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Investigation and comparative analysis of materials, efficiency, and design in microbial electrolysis cells for biomethane production

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ABSTRACT

The escalating global demand for energy and the imperative to address greenhouse gas emissions have spurred the exploration of alternative energy sources. Microbial Electrolysis Cells (MECs) have emerged as a promising technology, converting organic compounds into electrical energy and hydrogen gas. A recent breakthrough, namely a hybrid (H-MEC) system, integrates electromethanogenesis to convert CO_2 to methane, offering a novel avenue for efficiently harnessing renewable energy and mitigating emissions. This paper underscores the significance of optimizing the design, materials, and operational strategies to enhance the scalability and efficiency of MEC-based electromethanogenesis. Traditional anaerobic digestion processes, converting biomass residues and food waste into hydrocarbon bioenergy, are being redefined through the integration of H-MECs. This integration presents opportunities for improved effluent treatment, heightened methane production, and the generation of valuable compounds. Recent studies reveal the remarkable ability of ionic conductivity and electrochemical reactions within bacteria to synthesize hydrocarbons, emphasizing factors such as microbes, biofilm development, substrates, and electrode surfaces for amplified methane yields. H-MECs demonstrate exceptional versatility in consuming diverse substances, notably untreated food waste, positioning them as potent microbial biocatalysts. The diligent exploration of this domain has given rise to various H-MEC technologies for hydrogen generation and carbon dioxide reduction. This review delves into the mechanisms and methodologies of H-MECs for electromethanogenesis through varied biochemical reactions, shedding light on single or double-chambered MECs

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and reactor materials. Furthermore, it elucidates the production of methane and hydrogen via the hydrogen and organic water evolution process coupled with catalyst support systems. By comprehensively exploring H-MECs, this review contributes to a nuanced understanding of their potential and implications in advancing sustainable energy solutions and achieving emissions reduction goals. The integration of electromethanogenesis into MEFCs holds promise for ushering in a new era of cleaner energy production and environmental sustainability.

1. Introduction

Since the dawn of the 20th century, the world's energy demands have been predominantly met using fossil fuels, including coal, oil, gas, gasoline, and their derivatives [1]. While these resources have played a pivotal role in the global energy market, the finite nature of both renewable and non-renewable fossil resources is becoming increasingly evident. The relentless consumption of these energy sources, coupled with their finite availability, poses a significant risk of depletion within approximately 35 years [2]. Moreover, the combustion of fossil fuels has been linked to substantial environmental hazards, particularly the emission of carbon dioxide (CO_2) and other harmful gases, contributing to global warming and the acidification of bodies of water [3].

In response to the urgent imperative of mitigating environmental challenges associated with conventional energy sources, there is a growing emphasis on exploring carbon-free renewable technologies. Among these, H-MEC has emerged as a promising and ecologically friendly approach to energy generation. H-MEC operates by harnessing electrical energy through the catalytic conversion of chemical energy derived from diverse sources, including food waste, cellulosic materials, and wastewater, employing a biological electrocatalyst [4]. This interdisciplinary field integrates electrochemical processes, nanotechnology, microorganisms, and analytical chemistry to optimize energy conversion efficiency. The key innovation lies in the use of biological electrocatalysts, typically microorganisms, which play a central role in enhancing the overall efficiency of energy conversion [5]. By leveraging organic waste materials and integrating nanotechnology, H-MEC not only provides a sustainable and eco-friendly energy solution but also contributes to waste management and aligns with the broader global shift toward circular economies and regenerative practices. The emergence of H-MEC exemplifies a holistic and multidisciplinary strategy aimed at meeting the challenges of sustainable energy generation while minimizing environmental impact [6].

In an H-MEC, the oxidation of liquid occurs at the anode chambers, producing protons and electrons that are subsequently transferred to the cathode chamber under the influence of an external voltage differential. Redox processes occur at the cathode chamber in the presence of electrochemically active microorganisms [7]. Microbial Electrochemical Systems (MESs) encompasses various configurations such as microbial electrolysis cells (MECs), microbial desalination cells (MDCs), microbial fuel cells (MFCs), and microbial solar cells (MSCs), each tailored based on reactor structure, ambient conditions, and intended outputs [8-10]. While MFCs can generate energy from aerobic wastewater, MECs require an external electrical source to produce hydrogen from natural wastewater. MECs stand out for their proficiency in generating fuel and electricity from organic substances, providing renewable hydrogen, valuable products, and organic pollutant removal from wastewater in an energy-efficient, cost-effective, and environmentally friendly manner [11].

Although hydrogen has historically been the primary metabolic fuel produced by MECs, recent scientific attention has shifted towards methane (CH_4) production [12]. Biomethane (BioM), a sustainable fuel traditionally derived from the anaerobic decomposition of organic bio-waste, has garnered interest due to its potential as a clean energy source. Unlike traditional biomethane production processes that take several days, recent advancements in microbial electrochemical systems have facilitated the collection of CH_4 via

CO_2 electromethanogenesis, particularly during the hydrogen generation stage in MECs [13]. The production of BioM in MECs is influenced by various factors, including reactor design, substrate, inoculum, and catalyst loading, with methanogens playing a crucial role in the process. Efforts to reduce the formation of methanogens in MECs have been explored, but many existing methods are energy-intensive and often ineffective [14].

MECs present a marked departure from traditional anaerobic digestion (AD) methods, particularly in their approach to methane production. Unlike AD, which relies heavily on substantial amounts of organic material for microbial decomposition and subsequent methane generation, MECs offer a more direct and efficient pathway. This key distinction allows MECs to generate methane without the need for large quantities of organic matter, streamlining the process and enhancing versatility [15]. An additional operational advantage of MECs lies in their ability to operate effectively at room temperature, eliminating the necessity for external heating. This not only reduces energy input requirements but also simplifies the overall operational setup, contributing to improved energy efficiency and cost-effectiveness [16]. Furthermore, MECs exhibit notable resistance to hazardous chemicals, making them more resilient in the face of potentially inhibitory substances compared to anaerobic digestion processes. This resilience expands the scope of MEC applications, allowing for the efficient handling of diverse organic substrates, including those with complex compositions or contaminants [17]. The direct methane generation capabilities, operational efficiency, and chemical resilience of MECs position them as a promising and versatile technology for sustainable methane production with implications for a range of environmental and industrial applications.

This study delves into the expanding role of MECs in biomethanation, elucidating their function as a Microbial Electrochemical System aided by technologies such as nanoparticles and the hydrogen evolution reaction (HER). The paper provides a comprehensive exploration of the generalized mechanism of electromethanogenesis, including its electron transport technique. Furthermore, the characteristics of MECs, encompassing design, setup, reactor components, microbial species, and process parameters, are thoroughly examined to contribute to a deeper understanding of the potential and implications of MECs in advancing sustainable energy solutions and addressing environmental concerns.

2. MEC microbial pathway for enhanced BioM production

In the pursuit of enhancing biomethane production and mitigating environmental pollution, advanced designs, materials, and microbial strategies are crucial elements in the optimization of MECs. Innovations in MEC design involve exploring three-dimensional electrode configurations and biofilm-enhancing surfaces to maximize microbial activity and electron transfer efficiency. Concurrently, using novel electrode materials, such as conductive polymers and catalytic coatings, aims to improve conductivity and catalytic properties, thus enhancing biomethane yield. Additionally, investigating the synergistic effects of various microbial communities, including microbial consortia and genetically engineered strains, offers the potential to optimize electrogenic bacteria for methane production. This integrated approach addresses multiple facets of MEC functionality, fostering a sustainable and efficient system for biomethane generation while contributing to the broader goal of environmental sustainability. In conventional MEC systems, as illustrated in Fig. 1, there is a structural configuration comprising an anode and a cathode compartment, separated by a proton exchange membrane. Within the anode compartment, microorganisms, predominantly bacteria, play a pivotal role. These microorganisms engage in the oxidation of organic compounds, releasing electrons that are subsequently transferred to the anode electrode [18]. The electrons traverse an external circuit to reach the cathode electrode, where they combine with protons and oxygen to form water. Depending on the operational conditions, hydrogen gas can also be generated at the cathode. The performance of MEC systems is subject to various influencing factors, encompassing the types of microorganisms in the anode compartment, the organic substrate utilized, reactor design, and operational parameters [19].

Additionally, the choice of anode electrode material holds significance, impacting the efficiency and longevity of the system. Commonly employed anode materials include carbon-based options such as graphite or carbon cloth and metal-based materials like stainless steel or titanium. However, their efficiency is limited by several factors, including low current density, slow reaction rate, and high energy consumption [20]. New approaches have been developed to overcome these limitations, including hybrid MEC systems that incorporate additional steps, such as electromethanogenesis, to improve the efficiency and productivity of the system. MECs are a concept established from MES with an AD system in which an external voltage is utilized to exceed the metabolic potential barrier in order to drive biological processes.

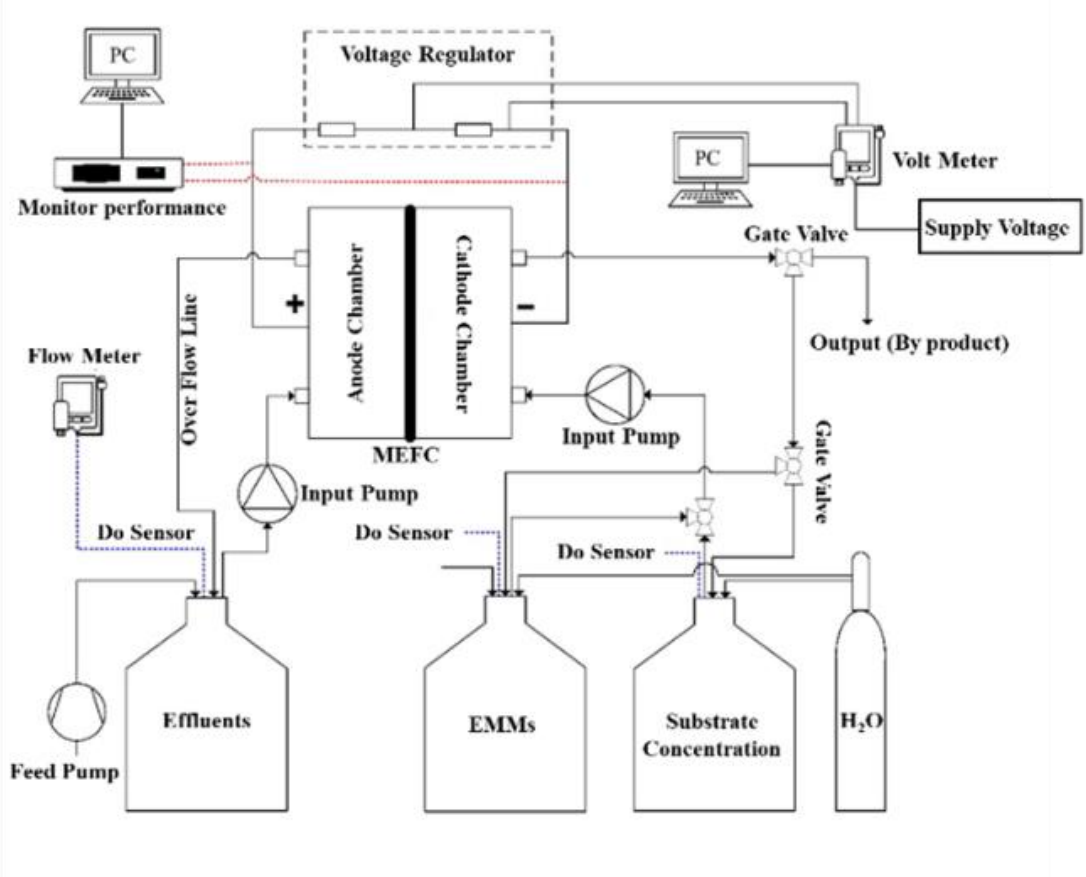


Fig. 1. Schematics of a two-stage bioelectrochemical system [12].

In AD, organic substances undergo decomposition in an oxygen-free environment, resulting in the production of a gas mixture termed biogas. This biogas comprises methane (50–70% volume), carbon dioxide (25–50% volume), and small amounts of hydrogen, hydrogen sulfide, ammonia, and various trace gases. Electromethanogenesis produces BioM in two different ways: directly through the uptake of electron density from an electron beam, as represented in Eq. 1, or indirectly through the production of hydrogen as well as other molecules, including acetate and formic acid, which are then mixed with CO_2 to form BioM and water as shown in Eqs. 2 and 3 [16].

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \rightarrow 240mV \text{ (Direct electromethanogenesis)} \quad (1)$$

$$2H^+ + 2e^- \rightarrow H_2 \rightarrow 400mV \text{ (Indirect electromethanogenesis)} \quad (2)$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (3)$$

Microorganisms that consume hydrogen exhibit the capability to receive electrons directly from the cathode, facilitating exclusive direct electromethanogenesis. On the other hand, methanogenic microorganisms present in the biocathode play a crucial role in both direct and indirect electromethanogenesis[17]. MECs that produce biomethane are made up of four core parts: anode, biocathode, ion exchange membrane, and voltage supplier, as depicted in Fig. 2. As shown in Fig. 2, MECs minor components include a water storage tank, a microbial storage tank, an electrode, a connecting pipe, a ball valve, a methane gas chamber, a pump and gas measuring meter, etc. Firstly, the anode undergoes oxidation, which is required to produce electrons for carbon dioxide reduction in the biocathode surface area. Furthermore, the biocathode is a key component in which methane is created with the aid of bacteria utilizing electrons supplied by the anode oxidation process.

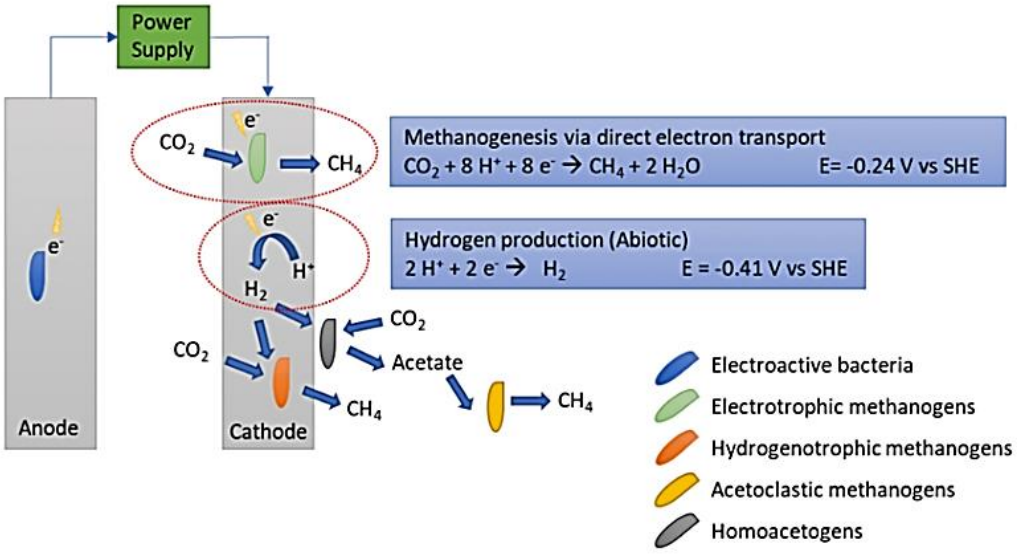


Fig. 2. Diagrams of a characteristic H-MEC [1].

An ion exchange membrane is required for ions with positive charges, such as H+, to migrate from the anodic to the cathodic chamber of the H-MEC system. Finally, external power electrical energy is essential to thermochemically drive the process. For the electrochemical conversion method to create BioM, a modest voltage source, such as a range of 100mV – 1000mV, is required [17]. Bacterial constructions in the microbiological storage tanks comprise mainly negative bacteria and Escherichia coli species. The bacteria's normal metabolism is used to make CH_4. Bacteria turn the substrates to create electrons. This method is an innovative and promising technique for converting CO_2 into sustainable biofuel (CH_4). Charged particles and ions are used by cathode oxygen, such as O_2, and create water at the cathode. To address the current issue, MFC may be more appealing. The table presenting electroactive microorganisms utilized in H-MECs for BioM yield (Table 1) highlights the diverse substrates, microbial species, morphologies, and applied voltages associated with microbial electrochemical cells (MECs). This overview underscores the critical role of electrogenic microorganisms such as Methanobacterium sp., Methanosaeta sp., and Geobacter sp., each exhibiting distinct electroactive properties and morphological traits [18,19,24]. Table 1 also differentiates between single-chamber and two-chamber MEC configurations, illustrating the variety in applied voltages ranging from 0.14 V to 0.85 V [25,27]. These distinctions provide insight into how substrate specificity and microbial characteristics influence MEC performance, showcasing the potential of electroactive microorganisms in optimizing bioenergy production [20,22].

Table 1. Electroactive microorganisms utilized in H-MECs for BioM yield.

Substrate	Electrogenic microorganisms	Electroactive Microbes Shape	MEC	Applied Voltage	Ref.
Food waste and Sewage sludge	*Methanobacterium sp.,*	Gram-negative, nonmotile, rod and shaped, obligately aerobic, and facultatively.	Two chamber MEC-AD, and single AD	0.4 V	[18]
	Methanosaeta sp.	Gram-negative, rod-shaped and non-motile, occurring singly or in pairs.			
Anaerobic digester sludge	*Methanobrevibacter sp.*	Gram-positive organisms form pairs, straight rods, helical chains and coccobacillus shapes.	Two chamber MEC	0.7V	[19]
Leachates Industrial waste	*Desulfuromondales sp.,*	Characterized by strict anaerobiosis, a rod-shaped morphology, lateral flagellation, and Gram-negative classification.	Two-chambered MEC-AD	0.7 V	[20]
	Pseudomonas sp	Gram-negative, rod-shaped, asporogenous, and mono-flagellated bacterium.			
Metropolitan wastewater	*Methanobacterium sp.*	In electron micrographs, the appearance ranges from rod-shaped, curved, or twisted rods to long and filamentous structures, all of which are characterized as gram-positive.	Two-chambered MEC-AD	0.8 V	[21]
Waste activated sludge	*Clostridium sp.*	Bacteria with a gram-positive classification, displaying a rod-shaped morphology, and demonstrating both spore production and motility through flagella.	Single-chamber membrane-free MEC and non-MECs	0.6V	[22-24]
	Methanocorpusculum sp.	Regular and irregular coccoidal cell shape and gram-negative.			
	Geobacter sp.	Rod-shaped, motile, gram-negative, and anaerobic bacterium			
	Methanosarcina sp.	Cocci with irregular shapes were found to be gram-negative and occurred either individually or in pairs. The cells were characterized by a lack of motility.			
Acetate	*Geobacter sulfurreducens sp.*	A rod-shaped, obligately anaerobic proteobacterium that reduces metals and sulfur, belonging to the Gram-negative category. Additionally, it is non-fermentative and possesses a flagellum.	Two chamber reactors.	0.85 V	[25]

Alkaline pretreated sludge	*Methanosaeta Sp.*	Gram negative, rod-shaped, non-motile, and usually found singly or in pairs.	Two identical MEC-AD reactors.	0.8 V	[26]
MR-1 Acetate	*Shewanella oneidensis sp.*	Gram-negative proteobacteria that are typically rod shaped.	Double chamber MFCs	0.14V	[27]

AD connected H-MEC-based electroactive microorganisms are shown in Table 1 for BioM production. Exoelectrogenic microorganisms metabolize organic materials in an MEC, producing CO_2, ions, and protons. The microorganisms deliver charged particles to the anode and produce protons into solutions. In principle, producing hydrogen at a MEC's cathode requires just approximately 0.1 V of independent power. Hence, owing to the over-potentials experienced at the electrodes, a voltage of 0.3 V or higher is necessary. This electrical input is significantly lower than the usual 1.8 to 2.0 V required for the process of water oxidation.

3. Principle of MECs materials innovation for CO_2 capture

In the quest for sustainable and environmentally conscious MECs, a pivotal focus lies in the development and characterization of novel materials for electrodes and membranes. The objective is to enhance the durability, selectivity, and overall performance of these critical components within MEC systems [28]. To achieve this, researchers are actively engaged in exploring advanced materials with properties that extend the lifespan of electrodes and membranes, withstand harsh operational conditions, and exhibit improved selectivity in terms of electron transfer and ion transport. Innovations in electrode materials include the investigation of conductive materials like graphene, carbon nanotubes, and advanced metal oxides. These materials not only bolster the electrical conductivity essential for efficient electron transfer but also contribute to the longevity of the electrodes [29]. Catalytic coatings on electrodes are being explored to improve their efficiency in facilitating reactions crucial for biomethane production. Simultaneously, there is a concerted effort to minimize the environmental footprint of MEC systems by incorporating sustainable and eco-friendly materials [30]. This involves scrutinizing the life cycle impact of materials, considering factors such as resource extraction, manufacturing processes, and end-of-life disposal. Researchers are exploring the use of biodegradable and recyclable materials, as well as those derived from renewable sources, to reduce the environmental impact associated with MEC technology [31]. By advancing materials science in MECs, the research community aims to develop components that not only enhance performance but also align with broader sustainability goals. This approach involves a holistic consideration of the environmental implications of materials throughout their life cycle, ultimately contributing to the development of MEC systems that are both efficient and environmentally responsible [32]. CH_4 growth response involves a classical two-electron transfer reaction with a singular catalytic stage, ultimately yielding CH_4 and capturing CO_2, as depicted in Fig. 3.

This process has the potential to establish the long-term viability of BioM production, characterized by its transferability, reusability, and adaptability in zero-emission conventional combustion fuel cells. The generation of hydrogen through BioM production H-MECs represents a sustainable technology, allowing for the production of BioM production from natural materials such as food waste under the influence of an electric charge [33].

4. Utilization of novel electrode materials investigated

In the quest to advance MECs for BioM production, the exploration of novel electrode materials is crucial. Materials like graphene, carbon nanotubes, and conductive polymers are being actively researched to enhance electrode conductivity and catalytic properties [31]. With its exceptional electrical conductivity, graphene facilitates efficient electron transfer, promoting enhanced biomethane yield [32]. Similarly, carbon nanotubes improve conductivity and serve as favorable scaffolds for microbial attachment, aiding biofilm formation. Conductive polymers

blend flexibility with electrical conductivity, enhancing electron transfer kinetics. Metal oxides and composite materials offer opportunities to optimize catalytic activity [33]. These materials not only boost MEC performance but also align with sustainable principles, marking strides in bioenergy technology, as shown in Fig. 4. Graphene, carbon nanotubes, and conductive polymers are chosen for their outstanding electrical conductivity, significantly impacting electron transfer efficiency in MECs [34]. Graphene, a hexagonal lattice of carbon atoms, serves as an excellent conductor with a large surface area for microbial adhesion, enhancing electron exchange [35]. Carbon nanotubes, cylindrical structures with high conductivity, improve electron transfer and provide a framework for microbial attachment [36]. Conductive polymers like polyaniline enhance electron transfer kinetics, promoting sustained electrogenic activity. The use of advanced conductive materials in MEC electrode design improves electron transfer kinetics, creating a symbiotic relationship between microorganisms and electrodes [37].

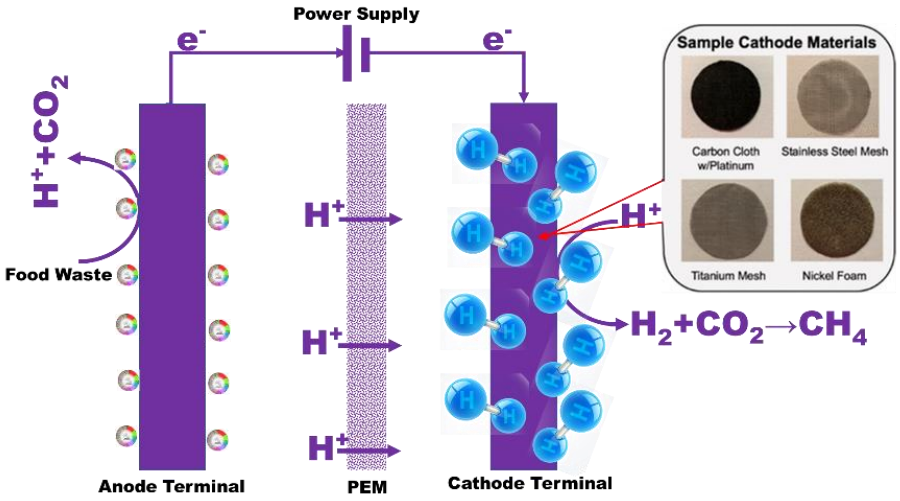


Fig. 3. MEC catalysts used in novel material for enhancing BioM production.

This synergy leads to more productive and sustainable biomethane generation, advancing renewable energy technologies. Despite nickel's continued dominance, hybrid materials and graphite show promise [38]. Catalysts like palladium and platinum efficiently catalyze hydrogen exchange, but alternatives like nickel, iron, tungsten, and molybdenum can reduce costs [39]. Non-metals and alloying elements enhance efficiency and reduce activation energy. Biocathodes, functioning as "electron sinks," utilize microorganisms for organic compound degradation, presenting an alternative approach to catalyze hydrogen growth response rate [40]. Nanocatalysts, especially MoS_2-based ones, show promise for hydrogen and methane production, warranting further investigation [41]. For instance, the exploration of advanced conductive materials in MECs holds the key to improving electron transfer kinetics, enhancing biomethane production, and advancing sustainable bioenergy technologies.

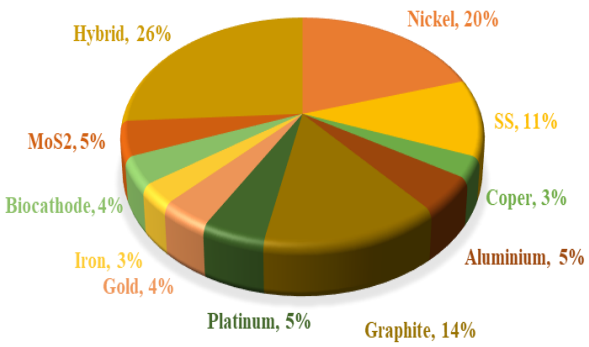
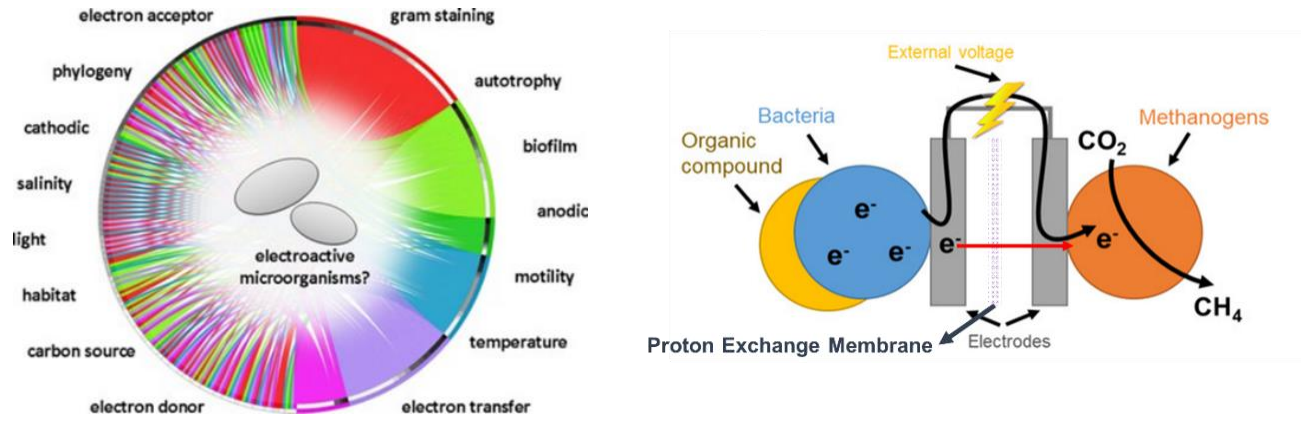


Fig. 4. MEC proportion of Novel Electrode Materials investigated.

5. Biocompatible materials: electrode surface and electroactive bacteria

The focus is on materials that are biocompatible and promote microbial adhesion without causing toxicity. This approach encourages a symbiotic relationship between the electrode surface and

microbial communities, fostering long-term stability and productivity. According to the findings, electroactive microorganisms do not have a single evolutionary path [42]. Significantly more electroactive microorganisms are likely to exist in the environment as well as established strain collections; however, their electron transfer mechanism capability is underutilized due to present culture procedures, as shown in Fig. 5. The inner-sphere process involves the sharing of a crossing molecule between two different metals, while the outer-sphere method involves the direct exchange of electrons between two different metals without the utilization of a crossing molecule.



(a) (b)

Fig. 5. MEC for (a) electroactive bacteria [42] and (b) electron transfer mechanism.

5.1. Exploring the anode chamber and its ETM

Different types of bacteria can grow in MECs on either the anode terminal or the cathode terminal. Gram-negative bacteria, including Geobacter spp. and Shewanella spp., are commonly found on the anode terminal, which also oxidizes organic materials and generates an electron flow, as shown in Fig. 6. The substrate concentration of specific species of bacteria that can create electrons or decrease CO_2 is used for this biodegradation process. Electroactive microorganisms are the name given to these microbes [42]. The development of volatile byproducts like methane in MECs is greatly partial by the interaction of microorganisms with other elements. Transfer of electrons from the organic substrate to the electrodes is crucial for the efficient operation of MECs.

The ability to effectively design MECs can be improved by having an improved considerate of this microbial extracellular electron transfer mechanism. Electrotrophic microorganisms are those that can take electrons, whereas exoelectrogens are those that can transmit electrons to cell membranes. Electroactive microorganisms have been discovered in a number of settings, including anaerobic sewage sludge, residential wastewater, and ocean and sea sediments [43].

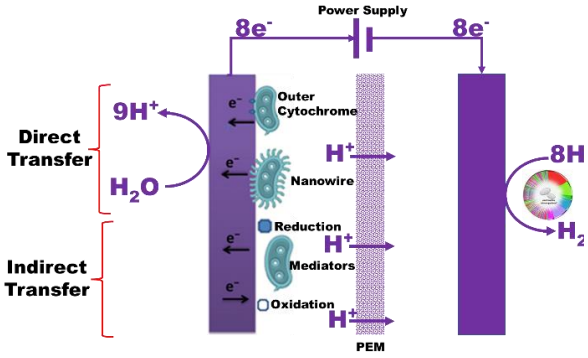


Fig. 6. Schematic diagram of ETM from exoelectrogen to anode and pathway in *Shewanella*.

5.2. Gram-negative bacteria and ETM

There are two ways that electrons are transferred: from the outside cell wall to the interior and vice versa. The first mechanism is the cytochrome complicated, which is found in electroactive bacteria such as Geobacter and Shewanella [44]. The subsequent structure includes Cyt coupled with cytochrome, which is typically found in bacteria that can oxidize iron, such as A. ferroxidans, in an

acidic environment [45]. In particular, Shewanella oneidensis, which represents the cytochrome mechanism, and Geobacter sulfurreducens nanowire are used as models for exocellular electron transmission. Fig. 7 illustrates the gram-negative bacteria Electron Transfer Mechanism. Normally, the lifespan of these bacteria depends on soluble electrophiles and donors, but they are also proficient in extracellular electron transfer, which can produce a low, erratic, or unpredictable current. They fall within the category of "moderate electricigens" as a result. There seem to be particular difficulties in recording their signal because of their low current output. This necessitates a thorough examination of the methods available in related domains.

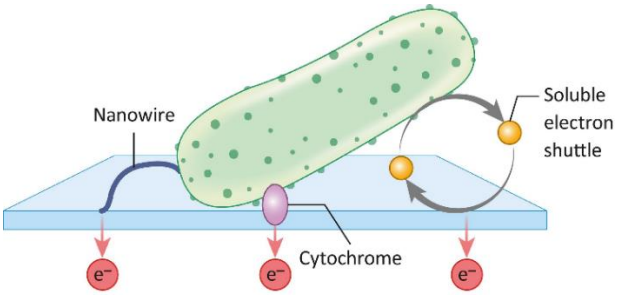


Fig. 7. Gram-negative bacteria Electron Transfer Mechanism [45].

5.3. Nanowires - geobacter sulfurreducens and electron transfer mechanism

A gram-negative, obligatory anaerobic bacterium known as Geobacter sulfurreducens belongs to the Delta Proteobacteria class [46]. In addition to new theories for protracted extracellular electron flow, the research of highly charged protein nanowires in Geobacter sulfurreducens has also sparked the creation of biodegradable superconductors and electronic gadgets with innovative uses. The multiheme c category cytochrome element aids in the electron carrier's pathway in G. sulfurreducens PCA [47]. CbcL, PpcD, ImcH, PpcA, and OMC are all found in C-type cytochromes, which also include B, C, S, and Z elements [48]. The cytoplasmic surface of the membrane surrounding CbcL and ImcH. PpcD and PpcA are found in the inner membrane region and aid in the subsequent transport of electrons into Omcs (B, S, C, S, Z). This substance helps an outside electrode by providing an electron. The transmission of an ion to an electrode is made easier by Omcz in particular, as depicted in Fig. 8. A 40–50 micrometers thick biofilm generates 0.005A of electricity [49]. Nanowires actually connect to the electrodes via organelles that resemble pili. Extremophiles, in addition to mesophiles, are crucial to H-MEC.

5.4. Extremophilic microorganisms and electron transfer mechanism

Extremophiles are remarkable bacteria that can survive and thrive in the harshest environments. Depending on the kinds of stress environments species can tolerate, extremeophiles can be classified as alkaliphiles, thermophiles, halophiles, acidophiles, psychrophiles, etc. [50].

Alkaliphiles: Extremophiles known as alkaliphiles may accept high alkalinity in the range of pH 8.5–11 [51]. Fig. 9 reveals that the different alkaliphilic strains Geoalkalibacter spp., alkaliphilic Bacillus, and S. oneidensis demonstrated significant current density production in MECs when used as a biocatalyst [52].

Alkaline anode circumstances and acidic cathode characteristics both resulted in higher terminal voltage. For S. oneidensis MR-1, the alkalinity boosted the oxidase production, which improved the output current [53].

Thermophiles: The ability to control the MEC in a heated atmosphere particularly leads to an increase in catalytic efficiency, which is one benefit of utilizing thermophiles in MEC. Fig.10 depicts that the MEC structure and the phylum Thermotogae are composed of anaerobic, gram-negative staining, hyperthermophilic, and mostly thermophilic bacteria. High mass and ion transfer rates, as well as good solubility of the medium, are further benefits of high temperatures.

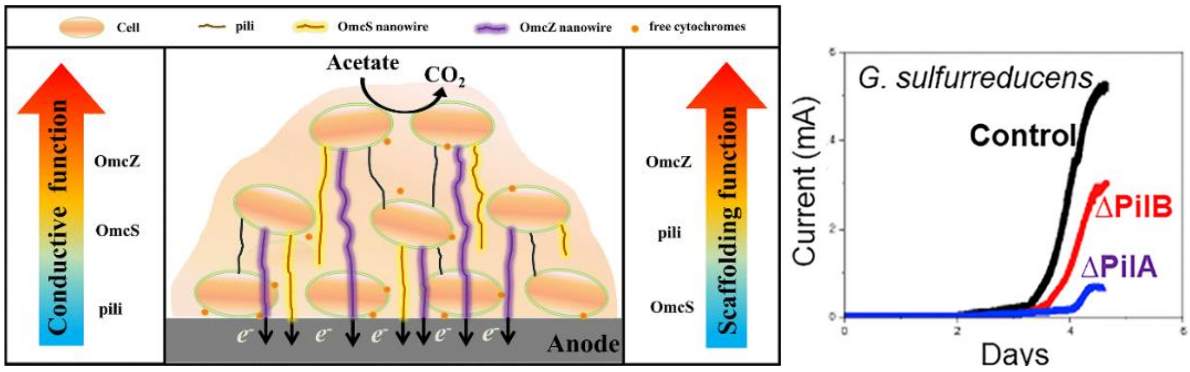


Fig. 8. Design of electron transfer in the G. sulfurreducens anode biofilm [49].

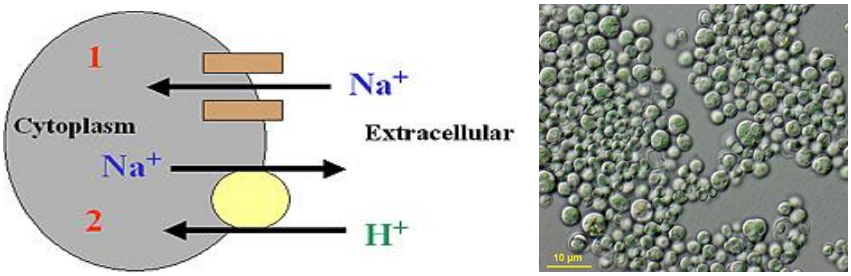


Fig. 9. Alkaliphiles Microorganisms Bacillus and S. oneidensis [53].

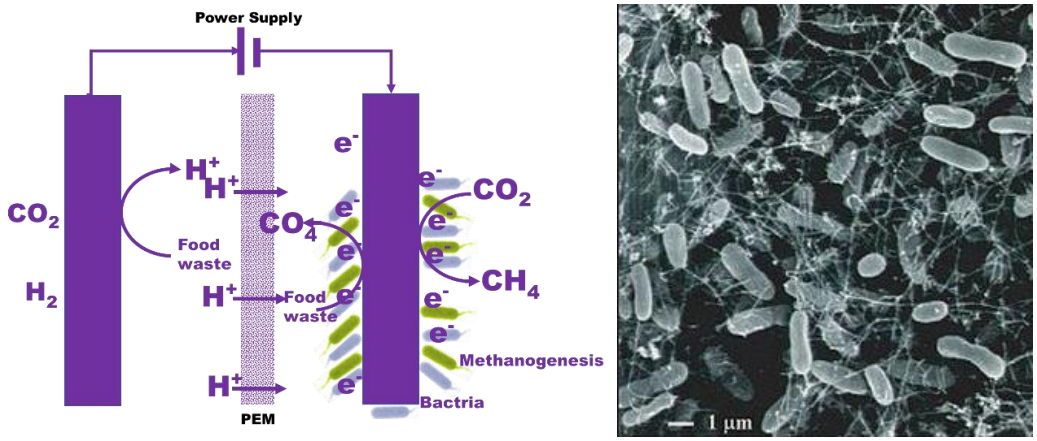


Fig. 10. Design of MEC and thermophile's *Thermotogae sp* [54].

While hybrid growth was used at 55°C, an MEC was maintained for 100 days and had high charge density production. It comprises a total of nine genera, viz. such as Thermotoga, Fervidobacterium, Petrotoga, Thermosipho, Marinitoga, Geotoga, Kosmotoga, Thermococcoides, and Thermopallium, all of which are presently segments of the family Thermotogaceae. According to research on the 16S rRNA clone library, 80% of the genus are capable of creating electricity and endospores. Increased power flow and conversion efficiency were noted in MECs operating under these conditions, as well as a decrease in sulfates [54].

Halophiles: In settings of extreme salinity, halophiles will develop. Proteobacteria, Actinobacteria, and Firmicutes are three phyla of Eubacteria that contain halophiles. Fig. 11 shows the design of MEC and halophile microorganisms Bacillus sp. and Oceanobacillus sp.

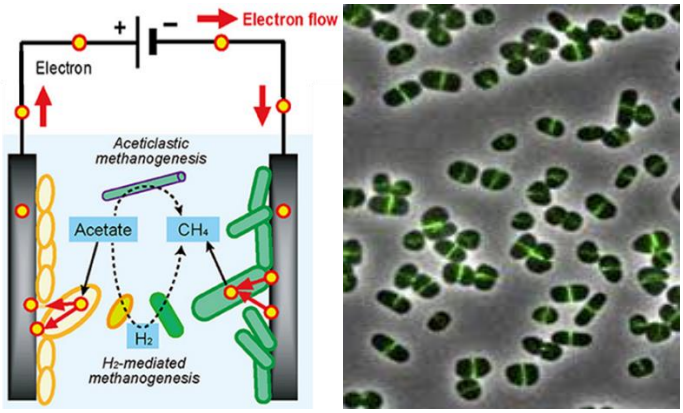


Fig. 11. MEC and halophile microorganisms Bacillus sp. and Oceanobacillus sp [55].

Because better proton transfer and greater resistivity help improve the final performance, the use of high salt concentrations in MECs has been very beneficial. As a result, halophilic electroactive microorganisms are beneficial for removing salty effluent and producing energy [55].

5.5. Anode terminal immobilization microbes for capture CO_2

In the context of sustainable technologies, anode terminal immobilization refers to the process of securely attaching or fixing microorganisms with CO_2-consuming capabilities to the anode terminal of an electrochemical cell. The anode terminal is a critical component in electrochemical systems, serving as the site where oxidation reactions occur [54]. The primary objective of this approach is to leverage the unique metabolic capabilities of microorganisms to capture carbon dioxide directly from the surrounding environment. Microbes are strategically positioned at the anode terminal, allowing them to come into direct contact with CO_2 as part of an electrochemical cell setup. In this electrochemical environment, the microorganisms utilize their metabolic pathways to catalyze reactions that convert captured CO_2 into other valuable compounds. The electrochemical processes involved in this setup enable the efficient transformation of CO_2 by facilitating electron transfer between the microbes and the anode terminal. This electron transfer is an essential step in the conversion of CO_2 into more complex compounds. Through the microbial activities at the anode terminal, CO_2 is transformed into products with potential applications, such as biofuels or other economically valuable substances [55]. This method offers a promising avenue for sustainable carbon capture and utilization, as it integrates biological processes with electrochemical principles. By harnessing the synergies between microorganisms and electrochemical cells, researchers aim to develop environmentally friendly technologies that not only capture CO_2 but also contribute to the production of valuable resources, thereby addressing both environmental and economic challenges.

Hybrid consortia are frequently used to operate MES. The problem with MEC is the excessive proliferation of undesirable non-electrogenic species and the lack of material in the anode terminal. Different methods have been developed to reduce the non-electrogenic species. Pre-treatment constitutes the most practical and relevant procedure in both cathodic MEC and anodic MFC. Pre-treatment is carried out to improve the electrochemical process efficacy and the way electroactive bacteria use the material to produce byproducts and power. The increase of electroactive bacteria is one method, while the suppression of the undesirable non-electrogenic bacterial community is another [56]. By using a constant anode voltage, a biological and physicochemical method, and the addition of electron acceptors, it is possible to increase electrocatalytic bacteria and speed up redox reactions in the anode terminal. Bioaugmentation using purified electrogene growth in hybrid seeds of electrocatalyst microorganisms is a potentially viable strategy. By using an electrode, non-electrogenic microorganisms induce resistance and

are prevented from the Electron Transfer Mechanism to the anode. In contrast, electrogenic microorganisms can be employed as microbial inoculants as they immediately contribute their electron to the anode, as shown in Fig. 12.

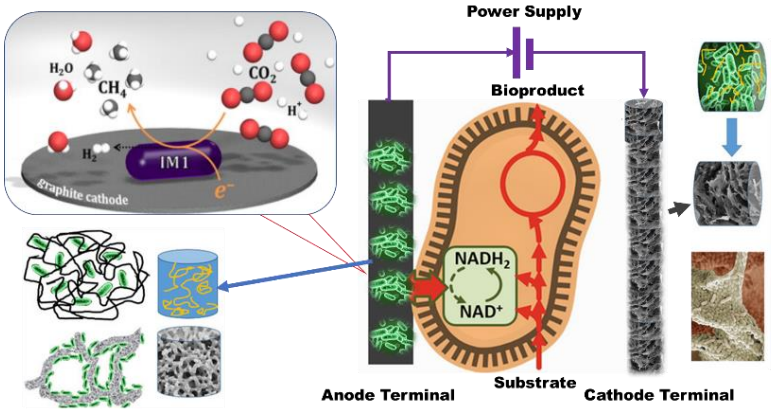


Fig. 12. Bioaugmentation by using pure electrogene of electroactive bacteria for MEC.

By accepting a bidirectional electron transfer mechanism with the synchronous effects of mycelium and heterogeneous inoculum, the anode can much more efficiently collect these electrons for the creation of current. Flavins-like oxidant exchangers, which move electrons from microorganisms to electrophiles, are secreted by Shewanella in its pure form [57]. As a result of the complementary interactions between the two strains, the electron transport in the electrode is improved. Continued growth might be achieved by boosting efficiency by establishing mixed bacterial isolation by adding new nutrients or alternative electron acceptors to encourage the development of certain microorganisms. In the anode surface, the bacterial community regulates the anode voltage. The electrogenic layer particularly influences bacterial communities, and the production of the total current and anode voltage are connected [58]. In an MEC system, the anode potential versus current density using microbial species refers to the relationship between the electrical potential at the anode and the resulting current density generated by the microbial community. This relationship is important for understanding how different microbial species can influence the electrical output of the MEC system and how variations in anode potential can impact the current density produced by the microbial community, as shown in Fig.13.

Fig. 13 shows that the higher charge density outputs might arise from the development of Geobacter sulfurreducens on the anode at the supply voltage of + 0.2 mV (vs. Ag/AgCl). In order to improve the electrogens and shorten the MFC's beginning time, an outer power supply might also be an alternative method [59].

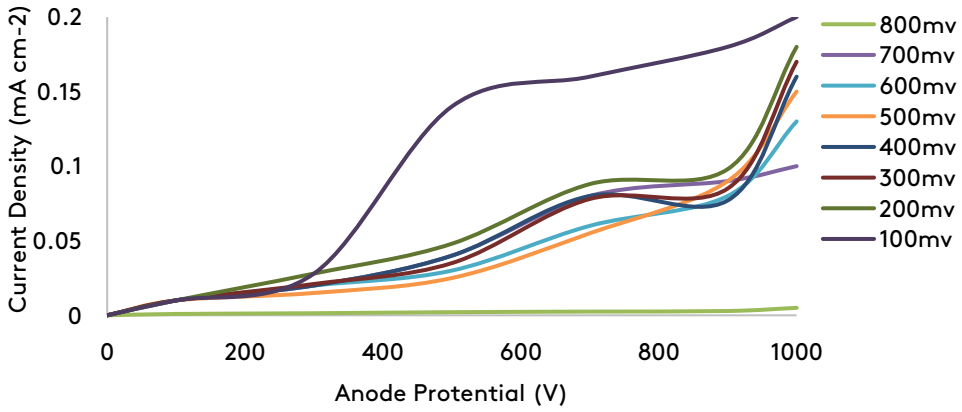


Fig. 13. MEC system anode protential vs current density using microbial.

5.6. Electron Transfer Mechanism at Cathode Terminal for CO_2 Capture

Protons and electrons produced through catalytic oxidation are used on the cathode surface to reduce CO_2 both directly and indirectly. Direct electromethanogenesis occurs in the biocathode via redox outside cell membranes in the presence of isoenzymes interacting with the negative electrode [60]. In contrast to cytochrome, other outer membrane enzymes implicated in electron transport include ferredoxin, rubredoxin, hydrogenase, and/or base-catalyzed dehydrogenase. Conducting biofilm participates in the Electron Transfer Mechanism of electromethanogenesis in the same way as bioanodes do, as shown in Fig. 14.

Alternatively, indirect electromethanogenesis can be conducted through three distinct sources: (1) electrochemical reactions and bioelectrochemically generated hydrogen, (2) formate, and (3) acetate [60]. Additional electron shuttlers or intermediaries, such as riboflavin, phenolic acid, and 40% of the total released by bacteria, can increase electron transport and, as a result, indirect electromethanogenesis. Transfer electrons organisms that convert CO_2 to CH_4, such as Methanosaeta and Methanosarcina, may be exoelectrogenic straight from primary iron [61].

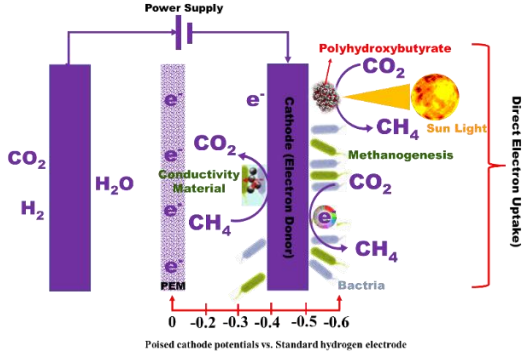


Fig. 14. Indirect microbial Electron Transfer Mechanism structure for BioM yield at the cathode.

A higher proportion of CH_4 is produced by the CO_2 reduction process depicted in Fig. 15. The metabolic pathway methanogenic microorganisms can develop, including both anode surfaces and cathode surfaces, although they prefer the cathode. Methanospirillum, Methanobacterium, Methanosarcina, Methanocorpusculum Methanoculleus, and Methanobrevibacter have been discovered to develop on the anode surface, implying the capability of methane production [62]. On the other hand, Methanosarcina may generate methane via the hydrogenotrophic and acetoclastic pathways. On the cathode chamber, Methanobrevibacter, Methanospirillum, and Methanoregula have been seen developing [63]. Microbes, including Methanosaeta and Methanobacterium, employ electrons to directly create CH_4 using carbon dioxide reduction. Increased CH_4 generation is observed while different based on recommendations of methanogens congregate to a certain amount and become linked with the electrode. Electromethanogen hydrogenotrophic interactions play a significant role in CH_4 generation by forming on the cathode side [64].

In contrast, methanogens, including Methanocorpusculum, are ineffective at arresting negative electrons and rely on the cross-species transfer of electrons performed by electroactive bacteria including, Geobacter or Acetobacterium [17]. The electro syntropy of specific bacterial communities for CH_4 yield is affected by the type of electrocatalyst used and the microorganisms existing in the experiment. To improve CH_4 synthesis in H-MECs, it is critical to comprehend the concept of electron transport between electroactive bacteria and an electrode. The precise process for electron transport has yet to be determined. Conversely, three recognized routes explain the production of CH_4 by MEC [65].

6. Electromethanogenesis chemical reaction for CO_2 to CH_4 yield

Every raw material within a species is the outcome of a metabolic process or route. Different physiological stages may be required to break, change, or develop biological structures and molecules. Various metabolic process byproducts can function as reactants in some other route. This section details the specific mechanisms of CH_4 anaerobic metabolism, also known as methanogenesis. Methane is produced through three main metabolic pathways: hydrogenotrophic, methylotrophic, and acetoclastic. Among these, the CO_2 reduction route, illustrated in Fig. 16, is considered the primary driver of methane yield. However, when

using starter cultures, alternative pathways gain greater significance [60].

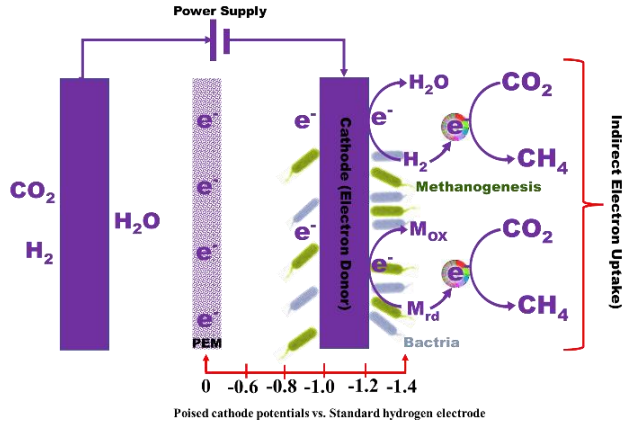


Fig. 15. Direct microbial ETM structure for enhanced BioM yield at the cathode.

Besides the M. barkeri that utilize all three routes, mostly all methanogens utilized in CH_4 electrochemical conversion processes utilize the CO_2 reduction route. On the other hand, microbes such as M. hollandica and M. thermophila can exclusively use methylotrophic and acetoclastic routes. The CO_2 reduction process is almost four times more common than the acetoclastic and methylotrophic routes mixed. This is due to the ease with which CO_2 and hydrogen are supplied throughout hydrogenotrophic methanogenesis. CO_2 is decreased and catalyzed to create formylmethanofuran, with decreased ferredoxin (Fdred) serving as an electrophile. The formyl group is transferred to tetrahydromethanopterin in the second phase (H_4MTP). The dehydration process generates methylene-H_4MTP, which is then decreased to methyl-H_4MTP using decreased F420 as an electron acceptor. Subsequently, methyl-CoM is reduced to CH_4 with coenzyme B (HS-CoB) both as an electron acceptor after the methyl group is transferred to coenzyme M (HS-CoM). To regenerate the coenzymes, the resultant CoM-S-S-CoB is decreased using H_2. It needs to be emphasized that certain methanogens can employ formic acid as an electron acceptor for CO_2 reduction rather than H_2.

The species Methanosarcina and Methanotrix synthesize CH_4 using acetate. Acetate should always be released for acetoclastic methanogenesis to emerge. This is accomplished by the synthesis of ATP and coenzyme A into acetyl-CoA, which is then divided by the CODH/acetyl-CoA polymerase combination.

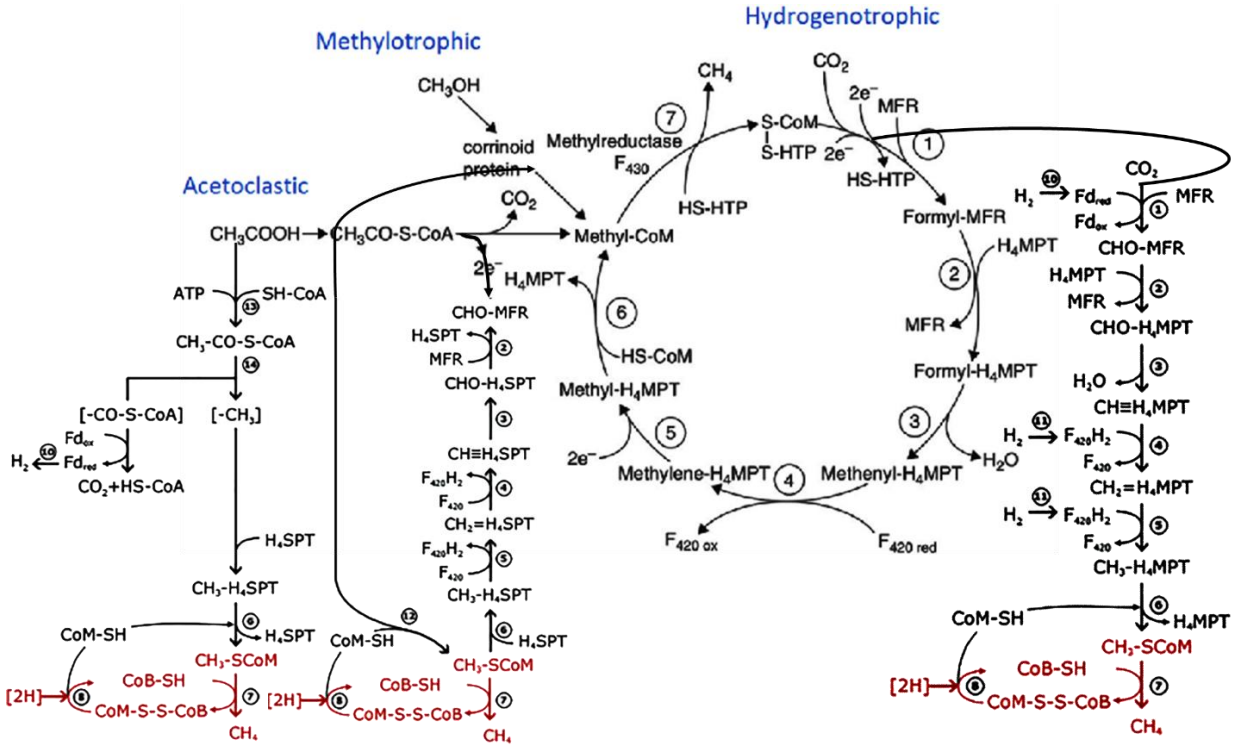


Fig. 16. Three metabolic pathways for electromethanogenesis include (a) Acetoclastic, (b) Hydrogenotrophic, and (c) Methylotrophic methanogenesis.

According to the hydrogenotrophic CH_4 generation process, the CH_3 group is converted to tetrahydrosarcinapterin (H_4SPT) and then transformed into CH_4. The final method of producing organic CH_4 uses substituent materials such as dimethyl sulphide, methanol, methanethiol, or methylamines. Methanosarcinales are a community of several methylotrophic microorganisms [66].

7. Exploring the building blocks: key materials utilized in MECs

Microbial Electrolysis Cells (MECs) represent a cutting-edge technology at the intersection of microbiology and electrochemistry. Understanding the intricate details of the materials used in MECs is crucial for harnessing their full potential in sustainable bioenergy generation. This exploration delves into the fundamental building blocks that constitute MECs, shedding light on the diverse range of materials carefully selected to optimize electron transfer, enhance conductivity, and facilitate catalytic processes. From advanced conductive materials like graphene and carbon nanotubes to innovative electrode coatings and biocompatible components, this investigation unravels the intricate tapestry of materials that drive the efficiency and functionality of MECs. As we delve into the realm of these essential materials, we gain insights into the technological advancements paving the way for a greener and more sustainable energy landscape.

7.1. Anode chamber materials

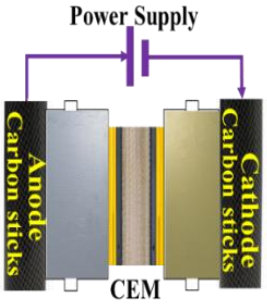
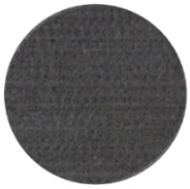
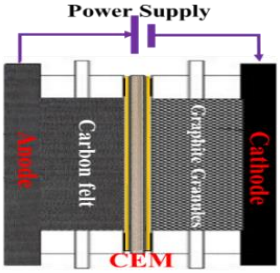
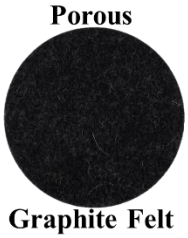
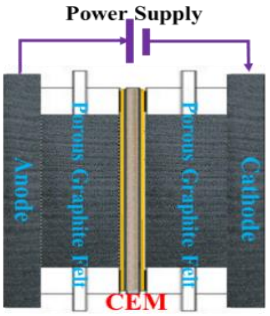
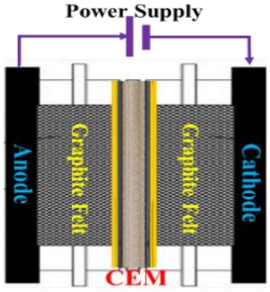
Desirable features for an anode in a Microbial Electrolysis Cell platform encompass high electrical conductivity, favorable biocompatibility, chemical stability, resistance to corrosion, scalability, low electrical resistance, resistance to fouling, robust mechanical strength, and a substantial surface area. These characteristics are considered essential for the effective utilization of anodes by acidogenic bacteria to execute aerobic metabolism within MECs. Due to their high electrical permeability, exceptional biocompatibility, cost-effectiveness, stability, and low overpotentials, carbon-based electrode materials emerge as the predominantly employed materials. As outlined in Table 2. various carbon-based anodes are employed for the conversion of CO_2 to CH_4, including carbon sticks, graphite felt, carbon paper, carbon cloth, carbon fiber, graphite granules, and porous graphite felt. MFCs often encounter challenges associated with a low operational voltage concerning the electrical potential of the cell, which is commonly termed as unsustainable kinetically determined possibilities. Nanoparticles are introduced into anodic transformation to address energy dissipation in multiple directions, including initiation loss, microbial metabolism loss, charge transport loss, and leakage currents. This technique enhances electron transport by promoting the development of electroactive bacteria, countering issues such as bacterial growth on the anode that hampers electron transfer from the bacterium to the anodic substance.

Different nano-metal or oxide metals, including MnO_2, iron oxides, and TiO_2, are utilized to modify the anode outer edge in order to maximize the inoculum's retaining capacities and increase the electron's electricity transfer rate. Iron oxide can induce the electron transfer mechanism via two mechanisms: as an electrical conductor inside the biofilm or as an interaction by developing on the cell membrane [67].

7.2. Cathode chamber materials

Cathode chamber materials are critical in both electrohydrogenesis and electromethanogenesis. Electromethanogenesis requires less electricity than electrohydrogenesis, which is used in a range of 0.23 V to 0.41 V. Therefore, more power is often needed to eliminate cathodic ionic conductivity. Cathode chamber material parameters, such as porous structure, high conductivity, and cytocompatibility, will now show a significant character in the MEC impact of development. According to Rozendal et al. [68], the cathode provides for 47% of the overall cost savings for constructing MECs. The total quality of MECs is determined by the electrodes and materials used to create devices. Methane is produced via CO_2 conversion on both the anode and cathode electrodes, using directly transferred electrons or oxidation reactions.

Table 2. Varieties of anodes employed in dual-chambered (MECs).

Ref.	Anode Terminal	Cation Exchange Membrane	Types of MEC	External Voltage	Methane Yield
[67]		CSO		The anode chamber was saturated with a 100-millimolar (mM) NaCl anolyte, while the potential across the system reached -900 volts	The enhancement of CO_2 flushing was successful, resulting in the production of 2.30 ± 0.34 mL of CH_4.
[68]		Ultrex CMI-7000		The MEC's anode reached a potential of -800 millivolts, yielding a rate of 14.46 grams of N-NH_4 per square meter per day	The conversion of CO_2 at the cathode resulted in the production of 79 liters of CH_4 per cubic meter per day.
[69]		CMI-7000		A potential of 200 millivolts was applied, and the anode was supplied with Sodium acetate (12.2 millimolar).	The CH_4 production was normalized to 0.113 mol/mol, and the current was standardized in the cathode.
[70]		CEM		The cathode reached a potential of -700 millivolts, and the current density at the projected cathode was 0.60 ± 0.16 A/m².	The production rate was 5.1 liters per square meter per day, with the detection of hydrogen (35.7% H_2, v/v) in the cathode.

For the construction of CO_2 to CH_4, different carbon-based cathodes, including carbon stick, nickel steel, carbon cloth, carbon fiber, graphite granules, and carbon felt, are utilized, as shown in Table 3. Nonspontaneous responses often occur in the cathode area, which necessitates the use of a particular material to catalyze oxidation and reduction. Platinum, for example, demonstrated its catalytic capability by optimizing oxidation and reduction. It is a valuable metallic element with excellent biocompatibility. However, there are other drawbacks, such as adverse environmental effects and expensive costs. Materials, including stainless steel alloys and nickel, have been found to be efficient options because of their ease of access, cheapness, consistency in alkaline conditions, and low activities. Stainless steel has been used to develop anaerobic digesters paired with single-chamber MECs to increase methane output [69]. Apart from stainless steel, advancements in

electrocatalysts have been made, relying on alloys such as iron-graphite and Ti/Ru, with the aim of boosting CH_4 production, especially in the presence of sewage sludge [22]. Carbon-based cathodes, constructed from materials like parietal graphite and porous carbon, could offer advantages in methane generation [69]. Siegert et al. [19] investigated CH_4 generation using both valuable metals like platinum, nickel, and stainless steel and nonprecious carbon-based materials like plain graphite, carbon black, and carbon brush. Notably, the study revealed that a simple graphite cathode yielded more methane than a cathode based on precious metals.

Cathodic materials made of carbon sticks and graphite felts had the best methane output and cathode conversion efficiency [19]. Catalytically modified multi-walled carbon nanotubes, including platinum, ammonia, iron phthalocyanine, nickel, and manganese oxide, have been employed as substitutes for cathodic materials to enhance the rate of methanogenesis [70].

7.3. Membrane materials

In MECs, the careful selection of membrane materials holds significant importance when aiming for efficient CO_2 capture. The choice of membranes profoundly influences the system's capability to transport and separate CO_2, directly impacting the overall effectiveness of the capture process. Optimal membrane materials play a crucial role in enhancing the diffusion of CO_2 toward the anode chamber, ensuring a conducive environment for microbial activity. Additionally, these materials facilitate the transport of ions necessary for electrochemical reactions, contributing to the overall efficiency of the CO_2 capture process. Importantly, the right membranes act as barriers, preventing the undesired crossover of various species between the anode and cathode chambers. This selective separation ensures that only the intended substances, such as CO_2 and ions, are transported, avoiding contamination and optimizing the performance of CO_2 capture within the MECs. The careful consideration and design of membrane materials thus emerge as a critical aspect of achieving successful and efficient CO_2 capture in microbial electrochemical systems.

Membranes serve as integral components in MECs, playing a crucial role in spatially segregating the cathode and anode within two-chambered configurations. These separators are essential for constructing MECs, acting as barriers that prevent the mass diffusion of substrates, hydrogen gas, hydrocarbons, and microorganisms between the anodic and cathodic chambers. Specifically designed to enable the movement of protons across electrodes, these membranes also function as safeguards against short circuits in MECs. Various types of membranes have been employed in MEC reactors, with Nafion, a proton exchange membrane, being widely utilized. Other examples include ion exchange membranes like AMI-7001, CSO monovalent-cation-selective exchange membranes, Ultrex CMI-17000, Ultrex CMI-7000, Non-woven fiber, and Tubular anion exchange membranes. It is crucial to consider pH fluctuations, especially the variations caused by cation exchange, which result in a lower pH at the anode and a higher pH at the cathode.

This pH shift can potentially impact microbial activity in both the anodic and cathodic chambers. Table 4 provides an overview of various membranes utilized in dual-chamber MECs and their corresponding methane production rates. In study [76], a membrane filter with a pore size of 0.45 micrometers was employed under an applied voltage of 300 millivolts, yielding a BioM production rate of 17.0 ± 1.6 L/d. The AD reactor underwent three distinct operational phases: start-up (day 1–69), intermediate steady state (day 70–289), and final steady state (day 290–365). In contrast, study [77] used a TAEM (thin anion exchange membrane) to separate the internal anodic and external cathodic chambers, with volumes of 3.14 L and 8.86 L, respectively. An applied potential of 200 mV facilitated the transfer of HCO_3^- ions across the membrane, resulting in a substantial daily production rate of 300 meq/d, emphasizing the importance of effective ion exchange in MEC performance.

Table 3. Categories of cathodes utilized in dual-chambered MECs.

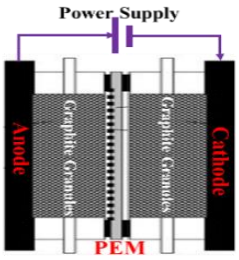
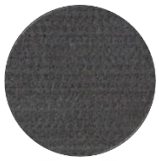
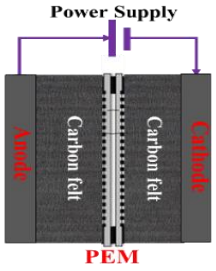
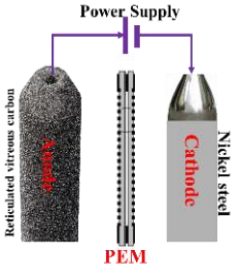
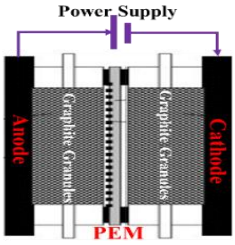
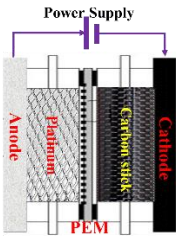
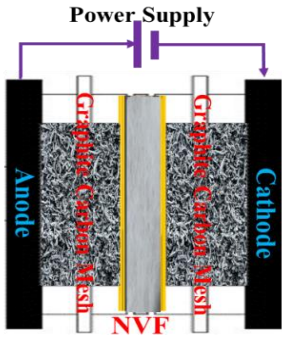
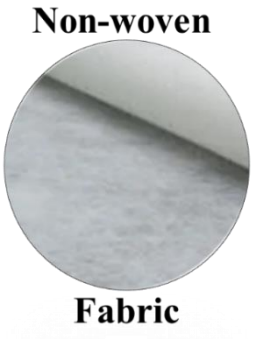
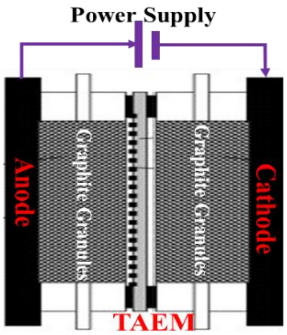
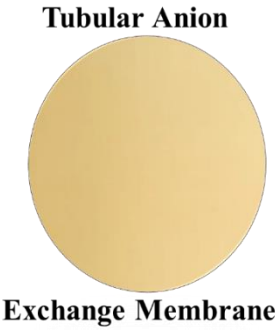
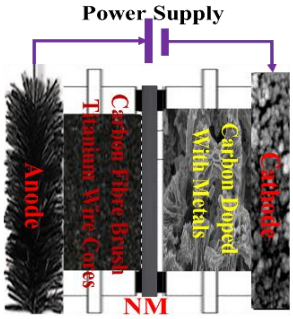
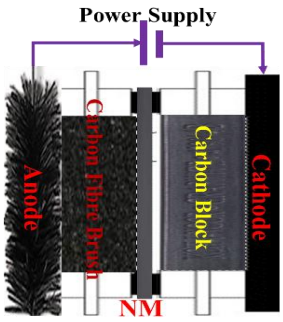
Ref.	Cathode Surface	Proton Exchange Membrane	Types of MEC	Voltage (mV)	Bacteria and Methane Yield
[71]	Graphite  Granules	Nafion 117		A potential of -200 millivolts was applied, resulting in the conversion of approximately 84–86% of the current into CH_4 at the cathode.	The microorganisms involved in this process include *Methanobrevibacter arboriphilus and Methanosarcina mazei*. The CH_4 production rate was measured at 47.7 ± 4.8 (meq/d).
[72]	 Carbon Felt	Proton Exchange Membrane		A potential of -800 millivolts was applied, resulting in the conversion of approximately 46–66% of the current into CH_4 at the cathode.	The enzyme involved in this process is phosphofructokinase, which facilitates the conversion of fructose-6-phosphate to fructose-1,6-bisphosphate. The total CH_4 production amounted to 62.8 milliliters.
[73]	 Nickel Steel	Nafion 117		A potential of +2000 millivolts was applied, leading to the conversion of approximately 67–97% of the current into CH_4 at the cathode.	The microorganisms involved in this conversion process include *Methanothermobacter marburgensis and M. thermautotrophicus*. The resulting CH_4 yield was measured at 68.7%.
[74]	Graphite  Granules	Nafion 117		A potential of +500 millivolts was applied, resulting in the conversion of approximately 67–86% of the current into CH_4 at the cathode	The microorganism involved in this conversion process is *G. sulfurreducens*. The CH_4 production rate reached 6.4 milliequivalents per liter per day.
[75]	 Carbon stick	Nafion 117		A potential of -1400 millivolts was applied, leading to the conversion of approximately 36–58% of the current into CH_4 at the cathode	The microorganisms responsible for this conversion belong to the *Methanomicrobiales* group. The resulting CH_4 concentration reached 80.9 milliliters per liter

Table 4. Kinds of membranes utilized in dual chambered MECs.

Ref.	Anode and Cathode of MEC	Membrane	Applied Voltage	Methane Production
[76]			A potential of 300 millivolts is applied, and a membrane filter with a pore size of 0.45 micrometers is employed.	The resulting BioM rate is measured at 17.0 ± 1.6 L/d. The AD reactor undergoes distinct phases, including start-up (day 1–69), intermediate steady state (day 70–289), and final steady state (d 290–365).
[77]			An applied potential of 200 mV is utilized, and the internal anodic chamber with a volume of 3.14 L is isolated from the external cathodic chamber (8.86L) by a TAEM.	A significant ion exchange process occurs across the AEM membrane, allowing the transfer of HCO3- ions from the cathodic chamber to the anodic chamber, resulting in a daily production rate of 300 meq/d.
[78]			An applied potential of -600 mV is employed, utilizing a system with an inner diameter of 2.4 cm and a length of 3.8 cm, sealed with an O-ring, and separated by a NM.	The resulting molar hydrogen production rates reach 247 ± 87 nmol cm^{-3} d^{-1}. Following a division by 4 in the Materials and Methods section, the calculated maximum potential for CH_4 production is obtained.
[79]			At a potential of -600 millivolts, the system features an inner diameter of 2.4 cm and a length of 3.8 cm, sealed with an O-ring, and separated by a NM.	The resulting molar hydrogen production rates are measured at 250 ± 30 nanomoles per cubic centimeter per day. This setup employs carbon fiber brushes (4 × 4 cm, 740 m^2) and graphite blocks (2 × 2 × 0.32 cm).

Studies [78] and [79] focused on MEC systems operating at an applied potential of -600 mV. Both utilized a non-selective membrane (NM) with identical system dimensions: an inner diameter of 2.4 cm and a length of 3.8 cm, sealed with O-rings. In study [78], the molar hydrogen production rate reached 247 ± 87 nmol cm^{-3} d^{-1}, with the maximum potential for CH_4 production calculated using data provided in the Materials and Methods section. Similarly, study [79] reported a slightly higher molar hydrogen production rate of 250 ± 30 nmol cm^{-3} d^{-1}, achieved using carbon fiber brushes (4 × 4 cm) and graphite blocks (2 × 2 × 0.32 cm). These results highlight the critical role of membrane

selection and reactor design in optimizing both hydrogen and methane production in dual-chamber MECs.

9. Configuration of hybrids MECs system

The layout of the chamber in MECs is critical in selecting the method to make or convert CO_2 to CH_4. The design of MEC has a direct impact on CH_4 outpt, overall fuel efficiency, and operational costs. Reactor operating designs, including single-chamber and double-chamber options, have been proposed. The existence or absence of proton or ionic exchange membranes in the system determines the chamber structure, which normally divides the structure into one or two chambers.

9.1. Configuration of Single-Chamber H-MEC

Decoupling membranes in double-chambered systems transforms them into single-chambered MECs, where both the anode and cathode reside in the same liquid within a unified chamber. This configuration mitigates the electromotive force voltage difference and reduces pH imbalances without the membrane barrier, minimizing associated risks [80]. The shift to a single-chamber design not only lowers the initial investment and simplifies construction but also streamlines manufacturing and purification processes by eliminating membrane-related challenges such as contamination and impedance, facilitating ease of maintenance. Various materials, including polypropylene, acrylic, and stainless steel, have been reported for constructing single-chamber reactors. Notably, this design encourages the proliferation of hydrogenotrophic methanogens, fostering methane production through hydrogen consumption. In one such prototype, a single-chamber MEC featured a flat stainless-steel cathode and a graphite block anode, illustrated in Fig. 17. The cathode incorporated a vertically positioned stainless-steel-based proton exchange membrane, while the anode, comprised of a vertically positioned graphite block, was situated at the reactor's bottom. This configuration, operating within an applied voltage range of 100mV-700mV, achieved a methane yield of approximately 0.028 m3/m3/d [81]. The anode terminal was constructed using graphite fiber brushes with a volume of 0.8m3. Stacked cathodes with a diameter of 0.05 m and 60 mesh were created, arranged in tiers using titanium wires, and differentiated by stainless-steel mesh layers on the abaxial surface, illustrating the innovative design and materials employed in single-chamber MECs. A substantial surface area was established, and an effective increase in CH_4 yield was observed when the volume ratio of the cathode's porous structure exceeded 2.5. Additionally, implementing concentric electrodes in a tubular configuration has been employed as an alternative MEC preparation, contributing to the enhancement of CH_4 yield in anaerobic digestion processes [82].

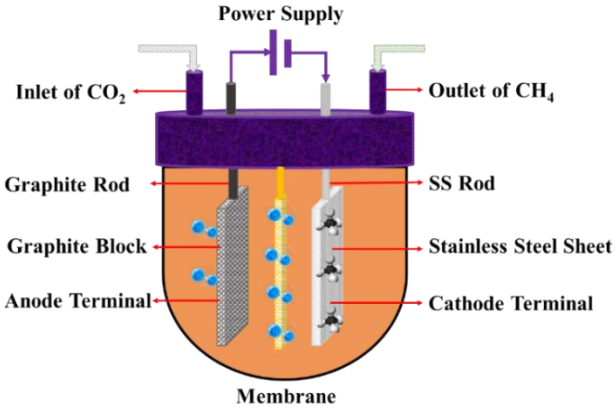


Fig. 17. Single-chambered H-MECs block diagram

9.2. AD based H-MEC of two-chamber configuration

The prevalent type of MEC is the two-chamber design, where the cathode and anode operate independently within two compartments isolated by a membrane [83]. The connection between the cathode and anode is established through an electrode surface, receiving an electrical supply from an external energy source throughout this configuration, as illustrated in Fig. 18.

Various membranes have been employed in the design of two-chamber MECs, with the most widely used being a proton exchange membrane designed with specific structural features, allowing for the passage of only free protons (H+) [80]. Additionally, charge-mosaic membranes, bipolar membranes, and anion-exchange membranes like AMI-7001 find application in two-chamber MECs. Under terminal voltages ranging from 200mV to 1200mV, the methane (CH_4) yield reached 656 millimoles per square meter per day. An innovative two-chamber MEC process was developed for CH_4 production from acetate, incorporating Geobacter

sulfurreducens as a microbial bioanode connected to a methanogenic microbial biocathode [25]. While the two-chamber MEC design is more intricate compared to the single-chamber reactor setup, drawbacks include the higher cost of membranes, their susceptibility to degradation, and the potential for pH imbalances introduced by their use.

10. Obstacles and influencing factors on the performance of MECs

Elements that impact the efficacy of MECs include the separator, substrate, microorganisms, operational aspects, reactor configurations, anode, and cathode. While certain parameters have been previously addressed, the essential challenges they encounter are elucidated below.

10.1. Substrate

In the process of CH_4 production, electroactive microbes oxidize the substrate and transfer electrons from the anode to the cathode. The effective selection of the substrate plays a pivotal role in determining the overall CH_4 production. Two crucial factors in MECs for achieving substantial CH_4 production are the organic content and substrate loading rate. MECs have the flexibility to utilize a range of organic substrates, spanning from simple sugars to more complex fermentable sources such as wastewater and biomass. Acetate is the most often utilized substrate in MECs, with a greater ionic conductivity of 91% [81]. Industrial, municipal, and household wastewater have all been tested for methane generation. Using all these waste items as a substrate for methane production also aids in pollutant removal, indicating that the MECs technique for manufacturing CH_4 is ecologically beneficial. Fig. 19 shows the average methane production and substrate consumption dynamics during incubation. Sodium acetate (CH_3COONa) is the most frequently utilized substrate for CH_4 production in MECs. In all cases, CH_4 production increased until the substrates were depleted. However, the CH_3COONa substrate was consumed the fastest, reaching the depletion point more rapidly than other substrates. Both the average CH_4 yield and substrate consumption rates were the highest, as shown in Fig. 19. During the first operation time, the bio-reactor was injected in the range of 0.2 g/L to 0.5 g/L CH3COONa.

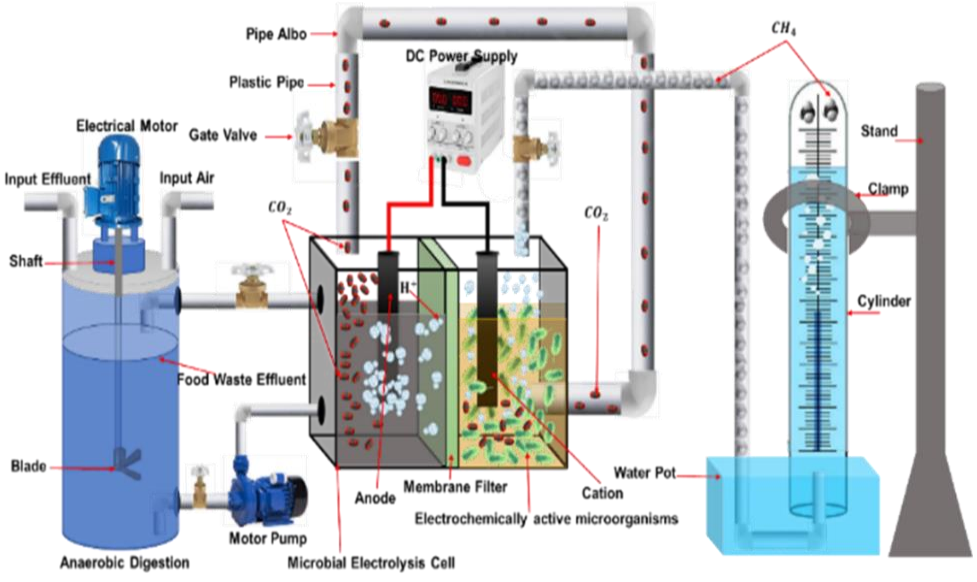


Fig 18. Block diagram of the two-chamber AD based H-MEC system.

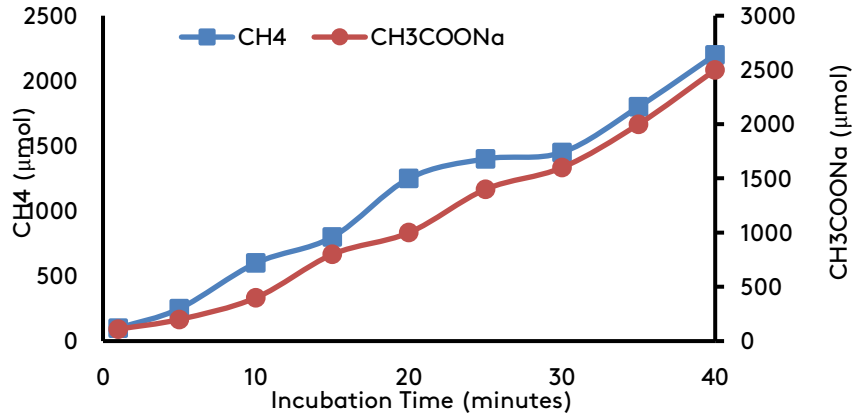


Fig. 19. Dynamics of substrate consumption and BioM production during incubation (../../../../nbbb01.xlsx).

For the second step of this process, the operating condition was changed to 0.4 g/L to 0.9 g/L, followed by increases in CH3COONa to 1 g/L and 1.8 g/L in the succeeding stages. In one liter of solution, the following elements of synthetic wastewater were formulated: 0.116 g NaCl, 0.31 g NH_4Cl, 4.4 g KH_2PO_4, 0.1 g $MgCl_2$ $6H_2O$, 3.4 g KH_2HPO_4, and 0.13 g KCl.

10.2. pH

Together with input voltage and temperature, pH influences CH_4 production in MECs. Because of the balanced behavior of microbes, the majority of CH_4 MECs function at a pH range of 4.5 to 7, as shown in Fig. 20. This is due to the electromethanogenesis sensitivity to its surroundings; even little variations in pH would elicit modifications in bacterial metabolic [82]. In addition to the mentioned factors, various parameters like ion transport, substrate oxidation, and liquid permeability are intricately connected to alterations in pH levels, either through direct or indirect mechanisms. Incorporating anaerobic digestion with MECs addresses the acidification process, providing a solution to treat substrates with elevated influent concentrations effectively [17]. This integration allows for a more comprehensive understanding of the complex interplay between different parameters, contributing to enhanced performance and efficiency in the treatment and conversion of various substrates within the MEC system.

Optimizing methane production involves careful consideration of pH and incubation time. In anaerobic digestion, maintaining a balanced pH range is crucial for the activity of acidogenic and methanogenic microorganisms. Acidogenic bacteria thrive in slightly acidic conditions, while methanogenic archaea prefer a more neutral pH. Achieving this balance enhances efficiency in methane generation. In microbial electrolysis cells, pH influences both microbial activity and electrochemical reactions at the electrodes, necessitating a compromise for optimal performance. Incubation time, representing the duration of microbial processes, is a critical factor, often experimentally tuned to maximize methane yield by aligning with microbial activity and overall process kinetics. Synergistic control of pH and incubation time is fundamental for successful methane production in diverse bioenergy systems.

10.3. Temperature

Temperature has a considerable impact on MEC efficiency. The changing temperature during MEC functioning causes variations in bacterial metabolism and species [83]. This alteration has an impact on the reactor's functioning. The majority of electromethanogenesis experiments have been conducted in two temperature ranges: room temperature of 22-25°C and mesophilic of 30-35°C settings, as depicted in Fig. 21.

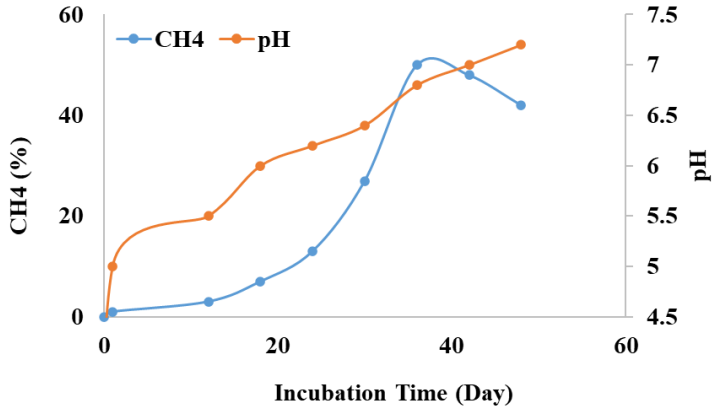


Fig. 20. The effect of pH and incubation time for methane production.

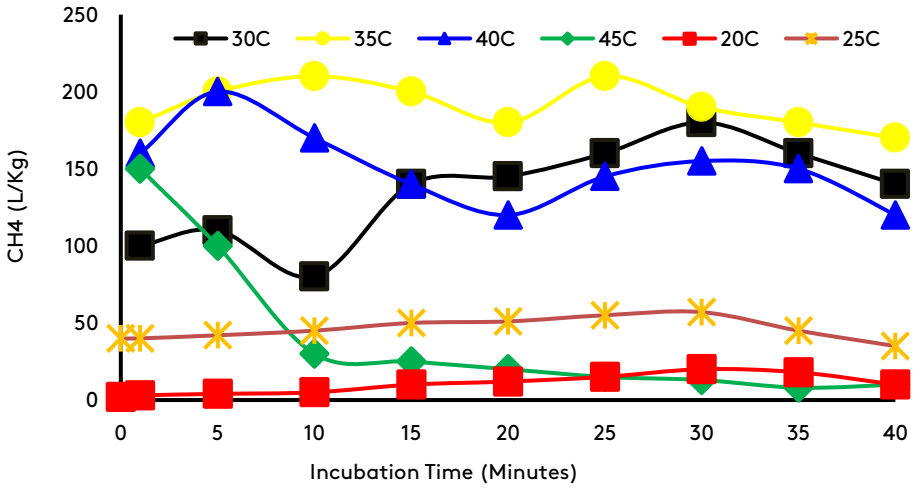


Fig. 21. The effect of temperatures and incubation time for CH_4 production using MECs.

The growth and mass transfer rate of electroactive microbe are affected by temperature changes [84]. The role of temperature in microbial processes, particularly in the context of methane (CH_4) production, remains a subject that requires a more comprehensive understanding. The available data is insufficient to precisely delineate the influence of temperature on cell growth and microbial community dynamics. Temperature is a crucial factor that can significantly affect the metabolic rates, enzymatic activities, and overall performance of microorganisms involved in methane-producing processes. The specific temperature requirements for optimal microbial activity can vary among different species, and understanding these nuances is essential for achieving maximum CH_4 yield. Further research and data acquisition on the temperature parameter are imperative to unlock the potential for enhanced efficiency and control in methane production processes.

10.4. Applied potential

One of the required physical criteria for the functioning of MECs to generate CH_4 is the electric potential or additional voltage. Changes in electric potential have a considerable influence on the growth and dispersion of electroactive microbes, as well as CH_4 formation as shown in Fig. 22. It is critical to remember that excessive amounts of supplied electron density may be harmful to the bacterium. This study suggested the necessity to examine the utilized potentials to maximize bacterial growth and promote activation. Gram-positive microorganisms were discovered to be the most often employed electroactive microbes in MECs paired with anaerobic digesting processes in several studies.

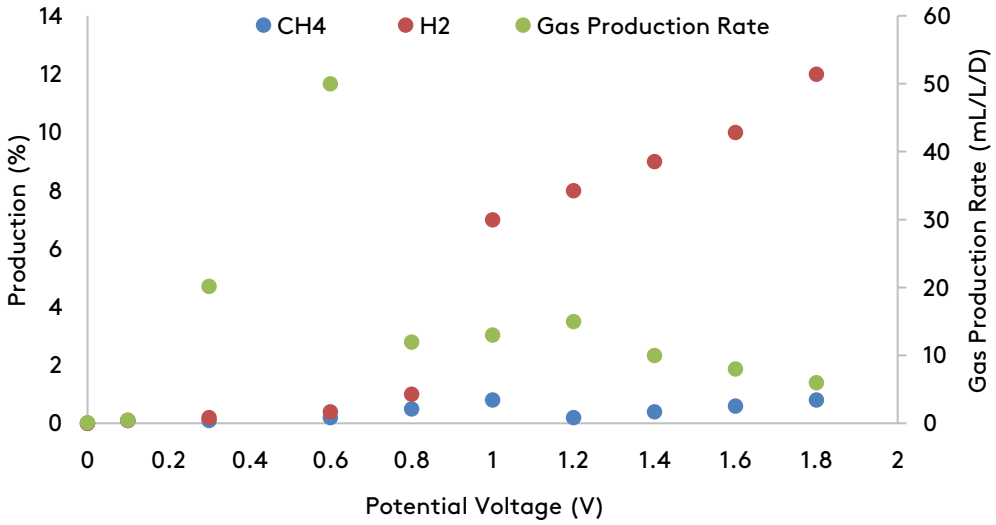


Fig. 22. The potential voltage effect for CH_4 production using MEC.

The three-dimensional design of their peptidoglycan cell wall affords substantial resilience to external shocks [85]. As a result, suitable external voltage must be considered for diverse materials in order to produce high rate CH_4 production. The technique of voltage supply and adequate utilization are required to calculate the process cost. Direct current power supplies are commonly employed in lab-scale reactors but fail when the methane generation mechanism is scaled up [86]. Standard voltage control and real-time control are required for the operation to be industrialized. Thus, several aspects like substrate type, cell layout, electrode composition, and microbes determine the appropriate potential difference in MECs. This reliance on many parameters highlights the necessity for voltage tuning for each MEC for improved system fuel efficiency.

10.5. Current density

The design process of MEC units that could significantly contribute to biomethanation underutilizes supplied current density, as demonstrated in Fig. 23. By raising the current density, bunched MECs can bypass the inherent drawbacks caused by a low oxide layer ratio [87]. Additionally, much research has found that using different electrode topologies can improve power density production as well as wastewater treatment, as shown in Fig 23.

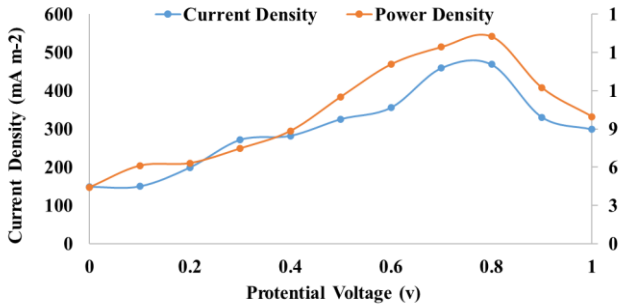


Fig. 23. Current density influencing the performance of MECs.

As illustrated in Fig. 23, the applied voltage is plotted against current and power density, using a 0.8 g/L sodium acetate substrate in a dual-chambered configuration. This setup overcomes various internal resistance levels, improving permittivity and resulting in the complete generation of methane.

11. Environmental factors affecting microbial electrolysis cells

Environmental factors, such as nutrient availability, microbial diversity, and abundance, significantly influence the performance and application of MECs in industrial settings. Adequate nutrient supply is crucial for the growth and metabolic activities of microorganisms involved in the electrochemical processes; deficiencies can lead to decreased efficiency in substrate conversion and lower biogas yields, while excess nutrients may disrupt microbial balance [61,75]. Additionally, a diverse microbial

community enhances the system's resilience and adaptability, promoting optimal substrate degradation and improved electrochemical performance. The natural selection of microbial populations is affected by varying environmental conditions such as temperature, pH, and the presence of inhibitors, making the maintenance of a balanced and diverse microbial community essential for sustaining high MEC performance [17,23,42]. Understanding these environmental factors is vital for optimizing MEC design and operation, enhancing their effectiveness in wastewater treatment and energy production, and showcasing their promising future in these applications [45,70].

11.1. Nutrient availability

Nutrient availability plays a crucial role in the performance of MECs, influencing the growth and activity of the microbial communities involved in the electrochemical processes [18]. Essential nutrients, such as nitrogen, phosphorus, and trace metals, are vital for the metabolic activities of microorganisms, which in turn affects the efficiency of biomethane production and the overall energy recovery from organic substrates [3]. In industrial applications, the concentration and type of nutrients can vary significantly based on the characteristics of the wastewater being treated. Therefore, optimizing nutrient levels tailored to specific waste streams is critical to achieving maximum performance from MECs [35]. Furthermore, inadequate nutrient supply can lead to imbalances in microbial communities, resulting in decreased efficiency in substrate conversion and lower biogas yields [27]. In contrast, excess nutrients can also disrupt the delicate equilibrium of microbial populations, potentially leading to adverse effects such as the proliferation of undesirable species [33]. Understanding the optimal nutrient conditions for MEC operation is essential for enhancing both wastewater treatment and energy production processes, making nutrient management a key consideration in the design and operation of MECs in industrial settings [67,77].

11.2. Microbial diversity and abundance

Microbial diversity and abundance are integral factors that directly influence the efficiency and stability of MECs [15]. A diverse microbial community can enhance the system's resilience and adaptability to varying operational conditions, promoting better substrate degradation and improved electrochemical performance [32]. Different microbial species may possess unique metabolic pathways and functions, enabling them to collectively optimize the conversion of organic matter into biogas [7]. For instance, specific bacteria may excel in hydrolyzing complex substrates, while others may be more efficient in electron transfer processes, thereby facilitating the overall conversion process in MECs [55]. In industrial applications, the natural selection of microbial populations can vary significantly based on environmental conditions, such as temperature, pH, and the presence of inhibitors [12]. Maintaining a balanced and diverse microbial community is essential for sustaining high performance in MECs, particularly in fluctuating operational environments. The abundance of key microorganisms can be monitored and adjusted through inoculation strategies or operational modifications, ensuring that the MECs remain effective over time [40]. This understanding of microbial diversity and abundance will not only enhance the performance of MECs but also provide insights into the best practices for their application in wastewater treatment and energy production, underscoring the technology's future prospects [71].

12. The Future prospects of microbial electrolysis cells (MECs) technology

MEC is a promising technology, particularly in the realm of sustainable energy production and wastewater treatment [66]. As global energy demands continue to rise alongside increasing environmental concerns, MECs offer a viable solution by converting organic waste into renewable energy sources, such as biomethane and hydrogen. Innovations in reactor design, materials, and operational strategies are continuously being explored to enhance the efficiency and cost-effectiveness of MECs, making them more attractive for large-scale industrial applications

[70,76]. Moreover, advancements in our understanding of microbial communities and their interactions within MECs can lead to tailored approaches that optimize performance based on specific waste streams and environmental conditions [35]. Integrating MEC technology with other renewable energy systems, such as solar and wind power, further expands its potential applications and benefits [17]. As regulatory frameworks increasingly support sustainable practices and renewable energy solutions, MECs are well-positioned to play a pivotal role in the future energy landscape, contributing not only to energy recovery but also to the mitigation of environmental impacts associated with waste disposal [52].

13. Conclusions

In light of escalating global warming concerns, the imperative for ecologically benign and sustainable technologies for methane generation is clear. MECs have emerged as a viable solution for methane, hydrogen, and wastewater treatment. Over the past two decades, the practical application of MECs in methane production has showcased significant progress. MECs' ability to produce methane in a single stage with cost-effective inputs at room temperature positions it as a promising option for effluent treatment, yielding methane as a substantial byproduct. Innovative approaches, such as the indirect method utilizing the highly efficient hydrogen evolution reaction, have been developed. Efficient electron transfer via electroactive microorganisms on conductive carbon electrodes within MEC reactors enhances feedstock breakdown and methane output. Nanotechnology as a catalyst has shown promise in boosting methane production and improving hydrogen evolution reaction performance. However, advancements in electron generation and transfer methods within the reactor components, including electrodes and membranes, are crucial for increased product output. Despite promising developments, there are still challenges to address, such as the need for innovative designs in electrode and membrane configurations to reduce losses from electron transport. Operating MECs in effluent not only promotes methane production but also mitigates harmful emissions. While the potential of methane-producing MECs is bright, commercialization hurdles, particularly high capital expenditures, need to be addressed. Improvement measures should focus on nanomaterials for enhanced catalytic performance and strategies to enhance microorganism adherence for improved biomethane quality and quantity. In this context, nanoparticles hold promise. Although MECs do not entirely replace the AD mechanism due to size and progress disparities, integrating MECs with AD, known as MEC-AD integrated MES, emerges as a more practical and promising solution for wastewater treatment. Electromethanogenesis in H-MEC-AD holds the potential to produce high-quality biogas by converting CO_2 to CH_4, reducing the costs of biogas upgrading. This review evaluated current applications and future prospects of MECs for methane production, highlighting significant findings in production mechanisms, electrode characteristics, use of electroactive microorganisms, and reactor configurations.

Abbreviations

MEC (Microbial Electrolysis Cell): A technology used in this study to evaluate biomethane production efficiency through comparative analysis of various materials and designs.

H-MEC (Hybrid Microbial Electrolysis Cell): A modified type of microbial electrolysis cell that combines elements of traditional MECs with additional features to enhance biomethane production efficiency and carbon dioxide capture, evaluated in this study through comparison of various design and material configurations.

MDCs (Microbial Desalination Cells): A technology utilized in this study for simultaneous desalination and energy production, where microbial processes are harnessed to remove salts from seawater while generating electrical energy.

MFCs (Microbial Fuel Cells): A bioelectrochemical system analyzed in this research that converts organic matter into electricity through microbial metabolism, providing a comparative basis for evaluating energy efficiency alongside biomethane production in H-MECs.

MSCs (Microbial Solar Cells): An innovative approach incorporated in this study that uses microbial communities to convert solar energy into electrical energy, facilitating discussions on integrating renewable energy sources with microbial technologies for enhanced biomethane production.

AD (Anaerobic Digestion): A biological process investigated in this study that involves the breakdown of organic matter by microorganisms in the absence of

oxygen, resulting in the production of biogas, primarily composed of methane and carbon dioxide. This process serves as a foundational mechanism for understanding the potential enhancements in biomethane production when integrated with microbial electrolysis cells.

HER (Hydrogen Evolution Reaction): A critical electrochemical reaction analyzed in this study that involves the production of hydrogen gas through the reduction of protons at the cathode of microbial electrolysis cells. Understanding HER is essential for evaluating the efficiency of H-MECs in converting organic substrates into renewable energy sources, including hydrogen and biomethane.

MES (Microbial Electrochemical System): A versatile technology examined in this study that integrates microbial processes with electrochemical reactions to convert organic waste into valuable biofuels and chemicals. MES encompasses various configurations, including microbial fuel cells, microbial electrolysis cells, and microbial desalination cells, allowing for the exploration of different operational strategies and materials to enhance biomethane production and carbon capture.

MEC-AD (Microbial Electrolysis Cell-Anaerobic Digestion): An integrated approach investigated in this study that combines microbial electrolysis cells with anaerobic digestion processes to enhance biomethane production. This system leverages the advantages of both technologies, utilizing microbial communities to efficiently convert organic waste into biogas while optimizing hydrogen production and carbon dioxide capture, thereby improving overall energy recovery and sustainability.

BioM (Biomethane): A renewable energy source produced through the anaerobic digestion of organic matter and microbial electrolysis processes, as investigated in this study. BioM serves as a sustainable substitute for natural gas, and the research focuses on optimizing its production efficiency through various designs and materials of microbial electrolysis cells, contributing to energy recovery and carbon dioxide mitigation.

Acknowledgments

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Chlamydomonas sp.(UKM6) and Scenedesmus sp.(UKM9) as biocatalysts for electricity production and water treatment. International Journal of Hydrogen Energy. 2023; 48(31), pp.11860-11873. https://doi.org/10.1016/j.ijhydene.2023.01.142

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