



# Microbial electrochemical approaches of carbon dioxide utilization for biogas upgrading

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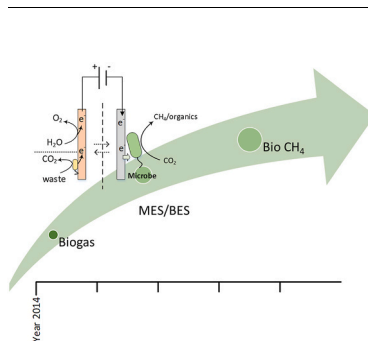
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## HIGHLIGHTS

- 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



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## ABSTRACT

Microbial electrochemical approach is an emerging technology for biogas upgrading through carbon dioxide (CO<sub>2</sub>) 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<sub>2</sub> reduction efficiency, methane (CH<sub>4</sub>) 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<sub>2</sub> to CH<sub>4</sub>. Most of the studies on the biogas upgrading process conclude hydrogen (H<sub>2</sub>) mediated electron transfer mechanism in BES biogas upgrading.

## 1. Introduction

Biogas, in general comprises a mixture of CH<sub>4</sub>, CO<sub>2</sub>, hydrogen sulfide

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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<sub>2</sub>S), ammonia (NH<sub>3</sub>), hydrogen (H<sub>2</sub>), nitrogen (N<sub>2</sub>), oxygen (O<sub>2</sub>), carbon monoxide (CO), and siloxanes. Some of the components present in biogas, notably CO<sub>2</sub>, H<sub>2</sub>S, 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). Physicochemical 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<sub>2</sub> and CH<sub>4</sub> 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<sub>2</sub> from biogas (Angelidaki et al., 2018; Fu et al., 2021). Additionally, exogenous H<sub>2</sub> supplemented microbial biogas upgrading has been tested in demonstration scale to convert CO<sub>2</sub> and upgrade CH<sub>4</sub> (Angelidaki et al., 2018; Aryal et al., 2021b). Recently, BESs have become promising biological technology to capture and convert CO<sub>2</sub> 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; Nancharaiyah et al., 2015; Rodríguez Arredondo et al., 2015). BES route of CH<sub>4</sub> production utilizing CO<sub>2</sub> reveals multiple benefits: (i) efficient conversion of waste CO<sub>2</sub> 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<sub>4</sub> 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<sub>2</sub> into CH<sub>4</sub> 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<sub>2</sub> reduction to produce CH<sub>4</sub> by utilizing the electrons from

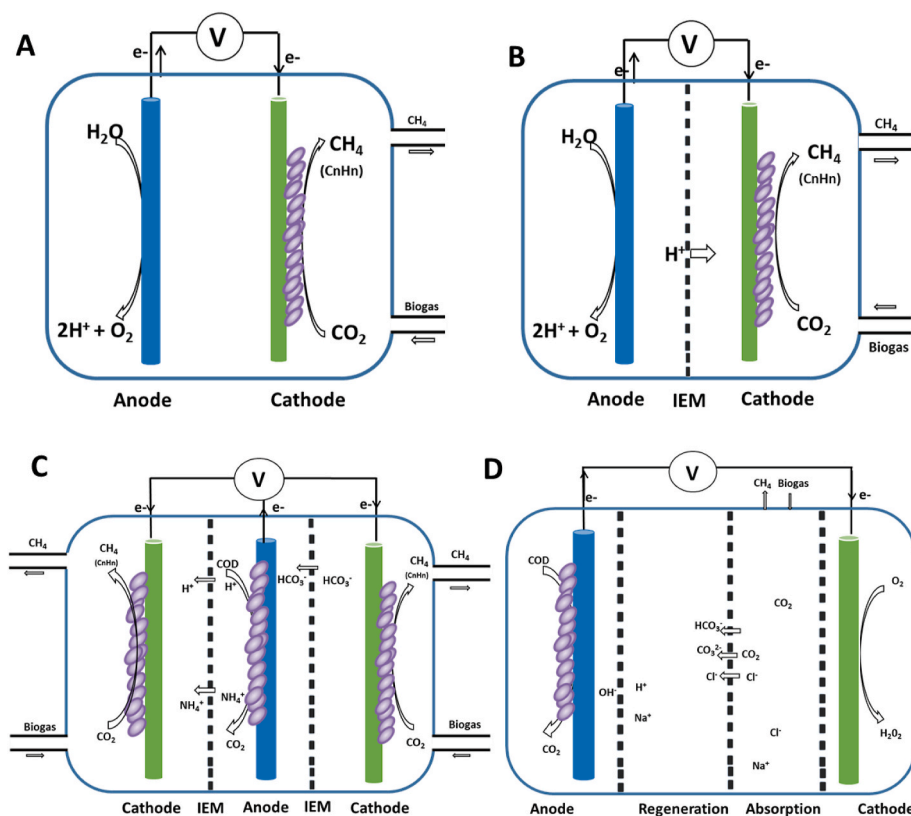
the cathode or reducing equivalents, e.g. H<sub>2</sub> derived from the poised cathode (Cheng et al., 2009). The proof-of-concept of bioelectrochemical upgrading of biogas was demonstrated in 2014 as a process attributed to CO<sub>2</sub> reduction through direct cathodic electron transfer to electroactive methanogens (Xu et al., 2014). Since then, researchers have widely applied BESs to remove and utilize of CO<sub>2</sub> to purify the biogas.

Within the recent five years, researchers have developed several laboratory-scale BESs to demonstrate the utilization of CO<sub>2</sub> 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<sub>2</sub>-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<sub>2</sub>) 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<sup>+</sup>, Na<sup>+</sup>) and acts as a separator to stop the crossover of bacterial liquid and O<sub>2</sub> 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  $\text{NH}_4^+$ ,  $\text{HCO}_3^-$  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  $\text{CO}_2$  removed from the biogas with the input of 0.9 kWh electricity per kg  $\text{CO}_2$  was reported by Zeppilli et al. (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,  $\text{CO}_2$  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  $\text{CO}_2$  removal and reduction from biogas. At the same time, the transport of  $\text{NH}_4^+$  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  $\text{CH}_4$  production,  $\text{CO}_2$  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,  $\text{CH}_4$  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  $\text{CH}_4$  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  $\text{CO}_2$  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<sub>4</sub> escape to the atmosphere while upgrading iv) recovery of CO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> 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<sub>2</sub> 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 <sub>2</sub> nanoparticles	<i>Ex-situ</i> (Batch)	AnOMBR-MEC separated by membrane	Mixed culture from WWTP sludge ( <i>Methanosaeta</i> , <i>Methanobacterium</i> and <i>Methanobrevibacter</i> )	$7.2 \times 10^4$ mA m <sup>-2</sup>	90% CH <sub>4</sub>	85	Gao et al. (2021)
Graphite granules	<i>in-situ</i> (Batch)	MEC integrated with ARS-HM	Enriched mixed culture/ Electromethanogenic)	$12.1 \pm 4.8 \times 10^4$ mA m <sup>-3</sup>	$73 \pm 8$ L <sub>CH<sub>4</sub></sub> m <sup>-3</sup> d <sup>-1</sup> (1.5 x improved)	23	Cerrillo et al. (2021)
Graphite plate	<i>in-situ</i> (Batch)	Two chambers separated by membrane	Mixed culture from synthetic wastewater sludge ( <i>Methanotherix</i> and <i>Methanobacterium</i> )	0.022 mA m <sup>-2</sup>	97% CH <sub>4</sub>	68.1	Liu et al. (2021)
Carbon felt	<i>Ex-situ</i> (Batch)	MEC membrane less two chamber separated by nylon cloth	Mixed culture from anaerobic sludge	250 mA	90% CH <sub>4</sub>	ng	Tartakovsky et al. (2021)
Ti-mesh coated with Pt/C	<i>Ex-situ</i> (Batch)	Two-chamber MEC separated by membrane	Mixed culture from WWTP ( <i>Methanobacterium</i> and <i>Azoarcus</i> )	$13.9 \pm 0.5A$ m <sup>-2</sup>	97.9% CH <sub>4</sub>	95	Zhou et al. (2020)
Carbon brush	<i>in-situ</i> (Batch)	MEC separated by membrane	Mixed culture from MWWTP ( <i>Methanosarcina</i> , <i>Methanobacterium</i> )	0.407 mA m <sup>-2</sup>	91.2% CH <sub>4</sub>	18.8	Liu et al. (2020)
Carbon paper	<i>Ex-situ</i> (Batch)	Cylindrical two chamber	Pure culture ( <i>Methanococcus maripaludis</i> )	ng	98.3% CH <sub>4</sub>	85.2	Fu et al. (2020)
Graphite granular	<i>Ex-situ</i>	Three compartment membrane separation	Mixed culture from thermophilic AD	$145 \pm 4$ mA $129 \pm 3$	$68 \pm 6$ $71 \pm 14$ mmol CO <sub>2</sub> removal-1	$69 \pm 4$ $95 \pm 4$ (cathodic capture)	Zeppilli et al. (2019b)
Carbon fiber	<i>In-situ</i> (Batch)	Single chamber membrane less	Mixed culture from WWTP sludge	15.54 mA (4 g/L glucose was added)	0.34 L CH <sub>4</sub> /gCOD higher CH <sub>4</sub> yield than control	ng	Lee et al. (2019)
Graphite plate	<i>In-situ</i> (Continuous)	AD-MES with two chambers separated by membrane	Mixed culture from WWTP sludge ( <i>Methanotherix</i> and <i>Methanobacterium</i> )	ng	>90% CH <sub>4</sub>	97.60	Liu et al. (2019)
Graphite coated with Cu-Ni & Fe	<i>In-situ</i> (Sequencing-Batch)	AD-MEC integrated in single chamber	Mixed culture from FWTP originated ( <i>Methanobacterium</i> <i>Methanosarcina</i> )	ng	1.7 fold faster than AD	ng	Park et al. (2018)
Stainless steel	<i>In-situ</i> (Batch)	Multi compartment MESC	Mixed culture from WWTP sludge	1490 mA m <sup>-2</sup>	99-100% CH <sub>4</sub>	ng	Kokkoli et al. (2018)
Carbon felt	<i>In-situ</i> (Batch)	Double chamber separated by membrane	Mixed culture from thermophilic sludge	120 mA	98% CH <sub>4</sub>	72.8	Liu et al. (2017)
Pt coated Ti wire mesh	<i>In-situ</i> (Batch)	MESC separated by membrane	Mixed culture from WWTP sludge	1700 mA m <sup>-2</sup>	97.5% CH <sub>4</sub>	81	Jin et al. (2017)
Graphite granular	<i>In-situ</i> (Batch)	Three chambers separated by membrane	Mixed culture from WWTP generated activated sludge	87 mA	90% CO <sub>2</sub> removal	86.4	Zeppilli et al. (2017)
MWCNT-RVC	<i>Ex-situ</i> (Batch)	Double chamber	Mixed culture from WWTPs sludge	$2 \times 10^5$ mA m <sup>-2</sup>	CO <sub>2</sub> removal as acetate	99	Jourdin et al. (2016)
Stainless steel (Wall of AD)	<i>In-situ</i> (Batch)	Single chamber barrel shaped membrane less	<i>Geobacter</i> and <i>Methanosarcina</i>	$3.04 \times 10^5$ mA m <sup>-3</sup>	24% higher CH <sub>4</sub> content than control	74.6	Yin et al. (2016)
Graphite	<i>In-situ</i> (Continuous)	Double chamber separated by membrane	Mixed culture from organic waste treating AD ( <i>Methanobacterium</i> , <i>Proteobacteria</i> )	$201.7 \pm 18.1$ mA m <sup>-2</sup>	85% CH <sub>4</sub>	69.9	Battle-Vilanova et al. (2015)
Graphite	<i>Ex-situ</i> (Batch)	AD connect to cathode chamber in H shape	Mixed culture from synthetic brewery ( <i>Methanobacterium</i> and <i>Methanosaeta</i> )	400 mA m <sup>-2</sup>	10% CO <sub>2</sub> removal	85.3	Xu et al. (2014)
Graphite	<i>in-situ</i> (Continuous)	Membrane less single chamber	Mixed culture from wastewater ( <i>Methanobacterium</i> and <i>Methanosaeta</i> )	3000 mA m <sup>-2</sup>	>8% CO <sub>2</sub> removal	90	Xu et al. (2014)
Stainless steel (Wall of AD)	<i>in-situ</i> (Batch)	MEC-AD in single chamber barrel shaped stainless-steel reactor	Mixed culture from wastewater treated MFC ( <i>Methanocorpusculum</i> , <i>Methanospirillum</i> , <i>Methanobacterium</i> , <i>Methanobrevibacter</i> , <i>Methanoculleus</i> )	ng	98% CH <sub>4</sub>	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<sub>4</sub> enrichment by comparing the single and double-chamber configuration (Liu et al., 2017). In contrast to previous studies, CH<sub>4</sub> enrichment in a double-chamber (77% CH<sub>4</sub>) configuration was more profound than single chamber (56% CH<sub>4</sub>). The higher CH<sub>4</sub> enrichment in a double-chamber is due to the alkalization of catholyte, promoting more CO<sub>2</sub> removal from raw biogas. Also, the use of membrane limits the migration of O<sub>2</sub> 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<sub>4</sub> 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<sub>2</sub> reduction into CH<sub>4</sub>. In *ex-situ* systems, the biogas collected from AD is passed into the BES reactor, where CO<sub>2</sub> from biogas is reduced to CH<sub>4</sub> either directly accepting the electron from the electrode or indirectly through H<sub>2</sub>. 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<sub>2</sub> 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<sub>2</sub> where 0.4 A/m<sup>2</sup> current density was observed in *ex-situ*, almost half of the current density observed in *in-situ* 1 A/m<sup>2</sup>; nevertheless, the charge transfer mechanism was not investigated thoroughly (Xu et al., 2014). Relatively, CO<sub>2</sub> gas-liquid mass transfer limitations caused lower current density in the *ex-situ* system where CO<sub>2</sub> 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<sub>2</sub> mass transfer because CO<sub>2</sub> 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<sub>2</sub> reduction. There could be multiple substrates available in the *in-situ* process in addition to the electricity input. In *ex-situ* systems, only CO<sub>2</sub> 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<sub>2</sub> utilization, pH, CH<sub>4</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>4</sub> formation from CO<sub>2</sub> 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<sub>2</sub> reduction.

The catalytic reactive sites of electrode materials support in accelerating the indirect and direct electron transfer to reduce CO<sub>2</sub> as shown in Fig. 2. Autotrophic microbes can reduce CO<sub>2</sub> 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<sub>4</sub> (Cheng et al., 2009). Another study reported that CH<sub>4</sub> production either directly via extracellular electron transfer or indirectly via H<sub>2</sub> mediated from electrode (Batlle-Vilanova et al., 2015) while upgrading biogas. Furthermore, direct electron transfer (DET) mechanism by an enriched mixed culture dominated by *Methanotrix* and *Azonexus* species were reported for CO<sub>2</sub> reduction to CH<sub>4</sub> (Yin et al., 2016). Direct flow of

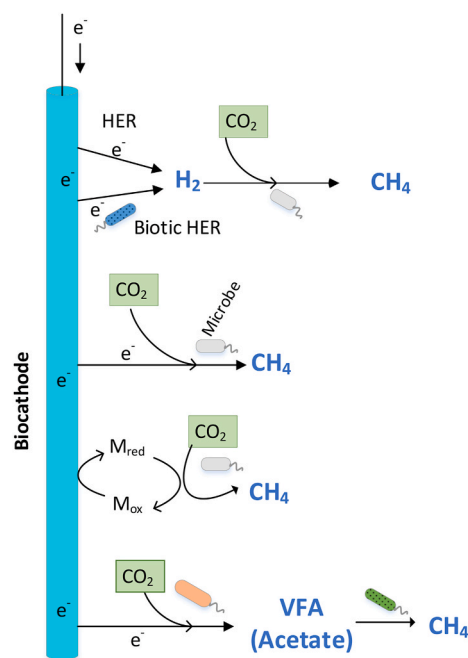


Fig. 2. Mechanism of electron transfer from biocathode in MES for methane production from CO<sub>2</sub>. HER: hydrogen evolution reaction; M: redox couple, VFA: volatile fatty acid.

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 biomaterials can enhance the HER (Aryal et al., 2019; Deutzmann et al., 2015). The study illustrated that the biological conversion of CO<sub>2</sub> to CH<sub>4</sub> has resulted from the reduction reaction with H<sub>2</sub> while upgrading biogas (Bo et al., 2014). Several research articles reported that the cathodic H<sub>2</sub> formation could be used in biological CO<sub>2</sub> reduction and CH<sub>4</sub> formation. High H<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> can also be absorbed or converted to acetate or formate at the cathode. Thereby, separating CO<sub>2</sub> from biogas can let the concentrated CH<sub>4</sub> at the outlet gas. A report demonstrated microbial CO<sub>2</sub> reduction to acetate in a biogas upgrading system by focusing on improving electrode design and operational parameters to utilize the CO<sub>2</sub> from synthetic biogas containing 70:30 v/v CH<sub>4</sub>: CO<sub>2</sub> (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<sub>2</sub> in the form of acetate when applying an applied cathode potential of  $-1.1$  V vs SHE with achieved  $-200$  Am<sup>-2</sup> current density. A similar observation was reported when SnO<sub>2</sub> nanoparticles were applied as a biocathode to upgrade the biogas where CO<sub>2</sub> was reduced to formate, stimulating the concentration of the 90% CH<sub>4</sub> 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<sub>2</sub> 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<sup>3</sup> of CH<sub>4</sub> was spent when 1000 m<sup>3</sup>/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<sub>4</sub> 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<sub>2</sub> (Christodoulou and Velasquez-Orta, 2016). Additionally, the case for the coupling of MES and AD were also presented considering the CO<sub>2</sub> conversions to acids (Christodoulou and Velasquez-Orta, 2016), but CO<sub>2</sub> utilization for CH<sub>4</sub> production was not explicitly analyzed. Likewise, the sustainability assessment aspect of acetate production from CO<sub>2</sub> 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<sub>4</sub><sup>+</sup>) can move 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<sub>4</sub><sup>+</sup> 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<sub>4</sub><sup>+</sup> ions migrate from anolyte to the accumulation compartment through the proton exchange membrane due to the electricity-driven migration. Likewise, CH<sub>3</sub>COO<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> 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<sub>4</sub><sup>+</sup>, CH<sub>3</sub>COO<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> without compromising the purity of CH<sub>4</sub> enrichment (Zeppilli et al., 2017, 2019b). Yet another study reported a recovered CO<sub>2</sub> using a three-compartment reactor system where CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> at the cathode compartment migrate through the anion exchange membrane to the middle regeneration compartment that allows the recovery of pure CO<sub>2</sub> while upgrading biogas (Jin et al., 2017). In the following study, the same research group recovered CO<sub>2</sub> *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 chlorine oxidation reaction is 45% less energy demanding compared to water oxidation (Du et al., 2015). Thus, anodic chlorine production while transforming the CO<sub>2</sub> containing effluent (e.g. biogas or wastewater) in the cathode of a BES into CH<sub>4</sub> 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<sub>4</sub>

loss is below 1.4%, and separated pure CO<sub>2</sub> 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<sup>0</sup>) recovery from anodic oxidation of H<sub>2</sub>S and cathodic biogas upgrading from CO<sub>2</sub> reduction (Fu et al., 2020). The author proposed applying electron shuttle Fe<sub>2</sub><sup>+</sup>/Fe<sub>3</sub><sup>+</sup> at anode to continuously drive the H<sub>2</sub>S 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<sub>4</sub><sup>+</sup>-N), while upgrading biogas at the cathode (Cerrillo et al., 2021). The recovered ammonia supported to regulate pH value that boosted CH<sub>4</sub> 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<sub>4</sub> 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<sub>2</sub> 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<sub>2</sub> reduction (Sleutels et al., 2009). Therefore, adding an acid or CO<sub>2</sub> 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<sub>4</sub> production in AD utilizing the accumulated H<sub>2</sub> 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<sub>4</sub> upgrading in different substrate conditions (Lee et al., 2019). The CH<sub>4</sub> 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<sub>4</sub> content was reached 97.9% from the initial 60% CH<sub>4</sub>, 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<sub>2</sub> removal by 113% compared to the potentiostatic condition (Zeppilli et al., 2021a). The polarization control to cathode rather than anode also promotes the CH<sub>4</sub> 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<sub>2</sub> to CH<sub>4</sub> by adding electron sources such as H<sub>2</sub>. However, inappropriate H<sub>2</sub> addition in AD process could accumulate the VFA that shifts the microbial dynamics, whereas low concentration favors stable dynamics to reduce CO<sub>2</sub> or CH<sub>4</sub> formation. Towards such argument, a report compared the effect of H<sub>2</sub> addition in *in-situ* biogas upgrading reactor and BES reactor (Tartakovsky et al., 2021). Due to the addition, of exogenous H<sub>2</sub>, 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<sub>2</sub> 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<sub>4</sub> and CO<sub>2</sub>. The persistence of acetoclastic methanogens could be due to the availability of acetate; even at autotrophic conditions, CO<sub>2</sub> was metabolized by other microbial consortia (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 (Gajjaraj 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> uptake capacity of the microorganisms. Further studies on the molecular mechanism and metabolic process of CO<sub>2</sub> capturing and conversion are required to advance in metabolic engineering attempts.

- II. Multi-compartment reactor configurations have shown 100% CH<sub>4</sub> 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<sub>2</sub> regeneration. *In-situ* and *ex-situ* approaches of biogas upgrading were widely applied where CH<sub>4</sub> 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<sub>2</sub> utilization into CH<sub>4</sub> (Corbellini et al., 2018). At the same time, the reactor design needs to be adapted to ensure an adequate supply of CO<sub>2</sub> when the system is scaled up. A high rate of uptake and conversion of CO<sub>2</sub> with stable performance and lower cell overpotentials have to be considered when practical applications are developed. The energy supply to produce electrons and H<sub>2</sub> 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<sub>2</sub> 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 renewable electrical energy (Christodoulou et al., 2017). In that context CO<sub>2</sub> 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<sub>4</sub> 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<sub>4</sub> production rate was increased up to 12.5 L CH<sub>4</sub>/L/d, by using redox flow battery design which was claimed as one of the highest production rate in BES; but, CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> reduction to CH<sub>4</sub> 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<sub>2</sub> utilization and biomethane production.

#### Credit author statement

Nabin Aryal: Conceptualization, Data curation, Writing – original draft, Writing – review & editing. Yifeng Zhang: Writing – review & editing, Suman Bajracharya: 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.

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