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Review article

Addressing scale-up challenges and enhancement in performance of hydrogen-producing microbial electrolysis cell through electrode modifications

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ABSTRACT

Bioelectrohydrogenesis using a microbial electrolysis cell (MEC) is a promising technology for simultaneous hydrogen production and wastewater treatment which uses electrogenic microbes. Microbial activity at the anode and hydrogen evolution reaction at the cathode can be controlled by electrode–microbe interaction and electron transfer. The selection of anode electrode material is governed by electrochemical oxidation of substrates and subsequent electron transfer to the anode. Similarly, a good cathodic material should reduce the overpotential at the cathode and enhance the hydrogen evolution reaction and H_2 recovery. This review mainly focused on modifications in electrode materials and cheaper novel alternatives to improve the performance for MEC and overcome its scale-up challenges for practical applications. Performance of various anode and cathode materials based on Ni alloys, stainless steel, polyaniline, palladium, and carbon has been discussed. The scalability of the material should consider its inexpensive fabrication procedure and efficiency.

Contents

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1. Introduction

The annual quantity of global wastewater discharge is approaching 359.4 billion m^3/year; however, about 48% of the wastewater generated worldwide is disposed to the environment without treatment (Jones et al., 2021). Thus, one of the industrialized world's major problems is resolving environmental contamination by identifying efficient wastewater treatment methods. In addition, several critical issues such as global warming, energy crisis, and water shortage became more pressing. As a result, wastewater is being regarded as alternative energy and water resource, not just a target to be purified (Smith et al., 2018). In this regard, the challenge of wastewater treatment and environmental pollution can be mitigated to a greater extent through the exploitation of anaerobic treatment systems to recover the energy in wastewater in various forms (Munoz-Cupa et al., 2021; Lin et al., 2021) in recent years, considerable attention has been paid to converting the chemical energy in organic constituents of wastewater to biogas and other usable fuels through anaerobic digestion systems and microbial electrochemical technologies (METs), termed as bioelectrochemical systems (BESs) (Zhao et al., 2021; Cabrera et al., 2021). Among the biological wastewater treatment technologies, the METs were found to be promising due to their several merits: potentials for easy convergence with other advanced water treatment systems (e.g., advanced oxidation process and membrane separation process), low sludge generation, and direct conversion of such energy into various forms of usable energy including electricity and hydrogen (Reddy et al., 2019; Anusha et al., 2018; Chae et al., 2009; Noori et al., 2018b). METs have evolved in wastewater treatment and work on the principle of extracellular electron transfer by microbes called exoelectrogens to produce energy (electricity) and other valuable products (hydrogen) for product recovery and wastewater treatment (Sahu and Parkhey, 2021). The emerging significance of hydrogen fuel to achieve a zero-carbon society has drawn a lot of attention to microbial electrolysis cells (MECs) that can produce high-purity hydrogen fuel with high efficiency.

1.1. Microbial electrolysis cell: An overview of operation mechanism

MECs were discovered in the last decade to meet the energy demand and simultaneously treat wastewater by two independent research groups in the USA and The Netherlands (Kadier et al., 2016; Liu et al., 2005). The production of hydrogen gas as a renewable energy source from MEC has gained so much attention recently. In the MEC, the electrogenic microbes oxidize organic matter in the substrates and produce electrons, protons, and carbon dioxide (Hu et al., 2008). The electrons are released to the anode electrode by microbial pili, cytochromes, and exocellular mediators such as pyocyanin and then transferred to the cathode by external electrical circuits (Logan et al., 2019; Kracke et al., 2015). The protons are transported to the cathodic chamber through a proton exchange membrane (PEM) for dual-chamber MECs and directly through the solution for single-chamber MECs. The protons that migrate to the cathode combine with electrons to produce hydrogen gas. However, H_2-production at the cathode is an endothermic reaction and thus needs an external energy supply ($\geq$0.2 V vs. SHE).

Interestingly, the overall energy demand for H_2-production in MECs is much lesser than the water electrolysis (1.23–1.8 V vs. SHE) (Liu et al., 2005). This less energy requirement is attributed to the involvement of microbial metabolism, which is more efficient than the abiotic H-evolution reaction (Rabaey and Rozendal, 2010). Therefore, the substrate degradation (acetate) at the anode and hydrogen evolution reaction at the cathode in MECs can be written as follows.

$$\text{Anode:} \quad C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+ \tag{1}$$

$$\text{Cathode:} \quad 8H^+ + 8e^- \rightarrow 4H_2 \tag{2}$$

1.2. Previous studies on factors governing the performance of MECs

As mentioned earlier, the mechanism for hydrogen production in MECs are quite simple. However, the hydrogen evolution performance of MEC is influenced by diverse parameters such as reactor configuration, substrate addition, catalyst, various metabolic processes, and electrode modifications. Therefore, this section will briefly summarize the factors affecting MEC performance, beginning with MEC configuration.

The most commonly used configurations of MEC are single and dual chambers. A dual-chamber MEC consists of an anodic and a cathodic chamber separated by a PEM, whereas in a single-chamber MEC, the anode and cathode share a common electrolyte (Gavilanes et al., 2019; Flores-Rodriguez et al., 2019; Montpart et al., 2015). Both reactor configurations have certain advantages and disadvantages. For example, a single-chamber MEC is a convenient design for practical applications due to its low fabrication cost (Noori et al., 2020b). However, the intermediate generation of hydrogen via electrolysis at anode could be highly detrimental to the microbial colony in the MECs. In addition, such a design has limitations of microbial hydrogen losses to methanogens (Chae et al., 2010a). By contrast, dual-chamber MECs efficiently stop the migration of O_2 and other harmful reactive oxygen species via a PEM to enter the cathode chamber, thus maintaining a favorable environment for H_2-evolution reaction (HER). The Nafion-117 membrane is the most commonly used PEM type to separate the anode and the cathode in MECs due to its selective proton transfer properties through SO_3^- functional groups (Tiwari et al., 2016; Kumar et al., 2018; Saha et al., 2018). However, a dual-chamber MEC has a few disadvantages, such as high fabrication costs associated with expensive PEM and increased internal resistance (contributed by PEM) (Miller et al., 2019).

The substrate also plays an essential role in MECs since it serves as a fuel and carbon source for the bacteria (Kadier et al., 2014). The substrate used for anodic oxidation affects the microbial colony developed on the anode, retrieved current, and

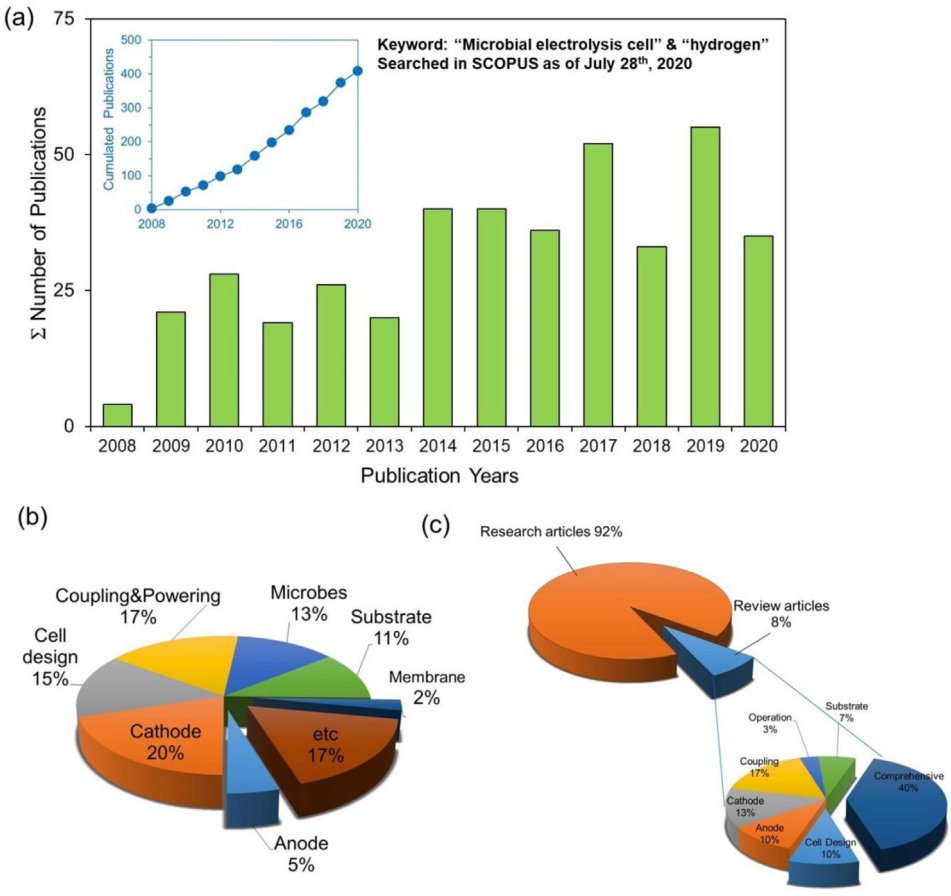

Fig. 1. Research trend articles related to microbial electrolysis cells (MECs) for hydrogen production as of July 31, 2020: (a) annual and cumulative publications of MEC papers based on Scopus database, (b) research topic-based distribution, and (c) article type-based distribution (research vs. review) and detailed composition of the published review articles. The list of research articles used for these figures was obtained by searching with two keywords, "microbial electrolysis cell" and "hydrogen" in Scopus, then manually eliminating unrelated articles from the list obtained from the search.

Coulombic efficiencies (CEs) in MECs. The most common substrates in MECs for hydrogen production are glucose, acetic acid, lactic acid, butyric acid, lingo-cellulose and complex wastewater, and industrial effluents. Among them, acetate is a popular carbon source in MECs as it is an end product of fermentation and is easily adaptable for microbes. A couple of earlier studies demonstrated very high (close to theoretical value) H_2 production rates in MECs using acetate as substrate and improved electrode materials (Jeremiasse et al., 2010; Call and Logan, 2008). Similarly, glucose has also been utilized as an efficient substrate for MECs operated at very low temperatures (∼4 °C) (Lu et al., 2012; Selembo et al., 2009b).

In addition, the source and type of bacterial inoculum also has a wide impact on the performance of MECs (Bajracharya et al., 2015). For example, the mixed culture inoculum obtained from an anaerobic fermentation unit contains different species of bacteria capable of using complex substrates at a wide range of operational and environmental conditions (Jiang et al., 2013; Marshall et al., 2012). On the contrary, the pure culture can be used only with simple substrates such as acetate and lactate (Newton et al., 2009; Call et al., 2009b). However, the major drawback in using mixed culture as inoculum is that it ensures substrate utilization for nonelectrogenic reactions such as methanogenesis and sulfate reduction, which reduces the Coulombic recovery in MECs (Rajesh et al., 2018b; Ray et al., 2017). The CEs of MECs are adversely affected by various determining factors such as the competitive electron acceptors (nitrate and sulfate), methanogenesis, and anaerobic fermentation. Since methanogens are prevalent in bioelectrochemical systems (BESs), they compete with electrogens for substrate and reduce the overall Coulombic recovery (Rismani-Yazdi et al., 2013). Various chemical inhibitors can inhibit methanogenesis, with several findings reported on this strategy (Rajesh et al., 2018a, 2014). Acetylene, various antibiotics, and 2-bromoethanesulfonate are the primary chemical inhibitors to suppress methanogenesis and enhance hydrogen production rate in MECs (Chae et al., 2010a; Wang et al., 2019b; Catal et al., 2015; Park et al., 2019; Chae et al., 2010b).

As stated earlier, many studies have addressed various issues such as the substrate and biocatalysts used in MECs, reactor design and configuration of MECs, inhibition of methanogenic activity, and application of MECs in anaerobic digestion (Kadier et al., 2016, 2014; Hasany et al., 2016; Lu and Ren, 2016; Yu et al., 2018a). For example, as shown in Fig. 1(a), when searching the "Scopus" database with the combination of two keywords "microbial electrolysis cell and hydrogen", more than 500 research articles were found and the number of published articles has been increasing steadily over the last decade, indicating a consistently growing interest. Furthermore, when categorizing those articles according to research topics, many studies have focused on cathode (20%), coupling and powering (17%), cell design (15%), microbes (13%), substrate (11%), anode (5%), and membrane (2%) (Fig. 1(b)).

In addition, with increasing interest in MEC technology, many review papers covering the state-of-the-art hydrogen-producing MEC have also been increasing steadily, accounting for 8% of total publications (Fig. 1(c)). Forty percent (40%) of these review papers

attempted to provide the principle, research progress, and challenges comprehensively. Several review papers also specifically focused on electrode material and catalyst (Kundu et al., 2013; Jafary et al., 2015; Kim et al., 2015; Yuan and He, 2017), biocatalyst and methanogen inhibition (Hasany et al., 2016; Karthikeyan et al., 2017; Kadier et al., 2018), cell configuration and scale-up (Kadier et al., 2016; Escapa et al., 2016; Kitching et al., 2017; Katuri et al., 2019), coupling with other processes (Bundhoo, 2017; Bakonyi et al., 2018; Yu et al., 2018b), substrate spectrum (Kadier et al., 2014; Yu et al., 2018a), membrane biofouling (Koók et al., 2019), and operation conditions for start-up (Kumar et al., 2017).

1.3. Aim of this review: Importance of electrodes

MEC research's ultimate goal is to achieve practical implementation of commercial hydrogen production using MEC processes. As briefly introduced in a previous section, many studies have made large efforts to clarify and resolve critical issues faced in MEC applications. However, commercial biohydrogen production using MECs is still a long way from being fully developed. To achieve this goal, materials that have high performance and are cost-effective for each component of MEC scale-up must be developed. In particular, researchers reduced the costs of electrodes of MECs and simultaneously enhanced their performance. However, not only do MEC electrodes contribute to a large portion of potential loss during MEC operation, but they also account for the highest percentage in the construction cost of MECs (Lee et al., 2015; Sleutels et al., 2009a; Aiken et al., 2019). Owing to the thermodynamically non-spontaneous hydrogen evolution in MECs, theoretically, at least 0.14 V of external energy input is required to overcome the thermodynamic potential for the hydrogen evolution reaction (Yang et al., 2021). However, during actual MEC operation, at least 0.25 V of external voltage needs to be supplied to produce hydrogen due to potential loss derived from the electrolyte, membrane, and electrodes (Yang et al., 2021) (Fig. 2(a)). According to a previous study (Lee et al., 2015), it was found that potential loss by anodic and cathodic electrodes accounts for nearly 50% of the total potential loss of MECs (Fig. 2(b)).

In addition, to reduce the construction cost of MECs, anodic and cathodic electrodes are key components. It has been mentioned that anodic and cathodic electrodes contribute to ∼79% of the total construction cost of MECs (Aiken et al., 2019) (Fig. 2(c)).

In this regard, we focus on recent progress in electrode materials and electrode modification in MECs. To the best of our knowledge, some review works intensively or comprehensively provided the summary of MEC research and suggested its research direction and perspective catalyst (Kundu et al., 2013; Jafary et al., 2015; Kim et al., 2015; Yuan and He, 2017). However, no intensive review that provides progresses made in the last 5 years on advances in MEC electrodes research is available. Hence, this review addresses the different electrode materials used and modifications made in MEC and our perspectives on potential MEC applications.

2. Electrode materials used in MECs

It is imperative to understand the critical features of the electrodes, having a direct impact on the microbial attachment, which will help choose a suitable electrode for a specific application.

2.1. Key features of electrode materials for MECs

In MECs, the anode and cathode electrodes play a pivotal role, and their favorable elements are essential to improve performance. The materials for the anode and cathode electrodes should have certain features such as electrocatalytic activity, conductivity, and large surface area.

Moreover, for the anode electrode, which is bio-catalyzed, biocompatibility to support enhanced bacterial repreparation is also a critical characteristic (Guo et al., 2015). If a biocatalyst is used as the cathode (thus, biocathode), then biocompatibility is important for consideration. The properties of electrode surfaces are of prime importance, which promotes the microbe–electrode interaction. It is crucial to overcome the repulsive surface energy to establish an electroactive biofilm on the surface of electrodes. Special types of cell wall-bounded protein structures such as cytochromes, and conductive nanowires available on some species of electroactive microbes such as *Geobacter sulfurreducens* and *Shewanella oneidensis* could easily overcome these negative energy barriers (Guo et al., 2015; Engel et al., 2019). Otherwise, the engineered electrode materials with the following properties: high porosity, randomized surface roughness, intentionally build micropillars, controlled surface charge distribution (hydrophobicity/hydrophilicity), etc. have shown remarkable improvement in the microbe–electrode interaction (Noori et al., 2020b). To begin with, doped ions (negative or positive) generate favorable electrostatic forces of attraction, thus enhancing biofilm development significantly. Similarly, electrode roughness and high surface area provide additional energy to the microbes to support their metabolism and form colonies (Noori et al., 2019). However, the bi-directional electron transfer mechanism (electrode to microbe and vice-versa) in MECs is still under investigation, making most of the electrode development processes empirical. Some excellent review articles explored electrode–microbe interaction in general (Aryal et al., 2017; Patil et al., 2012). It is clear that the surface properties of electrodes primarily govern the microbe–electrode interactions. Therefore, it is imperative to choose and modify an appropriate electrode material to optimize and enhance the MEC's performance.

Unlike the anode, the cathode needs to provide a flexible platform for hydrogen evolution reactions in MECs. However, the hydrogen evolution reaction (HER) rate on plain electrode materials, such as stainless steel containing low or no transition metal compositions (e.g., stainless steel 316 and 420) and carbon-based materials, is kinetically slow. Therefore, an efficient electrochemical catalyst is required to enhance HER efficiency. Platinum (Pt) is the most used cathode catalyst in MECs because of low overpotential for HER under optimized conditions. Another advantage is that it can be easily prepared in the laboratory by combining commercially available platinum with a chemical binder. However, platinum is expensive and can also be poisoned by chemicals such as sulfide or phosphate anion (Dai et al., 2016; Noori and Verma, 2019).

Recently, various transition metals such as nickel and molybdenum have been employed in MECs as electrodes and catalysts to enhance HER efficiency due to high electrochemical activity, abundance, low cost, and stability (Askari et al., 2019; Zhu et al., 2019; Leu et al., 2016; Jin and Chen, 2018; Jayabalan et al., 2019a). Based on these scales, nickel-based electrodes such as nickel alloys, nickel compounds, nickel nanoparticles, and stainless steel (stainless steel A286) containing a high percentage of nickel composition (up to 27 wt%) were the best materials (Selembo et al., 2009a; Kim et al., 2017a, 2019).

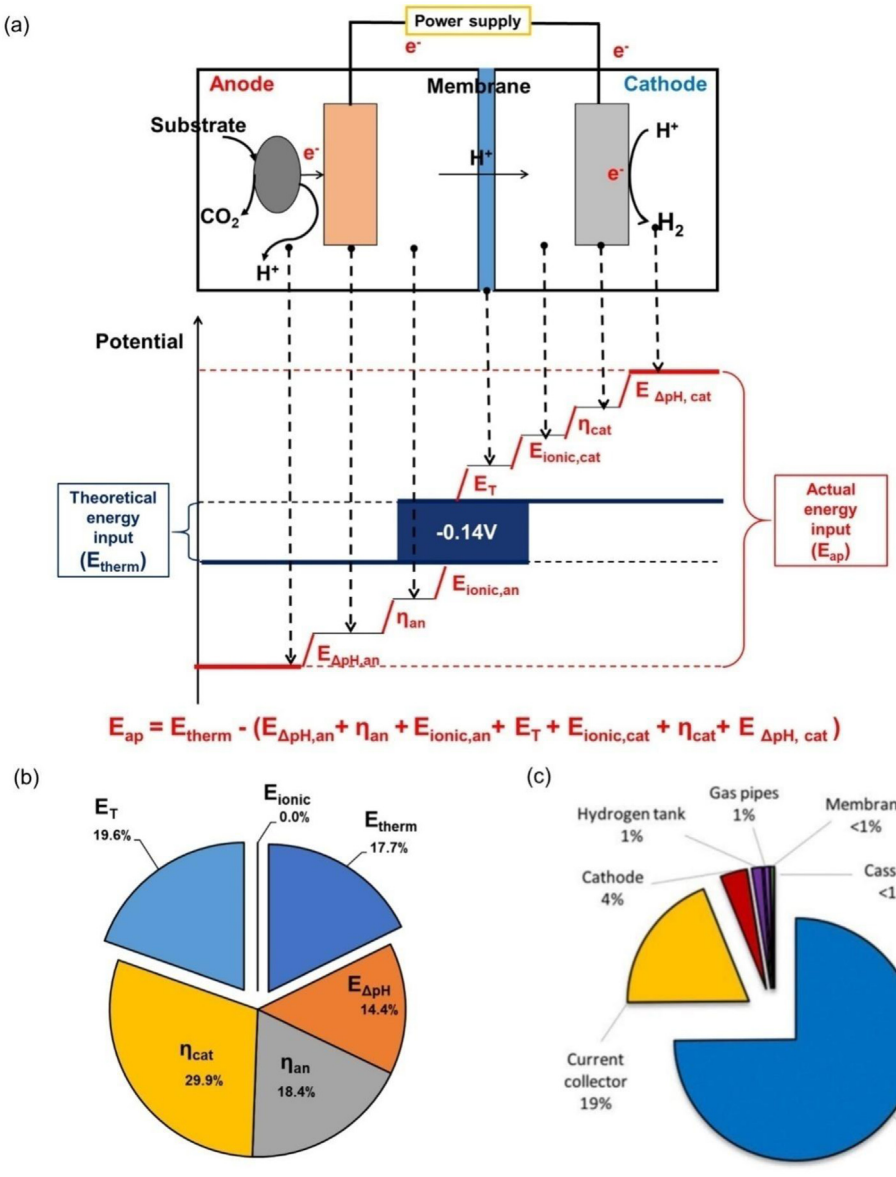

Fig. 2. (a) Potential losses occurring in a MEC: (1) $E_{\Delta pH,\ an}$: Potential loss caused by pH gradient in anode, (2) η_{an}: Anodic overpotential, (3) $E_{ionic,an}$: Anodic ionic loss, (4) E_T: Transport loss, (5) $E_{ionic,cat}$: Cathodic ionic loss, (6) η_{cat}: Cathodic overpotential, (7) $E_{\Delta pH,cat}$: Potential loss caused by pH gradient in the cathode, (8) E_{therm}: thermodynamically required potential (b) The percentage of each potential loss (Lee et al., 2015; Sleutels et al., 2009a; Yang et al., 2021) obtained from Lee et al. (2015). (c) Estimated capital cost of each component of a commercial MEC (Aiken et al., 2019).

2.2. Conventional electrode materials used in MECs

2.2.1. Anodic electrode materials

Carbon-based materials have been extensively used in MECs because of their biocompatibility, good conductivity, lower overpotentials, robust stability in a wide range of environmental conditions, and low cost (Logan et al., 2008; Zhang et al., 2016). Different C–C arrangements within the material frameworks of carbon allotropes induce remarkable electrochemical properties for specific applications (McCreery, 2008). The structural stability of carbon-based electrode materials under a rugged environment makes them exceptionally reliable for energy and environmental applications, including bioelectrochemical systems (Le et al., 2017; Nibel et al., 2017; Kim et al., 2016). Besides, some of the carbon allotropes possess high conductivity and surface area (Noori et al., 2017; Geppert et al., 2016; Olabi et al., 2020).

Among different carbon allotropes, graphitic carbon is the most commonly used anodic material in MECs, such as carbon paper (Ditzig et al., 2007), carbon cloth (Liu and Rodriguez, 2005), carbon felt (Zikmund et al., 2018), graphite felt (Rozendal et al., 2006), and graphite granules (Cheng and Logan, 2007). Liu et al. (2005) developed a modified MEC for hydrogen production from acetate using carbon cloth as an anodic material (Liu et al., 2005). Hydrogen could be efficiently produced by the augmentation of electrochemical potential caused by exoelectrogens in the MEC with a voltage of 250 mV. Overall hydrogen yield of 2.9 mol H_2/mol acetate and a hydrogen generation efficiency of 92% was obtained using carbon cloth electrodes. Rozendal et al. (2006) performed a bio-catalyzed electrolysis experiment using a disk-shaped piece of graphite felt as an anode electrode and achieved overall hydrogen efficiency of 53% at 0.5 V applied potential (Rozendal et al., 2006). A maximum CE of 26% and maximum hydrogen recovery of 42% with a chemical oxygen demand (COD) removal of 87%–100% was obtained in graphite granule packed MEC treating domestic wastewater. It could be feasible to treat domestic sewage efficiently from such a system, but increasing the overall hydrogen recovery modification is necessary.

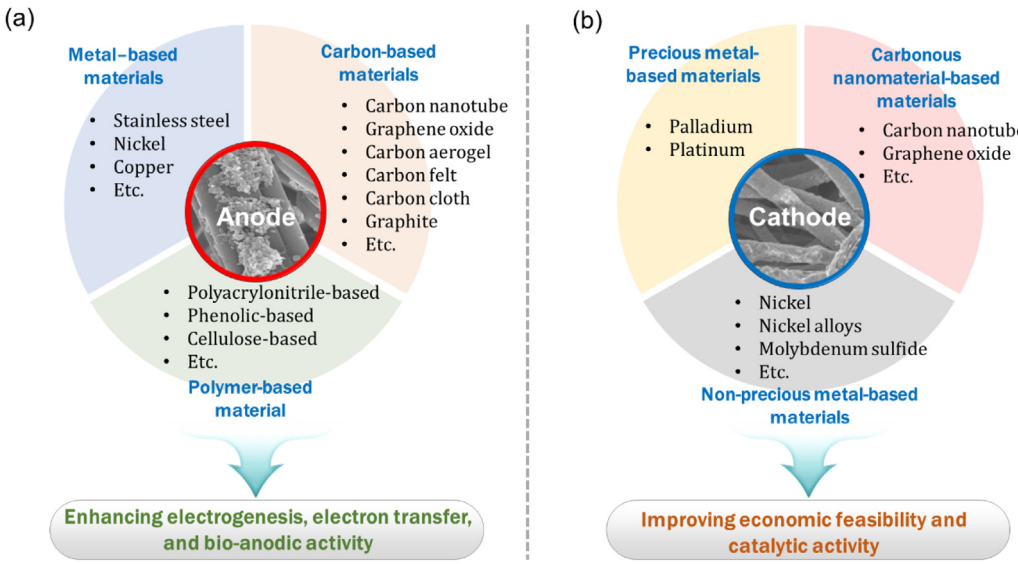

Fig. 3. Main research direction on the anode and cathode modifications for efficiency improvement and economic feasibility: (a) anode material and (b) cathode catalyst.

Graphite fiber brush anodes are the commonly used anodes in MECs due to their improved performance. A comparison of carbon felt and carbon brush anodes has been performed by Zikmund et al. (2018). The CEs of the MEC with brush and felt anodes were 74 ± 8% and 76 ± 6%, respectively. Despite placing the carbon felt anodes near the membrane, the anodes showed a minimal hydrogen gas production rate of 0.32 ± 0.02 m^3 $H_2/m^3/d$ compared to brush anodes (0.38 ± 0.02 m^3 $H_2/m^3/d$) due to mass transport limitations (Zikmund et al., 2018). This reduced performance of felt anodes could be ascribed to the substrate limited mass transfer. These results reveal that the brush anodes can be efficiently used to enhanced hydrogen production in MECs.

2.2.2. Cathodic electrode materials

As mentioned earlier, a cathodic electrode generally consists of a conductive electrode base providing the site for HER and a catalyst for facilitating the HER. As the traditional cathode materials in MECs, stainless steel, nickel, titanium, and carbon-based materials (e.g., carbon felt, carbon cloth, and graphite) are employed. Titanium and carbon-based materials possess poor HER catalytic activity, thus requiring coating using catalysts, such as platinum, to enhance HER in MECs. Call and Logan (2008) used Pt catalyst on carbon cloth in a single-chamber MEC reactor and achieved a hydrogen recovery of 96% and an overall energy efficiency of 75% (Call et al., 2009a). In a similar study, Rozendal et al. (2007) used a Pt-loaded titanium mesh cathode in one and two-chamber configurations. They obtained a hydrogen production rate of up to 0.3 m^3/m^3 reactor liquid/d at 1 V applied potential (Rozendal et al., 2007). A hydrogen production rate of 1.6 ± 0.0 m^3/m^3 reactor liquid/d and a CE of 85.0 ± 6.4% was obtained using Pt catalyst of particle size 0.002 μm mixed with 50-mg carbon black on carbon cloth (Selembo et al., 2010).

However, several stainless steel electrodes can offer relatively high hydrogen production yields without a precious metal catalyst in MECs because they contain nickel granules, which can act as a catalyst for hydrogen evolution (Roubaud et al., 2018). Furthermore, thanks to nickel's relatively good catalytic activity for HER, nickel-based electrodes have also been adopted in MECs (Siwek et al., 2019; Lu et al., 2016b; Hu et al., 2019).

Olivares-Ramirez et al. (2007) reported the HER and catalytic activation on different stainless steel electrodes in alkaline solutions (Olivares-Ramírez et al., 2007). The cyclic voltammetry behavior of stainless steel in an alkaline medium was performed. Results demonstrated that 316 stainless steel is preferred as a cathodic electrode for HER since it contains the highest nickel. In a similar study, stainless steel-containing nickel alloys were employed as cathodes. Stainless steel brush was evaluated under neutral pH conditions, and the effect of material composition on current generation was analyzed (Call et al., 2009a). An effective hydrogen production rate of 1.7 m^3 $H_2/$ m^3/d and an overall energy efficiency of 78% were obtained using stainless steel material at an applied voltage of 0.6 V.

Also, a stainless steel mesh (SS 304) woven and expanded mesh were employed as cathode materials in MEC (Zhang et al., 2010). The stainless steel mesh obtained a high hydrogen recovery (98 ± 4%) with a hydrogen production rate of 2.1 ± 0.3 m^3 $H_2/m^3/d$. Cyclic voltammetry tests showed three times higher electrochemically active surface area in stainless steel mesh than in a flat sheet. Moreover, the stainless steel mesh could be used as a scalable and cost-effective cathode material for scale-up.

More recently, the efficacy of stainless steel, nickel alloy, and graphite for hydrogen production at low cell voltage using carbonate solution was examined as a cathodic electrode by Roubaud et al. (2018) (Roubaud et al., 2018). The results showed that the electrocatalytic effect of HCO_3^- was found to be the highest on 316 and 254 SMO stainless steel.

2.3. Electrode modification for enhancing the performance of MECs

In investigating electrodes for MECs, it is of utmost interest to develop cheaper electrode materials that will give optimum performance and help reduce overpotential losses. Until now, researchers have made noticeable efforts to enhance the efficiency of MEC processes through electrode modification. Fig. 3 illustrates the overview of studies on each electrode modification in MECs. In this section, the various anode and cathode modifications to improve the performance of MECs by enhancing the essential characteristics of each electrode are described in detail.

2.3.1. Anode modification

The biofilm formation and electron transfer in MEC anodes depend on the anode's specific surface area, conductivity, surface charge, and surface wettability (Artyushkova et al., 2015; Noori et al., 2020a). In general, increasing the surface area available

Table 1
Performance of different anode materials used in MECs.

Anode material	Cathode potential (V)	Hydrogen production (m^3/m^3 reactor liquid/d[a])	Coulombic efficiency (%)	Cathodic hydrogen recovery (%)	References
Graphite granules	0.6	1.23	64	–	Cheng and Logan (2007)
Porous graphite felt	1	5.6	60	–	Sleutels et al. (2009b)
GAC	0.8	0.82 ± 0.01 mol H_2/mol acetate	100%	–	Liu et al. (2014b)
GAC/FeS	1	0.46	93.6	89.1	Yasri and Nakhla (2017)
GAC/Fe_3O_4	1	0.36	94.8	84.1	Yasri and Nakhla (2017)
GAC/CaS	1	0.55	96.7	93.7	Yasri and Nakhla (2017)
316L SS fiber felt	1	7.10 $l/l/d$	–	100	Guo et al. (2013)
Bioanode	0.7	7.4 $H_2/m^2/d$	45	–	Lim et al. (2017)
Carbon aerogel	0.3	0.37 mol/cm^2/h	–	–	Wang et al. (2019a)

[a]Unless stated otherwise.

for the bacterial attachment on the anode enhances the current density. It has been demonstrated that hydrophilic and positively charged surfaces enhance electrogenic microbial growth and development (Guo et al., 2013). For improving the performance of MECs, information on how the electrode properties affect the growth of the biofilm on the surface of the anode is mandatory. The performance comparison of various anodic materials used in MECs is described in Table 1.

2.3.1.1. Carbon-based materials. A compact reactor system consisting of chemically modified three-dimensional graphite granule anode was developed by Cheng et al. (2007) to increase the hydrogen generation rates. A high-temperature ammonia gas process was used to treat graphite granules to improve exoelectrogen adhesion and enhance overall performance (Cheng and Logan, 2007). Hydrogen gas was produced at a 2.01–3.95 mol/mol rate at applied voltages of 0.2–0.8 V using acetate as the substrate. Using glucose, volatile fatty acids, and cellulose, a maximum stoichiometric yield of 54%–91% and overall energy efficiencies of 64%–82% were obtained using graphite anode. The study pointed out that graphite granules can be efficiently employed as anodic materials in MECs for industrial applications.

The use of porous electrodes such as graphite felt, carbon cloth, and mat increased the specific surface area available microbes attachment, resulting in enhanced current densities (Kebaili et al., 2020). However, an increase in thickness of these porous electrodes led to mass and charge transport limitations in the core of the electrode, limiting the biofilm formation due to pore clogging (Blanchet et al., 2016). To further improve the characteristics of these electrodes, some treatments (e.g., plasma) have been applied (Rozenfeld et al., 2019). For example, a combined plasma treated carbon cloth was used as anode in MEC (Rozenfeld et al., 2019). The carbon cloth electrode materials were treated with plasma to enhance their surface morphology and hydrophilic properties. The highest biofilm viability and hydrogen production rate were obtained using these anodes in MECs.

Carbon nanotubes have recently gained so much importance due to the remarkable electrical, structural, chemical properties, and stability of nanomaterials and, therefore, applied as biohybrid electrodes in different BESs (Salvador et al., 2017; Liu et al., 2014a). However, some studies on CNTs have shown adverse effects on microbial colonies (Upadhyayula and Gadhamshetty, 2010). Therefore, graphite disk multianodes coated with gold (Au) and palladium (Pd) nanoparticles were developed by Fan et al. (2011) for the current generation in MEC (Fan et al., 2011). Au and Pd nanoparticle thin films were decorated on polished graphite disks by sputter coating for 0.5–1 min. Au nanoparticle-decorated anode produced a current density 20-fold higher than plain graphite anodes. However, the anode decorated with Pd nanoparticles had 50%–150% higher current than the control graphite electrode. Thus, the chemical composition, size, and shape of nanoparticles affect the performance of MECs.

Carbon nanosphere contains concentric graphitic layers within its surface with circular carbons (Dhand et al., 2014). Amorphous agglomerates of carbon nanospheres with 10–50 nm diameter were synthesized using the solution combustion method. Such carbon nanospheres can be used as potential candidates in energy storage devices to produce free hydrogen in MEC, as evident from electrochemical and thermocatalytic decomposition studies. Three-dimensional nanostructure material has been developed recently which has a large bacterial accessible specific surface area (Wang et al., 2021a). Wang et al. (2021) developed a three-dimensional (3D) nan-structure electrode by growing self-supported N-doped C/Fe_3O_4 nanotube composite array onto carbon fiber cloth using template-based deposition method. This material enhanced conductivity and areal capacitance of the electrode. Moreover, it reduced charge transfer resistance and enhanced the biocompatibility for microbial colonization.

Substrate diffusion limitation is a significant problem encountered in the anode of MECs with an increase in biofilm thickness. The anode biofilm must have access to the substrate for self-metabolism, and the bacteria at the outer part of the biofilm need to transfer electrons to the anode effectively. Flowable GAC particles were used in this study to facilitate additional surface area for the growth of exoelectrogenic bacteria (Liu et al., 2014b; Hagemann et al., 2018). Remarkably, the surface area of some GAC derived from lignocellulosic biomass could reach up to 3000 m^2/g (González-García, 2018). GAC particles with fluidization as anode material produced higher hydrogen gas recoveries and current densities than the controls by reducing the substrate diffusion limitations. This modification produced a hydrogen gas yield of 0.82 ± 0.01 mol H_2/mol acetate, which was 116% higher than that of control (no GAC) due to the intermittent contact of capacitive particles on the anode.

The utilization of GAC as a conductive and high specific surface area anode has widened its application in electrochemical systems such as MECs (Liu et al., 2018). It enhances substrate conductivity and mass transfer by increasing the electrode's specific surface area to form a 3D electrochemical cell system and creates bipolar fields on the granules. GAC doped with conductive (Fe_3O_4), semiconductive (FeS), nonconductive (CaS), or GAC without doping were evaluated by Yasri and Nakhla (2017) in MECs (Yasri and Nakhla, 2017). Higher current density and higher CE of 96.7%, hydrogen yield of 3.6 mol H_2/mol acetate, and attached biomass per anode mass (54.01 mg COD biomass/ g GAC) were obtained for 3D CaS doped electrode material. However, the higher surface area of the 3D MEC system did not improve the current density; doping 3D materials with species that naturally attract biota enhanced the performance of MEC.

The sluggish kinetics of organic matter oxidation made way for the search of excellent 3D materials. Carbon aerogels (CAs) are a promising bioanode material due to their anaerobic stability and low interfacial contact resistance. Wang et al. (2019) developed a self-supported 3D CA bioanode for studying the mechanism

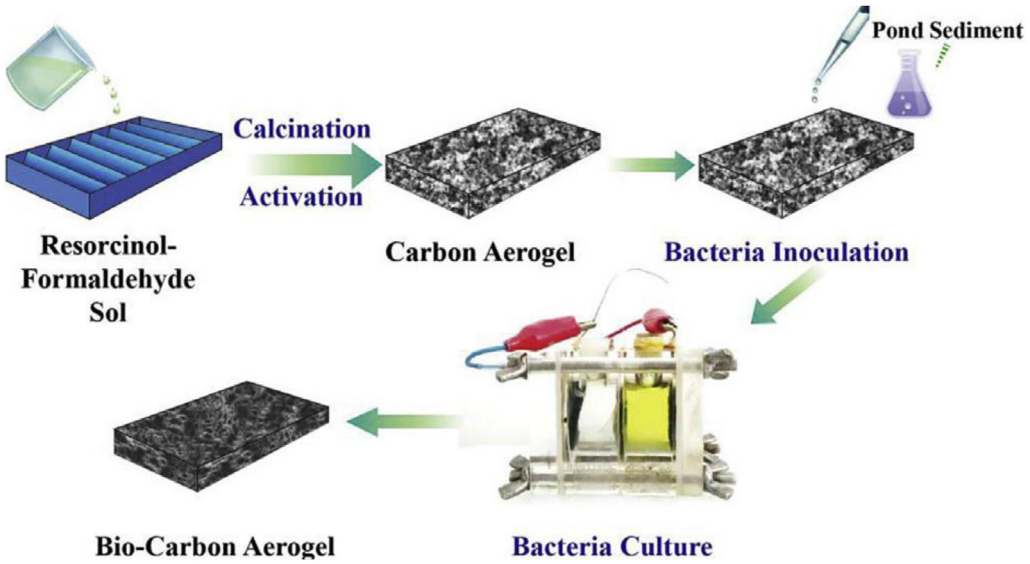

Fig. 4. Schematic diagram of carbon aerogel electrode preparation (Wang et al., 2019b).

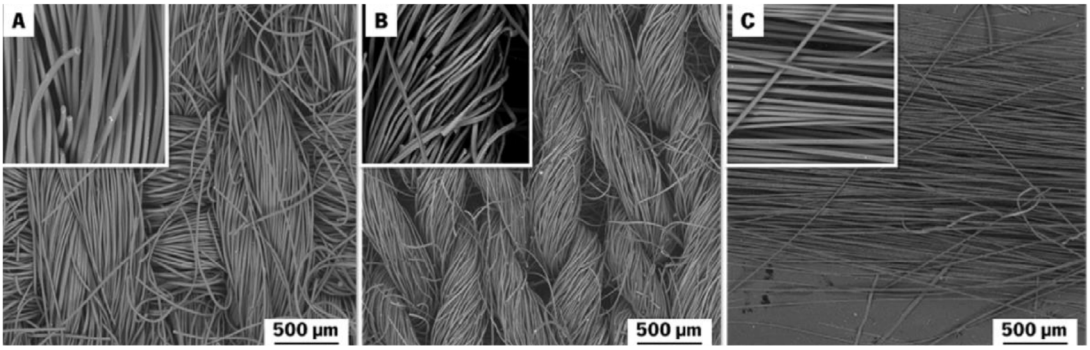

Fig. 5. SEM images of (a) Keynol, (b) C-Tex and (c) PAN (Barbosa et al., 2018).

of direct contact-based electron transfer and biocatalysts (Wang et al., 2019b). Fig. 4 shows the synthesis method of carbon aerogel. The CA bioanode developed improved electrical conductivity, enhanced interaction with microbes, and greatly enhanced bacterial incubation. In addition, the hydrogen production of bio-CA anode was found to be five-fold higher than that of biocarbon fiber at an applied voltage of 0.3 V in MEC.

2.3.1.2. Metal-based material. Metal-based electrodes, such as stainless steel, nickel, and copper, have gained enormous attention in BESs due to their high conductivity and mechanical strength
(Alqahtani et al., 2018). In fact, these properties are highly essential for scale-up applications (Sangeetha et al., 2016). For example, in a tubular design of MEC, Guo et al. (2017) used plated and tubular stainless steel (SS) anode for improving the volumetric current density with a reduction in Ohmic resistance due to the excellent conductivity of stainless steel (Guo et al., 2017). As a result, at an applied voltage of 1.0 V, the system yielded a hydrogen production rate of 7.10 $L/L/d$ with a hydrogen recovery of 100% and electrical energy efficiency of 149%.

2.3.1.3. Conductive polymer-based materials. During treatment of urine in MEC, Barbosa et al. (2018) studied the effect of different anode materials such as Keynol (phenolic based), C-Tex (cellulose-based), and PAN (polyacrylonitrile based) (Barbosa et al., 2018). The SEM images of such developed anode materials are shown in Fig. 5. C-Tex showed superior performance compared to Keynol and PAN electrode material in MEC. The highest current density of 904 mA/m^2 was obtained in C-Tex MEC—three-fold higher than Keynol MEC and eight-fold higher than PAN MEC. High current density revealed larger external surface area of C-Tex electrode, as evident from the textural, chemical, and electrochemical characteristics analysis. It was also apparent that anode properties did not influence microbial biodiversity in the developed biofilm.

2.3.2. Cathode modification

As stated earlier, the base materials of the cathode electrodes include stainless steel, titanium, carbonaceous materials, and other conductive materials. Since the hydrogen evolution reaction occurs very slowly on bare cathodes due to the high overpotential, a catalyst is required to accelerate HER. The most commonly used catalyst includes platinum due to its low free energy difference in Tafel reaction and low overpotential for HER. However, platinum is expensive, hence discovering different materials for commercializing the MEC system (Noori et al., 2018a). As a result, other catalytic materials such as nickel, nickel alloy, tungsten carbide, molybdenum disulfide, and some carbon-based nanomaterials were used for modifying cathodic electrodes. Table 2 describes the various electrode materials and catalysts used in MEC for hydrogen production and charge recovery.

2.3.2.1. Carbon-based nanomaterials. Nanostructured carbon materials are used as catalysts for oxygen reduction reactions in fuel cells and are widely used to support electrocatalysts. Also, carbon nanomaterials such as carbon nanotubes and graphene are widely

Table 2
Performance of different cathode materials and catalysts used in MEC.

Cathode Material/ catalyst	Cathode potential (V)	Hydrogen production rate (m^3/m^3 reactor liquid/d[a])	Coulombic efficiency (%)	Cathodic hydrogen recovery (%)	Reference
N-Fe/Fe_3C@C	0.8	0.0181 ± 0.0011 $m^3/m^2/d$	43.6 ± 0.8	79.8 ± 8.4	Xiao et al. (2012)
Pt/C	0.8	0.0230 ± 0.0031 $m^3/m^2/d$	39.8 ± 2.6	81.6 ± 5.0	Xiao et al. (2012)
NF + G	0.7	1.12 ± 0.06 mol Co/mol COD	64 ± 1.4	135 ± 2.9	Wang et al. (2015)
$Mg(OH)_2$/Gr	0.7	0.63 ± 0.11	83 ± 7	83 ± 9	Dai et al. (2016)
NF/NiO.rGO	1	4.38 mmol/l/d	56.64	21.16	Jayabalan et al. (2019b)
NF/Co_3O_4.rGo	1	3.66 mmol/l/d	54.67	18.16	Jayabalan et al. (2019b)
PtNi/C	0.4	0.064	82	–	Choi et al. (2019)
PtCu/C	0.4	0.044	77	–	Choi et al. (2019)
SS A286	0.9	1.50 ± 0.04	–	61 ± 3	Selembo et al. (2009a)
Ni 625	0.9	0.79 ± 0.27	–	43 ± 9	Selembo et al. (2009a)
Pt	0.9	1.37	–	98 ± 0.02	Ribot-Llobet et al. (2013)
SSW	0.9	0.06	–	70 ± 0.01	Ribot-Llobet et al. (2013)
SSFF100	0.9	3.66 ± 0.43	114.7	66.56 ± 2.07	Su et al. (2016)
SSW	0.9	1.3 ± 0.3 l-H_2/l/d	–	95	Kim et al. (2017c)
NiMo	0.6	2	75	86	Hu et al. (2009)
NiW	0.6	1.5	73	75	Hu et al. (2009)
NiMo	0.6	2.1	79	90	Hu et al. (2009)
Ni 210 + CB	0.6	1.2 ± 0.1	83.8 ± 1.2	94 ± 5	Selembo et al. (2010)
Ni 210	0.6	1.3 ± 0.3	92.7 ± 15.8	79 ± 10	Selembo et al. (2010)
Ni	1.0	4.1 $l/l_R/d$	68	103.3	Manuel et al. (2010)
Ni mesh	1.1	4.18 ± 1	–	119 ± 5	Kadier et al. (2015)
Pt/CC	1.1	4.25 ± 1	–	121 ± 3	Kadier et al. (2015)
NiFe LDH/Nickel foam	0.8	2.01 ± 0.01	77 ± 3	99 ± 0	Lu et al. (2016a)
Pt/Nickel foam	0.8	2.12 ± 0.09	66 ± 4	84 ± 3	Lu et al. (2016a)
NF-G	0.8	1.31 ± 0.07 ml H_2/ ml reactor/d	–	–	Cai et al. (2016)
Ni-P	0.7	1.42 *l/l/d*	97.6 ± 2.2	92.8 ± 4.8	Li et al. (2017)
NiW/Ni-foam	0.6	0.14 ± 0.01	–	78.9 ± 1.7	Mitov et al. (2017)
NiMo/Ni-foam	0.6	0.13 ± 0.01	–	88.6 ± 2.3	Mitov et al. (2017)
Pt/NF	0.8	0.71 ± 0.03	–	–	Bundhoo (2017)
AC-pNi4.8	0.9	0.38 ± 0.04 l-H_2/l/d	–	98 ± 5	Kim and Logan (2019)
MoS_2	0.8	2.72 ± 0.31	85 ± 5.2	100	Jeon et al. (2018)
MoS_2-EF	0.6	0.133	–	–	Rozenfeld et al. (2018)
PANI/MWCNT	0.9	0.67	72	75	Chen et al. (2015)
PANI/graphene on SSM	0.9	0.65	57	46	Ghasemi et al. (2020)
Pt on SSM	0.9	0.85	64	49	Ghasemi et al. (2020)
Pd	0.6	2.6 ± 0.5 $l/m^2/d$	56.0 ± 10.2	46.4 ± 8.5	Huang et al. (2011)
Pt	0.6	2.1 ± 0.3 $l/m^2/d$	52.0 ± 7.4	41.6 ± 6.1	Huang et al. (2011)

[a]Unless stated otherwise.

employed to develop high-performance catalysts in MECs (Xiao et al., 2012; Jayabalan et al., 2019b).

Novel carbon/iron-based composite nanorod (N-Fe/Fe_3C) catalysts as the core and graphite carbon as the shell were used as the cathode material and compared with Pt/C, CNT, and unmodified cathode (Xiao et al., 2012). The synthesis method of these hybrid materials is shown in Fig. 6. At an applied voltage of 1.0 V, the maximum hydrogen production rate of 4.38 ± 0.11 mmol/L/d and CE of 65.6% was obtained using NiO-rGO nanocomposite, which was found to be 1.19 and 2.68 times higher than Co_3O_4-rGO and uncoated Ni-foam, respectively. Furthermore, the addition of rGO with Ni and Co-metal oxide exhibited an excellent performance by coupling the high catalytic activity of Ni/Co with the high conducting capacity of graphene.

Hybrid catalysts of nickel oxide-reduced graphene oxide (NiO-rGO) and cobalt oxide-reduced graphene oxide (Co_3O_4-rGO)-coated nanocomposite cathodes were developed by Jayabalan et al. for the treatment of sugar industry wastewater and simultaneous production of biohydrogen (Jayabalan et al., 2019b). The synthesis method of these hybrid materials is shown in Fig. 6. At an applied voltage of 1.0 V, maximum hydrogen production rate of 4.38 ± 0.11 mmol/L/d and CE of 65.6% was obtained using NiO-rGO nanocomposite which was found to be 1.19 and 2.68 times higher than Co_3O_4-rGO and uncoated Ni-foam, respectively. The addition of rGO with Ni and Co-metal oxide exhibited an excellent performance by coupling high catalytic activity of Ni/Co with high conducting capacity of graphene.

Chen et al. (2015) developed a modified biocathode with polyaniline/multiwalled carbon nanotube (PANI/MWCNT) in a single-chamber membraneless MEC to improve hydrogen production (Chen et al., 2015). This composite was proposed to increase the electrochemical surface area and improve electrocatalysis. The microbial species and quantity were found to be different for the modified and unmodified biocathodes. The modified biocathode MEC generated a hydrogen production rate of 0.67 $m^3/m^3/d$ and a CE of 72%.

Recently, Ghasemi et al. (2020) compared the effect of three different catalysts such as Pt, PANI, and PANI/graphene on an SS base material (Ghasemi et al., 2020). Using dairy wastewater as substrate, MEC with SSM/PANI/graphene electrode exhibited a maximum hydrogen production rate of 0.805 m^3H_2/m^3 anolyte/d. This value was only 20% less than MEC using Pt. Although the MEC using Pt produced a CE 12% higher than SSM/PANI/graphene, this cathode reduced the fabrication cost by 39%. Compensating the CE, the cost economics of such catalyst reduced the overall cost and thus can be suitable for practical applications.

2.3.2.2. Stainless steel-based material. Stainless steel (SS) is the most promising material available in various shapes such as mesh, plates, highly porous wool, bushes, felt, and electroformed mesh. SS has excellent properties such as low cost, good durability, and high electrical conductivity. The hydrogen production rate of SS fiber (3.7 ± 0.4 l H_2/l -reactor/d) or SS brushes (1.7 ± 0.1 l H_2/l-reactor/d) cathode in MEC is similar to using Pt-based cathodes (Call et al., 2009a; Su et al., 2016).

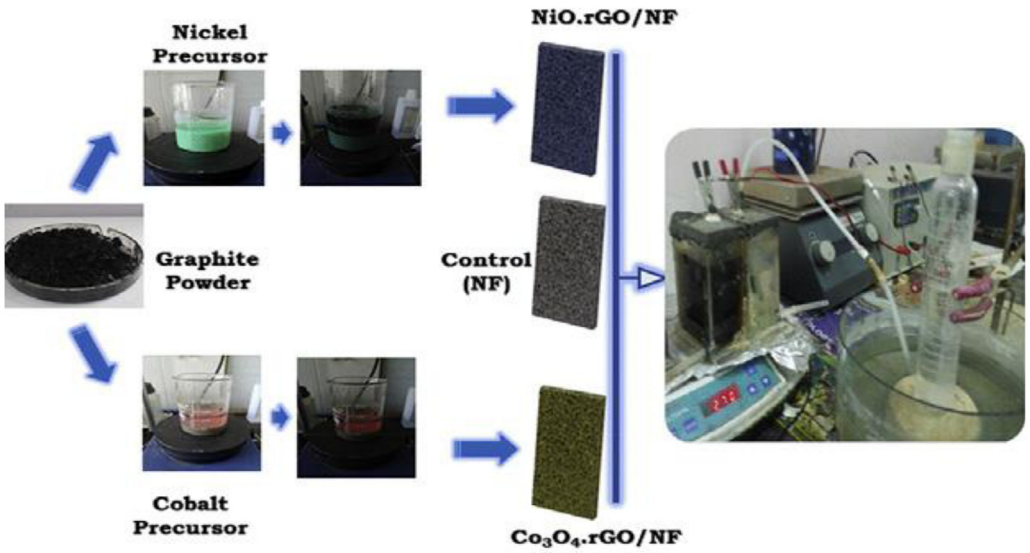

Fig. 6. Schematic diagram of synthesis of hybrid catalyst (NiO-rGO and Co_3O_4-rGO) and experimental setup (Jayabalan et al., 2019b).

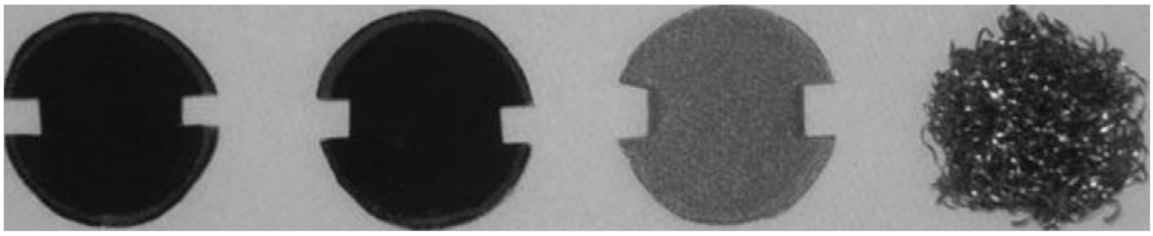

Fig. 7. Photographs (left to right) of platinum-coated SS mesh (Pt), molybdenum disulfide-coated SS mesh (MoS_2), nickel foam (NF), and SS wool (SSW) (Ribot-Llobet et al., 2013).

The phosphate charged species reduce the overpotential on cathodes and enhance the electrolyte conductivity. Stainless steel was shown that phosphate species undergo cathodic deprotonation, which enhances HER. Munoz et al. (2010) conducted a study to determine whether the corrosion occurring cathodic deprotonation by phosphate could be used to enhance H_2 production in neutral pH electrolysis (Munoz et al., 2010). A flat 254 SMO SS was fabricated as the cathode. Voltammetry and rotating disk electrodes proved that the current density of HER was enhanced by the presence of phosphate species through the cathodic deprotonation reaction. MEC with marine microbial anode and the fabricated cathode-produced hydrogen evolution rates up to 4.9 $l/h/m^2$.

Selembo et al. (2009) studied the effect of different nickel and SS alloy cathodes and compared them with platinum cathodes (Selembo et al., 2009a). The SS A286 was superior to platinum cathodes in terms of cathodic hydrogen recovery (61% vs. 47%). In another study, nickel foam (NF), SS wool (SSW), molybdenum disulfide-coated SS mesh (MoS_2), and platinum-coated SS mesh (Pt) were compared (Ribot-Llobet et al., 2013). The photographic image of the material used in this study is shown in Fig. 7. Again, the NF cathode outperformed all other catalyst materials. Furthermore, it was also found that overall hydrogen gas recoveries with MoS_2 (28.6 ± 1.3 ml), SSW (29.7 ± 0.5 ml), and NF (32.4 ± 2 ml) were slightly less than that of Pt (37.9 ± 0.5 ml).

Stainless steel fiber felt (SSFF) is a commercially available and cheap 3D porous filter material having the advantage of good conductivity, high specific surface area, and flexibility and have been used as efficient cathode materials (Su et al., 2016). The MEC using SSFF cathode exhibited a hydrogen recovery of 76.37 ± 15.04% and overall energy efficiency of 79.61 ± 13.07%. Moreover, the performance of MEC using SSFF cathode was found to be comparable with MEC using Pt/C cathode. The SSFF cathode material enhanced current density through improving electrochemical activity and reducing cathodic overpotential than the SSM.

The SS was a better cathode material when tested under static flow conditions. Kim et al. (2017) fabricated SS materials with different 3D structures such as mesh, fiber felt, wool, and brushes under catholyte recirculation and compared their performances with control Pt cathode (Kim et al., 2017c). The MEC with wool exhibited the highest hydrogen production rate (1.3 ± 0.3 l-H_2/l-reactor/d), similar to Pt control at a catholyte recirculation of 40 ml/min. The high specific surface area of wool (480 m^2/m^3 reactor volume) and catholyte recirculation reduced the cathode overpotential. Moreover, in the absence of flow, hydrogen production was depleted by 52% (wool) to 28% (brush).

2.3.2.3. Nickel-based materials. Nickel (Ni) has been widely used as an HER catalyst since Ni has a lower HER overpotential and is stable under alkaline conditions than other noble metals (Siwek et al., 2019; Lu et al., 2016b; Hu et al., 2019). Due to its lower electrical resistivity, Ni has also been used as a current collector instead of graphite or titanium (Wang et al., 2013). Different forms of Ni alloys (NiMo, NiW, NiFeMo, NiFe, NiFeP, NiFeCoP, and NiCr) can be efficiently used as HER catalysts and can be deposited electrochemically or chemically on carbon-based materials (Yang and Hu, 2019; Zhou et al., 2017; Xia et al., 2019; Zhang et al., 2018). Membraneless MEC with Ni-based cathodes has higher current densities, and volumetric H_2 production than MEC using Pt coated cathode (Jeremiasse et al., 2010). Non-precious metal cathodes were developed by electrodepositing NiMo and

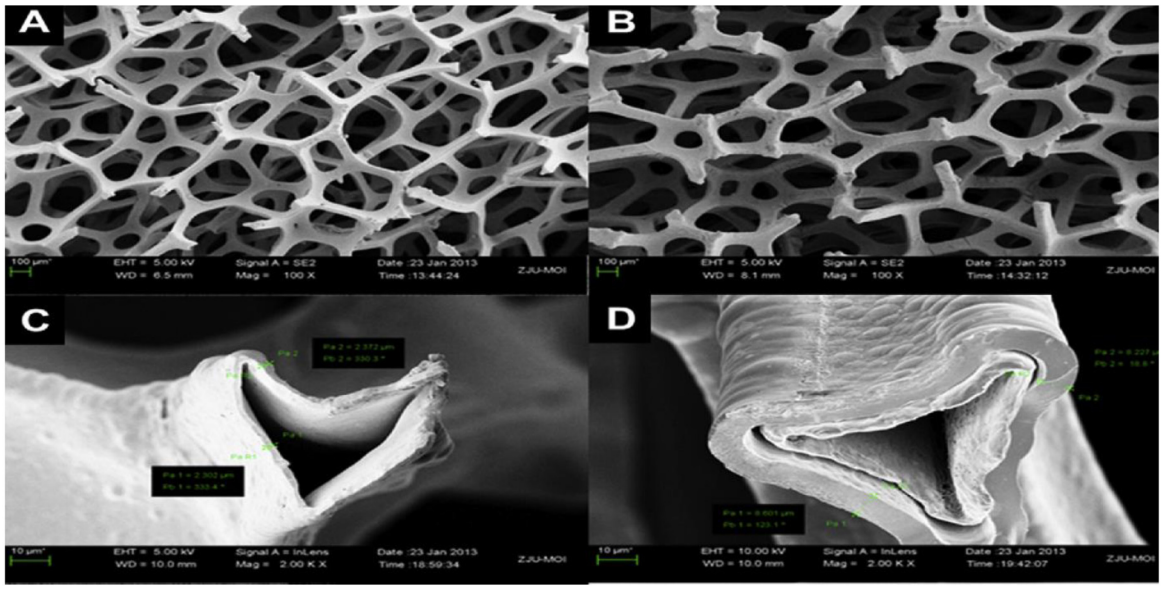

Fig. 8. SEM images of cathode materials: (A) plan view of Ni-foam and (B) 7.9% of P in NiP (C) sectional views of Ni-foam and (D) 7.9% of P in NiP (Li et al., 2017).

NiW on carbon fiber-weaved cloths (Hu et al., 2009). The energy efficiency based on electrical energy input of NiMo MEC reached 240% compared with NiW at an applied potential of 0.4 V. In another study using Ni powder cathode catalysts, the performance of MEC was comparable to that using Pt cathodes (Selembo et al., 2010).

Electrodeposition of Ni particles on porous material in a membraneless MEC reduced its methanogenic electron loss (Hrapovic et al., 2010). A maximum hydrogen production rate of 5.4 $l/l_R/d$ was obtained using electrodeposited Ni particles at a loading rate of 0.2–0.4 mg/cm^2. Other gas diffusion cathodes were developed using multicomponent cathodes containing Ni, Mo, Cr, and Fe chemically deposited at a catalyst loading of 1 mg/cm^2 with only 5% methane in the gas stream (Manuel et al., 2010).

A cathode's catalytic activity cannot be fully functionalized at neutral pH due to mass transport limitations. Hence MECs were operated under alkaline conditions when mass transport is not a limiting factor (Jeremiasse et al., 2011). In this study, copper sheets coated with nickel–molybdenum, nickel–iron–molybdenum, or cobalt–molybdenum alloys were used as cathode catalysts. MECs that employed these catalysts outperformed control nickel cathodes. The cobalt–molybdenum alloy exhibited a hydrogen production rate of 50 m^3 H_2/m^3 MEC/d. In another study, the electroformed Ni mesh cathode was compared with Pt/CC cathode. The CE (75 ± 4% vs. 72.7 ± 1%) and overall hydrogen recovery (89.3 ± 4% vs. 90.9 ± 3%) was comparable with the Pt cathode. This study demonstrated the potential of using a Ni mesh cathode instead of Pt cathode.

To reduce the manufacturing cost (of polymer binders and current collector), a one-step *in situ* growth of catalyst on nickel substrate is examined (Lu et al., 2016). In this study, a novel NiFe layered double hydroxide electrocatalyst was grown on NF cathode in MEC to treat brewery wastewater and simultaneously produce hydrogen (2.01–2.12 m^3H_2/m^3/d). Cai et al. (2016) fabricated a self-assembled 3D NF graphene cathode using the facile hydrothermal approach (Cai et al., 2016). Improved electrochemical activity and effective mass transport were obtained after binding NF with graphene. The hydrogen production rate, in this case, was comparable with Pt/C.

NF has superior mechanical strength and conductivity than carbon-based supports. In this view, Miltov et al. (2017) developed a NiW and NiMo catalyst having high intrinsic activity on NF. They found that NiW has about six times higher intrinsic electrocatalytic activity compared to NiMo (Mitov et al., 2017). This may be because the inner part of the thicker NiMo layer is inactive to HER reaction. The cathodic hydrogen recovery and energy efficiency of MEC using this catalyst was twice that of MEC using non-modified NF. Li et al. (2017) developed a Ni–P-coated NF cathode and compared its efficacy with plain NF and SS (Li et al., 2017). The SEM image of the NF and Ni-P is given in Fig. 8. Ni-P alloy has good physical and chemical properties along with superior hydrogen evolution performance. Moreover, the Ni-P catalyst was found to have less retention time for hydrogen escape and low ratio of hydrogen diffusion, which reduced the efficiency of hydrogenotrophic methanogens. More than 80% improvement in hydrogen production and 50% inhibition of methane production were obtained in this study. The hydrogen production rate using the Ni-P cathode was 7.5% higher than NF and 110% higher than SS.

Usually, multiple steps are required for electrodeposition and electroplating, which is not suitable for practical and commercial applications of MEC. Therefore, a one-step phosphorization of NF using phosphorous vapor without any additional binder was employed to synthesize a 3D structure with exposed active sites on the phosphide nanosheet matrix on the surface (Cai et al., 2018). Such biphasic Ni_5P_4–NiP_2 nanosheet matrix exhibited outstanding performance in hydrogen yield and hydrogen production rate, which might be due to the enhanced electron recovery and EET. A hydrogen production rate of 9.78 ± 0.38 $mL/d/cm^2$ was obtained in MEC using this catalyst found to be 1.5 times faster than that using plain NF. Also, the long-term durability in performance of this MEC was reported.

The excellent catalytic activity of Ni_2P to the negatively charged phosphorous atom contributed to the attraction of more positively charged protons and subsequently reduce the hydrogen binding energy (Liu and Rodriguez, 2005). Using the solution phase method, a carbon-supported Ni_2P nanoparticle (Ni_2P/C) was synthesized, and their efficacy was compared with Pt/C and Ni/C catalysts in MEC (Kim et al., 2019). The hydrogen production rate of Ni_2P/C (0.29 ± 0.04 l-H_2/l-reactor) was comparable with that of Pt/C (0.32 ± 0.03 l-H_2/l-reactor) and Ni/C (0.29 ± 0.02 l-H_2/l-reactor), and the mass normalized current density of Ni_2P/C was found to be 14 times higher than that of Ni/C with a reported stable performance of over 11 days.

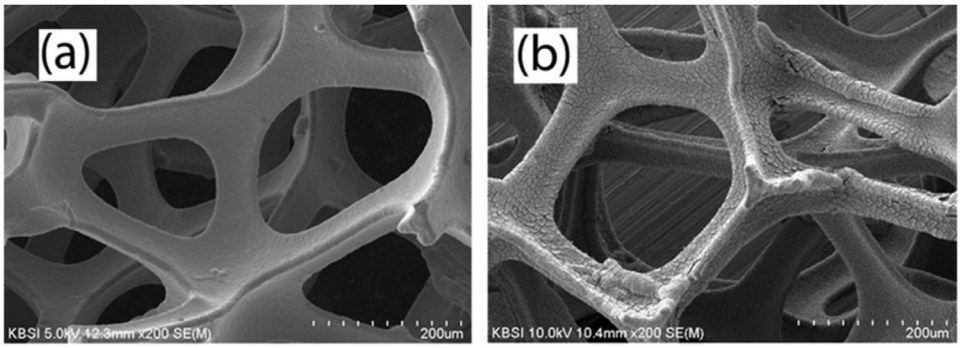

Fig. 9. SEM images of NF and NNR/NF electrodes (Eisa et al., 2019).

Considering the efficiency of other synthesis methods, the bromide anion exchange method effectively produces downsized nanoparticles without any need for organic molecules during synthesis. The performance of nickel-based metallic nanoparticles as a catalyst material in MEC was compared with homemade nickel mesh and high-purity nickel foil (Neto et al., 2019). The synthesized $Ni_{99}Pt_{01}$/C electrocatalyst performed better in current density and reduction in overpotential, notably in physiological conditions.

A 3D nickel electrode can have a greater electroactive surface area and produce more hydrogen than flat metal electrodes (Song et al., 2018). Although Ni catalysts can have a high rate of HER comparable to that of Pt electrodes, the amount of Ni loading needs to be reduced to make the system more economically favorable for scale-up applications (Alqahtani et al., 2018; Song et al., 2018). Kim and Logan (2019) developed cathodes by blending Ni powder with activated carbon (AC-pNi) to provide a higher surface area, thus enhancing HER with less nickel loading (Kim and Logan, 2019). The AC-pNi (with Ni loading of 4.8 mg/cm^2) resulted in an enhancement in hydrogen production rate (0.38 ± 0.04 l-H_2/l/d) than plane Ni (0.28 ± 0.02 l-H_2/l/d) with a 16 times less loading of Ni. Also, the cathodic hydrogen recovery was higher in AC-pNi ($98 \pm 5\%$) than plane Ni ($82 \pm 4\%$), indicating catalytic activities were improved by AC blending. Zhao et al. (2019) studied the effect of carbon-based Ni/NiO nanocomposite for HER in MEC and reported a decrease in performance due to the corrosion and Ni dissolution (Zhao et al., 2019).

Nickel nanoparticles were further used in MECs for electro-methanogenesis and also in an ethanol fuel cell. Electro-methanogenesis produces methane in a MEC from electrical current and CO_2 in the cathodic chamber. A Methanogenic bacteria symbiotically associated with exoelectrogens can promote direct interspecies electron transfer in methanogenic MECs using GAC and Ni nanoparticles (Ni-NP). The effect of Ni-NP/GAC composite on the performance of electro-methanogenesis in MECs was studied by Kim et al. (2017) (Kim et al., 2017b). The Ni-NP/GAC composite was found to produce methane gas (20.7 mL) higher than bare GAC (15.6 mL) and GAC free control (9.6 mL). In another study, Eisa et al. (2019) fabricated a nickel nanorod (NNR)/NF electrode as a cost-effective electrode for use in direct alcohol fuel cells (DAFCs) (Eisa et al., 2019). The SEM images of the fabricated electrode are shown in Fig. 9. Enhanced electrocatalytic activity and stability were reported in the DAFCs using NNR/NF electrode. Moreover, the current densities obtained using this electrode for ethanol oxidation were four times higher than that of pristine NF. MECs with electrodeposited cathodes (co-deposits of Ni, Ni–Co, and Ni–Co–P) were manufactured and studied for their treatment efficiency and hydrogen recovery using sugar industry wastewater (Chaurasia and Mondal, 2022). The Ni–Co–P electrodeposit achieved the maximum hydrogen production rate with 50% treatment efficiency in 7 days batch mode.

To maximize the electrode surface area, cathode coated with metal nanoparticles is evaluated and compared with cathodes without metal doping (Choi et al., 2019). Ni and Cu were the mainly used transition metals for doping. It performed slightly lower than Pt/C catalyst in terms of hydrogen generation efficiency and electrochemical behaviors. Moreover, the performance of Ni/C catalyst was shown to be better than that of other metals and carbon nanomaterials. Furthermore, Ni is inexpensive and corrosion-resistant, making it a suitable MEC catalyst for hydrogen production and sustainability.

2.3.2.4. Molybdenum sulfide-based materials. Molybdenum sulfides (MoS_X) are promising materials for higher HER, have excellent chemical stability, and are inexpensive. Molybdenum sulfides can be detailed as ionic compounds containing Mo^{4+} cations and sulfide (S^{2-}) as well as disulfide anions. For molybdenum sulfides, it has been shown that hydrogen atoms easily bind to sulfur anions at the edge of MoSx layers and contribute to a higher rate of HER. As a result, MECs with MoSx catalysts have higher hydrogen production rates than Pt catalyst, which promises an efficient catalyst material (Kokko et al., 2017).

Tokash et al. (2011) reported that molybdenum disulfide (MoS_2) composite cathode has electrochemical performance superior to SS and Pt cathode in phosphate of perchlorate electrolytes (Tokash and Logan, 2011). The MoS_2 and SS were evaluated as catalysts for treating wastewater in terms of treatment efficiency and energy recovery compared with platinum (Tenca et al., 2013). Methanol-rich industrial wastewater and food processing wastewater were assessed for treatment efficiency in MEC. The use of MoS_2 catalyst showed a better performance than SS, but the performance was lower than a platinum catalyst. For the treatment of acidic wastewater and hydrogen evolution, there is a need for a suitable and economical catalyst compatible with wastewater's complex chemical composition. Molybdenum sulfides (MoS_2) on different carbon substrates were used for HER in acidic wastewater (Kokko et al., 2017). For the most promising MoS_2 cathodes, the overpotential for HER was found to be slightly higher (40 mV) than that for a platinum electrode.

Recently, Jeon et al. (2018) fabricated a photo-assisted MEC (PAMEC) for hydrogen production with a p-type semiconductor cathode (Jeon et al., 2018). High-purity hydrogen with no methane and carbon dioxide was produced when Cu_2O coated MoS_2 cocatalyst was employed. Under visible light illumination, a hydrogen production rate of 2.72 m^3H_2/m^3/d was achieved. This improved performance could be related to the proton reduction activity of MoS_2 and p-type semiconductor characteristics of Cu_2O. The schematic representation of the electron transfer pathway in PAMEC is included in Fig. 10. Rozenfeld et al. (2018) synthesized an exfoliated molybdenum disulfide (MoS_2-EF) catalyst and tested it in MEC (Roubaud et al., 2018). Hydrogen evolution rates of a MEC tested with a *Geobactersulferreducens* anode and Pt, MoS_2-EF, and pristine MoS_2 cathodes were 0.106, 0.133, and 0.083 m^3/d/m^3, respectively.

Table 3
Comparison of scalable studies on MECs cited in the literature.

Reactor design					Operation condition			Performance		Ref.
Type	Reactor volume (L)	Anode electrode	Cathode electrode	Membrane	Operation mode	Substrate	Applied voltage (V)	COD removal (%)	H_2 production	
Single-chamber (eight electrode pairs)	2.5	Graphite brushes	Stainless steel 304 mesh sheet	–	Continuous	Acetate	0.9	31–47	Max. H_2 production rate: 0.53 $L/L/d$	Rader and Logan (2010)
Single-chamber (144 electrode pairs in 24 modules)	1,000	Graphite brushes	Stainless steel 304 mesh sheet	–	Continuous (HRT = 24 h)	Winery wastewater	0.9	62	Max. H_2 production rate: 0.19 $L/L/d$	Cusick et al. (2011)
Single-chamber (two five-liter reactors in series)	10	Carbon felt	Gas diffusion carbon paper with electrodeposited Ni	–	Continuous (HRT = 10 h)	Municipal wastewater	–	60–76	Max. H_2 production rate: 0.05 $L/L/d$	Gil-Carrera et al. (2013)
Cassette style design modules in reactor	120	Carbon felt	Stainless steel wire wool grade 1	Rhinohide membrane	Continuous	Urban wastewater	1.1	33.7	Max. H_2 production rate: 0.0015 $L/L/d$	Heidrich et al. (2013)
Two-chamber	60	Graphite plate	Stainless steel plates	Proton exchange membrane	Continuous (HRT = 29.52 h)	Wastewater	–	67	Current generation: 72 $\mu A/cm^2$	Brown et al. (2014)
Cassette style design modules in reactor	100	Carbon felt	Stainless steel wire wool grade 1	Rhinohide membrane	Continuous (HRT = 24 h)	Urban wastewater	1.1	~63.1	H_2 production rate: ~0.7 L/d	Heidrich et al. (2014)
Modular single-chamber (two 3-L reactors)	6	Graphite felt	Gas diffusion carbon paper with Ni	Porous geotextile	Continuous (HRT = 6–42 h)	Domestic wastewater	0.7	>10–70	H_2 recovery: ~20%	Escapa et al. (2015)
Multistack (10 anodes and 9 cathodes)	33	Reticulated vitreous carbon tubes	Ni steel	Proton exchange membrane (Nafion 117)	Continuous	Glucose	–	~1.5	H_2 production rate: ~0.026 L/d	Sugnaux et al. (2016)
Cassette style design modules in reactor (three modules)	182	Graphite felt	Stainless steel 316 mesh sheet	Rhinohide separator	Continuous (HRT = 5 h)	Wastewater	0.9	63.5	H_2 production rate: ~ $0.003L/L/d$	Cotterill et al. (2017)
Cassette style design modules in reactor (10 modules)	130	Carbon fiber	Stainless steel wire wool	Anion exchange membrane	Continuous (HRT = 24–48 h)	Wastewater	1.5	5.9–25.4	Max. H_2 production rate: ~ $0.032L/L/d$	Baeza et al. (2017)
Cassette style design modules in reactor	135	Carbon felt	Stainless steel wire wool grade 1	Rhinohide membrane	Continuous (HRT = 24 h)	Domestic wastewater	1.2	–	H_2 production rate: ~ $0.02L/L/d$	Cotterill et al. (2018)
Cassette style design modules in reactor (10 modules)	130	Graphite fibers	Stainless steel wire	Anion exchange membrane	Continuous (HRT = 48 h)	Urban wastewater	1	25.4	H_2 production rate: 4.1 L/d	Chen et al. (2019)
Cylindrical single-chamber	40	Graphite felt	Stainless steel 304 mesh sheet + graphite felt	–	Continuous (HRT = 48 h)	Acetate	0.5	96	H_2 production rate: 0.0039 $L/L/d$	Huang et al. (2019)
Single-chamber, membraneless reactor modules (stacking 45 cells)	32	–	–	–	Continuous (HRT = 72 h)	Municipal wastewater	0.7	72	CH_4 production rate: 4.4 $L/m^2/d$	Ceballos-Escalera et al. (2020)
Cassette style design modules in reactor (10 modules)	72	Carbon felt	Stainless steel wire wool	Rhinohide separator	Continuous	Urban wastewater	0.9	24.5	H_2 production rate: 0.0155 $L/L/d$	Leicester et al. (2020)
Cassette style design modules in reactor	360	Carbon cloth	Carbon cloth	–	Continuous (HRT = 144 h)	Sludge filtrate	0.9	86.6	CH_4 production: 282 mL/g COD	Wang et al. (2020)
Tubular two-chamber	12	–	–	Anion exchange membrane	Continuous (HRT = 12.6 h)	Acetate	–	56–92	CH_4 production: 261–449 meq/d	Zeppilli et al. (2020)
Single-chamber (seven anodes and three cathodes)	10	Carbon cloth	Carbon cloth (biocathode)	–	Continuous (HRT = 180 h)	Lignocellulosic hydrolyzate	1.36	99 (consumed substrate)	H_2 production rate: 0.71 $L/L/d$	Wang et al. (2021b)

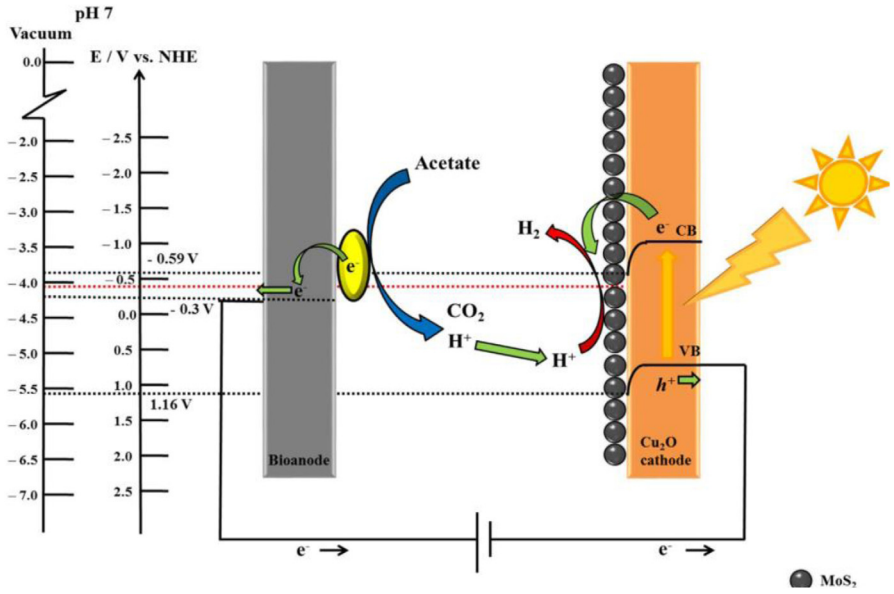

Fig. 10. Schematic representation of energy levels and electron transfer pathway in the PAMEC under illumination (Jeon et al., 2018).

2.3.2.5. Palladium-based materials. Palladium (Pd) has excellent catalytic performance and could be used efficiently as an HER catalyst. The catalytic efficiency normalized by the mass of the Pd nanoparticle was about 50 fold higher than that of the Pt black catalyst. Moreover, the Pd is at least 50 times more abundant in nature and cheaper than Pt. Therefore, successful HER could be obtained by co-depositing Pd and Au on Ni-foam base material in MEC (Chorbadzhiyska et al., 2015).

Pd nanoparticles were generated by bioelectrochemical reduction with *Shewanella onediensis* MR-1 directly on the cathode, and studies for HER in MECs were conducted (Wang et al., 2019b). This catalyst attained a hydrogen production rate of 61.8 ± 2.0 L. $H_2/m^3/d$ as compared to 38.5 ± 2.0 l-$H_2/m^3/d$ in MEC with Pd catalyst and low charge transfer resistance of 15.4 Ω. Huang et al. (2011) developed a carbon cloth-coated Pd nanoparticle cathode by electrochemical deposition and showed a lower overpotential than carbon paper coated with Pt black (Huang et al., 2011). The CE and cathodic hydrogen production achieved was slightly higher in Pd/C cathode assembly than Pt/C cathode in MEC. These results showed that Pd nanoparticles could be efficiently used as a cathodic catalyst in MEC while reducing the fabrication cost and voltage losses.

3. Scale-up and practical applications of MECs

3.1. Previous studies for MEC scale-up

Many trials on laboratory-scale MECs have been conducted successfully using novel catalyst and electrode *material* combinations; however, taking these laboratory-scale successes into account, several studies have been conducted to design scale-up MEC systems and test them in relevant environments (Rader and Logan, 2010; Cusick et al., 2011; Gil-Carrera et al., 2013; Heidrich et al., 2013; Brown et al., 2014; Heidrich et al., 2014; Escapa et al., 2015; Sugnaux et al., 2016; Cotterill et al., 2017; Baeza et al., 2017; Cotterill et al., 2018; Chen et al., 2019; Huang et al., 2019; Ceballos-Escalera et al., 2020; Leicester et al., 2020; Wang et al., 2020; Zeppilli et al., 2020; Wang et al., 2021b). Table 3 summarizes previous studies of scale-up MECs. The first pilot-scale MEC of 1000 L was tested by Cusick et al. (2011) for the treatment of winery wastewater. The designed system consists of 24 modules with 144 pair of electrodes (Cusick et al., 2011). Graphite fiber brush anode, and SS mesh cathode, and current collectors were used for the fabrication. Existing limitations of poor cathodic performance and electrode spacing were controlled in the MEC. Low power density (7.4 A/m^3) obtained in this pilot reactor was primarily due to reactor geometry, electrode materials, the inclusion of glass fiber separators, possible connection resistances, and other design constraints. Also, in 2013, considering the stacking arrangement, Gil-Carrera et al. connected MEC reactors with a capacity of 10 L in series and achieved a COD removal rate of 0.5 $g/l_{-Reactor}$ with an energy consumption rate of 0.9 Wh/g of removed COD, where the COD removal efficiency was 60%–76% (Gil-Carrera et al., 2013).

A prototype of a 60-L MEC was developed using a graphite plate anode and stainless steel cathode, where the performance could be improved by switching the reactor mode of operation from closed loop to continuous mode (Brown et al., 2014). In 2017, a modular MEC with a capacity of 130 L was applied for treating synthetic wastewater and produced hydrogen at a rate of 0.013 $m^3/m^3{\cdot}d$, thereby removing 26% of the COD (Baeza et al., 2017). Such cassette cells were accommodated in stainless steel tanks by maintaining an anode to cathode ratio of 3.5:1. In this study, selected cathode materials, i.e., stainless steel wool and stainless steel mesh wrapped with graphite fibers, showed good compromise between price and performance. Selecting electrically conductive electrode materials in MEC operation stimulate direct electron transfer by electrochemically active bacteria and promote the electrochemical redox reactions.

In actual practice, scale-up implementation depends on the long-term operation of MEC units and operational parameters, characteristics of the wastewaters, and cost of the system (Chen et al., 2019; Huang et al., 2019; Ceballos-Escalera et al., 2020). Hunag et al. (2019) scale-up single-chambered cylindrical MECs to 40-L capacity using graphite felt as the anode and cathode with surface areas of 18 m^2/m^3 and 22 m^2/m^3, respectively. This attempt suggested that the combination of acetate and metals showed higher treatment efficiency than MEC fed with acetate or metals alone (Huang et al., 2019). Further, a pilot-scale anaerobic baffled reactor with carbon cloth electrodes demonstrated technological and economic progress in anaerobic treatment of sludge filtrate (Wang et al., 2020). Tubular design of a 12-L MEC using graphite granule electrodes was proven to be a promising innovative biogas upgrade in technology (Zeppilli et al., 2020).

Most recently, Wang et al. (2021) achieved high hydrogen production yield of 91% (0.71 $L/L/d$ of hydrogen production rate) from lignocellulosic hydrolyzate using a 20-L biocathode MEC with multielectrodes (Wang et al., 2021b). Also, Baek et al. (2021) analyzed scalable MECs and established a relationship between the hydrogen production rate against the surface area-to-volume (S/V) ratio at an applied voltage of 1.1 V taken from a database of 90 experimental studies (Baek et al., 2021). Improper selection of the electrode material, S/V ratio, and biofilm formation can increase electrochemical losses and hinder the scalability of MECs.

3.2. Scale-up challenges of MECs

Research on MEC is a complex and multidisciplinary endeavor that includes the fields of electrochemistry, microbiology, materials science, environmental engineering, and related sciences. This can bring merits to MECs, but paradoxically, this can bring many hurdles for the practical application of the MEC. As stated earlier, MECs have experienced a rapid increase in the amount of scientific work and the number of publications, covering diverse domains such as electrode material, energy production, biohydrogen recovery as well as a few attempts toward pilot-scale applications. However, despite current research progress, previous scale-up trials have shown that MECs are far from real-life and commercial application.

For the practical application of MEC, many challenges must be addressed and resolved as follows. The first and foremost issue is to prevent decreased efficiency as reactor volume expands. As shown in Fig. 11(a), although there are very few exceptions, it is clear that the hydrogen production efficiency rapidly decreases as the volume increases due to many newly induced problems such as increased application of electrodes (explained in detail later). Therefore, maintaining proportionate hydrogen production with an increase in size is needed.

Among the many challenges described in Fig. 11(b), a variety of energy losses in MECs is inevitable and especially serious when the electrodes are enlarged due to increased electrode-based overpotentials. Therefore, a much greater external power support is required compared to the theoretical demand.

Another difficulty is the durability or physical strength of the electrode material. Until now, use of conductive carbon-based electrode materials, such as carbon fiber, carbon brush, and conductive stainless steel, for the current collector is preferred for scalable applications as revealed from past experience (Table 3). However, these electrode materials are fragile when expanded, which causes serious performance deterioration and maintenance difficulty. In addition, due to the limited experiences at a large scale, the available data of designing electrodes, such as electrode size, shape, and connection, are limited.

Owing to expensive core components, such as electrodes, current collector, and hydrogen tanks, practical-scale MECs require high construction costs compared to other competing biological wastewater treatment or energy recovery technologies (Jadhav and Chendake, 2019). According to a previous estimation, the material costs for electrode components, including current collectors, occupy nearly 94% of the total construction cost of a MEC system (Aiken et al., 2019). Therefore, the difficulties will continue unless there are price and performance innovations for these key components. Indeed, the most critical issues on scale-up MECs are mostly relevant to the electrodes, such as severe energy losses, cost economics, and difficulty in operation and maintenance (Mathuriya et al., 2018; Jadhav and Chendake, 2019).

Finally, operational and maintenance issues due to the complexity of the structure of the MEC should also be highlighted for scale-up. To increase MEC processing capacity, it is inevitably necessary to increase the electrode area. However, when simply increasing the electrode size, many of the problems mentioned above occur, so several MEC modules of an appropriate size must be stacked (i.e., modular stack design). Considering electrical wiring, operation and maintenance, and adaptability to conventional wastewater treatment systems, modular design on multiple electrode pairs can be a good design approach for consideration. This modular design can also be hydrodynamically maintained under uniform substrate conditions with substrate availability throughout the dimensions. However, if the maintenance of electrochemical components such as electrode replacements, electrical wiring, and cleaning of MEC modules is not properly considered in a stacked configuration, many operational problems incur and deteriorate the performance of this technology. In this regard, for electrode scale-up and modular design for large scale application, it is also a good idea to utilize the design know-how of a membrane bioreactor or plate type heat exchange system, which has achieved technological innovation based on similar concerns.

Similarly, optimization of operating conditions needs several trials to finalize the substrate characteristics and design aspects to move toward a scalable MEC. Newly developed electrode materials suggested in previous lab-scale studies must be demonstrated in large-scale MECs. Also, before commercialization, an understanding of microbial electrode interaction against applied potential needs to evaluate the electron transfer chain for enhancing the hydrogen production rate in the MEC is necessary. As discussed earlier, several more attempts will increase confidence to overcome these scale-up challenges as well as understand the commercialization perspectives.

4. Technoeconomic analysis and future perspectives

Low performance and capital cost investment are major barriers to scale-up a bioelectrochemical system, including MEC. The hydrogen that can be recovered with benchtop MEC models now approaches levels that come close to the requirements for practical applications (Rozendal et al., 2008). However, several microbial, electrochemical, engineering design and economic challenges need to be resolved to provide a sustainable solution for practical use. In cost comparison, the cost of MECs was almost ten-fold higher than the anaerobic digestion system due to the use of expensive electrode materials and membrane cost associated with the electrochemical system (Rozendal et al., 2008). As per financial feasibility analysis, the net present value (NPV) was estimated as –£ 42,900,000 for MECs, whereas NPV was –£ 2,000,000 for activated sludge process for 20 years against an organic loading rate of 140 g.COD/m^3/day (0.3 A/m^2) (Aiken et al., 2019). This feasibility analysis showed a major cost contribution of 99% from material cost (electrode and current collector cost), followed by the membrane cost.

Therefore, the success of realizing economically viable full-scale MEC systems substantially lies in cost-effective high-performance membrane and electrode components. Furthermore, it is critical for the commercialization of MECs to consider how to integrate conventional wastewater treatment systems such as activated sludge processes and anaerobic digesters. Substituting stand-alone MEC systems with conventional wastewater treatment and bioenergy production systems may be exceedingly difficult in the near future; the development of MECs should also be focused on improving the compatibility of conventional processes. For example, MEC systems can be employed as a booster system to enhance biogas generation in a conventional anaerobic digestion plant. For this, electrode materials and designs should be optimized under the consideration of operational conditions of anaerobic digestion plants.

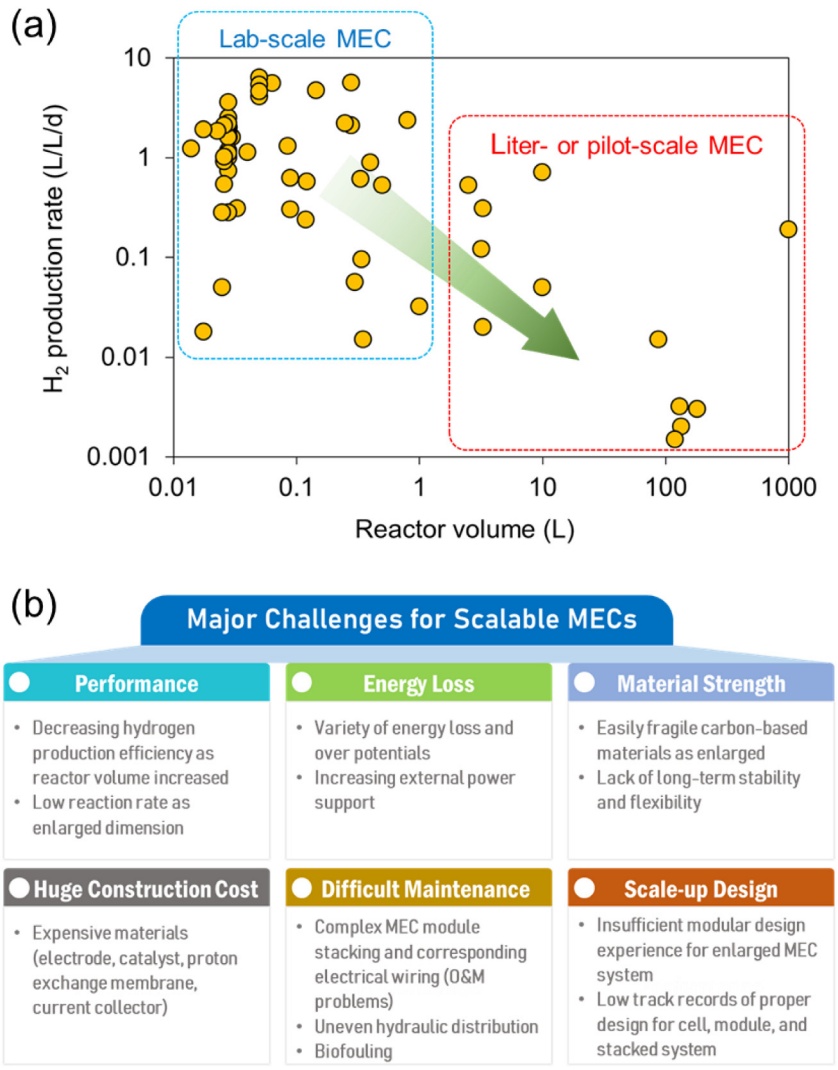

Fig. 11. (a) Hydrogen production rate comparison of lab-scale and pilot-scale MECs. (b) Major challenges of MECs technology for application at a large scale.

From the standpoint of engineering catalysts and electrodes, active efforts to exploit novel fabrication strategies and chemistry may bring more advanced and cost-effective materials in MEC electrodes. Moreover, leveraging nanomaterials of various morphology and size would provide new opportunities for high-performance electrodes with low cost. In this respect, carbon nanomaterials such as graphene and CNTs can be good options based on their excellent properties such as high aspect ratio, electrical conductivity, and chemical tunability to develop high-performance electrodes. The prices of these carbon nanomaterials have gradually decreased due to the developments of scalable production technologies.

In addition, in conjunction with cutting edge material science and engineering, exploiting advanced computational modeling could enable researchers to obtain valuable information on catalyst designs and interactions between catalysts, electrolytes, and molecules involved in hydrogen evolution. An in-depth understanding of the molecular level phenomena in MECs could offer great insight and information to enhance electrode material design.

5. Conclusions

Electrodes are an essential part of the MEC system. For system scalability, the cost of the electrode and the efficiency of electrode material are very important. The present review overviewed different electrode material options available for anode and cathode as well as suitable catalysts in MEC for scale-up applications. Biofilm formation and EET in the anodic chamber of MECs depend on the anode characteristics, such as specific surface area, conductivity, surface charge, and surface wettability. Among the tested anode materials, carbon-based materials such as graphite, carbon nanosphere, and granular activated material were useful and cheap. A suitable cathode material must have a large specific surface area, excellent electrical conductivity, good electrocatalytic activity, electrochemical stability, and low hydrogen overpotential. Platinum is the most widely used cathode material due to its enhanced properties, but its high cost prevents practical applications. Stainless steel, Ni alloys, molybdenum sulfide, polyaniline, and palladium are feasible, low-cost alternatives to platinum. Ni-based materials are found to exhibit higher hydrogen production and CE. The application of nanotechnology facilitated the development of materials with higher HER and specific surface area. Palladium nanoparticles exhibited higher HER and subsequent enhancement in cathodic hydrogen recovery.

Despite the research advancements in electrode materials at present, current MEC technology is not mature enough to be implemented practically in the near future and several advancements are still required in this direction. In particular, it is critical to build up experiences applying those developed materials in

pilot-scale MEC systems due to the lack of studies on scaled-up MECs. The continuous evaluation, improvement, and optimization of the discussed electrode materials in large-scale MEC treatment are able to play a key role toward the commercialization of MECs.

CRediT authorship contribution statement

Sung-Gwan Park: Writing – original draft, Investigation, Visualization, Writing – review & editing. **P.P. Rajesh:** Writing – original draft, Visualization, Investigation, Conceptualization. **Young-Uk Sim:** Investigation, Visualization. **Dipak A. Jadhav:** Writing – review & editing. **Md. Tabish Noori:** Writing – review & editing. **Dong-Ho Kim:** Visualization. **Siham Y. Al-Qaradawi:** Writing – review & editing. **Euntae Yang:** Writing – original draft, Visualization, Investigation, Writing – review & editing. **Jae-Kyung Jang:** Writing - review & editing. **Kyu-Jung Chae:** Writing – review & editing, Supervision.

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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