Chemosphere 291 (2022) 132843

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Microbial electrochemical approaches of carbon dioxide utilization for biogas upgrading

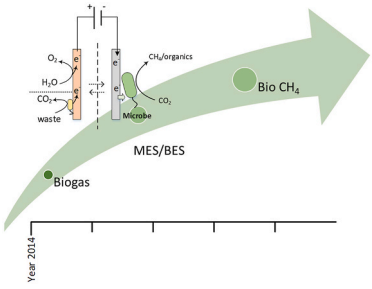
Nabin Aryal [a,*], Yifeng Zhang [b], Suman Bajracharya [c], Deepak Pant [d], Xuyuan Chen [a]

[a] Department of Microsystems, University of South-Eastern Norway, Borre, Norway
[b] Department of Environmental Engineering, Technical University of Denmark, Denmark
[c] Biochemical Process Engineering Department, Luleå University of Technology, Sweden
[d] Separation and Conversion Technology, Flemish Institute for Technological Research (VITO), Boeretang 200, Mol, 2400, Belgium

HIGHLIGHTS

- Microbial electrochemical approach for biogas upgrading is extensively scrutinized.
- Data related to operational parameters for process optimization are discussed.
- Applied potential and cathodic catalyst are the keys to reactor performances.
- Insight associated with reactor configuration and resource recovery are provided.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling Editor: Derek Muir

Keywords:
Biomethane
Bioelectrochemical system
CO_2 reduction
In-situ
Ex-situ
Electromethanogens

ABSTRACT

Microbial electrochemical approach is an emerging technology for biogas upgrading through carbon dioxide (CO_2) reduction and biomethane (or value-added products) production. There is limited literature critically reviewing the latest scientific developments on the bioelectrochemical system (BES) based biogas upgrading technologies, including CO_2 reduction efficiency, methane (CH_4) yields, reactor operating conditions, and electrode materials tested in the BES reactor. This review analyzes the reported performance and identifies crucial parameters considered for future optimization, which is currently missing. Further, the performances of BES approach of biogas upgrading under various operating settings in particular fed-batch, continuous mode in connection to the microbial dynamics and cathode materials have been thoroughly scrutinized and discussed. Additionally, other versatile application options associated with BES based biogas upgrading, such as resource recovery, are presented. Three-dimensional electrode materials have shown superior performance in supplying the electrons for the reduction of CO_2 to CH_4. Most of the studies on the biogas upgrading process conclude hydrogen (H_2) mediated electron transfer mechanism in BES biogas upgrading.

1. Introduction

Biogas, in general comprises a mixture of CH_4, CO_2, hydrogen sulfide

* Corresponding author.
E-mail address: nabin.aryal@usn.no (N. Aryal).

https://doi.org/10.1016/j.chemosphere.2021.132843
Received 21 July 2021; Received in revised form 11 October 2021; Accepted 7 November 2021
Available online 9 November 2021

Abbreviation

AD	Anaerobic digestion
AnOMBR	Anaerobic osmotic membrane bioreactor
ARS-HM	Ammonia recovery system based on hydrophobic membranes
AEM	Anion exchange membrane
BES	Bioelectrochemical system
CAPEX	Capital expenditure
CEM	Cation exchange membrane
DET	Direct electron transfer
FWTP	Food waste treatment plant
GHG	Greenhouse gas
HER	Hydrogen evolution reaction
IEM	Ion exchange membrane
MEC	Microbial electrolysis cell
MES	Microbial electrosynthesis
MWWTP	Municipal wastewater treatment plant
MFC	Microbial fuel cell
MSW	Municipal solid waste
MESC	Microbial electrolytic capture, separation and regeneration cell
MWCNT	Multiwall carbon nanotube
OPEX	Operating expense
PSA	Pressure swing absorption
RVC	Reticulated vitreous carbon
TRL	Technology readiness level
UASB	Upflow anaerobic sludge blanket digestion
VFA	Volatile fatty acid
WWTP	Wastewater treatment plant

(H_2S), ammonia (NH_3), hydrogen (H_2), nitrogen (N_2), oxygen (O_2), carbon monoxide (CO), and siloxanes. Some of the components present in biogas, notably CO_2, H_2S, and siloxanes, must be removed before direct gas application (Angelidaki et al., 2018), which is called biogas upgrading. Additionally, such impurities cause accumulation (siloxanes) on gas appliances (burner, gas engine) and also reduces the heating values of biogas (Aryal and Kvist, 2018). The increase in the emission of impurities in biogas is also hazardous for human health (Li et al., 2019). Physiochemical biogas upgrading approaches such as water scrubbing, pressure swing absorption (PSA), chemical adsorption, membrane separation, and cryogenic separation are currently applied on commercial scale (Angelidaki et al., 2018). However, these conventional technologies were shown to be energy-intensive, cause corrosion problems in upgrading plants, and significantly emit the CO_2 and CH_4 into atmosphere (Angelidaki et al., 2018; Aryal et al., 2018; Kvist and Aryal, 2019). Thereby, biological methods mostly utilizing microbes and photosynthetic microalgae are considered as effective approaches to utilize CO_2 from biogas (Angelidaki et al., 2018; Fu et al., 2021). Additionally, exogenous H_2 supplemented microbial biogas upgrading has been tested in demonstration scale to convert CO_2 and upgrade CH_4 (Angelidaki et al., 2018; Aryal et al., 2021b). Recently, BESs have become promising biological technology to capture and convert CO_2 from biogas (Aryal et al., 2021b; Schievano et al., 2018; Xu et al., 2014).

A BES reactor is equipped with an anode for oxidation and a cathode for reduction, which are typically divided by an ion-exchange membrane to transport the ions. The anode acts as a terminal electron acceptor where electroactive microorganisms oxidize the organic and inorganic materials (Kaur et al., 2021; Logan, 2010). The harvested electrons are transported *via* an external circuit to the cathode, where they are used to reduce the targeted compound, thereby producing value-added chemicals and fuels (Logan and Rabaey, 2012). BESs have been further proven to purify value-added multi-carbon organic chemicals and fuels and tested for resource recovery such as nutrients, metals and energy recovery from the waste stream (Aryal et al., 2017; Nancharaiah et al., 2015; Rodríguez Arredondo et al., 2015). BES route of CH_4 production utilizing CO_2 reveals multiple benefits: (i) efficient conversion of waste CO_2 to energy resources (ii) power-to-gas is possible integrating with renewable energy like wind and solar (iii) produced gas could be injected and stored into existing gas grid system (iv) CH_4 can be directly utilized for transportation and renewable resources (v) utilization of existing energy infrastructure could save extra investment cost (Nelabhotla et al., 2021).

The first report on reducing CO_2 into CH_4 described dates back to 1987 where methanogens utilized the electron from elemental iron as electron donor (Daniels et al., 1987). The terminology 'electromethanogenesis' was reported, where electroactive methanogens catalyzed the CO_2 reduction to produce CH_4 by utilizing the electrons from the cathode or reducing equivalents, e.g. H_2 derived from the poised cathode (Cheng et al., 2009). The proof-of-concept of bioelectrochemical upgrading of biogas was demonstrated in 2014 as a process attributed to CO_2 reduction through direct cathodic electron transfer to electroactive methanogens (Xu et al., 2014). Since then, researchers have widely applied BESs to remove and utilize of CO_2 to purify the biogas.

Within the recent five years, researchers have developed several laboratory-scale BESs to demonstrate the utilization of CO_2 fraction, electromethanogenesis activity, microbial dynamics, reactor design, electron transfer mechanism and resource recovery while purifying biogas to natural gas quality level. Few reviews have been previously accomplished on biogas upgrading primarily dedicated to physical, chemical, hydrogen mediated microbial and algal-based biological upgrading. However, a critical review of the latest scientific research on the BES-based biogas upgrading technology is still missing. Therefore, this report aims to summarize recent state-of-the-art followed by discussions on the electrode materials that transfer electrons to electroactive CO_2-reducing microbe, resource recovery, and future research prospective to overcome the BES technology bottleneck for biogas upgrading. Recent research publications have been selected for review by using biogas upgrading as a keyword, where secondary data collection and analysis were done.

2. State of the art on lab-scale studies

2.1. Reactor design and configuration applied in bioelectrochemical biogas upgrading

The most straightforward design so far is the single-chamber bioreactor used without membrane, which has simple reactor architecture and reduced capital cost (Lee et al., 2019). Nevertheless, the issue of oxygen (O_2) contamination in the single-chamber system hampers the survival of methanogens. Therefore, most BES studies have been tested in a dual-chamber reactor separated by an ion-exchange membrane that facilitates the transfer of charged species (H^+, Na^+) and acts as a separator to stop the crossover of bacterial liquid and O_2 from anode to cathode chamber. Fig. 1 (A, B, C & D) shows the representations of reactor configurations applied in bioelectrochemical biogas upgrading studies. The most commonly used reactor type is the H-shaped reactor, with two identical bottles or chambers (Fu et al., 2020). In double compartment systems, flat-parallel-plates configuration is also used where parallel plates help to create a uniform electric field across the reactor and avoid electrochemical disturbances due to reactor geometry. However, the volatile fatty acid, VFA (acetate) accumulation and toxicity associated with pH fluctuation are experienced in single and double chamber reactors. In the single-chamber reactor, VFAs

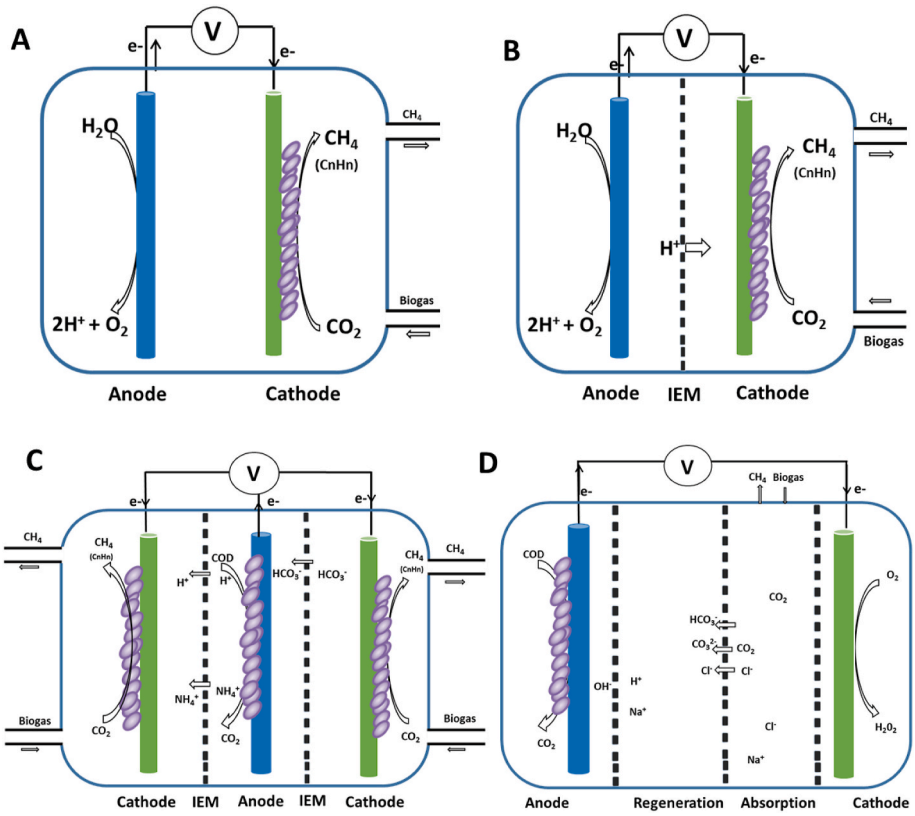


Fig. 1. Various reactor configurations used in microbial electrochemical approaches to purify biogas A) Single compartment configuration B) double compartments configuration C) triple compartments configuration with anode, cathode, and regenerative unit and D) Four compartments configuration with anode, regeneration, absorption and cathode compartment. IEM; ion exchange membrane.

(propionate and acetate) accumulation was observed that led to pH drop from 7 to 6; thereby, causing acidification which inhibit methanogens activity (Liu et al., 2017). Other operational parameters such as buffering capacity and partial alkalinity could support balancing the pH; however, high concentration caused acidification, resulting in the toxic condition for methanogens (Ahring et al., 1995; Murto et al., 2004). Furthermore, the addition of exogenous hydrogen inside the reactor could promote homoacetogenic activity; thereby, the accumulation of acetate and other VFA could occur. VFA accumulation reveals high acidogenic and acetogenic activities that cause the kinetic uncoupling between the acid producers (acidogens and acetogens) and acid consuming methanogens for biogas production (Murto et al., 2004). In a single chamber, the transport of ions is not limited, and energy losses could be minimized due to no transport limitations. But unwanted oxidation reactions at the anode may also hamper the performance in the single chamber. A double chamber reactor may demand slightly high energy input but the unwanted reactions can be minimized by creating only the cathodic condition.

With the aim of the BES up-scaling, three-compartment reactors having an accumulation chamber in-between anolyte and catholyte were also developed (Jin et al., 2017; Krieg et al., 2014; Zeppilli et al., 2017). The three-compartment system facilitated removing excess VFA and ions such as NH_4^+, HCO_3^- from either side, thereby overcoming the problem associated with VFA accumulation and toxicity as experienced in single and double chamber reactor configuration (Jin et al., 2017; Krieg et al., 2014; Zeppilli et al., 2017). Furthermore, above 90% of CO_2 removed from the biogas with the input of 0.9 kWh electricity per kg CO_2 was reported by Zeppilli et at. (2017), which illustrates the superiority of multi-compartment configuration over single or double. The electrical energy consumption in three-chamber BES can be invested simultaneously on chemical oxygen demand (COD) removal at the anode, CO_2 removal at the cathode, and recovery of ammonium bicarbonate at the accumulation compartment. In another study, the three-compartment configuration was used with a two-side cathode and one anode compartment for the CO_2 removal and reduction from biogas. At the same time, the transport of NH_4^+ from the anode to the cathode recovered nitrogen from AD digestate (see Fig. 1c) (Zeppilli et al., 2019b). The two-side cathode in the three-chamber BES configuration showed higher performance by combining CH_4 production, CO_2 removal and high purity of ammonium recovery than the conventional systems used for each process separately. The three-chamber BES technology should be comparable with the commercial biogas upgrading technology such as water scrubber. However, CH_4 production rate of laboratory-scale reactors has not been tested at the demonstration scale to compare the economic feasibility; thus, the technology readiness level (TRL) is low (Aryal et al., 2021a). The multi-compartment system are beneficial for multi-tasking purpose such as recovery of resources, however, the energy requirement in such system could be high. In addition, the reactor configuration may become complex. At the present stage of development of renewable energy technology, energy demand can be fulfilled with renewable sources (Gong et al., 2021). Thus, future research in BES field to incorporate renewable energy are recommended.

A further improvement on CH_4 production was achieved by a microbial electrolytic capture, separation and regeneration cell (MESC) reactor consisting of four compartments, e.g. cathode, absorption, regeneration, and anode compartments separated with bipolar membrane and anion exchange membrane as demonstrated in Fig. 1 D (Kokkoli et al., 2018). Such an approach simultaneously treated the domestic wastewater in the anode compartment and CO_2 removal at absorption compartment or reduced at the cathode, thereby improving the overall energy and process efficiency. Despite an increase in system complexity, the results from different studies suggest that the multi-compartment reactor configurations of BES in biogas upgrading

can offer intrinsic advantages in i) simultaneous wastewater treatment at the anode and biogas upgrading ii) *in-situ* production of chemicals such as VFA, acetate iii) lowering of possible CH_4 escape to the atmosphere while upgrading iv) recovery of CO_2, CO_3^{2-} and HCO_3^- at the regeneration and absorption chamber which can be further utilized v) further possibilities for easy modification (Jin et al., 2017; Kokkoli et al., 2018; Zeppilli et al., 2017, 2019b). The superiority of multi-compartment systems over single and double-compartment has been demonstrated based on the CO_2 removal, VFA accumulation, and pH regulations (Zeppilli et al., 2021b); nonetheless, further optimization

Table 1
Recent state-of-art for biogas upgrading in laboratory scale BES system.

Cathode material	Mode	Reactor design	Inoculum source/Most dominating microbes (genus or family level)	Current density/ draw	Upgrading/ improvement	CE (%)	Reference
SnO_2 nanoparticles	*Ex-situ* (Batch)	AnOMBR-MEC separated by membrane	Mixed culture from WWTP sludge (*Methanosaeta, Methanobacterium* and *Methanobrevibacter*)	7.2×10^4 mA m^{-2}	90% CH_4	85	Gao et al. (2021)
Graphite granules	*in-situ* (Batch)	MEC integrated with ARS-HM	Enriched mixed culture/ Electromethanogenic)	$12.1 \pm 4.8 \times 10^4$ mA m^{-3}	73 ± 8 L_{CH4} $m^{-3}d^{-1}$ (1.5 x improved)	23	Cerrillo et al. (2021)
Graphite plate	*in-situ* (Batch)	Two chambers separated by membrane	Mixed culture from synthetic wastewater sludge (*Methanothrix* and *Methanobacterium*)	0.022 mA m^{-2}	97% CH_4	68.1	Liu et al. (2021)
Carbon felt	*Ex-situ* (Batch)	MEC membrane less two chamber separated by nylon cloth	Mixed culture from anaerobic sludge	250 mA	90% CH_4	ng	Tartakovsky et al. (2021)
Ti-mesh coated with Pt/C	*Ex-situ* (Batch)	Two-chamber MEC separated by membrane	Mixed culture from WWTP (*Methanobacterium* and *Azoarcus*)	13.9 ± 0.5A m^{-2}	97.9% CH_4	95	Zhou et al. (2020)
Carbon brush	*in-situ* (Batch)	MEC separated by membrane	Mixed culture from MWWTP (*Methanosarcina*, *Methanobacterium*)	0.407 mA m^{-2}	91.2% CH_4	18.8	Liu et al. (2020)
Carbon paper	*Ex-situ* (Batch)	Cylindrical two chamber	Pure culture (*Methanococcus maripaludis*)	ng	98.3% CH_4	85.2	Fu et al. (2020)
Graphite granular	*Ex-situ*	Three compartment membrane separation	Mixed culture from thermophilic AD	145 ± 4 mA 129 ± 3	68 ± 6 71 ± 14 mmol CO_2 removal−1	69 ± 4 95 ± 4 (cathodic capture)	Zeppilli et al. (2019b)
Carbon fiber	*In-situ* (Batch)	Single chamber membrane less	Mixed culture from WWTP sludge	15.54 mA (4 g/L glucose was added)	0.34 L CH_4/gCOD higher CH_4 yield than control	ng	Lee et al. (2019)
Graphite plate	*In-situ* (Continuous)	AD-MES with two chambers separated by membrane	Mixed culture from WWTP sludge (*Methanothrix* and *Methanobacterium*)	ng	>90% CH_4	97.60	Liu et al. (2019)
Graphite coated with Cu–Ni & Fe	*In-situ* (Sequencing-Batch)	AD-MEC integrated in single chamber	Mixed culture from FWTP originated (*Methanobacterium Methanosarcina*)	ng	1.7 fold faster than AD	ng	Park et al. (2018)
Stainless steel	*In-situ* (Batch)	Multi compartment MESC	Mixed culture from WWTP sludge	1490 mA m^{-2}	99–100% CH_4	ng	Kokkoli et al. (2018)
Carbon felt	*In-situ* (Batch)	Double chamber separated by membrane	Mixed culture from thermophilic sludge	120 mA	98% CH_4	72.8	Liu et al. (2017)
Pt coated Ti wire mesh	*In-situ* (Batch)	MESC separated by membrane	Mixed culture from WWTP sludge	1700 mA m^{-2}	97.5% CH_4	81	Jin et al. (2017)
Graphite granular	*In-situ* (Batch)	Three chambers separated by membrane	Mixed culture from WWTP generated activated sludge	87 mA	90% CO_2 removal	86.4	Zeppilli et al. (2017)
MWCNT-RVC	Ex-situ (Batch)	Double chamber	Mixed culture from WWTPs sludge	2×10^5 mA m^{-2}	CO_2 removal as acetate	99	Jourdin et al. (2016)
Stainless steel (Wall of AD)	*In-situ* (Batch)	Single chamber barrel shaped membrane less	*Geobacter and Methanosarcina*	3.04×10^5 mA m^{-3}	24% higher CH_4 content than control	74.6	Yin et al. (2016)
Graphite	*In-situ* (Continuous)	Double chamber separated by membrane	Mixed culture from organic waste treating AD (*Methanobacterium, Proteobacteria*)	201.7 ± 18.1 mA m^{-2}	85% CH_4	69.9	Batlle-Vilanova et al. (2015)
Graphite	*Ex-situ* (Batch)	AD connect to cathode chamber in H shape	Mixed culture from synthetic brewery (*Methanobacterium* and *Methanosaeta*)	400 mA m^{-2}	10% CO_2 removal	85.3	Xu et al. (2014)
Graphite	*in-situ* (Continuous)	Membrane less single chamber	Mixed culture from wastewater (*Methanobacterium* and *Methanosaeta*)	3000 mA m^{-2}	>8% CO_2 removal	90	Xu et al. (2014)
Stainless steel (Wall of AD)	*in-situ* (Batch)	MEC-AD in single chamber barrel shaped stainless-steel reactor	Mixed culture from wastewater treated MFC (*Methanocorpusculum, Methanospirillum, Methanobacterium, Methanobrevibacter, Methanoculleus*)	ng	98% CH_4	66.7	Bo et al. (2014)

AnOMBR: Anaerobic osmotic membrane bioreactor, ARS-HM: Ammonia recovery system based on hydrophobic membranes AD: Anaerobic digestion, MWWTP: Municipal Wastewater treatment plant, WWTP: Wastewater treatment plant, MFC-Microbial fuel cell, BES: Bioelectrochemical system, MSW: Municipal solid waste, MESC: Microbial electrolytic capture, separation and regeneration cell, UASB: Upflow anaerobic sludge blanket digestion, FWTP: Food waste treatment plant, MWCNT: Multiwall carbon nanotube, RVC Reticulated vitreous carbon, ng: Not given, Cu: Copper, Ni: Nickel, Pt: Platinum, Fe: Iron, Ti: Titanium.

has not been done yet. The currently tested multi-compartment systems are far behind for upscaling due to high energy consumption, low mass transfer rate, difficulty to operate in continuous mode and electrode fouling, causing the low production rate. To overcome these issues, some authors proposed tubular reactor systems. Tubular reactors are still at an early stage to test in BES based biogas upgrading.

Another research group also elaborated the BES based CH_4 enrichment by comparing the single and double-chamber configuration (Liu et al., 2017). In contrast to previous studies, CH_4 enrichment in a double-chamber (77% CH_4) configuration was more profound than single chamber (56% CH_4). The higher CH_4 enrichment in a double-chamber is due to the alkalization of catholyte, promoting more CO_2 removal from raw biogas. Also, the use of membrane limits the migration of O_2 from the anolyte and hence restricts the loss of reducing equivalents by maintaining anaerobic environment at the cathode (Rozendal et al., 2008). Furthermore, VFA accumulation in either single or multi-chamber BES reactor negatively affects CH_4 upgrading (Liu et al., 2017). In a single-chamber system, propionate and acetate were gradually accumulated; thereby, pH dropped (Liu et al., 2017). In this aspect, *ex-situ* biogas upgrading would not suffer from the VFA accumulation as high organic loading is not available in BES for *ex-situ* biogas upgrading; but, it has not been experimentally demonstrated. Therefore, reactor operation modes, in particular, *ex-situ, in-situ,* batch, and continuous, have significant contributions to conclude the reactor set-up.

H-shaped reactors were frequently used in continuous and batch mode for biogas upgrading as shown in Table 1. To prove the concept of biogas upgrading in the bio-electrochemically assisted system, the authors used an H-type reactor where the membrane separated the anode from the cathode compartment then compared it with the single-chamber BES reactor in *in-situ* and *ex-situ* modes (Xu et al., 2014). In the case of *in-situ* biogas upgrading, the electrodes were directly inserted into the anaerobic digestion to stimulate the simultaneous anaerobic degradation of organic material and CO_2 reduction into CH_4. In *ex-situ* systems, the biogas collected from AD is passed into the BES reactor, where CO_2 from biogas is reduced to CH_4 either directly accepting the electron from the electrode or indirectly through H_2. A report compared *in-situ* and *ex-situ* biogas upgrading in the continuous and batch modes (Xu et al., 2014). It was claimed that the CO_2 reduction rate was higher in *in-situ* than in *ex-situ* biogas upgrading based on the current density. The current density illustrated the amount of the charge utilized per unit of the electrode for the reduction of CO_2 where 0.4 A/m^2 current density was observed in *ex-situ,* almost half of the current density observed in *in-situ* 1 A/m^2; nevertheless, the charge transfer mechanism was not investigated thoroughly (Xu et al., 2014). Relatively, CO_2 gas-liquid mass transfer limitations caused lower current density in the *ex-situ* system where CO_2 produced in independent AD was bubbled into the cathode compartment (Xu et al., 2014). The *in-situ* systems are not subjected to the same challenges of CO_2 mass transfer because CO_2 is supplied by organic matter degradation co-occurring in the electrode chamber. Likewise, the single chamber *in-situ* reactor configuration has shown better performance in current density and biogas upgrading due to the availability of more nutrients and active biomass developed on the surface of the electrode (Krieg et al., 2014; Lee et al., 2019; Nogueira et al., 2003; Xu et al., 2014). *In-situ* systems will have multiple anaerobic fermentations involved apart from CO_2 reduction. There could be multiple substrates available in the *in-situ* process in addition to the electricity input. *In ex-situ* systems, only CO_2 reduction is targeted, and electricity remains the only energy source. These observations demonstrated that the operation mode is one of the driving factors for selecting the reactor. Furthermore, fundamental studies such as the investigation of electrode-microbes interaction, electron transfer mechanism, the impact of membranes, and explorations of electrochemical parameters need to perform in *in-situ* vs *ex-situ* to conclude. Other factors (CO_2 utilization, pH, CH_4 yield) should be considered before concluding the superiority of *in-situ* over *ex-situ*. Furthermore, various types of membranes have been used in BES reactors, for example, proton exchange membranes (PEM), anion-exchange membranes (AEM) and bipolar membranes, which are different in the limitation of O_2 diffusivity from the anode to cathode (Batlle-Vilanova et al., 2019; Kokkoli et al., 2018; Zeppilli et al., 2017). However, the impact of membrane on biogas upgrading has not been investigated in detail yet.

2.2. Electrode materials and electron transfer mechanism

Various carbon-based electrodes such as carbon felt, carbon paper, carbon brush, carbon fiber, carbon brush, and reticulated vitreous carbon (RVC) have been employed to create a three-dimensional structure for CO_2 reduction as shown in Table 1. The three-dimensional architecture in the electrode offers a high active surface area to facilitate microbial colonization and electrode interaction, thus possesses maximum electron transfer rate. Of these, carbon felt is the most common three dimensional electrode material intensively explored in BESs, particularly for electromethanogenesis, sensor, MFC and MES applications (Table 1) (Geppert et al., 2016). Recently, researchers tested the graphite plate and carbon brush electrodes for biogas upgrading, where CH_4 formation from CO_2 reduction at carbon brush was almost four-fold higher than that from the graphite plate cathode (Liu et al., 2020), which illustrates that the topography of the electrode has a significant impact on CO_2 reduction.

The catalytic reactive sites of electrode materials support in accelerating the indirect and direct electron transfer to reduce CO_2 as shown in Fig. 2. Autotrophic microbes can reduce CO_2 by accepting electrons from the cathode surface; nonetheless, the electron transfer mechanism is very little known and a highly debated topic on BES. A research reported electromethanogenesis activity with direct electron uptake from the cathode surface as an electron donor to produce the CH_4 (Cheng et al., 2009). Another study reported that CH_4 production either directly *via* extracellular electron transfer or indirectly *via* H_2 mediated from electrode (Batlle-Vilanova et al., 2015) while upgrading biogas. Furthermore, direct electron transfer (DET) mechanism by an enriched mixed culture dominated by *Methanothrix* and *Azonexus* species were reported for CO_2 reduction to CH_4 (Yin et al., 2016). Direct flow of

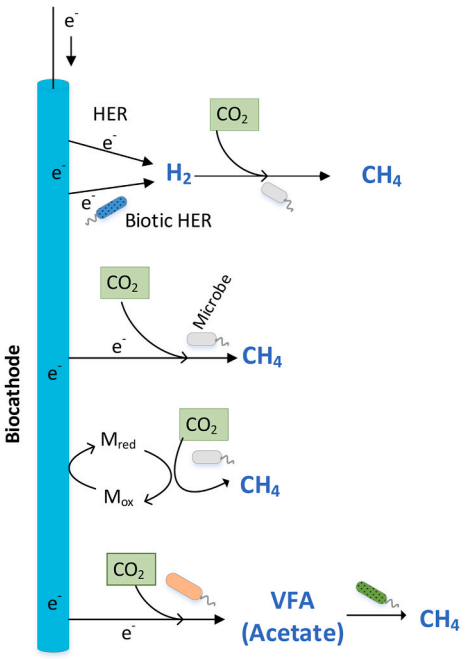


Fig. 2. Mechanism of electron transfer from biocathode in MES for methane production from CO_2. HER: hydrogen evolution reaction; M: redox couple, VFA: volatile fatty acid.

electrons to the electromethanogenesis activity could be more efficient than mediated electron transfer mechanism as DET does not involve the limitations pertaining to the redox activities and mass transfer of mediators (Yin et al., 2016).

The electrochemical interaction of bacterial cells on the metal-carbon composite electrode further accelerated the hydrogen evolution reaction (HER), and it has been proposed that redox enzymes or biometals can enhance the HER (Aryal et al., 2019; Deutzmann et al., 2015). The study illustrated that the biological conversion of CO_2 to CH_4 has resulted from the reduction reaction with H_2 while upgrading biogas (Bo et al., 2014). Several research articles reported that the cathodic H_2 formation could be used in biological CO_2 reduction and CH_4 formation. High H_2 production at the cathode and simultaneous biogas upgrading were achieved when using metallic electrodes such as Platinum coated titanium woven wire mesh or stainless steel (Blasco-Gómez et al., 2017). While exploring H_2 production from metal cathodes, metal-carbon composite electrodes of Cu–Ni and Fe coated onto graphite have also been utilized for biogas upgrading; however, the least insight has been given on the electrode performance (Park et al., 2018). In a related study, the metal-carbon composite electrode has been illustrated as one of the best electrode materials in BES (Gao et al., 2021; Zhou et al., 2020).

As another approach of biogas upgrading, CO_2 can also be absorbed or converted to acetate or formate at the cathode. Thereby, separating CO_2 from biogas can let the concentrated CH_4 at the outlet gas. A report demonstrated microbial CO_2 reduction to acetate in a biogas upgrading system by focusing on improving electrode design and operational parameters to utilize the CO_2 from synthetic biogas containing 70:30 v/v CH_4: CO_2 (Jourdin et al., 2016). Briefly, the authors developed multi-walled carbon nanotubes (MWCNT) from electrodeposited reticulated vitreous carbon (RVC) cathode, which generates multiple layers of micro, meso and macropores to provide high surface area cathodes with three-dimensional architecture to increase the bacteria-material interaction (Jourdin et al., 2016). The author reported 99% electron recovery to remove CO_2 in the form of acetate when applying an applied cathode potential of −1.1 V *vs* SHE with achieved −200 Am^{-2} current density. A similar observation was reported when SnO_2 nanoparticles were applied as a biocathode to upgrade the biogas where CO_2 was reduced to formate, stimulating the concentration of the 90% CH_4 in off-gas stream (Gao et al., 2021). These studies show that the electrode material development and its spatial surface modification are key strategies to optimize the electrode–microbe interactions, thereby reducing CO_2 fraction from biogas while upgrading (Elsamadony et al., 2021).

Economically cheap and bioelectrochemically efficient electrode materials are required to reduce the capital expenditure (CAPEX) of the BES reactor. This can support upscaling the technology. The cost of biogas upgrading by using physiochemical technology varies with CAPEX and operating expense (OPEX) (Angelidaki et al., 2018). A recent study revealed that around € 0.15/m^3 of CH_4 was spent when 1000 m^3/h biogas upgrading installation (conventional) was operated (IREA, 2017). Nevertheless, the per-unit cost decreased with larger installation capacities. If the plant capacity is high then the overall investment for upgrading will also be high. But when the output quantity is high, then the investment cost per unit output (here per cubic meter methane) will decrease (Sun et al., 2015). The economic assessment of BES technology is still the less explored; nevertheless, the economic evaluation reports of electricity production in MFC while treating municipality wastewater treatment have been available. It questioned the practical application to compete with conventional WWTP (Batlle-Vilanova et al., 2019). A report compared the different economic scenarios of the biogas upgrading process in BES, including the benefits of anodic chlorine production when combining wastewater treatment and biogas upgrading. The authors highlighted that the multiple purposes use of the BES system could gain an economic advantage in the future; nevertheless, the BES system has shown the least economic potential in the present scenario (Batlle-Vilanova et al., 2019). Future research has to focus on enhancing CH_4 production rate applying cheap renewable energy to compete with traditional commercial biogas upgrading plants. In another study, economic feasibility of BES technology was compared at the different scenarios of the cost-benefit assessment for chemical synthesis (acetic acid in particular) in MES technology from CO_2 (Christodoulou and Velasquez-Orta, 2016). Additionally, the case for the coupling of MES and AD were also presented considering the CO_2 conversions to acids (Christodoulou and Velasquez-Orta, 2016), but CO_2 utilization for CH_4 production was not explicitly analyzed. Likewise, the sustainability assessment aspect of acetate production from CO_2 in BES reported that significant improvement in production rate is essential to compete with fossil-based technology (Gadkari et al., 2021). The BES currently has a low technology readiness level (TRL); therefore, significant development is necessary before competing with current commercial physiochemical biogas upgrading technologies (Aryal et al., 2021b).

2.3. Adding value to the biogas upgrading: recovery of resources and ions

BES offers the unique capability to recover resources from wastes. For example, organics and biomasses can be converted into electricity at the anode, while nutrients and metals can be recovered at the cathode (Colombo et al., 2017; Patel et al., 2021). Recently, researchers demonstrated the recovery or removal of nitrogen and phosphorus from the waste stream through nitrification and bioelectrochemical denitrification (Bajracharya et al., 2016a; Zeppilli et al., 2017, 2019b).

Recovering nitrogen from waste is a sustainable approach to maintain nutrient cycling, which could minimize the cost of nitrogen fixation. The bioelectrochemically recovered nitrogen is an excellent source of nutrients that can be utilized as fertilizer in the agriculture field. The nitrogen recovery could be in the form of ammonium. Ammonium ions (NH_4^+) can moves across the ion exchange membranes due to either current-driven or diffusion-driven migration. It has been reported that a higher current density could enhance NH_4^+ transportation to the cathode compartment due to the electricity-driven migration, though the high pH of the catholyte can drive ammonia to escape during the recovery process (Kelly and He, 2013).

In multi-tasking approach of bioelectrochemical biogas upgrading, resource recovery was introduced where nutrients from the anode side was recovered while upgrading the biogas at the cathode (Zeppilli et al., 2017). The middle accumulation compartment was separated from the anode compartment by a CEM, while the cathode compartment was separated by an AEM. The NH_4^+ ions migrate from anolyte to the accumulation compartment through the proton exchange membrane due to the electricity-driven migration. Likewise, CH_3COO^- and HCO_3^- migrate from catholyte to the accumulation chamber through the anion exchange membrane. Moreover, the same research group has modified the reactor configuration by placing double cathode system to recover better NH_4^+, CH_3COO^- and HCO_3^- without compromising the purity of CH_4 enrichment (Zeppilli et al., 2017, 2019b). Yet another study reported a recovered CO_2 using a three-compartment reactor system where CO_3^{2-} and HCO_3^- at the cathode compartment migrate through the anion exchange membrane to the middle regeneration compartment that allows the recovery of pure CO_2 while upgrading biogas (Jin et al., 2017). In the following study, the same research group recovered CO_2 *in-situ* and then regenerated it *via* alkali and acid regeneration while treating wastewater in the anode compartment and biogas upgrading at the cathode (Kokkoli et al., 2018). It was also reported that the anodic chloride oxidation reaction is 45% less energy demanding compared to water oxidation (Du et al., 2015). Thus, anodic chlorine production while transforming the CO_2 containing effluent (e.g. biogas or wastewater) in the cathode of a BES into CH_4 is a better alternative to recover the disinfecting agent (Batlle-Vilanova et al., 2019). Authors further claimed that BES reactor has the potential to compensate current physiochemical biogas upgrading system because it can *in-situ* generate necessary chemicals, in particular acid and alkaline. Furthermore, CH_4

loss is below 1.4%, and separated pure CO_2 can be further utilized (Jin et al., 2017). The possibility of simultaneous biogas upgrading and resource recovery has been well illustrated *via* bioelectrochemical approaches.

Another report demonstrated the simultaneous sulfur (S^0) recovery from anodic oxidation of H_2S and cathodic biogas upgrading from CO_2 reduction (Fu et al., 2020). The author proposed applying electron shuttle Fe_2^+/Fe_3^+ at anode to continuously drive the H_2S oxidation and energy conservation in the BES reactor. Similarly, an electro-methanogenic microbial electrolysis cell (MEC) connected to an ammonia recovery system based on hydrophobic membranes (ARS-HM) was tested to recover ammonia from the anodic compartment (NH_4^+-N), while upgrading biogas at the cathode (Cerrillo et al., 2021). The recovered ammonia supported to regulate pH value that boosted CH_4 production rate almost two folds (Cerrillo et al., 2021). Therefore, BES is a reliable technology for simultaneous biogas purification and resource recovery; still, the profitability of recovered ions have not been compared yet.

2.4. Reactor operation modes

BES for biogas upgrading is currently limited to the laboratory scale reactor that has been operated in fed-batch and continuous operational modes, as shown in Table 1. Most of the BES reactors were operated in batch; conversely, continuous operation mode was reported with superior performance over batch and fed-batch mode. The CH_4 production rate was increased three times when the BES reactor was shifted from batch mode to continuous mode (Batlle-Vilanova et al., 2015). The continuous and gas recirculation modes are likely to supply substrate CO_2 to support overcoming the mass transfer limitations (Bajracharya et al., 2022; Bian et al., 2021). The continuous proton production at the anode resulted in acidification. In contrast, alkalization at the cathode due to the reduction reaction (consumption of proton) created the pH gradients, which could deteriorate the biofilm activities of electro-methanogens (Torres et al., 2008b). Apart from biofilm stability, a high pH gradient could cause increased power consumption where 59 mV for each unit of pH drop was reported, which explains the overpotential of the system and energy loss for CO_2 reduction (Sleutels et al., 2009). Therefore, adding an acid or CO_2 was proposed as an alternative approach to compensate for potential loss associated with the pH gradient over the cathode and anode compartment (Torres et al., 2008a).

Other operating parameters such as the applied voltage, VFAs profile during start-up period and pH may also directly impact on biogas upgrading (Park et al., 2018). The BES system accelerated the CH_4 production in AD utilizing the accumulated H_2 ions and VFAs degradation during the start-up period (Park et al., 2018). Another report applied 1 V of cell voltage in a single-chamber BES system to observe the CH_4 upgrading in different substrate conditions (Lee et al., 2019). The CH_4 production rate was doubled compared to the control; nevertheless, the stability of AD and the system performances was found heavily dependent on pH, VFAs profile and applied potential. A similar observation was reported when the applied cell voltage was increased from 0 to 4 V; the maximum CH_4 content was reached 97.9% from the initial 60% CH_4, thereby reported cell potential dependency for biogas upgrading (Zhou et al., 2020). Not limited to the cell potential of the BES reactor, the mode of electronic operation (potentiostat and galvanostatic) has a significant impact, especially in the multi-compartment reactor. Another group of researchers operated the simultaneous biogas upgrading and ammonium recovery using a three-compartment BES reactor. The author reported improvement in the current draw by galvanostatic operation, promoting CO_2 removal by 113% compared to the potentiostatic condition (Zeppilli et al., 2021a). The polarization control to cathode rather than anode also promotes the CH_4 generation while using system to treat chemical oxygen demand at the anode and biogas upgrading at the cathode (Zeppilli et al., 2019a).

2.5. Microbial communities in biocathode for methane enrichment

Microbial biogas upgrading requires the removal and consequent reduction of CO_2 to CH_4 by adding electron sources such as H_2. However, inappropriate H_2 addition in AD process could accumulate the VFA that shifts the microbial dynamics, whereas low concentration favors stable dynamics to reduce CO_2 or CH_4 formation. Towards such argument, a report compared the effect of H_2 addition in *in-situ* biogas upgrading reactor and BES reactor (Tartakovsky et al., 2021). Due to the addition, of exogenous H_2, accumulation of 6 g/l acetate was observed in the *in-situ* biogas upgrading reactor. In contrast, acetate accumulation was not observed in the BES reactor, and, thereby, superior performance of the BES reactor was claimed (Tartakovsky et al., 2021). *In-situ* H_2 generation by applying the BES could increase hydrogenotrophic methanogenic activity, thereby modifying the microbial dynamics (Cerrillo et al., 2021; Gao et al., 2021). The poised electrode in the BES contained significantly higher cathode-associated biomass, which was confirmed from protein analysis of biofilms developed at the cathode. The hydrogenotrophic methanogenic species were observed as the main dominating species in the microbial community in 16S rRNA sequences analysis (Bo et al., 2014).

Methanobacterium remained the most abundant species at the cathode when the reactor was operated in continuous and batch modes, as shown in Table 1. Microbial community analysis of biogas upgrading cathode reported that the relative dominance of *Methanospirillum* was increased from 16.0 to 68.4% when electrode potential was increased (Bo et al., 2014). Similarly, molecular biology investigation based on qPCR studies showed that the MEC coupling in AD did not significantly impact acetoclastic methanogens (Bo et al., 2014). Acetoclastic methanogens split acetate into CH_4 and CO_2. The persistence of acetoclastic methanogens could be due to the availability of acetate; even at autotrophic conditions, CO_2 was metabolized by other microbial consortiums (homoacetogens) to acetate which become available for further utilization by acetoclastic methanogens. In contrast, the abundance of hydrogenotrophic methanogens such as *Methanomicrobiales* and *Methanobacteriales* was enhanced up to 17.2 folds (Gajaraj et al., 2017). Thus, selective enrichment of hydrogenotrophic methanogens due to hydrogen production via bioelectrochemical pathways can be inferred.

Moreover, applying highly negative potential benefits hydrogenotrophic methanogens activity because of the associated *in-situ* H_2 evolution. A report observed enriched species of *Azonexus* (nitrogen-fixing bacteria) by 42% at cathode and <0.5% in the bulk sludge when −500 mV potential was applied at cathode. Interestingly, *Azonexus* species dropped by 28% within 9 days when external voltage supply was removed; this shows the microbial dynamics under the selectivity imposed due to externally applied voltage (Liu et al., 2019). In most research, hydrogenotrophic methanogens were dominated due to hydrogen production from the externally applied voltage; however, selectivity of acetoclastic methanogens was not observed during biogas upgrading.

3. Prospective and challenges

The prospect of the technology is encouraging as it is a sustainable platform for CO_2 utilization and biomethane synthesis, but the following prospective and challenges are identified.

I. Achieving high coulombic efficiency with low overpotential is the main challenge for the economic operation of biogas upgrading in the BES reactor. To tackle the challenge, BES requires improvements by establishing synergy from other scientific disciplines. Hence research has to be focused on improving CO_2 reduction rate by selecting/enriching the microbiome of active species of microbes (Jiang et al., 2019; Kracke et al., 2019). Exotic microbial habitats of chemolithotrophs such as deep saline sediments (Alqahtani et al., 2019, 2020) and underground caves and mines

etc. could be explored to find new active microbial species as biocatalysts. In another case, metabolically engineered species can also be developed to enhanced electroactivity and CO_2 uptake capacity of the microorganisms. Further studies on the molecular mechanism and metabolic process of CO_2 capturing and conversion are required to advance in metabolic engineering attempts.

II. Multi-compartment reactor configurations have shown 100% CH_4 enrichment (Kokkoli et al., 2018). However, optimal operational parameters must be investigated to achieve high rate biomethane production with simultaneous recovery (ions) and efficient CO_2 regeneration. *In-situ* and *ex-situ* approaches of biogas upgrading were widely applied where CH_4 enrichment up to natural gas quality was not achieved in most of the study; therefore, the synergy of *in-situ* and *ex-situ* (Hybrid) could support further CO_2 utilization into CH_4 (Corbellini et al., 2018). At the same time, the reactor design needs to be adapted to ensure an adequate supply of CO_2 when the system is scaled up. A high rate of uptake and conversion of CO_2 with stable performance and lower cell overpotentials have to be considered when practical applications are developed. The energy supply to produce electrons and H_2 has been claimed from renewable sources; however, real integration of renewable electricity and BES reactor is not yet reported. In the future, integration scenarios of BES reactor and renewable electricity should be done rather than commercial H_2 gas or commercial power supplies.

III. The combination of BES and fermentation technology was claimed as profitable bioprocess for the value-added product synthesis utilizing nenewable electrical energy (Christodoulou et al., 2017). In that context CO_2 can be supplied from biogas as a carbon source for electrochemically ctive microbes and renewable energy (wind, hydro etc) as energy source for up-scaling the reactor.

IV. In addition, membrane, reactor design, electrode materials and their arrangement in the reactor (surface area/volume ratio) for a pilot or large scale are still unknown. Membrane materials limit the CAPEX and OPEX of BES while up-scaling technology. Relatively cheap membranes such as agar-containing membranes could replace costly conventional membranes (Hernández-Flores et al., 2016).Moreover. the controlling cathode/cell potential has a significant contribution to operational cost. Further research to control the electric potential losses such as ohmic losses, charge transfer resistance, and pH gradient should be improved for up scaling the technology.

V. A new fermentation platform producing high-value products (sucrose, biofuels, biopolymers, proteins, and enzymes) apart from CH_4 can be promising in BES biogas upgrading. Thus, product diversification in reduction process could strengthen the technology for the commercially viable applications. Nonetheless, downstream recovery of the product is still challenging.

VI. The CH_4 production rate was increased up to 12.5 L CH_4/L/d, by using redox flow battery design which was claimed as one of the highest production rate in BES; but, CO_2 was supplied instead of biogas upgrading (Geppert et al., 2019). That illustrated the reactor design has significant role to optimize the process therefore redox flow battery design can be used for biogas upgrading (Bajracharya et al., 2016b; Geppert et al., 2019). Porous hollow fiber cathode designs have also been shown effective for delivering CO_2 immediately at the reduction site of the cathode thereby avoiding mass transfer limitation (Alqahtani et al., 2018, 2020; Bian et al., 2018) Biogas upgrading using such electrode in reactor set would be attractive to upgrade biogas. The electron transfer mechanism in MES has been poorly known among methanogens. Thus, multidisciplinary knowledge to engineer the electrode, configure the reactor system and energy supply that allows microbial interaction to enhance the electron transfer should be acquired (Singh et al., 2020).

4. Conclusion

This review provides an overview of research advances in microbial electrochemical approaches for biogas upgrading technology in different operating conditions, in particular *in-situ*, *ex-situ*, batch mode, continuous mode. Briefly, reactor configuration, electrode materials used for CO_2 reduction to CH_4 have been thoroughly summarized. Additionally, the possibility of integration of bioelectrochemical biogas upgrading with multiple applications, such as nutrient and resource recovery, are presented. The cathode material has significant influences on reactor performances, and the dynamics of the microbial community at biocathode can be controlled with the applied voltage. Further understanding and studies on the coupling of AD and BES is important for up scaling applications. The prospect of the technology is encouraging as it is a sustainable platform for CO_2 utilization and biomethane production.

Credit author statement

Nabin Aryal: Conceptualization, Data curation, Writing – original draft, Writing – review & editing. Yifeng Zhang: Writing – review & editing, Suman Bajaracharya: Writing – review & editing, Deepak Pant: Writing – review & editing, Xuyuan Chen: Writing – review & editing.

Declaration of competing interest

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

Acknowledgement

Aryal N. would like to thanks Regionalt Forskningsfond Vestfold og Telemark (RFFVT), Norway for "AddCar Project" and the strategic research plan “Energy and Climate Challenge” of University of South-Eastern Norway for financial support to perform the research. Zhang Y. thanks the Carlsberg Foundation for the Distinguished Fellowships Grant (CF18-0084), Denmark.

References

Ahring, B.K., Sandberg, M., Angelidaki, I., 1995. Volatile fatty acids as indicators of process imbalance in anaerobic digestors. Appl. Microbiol. Biotechnol. 43, 559–565. https://doi.org/10.1007/BF00218466.

Alqahtani, M.F., Bajracharya, S., Katuri, K.P., Ali, M., Ragab, A., Michoud, G., Daffonchio, D., Saikaly, P.E., 2019. Enrichment of marinobacter sp. and halophilic homoacetogens at the biocathode of microbial electrosynthesis system inoculated with red sea brine pool. Front. Microbiol. 10, 2563. https://doi.org/10.3389/fmicb.2019.02563.

Alqahtani, M.F., Bajracharya, S., Katuri, K.P., Ali, M., Xu, J., Alarawi, M.S., Saikaly, P.E., 2020. Enrichment of salt-tolerant CO_2–fixing communities in microbial electrosynthesis systems using porous ceramic hollow tube wrapped with carbon cloth as cathode and for CO_2 supply. Sci. Total Environ. 766, 142668. https://doi.org/10.1016/j.scitotenv.2020.142668.

Alqahtani, M.F., Katuri, K.P., Bajracharya, S., Yu, Y., Lai, Z., Saikaly, P.E., 2018. Porous hollow fiber nickel electrodes for effective supply and reduction of carbon dioxide to methane through microbial electrosynthesis. Adv. Funct. Mater. 28, 1–8. https://doi.org/10.1002/adfm.201804860.

Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., Kougias, P.G., 2018. Biogas upgrading and utilization: current status and perspectives. Biotechnol. Adv. https://doi.org/10.1016/j.biotechadv.2018.01.011.

Aryal, N., Ammam, F., Patil, S.A., Pant, D., 2017. An overview of cathode materials for microbial electrosynthesis of chemicals from carbon dioxide. Green Chem. 19, 5748–5760. https://doi.org/10.1039/c7gc01801k.

Aryal, N., Kvist, T., 2018. Alternative of biogas injection into the Danish gas grid system—a study from demand perspective. ChemEngineering 2, 43. https://doi.org/10.3390/chemengineering2030043.

Aryal, N., Kvist, T., Ammam, F., Pant, D., Ottosen, L.D.M., 2018. An overview of microbial biogas enrichment. Bioresour. Technol. https://doi.org/10.1016/j.biortech.2018.06.013.

Aryal, N., Mørck Ottosen, L.D., Bentien, A., Pant, D., Wegener Kofoed, M.V., 2021a. Bioelectrochemical Systems for Biogas Upgrading and Biomethane Production, Emerging Technologies and Biological Systems for Biogas Upgrading. INC. https://doi.org/10.1016/b978-0-12-822808-1.00013-1.

Aryal, N., Ottosen, L.D.M., Kofoed, M.V.W., Pant, D., 2021b. Emerging Technologies and Biological Systems for Biogas Upgrading. Elesvier.

Aryal, N., Wan, L., Overgaard, M.H., Stoot, A.C., Chen, Y., Tremblay, P.L., Zhang, T., 2019. Increased carbon dioxide reduction to acetate in a microbial electrosynthesis reactor with a reduced graphene oxide-coated copper foam composite cathode. Bioelectrochemistry 128, 83–93. https://doi.org/10.1016/j.bioelechem.2019.03.011.

Bajracharya, S., Krige, A., Matsakas, L., Rova, U., Christakopoulos, P., 2022. Dual cathode configuration and headspace gas recirculation for enhancing microbial electrosynthesis using Sporomusa ovata. Chemosphere 287, 132188. https://doi.org/10.1016/j.chemosphere.2021.132188.

Bajracharya, S., Sharma, M., Mohanakrishna, G., Dominguez Benetton, X., Strik, D.P.B.T.B., Sarma, P.M., Pant, D., 2016a. An overview on emerging bioelectrochemical systems (BESs): technology for sustainable electricity, waste remediation, resource recovery, chemical production and beyond. Renew. Energy 98, 153–170. https://doi.org/10.1016/j.renene.2016.03.002.

Bajracharya, S., Vanbroekhoven, K., Buisman, C.J.N., Pant, D., Strik, D.P.B.T.B., 2016b. Application of gas diffusion biocathode in microbial electrosynthesis from carbon dioxide. Environ. Sci. Pollut. Res. 23, 22292–22308. https://doi.org/10.1007/s11356-016-7196-x.

Batlle-Vilanova, P., Puig, S., Gonzalez-Olmos, R., Vilajeliu-Pons, A., Balaguer, M.D., Colprim, J., 2015. Deciphering the electron transfer mechanisms for biogas upgrading to biomethane within a mixed culture biocathode. RSC Adv. 5, 52243–52251. https://doi.org/10.1039/c5ra09039c.

Batlle-Vilanova, P., Rovira-Alsina, L., Puig, S., Balaguer, M.D., Icaran, P., Monsalvo, V. M., Rogalla, F., Colprim, J., 2019. Biogas upgrading, CO_2 valorisation and economic revaluation of bioelectrochemical systems through anodic chlorine production in the framework of wastewater treatment plants. Sci. Total Environ. https://doi.org/10.1016/j.scitotenv.2019.06.361.

Bian, B., Alqahtani, M.F., Katuri, K.P., Liu, D., Bajracharya, S., Lai, Z., Saikaly, P.E., 2018. Porous nickel hollow fi ber cathodes coated with CNTs for e ffi cient microbial electrosynthesis of acetate from CO_2 using Sporomusa ovata. J. Mater. Chem. 6, 17201–17211. https://doi.org/10.1039/c8ta05322g.

Bian, B., Xu, J., Katuri, K.P., Saikaly, P.E., 2021. Resistance assessment of microbial electrosynthesis for biochemical production to changes in delivery methods and CO_2 flow rates. Bioresour. Technol. 319, 124177. https://doi.org/10.1016/j.biortech.2020.124177.

Blasco-Gómez, R., Batlle-Vilanova, P., Villano, M., Balaguer, M.D., Colprim, J., Puig, S., 2017. On the edge of research and technological application: a critical review of electromethanogenesis. Int. J. Mol. Sci. 18, 1–32. https://doi.org/10.3390/ijms18040874.

Bo, T., Zhu, X., Zhang, L., Tao, Y., He, X., Li, D., Yan, Z., 2014. A new upgraded biogas production process: coupling microbial electrolysis cell and anaerobic digestion in single-chamber, barrel-shape stainless steel reactor. Electrochem. Commun. 45, 67–70. https://doi.org/10.1016/j.elecom.2014.05.026.

Cerrillo, M., Burgos, L., Bonmatí, A., 2021. Biogas upgrading and ammonia recovery from livestock manure digestates in a combined electromethanogenic biocathode—hydrophobic membrane system. Energies 14, 503. https://doi.org/10.3390/en14020503.

Cheng, S., Xing, D., Call, D.F., Logan, B.E., 2009. Direct biological conversion of electrical current into methane by electromethanogenesis. Environ. Sci. Technol. 43, 3953–3958. https://doi.org/10.1021/es803531g.

Christodoulou, X., Okoroafor, T., Parry, S., Velasquez-Orta, S., 2017. The use of carbon dioxide in microbial electrosynthesis: advancements, sustainability and economic feasibility. J. CO_2 Util. 22, 407–408. https://doi.org/10.1016/j.jcou.2017.11.006.

Christodoulou, X., Velasquez-Orta, S.B., 2016. Microbial electrosynthesis and anaerobic fermentation: an economic evaluation for acetic acid production from CO_2 and CO. Environ. Sci. Technol. acs.est.6b02101. https://doi.org/10.1021/acs.est.6b02101.

Colombo, A., Marzorati, S., Lucchini, G., Cristiani, P., Pant, D., Schievano, A., 2017. Assisting cultivation of photosynthetic microorganisms by microbial fuel cells to enhance nutrients recovery from wastewater. Bioresour. Technol. 237, 240–248. https://doi.org/10.1016/j.biortech.2017.03.038.

Corbellini, V., Kougias, P.G., Treu, L., Bassani, I., Malpei, F., Angelidaki, I., 2018. Hybrid biogas upgrading in a two-stage thermophilic reactor. Energy Convers. Manag. 168, 1–10. https://doi.org/10.1016/j.enconman.2018.04.074.

Daniels, L., Belay, N., Rajagopal, S.B., Weimer, J.P., 1987. Bacterial methanogenesis and growth from CO_2 with elemental iron as the sole source of electrons. Science 273, 509–511.

Deutzmann, J., Sahin, M., Spormann, A., 2015. Extracellular enzymes facilitate electron uptake in biocorrosion and. mBio 6, 1–8. https://doi.org/10.1128/mBio.00496-15.

Du, J., Chen, Z., Chen, C., Meyer, T.J., 2015. A half-reaction alternative to water oxidation: chloride oxidation to chlorine catalyzed by silver ion. J. Am. Chem. Soc. 137, 3193–3196. https://doi.org/10.1021/jacs.5b00037.

Elsamadony, M., Elreedy, A., Mostafa, A., Fujii, M., Gescher, J., Yekta, S.S., Schnu, A., 2021. Perspectives on potential applications of nanometal derivatives in gaseous bioenergy pathways: mechanisms, life cycle, and toxicity. ACS Sustain. Chem. Eng. https://doi.org/10.1021/acssuschemeng.1c02260.

Fu, S., Angelidaki, I., Zhang, Y., 2021. In situ biogas upgrading by CO_2-to-CH_4 bioconversion. Trends Biotechnol. 39, 336–347. https://doi.org/10.1016/j.tibtech.2020.08.006.

Fu, X.Z., Li, J., Pan, X.R., Huang, L., Li, C.X., Cui, S., Liu, H.Q., Tan, Z.L., Li, W.W., 2020. A single microbial electrochemical system for CO_2 reduction and simultaneous biogas purification, upgrading and sulfur recovery. Bioresour. Technol. 297, 122448. https://doi.org/10.1016/j.biortech.2019.122448.

Gadkari, S., Haji, B., Beigi, M., Aryal, N., Sadhukhan, J., Mirza Beigi, B.H., Aryal, N., Sadhukhan, J., 2021. Microbial electrosynthesis: is it sustainable for bioproduction of acetic acid? RSC Adv. 11, 9921–9932. https://doi.org/10.1039/d1ra00920f.

Gajaraj, S., Huang, Y., Zheng, P., Hu, Z., 2017. Methane production improvement and associated methanogenic assemblages in bioelectrochemically assisted anaerobic digestion. Biochem. Eng. J. 117, 105–112. https://doi.org/10.1016/j.bej.2016.11.003.

Gao, T., Zhang, H., Xu, X., Teng, J., 2021. Integrating microbial electrolysis cell based on electrochemical carbon dioxide reduction into anaerobic osmosis membrane reactor for biogas upgrading. Water Res. 190, 116679. https://doi.org/10.1016/j.watres.2020.116679.

Geppert, F., Liu, D., van Eerten-Jansen, M., Weidner, E., Buisman, C., ter Heijne, A., 2016. Bioelectrochemical power-to-gas: state of the art and future perspectives. Trends Biotechnol. https://doi.org/10.1016/j.tibtech.2016.08.010.

Geppert, F., Liu, D., Weidner, E., Heijne, A. ter, 2019. Redox-flow battery design for a methane-producing bioelectrochemical system. Int. J. Hydrogen Energy 44, 21464–21469. https://doi.org/10.1016/j.ijhydene.2019.06.189.

Gong, J., English, N.J., Pant, D., Patzke, G.R., Protti, S., Zhang, T., 2021. Power-to-X: lighting the path to a net-zero-emission future. ACS Sustain. Chem. Eng. 9, 7179–7181. https://doi.org/10.1021/acssuschemeng.1c03212.

Hernández-Flores, G., Poggi-Varaldo, H.M., Solorza-Feria, O., 2016. Comparison of alternative membranes to replace high cost Nafion ones in microbial fuel cells. Int. J. Hydrogen Energy 41, 23354–23362. https://doi.org/10.1016/j.ijhydene.2016.08.206.

IREA, 2017. Biogas for Road Vehicles Technologu Brief. IREA Int. Renew. Energy Agency.

Jiang, Y., May, H.D., Lu, L., Liang, P., Huang, X., Ren, Z.J., Lu, L., Liang, P., Huang, X., Ren, Z.J., 2019. Carbon dioxide and organic waste valorization by microbial electrosynthesis and electro-fermentation. Water Res. 149, 42–55. https://doi.org/10.1016/J.WATRES.2018.10.092.

Jin, X., Zhang, Y., Li, X., Zhao, N., Angelidaki, I., 2017. Microbial electrolytic capture, separation and regeneration of CO_2 for biogas upgrading. Environ. Sci. Technol. 51, 9371–9378. https://doi.org/10.1021/acs.est.7b01574.

Jourdin, L., Freguia, S., Flexer, V., Keller, J., 2016. Bringing high-rate, CO_2-based microbial electrosynthesis closer to practical implementation through improved electrode design and operating conditions. Environ. Sci. Technol. 50, 1982–1989. https://doi.org/10.1021/acs.est.5b04431.

Kaur, R., Singh, S., Chhabra, V.A., Marwaha, A., Kim, K.H., Tripathi, S.K., 2021. A sustainable approach towards utilization of plastic waste for an efficient electrode in microbial fuel cell applications. J. Hazard Mater. 417, 125992. https://doi.org/10.1016/J.JHAZMAT.2021.125992.

Kelly, P.T., He, Z., 2013. Nutrients removal and recovery in bioelectrochemical systems: a review. Bioresour. Technol. 153, 351–360. https://doi.org/10.1016/j.biortech.2013.12.046.

Kokkoli, A., Zhang, Y., Angelidaki, I., 2018. Microbial electrochemical separation of CO_2 for biogas upgrading. Bioresour. Technol. 247, 380–386. https://doi.org/10.1016/j.biortech.2017.09.097.

Kracke, F., Wong, A.B., Maegaard, K., Deutzmann, J.S., Hubert, M.A., Hahn, C., Jaramillo, T.F., Spormann, A.M., 2019. Robust and biocompatible catalysts for efficient hydrogen-driven microbial electrosynthesis. Commun. Chem. 2, 45. https://doi.org/10.1038/s42004-019-0145-0.

Krieg, T., Sydow, A., Schröder, U., Schrader, J., Holtmann, D., 2014. Reactor concepts for bioelectrochemical syntheses and energy conversion. Trends Biotechnol. 32, 645–655. https://doi.org/10.1016/j.tibtech.2014.10.004.

Kvist, T., Aryal, N., 2019. Methane loss from commercially operating biogas upgrading plants. Waste Manag. 87, 295–300. https://doi.org/10.1016/j.wasman.2019.02.023.

Lee, M., Nagendranatha Reddy, C., Min, B., 2019. In situ integration of microbial electrochemical systems into anaerobic digestion to improve methane fermentation at different substrate concentrations. Int. J. Hydrogen Energy 44, 2380–2389. https://doi.org/10.1016/j.ijhydene.2018.08.051.

Li, Y., Alaimo, C.P., Kim, M., Kado, N.Y., Peppers, J., Xue, J., Wan, C., Green, P.G., Zhang, R., Jenkins, B.M., Vogel, C.F.A., Wuertz, S., Young, T.M., Kleeman, M.J., 2019. Composition and toxicity of biogas produced from different feedstocks in California. Environ. Sci. Technol. https://doi.org/10.1021/acs.est.9b03003.

Liu, C., Sun, D., Zhao, Z., Dang, Y., Holmes, D.E., 2019. Methanothrix enhances biogas upgrading in microbial electrolysis cell via direct electron transfer. Bioresour. Technol. 291, 121877. https://doi.org/10.1016/j.biortech.2019.121877.

Liu, C., Xiao, J., Li, H., Chen, Q., Sun, D., Cheng, X., Li, P., Dang, Y., Smith, J.A., Holmes, D.E., 2021. High efficiency in-situ biogas upgrading in a bioelectrochemical system with low energy input. Water Res. 197, 117055. https://doi.org/10.1016/j.watres.2021.117055.

Liu, C., Yuan, X., Gu, Y., Chen, H., Sun, D., Li, P., Li, M., Dang, Y., Smith, J.A., Holmes, D. E., 2020. Enhancement of bioelectrochemical CO_2 reduction with a carbon brush electrode via direct electron transfer. ACS Sustain. Chem. Eng. 11368−11375 https://doi.org/10.1021/acssuschemeng.0c03623.

Liu, S.Y., Charles, W., Ho, G., Cord-Ruwisch, R., Cheng, K.Y., 2017. Bioelectrochemical enhancement of anaerobic digestion: comparing single- and two-chamber reactor

configurations at thermophilic conditions. Bioresour. Technol. 245, 1168–1175. https://doi.org/10.1016/j.biortech.2017.08.095.
Logan, B.E., Rabaey, K., 2012. Conversion of wastes into bioelectricity and chemicals by using microbial electrochemical technologies. Science 337, 686–690. https://doi.org/10.1126/science.1217412, 80-.
Logan, B.E., 2010. Scaling up microbial fuel cells and other bioelectrochemical systems. Appl. Microbiol. Biotechnol. 85, 1665–1671. https://doi.org/10.1007/s00253-009-2378-9.
Murto, M., Björnsson, L., Mattiasson, B., 2004. Impact of food industrial waste on anaerobic co-digestion of sewage sludge and pig manure. J. Environ. Manag. 70, 101–107. https://doi.org/10.1016/j.jenvman.2003.11.001.
Nancharaiah, Y.V., Venkata Mohan, S., Lens, P.N.L., 2015. Metals removal and recovery in bioelectrochemical systems: a review. Bioresour. Technol. 195, 102–114. https://doi.org/10.1016/j.biortech.2015.06.058.
Nelabhotla, A.B.T., Pant, D., Dinamarca, C., 2021. Power-to-gas for methanation. In: Emerging Technologies and Biological Systems for Biogas Upgrading. Academic Press, pp. 187–221.
Nogueira, R., Melo, L.F., Purkhold, U., Wuertz, S., Wagner, M., 2003. Erratum: nitrifying and heterotrophic population dynamics in biofilm reactors: effects of hydraulic retention time and the presence of organic carbon (Water Research (2002) 36 (469-481) PII: S0043135401002299. Water Res. 37, 2531. https://doi.org/10.1016/S0043-1354(02)00077-5.
Park, J., Lee, B., Tian, D., Jun, H., 2018. Bioelectrochemical enhancement of methane production from highly concentrated food waste in a combined anaerobic digester and microbial electrolysis cell. Bioresour. Technol. 247, 226–233. https://doi.org/10.1016/j.biortech.2017.09.021.
Patel, M., Patel, S.S., Kumar, P., Mondal, D.P., Singh, B., Khan, M.A., Singh, S., 2021. Advancements in spontaneous microbial desalination technology for sustainable water purification and simultaneous power generation: a review. J. Environ. Manag. 297, 113374. https://doi.org/10.1016/j.jenvman.2021.113374.
Rodríguez Arredondo, M., Kuntke, P., Jeremiasse, A.W., Sleutels, T.H.J.A., Buisman, C.J.N., ter Heijne, A., 2015. Bioelectrochemical systems for nitrogen removal and recovery from wastewater. Environ. Sci. Water Res. Technol. 1, 22–33. https://doi.org/10.1039/C4EW00066H.
Rozendal, A., Hamelers, H.V.M., Rabaey, K., Keller, J., Buisman, C.J.N., 2008. Towards practical implementation of bioelectrochemical wastewater treatment. Trends Biotechnol. 26, 450–459. https://doi.org/10.1016/j.tibtech.2008.04.008.
Schievano, A., Goglio, A., Erckert, C., Marzorati, S., Rago, L., Cristiani, P., 2018. Organic waste and bioelectrochemical systems: a future interface between electricity and methane distribution grids. Detritus 1, 57. https://doi.org/10.26403/DETRITUS/2018.6.
Singh, S., Noori, M.T., Verma, N., 2020. Efficient bio-electroreduction of CO_2 to formate on a iron phthalocyanine-dispersed CDC in microbial electrolysis system. Electrochim. Acta 338, 135887. https://doi.org/10.1016/J.ELECTACTA.2020.135887.
Sleutels, T.H.J.A., Hamelers, H.V.M., Rozendal, R.A., Buisman, C.J.N., 2009. Ion transport resistance in Microbial Electrolysis Cells with anion and cation exchange membranes. Int. J. Hydrogen Energy 34, 3612–3620. https://doi.org/10.1016/j.ijhydene.2009.03.004.
Sun, Q., Li, H., Yan, J., Liu, L., Yu, Z., Yu, X., 2015. Selection of appropriate biogas upgrading technology- a review of biogas cleaning, upgrading and utilization. Renew. Sustain. Energy Rev. 2015; 51 521-532.
Tartakovsky, B., Lebrun, F., Guiot, S.R., Bock, C., 2021. A comparison of microbial and bioelectrochemical approaches for biogas upgrade through carbon dioxide conversion to methane. Sustain. Energy Technol. Assessments 45. https://doi.org/10.1016/j.seta.2021.101158.
Torres, C.I., Lee, H.S., Rittmann, B.E., 2008a. Carbonate species as OH- carriers for decreasing the pH gradient between cathode and anode in biological fuel cells. Environ. Sci. Technol. 42, 8773–8777. https://doi.org/10.1021/es8019353.
Torres, C.I., Marcus, A.K., Rittmann, B.E., 2008b. Proton transport inside the biofilm limits electrical current generation by anode-respiring bacteria. Biotechnol. Bioeng. 100, 872–881. https://doi.org/10.1002/bit.21821.
Xu, H., Wang, K., Holmes, D.E., 2014. Bioelectrochemical removal of carbon dioxide (CO_2): an innovative method for biogas upgrading. Bioresour. Technol. 173, 392–398. https://doi.org/10.1016/j.biortech.2014.09.127.
Yin, Q., Zhu, X., Zhan, G., Bo, T., Yang, Y., Tao, Y., He, X., Li, D., Yan, Z., 2016. Enhanced methane production in an anaerobic digestion and microbial electrolysis cell coupled system with co-cultivation of Geobacter and Methanosarcina. J. Environ. Sci. (China) 42, 210–214. https://doi.org/10.1016/j.jes.2015.07.006.
Zeppilli, M., Cristiani, L., Armi, E.D., Villano, M., 2021a. Potentiostatic vs galvanostatic operation of a Microbial Electrolysis Cell for ammonium recovery and biogas upgrading. Biochem. Eng. J. 167, 107886. https://doi.org/10.1016/j.bej.2020.107886.
Zeppilli, M., Mattia, A., Villano, M., Majone, M., 2017. Three-chamber bioelectrochemical system for biogas upgrading and nutrient recovery. Fuel Cell. 17, 593–600. https://doi.org/10.1002/fuce.201700048.
Zeppilli, M., Paiano, P., Torres, C., Pant, D., 2021b. A critical evaluation of the pH split and associated effects in bioelectrochemical processes. Chem. Eng. J. 130155 https://doi.org/10.1016/j.cej.2021.130155.
Zeppilli, M., Paiano, P., Villano, M., Majone, M., 2019a. Anodic vs cathodic potentiostatic control of a methane producing microbial electrolysis cell aimed at biogas upgrading. Biochem. Eng. J. 152, 107393. https://doi.org/10.1016/j.bej.2019.107393.
Zeppilli, M., Simoni, M., Paiano, P., Majone, M., 2019b. Two-side cathode microbial electrolysis cell for nutrients recovery and biogas upgrading. Chem. Eng. J. 466–476. https://doi.org/10.1016/j.cej.2019.03.119.
Zhou, H., Xing, D., Xu, M., Su, Y., Zhang, Y., 2020. Biogas upgrading and energy storage via electromethanogenesis using intact anaerobic granular sludge as biocathode. Appl. Energy 269, 115101. https://doi.org/10.1016/j.apenergy.2020.115101.