

Review article

CO₂-refinery through microbial electrosynthesis (MES): A concise review on design, operation, biocatalysts and perspectives

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ABSTRACT

Microbial electrosynthesis cells (MES) are devices with demonstrated capability to treat CO₂-containing gaseous streams and alongside, generate certain valuable chemical products, particularly methane gas, carboxylic acids, alcohols, etc. Although there are many varieties of MES with their own individual characteristics, all systems have a lot in common, starting from their design and operational features to the underlying microbiological phenomena. With the support of literature publications and related numerical data, this paper reviews and analyses the most important features of MES to identify general tendencies and practical recommendations pertaining to their design (electrodes, membranes), operation (cathode potential, CO₂ feeding, temperature, pH) and biocatalysts ensuring an enhanced performance. As a result, several key-issues are provided to (i) successfully implement MES setups as well as to (ii) outline the perspectives of the technology towards the further promotion and development of this CO₂-refinery process.

1. Introduction

Microbial electrosynthesis cells (MES) are bioelectrochemical systems in which the reduced value-added products are generated at the anaerobic cathode electrode, usually by relying on the (electrotrophic) CO₂-utilizing biofilm formed there. Meanwhile, the anode reaction is mostly abiotic in the MES. As a matter of fact, the general MES scheme proposes the decomposition of water at the anode by the external energy supplied into the system, resulting formally in O₂, e⁻ and H⁺. In principle, the electrons enter the external circuit connecting the electrodes, and the protons migrate (in most cases through a membrane) to the cathode. Here, they participate in the biocatalysed synthesis of a particular substance with the incoming electrons via the reduction of CO₂ available in the catholyte. The simplest organic molecule in the broad range of products at the cathode is methane [1], realizing simultaneously the “power-to-gas” and “carbon capture and utilization (CCU)” technologies. Additionally, components with higher carbon numbers, such as alcohols (methanol, ethanol), organic acids (e.g., formic acid, acetic acid, propionic acid, butyric acid) and bioplastics (polyhydroxybutyrate, PHB) can also be derived using MES [2–4] as shown in Fig. 1. Furthermore, as auxiliary technologies to MES, other bioelectrochemical systems (e.g. microbial fuel cells, MFC, and microbial electrolysis cells, MEC) can also be used to obtain additional value-

added cathodic products, such as H₂O₂, NH₃ or reduced metals, where the anodic oxidation process is catalysed by electro-active bacteria, while the product synthesis does not necessarily require biocatalyst [5, 6]. Overall, based on the potentials and flexibility of MES in the low-carbon footprint electro-biotechnological production of chemicals, the enormous scientific attention paid to this emerging platform over the last decade or so is fully justified. As a result of the considerable R&D activity, MES – similar to the other representatives of the microbial electrochemical technology (e.g., microbial fuel cells, microbial electrolysis cells) – have been studied in-depth to find the most important factors influencing their effectiveness. Accordingly, it can be inferred that the actual efficiency of the MES is fundamentally determined by (i) the materials the system is built from, (ii) the operating conditions and finally, (iii) the qualities of biocatalysts on the cathode-surface.

Therefore, this review paper is contextualized around the objective of evaluating and presenting the international knowledge relevant to these major characteristics of MES. By assessing the topic in the light of these questions, we aim at the crucial, up-to-date analysis of how the different scientific solutions and strategies could support driving the segment of MES further on the way of technological progression and perspectives.

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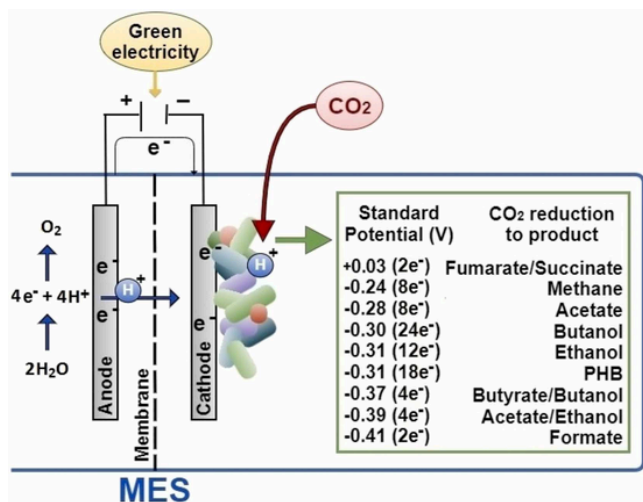


Fig. 1. Electrode potential dependence of cathodic products.

2. Influence of design factors (electrodes, membranes) in Microbial Electrolysis Cells

In the case of MES, most electrode developments focus on the cathode, with less attention paid to the anodes. The anodes used in MES, where water decomposition takes place, are mostly carbon-based, with a high overvoltage for O₂ formation, thus increasing the amount of energy to be invested [7,8]. Bian et al. identified 4 main directions for more efficient (and preferably cheaper) anodes:

1. coating the electrode surface with a small amount of precious metal,
2. using photoanodes,
3. replacing anodic water decomposition reaction to provide e⁻/H⁺ and
4. employing organic material oxidizing bioanodes [9,10].

Regarding cathodes, carbon-based materials are used most frequently, some of which are commercially available and some of them are still in the research and development phase. A detailed list of these materials can be found in the study by Aryal et al. [11]. Overall, the reasons behind favouring C-based materials are their low price, high specific surface area, good corrosion resistance and electrical conductivity, biocompatibility, and flexible manufacturing in a variety of forms [12]. In addition, cathode electrode materials often – and most promisingly in up-scaled technologies – needs to include additional catalyst (e.g. platinum coating) in order to provide hydrogen at sufficient rate for the bioelectrosynthesis [13]. Regarding the distance between the electrodes, Song et al. found (as expected) that keeping it as small as possible (in their work, 8 cm in a conventional H-cell reactor) could increase the current density as well as the volumetric productivity of MES (up to 0.21 g/(L*d) with the example of acetic acid as target product) [14].

Proton/cation exchange membranes (PEM, CEM) are standard solutions for electrode chamber separation, however, Gildemyn et al. [15] suggested that it may be worth extending research to anion exchange and bipolar membranes, as well, due to the ionic composition of the electrolytes of MES. In an acetic acid producer MES operated with an anion exchange membrane (AEM), the authors concluded that this design resulted in greater stability and required less external energy investment [15]. In general, the use of AEM can be advantageous for in-situ product separation of acetate and other compounds from the catholyte, and moreover, the concept of three-chamber reactors (having a recovery chamber between a CEM/AEM pair) can be adopted for further increasing the product extraction efficiency in MES [15,16].

The crucial role of membranes extends not only to accomplishing ion transfer, but also to the aspect of (hindered) oxygen transfer from the anolyte towards the cathode. Either as competitive electron acceptor at the cathode or as an inhibitor for the microbes involved in the electro-synthesis, substantial O₂ transport should be avoided in MES to achieve sufficient product yields and efficiency [17]. Therefore, the cost of membranes in return to oxygen retention is to be paid during reactor construction. Membrane-less designs lack the price and ohmic drop accompanying membrane including MES, however, in order to avoid the presence of O₂ – and the inherent consequences – at the cathode, higher distance between the electrodes has to be kept, which causes further potential losses in the system. In terms of electron utilization efficiency, it was shown in previous works that membrane-less reactors with vertically placed electrodes (O₂-generating anode on the top, cathode and gas flow at the bottom) can eliminate the disadvantageous effects of O₂ [17,18]. Moreover, it was also demonstrated previously that in membrane-less reactors, careful selection of the anode material (i.e. VITO-CoRE™ combined with stainless steel cover) together with sustaining only mild electrochemical activity in the MES could prevent O₂ evolution [19].

3. Influence of operating conditions on the efficiency of Microbial Electrolysis Cells

3.1. Cathode potential

The cathode potential (E_C) has a prominent role in MES to initiate the product formation (via CO₂ reduction) and to influence its rate. As the range of possible products is relatively wide, the distinct potentials must be chosen specifically for the particular target (Fig. 1). In the case of the simplest synthesizable organic molecule, methane, if water decomposition occurs at the anode, the theoretically necessary (practically larger) potential difference between the electrodes, is 1.06 V (pH=7, T = 298 K). For other components, data regarding bioelectrosynthesis – under the same boundary conditions – can be found in the paper of Bajracharya et al. [20]. Accordingly, it can be calculated that the theoretical E_C ranges from –0.24 to –0.48 V depending on the product. The formation of H₂ may also occur at the cathode (–0.414 V vs. SHE, pH=7). This H₂, produced electrochemically (abiotically) under anaerobic conditions, can be used by microbes (using their reversible bidirectional hydrogenase enzymes) to obtain electrons and protons. In this case the cathodic electron transfer mechanism is so-called indirect, mediated by hydrogen gas. It should be noted that H₂ can be also produced biologically by hydrogenotrophic bacteria present in the biofilm, e.g. through the enzymatic decomposition of formic acid (HCOOH = H₂ + CO₂) [21–23]. If such H₂ production occurs at the cathode, it is readily consumed by the cathodic biofilm and is involved in the substrate-product conversion.

E_C has a significant effect on the structure, diversity and efficiency of the resulting biofilm, therefore ensuring optimal E_C is essential. In case of methanogenic biocathode, Li et al. concluded that methane production was predominantly mediated by direct electron transfer in the bioelectrosynthesis cells started-up at $E_C = -0.7 - -0.8$ V (vs. Ag/AgCl, sat. KCl), while at $E_C = -0.9 - -1.1$ V (vs. Ag/AgCl, sat. KCl) values, CH₄ formation was mediated rather by indirect electron transfer [24]. Using a DC power supply (negative terminal: cathode, positive terminal: anode) Flores-Rodriguez and Min [25] investigated the process of methane bioelectrosynthesis in the range of 0.5–1.5 V and marked 1 V as the optimum. By examining the composition of the resulting cathodic microbial consortium, it was concluded that an interdependent (syntrophic) network of H₂-producing and H₂-consuming microbes developed there. The effect of the cathode potential on the acetate production efficiency in MES was first investigated by Mohanakrishna et al. [26], where it was clearly shown that more negative E_C (–0.8 V vs. –0.6 V) lead to significantly higher acetate productivity

(up to ~ 114 mg acetate/(L*d)) and provided more beneficial biofilm formation environment. In the case of organic acid-producing MES, Das et al. suggested that the energy requirements of the process should be considered to determine optimal E_C [27]. In the range of $E_C = -0.6 - -1$ V (vs. SHE), it was found that although more negative E_C is advantageous in terms of acid yields (acetic and butyric acids), it is linked to a higher demand of external energy. Considering this factor, $E_C = -0.7$ V (vs. SHE) was finally determined as the operational optimum for the organic acid production [27]. This kind of approach clearly shows that the cost-effectiveness of MES ultimately depends on the source of the auxiliary energy. Therefore, it may be worth considering (especially in terms of scaling-up) technical solutions where the process is carried out by connecting “green” power from a renewable energy source (e.g., solar energy). In this case, the energy produced in surplus can be stored by producing valuable components (electro-fuels, electro-commodities). In their study, del Pilar Anzola Rojas et al. showed that although the availability of “green” power for the MES operation can fluctuate in time, the microbial community developing on the biocathode and producing acetic acid may prove to be sufficiently robust in response to such a disturbance [28].

3.2. CO₂ feeding

In MES, the CO₂ feeding method is of great importance, since it may determine the formation rate of the products. The solubility of carbon dioxide in the catholyte depends on its composition, temperature and pressure. At 1 bar and 303 K (which is typical for biological systems), its value in water is relatively limited, 1.26 g/kg [29]. Its dissolution rate is influenced by factors such as:

1. the actual dissolved CO₂ concentration,
2. the specific area for mass transfer (determined by e.g. the input mode of gas bubbling) and
3. its consumption rate at the cathode.

According to the research of Mohanakrishna et al., the substrate concentration in MES also affects the rate of cathodic reaction as well as the product titre [30]. According to their results, raising the initial bicarbonate (substrate) concentration from 1 g/L to 4 g/L increased the rate of acetic acid production by approximately 4–5 times, and after 7 operating cycles the acetic acid concentration could be increased to 5 g/L (as opposed to 1.2–1.3 g/L in case of 1 g/L initial bicarbonate concentration). In a research by Dessi et al., various MES operating strategies were investigated, with CO₂ bubbling and NaHCO₃ feeding, fixing the cathode potential ($E_C = -1$ V vs. Ag/AgCl) [31]. According to their results, the efficient production of acetic acid and butyric acid required the suppression of methane producers using a chemical inhibitor (bromoethanesulfonic acid, BESA, 0.5 g/L in the catholyte), and the best acid productivity was obtained by the direct CO₂ feeding method (2.54 g CO₂/(m² × d) relative to the cathode surface area). Interestingly, the biofilm structure on the cathode surface was inhomogeneous and the electro-trophic microbes were physically closer to the current collection point. In order to feed CO₂ to the reactor efficiently, Bian et al. wrapped the cathode around a porous ceramic fibre, thus, allowing direct access for the microbes to CO₂ [32]. By varying the CO₂ dosing, it was found that higher flow rates in the range of 0.3–10 mL/min had a positive effect on acetic acid and methane production, and the cathodic biofilm was sufficiently stable when gas flow was interrupted, which could occur in real conditions as a result of operational uncertainties [32]. Del Pilar Anzola Rojas et al. [33] also found that higher CO₂ flow increased the productivity of MES, but underlined that the structure of the cathode could significantly affect its optimal value. As the development of MES is desirable for real industrial applications, it is needed to conduct research with real gas samples that contain other pollutants in addition to CO₂ instead of the pure CO₂ used in most labo-

ratory tests. For this purpose, Roy et al. examined the behaviour of MES using a feed gas mixture containing CO₂, N₂, O₂, and various aliphatic and aromatic hydrocarbons. Their results suggest that mixed-culture cathodic biofilms are more suitable for the treatment of these types of gases in MES thanks to their greater flexibility against contaminants, e.g., oxygen [34].

3.3. Temperature and pH

Regarding the operation of the MES, the effect of temperature and pH on the efficiency of MES should be investigated. Although, similar to the MFC and MEC systems, the mesophilic temperature range is the most typical, some studies suggest that it may be appropriate to systematically examine and adjust the temperature optimum for strains growing in cathodic biofilm. In this way, Faraghiparapari and Zengler demonstrated increased productivity of acetic acid at 60 °C by using *Moorella thermoacetica* and *Moorella thermoautotrophica* thermophilic microbes [35].

The effect of catholyte pH on product formation is complex. On the one hand, it affects the CO₃²⁻ ↔ HCO₃⁻ ↔ H₂CO₃ balance, i.e. the available number of protons, and on the other hand, the growth and metabolism of the strains in the cathodic biofilm is also affected by the pH. Regarding the impact of pH in bioelectrochemical systems, encompassing bioelectrosynthesis cells too, the recent paper published by Zeppilli et al. [16] could give some useful insights.

Actually, Battle-Vilanova et al. found that controlling the pH in MES at 5.8 made the formation of acetic acid thermodynamically more favourable and also met the needs of homoacetogenic bacteria, which prefer mainly slightly acidic media [36]. The effect of pH is also reflected in the spectrum of products formed, since, for example, acetic acid production can be shifted towards the formation of butyric acid by the so-called chain elongation reaction if the pH is low enough, and the partial pressure of H₂ is sufficiently high [37]. It is noteworthy that the pH can influence the product separation, as well, since it affects the behaviour of the charged molecules. Actually, using a membrane electro-dialysis technique, acids (as a function of their protonation) can be separated from the medium, as a relevant system was shown by Gildemyn et al. in connection with MES for producing acetic acid [38]. This technique was successfully applied for in-situ recovery of organic acids from a biohydrogen fermentation effluent, thereby increasing the stability of the process [39]. Furthermore, in the work of Bajracharya et al. an anion exchange resin (Amberlite™ FPA53) was found appropriate to extract and concentrate acetic acid (and prevent, thus, any inhibitory effect caused by its accumulation) over a longer period of time covering several consecutive production cycles [40].

4. Biocatalysts at the cathode of MES

A key-aspect for efficient cathodic CO₂ reduction is the supply of electrons to microbes as whole-cell biocatalysts used in the vast majority of MES. The electron transfer can take place using a mediator molecule or via direct mechanism. In the case of mediated electron transfer, a chemical component transports the electron picked up from the electrode to the cells. H₂ and/or formic acid (produced electrochemically and/or biotically at the cathode) play the role of electron donors in cases where the process takes place through an intermediary molecule. In the case of direct electron uptake, the electro-trophic microbes – connected to the cathode surface – directly utilize the available reducing power.

The cathodic biofilm typically contains methanogens, acetogens, and in some cases aerobic strains, which can be used alone or as part of a microbial consortium [6]. From the viewpoint of the (planktonic and immobilized) microbes present in the mixed culture MES, the high-throughput DNA sequencing techniques targeting e.g., the 16 S rRNA gene could be deployed for delivering fundamental understanding of

community interactions and population dynamics [41]. Certainly, the product portfolio in MES is notably determined by the properties of the underlying microbial population and their active metabolic pathways. Accordingly, several components may simultaneously appear at the cathode, e.g., acetate, methane, solvents such as ethanol and organic acids (e.g. propionic- and butyric acids) [26].

During the synthesis, the rate of the cathodic product formation is directly dependent on the generated (negative) current density. In this regard, research has concluded that instead of two-dimensional cathode structures, the use of three-dimensional electrodes capable of adhering specifically larger mass of active biomass (biocatalyst) is expedient [42]. The most typical products of MES are methane and acetic acid, however, it is also possible to produce other components with longer carbon-chain (Fig. 2), and the central molecule of the chain elongation (and thus, the product formation) cascade is the acetyl coenzyme A [43]. The synthesis of most target molecules takes places through the energetically favourable Wood-Ljungdahl metabolic pathway [44]. Microbes with the ability to generate these compounds can convert short-chain organic acids to medium-chain organic acids through reverse β -oxidation. Starting from acetic acid, C₄, C₆ and C₈ derivatives, while from acids with an odd number of C-atoms (e.g., propionic acid) C₅, C₇ derivatives can be synthesized [45]. Kracke et al. highlighted a selection of bacteria being the most promising to diversify the product spectrum of MES (underlining also the potential of metabolic engineering to further improve the process) [46]. This includes a series of species belonging to the class *Clostridia*, for instance *C. autoethanogenum* (ethanol), *C. beijerinckii* (iso-propanol), *C. caboxidivorans* (acetone), *C. tyrobutyricum* (butyrate), *C. acetobutylicum* (butanol) and *C. ljungdahlii* (2,3-butanediol) [46].

By taking up electrons at the cathode, microbes are able to increase the amount of available NADH ($\text{NAD}^+ + \text{H}^+ + \text{e}^- = \text{NADH}$) reduced coenzyme (electron carrier). This has a positive impact on the yield of more reduced metabolites, e.g., by the reduction of carboxylic acids (acetic acid, butyric acid) as terminal electron acceptors to the corresponding alcohol (carboxylic acid + $n\text{e}^- + n\text{H}^+ = \text{alcohol}$) [47]. Furthermore, the research of Izadi et al. showed that besides the polarized cathode (-1 V vs. Ag/AgCl) as an electron source, the addition of formic acid and ethanol as chemical electron donors may be advantageous for the chain elongation reaction [48]. For greater selectivity towards acid molecules with higher carbon numbers (butyric acid, caproic acid), Jourdin et al. recommended the operation of a continu-

ous MES ($E_c = -0.85$ V vs. SHE) with higher CO₂ load (173 L CO₂/d) and shorter hydraulic residence time (14 days) [49]. Resulting from the forced convection flow and continuous, fast supply of nutrients, a more robust cathodic biofilm had developed, which was capable of higher electron uptake rates, and thus, was more productive [49]. In contrast, the results of Das and Ghangrekar, according to which in the case of acetic, propionic and butyric acid-producing MES have shown that the batch mode resulted in better product yield compared to the continuous reactor [50]. The authors mentioned the higher CO₂ and H₂ retention achieved in batch mode (led to better availability for the microbes) as the reason behind the phenomenon [50].

Furthermore, Mateos et al. achieved increased acetic acid production by continuously recirculating the cathode-side headspace gas (containing CO₂) to the catholyte, thus, at a utilization rate of 171 mL CO₂/L-d, 261 mg acetic acid/L-d productivity could be attained [51]. In addition to acetogenic microbes (*Sporomusa*, *Clostridium*), *Desulfovibrio*, *Pseudomonas*, *Arcobacter*, *Acinetobacter* and *Sulfurospirillum* strains were present in the cathodic biofilm [51]. In terms of reactor stability of MES producing acetic acid, butyric acid and isopropanol, Arends et al. pointed out that the key to adequate long-term production was to control the hydraulic residence time, together with the appropriate adjustment of the catholyte pH [52]. The pH control of the catholyte (in the acidic range) can also play an important role (the product itself, e.g., acetic acid, can also contribute to this) in the elimination of competing methanogens. For this purpose, Bajracharya et al. proposed a multi-step, sequential inoculum selection and enrichment method for reducing methanogenic activity that does not require the use of specific chemical inhibitors during MES operation [53]. Enrichment and acclimatization of homoacetogenic microbes to higher bicarbonate concentrations also proved to be a suitable strategy in the research of Mohanakrishna et al., by which a maximum acetic acid titre of 15 g HCO₃⁻/L could be obtained [54]. If the goal is methane production, the so-called power-to-gas concept can be implemented in MES, by which the electrical energy can be stored in form of chemical energy [55].

Although the already discussed whole-cell biocatalysts are employed most frequently in MES, the use of immobilized enzymes also shows an increasing tendency. In this aspect, substrate-specific enzymatic cathodes mainly contain enzymes belonging to the oxidoreductases, which take up electrons from the electrode either by a direct or indirect (cofactor e.g., NADH, e⁻-transport molecule) mechanism. Enzymes that have been studied more widely so far include:

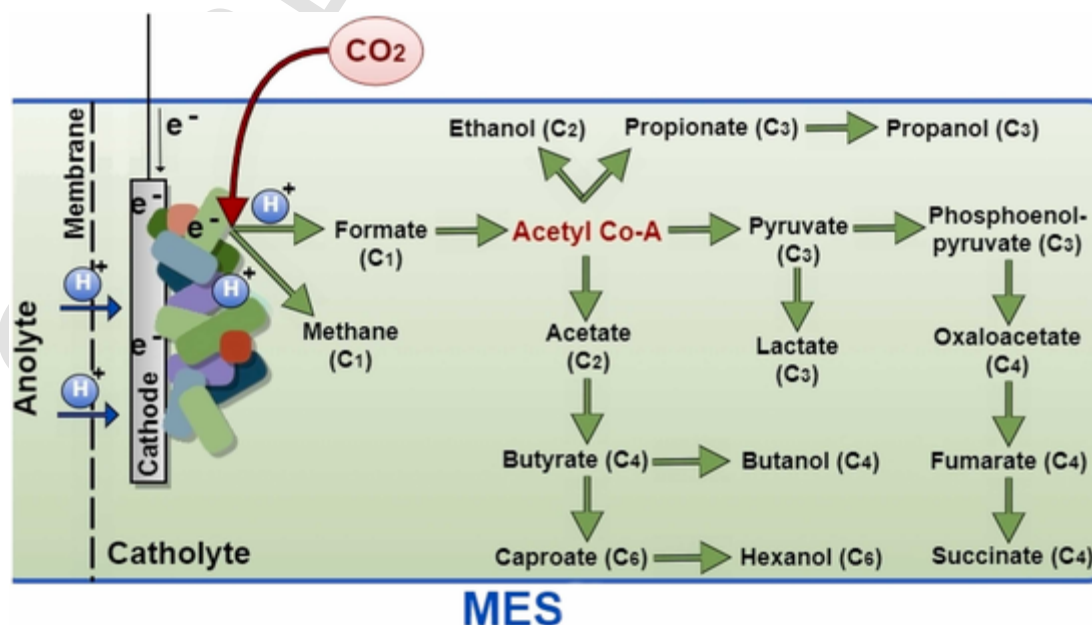


Fig. 2. Main biosynthetic chain elongation routes for cathodic products. (adapted with changes from Jiang et al. [43]).

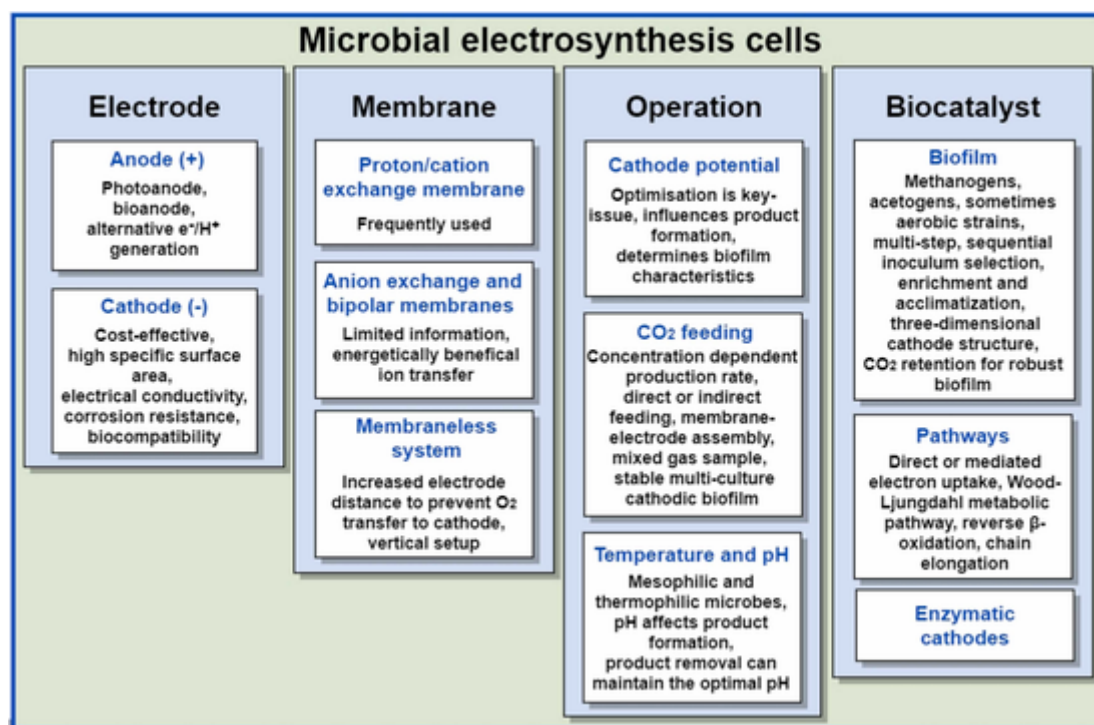


Fig. 3. The outline of operational and design factors to be considered for efficient microbial electrosynthesis.

1. formate dehydrogenases, which reduce CO₂ to formic acid and
2. nitrogenases, which convert N₂ to ammonia.

However, there are several more “exotic” examples in the literature which result in alkanes, polyhydroxybutyrate, etc. [56]. Furthermore, the use of carbonic anhydrase enzyme is gaining ground, as it accelerates the dissolution of CO₂ in the catholyte, and its presence has a beneficial effect on e.g., product formation by the formate dehydrogenase enzyme [57,58].

5. Perspectives

In the light of the above cited literature, diverse research work needs to be done to improve MES characteristics. The most essential aspects and developmental directions are summarized in Fig. 3. Additionally, in Table 1, tendencies of microbial electrosynthesis cells based on

Table 1 –

Number of MES themed articles published in the last 5 years. The search was made in the Scopus database using “microbial electrosynthesis cell” with different additional words listed below.

additional searching word	number of studies published (2017–2022)
cathode development	26
anode development*	9
membrane development	14
anion exchange membrane	8
cation exchange membrane	9
bipolar membrane	3
membraneless	1
free /extracellular/immobilized enzyme	12
formate dehydrogenases	5
optimization	22
membrane optimization	2
electrode optimization	15
operation optimization	4
microbiological/biocatalyst optimization	4

*There is no result between 2021 and 2022

the last 5 years could be observed. Although relatively wide and valuable knowledge has been collected in the recent years related to the operational parameters of MES (such as the effect of cathode potential, the C-source type and reaction conditions), the next phase of MES development and industrialization must rely on discoveries and technical solutions in material science, mass transfer and biocatalysis aspects of the systems. It can be said that electrodes and membranes should be optimized based on general considerations (e.g. high electrode surface area, sufficient ion exchange features, etc.) and at the same time, they should also be adjusted according to the desired operational mode and additional process parameters. The scale-up of MES will require a robust reactor design, which not only underlines the need for cost-effective parts and components, but also the potential exclusion of some of them, such as in case of membrane-less designs. In addition, further fundamental studies should evaluate the effect of the mass transfer of various compounds on the bioelectrosynthesis performance, as well as on the product recovery. Then, the effect of the overall system design on the biological apparatus ought to be understood extensively and investigated to fine-tune microbial electrosynthesis. Although the proposed objective requires significant innovation and research capacities, a successful accomplishment may contribute to a paradigm-shift, where microbial and conventional electrochemical processes powered by renewable energy and feedstocks are in the centre of a sustainable bioproduct generation chain. This concept (Fig. 4) can be realized in the so-called electro-biorefineries [59,60]. Such a technological approach was proven appropriate to produce not only acetate or methane, but biomass-based high-value chemicals, among others, drop-in fuels [61], polymer bricks such as C₅-dicarboxylates [62] or muconic acid [63,64], chiral alcohols [65], ectoine [66] and volatile fatty acids [67]. In addition to the proper design and operation of MES, the extension of the bioproduct variety can further accelerate their envisaged industrial deployment.

6. Conclusions

The main design-, operational- and microbiological aspects of MES and their developmental strategies were assessed and presented in this work. It can be concluded that establishing an attractive MES technol-

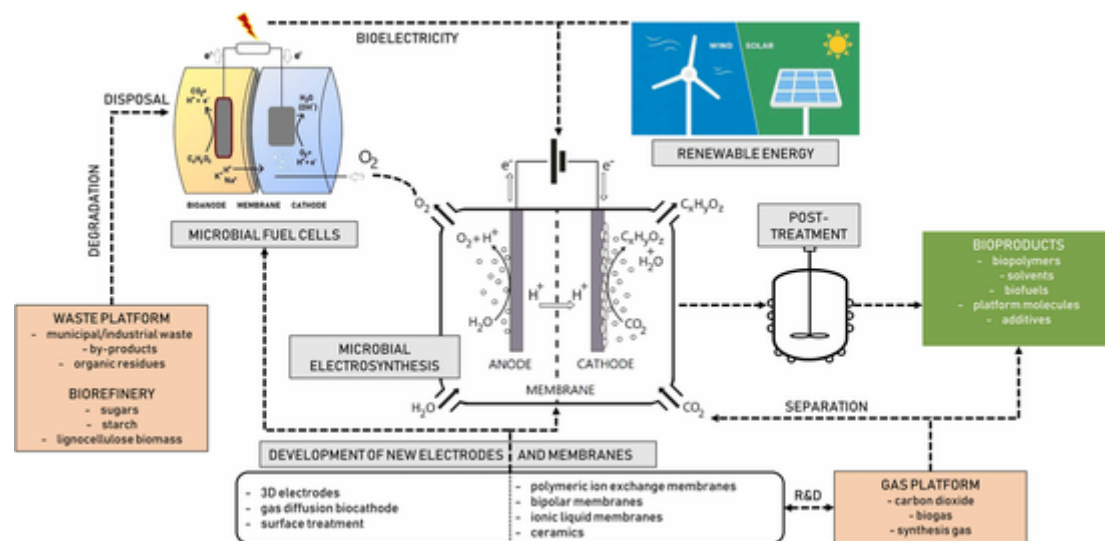


Fig. 4. Comprehensive scheme of electro-biorefineries for the production of value-added compounds.

ogy, which fits the concept of sustainable green chemical technology, requires optimization in these areas. Advanced electrodes and membranes can further improve the utilization efficiency of CO₂ feedstock, while targeted control of the operating conditions and knowledge of their effects on microbes and associated metabolic pathways are essential to diversify the spectrum of electro-commodities and hence increase the wider implementation of the MES as part of the bioelectrochemical platform.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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