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**Microbial electrosynthesis technology for CO<sub>2</sub> mitigation, biomethane production, and ex-situ biogas upgrading**

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## Abstract

Currently, global annual CO<sub>2</sub> emissions from fossil fuel consumption are extremely high, surpassing tens of billions of tons, yet our capacity to capture and utilize CO<sub>2</sub> remains below a small fraction of the amount generated. Microbial electrosynthesis (MES) systems, an integration of microbial metabolism with electrochemistry, have emerged as a highly efficient and promising bio-based carbon-capture-and-utilization technology over other conventional techniques. MES is a unique technology for lowering the atmospheric CO<sub>2</sub> and CO<sub>2</sub> in the biogas, and also simultaneously convert them to renewable bioenergy, such as biomethane and biogas. As such, MES techniques could be applied for biogas upgrading to generate high purity biomethane, which has the potential to meet natural gas standards. This article offers a detailed overview and assessment of the latest advancements in MES for biomethane production and biogas upgrading, in terms of selecting optimal methane production pathways and associated electron transfer processes, different electrode materials and types, inoculum sources and microbial communities, ion-exchange membrane, externally applied energy level, operating temperature and pH, mode of operation, CO<sub>2</sub> delivery method, selection of inorganic carbon source and its concentration, start-up time, and system pressure. It also highlights the current MES challenges associated with upscaling, design and configuration, long-term stability, energy demand, techno-economics, achieving net negative carbon emission, and other operational issues. Moreover, we provide a summary of current and future opportunities to integrate MES with other unique biosystems, such as methanotrophic bioreactors, and incorporate quorum sensing, 3D printing, and machine learning to further develop MES as a better biomethane-producer and biogas upgrading technique.

**Keywords:** microbial electrosynthesis, biogas upgrading, methane, CO<sub>2</sub> reduction, bioelectrochemical systems, microbial electrochemical technologies

## 1. Introduction

Carbon dioxide (CO<sub>2</sub>) is a crucial component of the global carbon cycle, which plays a vital role in regulating the temperature on earth (Zhang et al., 2021). However, CO<sub>2</sub> has been a main contributor to the anthropogenic greenhouse gas (GHG) emissions: CO<sub>2</sub> = 63%, CH<sub>4</sub> = 24%, and N<sub>2</sub>O = 3% (Bian et al., 2020; ElMekawy et al., 2016) resulting in catastrophic global warming. The massive CO<sub>2</sub> release is driven by anthropogenic activities (e.g., deforestation) and industrial processes, especially fossil fuel utilization and processing (Xiao et al., 2021; Zhang et al., 2021). For example, deforestation can lead to an excess of CO<sub>2</sub> in the atmosphere, trapping a substantial amount of heat from the sun. This causes an increase in Earth's temperature, contributing to the greenhouse effect and resulting in global warming (Cheah et al., 2015; Lekshmi et al., 2023). Main CO<sub>2</sub> emissions (92.4%) have been induced by the energy sector, where the energy generation, energy transport, and manufacturing industry contributed to 34.8%, 29.6%, and 15.4% of the total CO<sub>2</sub> emissions, respectively (Dessì et al., 2021). To date, annual CO<sub>2</sub> emission has already reached an unprecedented level (>38 billion tons) and the annual CO<sub>2</sub> discharge rate is expected to escalate further (Bajracharya et al., 2017b; Mao et al., 2021; Zhang et al., 2021). Regrettably, only a small fraction of emitted CO<sub>2</sub> (~2.2 billion tonnes/year) is being captured (Moseman and Harvey, 2023; Smith et al., 2024), and a portion of captured CO<sub>2</sub> (~45 million tons) is being utilized and sequestered (Lebling et al., 2023). For instance, some of the captured CO<sub>2</sub> could be used to generate bioenergy and valuable products like acids, biofuels, and platform chemicals (Finn et al., 2012). Additionally, there are no current industrial technologies that can achieve net-zero/net-negative CO<sub>2</sub> emissions (Bian et al., 2020; Dessì et al., 2021). Consequently, recent scientific and technological advancements have been concentrating on enhancing effective CO<sub>2</sub> emission management and lowering CO<sub>2</sub> concentrations (Bian et al., 2020; Dessì et al., 2021; Yuan et al., 2019; Zhang et al., 2021).

Various techniques are available to minimize the CO<sub>2</sub> emissions. One potential solution is to utilize low-carbon bioenergy to reduce reliance on fossil fuels (Chu et al., 2017; Liu et al., 2015b), but the world still cannot completely rely on these renewable energy resources alone. Alternatively, carbon-capture-and-utilization (CCU) and carbon-capture-and-storage (CCS) technologies have emerged as alternatives for enabling direct CO<sub>2</sub> mitigation (Bui et al., 2018; Li et al., 2013). CCS technologies include storage of a significant amount of CO<sub>2</sub>, with 194 large-scale CCS facilities

worldwide (capture a total CO<sub>2</sub> capture capacity of 244 million tonnes per annum (Zapantis et al., 2023)) in various locations, such as forests, oceans, and underground (Li et al., 2013). However, these facilities face many challenges, including (Zhang et al., 2021): (1) underground storage is very expensive and causes geological instability (Chu et al., 2020a); (2) marine storage may adversely impact the marine ecosystem (e.g., acidification) (Lainez-Aguirre et al., 2017); and (3) forest storage can lead to shrinking forest areas and deforestation (Lainez-Aguirre et al., 2017). Therefore, CO<sub>2</sub> conversion into renewable resources like industrial chemicals and clean energy using CCU technologies could be more appropriate, effective, and feasible (Bian et al., 2018a; Jayathilake et al., 2022; Nwanebu et al., 2022). CO<sub>2</sub>-capturing in CCU can be accomplished as via chemical, physical, and/or biological processes (Anwar et al., 2020). However, physical and chemical methods, such as absorption (Zhao et al., 2016a), adsorption (Webley, 2014), photochemical (Fang et al., 2021) often require high energy input and toxic chemicals (Tufa et al., 2020). A key challenge in utilizing CO<sub>2</sub> is its stability, requiring higher activation energy for chemical reactions, often resulting in simple state changes without transformation into target products during conversion processes. The electrochemical CCU options have poor selectivity of target products (Li and Sun, 2016; Ma and Kenis, 2013). Moreover, intensive energy demand and high operation costs limit the implementation of CCU methods (Spinner et al., 2012; Yaashikaa et al., 2019).

Biomethane or methane (CH<sub>4</sub>) is a more potent GHG than CO<sub>2</sub> but can be utilized as a renewable fuel (Lee et al., 2020; Patil et al., 2015; Zhang et al., 2021). Biogas generated from the anaerobic digestion (AD) process consists of approximately ~60% CH<sub>4</sub> and ~40% CO<sub>2</sub> along with other impurities (Antukh et al., 2022; Le Saché et al., 2019; Vilardi et al., 2020). An emerging research area that involves the carbon capturing process is biogas upgrading to renewable natural gas (RNG), by increasing CH<sub>4</sub> level in the biogas by > 95% (Antukh et al., 2022; Kim et al., 2022; Sun et al., 2015). Biogas upgrading is needed for various industrial and municipal facilities and sites, including anaerobic digesters, wastewater treatment plants, and landfills (Lecker et al., 2017). The upgraded biogas can directly be used as a transportation fuel, or injected into the natural gas grid, and/or used for power and heat generation (Antukh et al., 2022; Aryal et al., 2018; Nelabhotla and Dinamarca, 2019). The upgrading of biogas is typically achieved either by removing the CO<sub>2</sub> and other impurities through chemical/physical processes (e.g., adsorption and membrane separation) (Adnan et al., 2019; Awe et al., 2017), or by reducing the CO<sub>2</sub> in the biogas to CH<sub>4</sub> (Adnan et al.,

2019; Lecker et al., 2017). These physicochemical processes face challenges, such as high capital and operation costs, a large footprint, and the need for highly-skilled personnel (Adnan et al., 2019; Antukh et al., 2022). In this context, biological CCU technologies are more promising option for effective CO<sub>2</sub> reduction (Yuan et al., 2019; Zhang et al., 2021) and efficient biogas upgrading (Antukh et al., 2022; Khan et al., 2022). In enzymatic and microbe-dependent processes, energy efficiency and product selectivity remain high, even when dealing with elevated single-pass conversion rates (calculated by 100% x CO<sub>2</sub> consumed over CO<sub>2</sub> flowed in); microbes and enzymes also have the ability to self-regenerate (Jayathilake et al., 2022). However, the slower kinetics of biological systems remain a significant barrier compared to commercial processes. Boosting microorganism concentration can address slower biological system kinetics, allowing faster substrate utilization, including CO<sub>2</sub> reduction (considering the following relationship:  $\frac{dS_{CO_2}}{dt} = \frac{-q_{max}}{dt} \left( \frac{S_{CO_2}}{K_{S_{CO_2}} + S_{CO_2}} \right) X_a$ , where  $S_{CO_2}$  is the CO<sub>2</sub> substrate concentration,  $X_a$  is biomass concentration).

Among the biological CCU technologies for biogas upgrading, microbial electrochemical technologies (METs), an integration of microbial metabolism with electrochemistry, have gained attention as a potential strategy (Kim et al., 2022; Lee et al., 2020; Zhang et al., 2021). METs have been demonstrated for various energy and environmental applications (Chung et al., 2021; Rousseau et al., 2020; Sravan et al., 2021), including (1) microbial fuel cells (MFCs) for producing bioelectricity (Logan et al., 2006; Sravan et al., 2021); (2) microbial electrolysis cells (MECs) for generating biohydrogen (Hua et al., 2019; Rozendal et al., 2008); (3) combined MEC and AD, known as the microbial electrolysis cell-assisted anaerobic digestion (MEC-AD) systems for CH<sub>4</sub> production (Zakaria and Dhar, 2020; Zakaria and Dhar, 2019); (4) production of algal biomass in microbial carbon capture cells (MCCs) (Hu et al., 2015); and (5) bioelectrochemical sensors for environmental monitoring (Chung and Dhar, 2024; Chung et al., 2024; Chung et al., 2020a; Chung et al., 2022). More recently, METs also showed their ability to reduce and convert CO<sub>2</sub> to high-value bioproducts like alcohols, medium-chain fatty acids, and other industrial chemicals (Bian et al., 2020; Chu et al., 2021; Zakaria and Dhar, 2019; Zhang et al., 2021). Notably, METs that are designed to reduce CO<sub>2</sub> to produce bioproducts, such as CH<sub>4</sub>, are known as a microbial electrosynthesis (MES) system, which is a derivative of MECs (Baek et al., 2022; Thatikayala and

Min, 2021; Zhang et al., 2021). In general, MES focuses on the cathodic CO<sub>2</sub> conversion while other MET systems, such as MECs heavily focus on the anodic bio-oxidation (Zakaria et al., 2018; Zhang et al., 2021). Unlike other METs, MES mainly relies on an abiotic anode and a biocathode equipped with biocatalysts, such as methanogens for capturing CO<sub>2</sub> and reducing it to CH<sub>4</sub> (Bian et al., 2020; Kim et al., 2022; Lee et al., 2020; Zakaria and Dhar, 2019). In this regard, MES could serve as a unique CCU technology. Specifically, these methanogens demonstrated the ability to boost CH<sub>4</sub> content in biogas > 95% (or CO<sub>2</sub> content < 10%) (Antukh et al., 2022; Nelabhotla and Dinamarca, 2019), meeting the natural gas standards. MES is also considered a promising power-to-gas technology as it can utilize surplus electricity in the form of CH<sub>4</sub> (Götz et al., 2016; Kracke et al., 2020). Of note, the power-to-CH<sub>4</sub> storage is a promising platform leveraged by current natural gas infrastructure across the globe (Kracke et al., 2020). While past studies indicated the robustness and proficient process stability of MES as a CO<sub>2</sub>-mitigating/biogas upgrading technique (Aryal et al., 2022; Jayathilake et al., 2022; Nelabhotla and Dinamarca, 2019), further developments are needed for process scale-up and boosting process kinetics (Antukh et al., 2022; Batlle-Vilanova et al., 2019; Bian et al., 2020; Lee et al., 2020).

MES can be advantageous over traditional power-to-gas transformation routes like the Sabatier process, which involves water electrolysis and thermochemical methanation techniques (Götz et al., 2016; Jayathilake et al., 2022; Kracke et al., 2020). While high temperature and pressure are required for the Sabatier process, MES can be operated under ambient pressure and temperature (Götz et al., 2016; Kracke et al., 2020). MEC-AD could also be used for CH<sub>4</sub> generation using organics as a carbon source (Zakaria and Dhar, 2019). However, using a MEC-AD as a CCU technology has some downsides. For instance, the combination of the anodic bio-oxidation of organics, including ammonification, and the cathodic reduction reaction, increasing the pH of the cathode chamber, often results in free ammonia inhibition of cathodic methanogens (Zakaria and Dhar, 2019). Furthermore, incorporating the MEC with AD is still challenging, due to the lack of appropriate scale-up options (Zakaria and Dhar, 2019). In contrast, employing MES separately for ex-situ biogas upgrading is a more flexible option. MCCs could be used for CO<sub>2</sub> capture, with the main drawback being the low algae biomass yield due to nutrient limitations, leading to a low CO<sub>2</sub> fixation efficiency (Dragone et al., 2011; Zhang et al., 2021). Thus, the MES enables much more robust and stable CO<sub>2</sub> conversion to CH<sub>4</sub> by preventing the aforementioned challenges.

To date, several review articles have covered diverse MES applications, including the synthesis of chemicals, alcohols, acids, and biofuels (Bian et al., 2020; Dessì et al., 2021; Lee et al., 2020; Xiao et al., 2021; Zhang et al., 2021). Following an extensive literature search, only a few review-type papers were found, which focused on CO<sub>2</sub> conversion to CH<sub>4</sub> and biogas upgrading with a significant emphasis on anodic bio-oxidation, which lacked in discussions on sole MES configuration (Aryal et al., 2021; Aryal et al., 2022; Jayathilake et al., 2022). Some of the published reviews on electro-methanogenesis have been heavily focused on MEC-AD configuration and anodic bio-oxidation as well (Blasco-Gómez et al., 2017; Zakaria and Dhar, 2019). To the best of the author's knowledge, there is only a couple of review papers discussing MES and MEC-AD as a biogas upgrading technique (Aryal et al., 2022; Yuan, 2024), but a critical review on using sole MES for CO<sub>2</sub> mitigation, CH<sub>4</sub> production, and ex-situ biogas upgrading is still lacking. This critical review article does not discuss the other types of CH<sub>4</sub>-producing METs, such as MEC-AD (Nelabhotla and Dinamarca, 2019; Zakaria and Dhar, 2019; Zhang et al., 2021). In addition, MES studies applied CO<sub>2</sub> reduction to other value-added products, such as acetate to achieve higher CH<sub>4</sub> content by only reducing CO<sub>2</sub> fraction in biogas (Aryal et al., 2022; Gao et al., 2021; Jourdin et al., 2016) were also excluded. Ultimately, this critical review article aims to offer a thorough overview of published reports on MES for CO<sub>2</sub>-to- CH<sub>4</sub> and biogas upgrading as well as various performance metrics and operating conditions, such as inoculum sources, types of separators, temperature, pH, externally applied energy, etc. Moreover, the current challenges and prospects of CH<sub>4</sub>-producing- and biogas-upgrading MES on scaling up toward field applications are also thoroughly discussed.

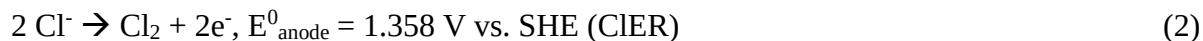
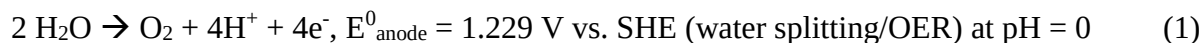
## **2. Brief overview of fundamental mechanisms of microbial electrosynthesis technology for CH<sub>4</sub> production and biogas upgrading**

### **2.1 Mechanisms**

MES typically features an abiotic anode and a biocathode, with the anode and cathode chambers divided by an ion-exchange membrane (IEM), such as cation-exchange membrane (CEM) (Lee et al., 2020; Zhang et al., 2021). MES operation requires significant energy input (Table 1) due to the electrochemical reactions in the anode, such as water splitting/oxygen evolution reaction (OER) and chlorine evolution reaction (ClER) for generating protons and electrons (Palaniselvam et al., 2017). In electro-methanogenesis, hydrogen (H<sub>2</sub>) produced in the cathode directly serves as the

electron donor for hydrogenotrophic and/or electrotrophic methanogen, enabling the conversion of CO<sub>2</sub> to CH<sub>4</sub> (Beese-Vasbender et al., 2015; Kracke et al., 2020; Kracke et al., 2019). Additionally, CO<sub>2</sub> reduction reactions are nonspontaneous, which requires an adequate amount of externally-applied energy (e.g., applied current, potential, or voltage) for overcoming the thermodynamic barriers (Christodoulou et al., 2017; Zakaria and Dhar, 2019). Overall, the CO<sub>2</sub> conversion process in MES is initiated by dehydrogenase catalysis after CO<sub>2</sub> is captured by an enzyme (e.g., carbonic anhydrase), which enables the enhancement of CO<sub>2</sub> solubility and the efficiency of its further conversion (discussed later) (Srikanth et al., 2017; Zhang et al., 2021). Figure 1 describes the typical MES configuration for CH<sub>4</sub> generation and biogas upgrading using CO<sub>2</sub> as the cathodic feedstock. A comprehensive discussion on different CH<sub>4</sub> production routes is provided later. Figures 2 and 3 described the anodic and cathodic pathways of MES. The operation of MES begins when enough energy is supplied (Table 1) to start the electrochemical reactions in the anode (water splitting/OER, ClER), which generate protons and/or electrons as shown below (Alqahtani et al., 2019; Bian et al., 2020; Jayathilake et al., 2022; Karlsson and Cornell, 2016):

\*Note SHE is an abbreviation for standard hydrogen electrode



From the aforesaid equations, a large amount of energy is being consumed by the OER reaction due to it being kinetically unfavorable. The OER is also quite complicated as it involves four-electron transfer (Palaniselvam et al., 2017), but it requires less activation energy compared to the ClER pathway (Karlsson and Cornell, 2016). Furthermore, the recovery of chlorine as a disinfection agent during ClER is an economical benefit (discussed later) (Batlle-Vilanova et al., 2019). However, past studies have indicated that oxygen can pass through a cation exchange membrane between the anodic and cathodic chambers, increasing the oxidation potential in the biocathode. This increased oxidation potential can stimulate the growth of aerobic heterotrophic bacteria and limit the growth of obligate anaerobes. Notably, it has been reported that oxygen diffusion can occur from the anode to the cathode in a dual-chamber MES (Alqahtani et al., 2019; Bian et al., 2020; Chung et al., 2021; Feng et al., 2013; Suzuki et al., 2016; Xiao et al., 2020a). Thus, the ClER could present another option, given the detrimental impacts of oxygen exposure

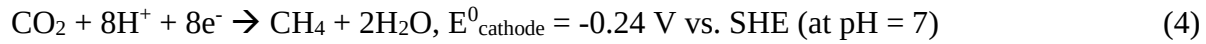
on the cathode biofilm containing chemolithoautotrophic microorganisms. CIER exhibits significantly higher selectivity compared to OER when using electrocatalysts, as it is kinetically more favorable due to the involvement of two electrons in chlorine evolution (Karlsson and Cornell, 2016). Moreover, CIER enables achieving a circular economy by offering much lower overpotential to initiate the reaction and the huge market demand (50-60 million tons/year) of Cl<sub>2</sub> gas (Bian et al., 2020; Gamble, 2019). Despite the benefits, CIER may need extra protons at the cathode since the reaction doesn't generate protons. Preventing chlorine gas diffusion from the anode to the cathode is essential to protect cathode biofilms. Alternatively, MES could be equipped with bioanode other than typical electroactive bacteria (EAB) (*Geobacter*, *Shewanella* species, etc.) which require organic carbon sources, such as non-fermentable substrates (acetate) and fermentable substrates (glucose, wastewater, etc.) (Chung and Dhar, 2021b; Chung et al., 2020a; Sravan et al., 2021; Zakaria et al., 2020). For instance, some SOB like *Desulfobulbus propionicus* and *Desulfuromonas* capable of performing bisulfide decomposition could serve as a biocatalyst in MES anode to produce electrons and protons (Gong et al., 2013). The following equation illustrates the decomposition of bisulfide using SOB as a biocatalyst within a specified working environment (at pH = 9, [Na<sup>+</sup>] = 1M) (Ni et al., 2019):



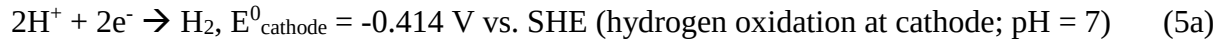
The bioanode enriched with sulfide-oxidizing bacteria (SOB) does not produce additional CO<sub>2</sub> like typical EAB as they do not oxidize organic matter (Chung and Dhar, 2021d; Zakaria et al., 2019). Compared to the abiotic electrochemical reactions, the bioelectrochemical mode is much more thermodynamically favorable and the electrons can be transferred from bisulfide to anode with fairly low applied energy (e.g., anode potential poised between 305 mV vs. SHE and 503 mV vs. SHE) (Ni et al., 2019; Ter Heijne et al., 2018). The ammonium oxidation reaction (Fig. 3d) has not been investigated thoroughly (as discussed later). Regardless of the selected anodic electrochemical reactions (Eq. 1-3), the generated electrons, first, move from the anode to the cathode via an external circuit because of the potential gradient (Zakaria and Dhar, 2019; Zhang et al., 2021). Then, the generated protons are transported to the cathode via a separator to maintain charge neutrality (Chung et al., 2020a; Dhar and Lee, 2013; Dhar et al., 2016). Despite the anion-exchange membranes (AEMs) being more beneficial for MET operation (Dhar and Lee, 2013; Leong et al., 2013), CEMs or proton-exchange membranes (PEMs) are often selected for their

effectiveness in proton transport from anode to cathode (Table 1). An overview of possible methanogenesis pathways in biocathode is shown in Figures 2 and 4.

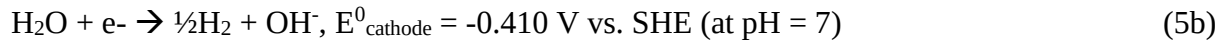
When the cathode biofilm is fed with external CO<sub>2</sub>, these electrons and protons in the cathode chamber are simultaneously consumed by the methanogens to perform indirect methanogenesis (indirect electron transport catalyzed by hydrogenotrophic methanogens) and/or direct methanogenesis (direct electron transport catalyzed by electro-methanogens/electrotrophs) (Batlle-Vilanova et al., 2015; Kim et al., 2022; Zakaria and Dhar, 2019; Zhang et al., 2021). Briefly, the key pathways in MES are direct- and indirect CH<sub>4</sub> formation (Nelabhotla and Dinamarca, 2019; van Eerten-Jansen et al., 2015; Villano et al., 2010). Eq. 4 describes the reaction associated with electro-methanogenesis via direct electron transfer pathway of CH<sub>4</sub> formation (also known as electro-methanogenesis):



Alternatively, CH<sub>4</sub> generation through indirect pathways involves intermediate compounds like H<sub>2</sub> or acetate (Nevin et al., 2011). In one of the pathways, hydrogen oxidation/electrocatalytically produced H<sub>2</sub> on the cathode or H<sub>2</sub> formed by the electroactive microorganisms (biologically produced due to the involvement of hydrogenases during MES operation; (Mayer et al., 2019)) act as the electron carrier and combine with CO<sub>2</sub> to produce CH<sub>4</sub>:



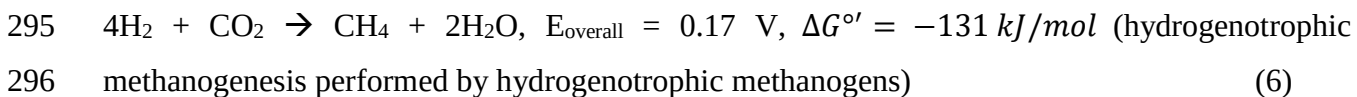
In certain instances, even though protons have a high diffusion coefficient in water (10<sup>-4</sup> cm<sup>2</sup>/s, Grotthuss mechanism), their low concentration in neutral media (10<sup>-10</sup> mol/cm<sup>3</sup>) results in water predominantly acting as the reactant in the hydrogen evolution reaction (HER), which creates a spike in local pH due to the hydroxide ion formation. Hence, the following reaction could occur in the cathode (Jayathilake et al., 2022):



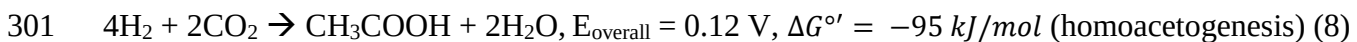
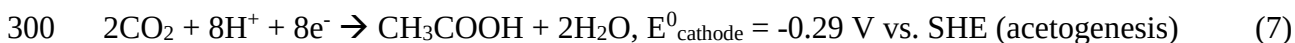
Moreover, for a cathode responsible for performing HER, the equation below represents the relationship between the electrode surface pH, diffusion layer thickness, and current density (Jayathilake et al., 2018; Jayathilake et al., 2022) (further discussed in a later section):

$$\text{Surface pH} = -\log [C^{*H^+} - (I\delta/nFD)] \quad (5c)$$

where  $\delta$  = diffusion layer thickness;  $D$  = diffusion coefficient of  $H^+$ ;  $I$  = current density;  $F$  = Faraday constant; and  $C^{*H^+}$  = bulk formal concentration of protons. In an electrochemical reaction, the concentration of reactants at the electrode surface is reduced relative to the bulk concentration (Jayatilake et al., 2018). The concentration gradient that forms as a result is referred to as the diffusion layer. Following Equation 5a, these produced  $H_2$  produced under anaerobic conditions is utilized by microorganisms through their reversible bidirectional hydrogenase enzymes to acquire electrons and protons (Bakonyi et al., 2023). Especially, the hydrogenotrophic methanogens utilize the generated  $H_2$  to perform indirect methanogenesis (also known as the indirect  $CH_4$  formation via indirect electron transfer (IET) pathway):



The other indirect pathway for  $CH_4$  formation involves the bioelectrochemical formation of acetate via acetogenesis or homoacetogenesis followed by acetoclastic methanogenesis (Molenaar et al., 2017; Vidales et al., 2019):



Note, the reactions from Equations 6-9 are based on Standard Temperature and Pressure (STP) condition ( $T = 298 \text{ K}$ ,  $P = 1 \text{ atm}$ ) and  $\text{pH } 7$ . Among the aforementioned pathways, the major pathway for  $CH_4$  generation is identified as  $CO_2$  reduction, and thus, the overall system performance is dominantly determined by the reaction rate of  $CO_2$  reduction (Blasco-Gómez et al., 2017). Furthermore, hydrogenotrophic methanogens, such as *Methanobacterium* or *Methanobrevibacter* were reported to play a main role (Equations 4 and 6) (Blasco-Gómez et al., 2017; Eerten-Jansen et al., 2013), especially in studies that investigated mixed culture biocathodes in  $CH_4$ -producing METs (Siegert et al., 2015). Fig. 5 describes an example diagram of a simplified native metabolic pathway of hydrogenotrophic methanogenesis in *M. maripaludis*. Briefly speaking, electrons from two moles of hydrogen are distributed between reducing ferredoxin and

regenerating coenzymes B and M through electron bifurcation. The reduced ferredoxin then participates in the initial step of CO<sub>2</sub> reduction in the pathway. The organism conserves energy in the form of ATP via a transmembrane sodium gradient. More explanations on the biomethanation and metabolic pathways of methanogens are provided in the literature (Blasco-Gómez et al., 2017; Kracke et al., 2020; Mou et al., 2022a; Yu et al., 2022; Zakaria and Dhar, 2019). However, the importance of the other methanogenic pathways and methanogenic archaeal species should not be overlooked, especially when working with mixed microbial consortia. The direct CH<sub>4</sub> formation pathway illustrated in Equation 4 is also considered to be the most energy-efficient process (Van Eerten-Jansen et al., 2012) due to the following reasons: (1) the lowest energy demand (van Eerten-Jansen et al., 2015), and; (2) not influenced or limited by the mass transfer of electron carriers (Zhen et al., 2018). As outlined in the literature (Junicke et al., 2016; Zakaria and Dhar, 2019), the process of homoacetogenesis is not as thermodynamically favorable when compared to hydrogenotrophic methanogenesis. This is evidenced by their respective standard Gibbs free energies, with hydrogenotrophic methanogenesis exhibiting a value of -32.68 kJ/mol of hydrogen, whereas homoacetogenesis shows -24.94 kJ/mol of hydrogen at pH 7. Compared to hydrogenotrophic methanogens, homoacetogens also have a higher K<sub>m</sub> (Michaelis–Menten constant) and lower  $\mu_{\max}$  (maximum specific microbial growth rate) (Peters et al., 1998; Zakaria and Dhar, 2019). More details on different methanogenic pathways are further elucidated in the literature (Antukh et al., 2022; Jayathilake et al., 2022; Molenaar et al., 2017; Vidales et al., 2019; Yuan et al., 2019; Zakaria and Dhar, 2019). Theoretically, considering water decomposition or OER has been selected as an anodic electrochemical reaction, the differences in potential between the two electrodes are 1.06 V (under pH = 7 and T = 298 K) for CH<sub>4</sub> synthesis at the biocathode (Bakonyi et al., 2023). More fundamental and basic information can be found in other review articles (Aryal et al., 2022; Blasco-Gómez et al., 2017; Chung and Dhar, 2023; Jayathilake et al., 2022; Lee et al., 2020; Zakaria and Dhar, 2019; Zhang et al., 2021).

## **2.2 Electron transfer mechanism in MES**

Electron utilization occurs inside microbial cells, while electron receptors are primarily in solid form and cannot go into the cell or microorganism, are found microorganism's outer surface (Chung and Dhar, 2023; Zhang et al., 2021). The electron transfer/uptake in the biocathode are accomplished by intracellular electron transfer (INT), extracellular electron transfer (EET), and

IET processes, which are vital for facilitating methanogen-electrode interaction (Blasco-Gómez et al., 2017; Choi and Sang, 2016; Zakaria and Dhar, 2019; Zhen et al., 2018). EET is the process through which microbes and electrodes exchange electrons. Enhancing the efficiency of EET can significantly boost CO<sub>2</sub> capture and conversion in MES (Zhang et al., 2021). There are two primary electron transfer mechanisms in MES biocathodes: “direct/unmediated electron transfer” and “mediated/indirect electron transfer”. These mechanisms facilitate the direct transport of electrons from the cathode to microbes like methanogens and electrotrophs (Aryal et al., 2022; Blasco-Gómez et al., 2017; Li et al., 2020a; Villano et al., 2010; Xiao et al., 2020b). Figure 6 summarizes different methanogenic pathways in the MES biocathode.

As briefly mentioned above, the electron exchange between the electrode and microbes is needed to initiate the CO<sub>2</sub> reduction reaction (Baek et al., 2022; Villano et al., 2010). Especially, the EET processes from cathode electrode to the methanogens and electrotrophic methanogens are accomplished in multiple ways (Bian et al., 2020; Lee et al., 2020; Zakaria and Dhar, 2019): (1) DET; direct transfer of electrons when the methanogens and microorganisms are physically attached to the cathode surface (Guzman et al., 2019; Walker et al., 2019); (2) IET; the electrons are transferred using various redox mediators (Harrington et al., 2015; Lee et al., 2020); (3) IET; the electrons are transferred using hydrogen generated from the cathode electrode facilitated by hydrogen-utilizing methanogens (Torella et al., 2015); and (4) interspecies hydrogen transfer (IHT); the electrons are transferred using the biologically produced H<sub>2</sub> by mixed-culture that are consumed by H<sub>2</sub>-utilizing methanogens (Barua and Dhar, 2017; Mayer et al., 2019). After all, the intracellular electron transfer process takes place followed by the EET processes. Also, the INT process further enables the delivery of the electrons to the inside of microbial cells by the intracellular electron carriers (e.g., NADH-delivering enzymes) (Nevin and Lovley, 2002). Of note, the EET kinetics is largely influenced by the cathode potential, and reducing this potential can slow down EET (Villano et al., 2010). EET for initiating the electro-methanogenesis in the MES is mainly governed by the level of externally supplied energy; for instance, CH<sub>4</sub> generation occurs under the cathode potential lower than -0.65 V. vs Ag/AgCl or -0.45 V vs. SHE) (Blasco-Gómez et al., 2017; Villano et al., 2010; Zakaria and Dhar, 2019). Therefore, it is exceptionally prominent to attain an efficient EET as it would maximize the overall electron utilization/transmission and CO<sub>2</sub> capture/utilization processes efficiencies.

There are still uncertainties in understanding the complete electron transfer process in MES, requiring further exploration. Additionally, claiming direct electro-methanogenesis as the primary mechanism in CH<sub>4</sub> production is premature, given the various pathways available for methanogenic archaea to utilize CO<sub>2</sub>, electrons, and protons (Aryal et al., 2022; Blasco-Gómez et al., 2017; Villano et al., 2010; Zakaria and Dhar, 2019). For instance, a study reported electro-methanogenesis mainly via DET from the surface cathode (Cheng et al., 2009), while another research claimed that biogas upgrading could also be accomplished using either EET and/or IET using H<sub>2</sub> mediated from cathode (Batlle-Vilanova et al., 2015). Hence, the exchange of electrons between the electrode and microbes is profoundly intricate and challenging to completely comprehend, as its mechanism relies on cell metabolism, electrode characteristics, and internal resistances within the system (Zhang et al., 2021). Additional information can be found in the literature (Chung and Dhar, 2023; Li et al., 2020a; Tian et al., 2023; Villano et al., 2010).

### **2.2.1 Direct electron transfer (DET)**

In MES, DET pathway involves electrotrophic methanogens that make direct contact with the cathode surface to receive electrons (Bian et al., 2020; Walker et al., 2019; Zakaria and Dhar, 2019; Zhang et al., 2021). These methanogens utilize the extracellular electron carriers, such as c-type cytochromes (Choi and Sang, 2016; Myers and Myers, 2001), nanowires (Reguera et al., 2005), and membrane vesicles (Zhao et al., 2021) to facilitate electron transfer. Additionally, the archaellum of *Methanospirillum hungatei* has been found to be electrically conductive, enhancing DET (Walker et al., 2019). It has also been observed that certain methanogens, like the *Methanobacterium*-like strain IM1, can engage in DET electro-methanogenesis under specific cathode potentials (e.g., -0.4 V vs. SHE), a potential under which hydrogenotrophic methanogens, such as *M. maripaludis* do not produce methane (Beese-Vasbender et al., 2015; Blasco-Gómez et al., 2017). Yin et al. (2016) found that the DET for transforming CO<sub>2</sub> to CH<sub>4</sub> was also done by a mixed culture consortium mainly enriched with *Methanothrix* and *Azonexus*. Such findings demonstrated that the DET as a single pathway could be used to produce CH<sub>4</sub>. Hence, more positive cathode potential (>-0.41 V vs. SHE) should be maintained to completely eliminate the IET pathway (e.g., eliminating HER) and to promote the DET electro-methanogenesis pathway (Zakaria and Dhar, 2019). The discussions on how externally applied energy promotes or favors the DET and/or IET electro-methanogenesis pathway are elucidated later. Past studies have

demonstrated that IET is relatively more inefficient compared to DET due to the loss of electrons and conversion of intermediates (Zhang et al., 2021). Therefore, the pathway of DET is often thought as a more ideal EET process. Some parameters, such as the cathode electrode characteristics, including specific surface area, conductivity, and biocompatibility, must be examined for optimizing the DET pathway (Bian et al., 2020; Zhang et al., 2021). However, numerous studies assert that DET accounts for only a minor fraction of methane production in MES, with the majority occurring through IHT and/or hydrogenotrophic methanogenesis (hydrogen-mediated electro-methanogenesis) (Batlle-Vilanova et al., 2015; Blasco-Gómez et al., 2017; Villano et al., 2010).

### 2.2.2 Indirect electron transfer (IET)

Methanogens that are unable to perform DET must go through a mediated pathway for the indirect transfer of electrons. The IET pathway in a MET is often accomplished through the diffusion of electron shuttles and redox mediators (Blasco-Gómez et al., 2017; Von Canstein et al., 2008). Furthermore, electron donors, such as  $H_2$ , formate, sulfide, and reduced metal ions are used by chemolithoautotrophs for reducing  $CO_2$  to  $CH_4$  through different pathways for the fixation of carbon (Bian et al., 2020). For instance, the  $H_2$  is generated via HER in the cathode (Equation 5) when enough external energy is applied (e.g.,  $E^0_{cathode} = -0.41$  V vs. SHE). Then,  $H_2$ -oxidizing methanogens, such as *Methanosarcina* consume this generated  $H_2$  at the cathode surface to transform  $CO_2$  to  $CH_4$  (Torella et al., 2015; Walker et al., 2019). However, although the IET pathway can be improved via dosing more redox mediators exogenously, more studies investigating the optimal dosage are needed as some of them could be toxic to some methanogens.

Other information on the fundamental aspects of MES, in terms of methanogens/electrotrophs and their roles (Eerten-Jansen et al., 2013; Li et al., 2020b; Siegert et al., 2014; Xiao et al., 2020b), biomethanation and metabolic pathways of methanogens (Kracke et al., 2020; Mou et al., 2022a; Yu et al., 2022), DET vs. IET (Li et al., 2020a; Tian et al., 2023; Villano et al., 2010), methanogen-electrode interactions (Choi and Sang, 2016; Modestra and Mohan, 2019), and electron flux (Patil et al., 2015) are further elucidated in the other review articles and book chapters (Aryal et al., 2022; Blasco-Gómez et al., 2017; Chung and Dhar, 2023; Jayathilake et al., 2022; Lee et al., 2020; Zakaria and Dhar, 2019; Zhang et al., 2021).

### 3. Summary of developments of biogas-upgrading MES

This section concisely lists key findings from published work of MES applied for biogas upgrading. The development of ex-situ biogas upgrading using MES over time is shown in Figure 7. Despite MES being such a promising platform for transforming CO<sub>2</sub> to CH<sub>4</sub>, only a few published reports have explored the real biogas upgrading application of MES. To the best of the author's knowledge, the digester biogas upgrading application of MES was first introduced in 2014 by Xu and their team (Xu et al., 2014). Specifically, their MES biocathode, dominated by *Methanobacterium petrolearium* (97-99%), could reduce the CO<sub>2</sub> content in the biogas to < 10%, demonstrating a feasible option for biogas-upgrading. Several years after, Das et al. (2018) demonstrated MES with real biogas (gas composition: 51% CH<sub>4</sub>, 36% CO<sub>2</sub>, 4% NH<sub>3</sub>, and other impurities, such as N<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>S). A year later, Batlle-Vilanova et al. (2019) further validated MES with real biogas produced from a full-scale AD facility. Recently, Kim et al. (2022) investigated MES fed with simulated AD biogas (60% CH<sub>4</sub> and 40% CO<sub>2</sub>), which could increase CH<sub>4</sub> content up to 96%, with a maximum CH<sub>4</sub> generation rate of 18.9 L/m<sup>2</sup><sub>cathode</sub>/d along with a very high CO<sub>2</sub>-conversion-to-CH<sub>4</sub> efficiency (95%). However, with real biogas (CH<sub>4</sub> = 60-65%, CO<sub>2</sub> = 30-35%, and a trace amounts of other gases), the CH<sub>4</sub> production rate decreased to 10.32 L/m<sup>2</sup><sub>cathode</sub>/d, despite CH<sub>4</sub> composition (96%) remained high. This decrease in CH<sub>4</sub> production rate is potentially attributed to the presence of impurities, such as sulfur compounds and siloxane impeding the methanogenic activity. Interestingly, the authors also compared the performances of 250 mL and 3 L MES reactors and observed inferior performance with 3 L MES (CH<sub>4</sub> generation rate: 18.9 vs. 4.78 L/m<sup>2</sup>/d; Faradaic efficiency: 95% vs. 60%). Considering the amount of energy applied to both systems (2.6-2.8 V and 5.6-5.8 V for 250 mL and 3 L reactors, respectively), this is potentially attributed to the insufficient amount of energy applied to the larger reactor. Other factors, such as electrode spacing, increased internal losses, and differences in configurations may have also played a substantial role in the inferior performance observed in 3L MES reactor. Still, such findings indicated that MES could be further developed for biogas upgrading. De la Puente et al. (2022) operated their MES with biogas containing CO<sub>2</sub> and CO, which successfully provided biogas upgrading by producing CH<sub>4</sub> content of ~100%. More recently, Carrillo-Peña et al. (2024) investigated various biogas upgrading strategies, comparing in situ direct feeding of raw biogas with ex situ indirect feeding of CO<sub>2</sub>. Their findings revealed that the MES system, when fed with

CO<sub>2</sub> separated from biogas, demonstrated better energy efficiency. Although both scenarios achieved effective biogas upgrading, with biomethane content in the biogas reaching approximately 95% and yielding 31.5-50.3% more usable energy compared to the base scenario, the raw biogas approach exhibited higher energy demand due to lower coulombic efficiencies. Lu et al. (2023) investigated the feasibility of in situ biogas upgrading using a bench-scale MES (1L working volume) at different pH conditions. This study comprehensively evaluated the optimal working pH, mainly in terms of enhanced methane content in AD biogas, electron utilization efficiency, biofilm morphology on the electrode surface, and microbial community in the cathodic region under optimal conditions. Their study concluded that their MES achieved the highest methane productivity (composition of ~88.3% in the biogas, a maximum production rate of 22.1±0.1 mmol/d) at pH 6.5. This was significantly greater than that of control (e.g., no applied energy), which only achieved a production rate of 1.7 mmol/d. Under the optimal pH environment, their biocathode had a much denser biofilm (51.3 µm) along with a dominant archaeal species of *Methanobacterium*. On the other hand, Tian et al. (2023) examined the electron transfer behaviors of cathode biofilms in MES during biogas upgrading, focusing on the influence of cathode potential. Their research indicated that the dominant electron transfer pathway shifted from DET to IET as the cathode potential decreased from -0.8 V to -1.0 V vs. Ag/AgCl. This shift was confirmed by the enrichment differences observed, with hydrogenotrophic methanogens being more prevalent at -1.0 V vs. Ag/AgCl, while more DET-related redox substances and methanogens were found at -0.8 V vs. Ag/AgCl. More details regarding the fundamentals of DET and IET in biogas-upgrading MES can be found in the literature (Tian et al., 2023).

#### **4. Operation strategies to enhance MES performance for CH<sub>4</sub>/biogas-upgrading**

Despite the promising results (see Table 1), addressing various challenges and limitations is crucial for the field application of MES. The biggest challenge lies in the scaling-up of reactors due to increased energy demand with increasing reactor size and electrode spacing (Chung and Dhar, 2021c; Dhar et al., 2016; Zakaria and Dhar, 2019). Moreover, longer startup periods often limit the feasibility of CH<sub>4</sub>-producing MES (Fu et al., 2015; Li et al., 2019). Therefore, it is crucial to scrutinize the potential strategies and modifications reported in the literature to effectively operate and optimize MES. Table 2 shows the overview of the selection criteria of MES materials and operating parameters, and this is further elucidated later.

#### 4.1 Engineering MES biocathode

A typical MES has a biotic cathode as the core platform where the methanogenic activities and CO<sub>2</sub> reduction occur (Chen et al., 2020a; Chen et al., 2020b). Water electrolysis at the anode produces protons, electrons, and oxygen. The protons travel to the cathode through an ion/proton exchange membrane, while the electrons move via an external circuit. The performance of MES heavily depends on the interaction between microbes and the cathode electrode (Liu et al., 2023). Therefore, choosing the cathode material is a critical design decision in MES, involving considerations like conductivity, surface area, corrosion resistance (or chemical stability), biocompatibility, porosity, redox potential, cost, and compatibility with the target product (Ibrahim et al., 2023). Moreover, high HER capability and minimized CO<sub>2</sub> mass transfer resistance are desirable features (Aryal et al., 2017; Logan et al., 2006; Noori et al., 2020; Zhang et al., 2021). Using precious metal catalysts (e.g. Pt, Ag, and Au) for electrochemical CO<sub>2</sub> reduction in MES would be questionable due to high costs (Zhao et al., 2016b). Instead, utilizing other low-cost metal catalysts (e.g., stainless steel, and nickel foam) can lower the activation energy and ensure efficient electron transfer from cathode to microbes/biofilms (Blanchet et al., 2015; Zhao et al., 2016b). However, poor biocompatibility, smooth electrode surface, and metal leaching limit the use of metal electrodes as biocathodes (Das et al., 2018; Das and Ghangrekar, 2018).

Biofilms containing methanogenic archaea established on the cathode significantly impacts the MET performance, in terms of CH<sub>4</sub> production (Garrett et al., 2008; Noori et al., 2020). For instance, the low CH<sub>4</sub> productivity in MES is often due to poor biofilm formation caused by the limited biocathode surface area (Li et al., 2020b). Therefore, using electrode materials that facilitate active biofilms adhesion is expedient. For effective biofilm development, electrode material should provide sufficient active sites and surface area. Increasing the surface roughness at the nanoscale is a common strategy adopted to promote bacterial adhesion and transfer of electrons (Flexer et al., 2013). Figures 8 and 9 show microscope images of different electrode materials used in MES. The deposition of metal-oxide nanostructures on a smooth carbon fiber surface offered rough shrub-like topography to the electrode, which allowed the microbes to infiltrate into the electrode matrix and enhance the electron transfer (Cui et al., 2017). Moreover, recent research on promising electrode material for MES emphasizes chemical or biological modification of the electrode surface. This suggests that positive charge accumulation on the

cathode surface, facilitated by surface treatments or the attachment of redox molecules, aids in sustaining electron transfer. This, in turn, ensures biofilm adhesion and activity for the CO<sub>2</sub> reduction reaction (Thulluru et al., 2023). Kracke et al. (2021) demonstrated doped carbons and graphene aerogels boosted the system performance of MES over using carbon black cathode because of reduced internal resistance. Liu et al. (2020a) also reported that MES equipped with a carbon brush cathode exhibited approximately 4-fold higher CH<sub>4</sub> formation rate from CO<sub>2</sub> reduction than their MES assembled with the graphite plate cathode. Moreover, Sharma et al. (2019) compared several commercial and VITO CORE<sup>®</sup> electrodes for MES and found that the usage of VITO CORE<sup>®</sup> electrode exhibited superior performance than typical carbon-based materials because of its high electro-exchange capacities and the presence of higher hydrophilic moieties. The VITO CORE<sup>®</sup> electrode is made up of an 80–20% carbon–polytetrafluoroethylen mix used for the assembly of activated carbon layers from both sides of a 316-grade stainless steel mesh. The authors also found that such electrode could provide roughness in the biologically amenable range. As discussed earlier, cathode selection is also directly related to the level of externally supplied energy. For instance, maintaining -0.414 V vs. SHE (or -0.214 V vs. Ag/AgCl) or more positive cathode potential is crucial for promoting the DET pathway during methanogenesis. However, in practice, a lower cathode potential is often required due to substantial electrode overpotential and internal resistance, leading to increased energy consumption for methane production (Geppert et al., 2016; Zakaria and Dhar, 2019). More recently, research related to identifying the impact of electrode geometry on biofilm development in biomethane-producing MES systems has gained interest. For instance, De la Puente et al. (2023) investigated this by comparing two different biocathode constructions: carbon brush and carbon felt. They assessed these configurations based on CO<sub>2</sub> capture efficiency and methane production. Their findings revealed that both MES setups achieved very high coulombic efficiencies (~100%) and methane production (>90%). Nevertheless, the carbon brush biocathode significantly enhanced current generation and electrical capacitance, resulting in higher peak hydrogen production than the carbon felt. This translated into increased CO<sub>2</sub> capture and methane generation. Furthermore, both biocathodes exhibited a higher prevalence of archaea over bacteria, with the carbon brush biocathode having 85% archaeal abundance compared to 53% on the carbon felt. Notably, the carbon felt cathode biofilm was primarily enriched with *Methanobacterium*, while the carbon brush cathode biofilm was dominated by *Methanobrevibacter*, underscoring the impact

of electrode geometry on the archaeal communities in MES biocathodes. Overall, selecting cathode materials with lower overpotential and resistance is critical to minimize energy requirements during MES operation. A summary of different MES cathode materials showing descriptions, properties, and pros and cons can be found elsewhere (Chu et al., 2021; Dessì et al., 2021; Lee et al., 2020; Zhang et al., 2021).

#### **4.1.1 Carbonaceous material as MES biocathode**

Carbonaceous materials have been extensively exploited for MES systems owing to their abundance, low-cost, chemical resistance, high surface area, porous structure, and biocompatibility (Aryal et al., 2017; Jayathilake et al., 2022; Zhang et al., 2021). The first proof-of-concept of CO<sub>2</sub> reduction in the MES system was demonstrated by Nevin et al. using unpolished graphite sticks as biocathode (Nevin et al., 2010). Carbonaceous materials are commercially available in different forms (e.g., carbon cloth, carbon felt, rods, etc.), (Zhang et al., 2021). Moreover, the low fabrication cost and abundant raw precursor availability make their use in the electrochemical processes scalable and practical (Jayathilake et al., 2022; Le et al., 2017). Among these carbon-based materials, the carbon-felt cathode has been intensively explored in various MET systems, particularly for electro-methanogenesis applications (Aryal et al., 2022; Geppert et al., 2016). However, not all carbon-based materials are suitable for MES biocathode. Nevin et al. (2010) tested the planar graphite block electrode and concluded that it would not be suitable as an MES cathode due to its relatively limited surface area, which is considered one of the major hurdles for biofilm formation. As expected, a reduced CO<sub>2</sub> conversion rate was achieved with a planar graphite block cathode. Moreover, carbon-based materials often lack sufficient mechanical strength and are prone to damage during operation; thus, the strengthening of carbon-based electrodes or replacing them with other sturdier electrodes is often required (Zhang et al., 2021).

#### **4.1.2 Metallic materials as MES biocathode**

Metal electrodes act as inorganic catalysts for HER (Blasco-Gómez et al., 2017; Deutzmann et al., 2015; Lee et al., 2020; Zakaria and Dhar, 2021), and exhibit excellent conductivity and high mechanical strength compared to carbon-based electrodes (Zhang et al., 2021). However, the high cost and potential toxicity associated with metals (creates a hostile environment for microbes) inhibit further development. Zakaria and Dhar (2021) and Blasco-Gómez et al. (2017)

demonstrated superior HER kinetics at the cathode with metal-based cathodes (Pt-coated titanium woven wire mesh, stainless steel mesh) along with high CH<sub>4</sub> generation and biogas upgrading rates; however, high cost of the Platinum-based electrode limits the field application (Jayathilake et al., 2022). To date, HER electrocatalysts, such as molybdenum carbide, nickel (Ni), perovskite, and zinc (Zn) were reported to enhance the CO<sub>2</sub> reduction process (Jayathilake et al., 2022; Jiang et al., 2019; Li et al., 2018; Tian et al., 2019), which has the potential to enhance methanogen-cathode interactions in MES. Moreover, these low-cost metals are recognized for their ability to exhibit a low overpotential HER in a neutral pH environment (Kracke et al., 2020; Kracke et al., 2019; Roger and Symes, 2015; Wang et al., 2019a), making them suitable for MES cathode. Therefore, metallic materials like iron (Dykstra and Pavlostathis, 2017), molybdenum (Siegert et al., 2014), nickel (Alqahtani et al., 2018), nickel-molybdenum (Kracke et al., 2019), rubidium (Das et al., 2021), and stainless steel (Bajracharya et al., 2015) have been utilized as MES biocathodes. However, the corrosion of metal electrodes followed by metal leaching can inhibit microbial activities (Zhang et al., 2021). Also, most metal-based cathodes are expensive, less biocompatible, and have a smaller specific surface area than carbonaceous electrodes, potentially leading to low performance. As a result, MES with metal-based cathodes is often considered impractical, prompting the exploration of alternative approaches for field applications.

#### **4.1.3 Surface-modified and composite MES cathodes**

Instead of a specific electrode material (metal or carbonaceous), surface modification of electrode could be another option. As such, fabricating hybrid/composite MES cathode using both carbonaceous and metallic materials can improve the conductivity, mechanical stability, and biocompatibility of the electrode (Bajracharya et al., 2015). Composite cathodes offer relatively greater specific surface area and amplified catalytic efficiency, which enable them to achieve higher current output and the formation of biofilms (Noori et al., 2020; Zhang et al., 2021). Another interesting method implies to doping/incorporation of metal nanoparticles/nanostructures into the carbon matrix or decoration on carbon electrode surface iron (Xu et al., 2012), nickel (Singh and Verma, 2015), and palladium (Siegert et al., 2014). For instance, the use of nickel nanowires anchored on graphite electrodes resulted in a 2.3-times increase in CO<sub>2</sub> bio-reduction compared to untreated graphite. This is credited to the enhanced interfacial surface area and the interaction between the cathode surface and the biocatalyst (Nie et al., 2013). Similarly, carbon-based

materials could be coated on the metallic cathode electrodes to achieve excellent biocompatibility, decent mechanical strength, and high conductivity (Das et al., 2018; Nwanebu et al., 2022; Zhang et al., 2021). Thus, combining carbon with metal counterparts enhances electrode performance in MES systems. Zhang et al. (2013) developed a composite cathode by applying chitosan onto a carbon cloth-based cathode, effectively increasing the rate of CO<sub>2</sub> adsorption. Moreover, the use of positively charged chitosan boosted the interaction between negative-charged microorganisms at the cathode. Another carbon electrode modified by Chen et al. (2016b) using reduced graphene oxide at the cathode augmented the CO<sub>2</sub> conversion rate. A cathode made with electropolymerization of a conductive poly 3,4-ethylene dioxythiophene (PEDOT) on graphene oxide (GO) film-modified carbon cloth (aka GO/PEDOT film cathode) also demonstrated a high potential to significantly improve the CH<sub>4</sub> production rate (e.g., 3.9-fold) (Li et al., 2020b).

#### **4.1.4 3D printed and other types of cathodes**

Using the method of 3D printing or additive manufacturing for electrode fabrication has attracted attention in the past few years. 3D printing allows to design of custom electrodes using different techniques including, inkjet printing, fused deposition modeling, stereolithography, and metal 3D printing (Zhang et al., 2017). Most importantly, the excellent patterning capability allows the patterning of complex 2D and hierarchical 3D structures. However, the major limitation is the lack of understanding of the process and material properties requirements. Nevertheless, the application of 3D-printed cathodes with a high surface area could be quite promising for increasing the volumetric productivity of MES without hindering energy efficiency as they have high stability, conductivity, and catalytic activity (Jayathilake et al., 2022; Yang et al., 2016). The optimization of 3D material design could enhance porosity and specific surface area, facilitating interaction between microbes and electrodes, as well as substrate transport within the electrode, eliminating the necessity for additional modifications (Aryal et al., 2022; Jourdin et al., 2018). Thus, the electron transfer rate could be maximized via 3D electrode architecture (Aryal et al., 2022). The application of porous electrodes with log-pile lattices facilitates the interaction between solution-phase microorganisms and hydrogen, and improves CH<sub>4</sub> generation at a given working cell voltage, thus achieving higher reaction rates (Jayathilake et al., 2022). Kracke et al. (2020) achieved a high CH<sub>4</sub> production rate using a 3D-printed cathode (2.2 L<sub>CH4</sub>/L<sub>Cathode</sub>/d) achieving nearly 100% utilization of *in situ* evolved H<sub>2</sub> at the cathode. Similarly, a cathode fabricated with 3D conductive

polylactic acid lattice (cPLA) and electrodeposition of metal electrocatalysts showed promising results in CH<sub>4</sub>-producing MES (Nwanebu et al., 2022).

#### 4.1.5 Types of cathodes explored in CH<sub>4</sub>-generating/biogas-upgrading MES

To date, several studies investigated how different cathodes could affect the MES performance for CH<sub>4</sub> production or biogas-upgrading. However, among the aforementioned MES cathodes, only a limited number are used for biomethane production and biogas upgrading applications. In 2018, Das et al. compared various MES configurations, MES-1 (anode – graphite felt, cathode – graphite felt), MES-2 (anode – nickel foam, cathode – graphite felt), MES-3 (anode – nickel foam, cathode – nickel foam) (Das et al., 2018). It was found that the graphite felt was not suitable as an anode as it is unable to catalyze water splitting reaction efficiently due to its inert and non-reactive characteristics; on the other hand, nickel foam can expedite the water splitting reaction, which can serve better as an anode (Das et al., 2018). Regarding the cathode, graphite felt is a porous-based material with cross-linking fibers, providing a much higher surface area, ultimately encouraging bacterial attachment. However, the anode fabricated with nickel foam is disadvantageous as it is toxic to microorganisms due to the leaching of nickel under acidic pH (Macomber and Hausinger, 2011; Xian et al., 2017). By reflecting on the aforesaid factors, Das et al. (2018) found the superior performance of MES-2 as it produced the highest acetate. Siegert et al. (2015) and Baek et al. (2022) determined that using platinum-coated cathode materials led to cathode biofilms predominated with *Methanobrevibacter* species, which was distinct from other MES systems (e.g., equipped with plain carbon, nickel, magnetite, steel, ferrihydrite, FeS, and MoS<sub>2</sub> cathodes) establishing cathode biofilms with *Methanobacterium* instead. This is due to platinum-based electrodes being an efficient H<sub>2</sub> generator by reducing the high overpotential of the proton reduction process, *Methanobrevibacter* is often pre-dominant. Such a finding highlighted the uniqueness of MES, in terms of selectivity (e.g., targeting specific end products) by simply enriching the cathode biofilm with desired electro-microorganisms.

Kracke et al. (2019) examined and characterized various non-precious metal HER catalysts, such as CoP, MoS<sub>2</sub>, and NiMo based on their HER kinetics and biocompatibility. Firstly, the maximum H<sub>2</sub> generation rate (48  $\mu\text{mol/h/cm}^2$ ; ~4 to 5 times greater than that of CoP and MoS<sub>2</sub> electrodes) and a very high coulombic efficiency (98%) were achieved using the NiMo alloy under -1.0 V vs.

SHE (or -1.2 V vs. Ag/AgCl) cathode potential. This finding is attributed to the HER being substantially impacted by electrochemical conditions, such as pH (Landers et al., 2018; Strmcnik et al., 2013), CO<sub>2</sub> exposure (Cave et al., 2018; Landers et al., 2018), and buffering anion concentration (Jeremiasse et al., 2009; Shinagawa and Takanabe, 2015). Overall, their MES assembled with NiMo cathode provided the optimal performance, in terms of stability, biocompatibility, efficiency, selectivity (100% H<sub>2</sub>-selectivity under biologically relevant conditions, such as circumneutral pH and microbial growth medium), and more importantly CH<sub>4</sub> productivity than the aforesaid electrodes (Kracke et al., 2019). Moreover, the NiMo alloy is cheap and highly available since both materials are earth-abundant, which can be easily electrochemically plated on most cathodes as a supplement.

Li et al. (2020b) modified their biocathode to boost the CO<sub>2</sub> reduction to CH<sub>4</sub> rate in MES. In their study, a novel GO/PEDOT cathode was constructed by electropolymerizing conductive PEDOT on GO film-modified carbon cloth and the fabricated GO/PEDOT cathode exhibited the highest CH<sub>4</sub> generation rate ( $315 \pm 13.2 \text{ mmol/m}^2_{\text{Cathode}}/\text{d}$ ), 3.9-fold greater than control MES equipped with carbon cloth cathode. This was due to the GO/PEDOT film deposited on carbon cloth improving the biofilm formation as well as providing a greater surface area for microbial colonization. Moreover, GO/PEDOT film allowed the MES operated under -0.9 V vs. Ag/AgCl (-0.7 V vs. SHE) to achieve a very high Faraday efficiency (>92%). Bian et al. (2022) developed a Ni-coated ceramic hollow fiber (Ni-CHF) cathode through electroless Ni plating on a TiO<sub>2</sub>/ZrO<sub>2</sub> ceramic membrane supported by TiO<sub>2</sub> to enhance MES performance. Evaluation of the Ni-CHF demonstrated its excellence in continuity, layer thickness, maintaining porous structures, water permeability, mechanical strength, and surface hydrophilicity. The cost-effective cathode production technique, utilizing Ni electroless plating, reduced material costs by approximately 29% versus metallic Ni hollow fibers and 94% versus ceramic hollow fibers wrapped with Ni foam, potentially enhancing economic viability. However, this technology should be further explored for methane-producing MES and biogas upgrading applications within MES systems.

Fu et al. (2022) showed their MES equipped with porous hollow stainless steel/graphene foam cathode had superior performance than carbon cloth. Especially, the graphene foam part of their cathode enabled the MES to produce a much higher current (e.g., 3 to 4 times greater than MES equipped with carbon cloth cathode) after the cultivation of biocathode for 15 days. Their modified

cathode was more adequate to colonize and proliferate the electroactive microorganisms. Moreover, their graphene foam-based biocathode was capable of producing 3.6 times greater maximum  $\text{CH}_4$  than the MES equipped with carbon cloth biocathode (or control) (848  $\text{mmol/m}^2_{\text{Cathode}}/\text{d}$  vs. 238.3  $\text{mmol/m}^2_{\text{Cathode}}/\text{d}$ ). He et al. (2022) proposed a new approach for the rapid establishment of a biocathode, by magnetically assembling a mixture of GO and  $\text{Fe}_3\text{O}_4$  nanoparticles and microbes (inoculum) biocomplex with carbon cloth. The characterization of the biocathode revealed that the GO/ $\text{Fe}_3\text{O}_4$  scaffold can facilitate the formation of thick biofilm containing methanogenic archaea (e.g., 3 mm) due to the existence of magnetic force (He et al., 2022). Their biocathode resulted in much higher  $\text{CH}_4$  output in MES, achieving 14.5 times higher  $\text{CH}_4$  compared to the MES equipped with carbon cloth cathode only (or control) (605 vs. 42  $\text{mmol/m}^2/\text{d}$ ).

On the other hand, Vidales et al. (2022) compared 3 different cathode materials (carbon felt, granular activated carbon, conductive acrylonitrile butadiene styrene (cABS) polymer) and determined that MES biocathode fabricated with plain carbon felt yielded the highest  $\text{CH}_4$  generation rate compared with other two cathode materials (1420  $\text{mL/V}_{\text{cathode}}/\text{d}$  vs. 720  $\text{mL/V}_{\text{cathode}}/\text{d}$ , 250  $\text{mL/V}_{\text{cathode}}/\text{d}$ , respectively) due to its large surface area, excellent conductivity, and adequate biocompatibility, and high porosity (Gonzalez-Garcia et al., 1999; Lin et al., 2019), promoting electroactive biofilm formation and providing higher bioelectrocatalytic activity (Vidales et al., 2019; Vidales et al., 2020). Their study also revealed that cathodes made with cABS polymer demonstrated the maximum specific activity for  $\text{CH}_4$  production. Thus, they further sophisticated the cABS polymer cathode by depositing Ni and Fe, which increased both biocatalytic activity and the current output of MES (e.g., 205 mA to 380 mA). However, cABS polymer biocathode offers a cost advantage due to its production using established techniques like extrusion, simplifying the scale-up process compared to the other mentioned electrodes (Vidales et al., 2019). Hence, if future research could further modify such a cathode to possess high surface area, high biocompatibility, easy scalability, low manufacturing cost, and optimal structural features, in terms of morphology, mechanical strength, and stability, it can enable MES to step forward towards its potential field application.

As mentioned earlier, 3D-printed electrodes demonstrated promising options for enhancing MET performance (Chung and Dhar, 2021a), such as electro-methanogenesis in MES (Kracke et al.,

2021; Nwanebu et al., 2022). For instance, Kracke et al. (2021) fabricated their MES cathode using carbon aerogel coated with a NiMo-alloy via the method of additive manufacturing (aka 3D printing technique). This novel 3D-printed cathode allowed their MES to achieve a stable electro-methanogenesis with a very high coulombic efficiency (>98%) (Kracke et al., 2021). Similarly, the increase in CH<sub>4</sub> recovery in MES was reported when electrodeposited metal electrocatalysts, such as Ni, Fe-Ni, and Fe-Mn-Ni were coated on 3D conductive polylactic acid lattice (cPLA) cathode (Nwanebu et al., 2022). In contrast, the control MES only equipped with a cPLA-biocathode showed inferior performance where the least amount of H<sub>2</sub> and CH<sub>4</sub> was produced along with reduced Coulombic efficiency. This could be attributed to the reduced electrocatalytic activity of cPLA for hydrogen generation and its higher electrode resistance (Nwanebu et al., 2022). Additionally, their research indicated that MES systems utilizing nickel-iron-manganese coatings exhibited optimal performance, achieving the peak methane production.

#### **4.2 Engineering MES anode**

Efficient anode is critical for MES as it serves as the site where the substrate is oxidized releasing electrons that are harvested for different applications. Therefore, it significantly impacts the functionality, efficiency, and overall performance of MES. In MES aimed at CO<sub>2</sub> generation, it is essential to use anode materials that promote water splitting or water electrolysis reactions and offer good stability for long-term operations. As such, noble metals (such as platinum, palladium, and titanium) are a common choice due to their high catalytic activity and good stability under harsh cell conditions. However, the scalability and commercialization of these systems strongly depend on the cost-effectiveness. Here, transition metals, metal alloys, and carbon materials could be an excellent option (Park et al., 2022). The anode plays a role in producing the protons and electrons and delivering them to the biocathode, which has great potential for augmenting electro-methanogenesis in MES. For efficient MES performance, H<sub>2</sub> generated at the cathode must be paired with an electrochemical (or abiotic) anodic oxidation reaction and the counter-reaction for the CO<sub>2</sub> reduction process should be sustainable and robust. OER (Equation 1) is the most widely adopted anodic reaction in MES due to the aforesaid advantages (Alqahtani et al., 2019; Bian et al., 2020; Jayathilake et al., 2022; Karlsson and Cornell, 2016). On the other hand, major drawbacks of oxygen production needed to be considered as oxygen could potentially diffuse to the cathode chamber, hampering the cathode biofilm containing methanogens and other anaerobic

microbes. this calls for strategic engineering of the anode electrode and cell design that prevents oxygen intrusion (Jayathilake et al., 2022; Salimijazi et al., 2020). Other concerns include high overpotential associated with OER and material instability in neutral to acidic environments. For instance, reducing the pH in the anode chamber to maintain proton transport across the membrane during water splitting would require additional energy, due to the increase in pH gradient between anode and cathode (0.59 V per one pH unit difference; discussed later) (Logan et al., 2008; Yasri et al., 2019). Thus, it is critical to define a technical solution that could shield the anolyte and catholyte compartment conditions and regulates the reaction kinetics at respective electrodes. The classification of commonly used MES anode materials and associated pros and cons for application in MES is outlined in other literature (Gupta et al., 2021; Lee et al., 2020; Zhang et al., 2021).

#### **4.2.1 Anode selection and modification**

Like cathode, identifying catalysts/materials suitable for an MES anode is also critical. Noble metal electrocatalysts, such as iridium and ruthenium are good candidates for OER in alkaline to acidic environments; however, they are priced prohibitively on a practical scale (Suen et al., 2017; Zheng et al., 2019). Plain electrodes like stainless steel, carbon-materials (carbon cloth, carbon fiber brush, graphite plate, and graphite stick) (Alqahtani et al., 2018; Bian et al., 2018a; Chen et al., 2016b; Gong et al., 2013; Nie et al., 2013), transition metals (such as nickel and molybdenum) (Askari et al., 2019; Jin and Chen, 2018), and polymer-based materials (polyacrylonitrile and cellulose) offer an interesting research direction for economic feasibility and efficiency improvement (Park et al., 2022). However, employing carbonaceous materials as an anode in MES is often suboptimal due to their intrinsic electrocatalytic OER activity, which necessitates an overpotential exceeding 0.6 V to achieve a satisfactory current density (5 mA/cm<sup>2</sup>) (Cheng et al., 2015). Similarly, metal catalysts, such as cobalt, nickel, iron, or manganese oxides often demand high overpotentials (e.g., greater than 0.4 V at 10 mA/cm<sup>2</sup>) in a neutral environment (Liu et al., 2020b; Melder et al., 2019). Conversely, titanium and platinum-based anodes are recognized for their effective OER performance and sustained stability in MES applications, efficiently mitigating concerns regarding corrosion (Bajracharya et al., 2016; Blanchet et al., 2015). Although nanoparticle-based catalysts show considerable promise for use as MES anodes, their practical implementation at a field scale presents significant challenges (Blasco-Gómez et al., 2017; Yang et al., 2016). Studies indicates that hybrid electrodes comprising carbon with metal catalysts like

platinum and nickel tend to degrade over relatively shorter periods in low pH electrolysis environments (Cheng et al., 2009; Clauwaert and Verstraete, 2009; Sato et al., 2013; Van Eerten-Jansen et al., 2012; Zhen et al., 2016). Additionally, the juxtaposition of noble metal catalysts (Ir and Pt) with cost-effective non-noble electrodes emerges as an innovative approach for enhancing MES efficiency (Bajracharya et al., 2017a; Bian et al., 2018a). In this regard, developing a cost-effective and durable OER catalyst with low overpotentials in both neutral to acidic environment is crucial for MES.

Different approaches have been explored for minimizing the energy requirement and the cost associated with MES anodes (Bian et al., 2020; Jayathilake et al., 2022). For example, selecting a non-noble electrode deposited with a stable noble catalyst prevents the use of expensive electrodes and simultaneously achieves higher OER (Bian et al., 2020). Interestingly, these integrated MES anodes could be sophisticated or modified (for instance, biosynthesized reduced graphene oxide doped with transition metals using EAB) for lowering preparation costs and attain long-term stability (Kalathil et al., 2019). These observations highlight a lack of development in determining the efficient MES anodes, and related research has not been gaining much attention. It is still questionable whether the MES anodes laminated with noble metal catalysts could provide long-term stability due to lack of relevant research data. Therefore, it is very crucial to explore and scrutinize various options for MES anode modifications.

#### **4.2.2 Different anodic reactions for deriving protons and electrons**

Considering the detrimental effect of  $O_2$  on the cathodic reaction, another effective alternative implies replacing the OER anode reaction to enhance the MES performance. Selecting OER as an anodic pathway in MES could result in oxygen intrusion (from anodic chamber to biocathode) (Alqahtani et al., 2019). Past studies have stated that oxygen diffusion via an IEM may occur, hindering the effectiveness of different METs (Chung et al., 2021; Feng et al., 2013; Suzuki et al., 2016; Xiao et al., 2020a). The energy demand is also much higher in OER than in other anodic reactions (discussed earlier). Thus, any anodic reaction that does not produce  $O_2$  (or  $H_2O_2$ ) can provide a way out of this dilemma. OER requires high overpotential on the majority of anode materials; therefore, oxidation of other alternate compounds like glycerol, and glucose at lower overpotentials seems attractive, in terms of energy efficiency (Jourdin and Burdyny, 2021), but

these options require anode biofilms (e.g., bio-oxidations of organic matters; this route is not discussed in this review article as it produces additional CO<sub>2</sub>, as discussed earlier). In this context, CLER maybe an attracting option over OER. Despite the less activation energy from selecting the OER (Eq. 1), the CLER exhibits higher selectivity with electrocatalysts and is more kinetically favorable than OER due to the involvement of a two-electron reaction (Karlsson and Cornell, 2016). A study investigated the OER and CLER activities utilizing TiO<sub>2</sub> electrocatalysts developed through atomic layer deposition (Finke et al., 2019). The study found that CLER performed more effectively, demonstrating lower anode potentials and higher current outputs (700 mV vs. 900 mV; ~2 mA/cm<sup>2</sup> vs. ~0.05 mA/cm<sup>2</sup>) when employing a fluorine-doped tin oxide electrode enhanced with ten cycles of TiO<sub>2</sub> atomic layer deposition (Finke et al., 2019). Furthermore, the larger market demand for chlorine gas, estimated between 50 to 60 million tons annually, underscores the practical advantage of CLER (Gamble, 2019).

Similarly, bio-oxidation of inorganic compounds can be a cost-effective and less energy-intensive option over OER (Bian et al., 2020). For the bio-oxidation of the reduced inorganic compounds, bisulfide and sulfur often serve as electron donors to SOB in the anode biofilms, which can substantially lower the overpotential (Gong et al., 2013; Ter Heijne et al., 2018). A previous study have demonstrated the successful MES applications with a SOB-enriched anode biofilm (Gong et al., 2013). The main benefit of SOB anode biofilm and bio-oxidation of sulfide and sulfur is that the electron and proton productions can be done with relatively lower energy input (Ni et al., 2019; Ter Heijne et al., 2018).

#### **4.2.3 Types of anodes explored in CH<sub>4</sub>-generating/biogas-upgrading MES**

According to past studies, titanium-based anodes can perform stable water splitting (van Eerten-Jansen et al., 2015; Zhou et al., 2021). Similar to the discussions on MES cathodes, only a handful of anodes have been investigated for biomethane-producing and biogas-upgrading MES. In this regard, Baek et al. (2022) demonstrated that platinized titanium felt anode could provide improved CH<sub>4</sub> generation than the carbon-felt anode. The type of anolyte solution could also impact the system performance. For instance, Das et al. (2018) experienced corrosion when they used nickel foam as an anode with a phosphate buffer solution. Specifically, their nickel foam anode shrunk in size and became brittle due to the reaction between Ni foam and phosphate in the buffer solution

to form  $\text{Ni}_3(\text{PO}_4)_2$  (Nickel (II) phosphate) during MES operation. However, replacing the phosphate buffer solution with other anolyte solutions, such as nickel sulfate can ensure the longevity of the anode. Batlle-Vilanova et al. (2019) used NaCl solution as an anolyte for their MES, which is highly beneficial over water splitting reaction as the oxidation of chloride to chlorine ( $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$ ,  $E^0 = -1.36 \text{ V vs. SHE}$ ,  $\Delta G^0 = 2.72 \text{ eV}$ ), requiring 45% less energy compared to OER ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$ ,  $E^0 = -1.23 \text{ V vs. SHE}$ ,  $\Delta G^0 = 4.92 \text{ eV}$ ). With this anolyte, the total  $\text{CH}_4$  generation increased by 17.5%, with a reduced total  $\text{CO}_2$  emission below < 42.8%. In addition, the produced  $\text{Cl}_2$  can be utilized as a water disinfection agent for the tertiary treatment of wastewater. Overall, CIER can be a more efficient and suitable alternative as an anodic reaction in MES. An opinion written by Sivalingam et al. (2020) stated that ammonium ions could serve as a unique carbon-free electron donor ( $2\text{NH}_4^+ \rightarrow \text{N}_2 + 8\text{H}^+ + 6\text{e}^-$ ,  $E^0 = -0.273 \text{ V vs. SHE}$ ) for  $\text{CH}_4$ -generating or biogas-upgrading MES systems. Zhan et al. (2014) also showcased the successful application of such a method where the anode biofilm enriched with *Nitrosomonas*, *Comamonas*, and *Paracoccus* bacteria for oxidizing the ammonium to nitrogen gas under 0.6 V vs. Ag/AgCl or 0.8 V vs. SHE (anode potential).

Recently, Dinh et al. (2022) used anolyte containing  $\text{HS}^-$  ions to allow electrons to be harvested from  $\text{HS}^-$  oxidation to  $\text{SO}_4^{2-}$  ( $\text{HS}^- \rightarrow \text{S}_{(\text{s})} + 2\text{e}^- + \text{H}^+$ ;  $E^0 = -0.22 \text{ V vs. SHE}$ ; Eq. 3). This anodic oxidation reaction could allow the MES to generate  $\text{CH}_4$  with a substantially minimal applied voltage (considering the theoretical required energy input is only 0.02 V) without the need for organic compounds as substrates for anode biofilms (Dinh et al., 2022). After introducing 4 mg/L of sulfide to the anode chamber, their MES was capable of producing  $\text{CH}_4$  with a significantly low amount of voltage (0.1 V). On the other hand, Kambara et al. (2023) utilized bioanode enriched with anaerobic chemolithoautotrophs (dominated by *Dessulfurimicrobium*), which can grow by the disproportionation of a sulfur element, thiosulfate, and sulfite (Slobodkin et al., 2016) to perform anodic sulfide oxidation ( $\text{HS}^- + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 9\text{H}^+ + 8\text{e}^-$ ) to produce the necessary electrons for electro-methanogenesis. This integration of different microbial consortia in the biocathode and bioanode led to successful  $\text{CH}_4$  generation even with a very small amount of voltage supply (0.2 – 0.8 V) (Kambara et al., 2023). More importantly, these findings demonstrated a great potential for MES to be implemented for field applications by alleviating high energy demand (Chung and Dhar, 2021c; Chung et al., 2021; Dinh et al., 2022).

## 4.3 Optimization of MES operating parameters

### 4.3.1 Biocathode inoculum sources and microbial communities

In CH<sub>4</sub>-producing MES, inoculum sources usually do not require extensive chemical/thermal pre-treatment, unlike other MES types, such as MES for acetic acid production (Bajracharya et al., 2017b; Dessì et al., 2021; Marshall et al., 2013; Mou et al., 2022b). Acetic acid is successfully produced in MES using both pure and mixed microbial cultures, utilizing a variety of inorganic carbon sources including bicarbonate (Jourdin et al., 2015), pure CO<sub>2</sub> gas (Song et al., 2017), and brewery flue gas (Roy et al., 2021a). Therefore, there is potential for highly selective production of CH<sub>4</sub> with MES; however, several challenges still exist. As discussed earlier, the cathode with biofilm grants electrotrophic methanogens direct access to hydrogen generated via HER, but the use of biofilm could result in higher interfacial resistance between the catholyte and cathode electrode, which contributes to the addition of ohmic resistance on the biocathode (Arunasri and Mohan, 2019; Jayathilake et al., 2022; Salimijazi et al., 2020). Furthermore, the higher ohmic resistance on the biocathode could impose diffusion barriers on reactants, such as protons, CO<sub>2</sub>, and other end products, which could decrease the MES energy efficiency. Opposingly, the hydrogen-mediated biomethanation pathway could be more attractive at both commercial and research levels (Prévot et al., 2020). H<sub>2</sub>-consuming methanogens are often more stable, especially during long-term operation even with fluctuation in HER rates, demonstrating their resilience for field applications (Mateos et al., 2020; Rojas et al., 2018) (further discussed later). Hence, choosing the optimal microbial inoculation strategy would greatly assist in optimizing MET system performance (Chung and Dhar, 2021b; Chung and Dhar, 2021d; Hengsbach et al., 2022; Zakaria and Dhar, 2019). Especially, different inoculum sources could shift the cathodic microbial communities, governing their selective performance (Alqahtani et al., 2021).

The microbial communities in MES biocathode enable various methanogenic pathways; for instance, having high abundances of hydrogenotrophic methanogens, such as *Methanobacteriaceae* and *Methanomicrobia* indicates CH<sub>4</sub> production occurred via hydrogenotrophic methanogenesis (Geppert et al., 2016; Geppert et al., 2019; Liu et al., 2018; van Eerten-Jansen et al., 2015). *Methanobacterium* species have been mostly dominated in bioelectrochemical biogas upgrading applications (Aryal et al., 2022). The engineering of microbial communities within the biocathode has become increasingly significant, given that only

a limited number of methanogens have been identified as electrotrophic during MES operations thus far (Logan et al., 2019). For instance, the productivity of CH<sub>4</sub> productivity and the selectivity of MES can differ significantly between biocathodes enriched with pure cultures and those enriched with mixed cultures (Hengsbach et al., 2022). Therefore, selecting the most suitable method for enriching these microbial communities is essential for optimizing MES performance. To the best of our knowledge, MES inoculated with pure culture methanogen was first examined by Beese-Vasbender et al. (2015). Their MES was inoculated with marine lithoautotrophic *Methanobacterium*-like archaeon strain IM1, which could take a DET pathway to directly use electrons from the cathode surface for achieving high selectivity towards CH<sub>4</sub> generation. The authors also noticed generations of biologically catalyzed hydrogen at cathode potentials more positive than abiotic HER on graphite. This was an indication of excessive electron supply to strain IM1, which could result in the reduction of protons ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ) rather than a further increase in CH<sub>4</sub> generation. Overall, their study achieved a high CH<sub>4</sub> generation rate (350 nmol/d/cm<sup>2</sup>) and coulombic efficiency (80%) even under a relatively low negative cathode potential (-0.4 vs. SHE). In 2017, a study reported that the use of co-cultures, such as strain IS4 and *M. maripaludis* could enhance CH<sub>4</sub> production in MES (Deutzmann and Spormann, 2017). The authors specifically indicated that the enhancement of CH<sub>4</sub> generation was associated with the coupling of co-cultures, cathodic electron uptake, and synthesis reactions, which mainly promoted the interspecies hydrogen transfer. Hence, the strain IS4 cells (highly efficient H<sub>2</sub> producer) were coupled with hydrogenotrophic methanogen (*M. maripaludis*) to achieve no accumulation/rapid consumption of hydrogen. Under an optimal cathode potential (-0.4 to -0.6 V vs. Ag/AgCl or -0.2 to -0.4 V vs. SHE), electrons/hydrogen, and other end products and intermediates were effectively scavenged by the methanogens to promote the methanogenesis in MES (Deutzmann and Spormann, 2017). Mayer et al. (2019) cultured different methanogenic strains (*M. maripaludis*, *Methanococcus vannielii*, *Methanoculleus submarinus*, *Methanolacinia petrolearia*, and *Methanobacterium congolense*) in MES biocathode and compared their performances. The authors reported that the MES enriched with *Methanococcus* species (found in different environmental habitats, such as salt marches and marine mud) achieved the maximum growth rate (Generation Time of 4.1 – 4.7 h) compared with the aforesaid methanogenic strains when it was fed with a mixed of H<sub>2</sub> and CO<sub>2</sub>. Furthermore, the authors observed that *M. maripaludis* achieved the highest cell densities, with an optical density (OD<sub>600</sub>) of 3, when cultivated with a H<sub>2</sub>/CO<sub>2</sub> gas mixture. Conversely,

*Methanoculleus submarinus* yielded the lowest growth rate (Generation Time of 18.7 h) during its cultivation in MES. For instance, *Methanoculleus submarinus* produced cell mass first, before catalyzing CH<sub>4</sub> formation, which could be seen as unusual considering the following two facts: (1) the growth rate of methanogens is proportional to CH<sub>4</sub> generation; (2) the main product of methanogen's energy metabolism is CH<sub>4</sub> (Mayer et al., 2019; Thauer et al., 2008). More importantly, their MES biocathode enriched with electroactive *M. maripaludis* (Lohner et al., 2014) exhibited the highest CH<sub>4</sub> generation rate (8.81 mmol/m<sup>2</sup>/d). Similarly, Mayer et al. (2022) investigated two pure iron-corroding methanogens (*M. maripaludis* Mic1c10 and KA1) due to their natural ability for electron uptake. In their study, the MES enriched with the strain Mic1c10 yielded higher current density (120% higher) and CH<sub>4</sub> generation rate (84% higher) than MES biocathode enriched with non-corrosive strain *M. maripaludis* S2. More recently, the effect of different inoculum sources on MES selectivity was further studied (Alqahtani et al., 2021). Alqahtani et al. demonstrated that their MES inoculated with mangrove (MG) sediment produced higher levels of acetate, albeit with lower CH<sub>4</sub> generation, compared to a salt marsh (SM)-inoculated MES. This was attributed to the greater relative abundance of the genus *Acetobacterium* (phylum Firmicutes) in the MG-inoculated MES (3.1 mmol vs. 1.5 mmol of acetate) (Alqahtani et al., 2021). MES inoculated with SM produced higher CH<sub>4</sub> compared to their other inoculum sources, such as MG sediment (4.9 vs. 3.8 mmol of CH<sub>4</sub>); thus, the pure culture could enable the selective CH<sub>4</sub> generation in MES.

A review by Dessì et al. (2021) indicated that the greatest methane generation was achieved by Geppert et al., with a generation rate of 12.5 L<sub>CH<sub>4</sub></sub>/(L·d) and 65% current-to-CH<sub>4</sub> efficiency with mixed culture (Geppert et al., 2019). Geppert et al. (2019) also revealed the importance of the microbial communities in their double-layered biocathode; for instance, the biocathode layer facing the current collector side had high relative abundances of hydrogenotrophic *Methanobacteriaceae* and *Methanomicrobia*, while the biocathode layer facing the membrane side was dominated by *Methanobacteriaceae* and *Proteobacteria*. However, more future studies are still required to justify whether a pure culture/co-culture or a mixed culture should be selected over another.

#### 4.3.2 Ion-exchange membrane (IEM)/separator and membrane-less/microfluidic cell mode

The most MES designs include an ion exchange membrane (IEM) to separate the anodic and cathodic chambers. Common practices to prevent oxygen intrusion include introducing a membrane or separator between the two chambers, modifying reactor design and configuration, and altering electrode geometry to direct electrolyte flow (Jayathilake et al., 2022). This limits the O<sub>2</sub> penetration and offers the excellent ion conductivity that is required. The primary function of membrane is to regulate the passage of selective ions while preventing the movement of microorganisms and large molecules to avoid cross-contamination. The selectivity and overall performance of MES can be greatly influenced by membranes. For instance, poor membrane permeability and cation gradient could result in proton accumulation in anolyte which affects the pH disparity across the cell. This leads to a longer start-up period and delayed biofilms formation (Fornero et al., 2010; Rozendal et al., 2006). Figure 10 describes MES configurations equipped with different types of membranes and separators. IEM, such as cation exchange membrane (CEM), anion exchange membrane (AEM), and bipolar membranes (BPMs) are imperative for facilitating ion transports between the anode chamber and cathode chamber, and adequately maintaining electroneutrality (Chung and Dhar, 2021a; Dhar and Lee, 2013; Jayathilake et al., 2022; Leong et al., 2013). Especially, in MES, the selection of IEMs is dependent on the anolyte and catholyte pH, which facilitates the proton and hydroxide ion transports (Jayathilake et al., 2022). IEMs can significantly impact various operating parameters in METs, such as current density. This effect is influenced by the IEM's surface area and material type, which are linked to ionic conductivity and internal resistance within the MET system (Philamore et al., 2015; Zuo et al., 2007). IEM or a dual-chamber reactor configuration is often implemented for facilitating the delivery of charged species, such as H<sup>+</sup> and Na<sup>+</sup> (Aryal et al., 2022). It could also act as a physical separator to prevent the bacterial aqueous solution and oxygen crossover between two chambers (Aryal et al., 2022; Chung et al., 2020b). Moreover, by equipping an IEM, the working condition of each chamber can be further optimized (Chung et al., 2020b; Zakaria and Dhar, 2019). Therefore, the selection of IEMs or separators is important for achieving optimal MES performance.

Among the different PEMs, Nafion<sup>®</sup>-based membranes, are mostly used to transport protons from anode to cathode (Ceballos-Escalera et al., 2020; Kracke et al., 2020; Kracke et al., 2019). The conductivity of protons in PEMs is temperature- and hydration-dependent, and it can be up to 0.2

S/cm for Nafion<sup>®</sup> (Kusoglu and Weber, 2017). Nafion offers a unique structure consisting of a hydrophobic perfluorinated polyethylene backbone and hydrophilic sulfonic acid terminated perfluoro vinyl ester side group (Mauritz and Moore, 2004). The proton conduction is governed by the relationship between the proton solvation energy (inversely proportional to the dielectric constant) and the electrostatic interactions (Li et al., 2020d). The proton transport mechanism is governed by two proposed models namely, the vehicular mechanism and the Grotthuss mechanism. The vehicular mechanism defines proton conductivity through the concentration gradient developed during the diffusion of protons involving water molecules ( $\text{H}_3\text{O}^+$ ,  $\text{H}_5\text{O}_2^+$ , and  $\text{H}_9\text{O}_4^+$ ) and uncharged molecules. Thus, the remaining carriers reverse their diffusion and facilitate proton transport. This model is dominant under low-hydration conditions incomplete  $\text{H}_2$  bonding. While Grotthuss model emphasizes that transport of hydrogen-bonded network of water molecules along water channel caused continuous conversion between hydrated complexes. This is characterized by high proton mobility and activation energy as  $\text{H}_2$  bond cleavage requires energy loss (Zhu et al., 2022). On the contrary, are employed in alkaline conditions to transport hydroxide ions generated at the cathode to the anode chamber in MES. However, AEMs often exhibit poor ion conductivity in neutral media (Cheng et al., 2009; Jayathilake et al., 2022). Additionally, during the biocatalytic conversion of  $\text{CO}_2$ , they have been reported to non-selectively transport bicarbonate and anionic liquid products from the cathode to the anode (Dharmalingam et al., 2019; Divekar et al., 2020; Geppert et al., 2016). BPMs, which combine a PEM with an AEM layer, can also be used in MES. Unlike the other two types of membranes BPMs facilitate water dissociation at their center, maintaining a pH difference between the cathode and anode (Jayathilake et al., 2022). However, BPMs may lead to high internal resistance (Jayathilake et al., 2022). PEMs have been widely utilized in MES studies for not only allowing for proton transport but enabling the production of high-purity end products and protecting the cathode biofilms from toxic compounds, which could potentially be produced at the anode (Vidales et al., 2019; Villano et al., 2010). However, PEM could limit the field application of MES due to its high cost, increased ohmic resistance, fouling, and scaling problems (Clauwaert and Verstraete, 2009; Dhar and Lee, 2013; Leong et al., 2013). Also, the pH gradient created between the anode and cathode chambers necessitates the use of pH control (Dhar and Lee, 2013; Leong et al., 2013; Zhang et al., 2019).

In most cases, biogas-upgrading or CH<sub>4</sub>-generating MES is operated using a dual-chamber mode (separated by IEM) (see Table 1), and it has been reported that the dual-chamber mode could enable higher biogas upgrading performance over single-chamber mode (Aryal et al., 2022; Liu et al., 2017). To date, however, the impact of membranes on biogas upgrading applications is still ambiguous (Aryal et al., 2022). To the best of the author's knowledge, only a single study has examined the effect of different membrane types and reported it could interfere with CH<sub>4</sub> productivity in MES (Babanova et al., 2016). When Babanova et al. studied PEM (Nafion 117) vs. CEM (Ultrex CMI-7000), CH<sub>4</sub> production was slightly higher in MES equipped with PEM during the start-up, potentially due to less internal resistance (e.g., membrane resistance) (Babanova et al., 2016). Instead of IEMs, the chambers in MES could be separated using other separator materials, such as nylon cloth (Vidales et al., 2020). However, using such a separator could be highly disadvantageous as the oxygen molecules generated at the anode could easily diffuse to the cathode chamber, potentially inhibiting methanogens (Van Eerten-Jansen et al., 2012; Vidales et al., 2020). Hence, it is crucial to maintain only trace amounts of O<sub>2</sub> to avoid the interference of methanogenic activity if one decides to use a separator over an IEM. Ultimately, more studies are still required to further scrutinize the effect of different membranes on biogas upgrading or CH<sub>4</sub>-producing MES. Modified PEMs could provide a rational design considering the proton transport, fuel permeability, and material stability concerns. For instance, hygroscopic inorganics such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and SiO<sub>2</sub> could be cross-linked with the sulfonic acid group of Nafion<sup>®</sup>, improving the porosity, and water retention and reducing gas cross-over (Son et al., 2019). These modified or composite membranes could readily scavenge free radicals produce and enhance the durability of PEMs (Zhu et al., 2022). Despite the variety of available membranes and separators, Nafion PEMs remain the ideal choice for optimizing system performance in methane-producing MES (Bian et al., 2018a; Jayathilake et al., 2022; Vidales et al., 2019; Villano et al., 2010).

A single-chamber MES can eliminate the associated costs and ohmic losses. To the best of our knowledge, the first membrane-less MES for the CH<sub>4</sub> production was demonstrated by Giang et al. (2018), achieving CH<sub>4</sub> production of up to 4.7 L/m<sup>2</sup>-d from CO<sub>2</sub>. The membrane-less MES is also quite close to the microfluidic cell mode (Dessi et al., 2021), where the anode and cathode are separated by a thin layer of electrolyte to allow CO<sub>2</sub> diffusion. In fact, microfluidic cells for CO<sub>2</sub> electrolysis, which could bring a new paradigm to the field of MES by alleviating the need of

membranes (Dessì et al., 2021; Weekes et al., 2018). However, several limitations, such as oxygen intrusion from anode to cathode, must be effectively prevented for cathode biofilms (Aryal et al., 2022; Butler and Lovley, 2016). Furthermore, the scaling-up of such an approach could be more challenging than the conventional design with membranes/separators (Dessì et al., 2021; Sánchez et al., 2019).

#### 4.3.3 Externally applied energy

The externally applied energy has a substantial influence on the start-up and system performance of MES (Bian et al., 2020; Zakaria and Dhar, 2019). The cathode potential has a prominent role in initiating the CO<sub>2</sub> reduction to CH<sub>4</sub> and determining its kinetics (Bakonyi et al., 2023; Mao et al., 2021; Zakaria and Dhar, 2019). Cathode potential also influences the structure, diversity, and efficiency of the cathode biofilm (Bakonyi et al., 2023). As discussed earlier, maintaining the cathode potential more positive than -0.414 V vs. SHE results in promoting the DET pathway during methanogenesis as it eliminates the electrochemical H<sub>2</sub> generation (Zakaria and Dhar, 2019). This is directly connected to cathode selection, as a more negative cathode potential is often necessary to offset the high electrode overpotential and internal resistance within the system (discussed earlier). Applying highly negative cathode potential usually benefits the activities of hydrogenotrophic methanogens due to the *in-situ* HER (Aryal et al., 2022). Additionally, the externally applied energy could also be manipulated to maximize the abundance of useful methanogens in the biocathode for biogas upgrading. For instance, Bo et al. (2014) reported a boost in the relative abundance of *Methanospirillum* from 16 to 68.4% when the cathode potential was increased. The past published literature comprehensively investigating the effect of externally applied energy on MES operation is discussed below.

Villano et al. (2010) indicated that the applied energy governs the level of CH<sub>4</sub> generated via promoting the DET process. Under the applied cathode potential of -0.65 V vs. SHE or more negative, the authors achieved a very high rate of CH<sub>4</sub> production (0.055 mmol/d/mg VSS) and coulombic efficiency (>85%). A few years later, Jiang et al. (2013) found that their MES cathode operated under -0.85 to -0.95 V vs. Ag/AgCl (-0.65 to -0.75 V vs. SHE) selectively produced CH<sub>4</sub> and H<sub>2</sub>. The authors further elucidated that operating the MES with lower cathode potential (e.g., -0.95 V vs. Ag/AgCl or -0.75 V vs. SHE or more negative) could result in the production of other

end products, such as acetate (Jiang et al., 2013). Similarly, another study indicated a superior CH<sub>4</sub> formation rate (from 0.1 – 0.14 to 0.6 – 0.9 μmol/cm<sup>2</sup>/h) with more negative cathode potential (from -0.4 to -0.5 V vs. SHE) (Deutzmann and Spormann, 2017). More recently, a method of polarity reversal was implemented to optimize the MES performance (Li et al., 2019). Li et al. (2019) initiated their experiment by first setting up a system equipped with a bioanode, which was operated under -0.2 V vs. SHE (anode potential). Then, they utilized the established bioanode as a biocathode by moving it to the cathode compartment and fixing -0.5 V vs. SHE cathode potential. This reverse polarization greatly reduced the start-up (e.g., from >30 days to 18 days) as well as increased the current density (580 mA/m<sup>2</sup> vs. 299 mA/m<sup>2</sup>), which resulted in 1.2 times greater maximum CH<sub>4</sub> generation rate than the control (49 mmol/m<sup>2</sup>/d vs. 29 mmol/m<sup>2</sup>/d) (Li et al., 2019). Similarly, Baek et al. (2022) also indirectly showed a polarity reversal. In their study, the authors used the anode biofilm established using MEC mode (applied voltage of 0.8 V on the anode), then it was used as the cathode biofilm with an applied voltage of 2.0 – 3.1 V.

Vidales et al. (2019) reported a decrease in CH<sub>4</sub> production when they decreased the applied voltage from 2.8 to 2.6 V (from -0.9 V to -0.7 V vs. NHE) in MES. Li et al. (2019) stated that while decreasing cathode potential improves the current density, implementing a significantly more negative potential (e.g., -0.7 V vs. SHE) could favor an IET pathway, leading to the production of excessive H<sub>2</sub>, which is not desirable as it facilitates imbalance between DET and IET (Mohanakrishna et al., 2018; Mohanakrishna et al., 2016; Rojas et al., 2018). Nelabhotla and Dinamarca (2019) found their CH<sub>4</sub> production rate was elevated when the cathode potential increased from -0.8 V to -0.65 V vs. SHE (from 3 mmol/L/d to 6.1 mmol/L/d) but noticed a drastic drop in CH<sub>4</sub> yield when the cathode potential was further increased to -0.55 V vs. SHE. Overall, although their study used reject wastewater containing both CO<sub>2</sub> and COD as a substrate, their MES was capable of producing biogas with high CH<sub>4</sub> content (83-87% under -0.65 V vs. SHE and 90-93% under -0.60 V vs. SHE) when they implemented more positive cathode potentials. The authors also stated that the CO<sub>2</sub> reduction to CH<sub>4</sub> is limited if the cathode potentials are greater than (or more positive) -0.65 V vs. SHE whereas cathode potentials more negative than -0.65 V vs. SHE supports the transformation of CO<sub>2</sub> to CH<sub>4</sub>. More recently, Flores-Rodriguez and Min (2020) investigated a wider range of applied voltage (0.5 – 1.5 V), and 1 V was determined to be

optimal for their MES. This optimal level of the applied voltage was similar to the theoretical applied voltage level discussed earlier.

Li et al. (2020a) conducted a comprehensive analysis of various start-up cathode potentials ranging from -0.7 to -1.1 V vs. Ag/AgCl (-0.5 to -0.9 V vs. SHE). They discovered that biocathodes initiated at -0.7 and -0.8 V vs. Ag/AgCl (-0.5 to -0.6 V vs. SHE) exhibited characteristic sigmoidal catalytic currents indicative of CO<sub>2</sub> reduction. Their results, including CH<sub>4</sub> production rate, Faradaic efficiency, scanning microscopy, and microbial community composition, demonstrated that these cathode potentials favored the DET pathway. In contrast, more negative potentials (-0.9 to -1.1 V vs. Ag/AgCl or -0.7 to -0.9 V vs. SHE) supported the IET pathway. Notably, potentials in the range of -1.0 to -1.1 V vs. Ag/AgCl (-0.8 to -0.9 V vs. SHE) accelerated system start-up by over an order of magnitude compared to less negative potentials, due to a larger driving force for the electrochemical reaction. Although these more negative potentials increased methane production, they significantly reduced Faradaic efficiency because hydrogen generation outpaced its conversion to methane (Li et al., 2020a). Similarly, Ragab et al. (2020) reported that lowering the cathode potential from -1.0 V to -0.7 V vs. Ag/AgCl (-0.8 to -0.5 V vs. SHE) negatively impacted both current density and gas production (CH<sub>4</sub> and H<sub>2</sub>). They also observed that gas products were undetectable when the MES operated at -0.7 V vs. Ag/AgCl (-0.5 V vs. SHE) for 90 minutes. Kim et al. (2022) explored different applied cathode potentials (-0.6, -0.8, and -1.0 V vs. Ag/AgCl or -0.4, -0.6, and -0.8 V vs. SHE) and found that more negative potentials (-1.0 V vs. Ag/AgCl or -0.8 V vs. SHE) were advantageous for CH<sub>4</sub> production due to a greater driving force for cathodic CO<sub>2</sub> reduction and concurrent anodic water electrolysis (Wagner et al., 2010). However, they cautioned that excessively negative potentials (<-1.1 V vs. Ag/AgCl or <-0.9 V vs. SHE) could lead to hydrogen accumulation due to overproduction. By optimizing the cathode potential to -1.0 V vs. Ag/AgCl (-0.8 V vs. SHE), they achieved a maximum CH<sub>4</sub> production rate of 18.9 L/m<sup>2</sup>/d and a 95% CH<sub>4</sub> yield from CO<sub>2</sub> (Kim et al., 2022).

Mateos et al. (2020), on the other hand, demonstrated how MES performance, electro-methanogenesis, and biocathode microbial community evolution could be enhanced by implementing a long-term open circuit mode (e.g., power off for 6 weeks). After reconnection of the power supply, the biocathode was dominated by syntrophic acetate-oxidizing and H<sub>2</sub>-producing bacteria (e.g., *Clostridium*) and H<sub>2</sub>-consuming methanogens, which ultimately led to

CH<sub>4</sub> production. Thus, MES system can be resilient to a long-term power interruption. A few years later, Baek et al. (2022) conducted an experiment with cathode potentials set at -0.7 and -0.9 V vs. SHE, which resulted in an archaeal community predominantly composed of *Methanobacterium*. However, at more negative cathode potentials (-1.1 V vs. SHE), there was a higher abundance of *Methanobrevibacter*. The enrichment of *Methanobrevibacter* at these more negative potentials is favorable due to their higher H<sub>2</sub> thresholds (2.0 – 5.8 Pa) compared to *Methanobacterium* (Kim, 2012). Additionally, a significantly higher relative abundance of *Methanobrevibacter* (80-99%) was observed over *Methanobacterium* under conditions of higher current and H<sub>2</sub> production. In contrast, their abundance markedly decreased to 27% with lower H<sub>2</sub> production (Werner et al., 2016).

Mao et al. (2021) systematically examined the effect of different electrochemical operations. For instance, various electrochemical operation methods, such as applying constant voltage, galvanostatic, and potentiostatic modes were selected, and the authors observed their impact on the start-up process. The CH<sub>4</sub> generated from applying the constant voltage mode is higher than that of the galvanostatic and potentiostatic modes (145% and 238% higher, respectively). Additionally, their electrochemical impedance spectroscopy (EIS) analysis indicated that the superior biocathode performance achieved with applying constant voltage was mainly due to significantly lowered charge transfer resistance. Geppert et al. (2019) demonstrated superior performance, in terms of CH<sub>4</sub> production rate by increasing the applied current (in the range of 5 – 35 A/m<sup>2</sup>; measured cathode potential = -0.76 to -1.08 V vs. SHE). The highest CH<sub>4</sub> yield was achieved at 35 A/m<sup>2</sup> applied current (12.5 L<sub>CH<sub>4</sub></sub>/L/d) with an adequate current-to-CH<sub>4</sub> efficiency (64%). Their study also detected some H<sub>2</sub> when their MES was supplied with a current density > 25 A/m<sup>2</sup>, which was attributed to the metabolic limitations of the cathodic biocatalyst. Kracke et al. (2021) explored the effect of various current densities (0.6 – 1.3 mA/cm<sup>2</sup>) on MES and observed the amount of H<sub>2</sub> consumed by *Methanococcus maripaludis*. They found the MES operated under 0.6 mA/cm<sup>2</sup> of current density allowed highly efficient CH<sub>4</sub> production (~0.095 mL/min) with a very high coulombic efficiency (>97%), which was comparable to the performance of MES supplied with 1.3 mA/cm<sup>2</sup> (<0.01 mL/min). Specifically, their MES operated with higher current densities (0.9 – 1.3 mA/cm<sup>2</sup>) resulted in significant insufficient usage of hydrogen, leading to a decrease in CH<sub>4</sub> generation and very low coulombic efficiency (<20%) (Kracke et al., 2021). These

findings underscore the significance of regulating the cathodic current density to enhance the performance of methane-producing MES. In contrast, Cai et al. (2022) found that increasing the level of applied current (e.g., from 1 to 5 A) on moving bed biofilm reactor-based MES could instantaneously increase the CH<sub>4</sub> productivity (from 0.57 to 1.47 L/L/d for 3 days). However, continuous operation of the MES system under such high applied energy is unfavorable as it deteriorates the CH<sub>4</sub> productivity (sharply decreased after operating for 34 days) due to the alkalization of the catholyte and floatation of microbes resulting from H<sub>2</sub> evolution (Cai et al., 2022). The alkalization in the cathode chamber leads to the deposition of useful cations, such as Mg<sup>2+</sup> and Ca<sup>2+</sup>, that are critical for cathodic microbial growth (Cai et al., 2022). The authors found that operating their MES with <1 A of applied current was optimal as CH<sub>4</sub> was the predominant product, which also corresponded to the highest coulombic efficiency (96.5%) and the highest energy efficiency (43.4%) compared to their other MES operated under higher applied current (2-5 A). Overall, the findings from these studies suggested the importance of optimal energy input for a highly selective CH<sub>4</sub> production in MES.

The bioelectrochemical production of CH<sub>4</sub> via electron transfer mechanisms in METs has been reported at specific cathode potentials (e.g., between -0.6 V and -1.0 V vs. NHE, normal hydrogen electrode) (Vidales et al., 2019). According to the previous findings, a less negative cathode potential (e.g., < -0.75 V vs. NHE) promotes a direct electro-methanogenesis pathway, whereas a higher cathode potential (e.g., > -0.75 V vs. NHE) is expected to facilitate indirect CH<sub>4</sub> formation via intermediates such as H<sub>2</sub> and acetate (Marshall et al., 2012; Villano et al., 2010). However, it is still very challenging to determine the relative contribution of direct- and indirect pathways for CO<sub>2</sub> fixation to CH<sub>4</sub> due to the co-existence of multiple pathways and the complexity of cathodic biofilm communities (Vidales et al., 2019; Zhen et al., 2018). Other CH<sub>4</sub> formation pathways were hypothesized and discussed in the past (Zhang et al., 2019). The elucidations on different electron transfer processes are also discussed later. The external CO<sub>2</sub> can be dosed in various ways, such as in the form of bicarbonates (aqueous form), from ambient air, greenhouse gases, biogas generated from AD digesters, CO<sub>2</sub>-rich flue gases generated from industrial activities, etc. (Batlle-Vilanova et al., 2019; Cheng et al., 2019; Dessì et al., 2021; Irfan et al., 2019; Mao et al., 2021; Tartakovsky et al., 2021). Therefore, regardless of the CO<sub>2</sub> sources, MES enables both CH<sub>4</sub> production and biogas upgrading.

Past research has investigated how energy application impacts methane formation in MES, with a focus on the resultant electron carrier intermediates (Li et al., 2020a; Marshall et al., 2012; Vidales et al., 2019; Villano et al., 2010; Xiao et al., 2020b). Firstly, Marshall et al. (2012) reported that at  $-0.59$  V vs. NHE (applied potential on the cathode), both direct and indirect pathways contributed to  $\text{CH}_4$  production, but no distinction was made between the two mechanisms. Similarly, Villano et al. (2010) found that  $\text{CH}_4$  was primarily formed via direct pathway when their MES was operated under  $-0.75$  V vs. NHE or less negative cathode potential, whereas it was mostly formed via indirect pathway using  $\text{H}_2$  at cathode potentials more negative than  $-0.75$  V vs. NHE. However, when Vidales et al. (2019) fixed their cathode potentials between  $-0.9$  V and  $-0.7$  V vs. NHE in MES, the  $\text{CH}_4$  production pathway at both cathode potentials appeared to be similar. Although numerous studies have explored MES for biomethane production, the optimal cathode potential can vary based on working conditions due to differences in overpotential across studies. As previously discussed, a cathode potential that favors the DET pathway is considered the most energy efficient. This efficiency arises from its lower energy demand and avoidance of reliance on electron carriers, which can also lead to mass transfer limitations as discussed previously (Van Eerten-Jansen et al., 2012; van Eerten-Jansen et al., 2015; Zhen et al., 2018). On the other hand, IET pathway can accommodate other hydrogenotrophic and electrotrophic methanogens that lack the capacity for DET. However, determining the relative contribution of direct and indirect  $\text{CO}_2$  fixation pathways to biomethane production is still challenging due to the co-existence of multiple pathways and the complexity of the cathodic biofilm communities (Vidales et al., 2019; Zhen et al., 2018). Hence, it remains ambiguous which pathway or combination of pathways is most effective for methane production under specific cathode potentials in MES. Therefore, it is crucial to determine a precise working cathode potential to enhance a specific  $\text{CH}_4$  formation pathway remains unclear, requiring further research.

#### **4.3.4 Temperature and pH**

The operating temperature is crucial in MES operation since the growth kinetics of methanogens or electro-microorganisms are sensitive to temperature (Xiao et al., 2020b; Yang et al., 2018a). Yang et al. (2018a) observed the effect of different temperatures ( $15 - 70^\circ\text{C}$ ) and revealed that the optimal  $\text{CH}_4$  generation was attained when their MES was operated  $<50^\circ\text{C}$ . Other studies indicated that the thermophilic condition is favorable for increasing biogas production, reducing oxygen

solubility, and promoting the proton mass transfer rate through the electrolyte (Bolzonella et al., 2012; Jong et al., 2006). Moreover, obtaining higher coulombic efficiency is important as generated electrons do not always get converted to CH<sub>4</sub>; for instance, they are utilized by other by-products, such as organic acids and H<sub>2</sub> on the cathode (Yang et al., 2018a). Of note, operating the MES under thermophilic conditions (Fu et al., 2015; Yang et al., 2018a) could yield a higher coulombic yield than that under mesophilic conditions during CH<sub>4</sub> generation process (Marshall et al., 2012; Van Eerten-Jansen et al., 2012; van Eerten-Jansen et al., 2015; Villano et al., 2010; Xu et al., 2014). Conversely, when Xiao et al. (2020b) tested a smaller temperature range (15 – 55 °C), 35 °C yielded the highest current density, CH<sub>4</sub> production (205.3 L/m<sup>3</sup>/d) and Faradaic efficiency (93.1%). Xiao et al. (2020b) found that temperature > 35 °C led to a drastic attenuation of produced current density due to the potential inhibition of microbes enriched from the mesophilic mixed culture, which contradicted the findings from the earlier study (Yang et al., 2018a). The authors further indicated that lowering the temperature <35 °C results in the retardation of microbial metabolism due to the low enzymatic turnover rate (Xiao et al., 2020b). Two aforesaid studies (Xiao et al., 2020b; Yang et al., 2018a) clearly had distinct findings; hence this indicates that having different inoculum sources might have played a role when determining the optimal working temperature. Hence, more holistic studies are needed to fully reveal the pros and cons of using different inoculums for MES.

The pH gradient is one of the main reasons for the bioelectrochemical system's overpotential (Aryal et al., 2022; Sleutels et al., 2009). The pH changes in catholyte could affect the balance of CO<sub>2</sub> equilibrium reactions ( $\text{CO}_2 \leftrightarrow \text{CO}_3^{2-} \leftrightarrow \text{HCO}_3^- \leftrightarrow \text{H}_2\text{CO}_3$ ) (Bakonyi et al., 2023) and create a pH gradient, which would increase the power consumption (~59 mV per each unit of pH drops) and energy loss for CO<sub>2</sub> reduction (Aryal et al., 2022; Sleutels et al., 2009). As discussed earlier (Eq. 5c,  $\text{Surface pH} = -\log [\text{C}^{*\text{H}^+} - (\text{I}\delta/\text{nFD})]$ ), cathode electrode surface pH is also an important component when optimizing HER (Jayathilake et al., 2018; Jayathilake et al., 2022). pH also influences the ions transport; for instance, at neutral pH, the poor activities of protons and hydroxides were reported, which was evident by their limited rate of transport, particularly when the supporting cation and anion concentrations were greater than 4-5 orders of magnitude (Jayathilake et al., 2022; Logan et al., 2008; Sleutels et al., 2017). Hence, the MES biocathode requires pH control or a specialized CO<sub>2</sub> delivery system to buffer the pH, since the catholyte pH

could become strongly alkaline (7.7 – 10.1) during operation (Baek et al., 2022; Bian et al., 2021; Liu et al., 2017; Mohanakrishna et al., 2016; van Eerten-Jansen et al., 2015). Hence, it is greatly desirable to maintain an adequate pH level (e.g., 6.8-7.8) because an alkaline environment could lead to inferior MES performance (Kim et al., 2022; Wagner et al., 2010; Ward et al., 2008; Zakaria and Dhar, 2019). Nelabhotla and Dinamarca (2019) reported a gradual increase in pH to 8.7 (moderately alkaline) during their MES operation due to the consumption of protons via electrochemical activity, which ultimately hindered the heterotrophic methanogenesis process and lowered CH<sub>4</sub> production rate. Their MES yielded the highest CH<sub>4</sub> generation rate under pH 8.1, which was within the optimal range mentioned earlier. Xiao et al. (2020b) reported that increasing pH from 6.0 to 7.5 led to a boost in current density from 36.3 to 86.0 A/m<sup>3</sup>, but further raising the pH to 8.0 led to a decrease in current density from 86.0 to 51.5 A/m<sup>3</sup>. This was potentially attributed to the inhibition of microbial activity and the biocatalytic reduction process under acidic and alkaline pH (Xiao et al., 2020b). Their study also found the highest CH<sub>4</sub> production rate (213.4 L/m<sup>3</sup>/d) were achieved at pH 7.5. Similarly, Vidales et al. (2021) further confirmed the suppressed CH<sub>4</sub> generation when their MES was operated with a cathodic pH of ~9.5. Recently, Baek et al. (2022) proposed an integration of a vapor-fed anode chamber and zero-gap electrode spacing to maintain neutral catholyte pH (6.6 – 7.2) in MES, which allowed a selective protons transport, restricting the flow of other cations. Moreover, minimizing the space between anode and cathode was also highly beneficial as it enabled effective proton transport from the anode to the biocathode, which eliminated the local pH changes and mass transfer limitation issues. As a result, maintaining a stable pH throughout the MES operation led to less energy input due to the minimization of the pH gradient (Baek et al., 2022).

#### **4.3.5 Mode of operation**

The MES for biogas applications is influenced by the operational mode. Presently, MES for biogas is primarily confined to lab-scale, either in semi-continuous or continuous modes (Table 1). In general, the continuous operation mode demonstrated superior performance over semi-continuous or batch modes. For instance, the CH<sub>4</sub> generation rate increased by 3 times when Batlle-Vilanova et al. (2015) switched their MES operation from batch to continuous. The continuous mode and gas recirculation assisted in overcoming the mass transfer limitations of CO<sub>2</sub> in the system (Bajracharya et al., 2022; Bian et al., 2021). Similarly, Mao et al. (2021) operated their MES in

continuous mode with a hydraulic retention time of 5.88 h, which significantly improved CH<sub>4</sub> generation (0.43 m<sup>3</sup>/m<sup>3</sup>/d or 7.99 L/m<sup>2</sup>/d) by 14.3 times compared to their previous study using fed-batch mode (Cheng et al., 2009). Kim et al. (2022) operated their MES in batch mode, highlighting the importance of selectively excluding electrode-attached and suspended microbes to enhance the CO<sub>2</sub> conversion process. They emphasized the crucial role of attached-growth cells on the electrode surface during batch operation, facilitating direct electron uptake from the cathode electrode through DET and interspecies electron transfer (Kim et al., 2022). In a recent study, Tanguay-Rioux et al. (2023) focused on ensuring long-term stability in MES operation. Their lab-scale MES systems (0.5 – 1 L) successfully produced volumetric methane rates of 0.8 – 1.4 L/L/d, maintaining a nearly constant CO<sub>2</sub> content in the cathode off-gas. Although further investigations are necessary to definitively determine the most effective operating mode for biomethane-producing MES, operating in continuous mode appears highly beneficial for achieving superior methane yield. Additionally, future studies should include a detailed examination of the different mechanisms associated with various operating modes to fully understand their impacts on system performance and efficiency.

#### **4.3.6 CO<sub>2</sub> delivery methods**

CO<sub>2</sub> delivery methods are also critical for MES performance (Bakonyi et al., 2023; Liu et al., 2022). In most cases, CO<sub>2</sub> in gaseous form is used, which is done through either bubbling or sparging in the cathode chamber (Table 1). This method is known to be the most economical way of delivering CO<sub>2</sub> (Liu et al., 2022). It's crucial to also take into account the solubility of CO<sub>2</sub> in the catholyte, which depends on factors such as its composition, temperature, and pressure (Bakonyi et al., 2023). In a typical bioreactor setting (P = 1 bar, T = 303 K), unfortunately, the CO<sub>2</sub> solubility is quite limited (e.g., 1.26 g/kg) (Duan and Sun, 2003). Moreover, other components like the actual dissolved CO<sub>2</sub> concentration, specific area for mass transfer (calculated the input mode of gas bubbling), and the CO<sub>2</sub> uptake rate should also be considered as they also influence the dissolution rate of CO<sub>2</sub> (Bakonyi et al., 2023). Regarding the gaseous CO<sub>2</sub> feeding mode, the gas-liquid mass transfer is considered a major hurdle considering the low solubility of gaseous CO<sub>2</sub> in water (Jiang and Zeng, 2018); for instance, the low solubility of CO<sub>2</sub> in water (limited to 0.0383 mol/L) would lead to inferior MES performance (Mohanakrishna et al., 2018). In such a case, more intense mixing/re-circulation (Mateos et al., 2019; Rojas et al., 2021) or sophisticating the MES

biocathode, such as introducing a hybrid biosystem combining biocompatible Ni-based conductive, catalytic, and porous hollow-fiber cathode (Ni-CCPHF) would be required to provide an effective CO<sub>2</sub> supply and a CO<sub>2</sub>-reduction-to-CH<sub>4</sub> (Alqahtani et al., 2018); but this implies a potential increase in both the capital and operation costs as a trade-off for maintaining an adequate MES performance. Therefore, the optimal selection of CO<sub>2</sub> feeding method is crucial. In this regard, Bian et al. (2021) comprehensively investigated how the CO<sub>2</sub> feeding method affects the overall performance of MES. They compared direct- (directly delivering the pure CO<sub>2</sub> gas from the gasbag) and indirect- (pure CO<sub>2</sub> from the gasbag sparged through the nickel foam coated with multi-walled carbon nanotubes cathode and ceramic hollow tube) CO<sub>2</sub> feeding methods and determined that a higher CH<sub>4</sub> production rate was obtained using MES with direct feeding of CO<sub>2</sub> (76.9 vs. 43.5 mmol/m<sup>2</sup>/d) (see Figure 11). However, the authors initially hypothesized that the detachment of microbial cells from the biocathode might have occurred during indirect dosing of CO<sub>2</sub>. The highest CH<sub>4</sub> generation rate was achieved using a direct CO<sub>2</sub> flow rate of 10 mL/min (240 mmol/m<sup>2</sup>/d) among various CO<sub>2</sub> flow rates (0.3 – 10 mL/min). Similarly, Fu et al. (2022) also compared two different CO<sub>2</sub> delivery methods: (1) mode 1 - sparging of CO<sub>2</sub> directly into the medium; and (2) mode 2 - sparging CO<sub>2</sub> directly through their porous hollow-stainless-steel-cathode. The authors found that mode 2 overcame the limitations of the low CO<sub>2</sub> solubility in aqueous solution. This was attributed to the fact that microorganisms colonize the outer surface of the cylindric electrode, allowing direct CO<sub>2</sub> delivery to the cathodic microorganisms through their porous hollow structured cathode (Fu et al., 2022). More importantly, MES fed with mode 2 exhibited 1.47 times greater maximum CH<sub>4</sub> generation than that fed with mode 1. It has also been reported that bubbling CO<sub>2</sub> can enhance CH<sub>4</sub> production due to the slow and limited mass transfer of gaseous CO<sub>2</sub> into the medium solution (Xiao et al., 2020b). Flushing the biocathode with CO<sub>2</sub> bubbles can improve CO<sub>2</sub> mass transfer from the bulk solution to the biofilms, promoting more efficient methane generation (Xiao et al., 2020b). Additionally, this method helps to minimize local pH differences between the bulk solution and the biofilms (Xiao et al., 2020b). The biocathode also exhibited a much faster response (e.g., several minutes), when CO<sub>2</sub> was provided in the form of bubbles, highlighting the importance of optimizing the CO<sub>2</sub> feeding method (Xiao et al., 2020b). Xiao et al. also investigated different CO<sub>2</sub> feeding rates (20 – 60 mL/min) and found that increasing the flow rate of gaseous CO<sub>2</sub> could slightly increase the methane generation in MES (Xiao et al., 2020b). However, the benefit of maximizing the CO<sub>2</sub> feeding rate for only a slight

increase in CH<sub>4</sub> generation is questionable. It is essential to focus on analyzing and optimizing effective flow, including velocity distribution at the cathode biofilm surface, to enhance MES performance. Although computational fluid dynamics (CFD) can address this (Chung et al., 2021; Quaglio et al., 2019), its application in CH<sub>4</sub>-producing or biogas-upgrading MES is still lacking (de Smit et al., 2023; Jourdin and Burdyny, 2021).

#### **4.3.7 Selection of inorganic carbon sources**

There are various methods to introduce external CO<sub>2</sub> into MES systems. Potential sources include ambient air, bicarbonate (in aqueous form), biogas from AD reactors, and CO<sub>2</sub>-rich industrial flue gases such as those from steel mills (20-30%), refineries (10-20%), cement industries (25-35%), and power plants (10-15%) (Batlle-Vilanova et al., 2019; Cheng et al., 2019; Dessì et al., 2021; Irfan et al., 2019; Mao et al., 2021; Tartakovsky et al., 2021). Given the equilibrium relationships among CO<sub>2</sub>, H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> in aqueous solutions, bicarbonate is more prevalent at neutral pH, making it a favorable option for MES systems typically operated under neutral pH conditions (Xiao et al., 2020b). However, there is a scarcity of studies examining the impact of different inorganic carbon sources on MES performance. Therefore, more comprehensive research is needed to determine the most effective inorganic carbon source for these systems.

#### **4.3.8 Effect of CO<sub>2</sub> concentration and its bubble sizes**

The CO<sub>2</sub> concentrations and bubble sizes are also critical, which can affect the CO<sub>2</sub> fixation, microbial growth, and methanogen-electrode interactions (Bian et al., 2020). The CO<sub>2</sub> reduction rate is significantly influenced by the efficiency of CO<sub>2</sub> mass transfer from the bulk solution to the biofilm (Xiao et al., 2020b), as the CO<sub>2</sub> reduction kinetics is influenced by the concentrations of substrates (i.e., CO<sub>2</sub> and bicarbonate) (Mohanakrishna et al., 2018). Xiao et al. (2020b) examined the effect of different bicarbonate concentrations (1-8 g/L) in MES and found that increasing the concentration from 1 to 4 g/L resulted in higher current output. This was attributed to the increased catholyte conductivity by HCO<sub>3</sub><sup>-</sup>. Especially, the transfer of H<sup>+</sup> from the bulk liquid to the cathode biofilm could also be enhanced by increased conductivity (Lefebvre et al., 2012). Conversely, a further increase in bicarbonate concentration (>4 g/L) could lead to a high saline condition, which is detrimental to biocathodes. Especially, the highly saline environment inhibits the methanogens and will eventually decrease the performance. The overdosing of CO<sub>2</sub> could also inhibit the

methanogens in the biocathode as the excessive amount of CO<sub>2</sub> would create an acidic pH environment in the cathode (e.g., bringing the pH down between a range of 5-6), inhibiting the methanogenic activity (Bian et al., 2020; Zakaria and Dhar, 2019). Hence, either lowering the CO<sub>2</sub> feeding rate or an alternative CO<sub>2</sub> dosing method is required for handling high CO<sub>2</sub> concentration and minimizing the pH fluctuations. Ryu et al. (2009) have indicated that the smaller CO<sub>2</sub> bubble sizes (e.g., 31-61 mm) would promote microbial growth. This is potentially due to the smaller bubble sizes enhancing the gas-liquid interfacial area and mass transfer rate (Ryu et al., 2009).

#### **4.3.9 Start-up time**

The typical start-up time (time required to reach stable operation and/or steady-state) of ~28 days has been reported for CH<sub>4</sub>-producing MES systems (Li et al., 2019; Liu et al., 2018; Mao et al., 2021; Yang et al., 2018a). However, the process could be prolonged further (e.g., > 40 days) (Li et al., 2019; Saheb-Alam et al., 2018). Hence, it is imperative to deeply understand the underlying mechanism associated with the start-up of biocathode to facilitate the field applications of MES. To date, some efforts have been dedicated to lowering the start-up time of MES (Li et al., 2019; Mao et al., 2021). Li et al. (2019) implemented polarity reversal as an electrochemical operation method, which was to establish a bioanode with a simple organic substrate, such as acetate using a fixed potential first (-0.2 V vs. SHE), and then use it as a cathode biofilm by reversing the potential (-0.5 V vs. SHE), which reduced the start-up time approximately by 40% from >30 days than the control MES. This approach also led to >1.2 times higher maximum CH<sub>4</sub> production than the control. Baek et al. (2022) also implemented a similar approach, where they established the anode biofilm under MEC mode (0.8 V), then used as the cathode biofilm (2.0 – 3.1 V) later on. Additionally, Mao et al. (2021) compared three different electrochemical operation techniques, such as applying constant voltage (ACV), galvanostatic (GS), and potentiostatic (PS), and determined that MES operated with the ACV method greatly reduced the start-up time than the other two methods (20 vs. 30 days).

#### **4.4 Strategies for enhancing electron transfer processes**

In MES, the electron transfer could be improved by establishing kinetically efficient microbes in the cathode (Liu et al., 2022; Shin et al., 2017). For instance, Alqahtani et al. (2021) selectively enriched their MES biocathode mostly with methanogenic archaea, *Methanococcus*, and optimize

their electron uptake rate by using cell-derived enzymes, such as hydrogenases and presumably formate dehydrogenases (Deutzmann et al., 2015). Alternatively, it has been reported that the introduction of exogenous mediators could promote the electron transfer process which ultimately increases CH<sub>4</sub> generation rate (Cai et al., 2018; Liu et al., 2022; Yang et al., 2020; Yuan et al., 2019; Zhang et al., 2021). For instance, Yang et al. (2020) incorporated neutral red and anthraquinone-2,6-disulfonate into their MES biocathode, resulting in a substantial increase in CH<sub>4</sub> production rates—5.8-fold and 3.5-fold higher than the control, respectively. This improvement was due to the enhanced IET by methanogenic archaea and a decrease in the system's internal resistance. Cai et al. (2018) also reported that when VFe nitrogenase with cobaltocenium, 1-carboxycobaltocenium, and 1,1'-dicarboxycobaltocenium was used as mediators, they supported the electroenzymatic formation of CH<sub>4</sub> from CO<sub>2</sub>.

#### **4.5 Effect of the presence of other compounds and substances in the biogas**

Biogas from landfill and the AD process is primarily composed of CH<sub>4</sub> and CO<sub>2</sub> (Aghel et al., 2022). However, raw biogas also contains hydrogen sulfide, hydrogen, ammonia, carbon monoxide (CO), nitrogen, and oxygen (Aghel et al., 2022). In this regard, Chu et al. (2020b) showed that the increase in CO content could decrease the MES performance. Kim et al. (2022) also reported that the presence of sulfur compounds and siloxane in biogas impeded the overall performance of their MES applied for biogas upgrading.

#### **4.6 Effect of micronutrients**

The presence of different trace metal levels could potentially affect the MES performance (Reddy et al., 2021; Vidales et al., 2021; Vidales et al., 2020). The explicit biochemical function of trace metals could stimulate the microbial metabolism (Reddy et al., 2021). As summarized in Table 3, each trace metal in the catholyte plays a vital role in CO<sub>2</sub> reduction. Vidales et al. (2020) and Vidales et al. (2021) reported an increase in CH<sub>4</sub> production (39% and 38%, respectively) when Ni and Fe were introduced to MES cathode. After removing Ni and Fe salts from the cathode chamber, the MES performance remained unchanged due to their catalytic effects and their permanent *in-situ* deposition on the carbon felt cathode, which improved its conductivity and the electron transfer process. Vidales et al. (2021) further highlighted that both Ni and Fe metals could also serve as catalysts for the HER (Kim et al., 2017). Similarly, Reddy et al. (2021) examined the

impact of various trace metal concentrations (TM1 = low level-; TM2 = medium level-; TM3 = high-level concentrations of trace metals on MES performance. The highest current and CH<sub>4</sub> generation and CH<sub>4</sub> content in biogas were all achieved using TM2-MES. Excessive trace metal dosing (TM3) was detrimental to the MES (Reddy et al., 2021) due to toxic effects on microbes [23,28]. Hence, optimizing trace metal dosages is crucial for enhancing electron transfer and activating essential enzymes and coenzymes for CO<sub>2</sub> reduction (Pobeheim et al., 2010; Reddy et al., 2021). More recently, Gharbi et al. (2024) also examined the effects of various trace metals, including bismuth and tin, on methane production in MES. Their findings revealed that continuous CO<sub>2</sub> supply in the presence of Bi<sup>3+</sup> ions enhanced methane production, whereas Sn<sup>2+</sup> ions showed no significant impact. Additionally, the presence of Cu<sup>2+</sup> ions markedly inhibited methanogenic activity, resulting in decreased methane output.

## **5.0 Challenges and research gaps**

### **5.1 Challenges in advancing MES for field applications**

For the transition of MES from lab to field applications, the key challenges posed include scaling up the MES system with the same efficiency and cost-effectiveness, maintaining the microbial community dynamics, electrode material stability for the overall longevity of the setup, and product selectivity. Moreover, regulatory compliance and public perception and awareness are critical to unlock the full potential of the technology in the sustainable production process.

#### **5.1.1 MES upscaling and long-term stability**

The upscaling of MES still requires optimization of the components, further developments of innovative electrode and membrane materials. Notably, developing scalable and durable OER catalysts for neutral to acidic media or enhanced ion transport separators would be critical (discussed later). Hence, researchers should revisit MES development, focusing on reactor and electrode geometry, flow engineering, specialty electrolytes, and specific biocatalysts. Achieving commercially relevant productivity in MES systems requires understanding the final scale, the path to upscale, and translating novel designs for mass manufacturability.

Although many studies focused on scalable design of METs (Hiegemann et al., 2016; Liang et al., 2018), there is an enormous gap between the smaller-scale (bench/lab-scale) and larger-scale (pilot

and larger) METs, in terms of performance. Commercializing METs faces challenges in electrode spacing selection (minimizing internal resistance) and extensive energy demands (Chung and Dhar, 2021a; Chung and Dhar, 2021b; Chung and Dhar, 2021c; Chung et al., 2021; Chung et al., 2020b; Zakaria and Dhar, 2019). Microbiological restrictions (metabolic and electron transfer pathways and kinetics), material cost and efficiency, and fluid dynamics are other major concerns (Katuri et al., 2019; Liu and Cheng, 2014). Moreover, the long-term stability of systems are still ambiguous (Katuri et al., 2019; Liu and Cheng, 2014). To address these challenges, several studies have examined the feasibility of upscaling MES (Ceballos-Escalera et al., 2020; Enzmann and Holtmann, 2019; Liu et al., 2022; Shang et al., 2023). In 2019, the first scaling-up attempt of MES by Enzmann et al. came up with a 50 L MES reactor enriched with *M. maripaludis*, which was the largest pure culture electro-methanogenesis experiment and achieved a CH<sub>4</sub> production rate of 11.7 mmol/d (Enzmann and Holtmann, 2019). Ceballos-Escalera et al. (2020) enlarged their MES size to 50 L, which achieved a CH<sub>4</sub> generation rate of 0.01 L/L/d or 0.25 L/m<sup>2</sup>/d. A few years later, Shang et al. (2023) developed a 20 L electrochemical continuous stirred tank reactor (E-CSTR) to study the performance MES for CO<sub>2</sub>-to-CH<sub>4</sub>. A relatively higher CH<sub>4</sub> generation rate (0.68 L/L/d or 407.8 L/m<sup>2</sup>/d) was observed due to the agitation in the CSTR facilitating more uniform conditions for mass and heat transfer. Despite these promising findings, only a single study investigated upscaling of biogas-upgrading MES. Kim et al. (2022) compared two different MES sizes (250 mL vs. 3 L) and found that 3 L provided inferior CH<sub>4</sub> generation rate (18.9 vs. 4.78 L/m<sup>2</sup>/d), while CH<sub>4</sub> content in the final biogas was 95% in both reactors. Considering the level of applied voltages (2.6-2.8 V on 250 mL and 5.6-5.8 V on 3 L reactors), this might be potentially due to insufficient energy input. Hence, future studies are still needed to overcome the configuration and design limitations of larger-scale MES.

Besides MES, other researchers have identified common challenges associated with scaling up METs (Chung and Dhar, 2021b; Heidrich et al., 2014; Hiegemann et al., 2016; Liang et al., 2018; Sim et al., 2018; Zakaria et al., 2024). For instance, Sim et al. (2018) highlighted the difficulties in sourcing appropriate inocula for large-scale applications, noting that effluents from lab-scale MET reactors are often unsuitable for full-scale operations. This challenge is relevant to the scaling of MES as well. Moreover, the transition from lab-scale to larger-scale reactors often introduces significant design changes that can increase overpotential and reduce the performance of METs

(Liang et al., 2018; Sim et al., 2018). For instance, Liang et al. (2018) reported performance deterioration in a 1 m<sup>3</sup> MFC due to water leakage and insufficient electrolyte solution. Additionally, anodic mass transfer limitations in larger-scale METs can lead to diminished current density outputs over time, often exacerbated by potential acidification issues (Sim et al., 2018). Another notable challenge is the increase in dead space caused by the insertion of large online probes, which can affect reactor efficiency (Hiegemann et al., 2016). Hence, exploring alternative methods for implementing online probes in larger designs is recommended.

In this regard, numerous efforts have focused on advancing potential practical solutions. For example, configuring small multiple reactors in series could mitigate operational issues commonly faced by larger single reactors (Heidrich et al., 2014; Walter et al., 2017; Walter et al., 2020). However, such stacked systems may encounter limitations, such as increased overpotential due to inactive biomass accumulation and other operational challenges, including membrane fouling and wire connection issues. Additionally, the implementation of a multi-electrode configuration, previously proposed (Hiegemann et al., 2016; Sonawane et al., 2013), has yet to be explored for biomethane-producing MES. Future studies should investigate this configuration to potentially reduce overpotential and minimize energy inputs. These advancements could also address biocathode and mass transfer limitations in MES. As previously noted, securing adequate and environmentally sustainable power sources is crucial during MES scale-up, given its significantly higher energy consumption compared to other types of METs. It has been suggested that the external power required for spontaneous reactions in METs should be sourced from renewable energies, such as solar and wind power, to ensure MES operations are both sustainable and feasible (Karthikeyan et al., 2019; Thatikayala and Min, 2021). More comprehensive discussions on overcoming the challenges in scaling up METs can be found in other review articles (Jadhav et al., 2022; Jadhav et al., 2021; Janicek et al., 2014; Logan, 2010; Tan et al., 2021). Ultimately, moving forward, it is imperative to apply and further investigate these approaches to overcome scalability barriers in biomethane-producing/biogas-upgrading MES.

### **5.1.2 Selection of MES membranes**

The material cost has been a significant challenge for METs (Aryal et al., 2022; Chung and Dhar, 2021d; Jayathilake et al., 2022; Zakaria and Dhar, 2021); the cost of membranes is typically

represent a significant portion of capital expenses (Jayathilake et al., 2022). Hence, IEMs must be selected based on their efficiency, robustness, and cost. Developing cross-linked PEMs, such as Ultrex CMI-7000 showed potential for reducing the cost (Babanova et al., 2016; Jayathilake et al., 2022). Inexpensive membranes along with some advantageous features, such as enhanced proton conductivity under a neutral pH environment and higher oxygen rejection, may contribute to the commercialization of MES. AEMs are useful in alkaline conditions, particularly for transporting hydroxide ions from the cathode to the anode (Figure 10). Cheng et al. (2009) tested if the AEMs are suitable for electro-methanogenesis and stated that poor ion conductivity was inevitable in neutral media. Furthermore, AEMs allow the non-selective transport of anionic liquid products including carbonate and bicarbonate (Dharmalingam et al., 2019; Divekar et al., 2020; Geppert et al., 2016). Unless the AEM's hydroxide transport process is further improved, PEM/CEM could be a better option, in terms of efficiency and cost. BPMs, composed of a PEM layer and an AEM layer, can enable the anode and cathode chambers to maintain a pH difference by catalyzing water dissociation in the middle. A previous MES study found that a BPM under acidic cathode environment outperformed an AEM under neutral cathodic pH (Wang et al., 2019b). However, utilizing BPM involves extra energy due to higher internal resistance and the potential risk of irreversible performance degradation from layer delamination (Jayathilake et al., 2022). Also, more studies revealing the long-term stability of BPMs are still greatly needed.

### **5.1.3 Energy and Economic Barriers**

Detailed techno-economic assessments for MES systems are lacking, with the electrical energy input being a significant cost for MES operation. For instance, assuming an optimal condition (coulombic efficiency = 90%, externally applied voltage = 3 V), it is estimated that approximately 12 kWh of energy are required to produce 1 kg of acetic acid, and this power consumption will be doubled when generating medium-chain fatty acids, such as caproic acid (Dessi et al., 2021; PrévotEAU et al., 2020). Thus, the energy cost of producing value-added products in MES may exceed its commercial value even without considering other operational costs, maintenance, and downstream processing (Child et al., 2019; Dessi et al., 2021), which may not be economically feasible (Ferry, 2010; Jayathilake et al., 2022; Jourdin et al., 2020). For MES in biogas upgrading, the critical consideration is the availability of free electrical energy, such as surplus or renewable energy. Therefore, future research should focus on identifying more cost-effective renewable

energy sources for MES, enabling it to be competitive with conventional commercial biogas upgrading facilities. Moreover, the current stage of MES, especially for CH<sub>4</sub> production and biogas upgrading, requires substantial development to rival existing commercial biogas upgrading technologies (Aryal et al., 2021; Aryal et al., 2022). Hence, future research should prioritize developing cost-effective components like noble metal-free anodes for OER and cathode electrodes for HER.

A recent study indicated that ~€ 0.15/m<sup>3</sup> CH<sub>4</sub> (equivalent to 0.16 USD considering €1 = 1.09 USD) was spent during the operation of biogas upgrading with an installation capacity of 1000 m<sup>3</sup>/h (Agency, 2018). While the per-unit cost decreases with larger capacities, a higher plant capacity necessitates a substantial overall capital investment (Aryal et al., 2022). Conversely, increased upgrading efficiency leads to reduced costs (Aryal et al., 2022; Sun et al., 2015). Batlle-Vilanova et al. (2019) conducted economic assessments of different biogas upgrading scenarios with MES and found that coupling wastewater treatment with MES biogas upgrading would be advantageous. This integration allows for selecting ClER as the anodic pathway to produce chlorine, which can be used for wastewater disinfection (see Section 2.1). The economic viability of MES was assessed by comparing various scenarios through cost-benefit analysis for chemical synthesis (e.g., acetic acid) from CO<sub>2</sub> reduction in MES (Christodoulou and Velasquez-Orta, 2016). The sustainability assessment of the acetic acid production process via MES indicated that significantly increasing the generation rate would be crucial to competing with fossil-based technologies (Gadkari et al., 2021). Thus, more novel, and unique approaches and their techno-economic assessments must be considered for CH<sub>4</sub> production and biogas upgrading applications of MES.

#### **5.1.4 Net negative carbon emission and use of renewable energy sources**

If powered by fossil fuels, MES can increase carbon emissions instead of mitigating them (Christodoulou et al., 2017; Dessì et al., 2021). To ensure sustainability, renewable and cost-effective energy sources like solar, wind, geothermal, hydro, or bioenergy are crucial for MES biorefineries (Dessì et al., 2021). Direct powering of MES could also be done via solar-to-product conversion by equipping the photoactive electrodes, which might generate enough power density for the system (discussed later) (Bushuyev et al., 2018). However, the intermittent nature of electrical energy supply from renewable sources such as solar power may intermittently lower

production rates in MES, or potentially alter metabolic pathways (Dessi et al., 2021; Mateos et al., 2020). Thus, providing a constant level of energy to the MES system is critical, which could be done by using power storage units or light-emitting diodes for ensuring continuous electron/current delivery to the system (Dessi et al., 2021). Ongoing research on these strategies is crucial to achieve a net-negative carbon emission from MES systems.

## **5.2 Biocathode limitations**

During MES operation, other microbes, such as acetogens could compete with methanogens for H<sub>2</sub> and electrons (Marshall et al., 2017; Patil et al., 2015). Especially, when the operating parameters in MES become favorable for acetogenic activities (e.g., pH drop), methanogens can be outcompeted and acetogens will start utilizing H<sub>2</sub>/CO<sub>2</sub> to generate organic acids (Baek et al., 2022). Thus, an effective biocathode is critical to avoid the production of unwanted by-products. Bajracharya et al. (2015) compared the effect of pure culture (*Clostridium ljungdahlii* DSM 13528) and mixed cultures on the acetate production in MES and found the pure culture MES reactor exhibited higher acetate production (1.3 mM/d vs. 2.4 mM/d). However, this study primarily targeted acetate production, and further research is needed to confirm whether utilizing a pure culture or co-culture would effectively enhance CH<sub>4</sub> generation in MES, given the challenges of maintaining pure culture/co-culture reactor. However, designing the MES reactor that relies on mixed-culture biofilms facilitating DET pathways, may provide higher efficiency and productivity (Jayathilake et al., 2022; Jourdin et al., 2020). Improving the conductivity of cathode biofilm by adding exogenous conductive particles, molecules, and/or ions for enhanced DET can be an option (Noori et al., 2020; Ren et al., 2019). Conversely, relying on a H<sub>2</sub>-mediated MES system and solution phase microbes could be another alternative (PrévotEAU et al., 2020). The hydrogenotrophic methanogens are reported to be much more stable in the long term despite the fluctuations of electrochemical H<sub>2</sub> generation, indicating their high resiliency and potential for practical applications (Mateos et al., 2020; Rojas et al., 2018), which could reduce the kinetic barrier and internal resistance induced by the biofilms (Zhen et al., 2018). However, it's also critical to efficiently transfer in-situ generated H<sub>2</sub> to suspended methanogens. (Suen et al., 2017). Therefore, frequent maintenance and surveillance of the catholyte with suspended microbes including methanogens would be necessary. Otherwise, their rapid proliferation and buildup of

dead cell mass could decrease the ionic conductivity of both the electrolyte and the membrane (Jayathilake et al., 2022).

### **5.3 Mass transfer limitations**

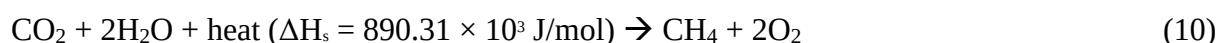
MES systems often provide low CH<sub>4</sub> production rates due to the low solubility of CO<sub>2</sub> and H<sub>2</sub> gases in liquid media and the slow diffusion rates of H<sub>2</sub> bubbles (Kracke et al., 2019; Wang et al., 2014). Such limitations restrict the MES from operating at the intrinsic turnover rate (Guiot et al., 2011; Zabranska and Pokorna, 2018). Interestingly, a past study indicated that the hydrocarbon biosynthesis from CO<sub>2</sub> is limited by H<sub>2</sub> uptake, not much by the slow CO<sub>2</sub> utilization rate. Thus, sufficient H<sub>2</sub> supply to cathodic microorganisms is essential to increase the reaction rate (Liu et al., 2016; Xiu et al., 2019). To enhance hydrogen utilization, systems with high-pressure H<sub>2</sub> gas input, advanced gas diffusers, dispersion and recirculation systems, and large mixing/agitation rates can be employed, albeit with increased energy consumption (Ferry, 2010; Geppert et al., 2016; Guiot et al., 2011). As discussed earlier, MES equipped with IEMs often leads to sluggish ion conductivity across the membrane (Jayathilake et al., 2022). This can significantly elevate cathodic pH due to water electrolysis reactions (Jayathilake et al., 2022). High internal resistance and voltage drop between the anode and cathode may also occur, diminishing overall energy efficiency (Jayathilake et al., 2022). Membrane fouling, bubble trapping, and interactions between membrane functional groups and microbial media components are critical factors to consider, to prevent membrane failure (Dharmalingam et al., 2019; Jayathilake et al., 2022). Therefore, developing a conductive and robust ion-selective membrane that operates effectively under neutral pH conditions is urgently needed.

## **6.0 Future prospects**

### **6.1 Integrated MES systems for CO<sub>2</sub> recycling**

As discussed earlier, MES equipped with water splitting reaction in anode greatly suffers due to high overpotentials and require expensive catalysts for the OER that is critical for CO<sub>2</sub> reduction reaction in cathode (Bian et al., 2020; Dessì et al., 2021). Also, the partial intrusion of produced oxygen from the anode could result in the inhibition of anaerobic cathodic microorganisms. Therefore, MEC-AD design, where combining CO<sub>2</sub> reduction as a cathodic reaction and oxidation of organics or pollutants as an anodic reaction could be a more practical approach (Dessì et al.,

2021; Zakaria and Dhar, 2019). Furthermore, the additional CO<sub>2</sub> generation from the anodic bio-oxidation of organics could be recycled to the biocathode and act as a precursor for chemical production (Zhao et al., 2012). In this regard, further efforts have been made for selective oxidation of target compounds, such as alkenes via photocatalytic oxidation to enhance the anodic reaction (Dessi et al., 2021; Farràs et al., 2016). However, extra CO<sub>2</sub> can be produced via anodic bio-oxidation should be managed. One possible option could be injecting that extra CO<sub>2</sub> into the cathode chamber. Moreover, targeting CH<sub>4</sub> production in MES might be energy negative considering the following reverse CH<sub>4</sub> combustion reaction (or overall reaction in MES equipped with OER):



Theoretically, the minimum amount of energy required for synthesizing one mol of CH<sub>4</sub> from one mol of CO<sub>2</sub> is 890 kJ. However, if the generated CH<sub>4</sub> is combusted for heat and power with approximately 32-64% efficiency (Gür, 2016; Li et al., 2020c; Wood et al., 2023), the MES for CH<sub>4</sub> production would become energy negative, and it would no longer capture carbon, as it would release CO<sub>2</sub> back into the environment. Notably, the energy transfer efficiency of methane in biogas to electricity typically falls within the lower end of the aforementioned range (e.g., 33-38%), largely due to its composition (~60-80%) (Lang et al., 2017; Shin et al., 2014; Shin et al., 2021). In this regard, converting the produced CH<sub>4</sub> to other higher-value bioproducts, such as polyhydroxyalkanoates (PHA) and polyhydroxybutyrate (PHB) bioplastics and methanol could be a unique option (Myung et al., 2017; Myung et al., 2016; Myung et al., 2018). Moreover, it has been demonstrated that biogas can be directly utilized in methanotrophic systems to produce value-added products, such as PHBs (Pham et al., 2024; Sahoo et al., 2021), offering additional advantages given the low conversion efficiency of biomethane. In the past, the two-stage system combining methanotrophic bacteria and METs has been demonstrated, methanotrophic bacteria first converted CH<sub>4</sub> to methanol, followed by using a MFC to convert methanol into electricity (Myung et al., 2018). Recently, an MES-methanotrophic system was also proposed to synthesize a single-cell protein from CH<sub>4</sub> produced via electro-methanogenesis (Xu et al., 2021) (Figure 12); however, more work is still needed regarding this hybrid system. Incorporating the methanotrophic process followed by CH<sub>4</sub> production in MES could be another feasible option for CO<sub>2</sub> mitigation and producing high-value products from CH<sub>4</sub>. Despite the promising approach of combining MES

systems with methanotrophs, a more comprehensive investigation into the economic viability of such a hybrid system is crucial for advancing and moving MES systems closer to practical application. Additionally, optimizing the cathodic and anodic reactions in these integrated systems remains a significant challenge. Another potential issue is producing high-purity biomethane using MES prior to methanotrophy, as methanotrophs are primarily known for converting methane (Gęsicka et al., 2021; Strong et al., 2016) rather than other impurities present in biogas. Given the typically low methane content in raw biogas, upgrading the biogas could be more desirable for methanotrophic systems. However, as noted earlier, methanotrophs can still convert both CO<sub>2</sub> and methane into other value-added products (Pham et al., 2024; Sahoo et al., 2021). In this context, the dependency on MES performance prior to methanotrophy might be less critical, making this hybrid system a more feasible and viable option for utilizing biomethane and biogas. Future studies should consider these aspects to further advance MES systems.

## **6.2 Application of quorum sensing (QS) gene for stimulating microbes in MES**

Quorum sensing (QS) in biosystems and biotechnologies is of great interest due to its crucial role in microbial interactions (Chung et al., 2022; Dai et al., 2023; Li et al., 2023). Intercellular communication among microbes, facilitated by extracellular signaling molecules or autoinducers like acylated homoserine lactones (AHLs), is known as QS (Christwardana et al., 2019; Papenfort and Bassler, 2016; Shi et al., 2023; Yang et al., 2018b). This crucial process coordinates cell-to-cell communication, regulating gene expression to control various physiological behaviors such as competence, cell motility, virulence, conjugation, symbiosis, electron transfer processes, and biofilm formation (Dai et al., 2023; Yang et al., 2018b; Yin et al., 2020; Yong et al., 2011). QS can be artificially enhanced by introducing exogenous autoinducers, which can lead to higher current and power densities (Christwardana et al., 2019; Chung et al., 2022; Yong et al., 2011). The literature provides numerous examples of QS applications and their roles in electron transfer and biofilm formation (Dang et al., 2022; Yin et al., 2020; Zhou et al., 2022). Li et al. (2023) demonstrated that exogenous AHLs enhanced the electrochemical activities of cathodic electroactive bacteria (EABs) by promoting microbial attachment to electrodes, increasing the live-to-dead cell ratio, and boosting the abundance of key microbes. Furthermore, Zhou et al. (2022) reported improved cathode biofilm formation, CO<sub>2</sub> reduction, and acetate production in MES through N-Hexanoyl-L-homoserine lactone (C6HSL)-based QS regulation. QS in the biocathode

can significantly influence methanogenesis and enhance MES performance (Li et al., 2023; Yin et al., 2020). Despite its potential, the application of exogenous autoinducers to improve MES performance has been infrequently reported (Chung et al., 2022; Pan et al., 2020). No studies have explored the impact of QS on methanogens and electrotrophs in CH<sub>4</sub>-generating MES. Future research should thoroughly investigate QS application for enhanced CH<sub>4</sub> generation and biogas upgrading rates.

### **6.3 Applications of advanced fabrication and computational tools**

The MET systems are inherently complex, time-variant, and nonlinear, with performance often influenced by various design and operating parameters as well as environmental conditions (Chung and Dhar, 2021d; Fang et al., 2013; Yewale et al., 2020). A specialized modeling tool is essential to understand these intricate nonlinear interactions and optimize MES. However, the lack of such models has traditionally forced a heavy reliance on experimental investigations, making MET research labor-intensive and time-consuming (Chung et al., 2023). Recently, machine learning (ML) algorithms have emerged as a promising approach in bioprocess research (Cai et al., 2019; Chung et al., 2023; Haffiez et al., 2022; Lesnik and Liu, 2017), providing valuable tools to decipher the core nonlinear interactions among various operating and design parameters in METs (Chung et al., 2023). For instance, Artificial Neural Networks (ANN) could be used to optimize physical design parameters, such as anode angle, inlet flow rate, and flow direction in METs (Chung and Dhar, 2021b; de Ramón-Fernández et al., 2020; Jaeel et al., 2016). Additionally, ML models can predict other key operating parameters, such as microbial community composition (Lesnik and Liu, 2017), temperature (Yewale et al., 2020), maximum power density (Fang et al., 2013), and types of substrate (Cai et al., 2019). Notably, previous studies have shown that MET-related ML models can achieve algorithm validation with a relatively small amount of training data (e.g., as few as 17 data points) (Chung et al., 2023; Tsompanas et al., 2019; Vabalas et al., 2019). In the context of methane and biogas applications, Quashie et al. used a backpropagation neural network model to estimate biogas production from MEC-AD, considering variables such as chemical oxygen demand (COD), pH, and organic loading rate (OLR) (Quashie et al., 2021). Their ML model demonstrated high accuracy (determination coefficient,  $R^2 = 0.8902$ ; index of agreement,  $IA = 0.925$ ; and fractional variance,  $FV = 0.0715$ ), accurately predicting the impact of these parameters on system performance. Such ML applications could be further modified for the MES

optimization, including the selections of the most efficient functional anode/biocathode and inoculum sources, membranes, applied energy, operating temperature and pH, CO<sub>2</sub> delivery method, CO<sub>2</sub> concentrations, inorganic carbon source, start-up time, and system operating pressure.

Furthermore, unique manufacturing techniques, such as 3D printing (three-dimensional printing; 3DP) could significantly aid the scale-up opportunities of METs (Chouler et al., 2018; Chung and Dhar, 2021a). The 3D printing applications already have been demonstrated for the accurate manufacturing of different operating components of METs (Chung and Dhar, 2021a), such as reactor bodies (Di Lorenzo et al., 2014), electrodes (Bian et al., 2018b), EAB biofilms (Freyman et al., 2020), and membranes (Philamore et al., 2015). Similar approaches can be implemented for MES applied for CH<sub>4</sub>/ biogas applications. For instance, 3D-printed gas diffusion electrodes showed promising results by improving the single-pass reactant conversion efficiency during the DET process (Higgins et al., 2018). Although their ability needs to be further assessed and evaluated in IET- or H<sub>2</sub>-mediated CO<sub>2</sub> conversion systems (Jayathilake et al., 2022). The advancement of 3D electrodes enables the optimization of electrode geometry and topology to align with the reactor volume and housing. This integration facilitates fluid flow to enhance turbulent mixing and reduce the diffusion layer thickness, resulting in higher current densities (Ambrosi and Pumera, 2016; Palmara et al., 2021; Zhu et al., 2017). Consequently, the fabrication of 3D biocathodes is crucial for enhancing reactor efficiency and reducing the diffusion layer, enabling increased current densities without compromising microbial activities. If the final products of the bioelectrochemical systems are gases just like CH<sub>4</sub>-producing MES, the management of bubbles is also imperative for minimizing the system resistance (Jayathilake et al., 2022). For instance, the physical blockage of electrodes and membranes due to bubbles can lead to unnecessary internal resistance in MES (Jayathilake et al., 2022). Creating gas transport channels on the electrodes or flowing electrolytes through them could be an option to mitigate bubble-related issues (Kou et al., 2020). In this regard, 3D-printed electrodes are highly promising for custom-design to include gas transport channels at both micro and macro scales. 3D metallic cathodes manufactured using emerging 3DP methods were also quite promising, but their speed, cost, processing methods, and material scalability need to be improved (Jayathilake et al., 2022). A newer form of additive manufacturing, electrochemical 3DP, has emerged, creating metallic structures through the electrochemical reduction of metal ions onto conductive substrates

(PrévotEAU et al., 2020). However, more studies and development are required prior to their adoption for MES. Despite several promising applications of 3DP in MES, more studies are needed to clearly identify the benefits of using 3DP for MES fabrication. Figure 13 shows a conceptual schematic of how METs can be incorporated with emerging manufacturing and computational tools, such as computational fluid dynamics (discussed earlier), machine learning, and 3D printing.

#### **6.4 Advanced cathode materials**

Commercial carbonaceous materials are frequently chosen as biocathodes in MES due to their exceptional stability, high conductivity, and catalytic activity (Aryal et al., 2016; Blasco-Gómez et al., 2017; Ceballos-Escalera et al., 2020; Zhen et al., 2018). Additionally, biochar (Cheng et al., 2020) and gas diffusion-activated carbon electrodes (Bajracharya et al., 2016; Dong et al., 2018) have been utilized effectively as MES electrodes. Aryal et al. (2016) reported significantly enhanced acetate productivity using a 3D-graphene-modified carbon felt composite, achieving approximately 6.8 times higher production compared to untreated carbon felt cathodes due to the increased specific surface area. Similarly, MES systems using nitric acid-treated graphite granular cathodes have shown improved electron transfer and a larger specific surface area, facilitating greater bacterial adhesion and effective microbe-electrode interactions, thus optimizing acetate productivity (Marshall et al., 2013; Shakeel et al., 2020). Moreover, improving electrode material conductivity using doped carbons and graphene aerogels over carbon black electrodes can reduce internal resistance, boosting overall system performance (Jayathilake et al., 2022; Kracke et al., 2021).

Some metal-based cathodes and composite cathodes also have been adopted as MES biocathodes. Platinum electrodes are usually known to be the benchmark MES anode material, but they are not practical at larger scales due to high price. Thus, more common and cheaper metals, such as copper, nickel, and alloys (e.g., nickel-molybdenum) would be more feasible for MES biocathode as they can still efficiently achieve low overpotential HER under neutral working conditions (Kracke et al., 2020; Kracke et al., 2019; Roger and Symes, 2015; Wang et al., 2019a). Jiang et al. (2019) investigated the impact of various metal-based cathodes, including copper, indium, titanium, and zinc, on biodiversity, noting that metal leaching could influence microbial communities. They found that zinc-based biocathodes led to higher acetic acid and titer production, and zinc proved

less toxic than copper in acute toxicity tests. Consequently, zinc-based cathodes may enhance methanogenesis in MES. Additionally, molybdenum carbide-modified cathodes were used to increase acetate production (Tian et al., 2019) due to their role as HER electrocatalysts, potentially boosting electro-methanogenesis in MES. Low CO<sub>2</sub> and H<sub>2</sub> solubilities are significant limitations in MES performance (PrévotEAU et al., 2020), and perovskite-based electrodes might be promising as they improve HER and CO<sub>2</sub> adsorption (Tian et al., 2020; Zhu et al., 2019). Perovskite-based cathodes, known for their biocompatibility, facilitate denser biofilm formation, enhancing MES performance (Tian et al., 2020). Li et al. (2018) demonstrated that composite biocathodes with nickel nanoparticles embedded in nitrogen-doped nanotubes significantly increased the CO<sub>2</sub>-to-poly-β-hydroxybutyrate conversion rate in MES. Another study showed that a graphite rod biocathode with magnetite nanoparticles yielded higher acetate production (~8.5 times more than the control) (Viggi et al., 2020), attributed to magnetite's ability to catalyze microbiologically-driven H<sub>2</sub> production and promote DET processes. This was attributed to the fact that magnetite nanoparticles were capable of catalyzing microbiologically-driven H<sub>2</sub> production and promoting the DET processes (Viggi et al., 2020). Reduced graphene oxide supported with copper ferrite also showed promise in enhancing the bioelectrosynthesis of VFAs from CO<sub>2</sub> (Thatikayala and Min, 2021). Electrode materials can be further optimized by applying a catalytic layer via electrodeposition to reduce overpotential (Jayathilake et al., 2022). Zakaria and Dhar (2021) reported that stainless steel cathodes outperformed carbon fiber cathodes due to denser methanogenic biofilm formation. Furthermore, alternative cathode types, such as flow-through and gas diffusion electrodes (Alqahtani et al., 2018; Bajracharya et al., 2016; Bajracharya et al., 2017b; Jourdin et al., 2018), can enhance CO<sub>2</sub>-to-CH<sub>4</sub> conversion by improving the CO<sub>2</sub> mass transfer rate (Bajracharya et al., 2016). A forced flow-through configuration with a carbon fiber-based cathode can increase mass transfer and electrode surface area (Bajracharya et al., 2017b; Jourdin et al., 2018). Additionally, supplying CO<sub>2</sub> directly through a dual-functional porous Ni-hollow fiber membrane cathode can mitigate CO<sub>2</sub> mass transfer limitations, leading to superior CO<sub>2</sub> reduction to methane in MES (Alqahtani et al., 2018; Bian et al., 2018a). Although most studies emphasized optimizing the biocathode for increased productivity of other products like acetate, these findings can aid in achieving better MES performance for CH<sub>4</sub> production and biogas upgrading.

## **6.5 Advanced membranes**

Advanced membranes, such as amphoteric membranes (AMPs), incorporating both cation and anion exchange features within one layer, present a promising option as separators in MES (Jayathilake et al., 2022). These membranes have demonstrated high proton conductivity and exceptional ionic selectivity in redox battery applications (Chu et al., 2019; Jayathilake et al., 2022; Yan et al., 2017). AMPs are particularly advantageous for neutral media electrolysis, as they can conduct both cations and anions, offering a superior alternative to single-type IEM (Liao et al., 2020). However, further fundamental research on polymer morphology and the distribution of cationic and anionic groups within AMPs is necessary before they can be effectively implemented in MES systems (Jayathilake et al., 2022). Porous separators (POS) represent another viable option. Unlike selective ion transport regulated by charge, POS made from materials like nylon or poly(propylene) can be designed for selective transport by controlling pore sizes (Jayathilake et al., 2022; Vidales et al., 2021; Vidales et al., 2022). These separators have been explored in various electrochemical systems, including solid-state aqueous batteries and alkaline electrolyzers (Jayathilake et al., 2022). Their low internal resistance can enhance the system's voltaic efficiency and enable faster ion transport compared to IEMs, while maintaining pH during electrolysis in neutral environments (Jayathilake et al., 2022; Sato et al., 2013). Despite their use in MES for methane and acetic acid production (Vidales et al., 2021; Vidales et al., 2022; Vidales et al., 2019; Vidales et al., 2020), the porous nature of POS allows for the crossover of dissolved oxygen and charge-neutral molecules (Jayathilake et al., 2022). Innovative approaches are needed to reduce gas permeation, prevent non-selective crossover, and minimize biofilm growth on the membrane (Jayathilake et al., 2022). Overall, if this pore-size engineering and surface modification can be done successfully, POS could significantly contribute to the upscaling of MES.

## **6.6 Photo-electrodes as a solution for minimizing energy demand**

To meet MES energy demands, utilizing a solar-powered photoanode can be a promising solution. Harnessing abundant light energy can offset the significant thermodynamic barrier, such as the system overpotential, associated with the OER in MES—a process called artificial photosynthesis (Fu et al., 2018). The photoelectrochemical cells for water splitting are capable of supplying currents as high as 5.8 mA/cm<sup>2</sup> for driving electrochemical CO<sub>2</sub> reduction (Dessì et al., 2021; Kirner and Finke, 2017). Previous studies combining the photoelectrochemical anode and

biological cathode (known as photo-bioelectrochemical systems or photo-MES) demonstrated self-sustained productions of isopropanol, acetic acid, and more importantly, CH<sub>4</sub> from CO<sub>2</sub> (Dessi et al., 2021; Kistler et al., 2018; Yang et al., 2017).

In particular, OER catalysts based on metal oxides, like titanium dioxide in the configuration of nanowire arrays, can efficiently harness solar energy during MES operation (Fu et al., 2018; Liu et al., 2015a; Xiao et al., 2020c). Liu et al. (2015a) integrated TiO<sub>2</sub> nanowires as a photocatalyst at the anode in their MES, which was enriched with *S. ovata* as the biocatalyst at the cathode. This setup produced acetic acid concentrations up to 6 g/L, comparable to those achieved in conventional MES systems (PrévotEAU et al., 2020). More recently, Xiao et al. (2020c) reported an average solar conversion efficiency of 0.62%—approximately six times higher than global natural photosynthesis—for the biological conversion of CO<sub>2</sub> to CH<sub>4</sub>, utilizing a TiO<sub>2</sub>-CdS photoanode in MES. Their study further demonstrated that dosing a Cu<sub>2</sub>ZnSnS<sub>4</sub> light-absorbing sensitizer to the photoanode could enhance bio-cathodic methane production even more. Thus, using a photo-absorber as an anode proves to be highly promising to mitigate the energy demand associated with enhancing the OER in MES and holds potential for application in MES for CH<sub>4</sub> generation and biogas upgrading.

## 6.7 Adding additional value to the biogas upgrading process

Enhancing the economic feasibility of MES for methane production and biogas upgrading can be achieved by recovering additional resources, ions, and value-added products. Chu et al. (2020b) demonstrated the potential for selective recovery of C<sub>4</sub> and C<sub>6</sub> carboxylates in the presence of carbon monoxide. Sustainable nitrogen recovery maintains nutrient cycling, potentially reducing nitrogen fixation costs (Aryal et al., 2022). Bioelectrochemically recovered nitrogen, particularly as ammonium (NH<sub>4</sub><sup>+</sup>), serves as an excellent fertilizer for agriculture (Aryal et al., 2022; Barua et al., 2019). The recovery of nitrogen could be in the form of ammonium (NH<sub>4</sub><sup>+</sup>), where the acidic environment would favor the production of ammonium ( $\text{H}_2\text{O} + \text{NH}_3 \rightleftharpoons \text{OH}^- + \text{NH}_4^+$ ). However, alkaline catholyte pH could drive ammonia escape during recovery (Aryal et al., 2022; Kelly and He, 2014). The implementation of anodic CIER could simultaneously reduce the energy demand by 45% (Du et al., 2015) and recover the disinfecting agent, such as chlorine (Aryal et al., 2022; Battle-Vilanova et al., 2019). Such added features could potentially compete with the conventional

physiochemical biogas upgrading methods due to the additional production of chemicals. Additionally, Fu et al. (2020) showed that simultaneous sulfur recovery from anodic H<sub>2</sub>S oxidation is feasible by incorporating exogenous electron shuttles such as Fe<sup>2+</sup>/Fe<sup>3+</sup>, further improving the system's utility and efficiency. However, this study was limited to in-situ biogas upgrading or MEC-AD mode where H<sub>2</sub>S was exposed to anode electrode, and it would be questionable whether the recovery of sulfur could be accomplished in MES configuration. In this regard, resource recovery, such as nutrient recovery could be done more efficiently in MEC-AD mode or during *in situ* biogas upgrading process due to the presence of biotic anode (Bajracharya et al., 2016; Cerrillo et al., 2021; Zeppilli et al., 2017; Zeppilli et al., 2019). Since the target of this article is not on the *in situ* biogas upgrading in MEC-AD mode, more comprehensive discussions on the recovery of value-added products along with biogas upgrading via bioelectrochemical process is found in the recent review (Aryal et al., 2022). Considering that biomethane derived from biogas is inexpensive and has limited applications (e.g., as a direct transportation fuel and for producing heat and electricity; discussed earlier), and that it typically exhibits low energy conversion efficiencies (around 33-38%) (Shin et al., 2014; Shin et al., 2021), converting the CO<sub>2</sub> in biogas into other value-added products, such as acetic acid, offers a promising alternative to enhance the value of biogas (Roy et al., 2023; Roy et al., 2021b). Additionally, the market for acetic acid is considerably larger, and acetic acid itself has diverse applications (Christodoulou and Velasquez-Orta, 2016; Gadkari et al., 2021; Naidu and Mathews, 2019; Pal and Nayak, 2017), providing a significant advantage over biomethane. In this regard, Roy et al. (2021b) developed an MES system enriched with *Acetobacterium* spp., demonstrating the conversion of CO<sub>2</sub> in biogas to acetic acid under a fixed cathode potential of -1 V vs. Ag/AgCl. This process not only produced a maximum acetic acid concentration of 1.5±0.5 g/L but also enhanced the methane content of the biogas from 61% to 86%. Building on this, the same research group later enhanced their MES performance, achieving higher acetic acid concentrations (3.6±0.5 g/L) and improved biogas upgrading efficiency (methane content increased from 56% to 86%) (Roy et al., 2023). Their studies also reported satisfactory coulombic (82%) and energy efficiencies (36%) during the biogas upgrading process. However, potential drawbacks of acetic acid production from biogas include the higher energy demand associated with the homoacetogenesis process (considering the standard Gibbs free energy), the possible enrichment of slow-growing acetoclastic methanogens during long-term operations, the need to add substances like chemicals to control methanogenesis, and the risk of

acidification from accumulated acetic acids if methane production is also targeted (which requires precise process monitoring). Despite these challenges, the unique findings from the aforesaid studies demonstrate that MES systems could also be employed to produce other higher-value products from biogas, such as medium-chain fatty acids (Chu et al., 2021), thereby enhancing the potential applications of biogas upgrading via MES. Overall, future studies should investigate innovative MES configurations and designs to recover other higher-value products from other gas components of feedstock biogas.

## **7.0 Conclusions**

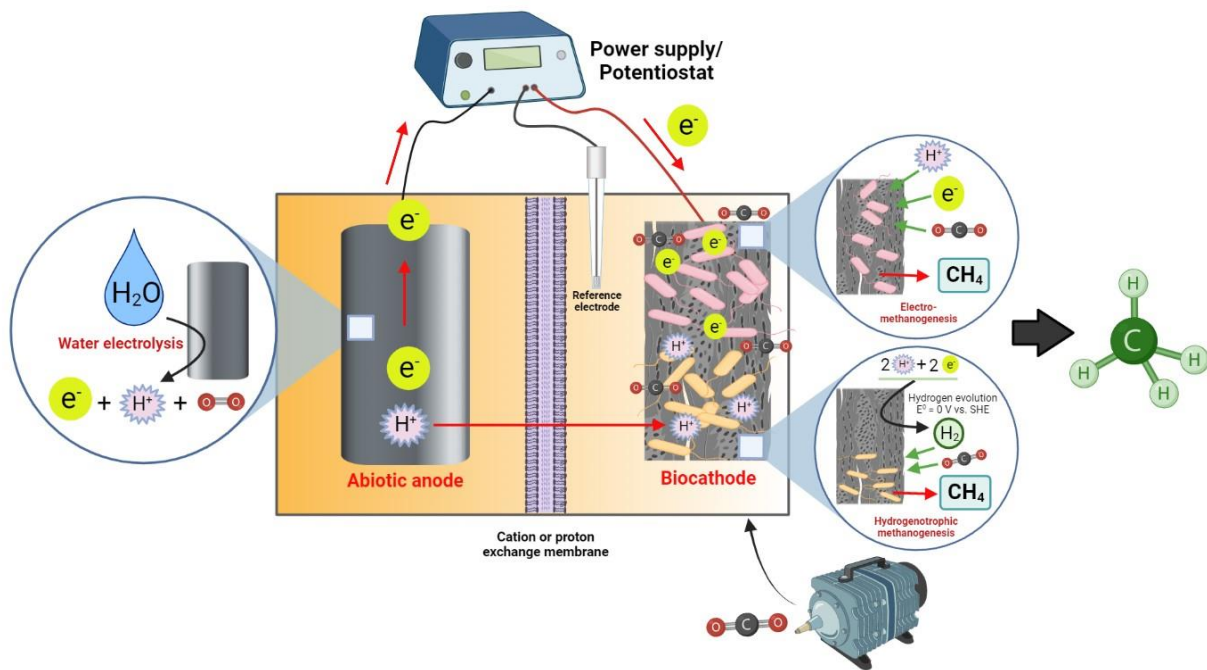
In summary, this review article highlights the applications of MES for simultaneous CO<sub>2</sub> mitigation and reduction, CH<sub>4</sub> generation, and biogas upgrading. Previous studies have confirmed the feasibility of MES for efficiently producing CH<sub>4</sub> from CO<sub>2</sub> and stated that many different factors, such as electrode materials and types, methanation routes and associated electron transfer pathways, inoculum sources and microbial communities, ion-exchange membrane, externally applied energy level, operating temperature and pH, mode of operation, CO<sub>2</sub> delivery method, inorganic carbon source and its concentration, start-up time, and system pressure, can influence and govern the performance of MES. Despite the promising results of MES, however, several research gaps and challenges were highlighted for further research. Several hurdles, such as design and configuration, long-term stability, high energy demand, techno-economics, achieving net negative carbon emission, and other aforementioned operational issues, must be addressed to implement this CH<sub>4</sub>-producing and biogas-upgrading MES for practical applications. Based on the evaluation of previous studies, we suggest that future studies should focus on developing an integrated MES system and exploring the QS mechanisms in the biocathode and incorporating MES with other emerging manufacturing and computational tools, such as 3D printing and machine learning for more efficient and sustainable CO<sub>2</sub> recycling and the production of renewable energy. Introducing a methanotrophic bioreactor as a following step can further convert the CH<sub>4</sub> produced from MES to value-added products, such as bioplastics, methanol, and single-cell protein, which further adds value to CH<sub>4</sub> and enables sustainable CO<sub>2</sub> recycling. Enhancing QS in the MES biocathode could further facilitate the formation of biofilm and electron transfer processes for increasing the rates of CO<sub>2</sub> reduction and CH<sub>4</sub> production. Adopting 3D printing techniques and machine learning algorithms could also optimize various operating parameters of MES. Ultimately,

with the assist of more future studies and research, the MES can potentially be a clean, efficient, low-cost, and promising technology for capturing, mitigating, and reducing CO<sub>2</sub> in the environment and sustainably providing renewable energy across the globe.

### **Acknowledgements**

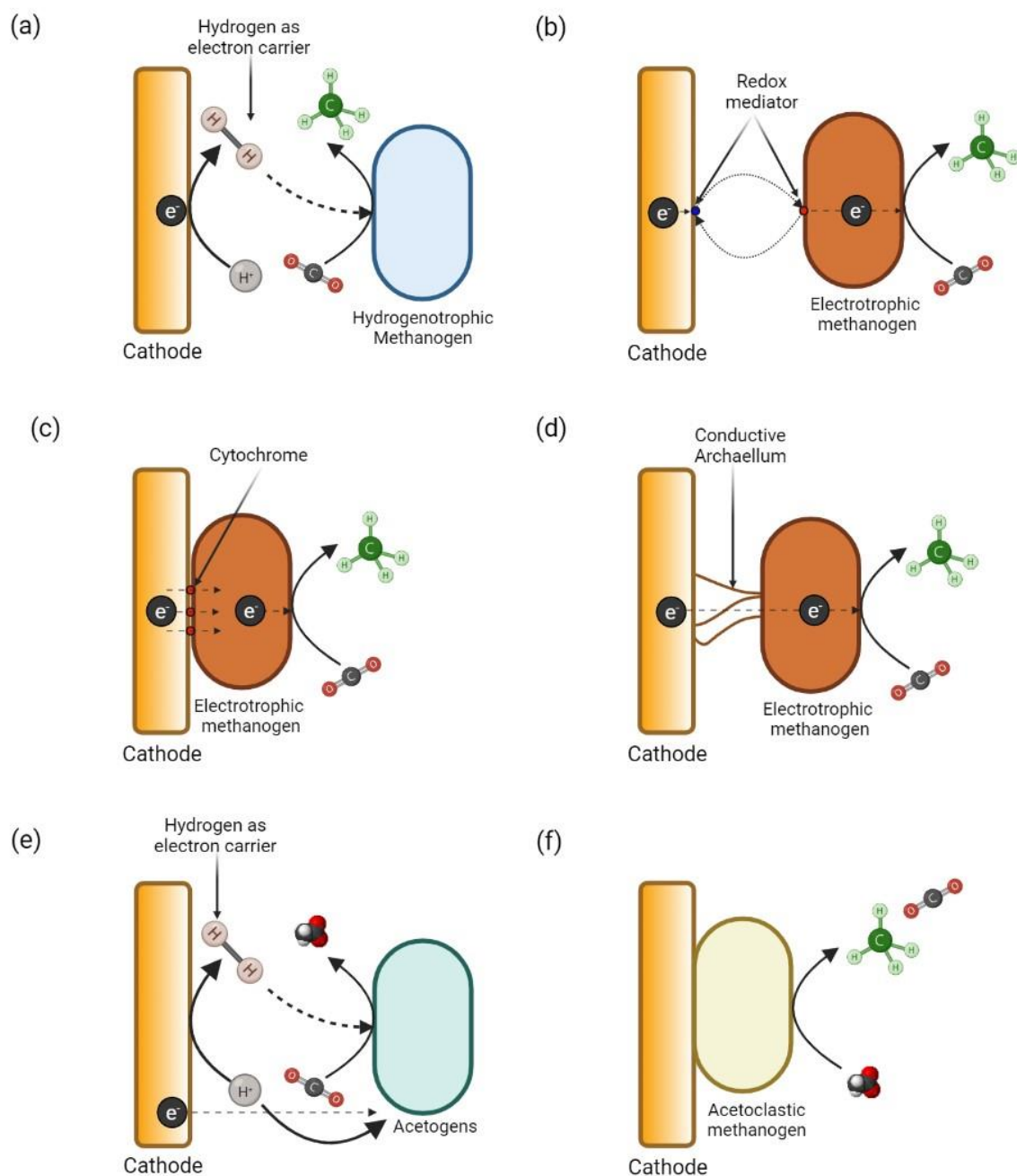
We acknowledge financial support from the Natural Sciences and Engineering Research Council (NSERC) Discovery Grants and Canada Research Chair (CRC Tier 2) in Microbial Electrocatalysis for Energy and Environment (Dr. Dhar). T.H. Chung acknowledges the Izaak Walton Killam Memorial Scholarship, NSERC Alexander Graham Bell Canada Graduate Scholarship, Alberta Innovates Graduate Student Scholarship (AIGSS), and University of Alberta's Graduate Scholarships (ConocoPhillips Canada Limited Graduate Scholarship in Hydrocarbon Development, Ivy A Thomson and William A Thomson Graduate Scholarship, and Westmoreland Coal Company Graduate Student Scholarship in Environmental Engineering).

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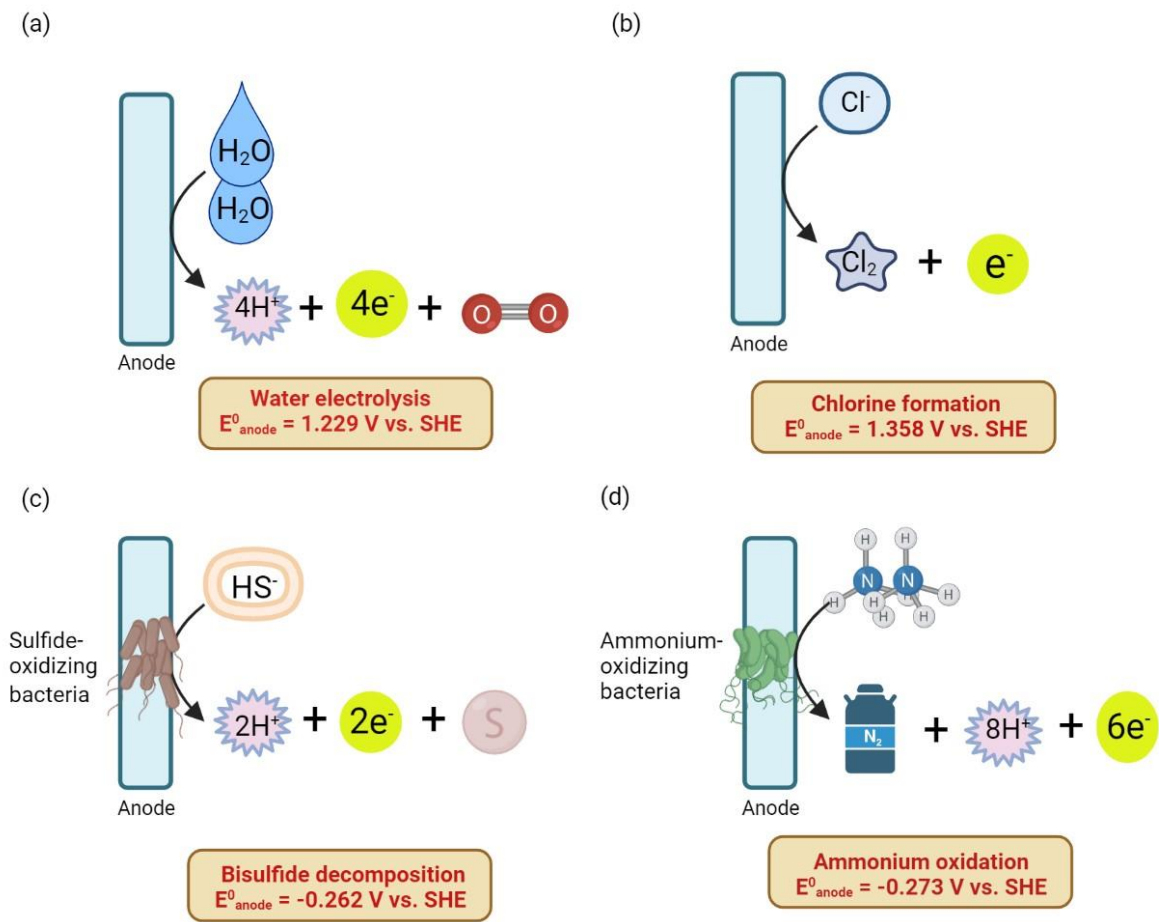
1971 **Figure 1.** A schematic showing a conventional MES system for  $\text{CH}_4$  production (Created with  
1972 BioRender.com)



**Figure 2.** An illustration describing possible  $\text{CH}_4$  production routes using methanogens in biocathode; (a) hydrogenotrophic methanogenesis; (b) electrotrophic methanogenesis using redox mediator as an electron carrier; (c) electrotrophic methanogenesis using cytochrome as an electron carrier; (d) electrotrophic methanogenesis using direct electron transfer pathway; and (e-f) acetoclastic methanogenesis pathway (Created with BioRender.com)

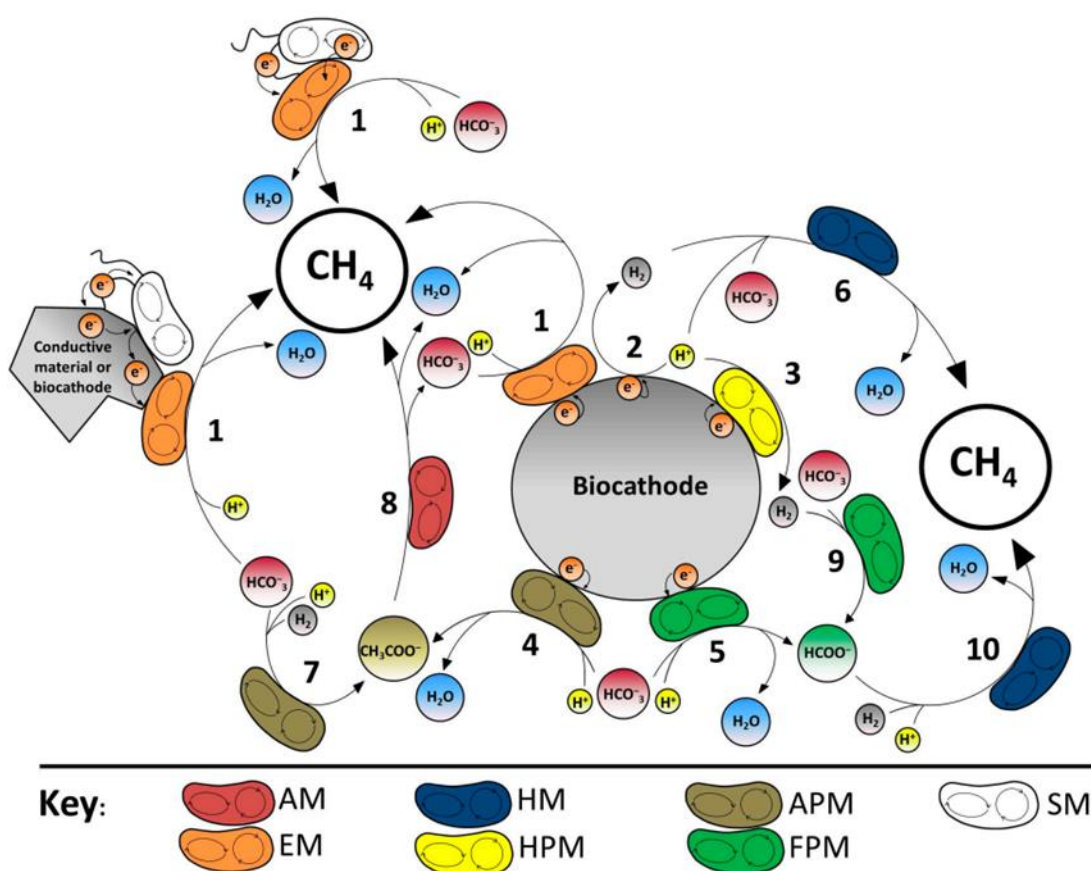
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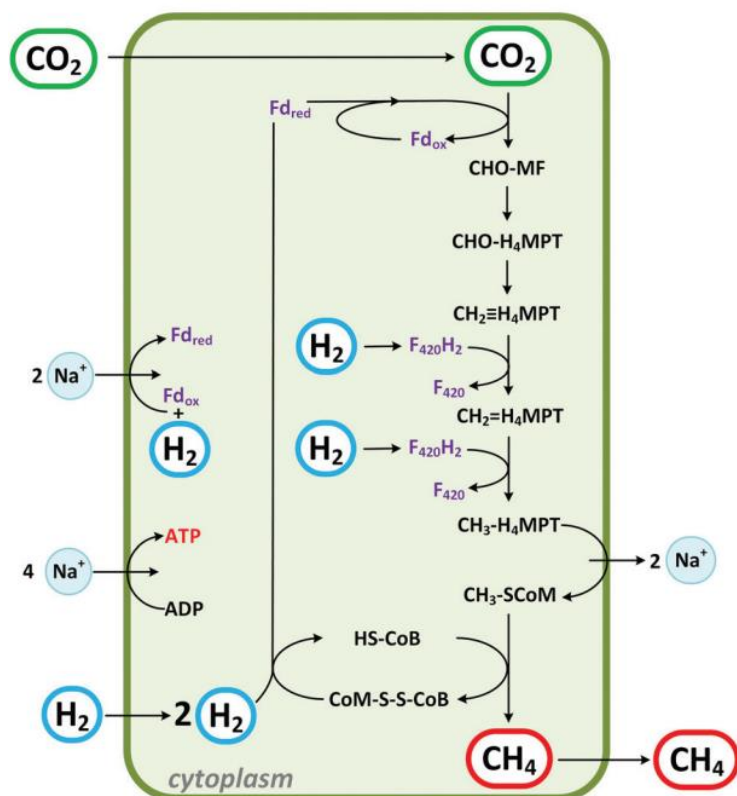


1981

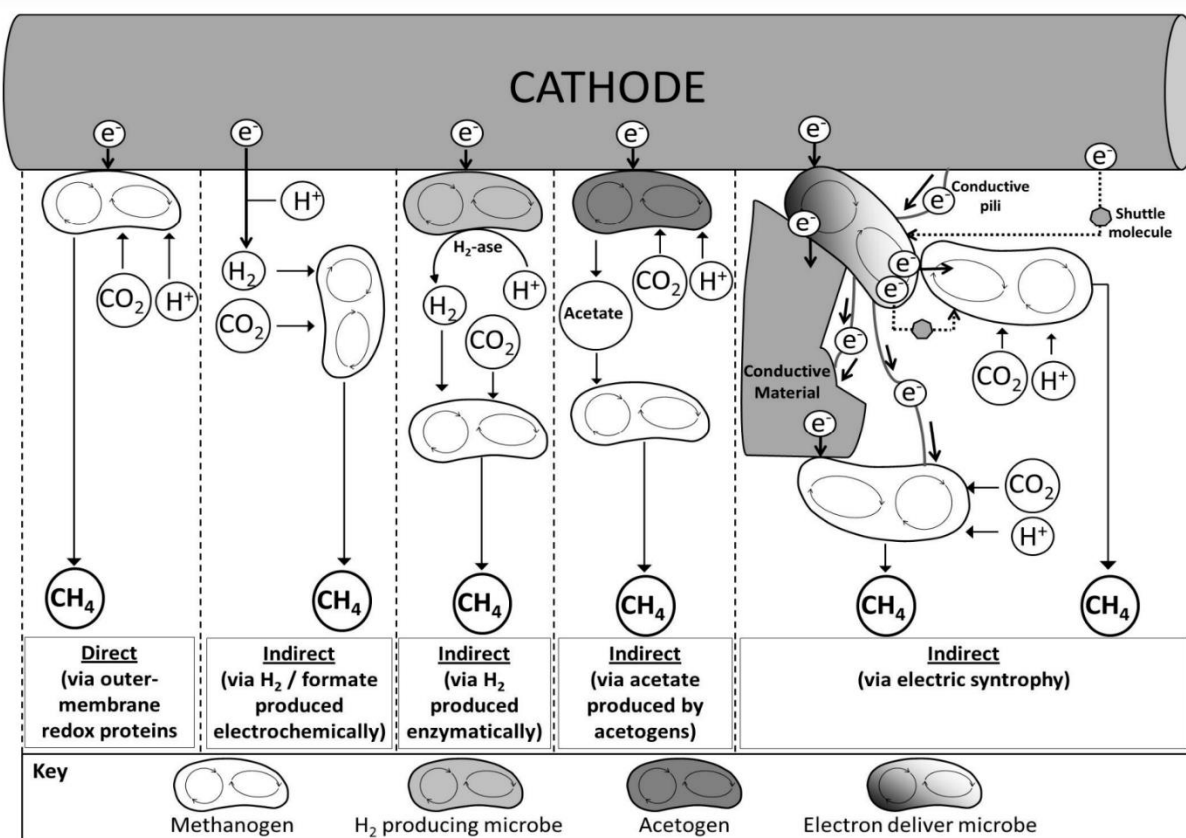
1982 **Figure 3.** An illustration of possible MES anodic reactions; (a) water electrolysis; (b) chlorine  
1983 formation; (c) bisulfide decomposition; and (d) ammonium oxidation (Created with  
1984 BioRender.com).



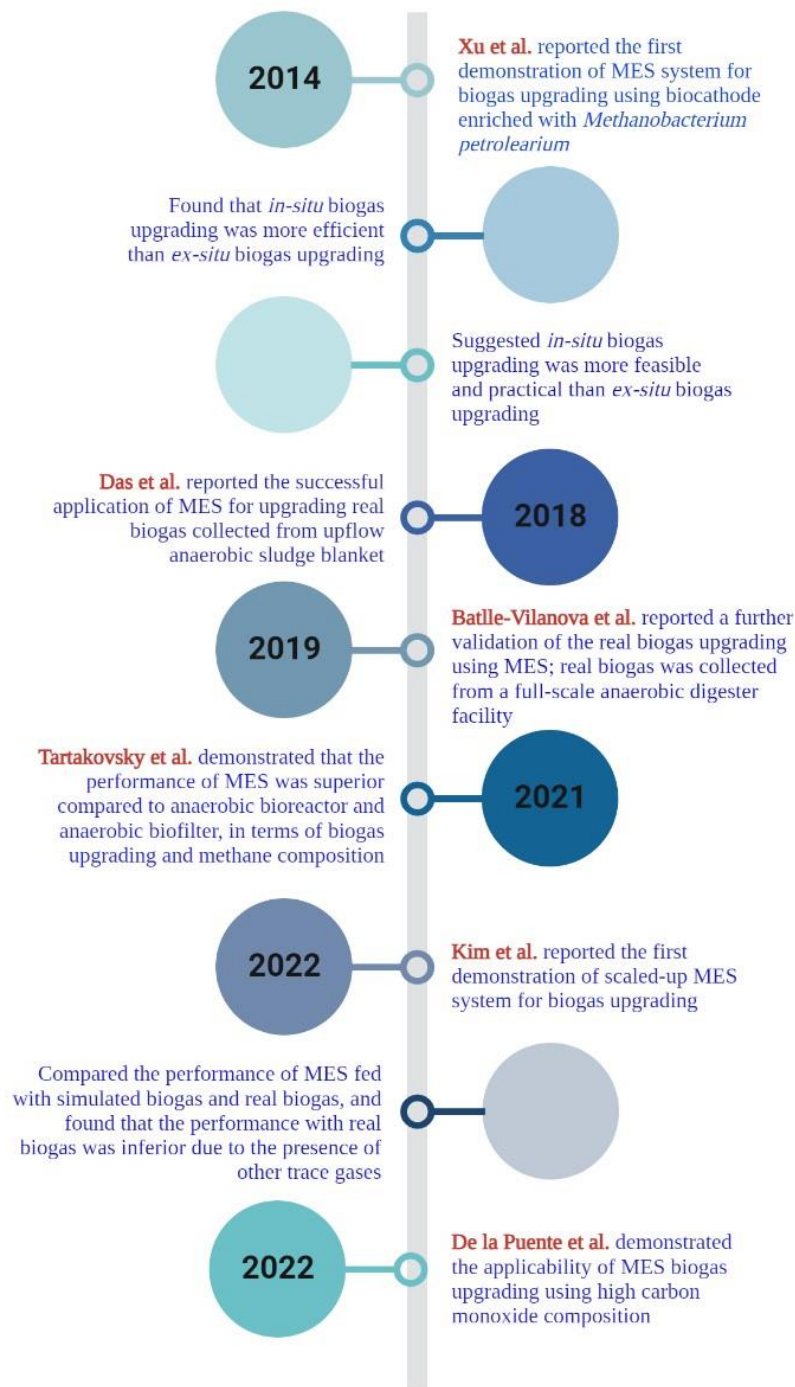
**Figure 4.** Illustrated electro-methanogenesis pathways in mixed culture biocathodes: 1. Direct electro-methanogenesis, 2. Abiotic  $H_2$  production, 3. Biotic hydrogen production, 4. Bioelectrochemical acetate production, 5. Bioelectrochemical formate production, 6. Hydrogenotrophic methanogenesis, 7. Mediated acetate production, 8. Acetoclastic methanogenesis, 9. Mediated formate production, and 10. Indirect methane production from formate. The sizes of the circles do not correspond to any specific proportions. AM: Acetoclastic methanogens; EM: Electrotrophic methanogens (includes species capable of performing direct and mediated electro-methanogenesis); HM: Hydrogenotrophic methanogens; HPM: Hydrogen-producing microorganisms; APM: Acetate-producing microorganisms; FPM: Formate-producing microorganisms; SM: Syntrophic microorganisms;  $M_{red}$ : Reduced mediator;  $M_{ox}$ : Oxidized mediator. The figure was taken from Blasco-Gómez et al. (2017) and reprinted with permission from MDPI.



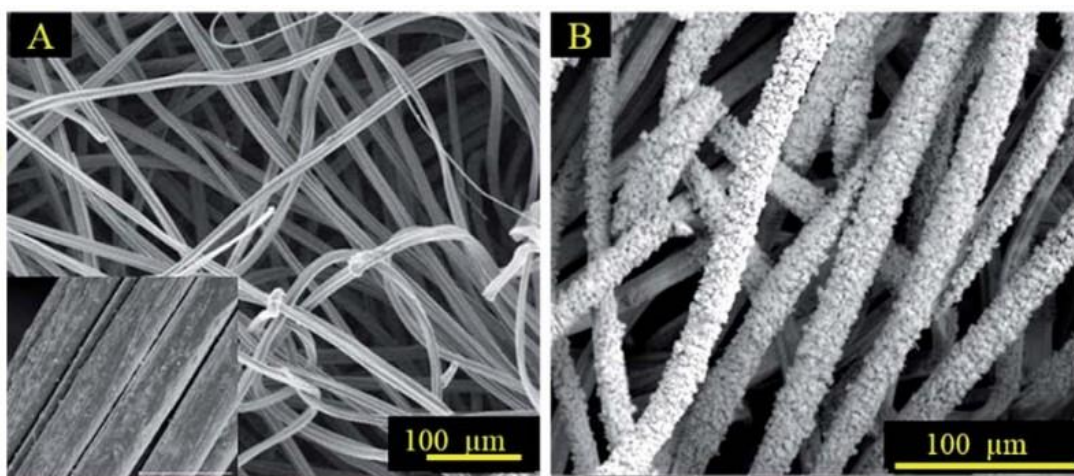
**Figure 5.** Simplified native metabolic pathway of hydrogenotrophic methanogenesis in *M. maripaludis*. The organism conserves energy in the form of adenosine triphosphate (ATP) via a transmembrane sodium gradient. Abbreviations for metabolites in the figure are coenzyme M (CoM), coenzyme B (CoB), coenzyme  $\text{F}_{420}$  ( $\text{F}_{420}$ ), reduced ferredoxin ( $\text{Fd}_{\text{red}}$ ), oxidized ferredoxin ( $\text{Fd}_{\text{ox}}$ ), methanofuran (MF), and methanopterin (MPT). The figure was reproduced from Kracke et al. (2020) with permission from the Royal Society of Chemistry.



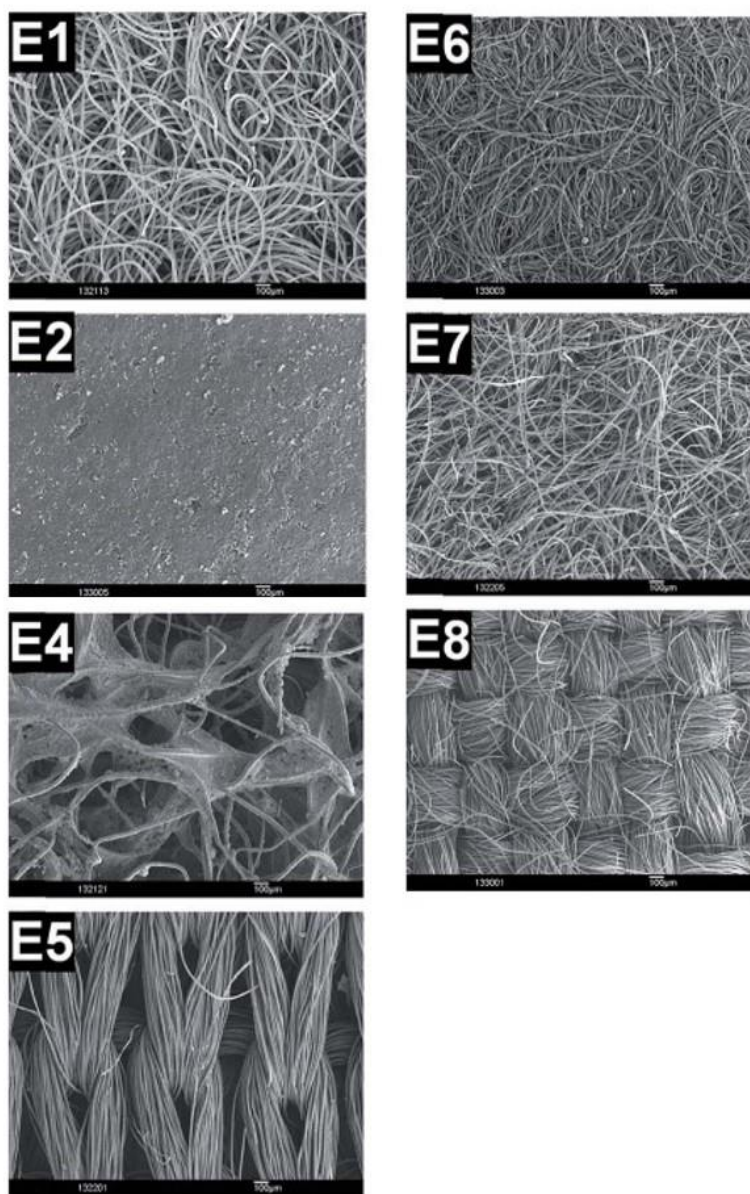
**Figure 6.** Proposed electron transfer mechanisms within the biocathode chamber. Although  $H_2$  is the sole intermediate molecule biologically or electrochemically produced on the electrode surface depicted in the figure, formate and other molecules should also be considered as potential electron carriers. The sizes of the circles do not correspond to any specific proportions. Reprint permission. The figure was taken from Blasco-Gómez et al. (2017) and reprinted with permission from MDPI.



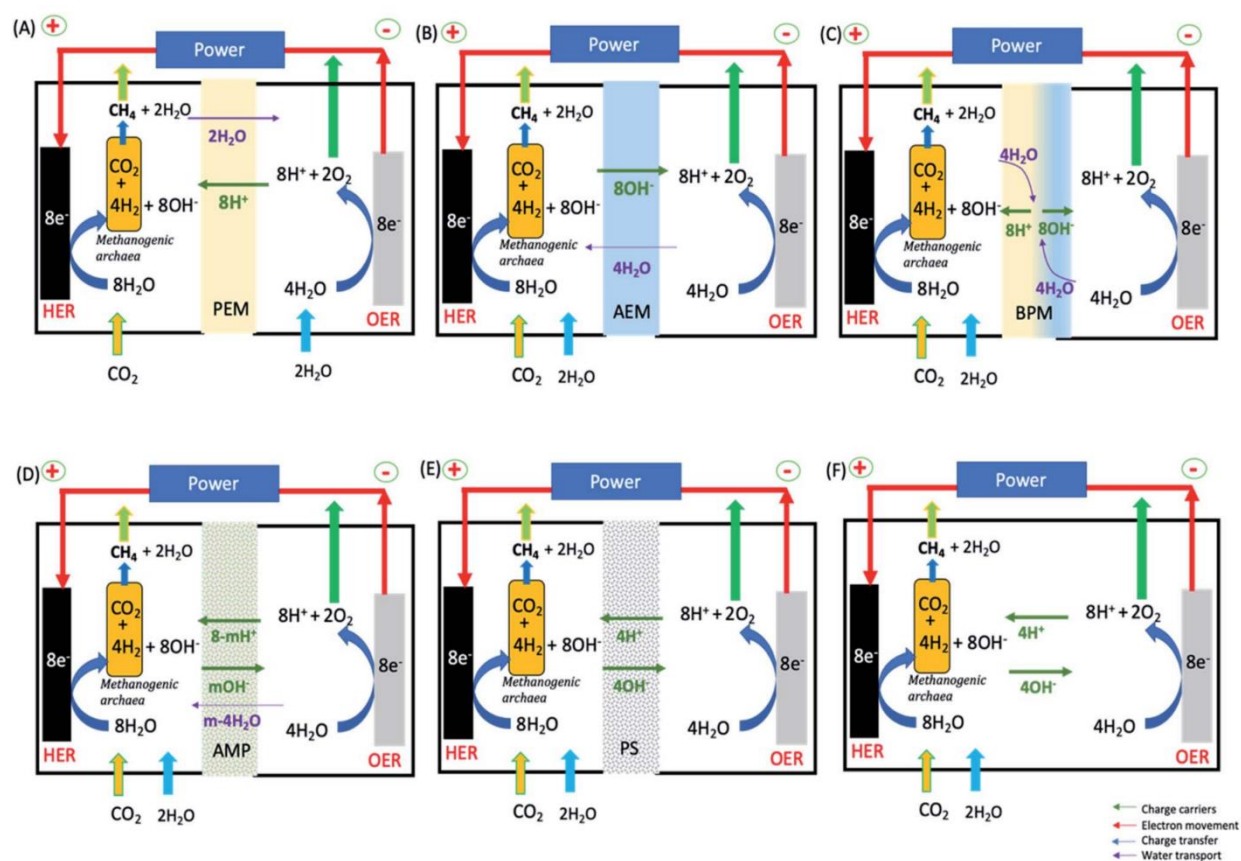
**Figure 7.** Historical overview of major achievements towards biogas upgrading application in MES.



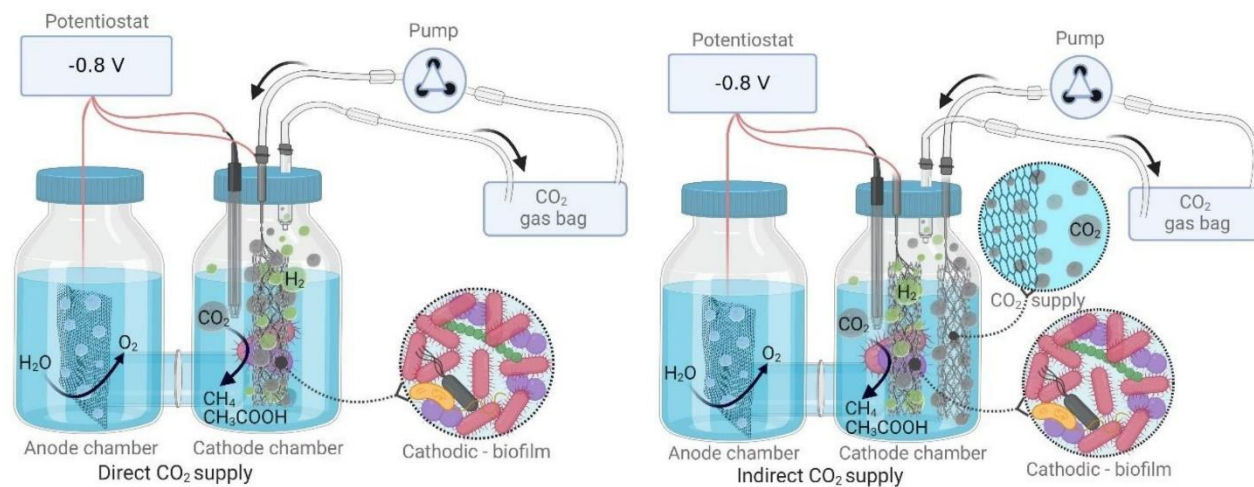
**Figure 8.** Scanning electron microscope images of (a) untreated carbon fibers, and (b) carbon fibers with the deposition of the hybrid layer of carbon and iron oxide. The figure was reproduced from Cui et al. (2017) with permission from Royal Society of Chemistry.



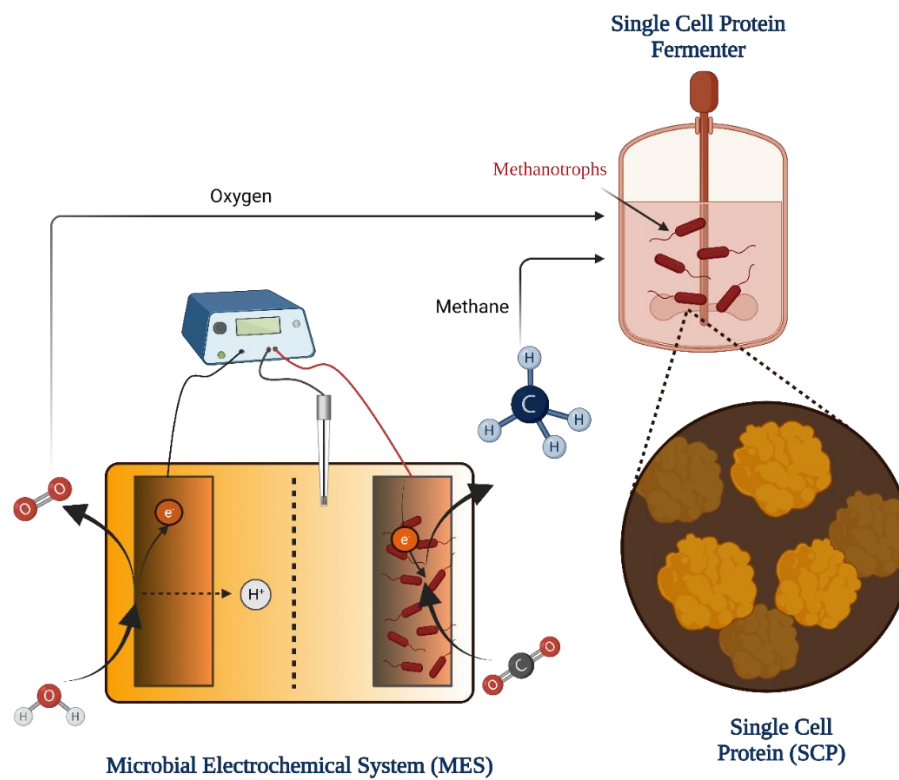
**Figure 9.** Scanning electron microscope images of (E1) glass wool filter; (E2) activated carbon-based VITO CORE™; (E4) activated carbon fleece; (E5) activated carbon fabric; (E6) carbon paper; (E7) carbon felt; and (E8) paxitech. This was the first study comparing several commercial and VITO CORE™ electrodes for MES. The figure was reproduced from Sharma et al. (2019) with permission from Royal Society of Chemistry.



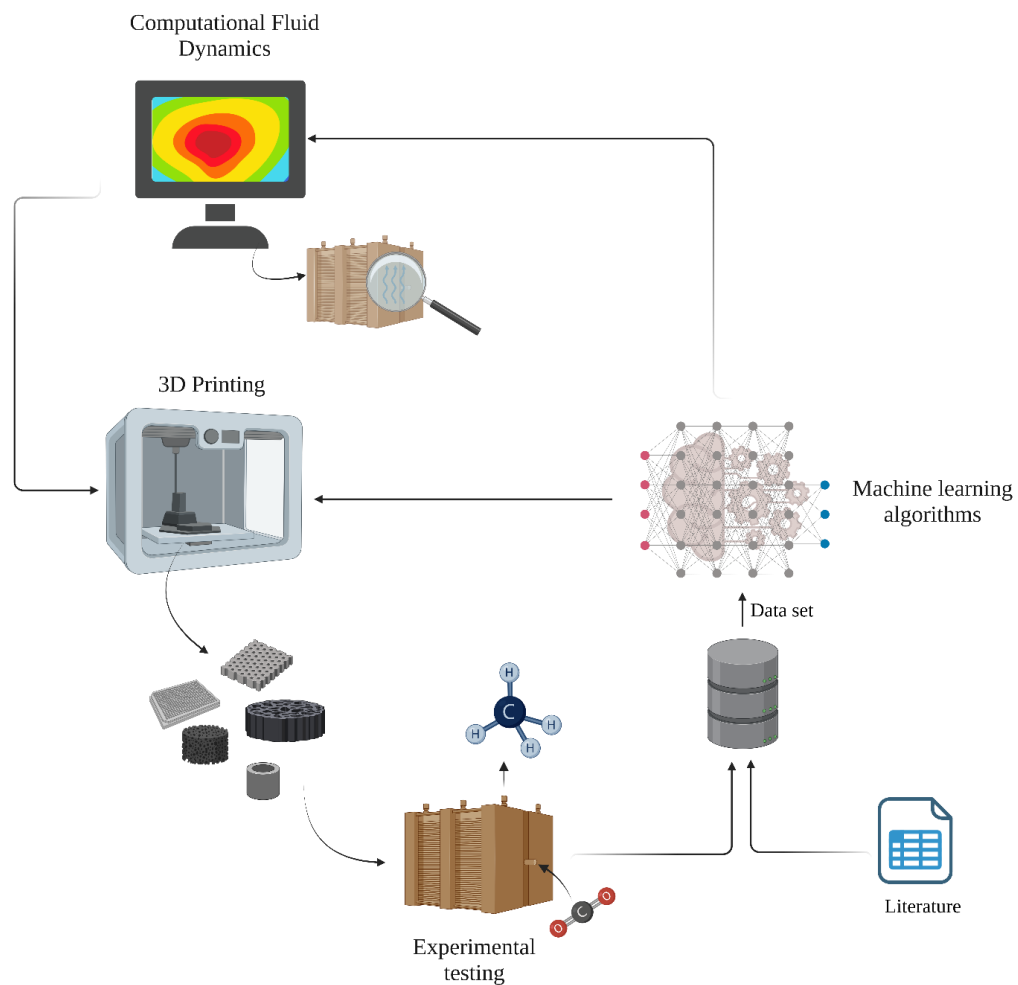
**Figure 10.** MES configurations featuring various membranes and separators. The diagrams are not to scale. The configurations include: (a) proton exchange membrane (PEM); (b) anion exchange membrane (AEM); (c) bipolar membrane (BPM); (d) amphoteric membrane (AMP); (e) porous separator (POS); and (f) membrane-less system. Membrane selection and design focus on ensuring fast ion transport and preventing oxygen permeability. Sustainable operation requires careful water input management and engineering of water movement across ion-selective membranes. While the diagrams show gaps between electrodes and separators to illustrate chemical and electrochemical conversions and ion/molecule transport, actual systems typically have little to no gap. The figure was reproduced from Jayatilake et al. (2022) with permission from the Royal Society of Chemistry.



**Figure 11.** Direct CO<sub>2</sub> delivery to microbes through pores of biocathode (left) and indirect CO<sub>2</sub> sparging through an electrically insulated ceramic hollow tube (right). The figure was taken from Bian et al. (2021) and reprinted with permission from Elsevier.



**Figure 12.** Two-stage MES-methanotrophic hybrid system for single-cell protein production using  $CO_2$  and generated  $CH_4$  as substrates (Created with BioRender.com).



**Figure 13.** Incorporating METs with emerging manufacturing and computational tools, such as computation fluid dynamics, machine learning, and 3D printing (Created with BioRender.com).

**Table 1.** A summary table containing up-to-date MES applications on CH<sub>4</sub> production and biogas upgrading.

| Anode electrode                                 | Anolyte condition                                               | Cathode electrode                         | Catholyte condition                                                                 | Inoculum                                                                                                                       | Temp.  | Applied energy on the cathode | Chamber type                     | Selection of inorganic carbon                    | CO <sub>2</sub> feed rate                                                             | Methanogens/electrotrophs                                         | Target application                                                                   | Productivity / cathodic electron efficiency (CEE)                                                            | Ref.                           |
|-------------------------------------------------|-----------------------------------------------------------------|-------------------------------------------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------|--------|-------------------------------|----------------------------------|--------------------------------------------------|---------------------------------------------------------------------------------------|-------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|--------------------------------|
| Graphite                                        | Anaerobic medium without vitamin                                | Graphite                                  | 0.2 L (in-situ) and 0.8 L (ex-situ); Anaerobic medium containing buffer and vitamin | Crushed anaerobic granular sludge                                                                                              | 37°C   | 0.7 V vs. SHE                 | Dual; Separated by CEM           | Digester biogas (CO <sub>2</sub> content ~48%)   | Batch mode for in-situ biogas upgrading, Continuous mode for ex-situ biogas upgrading | Dominated by <i>Methanobacterium petrolearium</i>                 | Biogas upgrading (Lowering of CO <sub>2</sub> content)                               | Under both in-situ and ex-situ mode, the upgraded biogas achieved a CO <sub>2</sub> content of less than 15% | (Xu et al., 2014)              |
| Platinum sheet laser-welded to a Titanium plate | 16 mL;                                                          | Graphite felt with stainless steel mesh   | 16 mL; pH = 6.5 – 7.5; Phosphate buffer solution                                    | anaerobic culture of carboxydophilic actinomycete <i>Streptomyces thermospinisporus</i> DSM 41779 mixed with wastewater sludge | *NR    | -1.1 V vs. Ag/AgCl            | Dual; Separated by CEM           | 5% w/v sodium bicarbonate                        | 10-30 mL per cycle                                                                    | *NR                                                               | CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production)     | Up to 10% (v/v) in the first batch                                                                           | (Bajracharya et al., 2015)     |
| Graphite rod                                    | 350 mL;                                                         | Graphite rod                              | 350 mL; anoxic artificial seawater                                                  | Cultures of the marine lithoautotrophic <i>Methanobacterium</i> -like archaeon strain IM1                                      | 21°C   | -0.4 V vs. SHE                | Dual; Separated by a salt bridge | CO <sub>2</sub> /N <sub>2</sub> (v/v, 10/90) gas | 10 mL/min                                                                             | Pure culture of <i>Methanobacterium</i> -like archaeon strain IM1 | CH <sub>4</sub> production                                                           | 350 nmol/h/cm <sup>2</sup>                                                                                   | (Beese-Vasbender et al., 2015) |
| Titanium mesh                                   | 110 mL; pH = 6.8; Modified <i>Methanosarcina barkeri</i> medium | Carbon cloth                              | 110 mL; pH = 6.8; Modified <i>Methanosarcina barkeri</i> medium                     | Rice paddy soil inoculated MES effluent                                                                                        | *NR    | -0.7 V vs. Ag/AgCl            | Dual; Separated by CEM           | CO <sub>2</sub> /N <sub>2</sub> (v/v, 20/80) gas | *NR                                                                                   | Dominated by <i>Methanobacteriales</i>                            | CH <sub>4</sub> production                                                           | *Exact value NR; see figures in the literature                                                               | (Babanova et al., 2016)        |
| Conductive graphite bars                        | 150 mL;                                                         | Conductive graphite bars                  | 150 mL;                                                                             | Artificial seawater medium containing <i>A. woodii</i> (DSM 1030) and <i>M. maripaludis</i> strain MM901                       | 30°C   | -0.5 V vs. SHE                | Dual; Separated by CEM           | CO <sub>2</sub> /N <sub>2</sub> (v/v, 20/80) gas | *NR                                                                                   | Co-culture of strain IS4 and <i>M. maripaludis</i>                | CH <sub>4</sub> production                                                           | 0.6 – 0.9 µmol/cm <sup>2</sup> /h                                                                            | (Deutzmann and Spormann, 2017) |
| Platinum/iridium-coated titanium plates         | 120 mL; pH = 7.5; Phosphate buffer                              | Stainless steel plate with graphite paper | 180 mL; pH = 5.5; MilliQ water containing vitamin solution and trace metal solution | A mixture of activated sludge from an anaerobic digester and cow manure                                                        | 32±1°C | -0.9 V vs. Ag/AgCl            | Dual; Separated by CEM           | CO <sub>2</sub> gas                              | 80 mL/min                                                                             | *NR                                                               | CH <sub>4</sub> production; however, the target production was acetate in this study | *Exact value NR; see figures in the literature (Partial pressure of CO <sub>2</sub> reduced                  | (Molenaar et al., 2017)        |

|                                                                     |                                                |                                           |                                                                        |                                                           |        |                                                         |                                        |                                                                                                           |                                    |                                                                    |                                                                                                    |                                                                                                                                      |                                |
|---------------------------------------------------------------------|------------------------------------------------|-------------------------------------------|------------------------------------------------------------------------|-----------------------------------------------------------|--------|---------------------------------------------------------|----------------------------------------|-----------------------------------------------------------------------------------------------------------|------------------------------------|--------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------|--------------------------------|
|                                                                     |                                                |                                           |                                                                        |                                                           |        |                                                         |                                        |                                                                                                           |                                    |                                                                    |                                                                                                    | from 85% to 5-10%)                                                                                                                   |                                |
| Nickel foam                                                         | 25 mL; pH = 5.2; Phosphate buffer solution     | Graphite felt                             | 25 mL; pH = 5.2; Phosphate buffer solution                             | 5 mL mixed anaerobic sludge                               | 27±5°C | -0.7 V vs. SHE                                          | Dual; Separated by CEM                 | Biogas from the UASB reactor                                                                              | 3 L/d                              | *NR                                                                | Biogas upgrading, CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production) | *Exact value NR; see figures in the literature                                                                                       | (Das et al., 2018)             |
| Carbon felt with titanium wire                                      | 600 mL; Phosphate buffer solution              | Carbon felt with titanium wire            | 600 mL; pH = 6.8; Buffer solution containing vitamins and minerals     | Anaerobic sludge supernatant                              | 50°C   | -0.9 V vs. Ag/AgCl                                      | Dual; Separated by CEM                 | 5 g/L of sodium bicarbonate                                                                               | Fresh medium per batch cycle       | Dominated by <i>Methanobacterium</i>                               | CH <sub>4</sub> production                                                                         | 0.094 mmol/h (CE = 19 – 74%)                                                                                                         | (Yan g et al., 2018 a)         |
| Ti-MMO with titanium wire                                           | 0.5 L; NaCl solution;                          | Graphite granules                         | 0.3 L;                                                                 | A mixed culture dominated by <i>Methanobacterium</i> spp. | 25±1°C | -0.8 V vs. SHE                                          | Dual; Separated by CEM                 | Biogas (65% CH <sub>4</sub> , 35% CO <sub>2</sub> )                                                       | 60 mL/h                            | Dominated by <i>Methanobacterium</i> spp.                          | Biogas upgrading                                                                                   | *NR (see figures in the literature)                                                                                                  | (Batlle-Vilanova et al., 2019) |
| Iridium-oxide coated titanium mesh; layers of spacer cloth material | 85 cm <sup>3</sup> ; Phosphate buffer solution | Double-layered graphite felt              | 3 L; Phosphate buffer solution containing vitamins and minerals        | Seed from a biogas plant                                  | 30°C   | 5 – 35 A/m <sup>2</sup> (-0.76 to -1.08 V vs. SHE)      | Dual; Separated by CEM                 | Bicarbonate (5 g/L)                                                                                       | Fresh medium (2 L) per cycle       | Dominated by <i>Methanobacteriaceae</i> and <i>Methanomicrobia</i> | CH <sub>4</sub> production                                                                         | Highest CH <sub>4</sub> yield rate = 12.5 L <sub>CH4</sub> /L/d (Current-to-CH <sub>4</sub> efficiency = 64%) at 35 A/m <sup>2</sup> | (Gepert et al., 2019)          |
| Ti/IrO <sub>2</sub> mesh                                            | 325 mL;                                        | Carbon felt with Ti/IrO <sub>2</sub> mesh | 650 mL;                                                                | Anaerobic sludge                                          | 30°C   | 2.6 – 2.8 V (-0.9 to -0.7 V vs. NHE)                    | Dual; Separated by PEM and nylon cloth | CO <sub>2</sub> gas (99.99%)                                                                              | 50 mL/d                            | *NR                                                                | CH <sub>4</sub> production                                                                         | 0.72 L/d (CO <sub>2</sub> level below detection limit)                                                                               | (Vidales et al., 2019)         |
| Platinized titanium mesh                                            | 150 mL; Mixture of buffer and growth medium    | Transition-metal-based cathodes (NiMo)    | 150 mL; Mixture of buffer and growth medium                            | <i>M. maripaludis</i> (wild-type strain MM901)            | 30°C   | -1.0 V vs. SHE                                          | Dual; Separated by PEM                 | Cathode medium containing bicarbonate buffer purged with CO <sub>2</sub> /N <sub>2</sub> gas (v/v, 20/80) | Fresh cathode medium per batch     | <i>M. maripaludis</i> (wild-type strain MM901)                     | CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production)                   | *NR (see figures in the literature)                                                                                                  | (Kracke et al., 2019)          |
| Carbon cloth with titanium wire                                     | 360 mL; Buffer solution                        | Carbon cloth with titanium wire           | 360 mL; Buffer solution                                                | MES effluent                                              | 30±1°C | -0.7 V vs. SHE (Polarity reversal after -0.2 V vs. SHE) | Dual; Separated by CEM                 | CO <sub>2</sub> gas (99.999%) with 1mL He as an inert internal standard                                   | Gauge pressure of 8 kPa for 15 min | *NR                                                                | CH <sub>4</sub> production                                                                         | 61 mmol/m <sup>2</sup> /d (*NR)                                                                                                      | (Li et al., 2019)              |
| Graphite rods with titanium wire                                    | 550 mL;                                        | Graphite rods with titanium wire          | 550 mL; Buffer solution containing trace elements and vitamin solution | <i>M. mazei</i>                                           | *NR    | -0.7 V vs. SHE                                          | Dual; Separated by PEM                 | Cathode medium containing 5 g/L bicarbonate buffer purged with CO <sub>2</sub> /N <sub>2</sub> gas        | Sparged for 30 min                 | <i>M. mazei</i>                                                    | CH <sub>4</sub> production                                                                         | 0.14 mmol/m <sup>2</sup> /d                                                                                                          | (Mayer et al., 2019)           |

|                                  |                                  |                                  |                                                                        |                           |      |                 |                        |                                                                                                                 |                                                                |                       |                                                    |                                          |                                   |
|----------------------------------|----------------------------------|----------------------------------|------------------------------------------------------------------------|---------------------------|------|-----------------|------------------------|-----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------|-----------------------|----------------------------------------------------|------------------------------------------|-----------------------------------|
| Graphite rods with titanium wire | 550 mL;                          | Graphite rods with titanium wire | 550 mL; Buffer solution containing trace elements and vitamin solution | <i>M. congolense</i>      | *NR  | -0.7 V vs. SHE  | Dual; Separated by PEM | Cathode medium containing 5 g/L bicarbonate buffer purged with CO <sub>2</sub> /N <sub>2</sub> gas (v/v, 20/80) | Sparged for 30 min                                             | <i>M. congolense</i>  | CH <sub>4</sub> production                         | 4.12 mmol/m <sup>2</sup> /d (CE = 51.3%) | (Mayer et al., 2019)              |
| Graphite rods with titanium wire | 550 mL;                          | Graphite rods with titanium wire | 550 mL; Buffer solution containing trace elements and vitamin solution | <i>M. submarinus</i>      | *NR  | -0.7 V vs. SHE  | Dual; Separated by PEM | Cathode medium containing 5 g/L bicarbonate buffer purged with CO <sub>2</sub> /N <sub>2</sub> gas (v/v, 20/80) | Sparged for 30 min                                             | <i>M. submarinus</i>  | CH <sub>4</sub> production                         | 7.90 mmol/m <sup>2</sup> /d (CE = 45.3%) | (Mayer et al., 2019)              |
| Graphite rods with titanium wire | 550 mL;                          | Graphite rods with titanium wire | 550 mL; Buffer solution containing trace elements and vitamin solution | <i>M. petrolearia</i>     | *NR  | -0.7 V vs. SHE  | Dual; Separated by PEM | Cathode medium containing 5 g/L bicarbonate buffer purged with CO <sub>2</sub> /N <sub>2</sub> gas (v/v, 20/80) | Sparged for 30 min                                             | <i>M. petrolearia</i> | CH <sub>4</sub> production                         | 7.49 mmol/m <sup>2</sup> /d (CE = 56.6%) | (Mayer et al., 2019)              |
| Graphite rods with titanium wire | 550 mL;                          | Graphite rods with titanium wire | 550 mL; Buffer solution containing trace elements and vitamin solution | <i>M. vanniellii</i>      | *NR  | -0.7 V vs. SHE  | Dual; Separated by PEM | Cathode medium containing 5 g/L bicarbonate buffer purged with CO <sub>2</sub> /N <sub>2</sub> gas (v/v, 20/80) | Sparged for 30 min                                             | <i>M. vanniellii</i>  | CH <sub>4</sub> production                         | 8.76 mmol/m <sup>2</sup> /d (CE = 55.4%) | (Mayer et al., 2019)              |
| Graphite rods with titanium wire | 550 mL;                          | Graphite rods with titanium wire | 550 mL; Buffer solution containing trace elements and vitamin solution | <i>M. maripaludis</i>     | *NR  | -0.7 V vs. SHE  | Dual; Separated by PEM | Cathode medium containing 5 g/L bicarbonate buffer purged with CO <sub>2</sub> /N <sub>2</sub> gas (v/v, 20/80) | Sparged for 30 min                                             | <i>M. maripaludis</i> | CH <sub>4</sub> production                         | 8.81 mmol/m <sup>2</sup> /d (CE = 58.9%) | (Mayer et al., 2019)              |
| Graphite rod                     | 135 mL; pH = 7.8<br>Reject water | Carbon felt with titanium wire   | 135 mL; pH = 7.8; Rejected water                                       | Digested anaerobic sludge | 35°C | -0.65 V vs. SHE | Single                 | Reject wastewater containing COD and CO <sub>2</sub>                                                            | Operated continuously with a hydraulic retention time of 1-day | *NR                   | CH <sub>4</sub> production                         | 6.1 mmol/L/d                             | (Nela bhotla and Dinamarca, 2019) |
| Iridium- and ruthenium-coated    | 120 mL; Phosphate buffer         | Carbon felt                      | 120 mL; Phosphate buffer                                               | *NR                       | *NR  | *NR             | Dual; Separated by CEM | Bicarbonate                                                                                                     | *NR                                                            | *NR                   | Inhibition of electron recovery to CH <sub>4</sub> | Electron recovery to                     | (Chuet al.,                       |

|                                     |                                                                                 |                                  |                                                                                 |                                                 |     |                            |                        |                                                                                                                  |                                       |                                                                                                                                                                 |                                     |                                                                           |                       |
|-------------------------------------|---------------------------------------------------------------------------------|----------------------------------|---------------------------------------------------------------------------------|-------------------------------------------------|-----|----------------------------|------------------------|------------------------------------------------------------------------------------------------------------------|---------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------|---------------------------------------------------------------------------|-----------------------|
| titanium mesh                       |                                                                                 |                                  |                                                                                 |                                                 |     |                            |                        |                                                                                                                  |                                       |                                                                                                                                                                 | (C4 and C6 carboxylates production) | CH <sub>4</sub> (67.39% to 36.19%)                                        | 2020 b)               |
| Platinized titanium mesh            | 100 mL; Medium-JD containing various salts and supplements (see the literature) | NiMo-plated graphite rods        | 100 mL; Medium-JD containing various salts and supplements (see the literature) | <i>Methanococcus maripaludis</i> (strain MM901) | *NR | -50 mA Constant current    | Dual; Separated by PEM | 100% CO <sub>2</sub> , H <sub>2</sub> /CO <sub>2</sub> (v/v, 80,20), H <sub>2</sub> /CO <sub>2</sub> (v/v 75,25) | 0.14 mL/min – 0.49 mL/min             | <i>Methanococcus maripaludis</i> (strain MM901)                                                                                                                 | CH <sub>4</sub> production          | 1.4 L <sub>CH4</sub> /L/d (CE = >90%)                                     | (Kracke et al., 2020) |
| *NR                                 | *NR                                                                             | *NR                              | Bicarbonate buffer                                                              | MES effluent                                    | *NR | -1.0 V vs. Ag/AgCl         | *NR                    | CO <sub>2</sub> gas and bicarbonate                                                                              | *NR                                   | Dominated by <i>Methanobacteriaceae</i>                                                                                                                         | CH <sub>4</sub> production          | ~80% in the off-gas                                                       | (Mateos et al., 2020) |
| Carbon felt                         | 360 mL; Medium solution                                                         | Carbon cloth                     | 360 mL; Anaerobic medium solution, prepared culture medium                      | MEC effluent                                    | *NR | -0.9 V vs. Ag/AgCl         | Dual; Separated by CEM | Headspace filled with CO <sub>2</sub> gas (99.999%)                                                              | *NR                                   | *NR                                                                                                                                                             | CH <sub>4</sub> production          | 81 mmol/m <sup>2</sup> /d (FE = ~90%; see the figure in the literature)   | (Li et al., 2020 b)   |
| Carbon felt                         | 360 mL; Medium solution                                                         | Carbon cloth with GO             | 360 mL; Anaerobic medium solution, prepared culture medium                      | MEC effluent                                    | *NR | -0.9 V vs. Ag/AgCl         | Dual; Separated by CEM | Headspace filled with CO <sub>2</sub> gas (99.999%)                                                              | *NR                                   | *NR                                                                                                                                                             | CH <sub>4</sub> production          | ~90 mmol/m <sup>2</sup> /d (FE = ~90%; see the figure in the literature)  | (Li et al., 2020 b)   |
| Carbon felt                         | 360 mL; Medium solution                                                         | Carbon cloth with PEDOT          | 360 mL; Anaerobic medium solution, prepared culture medium                      | MEC effluent                                    | *NR | -0.9 V vs. Ag/AgCl         | Dual; Separated by CEM | Headspace filled with CO <sub>2</sub> gas (99.999%)                                                              | *NR                                   | *NR                                                                                                                                                             | CH <sub>4</sub> production          | ~100 mmol/m <sup>2</sup> /d (FE = ~90%; see the figure in the literature) | (Li et al., 2020 b)   |
| Carbon felt                         | 360 mL; Medium solution                                                         | Carbon cloth with GO/PEDOT       | 360 mL; Anaerobic medium solution, prepared culture medium                      | MEC effluent                                    | *NR | -0.9 V vs. Ag/AgCl         | Dual; Separated by CEM | Headspace filled with CO <sub>2</sub> gas (99.999%)                                                              | *NR                                   | *NR                                                                                                                                                             | CH <sub>4</sub> production          | 315.3 mmol/m <sup>2</sup> /d (FE = >92%)                                  | (Li et al., 2020 b)   |
| Carbon cloth with titanium wires    | 360 mL; Medium solution                                                         | Carbon cloth with titanium wires | 360 mL; Medium solution                                                         | MES effluent                                    | *NR | -0.5 to -0.9 V vs. Ag/AgCl | Dual; Separated by CEM | CO <sub>2</sub> /N <sub>2</sub> (v/v, 20/80) gas                                                                 | Gauge pressure of 8 kPa for 30 min    | Dominated by <i>Methanobacteria</i> of the phylum <i>Euryarchaeota</i>                                                                                          | CH <sub>4</sub> production          | *NR (see figures in the literature)                                       | (Li et al., 2020 a)   |
| Titanium plates with titanium wires | 300 mL;                                                                         | Carbon cloth                     | 300 mL;                                                                         | Previously used as a MEC cathode                | *NR | -0.7 vs. Ag/AgCl           | Dual; Separated by CEM | CO <sub>2</sub> gas and sodium bicarbonate                                                                       | Purging CO <sub>2</sub> gas for 5 min | Dominated by hydrogenotrophic <i>Methanobacterium</i> sp. (5 OTUs), <i>Methanobrevibacter</i> sp. (1 OTU) and the mixotrophic <i>Methanosarcina</i> sp. (1 OTU) | CH <sub>4</sub> production          | 0.08 µmol/cm <sup>2</sup>                                                 | (Ragab et al., 2020)  |
| Titanium plates with                | 300 mL;                                                                         | Carbon cloth                     | 300 mL;                                                                         | Previously used as a MEC cathode                | *NR | -1.0 vs. Ag/AgCl           | Dual; Separated by CEM | CO <sub>2</sub> gas and sodium bicarbonate                                                                       | Purging CO <sub>2</sub> gas for 5 min | Dominated by hydrogenotrophic <i>Methanobacterium</i> sp.                                                                                                       | CH <sub>4</sub> production          | 0.10 µmol/cm <sup>2</sup>                                                 | (Ragab et al.,        |

|                                                     |                                     |                                                                          |                                                    |                                  |      |                       |                                                                                     |                                                              |                                                                           |                                                                                                       |                                                                                  |                                                    |                           |
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| titanium wires                                      |                                     |                                                                          |                                                    |                                  |      |                       |                                                                                     |                                                              |                                                                           | (5 OTUs), <i>Methanobrevibacter</i> sp. (1 OTU) and the mixotrophic <i>Methanosarcina</i> sp. (1 OTU) |                                                                                  |                                                    | 2020 )                    |
| *NR                                                 | A solution containing ammonium ions | *NR                                                                      | *NR                                                | *NR                              | *NR  | *NR                   | *NR                                                                                 | Biogas containing CO <sub>2</sub>                            | *NR                                                                       | *NR                                                                                                   | CH <sub>4</sub> production                                                       | *NR                                                | (Sivalinga et al., 2020 ) |
| Ti/IrO <sub>2</sub> mesh and carbon felt            | 250 mL;                             | Carbon felt with stainless steel mesh                                    | 500 mL; Nutrient solution containing Ni salt       | *NR                              | 30°C | 2.8 V                 | Dual; Separated by nylon cloth (anode-cathode exchange area of 96 cm <sup>2</sup> ) | CO <sub>2</sub> gas (99.999%)                                | 500 – 4380 mL/d of CO <sub>2</sub> gas with nutrient solution of 120 mL/d | *NR                                                                                                   | CH <sub>4</sub> production                                                       | 422 mL/d (0.81 L/L/d; CE = 94%)                    | (Vidales et al., 2020 )   |
| Carbon fiber brush with titanium wires              | 300 mL; Medium solution             | Carbon fiber brush with titanium wires                                   | 300 mL; Medium solution                            | MES effluent                     | 30°C | -0.9 V vs. Ag/AgCl    | Dual; Separated by CEM                                                              | Ultrapure CO <sub>2</sub> gas (99.999%), bicarbonate (4 g/L) | Purge for 30 min                                                          | *NR                                                                                                   | CH <sub>4</sub> production                                                       | 213.4 L/m <sup>3</sup> /d (FE = >90%)              | (Xiao et al., 2020 b)     |
| Titanium plates                                     | 300 mL; Artificial seawater         | Carbon cloth                                                             | 300 mL; Mimic Red Sea Water                        | Mangrove sediment                | *NR  | -1.0 V vs. Ag/AgCl    | Dual; Separated by CEM                                                              | 100% CO <sub>2</sub> gas in a gas bag                        | 12 mL/min                                                                 | Dominated by <i>Methanococcus</i>                                                                     | CH <sub>4</sub> production                                                       | 1.5 mmol (*NR)                                     | (Alqahtani et al., 2021 ) |
| Titanium plates                                     | 300 mL; Artificial seawater         | Carbon cloth                                                             | 300 mL; Mimic Red Sea Water                        | Salt marsh sediment              | *NR  | -1.0 V vs. Ag/AgCl    | Dual; Separated by CEM                                                              | 100% CO <sub>2</sub> gas in a gas bag                        | 12 mL/min                                                                 | Dominated by <i>Methanococcus</i>                                                                     | CH <sub>4</sub> production                                                       | 4.9 mmol (*NR)                                     | (Alqahtani et al., 2021 ) |
| Titanium plates                                     | 275 mL;                             | Nickel foam coated with multi-walled carbon nanotubes                    | 275 mL; A solution containing minerals and vitamin | Anaerobic sludge                 | 30°C | -0.8 V vs. Ag/AgCl    | Dual; Separated by CEM                                                              | CO <sub>2</sub> gas (bicarbonate used for startup)           | 0.3 – 10 mL/min                                                           | Dominated by <i>Methanobacterium</i> (and <i>Acetobacterium</i> )                                     | CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production) | 240 mmol/m <sup>2</sup> /d (CE = >90%)             | (Bian et al., 2021 )      |
| Platinized titanium mesh                            | 100 mL;                             | Carbon aerogel cathode coated with NiMo-alloy fabricated via 3D printing | 100 mL;                                            | <i>Methanococcus maripaludis</i> | 30°C | 50 – 80 mA            | Dual; Separated by PEM                                                              | 100% CO <sub>2</sub> gas                                     | 0.15 mL/min                                                               | Dominated by <i>Methanococcus maripaludis</i>                                                         | CH <sub>4</sub> production                                                       | 2.2 L/L/d (CE = 99%)                               | (Kracke et al., 2021 )    |
| Ti/IrO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub> | 13 mL; Phosphate buffer solution    | Nickel foam                                                              | 13 mL; Phosphate buffer solution                   | MEC effluent                     | 30°C | -0.9 V vs. Ag/AgCl    | Dual; Separated by CEM                                                              | 99.999% CO <sub>2</sub> gas                                  | Sparged for 2 h before the start of each batch                            | Dominated by <i>Methanocalculus</i>                                                                   | CH <sub>4</sub> production                                                       | 0.08 m <sup>3</sup> /m <sup>3</sup> /d (CE = <40%) | (Mao et al., 2021 )       |
| Ti/IrO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub> | 13 mL;                              | Nickel foam                                                              | 13 mL; Phosphate buffer solution                   | MEC effluent                     | 30°C | 2.14 A/m <sup>2</sup> | Dual; Separated by CEM                                                              | 99.999% CO <sub>2</sub> gas                                  | Sparged for 2 h before the                                                | Dominated by <i>Methanobacterium</i> and <i>Methanocalculus</i>                                       | CH <sub>4</sub> production                                                       | 0.10 m <sup>3</sup> /m <sup>3</sup> /d (CE = <40%) | (Mao et al.,              |

|                                                         |                                                                          |                                                                             |                                                                          |                                                                           |      |                                        |                                                                     |                                                                                       |                                                           |                                                                                                        |                                                                                               |                                                                       |                            |
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|                                                         | Phosphate buffer solution                                                |                                                                             |                                                                          |                                                                           |      |                                        |                                                                     |                                                                                       | start of each batch                                       |                                                                                                        |                                                                                               |                                                                       | 2021)                      |
| Ti/IrO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub>     | 13 mL; Phosphate buffer solution                                         | Nickel foam                                                                 | 13 mL; Phosphate buffer solution                                         | MEC effluent                                                              | 30°C | 1.98 V                                 | Dual; Separated by CEM                                              | 99.999% CO <sub>2</sub> gas                                                           | Sparged for 2 h before the start of each batch            | Dominated by <i>Methanocalculus</i> (The highest abundance of <i>M. taiwanensis</i> )                  | CH <sub>4</sub> production                                                                    | 0.27 m <sup>3</sup> /m <sup>3</sup> /d (CE = 93%)                     | (Mao et al., 2021)         |
| Carbon brush                                            | 350 mL; Phosphate buffer solution containing minerals and trace elements | Carbon brush                                                                | 350 mL; Phosphate buffer solution containing minerals and trace elements | *NR                                                                       | 33°C | 1.0 V                                  | Single chamber                                                      | 99.9% CO <sub>2</sub> gas                                                             | 5 mL/min                                                  | *NR                                                                                                    | CH <sub>4</sub> production                                                                    | *NR (see figures in the literature)                                   | (Reddy et al., 2021)       |
| IrO <sub>2</sub> -covered titanium meshes               | 250 mL; Nutrient solution                                                | Carbon felt pieces hooked up with IrO <sub>2</sub> -covered titanium meshes | 500 mL; Nutrient solution                                                | *NR                                                                       | *NR  | 100 – 250 mA (equivalent to 2.5-4.5 V) | Dual; Separated by nylon cloth (membraneless)                       | Synthetic biogas (35% CO <sub>2</sub> , 60% CH <sub>4</sub> , and 5% N <sub>2</sub> ) | 50 mL/d liquid recirculation purged with synthetic biogas | *NR                                                                                                    | Biogas upgrading                                                                              | 92% CH <sub>4</sub> purity with max. CO <sub>2</sub> removal of 98.1% | (Tartakovsky et al., 2021) |
| Ti/IrO <sub>2</sub> mesh and carbon felt                | 325 mL;                                                                  | Stainless steel mesh and carbon felt                                        | 625 mL; A nutrient solution containing nickel                            | *NR                                                                       | 30°C | -0.7 V vs. SHE                         | Dual; Separated by nylon cloth                                      | CO <sub>2</sub> gas (plus bicarbonate initially)                                      | 500 – 4380 mL/d                                           | Dominated by <i>Methanosaeta</i> , <i>Methanobrevibacter</i> , and <i>Methanobacterium</i>             | CH <sub>4</sub> production (Simultaneous volatile fatty acids and CH <sub>4</sub> production) | 0.83 L/L/d                                                            | (Vidales et al., 2021)     |
| Titanium mesh                                           | *NR                                                                      | Ni-coated ceramic hollow fiber cathode                                      | *NR                                                                      | Anaerobic sludge from continuous stirred-tank reactor                     | 30°C | -1.1 V vs Ag/AgCl                      | Dual; Separated by CEM                                              | 100% CO <sub>2</sub> gas                                                              | 1 mL/min                                                  | Not applicable since the study focused on acetate production                                           | CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production)              | 6.9 mmol per batch cycle (CE = 25.4%)                                 | (Bian et al., 2022)        |
| Carbon cloth coated with Pt/C, platinized titanium felt | 4.5 mL; DI water                                                         | Carbon felt                                                                 | 4.5 mL;                                                                  | MFC effluent (50% v/v with medium) and anaerobic digester sludge (1% v/v) | 30°C | 3.1 V                                  | Dual; Separated by CEM                                              | Medium purged with mixed gas (80% N <sub>2</sub> , 20% CO <sub>2</sub> ).             | 2.5 mL/min                                                | Dominated by <i>Methanobrevibacter</i> , <i>Clostridium sensu stricto 1</i>                            | CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production)              | 2.9 L/L/d (CH <sub>4</sub> ), 940 mmol/m <sup>2</sup> -d (acetate)    | (Bae et al., 2022)         |
| IrO <sub>2</sub> -coated Ti mesh                        | 1 L; Phosphate buffer solution                                           | Stainless steel perforated mesh                                             | 4.5 L; Modified M9 medium with NaOH as pH control                        | Glucose-fed MEC effluent                                                  | 37°C | 1 A                                    | Moving bed biofilm reactor-based MES dual chamber; Separated by CEM | CO <sub>2</sub> gas                                                                   | 2 L/h                                                     | Dominated by <i>Methanobrevibacter</i>                                                                 | CH <sub>4</sub> production                                                                    | 0.57 L/L/d (CE = 96.5%; Energy efficiency = 43.4%)                    | (Cai et al., 2022)         |
| IrO <sub>2</sub> -coated Ti mesh                        | 1 L; Phosphate buffer solution                                           | Stainless steel perforated mesh                                             | 4.5 L; Modified M9 medium with NaOH as pH control                        | Glucose-fed MEC effluent                                                  | 37°C | 5 A                                    | Moving bed biofilm reactor-based MES dual chamber; Separated by CEM | CO <sub>2</sub> gas                                                                   | 2 L/h                                                     | Dominated by <i>Methanobrevibacter</i>                                                                 | CH <sub>4</sub> production                                                                    | 1.42 L/L/d (CE = 45.7%; Energy efficiency = 29.7%)                    | (Cai et al., 2022)         |
| Platinum powder coated carbon cloth                     | 70 mL; Medium containing buffer, trace                                   | Carbon cloth                                                                | 70 mL; Medium containing buffer, trace metals, and HS <sup>-</sup>       | Anaerobic sludge from upflow sludge blanket                               | 30°C | 0.1-0.8 V                              | Dual; Separated by CEM                                              | 200 mg/L sodium bicarbonate                                                           | Fresh medium per batch cycle                              | Methanogen strain dominated by <i>Methanosaeta</i> , <i>Methanobacterium</i> , and <i>Methanolinea</i> | CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production)              | *NR (see figures in the literature)                                   | (Dinh et al., 2022)        |

|                                    |                                                           |                                                                          |                                                                        |                                                  |      |                    |                        |                                                                                                                                                    |                                |                                                  |                                              |                                                                                                                |                             |
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|                                    | metals, and HS                                            |                                                                          |                                                                        |                                                  |      |                    |                        |                                                                                                                                                    |                                |                                                  |                                              |                                                                                                                |                             |
| Platinum mesh                      | 0.5 L; Synthetic medium without trace metals and vitamins | Four carbon-based electrode (2 carbon felts, two carbon brushes)         | 0.5 L; Synthetic medium containing trace metals and vitamins           | *NR                                              | 30°C | -1 V vs. Ag/AgCl   | Dual; Separated by CEM | Biogas containing CO <sub>2</sub> and CO (v/v 50/50, and v/v 75/25)                                                                                | *NR                            | Dominated by <i>Methanobrevibacter</i>           | Biogas upgrading                             | CH <sub>4</sub> composition >90% (CE ~100%) =                                                                  | (De la Puente et al., 2022) |
| Carbon felt                        | 250 mL; MES medium                                        | Carbon cloth                                                             | 250 mL; MES medium                                                     | MES effluent                                     | *NR  | -1.0 V vs. Ag/AgCl | Dual; Separated by CEM | CO <sub>2</sub> gas                                                                                                                                | 10 mL/min                      | *NR                                              | CH <sub>4</sub> production                   | 238.3 mmol/m <sup>2</sup> /d (FE = 84.2%)                                                                      | (Fu et al., 2022)           |
| Carbon felt                        | 250 mL; MES medium                                        | Porous hollow stainless steel/graphene foam                              | 250 mL; MES medium                                                     | MES effluent                                     | *NR  | -1.0 V vs. Ag/AgCl | Dual; Separated by CEM | CO <sub>2</sub> gas                                                                                                                                | 10 mL/min                      | *NR                                              | CH <sub>4</sub> production                   | 848.0 mmol/m <sup>2</sup> /d (FE = 84.2%)                                                                      | (Fu et al., 2022)           |
| Carbon felt                        | 260 mL; Medium source                                     | GO/Fe <sub>3</sub> O <sub>4</sub> /microbes biocomplex with carbon cloth | 260 mL; Medium source                                                  | MEC effluent                                     | *NR  | -0.9 V vs. Ag/AgCl | Dual; Separated by CEM | 99.999% CO <sub>2</sub> gas                                                                                                                        | Purged for 30 min              | Dominated by <i>Methanobacterium</i>             | CH <sub>4</sub> production                   | 605 mmol/m <sup>2</sup> /d (FE = 91.5%)                                                                        | (He et al., 2022)           |
| Graphite felt                      | 3L;                                                       | Graphite felt                                                            | 3L; Phosphate buffer solution containing trace metals and vitamins     | Anaerobic digester sludge                        | 30°C | -1.0 V vs. Ag/AgCl | Dual; Separated by PEM | A mixed gas containing 60% CH <sub>4</sub> and 40%                                                                                                 | 50 mL/min for 1.5 h            | Dominated by <i>Methanobacterium</i>             | Biogas upgrading, CH <sub>4</sub> production | CH <sub>4</sub> composition = 95%, CH <sub>4</sub> production rate = 4.78 L/m <sup>2</sup> /d (FE = 60%)       | (Kim et al., 2022)          |
| Graphite felt                      | 250 mL;                                                   | Graphite felt                                                            | 310 mL; Phosphate buffer solution containing trace metals and vitamins | Anaerobic digester sludge                        | 30°C | -1.0 V vs. Ag/AgCl | Dual; Separated by PEM | A mixed gas containing 60% CH <sub>4</sub> and 40%                                                                                                 | 10 mL/min for 30 min per cycle | Dominated by <i>Methanobacterium</i>             | Biogas upgrading, CH <sub>4</sub> production | CH <sub>4</sub> composition = 96%, Max. CH <sub>4</sub> production rate = 10.32 L/m <sup>2</sup> /d (FE = 95%) | (Kim et al., 2022)          |
| Graphite felt                      | 250 mL;                                                   | Graphite felt                                                            | 310 mL; Phosphate buffer solution containing trace metals and vitamins | Anaerobic digester sludge                        | 30°C | -1.0 V vs. Ag/AgCl | Dual; Separated by PEM | Real AD effluent gas (60-65% CH <sub>4</sub> , 30-35% CO <sub>2</sub> , trace amount of other gases, such as NH <sub>3</sub> and H <sub>2</sub> S) | 10 mL/min for 30 min per cycle | Dominated by <i>Methanobacterium</i>             | Biogas upgrading, CH <sub>4</sub> production | CH <sub>4</sub> composition = 96%, Max. CH <sub>4</sub> production rate = 10.55 L/m <sup>2</sup> /d (FE = 95%) | (Kim et al., 2022)          |
| Graphite rods with a platinum wire | 500 mL;                                                   | Graphite rods with a platinum wire                                       | 500 mL;                                                                | <i>Methanococcus maripaludis</i> Mic1c10 and KA1 | 37°C | -0.7 V vs. SHE     | Dual; Separated by PEM | N <sub>2</sub> /CO <sub>2</sub> (v/v, 80/20)                                                                                                       | 1.7 bar                        | <i>Methanococcus maripaludis</i> Mic1c10 and KA1 | CH <sub>4</sub> production                   | 16.2 mmol/m <sup>2</sup> /d                                                                                    | (May et al., 2022)          |

|                          |                                      |                                                     |                            |                                                         |     |                                 |                                               |                         |          |     |                                                                                  |                                                             |                         |
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| Ti/IrO <sub>2</sub> mesh | 50 mL; NaOH solution (maintain pH 7) | cPLA lattice electrode                              | 100 mL; Carbonate solution | *NR                                                     | *NR | 2.8 V (0.8 – 0.9 V vs. Ag/AgCl) | Dual; Separated by nylon cloth (membraneless) | Carbonate solution      | 160 mL/d | *NR | CH <sub>4</sub> production                                                       | ~15 mL/d (CE = ~>20%; see the figure in the literature)     | (Nwa nebu et al., 2022) |
| Ti/IrO <sub>2</sub> mesh | 50 mL; NaOH solution (maintain pH 7) | Ni-coated cPLA electrode                            | 100 mL; Carbonate solution | *NR                                                     | *NR | 2.8 V (0.8 – 0.9 V vs. Ag/AgCl) | Dual; Separated by nylon cloth (membraneless) | Carbonate solution      | 160 mL/d | *NR | CH <sub>4</sub> production                                                       | ~20 mL/d (CE = ~>80%; see the figure in the literature)     | (Nwa nebu et al., 2022) |
| Ti/IrO <sub>2</sub> mesh | 50 mL; NaOH solution (maintain pH 7) | NiFe-coated cPLA electrode                          | 100 mL; Carbonate solution | *NR                                                     | *NR | 2.8 V (0.8 – 0.9 V vs. Ag/AgCl) | Dual; Separated by nylon cloth (membraneless) | Carbonate solution      | 160 mL/d | *NR | CH <sub>4</sub> production                                                       | ~45 mL/d (CE = ~>80%; see the figure in the literature)     | (Nwa nebu et al., 2022) |
| Ti/IrO <sub>2</sub> mesh | 50 mL; NaOH solution (maintain pH 7) | NiFeMn-coated cPLA electrode                        | 100 mL; Carbonate solution | *NR                                                     | *NR | 2.8 V (0.8 – 0.9 V vs. Ag/AgCl) | Dual; Separated by nylon cloth (membraneless) | Carbonate solution      | 160 mL/d | *NR | CH <sub>4</sub> production                                                       | ~50 mL/d (CE = ~>100%; see the figure in the literature)    | (Nwa nebu et al., 2022) |
| Ti/IrO <sub>2</sub> mesh | 650 mL;                              | Granular activated carbon                           | 650 mL; Nutrient solution  | Anaerobic sludge from food waste-fed anaerobic digester | *NR | 2.8 V                           | Dual; Separated by nylon cloth                | 99.999% CO <sub>2</sub> | 3 L/d    | *NR | CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production) | 225 mL/d                                                    | (Vida les et al., 2022) |
| Ti/IrO <sub>2</sub> mesh | 650 mL;                              | Granular activated carbon                           | 650 mL; Nutrient solution  | Anaerobic sludge from food waste-fed anaerobic digester | *NR | 3.0 V                           | Dual; Separated by nylon cloth                | 99.999% CO <sub>2</sub> | 3 L/d    | *NR | CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production) | 410 mL/d                                                    | (Vida les et al., 2022) |
| Ti/IrO <sub>2</sub> mesh | 650 mL;                              | Conductive ABS polymer rod                          | 650 mL; Nutrient solution  | Anaerobic sludge from food waste-fed anaerobic digester | *NR | 2.8 V                           | Dual; Separated by nylon cloth                | 99.999% CO <sub>2</sub> | 3 L/d    | *NR | CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production) | *Exact value not reported see the figures in the literature | (Vida les et al., 2022) |
| Ti/IrO <sub>2</sub> mesh | 650 mL;                              | Conductive ABS polymer rod deposited with Ni and Fe | 650 mL; Nutrient solution  | Anaerobic sludge from food waste-fed anaerobic digester | *NR | 2.8 V                           | Dual; Separated by nylon cloth                | 99.999% CO <sub>2</sub> | 3 L/d    | *NR | CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production) | *Exact value not reported see the figures in the literature | (Vida les et al., 2022) |
| Ti/IrO <sub>2</sub> mesh | 650 mL;                              | Carbon felt with stainless steel mesh               | 650 mL; Nutrient solution  | Anaerobic sludge from food waste-fed anaerobic digester | *NR | 2.8 V                           | Dual; Separated by nylon cloth                | 99.999% CO <sub>2</sub> | 3 L/d    | *NR | CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production) | 410 mL/d (1420 mL/V <sub>cathode</sub> /d)                  | (Vida les et al., 2022) |
| Ti/IrO <sub>2</sub> mesh | 650 mL;                              | Carbon felt with stainless steel mesh               | 650 mL; Nutrient solution  | Anaerobic sludge from food waste-fed anaerobic digester | *NR | 3.0 V                           | Dual; Separated by nylon cloth                | 99.999% CO <sub>2</sub> | 3 L/d    | *NR | CH <sub>4</sub> production (Simultaneous acetate and CH <sub>4</sub> production) | 825 mL/d                                                    | (Vida les et al., 2022) |

|                               |                                                                                                         |                                 |                                               |                                             |         |                                                       |                                                                    |                                                                                      |                                                          |                                                                                                                             |                                                 |                                                                                                                                       |                                |
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| Carbon cloth                  | 70 mL; Bioanode fed with a solution containing sulfide (280 mmol/L Na <sub>2</sub> S-9H <sub>2</sub> O) | Carbon cloth                    | 70 mL; Nutrient solution                      | Anaerobic sludge from upflow sludge blanket | 30°C    | 0.8 V                                                 | Dual; Separated by CEM                                             | *NR                                                                                  | *NR                                                      | Dominated by <i>Methanosaeta</i>                                                                                            | CH <sub>4</sub> production                      | 12.1 mmol/m <sup>2</sup> /d                                                                                                           | (Kambara et al., 2023)         |
| Platinum mesh                 | 0.5 L                                                                                                   | Carbon felt, carbon brush       | 0.5 L; Nutrient solution                      | Another MES reactor operated for >300 days  | 30°C    | -1.0 V vs. Ag/AgCl                                    | Dual; Separated by CEM                                             | 200 mL CO <sub>2</sub> , 100 mL H <sub>2</sub>                                       | 200 mL CO <sub>2</sub> , 100 mL H <sub>2</sub> per cycle | Carbon felt dominated by <i>Methanobacterium</i> and carbon brush dominated by <i>Methanobrevibacter</i>                    | CH <sub>4</sub> production                      | Achieved >90% methane                                                                                                                 | (De la Puente et al., 2023)    |
| Titanium iridium oxide meshes | 50 mL; used NaOH with H <sub>2</sub> SO <sub>4</sub> as a pH controller                                 | Carbon felt pieces with Ti wire | 200 mL; Buffer solution containing metal ions | Anaerobic sludge from an UASB reactor       | 25–27°C | Applied constant current up to 80 mA                  | Dual; Separated by dialysis membrane with nylon cloth on each side | CO <sub>2</sub> gas, concentration not specified                                     | 720 mL/d                                                 | *NR                                                                                                                         | CH <sub>4</sub> production                      | 275 – 835 mL/L/d under Bi and Sn electrodeposition; 860 – 1010 mL/L/d under Bi <sup>3+</sup> and Sn <sup>2+</sup> metal ion injection | (Gharbi et al., 2024)          |
| Graphite rod                  | *NR                                                                                                     | Carbon felt                     | 1L; Nutrient solution                         | Anaerobic granular sludge from AD process   | 37±1°C  | -0.4 V vs. SHE                                        | Dual; Separated by CEM                                             | Bicarbonate and biogas generated from the operation                                  | *NR                                                      | Dominated by <i>Methanobacterium</i>                                                                                        | In situ biogas upgrading                        | Methane production rate of 22.1±0.1 mmol/d with methane content in the biogas to ~88.3%                                               | (Lu et al., 2023)              |
| Titanium iridium oxide meshes | 250 mL                                                                                                  | Carbon felt                     | 500 – 900 mL; Nutrient solution               | Anaerobic sludge                            | 28–30°C | -1.2 V vs. Ag/AgCl (not all potentials were reported) | Dual; Separated by a non-conductive nylon cloth                    | Pure CO <sub>2</sub> , synthetic biogas (40% CO <sub>2</sub> , 60% CH <sub>4</sub> ) | Recirculation of cathode off-gas at a rate of 12 L/d     | *NR                                                                                                                         | CH <sub>4</sub> production and biogas upgrading | Achieved volumetric rate of methane of 0.8 – 1.4 L/L/d                                                                                | (Tan guay-Riou x et al., 2023) |
| Pt-coated Ti mesh             | 140 mL                                                                                                  | Carbon felt                     | 140 mL; Buffer solution                       | Anaerobic granular sludge                   | *NR     | -0.8 to -1.0 V vs. Ag/AgCl                            | Dual; Separated by CEM                                             | *NR                                                                                  | *NR                                                      | Dominated by hydrogenotrophic methanogens at -1.0 V vs. Ag/AgCl, dominated by DET-related methanogens at -0.8 V vs. Ag/AgCl | CH <sub>4</sub> production                      | Achieved a maximum total CH <sub>4</sub> yield of 72.9%                                                                               | (Tian et al., 2023)            |

Note: CE = Coulombic efficiency; FE = Faradaic efficiency; PEM = proton-exchange membrane; SHE = standard hydrogen electrode; UASB = upflow anaerobic sludge blanket; \*NR = not reported.

**Table 2.** Overview of selection criteria of MES materials and operating parameters that are to be considered during the design of MES for CO<sub>2</sub> mitigation, CH<sub>4</sub> production, and biogas upgrading.

| Parameter        | Type     | Selection criteria, factors, descriptions                                                               |                                       |                                                                                              | References                                                                                                                                                                               |
|------------------|----------|---------------------------------------------------------------------------------------------------------|---------------------------------------|----------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Carbon electrode | Material | Lower overpotential and resistance                                                                      | Low cost or cost-effectiveness        | High active biocompatibility and interactions with the biocatalyst                           | (Aryal et al., 2017; Logan et al., 2006; Noori et al., 2020; Zhang et al., 2021)                                                                                                         |
|                  |          | High durability and long-term stability                                                                 | High electroactivity and conductivity | Large specific surface area for cell adhesion and biofilm formation                          |                                                                                                                                                                                          |
|                  |          | High chemical stability                                                                                 | High HER capability                   | High CH <sub>4</sub> productivity and CO <sub>2</sub> reduction rate                         |                                                                                                                                                                                          |
|                  |          | Low CO <sub>2</sub> mass transfer resistance                                                            | High flexibility                      | High availability and field applicability                                                    |                                                                                                                                                                                          |
| Anode electrode  | Material | Lower overpotential under acidic to neutral environment                                                 | Low-cost materials                    | Materials that can minimize energy demand                                                    | (Bajracharya et al., 2016; Bian et al., 2020; Blanchet et al., 2015; Jayathilake et al., 2022; Suen et al., 2017; van Eerten-Jansen et al., 2015; Zheng et al., 2019; Zhou et al., 2021) |
|                  |          | High material stability under acidic to neutral environment                                             | High electroactivity and conductivity | Ability to efficiently drive anodic reaction (e.g., tendency to catalyze water electrolysis) |                                                                                                                                                                                          |
|                  |          | High durability under acidic to neutral environment (e.g., degradation over relatively short periods of |                                       |                                                                                              | (Cheng et al., 2009; Clauwaert and                                                                                                                                                       |

|                                    |                     |                                                                                                                                 |                                                 |                                                                                                          |                                                                                                                                                        |
|------------------------------------|---------------------|---------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------|----------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                    |                     | low pH electrolysis)                                                                                                            |                                                 |                                                                                                          | Verstraete, 2009; Sato et al., 2013; Van Eerten-Jansen et al., 2012; Zhen et al., 2016)                                                                |
|                                    |                     | Lacks intrinsic electrocatalytic OER activity, requiring an overpotential exceeding 0.6 V to generate sufficient current output |                                                 |                                                                                                          | (Cheng et al., 2015)                                                                                                                                   |
| Ion-exchange membrane separator or | Material design and | Low cost, highly durable, and long-term stable materials                                                                        | Prevents oxygen diffusion from cathode to anode | High CH <sub>4</sub> productivity (e.g., low resistance to achieve a larger consumption rate of current) | (Jayathilake et al., 2022; Philamore et al., 2015; Zuo et al., 2007)                                                                                   |
|                                    |                     | High and selective ion transport efficiency                                                                                     | Low ohmic resistance                            | Minimize alteration on current generation and pH gradient/control                                        | (Ceballos-Escalera et al., 2020; Dharmalingam et al., 2019; Divekar et al., 2020; Geppert et al., 2016; Kracke et al., 2020; Kracke et al., 2019)      |
|                                    |                     | Prevents the crossover of the bacterial aqueous solution                                                                        | Ability to maintain electroneutrality           | Prevents or minimizes fouling and scaling problems                                                       | (Aryal et al., 2022; Chung and Dhar, 2021a; Chung et al., 2020b; Dhar and Lee, 2013; Jayathilake et al., 2022; Leong et al., 2013; Zhang et al., 2019) |

|                                                      |           |                                                                                                                                                                                                                  |                                                                                                                                                       |                                                                                                       |
|------------------------------------------------------|-----------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------|
| Inoculum sources                                     | Material  | Pure culture for selectivity, mixed culture for CH <sub>4</sub> productivity                                                                                                                                     | Microbes remain in suspension vs. form a biofilm (biofilm leads to higher interfacial resistance, the addition of ohmic resistance on the biocathode) | (Arunasri and Mohan, 2019; Hengsbach et al., 2022; Jayathilake et al., 2022; Salimijazi et al., 2020) |
|                                                      |           | Low ohmic resistance on the biocathode (high resistance acts as a barrier to diffusion for reactants such as protons, CO <sub>2</sub> , and other end products)                                                  |                                                                                                                                                       | (Arunasri and Mohan, 2019; Jayathilake et al., 2022; Salimijazi et al., 2020; Zhen et al., 2018)      |
|                                                      |           | Microbes favoring the hydrogen-mediated CH <sub>4</sub> production pathway (attractive at both commercial and research levels)                                                                                   |                                                                                                                                                       | (PrévotEAU et al., 2020)                                                                              |
|                                                      |           | H <sub>2</sub> -consuming methanogens: (1) often more stable, especially during long-term operation even with fluctuations in electrochemical H <sub>2</sub> production, (2) resilient during field applications |                                                                                                                                                       | (Mateos et al., 2020; Rojas et al., 2018)                                                             |
| CO <sub>2</sub> concentration                        | Substrate | Avoiding excessive bicarbonate concentration (Concentrations greater than 4 g/L lead to a high saline condition that is detrimental to biocathode and CO <sub>2</sub> fixation process)                          |                                                                                                                                                       | (Lefebvre et al., 2012)                                                                               |
|                                                      |           | Avoiding continuous CO <sub>2</sub> sparging (acidifies the catholyte, creates an unfavorable environment for the methanogenic activity to occur)                                                                |                                                                                                                                                       | (Bian et al., 2020; Zakaria and Dhar, 2019)                                                           |
|                                                      |           | Higher bicarbonate concentration (higher catholyte conductivity, current output, and proton transport from the bulk liquid to the cathode biofilm)                                                               |                                                                                                                                                       | (Xiao et al., 2020b)                                                                                  |
| Inorganic carbon source, CO <sub>2</sub> bubble size | Substrate | Dosing inorganic carbon as a form of bicarbonate is favorable                                                                                                                                                    |                                                                                                                                                       | (Xiao et al., 2020b)                                                                                  |
|                                                      |           | Smaller CO <sub>2</sub> bubble sizes (31 – 61 mm): enhanced gas-liquid interfacial area and mass transfer, higher bacterial growth                                                                               |                                                                                                                                                       | (Ryu et al., 2009)                                                                                    |

|                                 |                      |                                                                                                                                                                                                            |                                                                                                                                                   |                                                                                                    |
|---------------------------------|----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------|
| CO <sub>2</sub> delivery method | Substrate design and | Ability to maintain catholyte pH                                                                                                                                                                           | Enhanced gas-liquid mass transfer                                                                                                                 | (Alqahtani et al., 2018; Bakonyi et al., 2023; Jiang and Zeng, 2018; Mohanakrishna et al., 2018)   |
|                                 |                      | Enhanced solubility of CO <sub>2</sub> in water                                                                                                                                                            | Enhanced the mass transfer of CO <sub>2</sub>                                                                                                     |                                                                                                    |
|                                 |                      | Direct vs. indirect delivery method (e.g., direct delivery to microbes via pores of the biocathode contrasts with indirect CO <sub>2</sub> sparging through an electrically insulated ceramic hollow tube) |                                                                                                                                                   | (Bian et al., 2021)                                                                                |
| Operating mode                  | Design and operation | Continuous mode                                                                                                                                                                                            | Batch mode                                                                                                                                        | (Batlle-Vilanova et al., 2015; Cheng et al., 2009; Kim et al., 2022; Mao et al., 2021)             |
| Startup time                    | Design and operation | Startup takes approximately 28 days and can be prolonged to 40 days                                                                                                                                        | Startup time is influenced by various operating parameters, including the source of the inoculum, temperature, pH, and externally applied energy. | (Li et al., 2019; Liu et al., 2018; Mao et al., 2021; Saheb-Alam et al., 2018; Yang et al., 2018a) |
| Externally applied voltage      | Operation            | Optimal CO <sub>2</sub> reduction and CH <sub>4</sub> formation rates                                                                                                                                      | Often, a more negative cathode potential is required to counteract high electrode overpotential and internal resistance within the system.        | (Bakonyi et al., 2023; Mao et al., 2021; Zakaria and Dhar, 2019)                                   |
|                                 |                      | Cathode potential > -0.414 V vs. SHE: eliminates the electrochemical generation of H <sub>2</sub> , promotes the DET pathway during methanogenesis                                                         |                                                                                                                                                   | (Zakaria and Dhar, 2019)                                                                           |
|                                 |                      | Cathode potential of -0.7 V vs. SHE: promotes an IET pathway (hydrogen production), supporting the catalysis of hydrogenotrophic methanogens in mixed culture MES (undesirable)                            |                                                                                                                                                   | (Li et al., 2019; Mohanakrishna et al., 2018; Mohanakrishna                                        |

|                 |           |                                                                                                                                                                                                                                        |                                                                         |                                                                                                                               |
|-----------------|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------|
|                 |           |                                                                                                                                                                                                                                        |                                                                         | et al., 2016; Rojas et al., 2018)                                                                                             |
|                 |           | Cathode potential < -0.75 V vs. SHE: production of other end products, such as acetate                                                                                                                                                 |                                                                         | (Jiang et al., 2013)                                                                                                          |
|                 |           | Cathode potential that influences the structure, diversity, and efficiency of the resulting cathode biofilm                                                                                                                            |                                                                         | (Bakonyi et al., 2023)                                                                                                        |
| System pressure | Operation | Higher pressure: optimal performance                                                                                                                                                                                                   | Solubility of H <sub>2</sub> is often poor under atmospheric conditions | (Kobayashi et al., 2017; Mayer et al., 2019)                                                                                  |
|                 |           | MES under an initial pressure between 1.6-1.7 bar: enhanced the gas availability of H <sub>2</sub> in solution for methanogenic uptake                                                                                                 |                                                                         |                                                                                                                               |
| Temperature     | Operation | Mesophilic environment                                                                                                                                                                                                                 | Thermophilic environment                                                | (Fu et al., 2015; Xiao et al., 2020b; Yang et al., 2018a)                                                                     |
|                 |           | High temperature above 35°C: Reduce current density and inhibit electro active microbes from the mesophilic mixed culture in the biocathode                                                                                            |                                                                         |                                                                                                                               |
|                 |           | Thermophilic condition: (1) provides optimal microbial activity, (2) has a rate advantage, (3) increases biogas production, (4) reduces oxygen solubility, (5) promotes proton mass transfer rate through the electrolyte              |                                                                         |                                                                                                                               |
| pH              | Operation | Maintaining an adequate pH (6.8-7.8): optimizing the electro-methanogenesis                                                                                                                                                            | One of the main reasons for MES overpotential                           | (Aryal et al., 2022; Kim et al., 2022; Sleutels et al., 2009; Wagner et al., 2010; Ward et al., 2008; Zakaria and Dhar, 2019) |
|                 |           | At a neutral pH: (1) Proton and hydroxide activities are typically low, and (2) There's a restricted rate of transport, especially noticeable when the concentrations of supporting cations and anions exceed 4-5 orders of magnitude. |                                                                         | (Jayathilake et al., 2022; Logan et al., 2008; Sleutels et al., 2017)                                                         |

**Table 3.** The function of each trace metal. Information was adapted from Reddy et al. (2021).

| Trace metal type and its relationship with enzyme | Function and role during MES operation                                                                                                                                                                                                            | References                                                                                                       |
|---------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------|
| Fe and formylmethanofuran dehydrogenase (Fmd)     | <ul style="list-style-type: none"> <li>The CO<sub>2</sub> conversion process is catalyzed by Fmd, which necessitates Fe for the formation of Fe<sub>4</sub>S<sub>4</sub> clusters.</li> </ul>                                                     | (Pobeheim et al., 2010; Srikanth and Mohan, 2012)                                                                |
| Mo                                                | <ul style="list-style-type: none"> <li>Facilitates the binding of approximately nine Fe<sub>4</sub>S<sub>4</sub> clusters in the Mo/W-pterin and polyferredoxin by the Fmd, the primary enzyme in the CO<sub>2</sub> reduction pathway</li> </ul> | (Pobeheim et al., 2010; Srikanth and Mohan, 2012)                                                                |
| Zn                                                | <ul style="list-style-type: none"> <li>Crucial for various cellular processes, thus essential for the survival and growth of the biocatalyst</li> </ul>                                                                                           | (Pobeheim et al., 2010; Srikanth and Mohan, 2012)                                                                |
| Fe-S Zn clusters                                  | <ul style="list-style-type: none"> <li>The enzyme responsible for heterodisulfide (CoM-S-S-CoB) reduction in the final stages of methanogenesis contains Fe-S Zn clusters</li> </ul>                                                              | (Glass and Orphan, 2012; Thanh et al., 2016)                                                                     |
| Hydrogenases                                      | <ul style="list-style-type: none"> <li>Hydrogenases involved in methanogenesis assist in hydrogen oxidation and reduce ferredoxin and other electron carriers, including coenzyme F420.</li> </ul>                                                | (Glass and Orphan, 2012; Thanh et al., 2016)                                                                     |
| Ni and M methyltransferases (Mtr)                 | <ul style="list-style-type: none"> <li>Nickel aids in the uptake of cellular constituents</li> <li>Mtr containing Co are necessary for forming methyl coenzyme M, which transfers the methyl group to HS-CoM</li> </ul>                           | (Chen et al., 2016a; Feng et al., 2010; Glass and Orphan, 2012; Pobeheim et al., 2010; Srikanth and Mohan, 2012) |
| Mg                                                | <ul style="list-style-type: none"> <li>Acts as an active component of various enzymes required for hydrogenotrophic methanogenesis and assists in ATP transport within the biocatalyst</li> </ul>                                                 | (Chen et al., 2016a; Feng et al., 2010; Glass and Orphan, 2012; Pobeheim et al., 2010; Srikanth and Mohan, 2012) |
| Mn                                                | <ul style="list-style-type: none"> <li>Plays a multifaceted role, existing in 11 oxidation states, typically as divalent Mn clusters in biological systems</li> </ul>                                                                             | (Chen et al., 2016a; Feng et al., 2010; Glass and Orphan, 2012; Pobeheim et al., 2010; Srikanth and Mohan, 2012) |

|    |                                                                                                                                                       |                                                    |
|----|-------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------|
|    |                                                                                                                                                       | 2010; Srikanth and Mohan, 2012)                    |
| Fe | <ul style="list-style-type: none"> <li>Trace metals primarily exist as Fe-S complexes, aiding in electron transfer and catalytic reactions</li> </ul> | (Glass and Orphan, 2012; Srikanth and Mohan, 2012) |

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