with mostly positive results.

The other aim of the modification with coating is to increase the conductivity. The N-groups in the NH_4Cl interfered with the electrode surface, via changing the porosity of the graphite and the conductivity increased [162].

8. BES operational parameters

Numerous factors and parameters are variable in BES reactors as discussed above. In addition, the introduction of various sludge, substrates, electron donors make the comparison of the systems [114] very difficult. In 2016 Rosa et al. recommended a design for general use but it did not receive widespread acceptance [163]. Several models have been developed instead and the experimental data are fitted to them in order 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 [164]. The modified Gompertz model and a first-order kinetic model predicts the biomethane production precisely [165]. The modified Gompertz model and the first-order kinetic model describe the process with an error of 1.2-3.4% and 4.6-18.1%, respectively.

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

M is the cumulative methane production (mL/g COD), P is methane production potential (mL/g COD), Rmax is maximum methane production rate (mL/g COD $*$ day), λ is lag phase (day), t is time (day), e is the exp(1) = 2.7183 [165,166].

8.2. Coulombic efficiency

Coulombic efficiency is often calculated in the scientific reports and the formula can change according to the authors' definition of coulombic efficiency. Although η indicates the coulombic efficiency in physics [167], in many cases "CE" is used instead of η. CE represents the efficiency of electron utilization for product conversion, taking into account the various losses in a BES system, e.g. thermodynamic, side reactions, recombination of the products, etc. Faraday efficiency (FE), faradaic efficiency, faradaic yield or current efficiency are the frequently mentioned synonyms [96]. To calculate CE there are variations of the basic formula according to the available data sets. A very simple equation [79] is as follows

$$CE(\%) = \frac{mnF}{\int_0^t Idt} \quad \text{(eq. 6)}$$

where m is the number of moles of products harvested, n is the number of electrons required for the formation of 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:

$$CE(\%) = \frac{[m_{CH_4}*n_{CH_4}+m_{H_2}*n_{H_2}]*F}{\int_0^t Idt} \quad \text{(eq. 7)}$$

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 [80].

If the CE represents the electrons utilized to produce a specific product, then current-to-product name is in use as well [112]. For example, current-to-methane calculation:

$$CE(\%) = \frac{n_{CH_4}*z_{CH_4}*F}{\int_0^t Idt} \quad \text{(eq. 8)}$$

n_{CH_4} (mol) is total moles of CH_4 produced; z_{CH_4} is moles of electrons per mole of CH_4 [168].

Optimally CE = 100 %, though there are examples in the literature of higher numbers [25,80,169,170]. 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 [144]:

$$CE(\%) = \frac{\int_0^t Idt}{n*F*\Delta COD*V} \quad \text{(eq. 9)}$$

where n is the stoichiometric number of electrons produced per mole of substrate (24 for glucose),), V (L) is the liquid volume of the reactor and ΔCOD is the removed COD (mol glucose/L) [144]. Other parameters are the same as above.

8.3. Current density

Current density (j) is the amount of charge per unit time that flows through a unit area of a chosen cross section [171]. 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 [51,77]. There are several methods to resolve this situation, such as increasing the conductivity of the catholyte [77], leaving the membrane out from the reactor [18], enrichment of electroactive microorganisms and modification of electrode materials [51].

$$j = \frac{I}{A} \quad \text{(eq. 10)}$$

I (A) is the current, A (m^2) is the projected surface area of the electrode [172]. Alternatively, the current density of the whole system can be calculated, in this case A (m^3) stands for the liquid volume [53].

8.4. Methane production rate

Methane production rate (MPR) gives information about the methane producing capacity of reactors. The formula is used not only in BES [50,91], but conventional AD reactors [173,174] so MPR can be considered as a bridge across the gap between the BES and conventional AD system.

$$\gamma_{CH_4} = \frac{V_{CH_4}}{V_{liquid} * t} \quad \text{(eq. 11)}$$

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) [50,174]. The formula is expressed taking into account the projected surface area ratio.

$$\gamma_{CH_4} = \frac{V_{CH_4}}{A_{proj} * t} \quad \text{(eq. 12)}$$

Here A_{proj} refers to the projected surface area, which could be the membrane, anode, cathode, both electrodes, or all three together [168].

8.5. CO_2 conversion rate

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

$$\eta_C = \frac{m_{C/CH_4}}{TIC_0 - TIC_{end}} \quad \text{(eq. 13)}$$

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) [112].

8.6. Other indicative parameters

Additional parameters are usually considered as less important for the thorough characterization of the BES electrobiomethanation systems although they could be important for the comparison of the various constructs [55]. For example, Reynold number (Re) is used to predict the flow regimes, since it combines viscous and internal forces [175], 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 describe the relationship between the resistance force and inertia force [176]. In reactors, it is commonly used to describe the power requirements for stirring purposes [114].

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 [95]. To achieve electrosynthesis, the microorganisms have to pick-up electrons to use them for the reduction of CO_2 to CH_4 or other 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 [177]. 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 [178]. To achieve DEET, electroactive microorganisms, called electrogens or electrotrotrophs are needed in the system [179]. DEET is achieved via soluble electron shuttles, conductive particles, or direct contact by a cellular structures between the electron donor and electron acceptor partners [177]. If DEET takes place between two microorganisms without any external conductor, the phenomenon is called direct interspecies electron transfer (DIET) [60]. Complex enzyme structures are not required for DEET/DIET, so the speed of the electron transfer is 10^6 times faster than in IEET [66]. Hence the reduction of CO_2 is more efficient, results in higher product yield [4], lower CO_2 content [60] and more stable reaction [180]. The electroactive microorganisms need special structures for the electron conduction, like electroactive pili, c-type cytochromes or archaellum [144,181]

Both mixed [42,84,154,159] and pure cultures [25,55,163,182,183] have been employed in BES applications. The first conclusive evidences for DEET and DIET was made with well-defined co-cultures [16,69]. Since then, *Geobacter sulfurreducens* strain PCA and KN 400 and *Shewanella oneidensis* strain MR-1 became the preferred model organisms of microbial electrochemistry [184]. The experimental potential in sterile cultures is straightforward, there is less unknown biochemical events, while the different microbial metabolism pathways involved in the process is 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 application [31,65]. Up to now, more than 100 microorganisms have been described as electroactive [57], the majority (about 80 %) of them is gram negative [184], and 91% possess biofilm building ability [184]. Biofilm formation was observed after 24 h on the electrode surface [76]. Certain microorganisms act as an anchor to help the attachment of methanogens, while the electroactive microorganisms [166]., for example *Shewanella*, secretes redox shuttles, to improve the electron transfer [57]. In mixed cultures, many microorganisms can accomplish the 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 ≤–0.44V versus NHE	[90]
Acetobacterium spp.	cathode	Most prevalent and active bacteria on the electrode in acetate production	[24]
Clostridium sp.	Bulk solution	Transferred electrons directly to outside electron acceptor	[144]
Geobacter sp.	cathode	Well known DIET partner	[83,166]
Hydrogenophaga sp	cathode	Electroactive bacterium. Its role in electromethanogenesis is unclear	[166]

Azoarcus sp.	cathode	Facultative electroactive, the role in BES needs further investigation	[151]
Tangfeifania sp.	cathode	It is detected frequently in BES reactors, they probably facilitate methanogenesis	[92]
Aminomonas sp.	cathode	Syntrophic methanogen partner electron transfer has not been documented	[92]
Desulfuromonas sp.	anode	Electroactive microbe	[78]
Bacteroidia sp.	Bulk solution	Hydrolyzes proteins and transforms the amino acids generated in the process into acetate	[86]
Azonexus sp.	cathode	Acetate oxidising bacterium, capable for DIET and to DEET, it can be found frequently on anode as well	[93]

Since electroactive microorganisms have an impact on CO_2 reduction [48], enrichment of them enhances the production of valuable commodities [93]. Several approaches have been tested to improve the microbial community in BES reactors, such as applying fixed potential [57], bioaugmentation with pure electroactive cultures, *Geobacter* species [78]. Inocula taken from already running reactors [36], or genetically modified microbes have proven promising results [51]. **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.[24,51,86,93,112,117,143,151,166].

Table 7. Most frequently detected archea in BES reactors.

Archea	References
Methanobacterium palustre	[90]
Methanobacterium aarhusense	[90]
Methanothermobacter thermoautotrophicus	[81,185]
Methanothrix concillii	[29,92,93,186]
Methanospirillum hungatei	[29]
Methanosarcina flavescens	[29]
Methanoculleus bourgensis	[29]
Methanosphaera cuniculi	[29]
Methanobacterium formicicum	[84,86]
Methanobacterium petrolearium	[186]
Methanobacterium subterraneum	[35,186]
Methanosarcina thermophile	[86]

10. Conclusions

1. In this review, we compiled a cross section of the ongoing research on bioelectrochemical systems (BES) with emphasis on the electrochemical biomethane formation. In this endeavor the first observation has been the large number and exponential growth of the relevant scientific publications. In light of the recommenced interest towards renewable energy research and development, this is not surprising.
2. We note that the various BES systems developed in numerous laboratories all over the world, 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 be rationalized as well, when the multitude reactor designs, electrodes, membranes are selected to perform

optimally in specific applications. Unfortunately, the almost chaotic infrastructural assortments make the comparison of the various BES systems extremely difficult. Therefore, it is advised to specify a few "general or basic BES reactor systems" to be included in the related studies as sort of built–in 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 the diverse laboratory studies using a number of reactor designs and components' selection.
4. A consensus is needed regarding the indicator parameters in the evaluation of the various BES performances.
5. Equally important aspect is the need to take into account that all BES systems employs biological components, i.e. pure strains of specific microbes or mixed microbial communities. These microbes do fundamental contribution to the job accomplished and thus they have a great share in the success of the BES electrobiomethanization systems. The complexity of the physiology and biochemistry of these microbial participants significantly alter the success of the electrochemical process. The associated tasks to optimize electrochemistry with microbial fermentation/conversion is 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 many related research.

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