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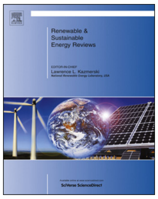

Recent advances and emerging challenges in microbial electrolysis cells (MECs) for microbial production of hydrogen and value-added chemicals

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ABSTRACT

Microbial electrolysis cell (MEC) is a potentially attractive green technology to tackle the global warming and energy crisis, which employs electrochemically active bacteria to convert organic matter into hydrogen or a wide range of chemicals, such as methane, acetate, hydrogen peroxide, ethanol, and formic acid, without causing environmental pollution. Until now, probably the cleanest and the most efficient method of producing hydrogen has been MEC. However, this technology is still in its infancy period and poses various challenges towards up-scaling and widespread applications, such as such as lower hydrogen production rate (HPR), high internal resistance, complicated architecture, and expensive materials. New advances are needed in biofilm engineering, materials for electrodes and reactor configuration for successful real-world application of this technology. Thus, the present review deals with development of practical MEC technology and includes the following sections: firstly a general introduction to MECs; their operating principles, thermodynamics of MEC, and energy or voltage losses in the MEC system were provided. Followed by a section on the critical factors affecting MEC performance; microorganisms, anode, cathode, membrane or separator, fuel sources, the state-of-art MECs designs, other key operational factors, and its potential application in microbial production of value added products are discussed in detail. Afterwards, current challenges involved in developing practical MEC systems are highlighted, and outlooks for future development are also suggested. The review aims to assist researcher and engineers to gain fundamental understandings of MEC, and it also provides several future

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Abbreviations: AEM, Anion-exchange Membrane; ARB, Anode-respiring Bacteria; BBS, Bicarbonate Buffer Solution; BEAMR, Bio-electrochemically Assisted Microbial Reactor; BEC, Biocatalyzed Electrolysis Cell; BPEC, Bio-photo Electrochemical Cell; C_E, Coulombic Efficiency; CEA, Cloth Electrode Assemblies; CFCs, Chlorofluorocarbons; CNTs, Carbon Nanotubes; DC, Direct Current; DSSC, Dye Sensitized Solar Cell; DWW, Domestic Wastewater; EAB, Electrochemically Active Bacteria; E°_{an}, The Standard Electrode Potential for Acetate Oxidation; E_{ap}, Applied Voltage; E°_{cat}, The Standard Electrode Potential for Hydrogen; EEA, Extracellular Electron Acceptors; EET, Extracellular Electron Transfer; F, Faraday's constant (96485 C/mol e^-); FP, Food Processing; GDE, Gas Diffusion Electrode; GHG, Greenhouse Gas; GM, Green Methods; HER, Hydrogen Evolution Reaction; HPRs, Hydrogen Production Rates; IEA, International Energy Agency; IW, Industrial Wastewater; MECs, Microbial Electrolysis Cells; MFCs, Microbial Fuel Cells; MRECs, Microbial Reverse-electrodialysis Electrolysis Cells; MDC, Microbial Desalination Cell; MEDC, Microbial Electrodialysis Cell; MSC, Microbial Saline-wastewater electrolysis cell; MEDCC, Microbial Electrolysis Desalination and Chemical Production Cell; MV, Methyl Viologen; MWCNT, Multi-Walled Carbon Nanotube; NF, Nickel Foam; NHE, Normal Hydrogen Electrode; PBS, Phosphate Buffer Solution; PEM, Proton Exchange Membrane; Pt/CC, Pt Contained Carbon Cloth; R, The Universal Gas Constant (8.314 J/K/mol); R_{in}, Internal Resistance; R_{CAT}, Cathodic Hydrogen Recovery; R_{H2}, Overall Hydrogen Recovery; SHE, Standard Hydrogen Electrode; SS, Stainless steel; T (K), The Absolute Temperature; VFA, Volatile Fatty Acids; Y_{H2}, Hydrogen Yield

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research directions and a road map on how to overcome the barriers, so the MEC technology can be further advanced and applied in larger scale.

Contents

1. Introduction

In today's world, global warming and energy crisis are two of the most crucial issues. As world population continues to multiply and non-renewable fossil fuels begin to diminish. According to the International Energy Agency (IEA), at present, fossil fuels (oil, coal, and natural gas) represent more than 86% of global energy consumption, and transport in particular depends 95% on oil [1].

However, the use of fossil fuels has some major drawbacks. Firstly, the fossil fuels are finite and they will eventually run out. It is an inconvenient truth that known petroleum reserves are predicted to be depleted in less than 50 years at the current rate of consumption [2,3]. Moreover, the use of fossil fuels raises serious environmental issues and concerns. The burning of fossil fuels is directly linked to global warming as CO_2 is a primary greenhouse gas (GHG) [4,5]. GHG are defined as water (H_2O), CO_2, methane (CH_4), nitrous oxide (N_2O), chlorofluorocarbons (CFCs) and aerosols [6]. Scientists are concerned that the highest GHG emissions in the atmosphere of earth are causing an increase in global mean temperatures, with potentially harmful consequences for the environment and human and animal health [7]. This has triggered the researchers in energy sector to find a carbon-neutral and renewable energy sources to replace the fossil fuels [8,9].

Of late years, hydrogen fuel is exhibiting perhaps the best potential as an alternative energy carrier and source to conventional fossil fuels. Compared to other alternative energy sources, H_2 has many advantages. Firstly, hydrogen is a green fuel that is almost free of CO_2 and other pollutant emissions, burning H_2 does not contribute to GHG emissions, ozone depletion or acid rain due to its oxidation product is only H_2O vapor [10–12]. Secondly, H_2 is high calorific value fuel. Compared to other gaseous fuels, H_2 has the highest energy content per unit weight. Energy content of 120–142 MJ/kg for H_2, other possible biofuels CH_4: 50 MJ/kg or ethanol: 26.8 MJ/kg and 44 MJ/kg for gasoline [13–15]. Thirdly, H_2 can be derived from a wide variety of renewable feedstock and domestic waste materials. So, H_2 can be cost effective, clean, sustainable and renewable [16,17]. Fourthly, H_2 is an important feed stock to the chemical industry.

Although H_2 is often presented as a clean energy vector not directly contributing greenhouse gas effect, currently, 96% of commercial H_2 produced today is delivered from fossil fuels via steam reforming, thermo-chemical conversion (pyrolysis) and gasification [18,19]. Apart from abovementioned methods, electrolysis of alkaline solutions at high temperature has been extensively studied in recent years, accounting for 4% of the current total H_2 production [20]. Whereas, abovementioned methods are all energy intensive processes requiring high temperatures ($>850\ ^\circ C$), not always environment-friendly and thus they are not considered long-term sustainable method of green H_2 production [21]. The development of advanced technologies for producing H_2 from biomass and other renewable energy resources that reduce environmental problems is now given high priority.

The production of hydrogen from renewable resources has gained increasingly attention as it is a clean energy carrier with no carbon emission. Regarding to hydrogen production, there are several established and developing renewable and green methods (GM) available for sustainable hydrogen production, such as water electrolysis, biophotolysis, photo-fermentation, dark fermentation [22–24]. Each of those processes has their own advantages and disadvantages. Water electrolysis is one of the easiest methods for pure hydrogen production. Hence, one of the key advantages of this method is providing clean hydrogen with no carbon and sulfur contamination. However, it requires a high electrical input (50 kWh/kg-H_2) with a typical energy efficiency of 56–73% [25,26]. The challenges for widespread use of water electrolysis are to reduce energy consumption, cost and maintenance and to increase reliability, durability and safety. Biophotolysis is a biological process that uses algae or photosynthetic bacteria to split water into H_2 and O_2. Production of H_2 through bio-photolysis is classified into direct or indirect biophotolysis. Major constraint in biophotolysis is oxygen inhibition, which leads to its low efficiency. The maximum energy production rates obtained through biophotolysis are no more than $0.38\ kJ\ L^{-1}\ h^{-1}$ [27]. Photo-fermentation uses photosynthetic microbes' (green algae, and cyanobacteria) ability to fix nitrogen to produce H_2. The nitrogenase enzyme creates hydrogen when fixing N_2 under nitrogen limiting condition and H_2 is produced as a byproduct. One of the most important concerns of photo-fermentation is enhancement of H_2 production in photo-fermentation is hindered by modification of the nitrogenase and the hydrogenase enzymes (both enzymes are very sensitive to the presence of oxygen). In addition, this process is energy intensive and requires large and complex design of anaerobic photo reactors [28]. As compared to other various biological hydrogen production methods, dark fermentation appears to be more promising. It does not require light energy, requires moderate process conditions, adaptability to versatile organic substrates, and has lower energy demands [29]. However, the thermodynamic limitations of dark fermentation process result in lower conversion of the substrate (in this process recovers at best 23–25% of the hydrogen present in the substrate) [30,31]. Improving hydrogen yield over 4 mol H_2/mol glucose can make hydrogen economy viable [32]. Dark fermentation leaves many hydrogen-containing components as end-products for example, acetic acid, butyric acid and ethanol [33,34], which cannot be further converted to H_2 without adding an external energy input [35,36]. However, biophotolysis and photo-fermentation conversion rates are much lower than dark fermentation [37].

A novel biological hydrogen-producing technology from biomass, microbial electrolysis cells (MECs) provide completely new avenue for clean, sustainable hydrogen production from renewable biomass and wastewaters [38–40]. This process analogous to microbial fuel cells (MFCs), but the cathode of MECs was not exposed to air. In contrast, MFCs operate with cathodes exposed to air resulting in O_2 reduction reaction at the cathode and electricity production [41]. It has previously been referred to as bio-electrochemically assisted microbial reactor (BEAMR) [42,43], biocatalyzed electrolysis cell (BEC) [44,45], and electrohydrogenesis [22,46,47]. The MEC research is highly multidisciplinary involving bio-electrochemistry, microbiology, molecular biology, physics, chemical engineering and environmental engineering among others.

In comparison to other conventional methods (photo fermentation, dark fermentation, and water biophotolysis), the advantages of MEC to produce hydrogen from organic wastes are multifold. Firstly, the MECs theoretically offer the possibility to produce H_2 at relatively low energy inputs; $0.6\ kWh/m^3H_2$ [42] and $1\ kWh/m^3H_2$ [48], which are much lower than the typical energy requirement of $4.5–50.6\ kWh/m^3H_2$ for water electrolysis [49]. Secondly, no precious metals were needed on the anode of MEC, because of self-sustaining microbial biocatalysts (electrochemically active microorganisms). Thirdly, high conversion efficiency to hydrogen is achievable in MECs. The hydrogen can be fully recovered from the end products of fermentation processes, and obtaining greater overall hydrogen yield than any types of fermentation. For example, Cheng and Logan [8] reported an efficiency of 8.55 mol H_2/mol-glucose at 0.6 V compared with the typical 4 mol H_2/mol-glucose obtained by dark fermentation [36]. Fourthly, relatively pure hydrogen is produced in the cathode chamber and thus expensive gas purification processes are not required [50], in contrast, for direct biophotolysis, hydrogen purification processes are necessary, since hydrogen and oxygen are concurrently generated by the light-driven dissociation of water ($2H_2O + light \rightarrow 2H_2 + O_2$). Lastly, the MEC using microbes as biocatalysts that produce other value added products such as CH_4 [51], H_2O_2 [52,53], C_2H_5OH (ethanol) [54], while using final electron acceptors like protons, CO_2 and acetate. Hence, the MEC systems have the potential to provide clean, renewable and sustainable energy for our future.

MEC is a very promising technology, since it can convert organic waste to hydrogen and other value-added chemicals with only a small energy input. Crucially, there are several parameters that can affect the performance of the MEC, these include bacteria, the materials being used (e.g., anode, cathode, membrane); substrate composition; the MEC designs and configuration

2. Working principles and thermodynamics of MEC

Fig. 1 shows the essential physical components of an MEC that consists of an anode, a cathode, a membrane, electrochemically active microbes, and a power supply. In an MEC, electrogenic microorganisms colonized on the anode surface and decompose the organic matter or wastes into CO_2, electrons (e^-), and protons (H^+) as a part of its metabolism. The bacteria transfer the electrons to the anode, while the protons are released directly into the MEC solution. An anode reaction is shown below using sodium acetate as an example:

$$CH_3COO^- + 4H_2O \rightarrow 2HCO^{3-} + 9H^+ + 8e^- \quad (1)$$

In the meanwhile, the electrons then travel through an electronic wire with help of power supply to a cathode and combine with the free protons in the solution generate H_2 (cathode reaction).

$$8H^+ + 8e^- \rightarrow 4H_2 \quad (2)$$

$$(E_{H+/H_2} = -0.414\ \text{V vs. NHE})$$

However, this reaction does not occur spontaneously. In order to produce H_2 at the cathode of MEC from the combination of these protons and electrons, a cathode potential of at least > -0.414 V vs NHE (normal hydrogen electrode) is needed under standard biological conditions of pH=7, T=25 °C, $P_{H_2}=1$ atm as shown in Eq. (4) [45,56,57].

Overall reaction in an MEC;

$$CH_3COO^- + 4H_2O \rightarrow 2HCO^{3-} + H^+ + 4H_2 \quad (3)$$

For electrode reactions in MECs at a pH of 7, the theoretical reduction potential of each half cell reaction are written and calculated based on the Nernst equation. For the cathode reaction, the theoretical reduction potential are written and calculated according to Eq. (4):

$$E_{cat} = E^{\circ}_{cat} - \frac{RT}{2F} 1n \frac{P_{H_2}}{[H^+]^8}$$

$$= 0 - \frac{8.314 \times 298.15}{2 \times 96485} 1n \frac{1}{\left[10^{-7}\right]^8} = -0.414\ V \quad (4)$$

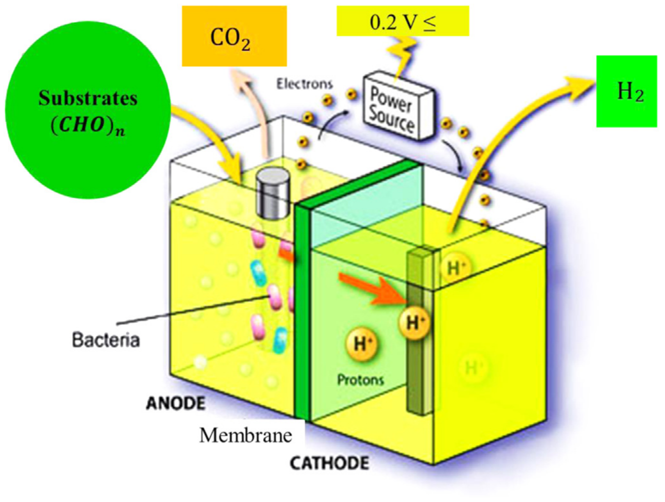


Fig. 1. Schematic diagrams of a typical two-chamber MEC reactor and its operation.

where E°_{cat} is the standard electrode potential for hydrogen (0 V), R (8.314 J/K/mol) is the universal gas constant, T (K) is the absolute temperature, and F (96485 C/mol e^-) is Faraday's constant. For the anode reaction, the theoretical reduction potential are written and calculated according to Eq. (5):

$$E_{an} = E^{\circ}_{an} - \frac{RT}{8F} 1n \frac{[CH_3COO^-]}{\left[HCO^{3-}\right]^2 [H^+]^9}$$

$$= 0.187 - \frac{8.314 \times 298.15}{8 \times 96485} 1n \frac{0.0169}{[0.005]^2 \left[10^{-7}\right]^9} = -0.3000\ V \quad (5)$$

where E°_{an} (0.187 V) is the standard electrode potential for acetate oxidation, for a solution with HCO^{3-}=0.005 M, CH_3COO^-=0.0169M, pH=7 [57]. Thus the cell voltage (E_{cell}) necessary for a MEC to produce H_2 at the cathode under these conditions is

$$E_{cell} = E_{cat} - E_{an} = (-0.414V) - (-0.300V) = -0.114V \quad (6)$$

Eq. (6) shows that the E_{cell} is negative which evidences that H_2 cannot be produced from acetate spontaneously and in order for the reaction becomes favorable and produce H_2 an additional input voltage (>0.114 V) has to be supplied. In practice, the applied voltage (E_{ap}) is normally higher than the theoretical (E_{cell}) due to ohmic loss, activation loss, and mass transport loss in the MEC system. Previous MEC studies have demonstrated that E_{ap}=0.2 V or more is needed to obtain measurable current and hydrogen production in MEC [45,46]. Nevertheless, this voltage is much lower than the voltages required for water electrolysis (typically 1.23–2.0 V) [58].

3. Energy or voltage losses in MEC and strategy to reduce voltage losses

As discussed above, in an MEC hydrogen gas is formed at the cathode theoretically at minimum applied voltage of 0.114 V. However, in practice, more than 0.135 V has to be employed to the MEC .This is due to a whole variety of voltage losses occurring in the system, which increase the voltage requirements in MEC. Voltage losses in MEC systems can be divided into electrode overpotentials and ohmic losses of the system. The real voltage requirements for an MEC can be calculated as in equation 1.10 [59,60].

$$E_{ap} = E_{therm} - (\eta_{Cathode} + \eta_{anode} + \eta_{ohm}) \quad (7)$$

where E_{thermo} is the thermodynamically predicted voltage, $\eta_{cathode}$ is the overpotential of cathode, η_{anode} is anodic overpotential, and η_{ohm} is overall ohmic loss of the system, which are from ionic and electronic resistances.

3.1. Electrode overpotentials

The overpotentials of both the cathode and the anode can be calculated as the difference between the real (measured) electrode potential and the theoretical reduction potential at specific conditions:

$$\eta_{cathode} = E_{cathode} - E_{theor(C)} \quad (8)$$

$$\eta_{anode} = E_{anode} - E_{theor(A)} \quad (9)$$

where $E_{cathode}$ (V) and E_{anode} (V) are real electrode potentials for the cathode and the anode, respectively. Moreover, electrode overpotentials are the result of activation losses, bacterial metabolic losses, and concentration losses. Thus, the following can be stated [59,61]:

$$\eta_{Cathode} = \eta_{act(C)} + \eta_{conc(C)} \tag{10}$$

$$\eta_{anode} = \eta_{act(A)} + \eta_{conc(A)} + \eta_{bact(A)} \tag{11}$$

where $\eta_{act(C)}$ (V) and $\eta_{act(A)}$ (V) are the activation losses for the cathode and the anode, respectively, $\eta_{conc(C)}$ (V) and $\eta_{conc(A)}$ (V) are the concentration losses for the cathode and the anode, respectively and $\eta_{bact(A)}$ (V) are the bacterial metabolic losses for the anodic biofilm. Overpotential is specific to each cell design and varies across cells and operational conditions, even for the same reaction. Overpotentials can be grouped into three categories: activation, bacterial metabolic activity, and concentration.

3.1.1. Activation losses

A certain proportion of energy or voltage is needed to initiate the chemical reaction at electrode surface in MEC. This phenomenon produces a non-linear voltage drop called activation losses. It can be represented by region A in Fig. 2 is observed as a sharp decrease in MFC or MEC voltage (low polarization) at the initial low current densities, but it is steadily overshadowed by ohmic and concentration losses which usually occur at intermediate or high current densities (region B in Fig. 2).

Activation losses or overvoltage is the most important irreversibility and cause of voltage drop, which occurs at both anode and the cathode, and it is important to note that the cathodic overpotentials are much larger than anodic overpotentials. The activation losses can be explained from the Tafel equation shown by Eq. (8).

$$\eta_{act} = A\ln\left(\frac{i}{i_o}\right) \quad \text{or} \quad \eta = \frac{2.303RT}{\alpha nF}\log\left(\frac{i}{i_o}\right) \tag{12}$$

where = the over-potential, b is Tafel slope $\left(b = \frac{2.303RT}{\alpha nF}\right)$ is the main indicator for activation losses, the parameter α is the charge transfer coefficient. It depends on the type of reaction and the electrode material. Its value is theoretically between 0 and 1 depending on the catalyst material [62]. i is the current density, A/m^2 and i_0 "exchange current density" is considered as the current density at which the overvoltage begins to move from zero.

The activation losses are generally the dominant effect on the energy efficiency of MECs. Some steps that can be taken to minimize the activation losses are:

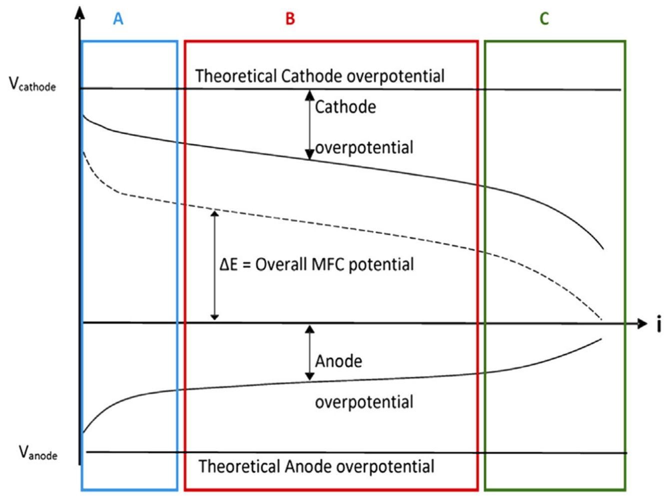


Fig. 2. The polarization curve for a typical MFC [60].

(1) *Increasing anode surface area:* Increasing the surface area is a reliable approach to decrease the activation potential as when the surface area is increased the current density gets reduced. This can be done by increasing the electrode surface porosity and roughness.

(2) *Improving anode-microbe interactions:* In order to decrease the activation losses at the bacteria, it is necessary to improve anode-microbe interactions. Using the correct mediator would eliminate this problem by enhancing electron transfer. As mediators would go inside the cell membrane it can reduce the intracellular activation losses as well. MEC systems employing microorganisms that produce conducting pili have relatively low activation polarization.

(3) *Increasing the operating temperature:* In an inorganic fuel cell raising the temperature would reduce the activation overpotential but in the MEC or in MFC it is not possible to increase the temperature unless the bio-reaction section is separate from the anode chamber.

(4) *Decreasing the activation loss at the electrode surface:* The activation energy at the electrode surface can be decreased by adding catalyst to the electrode. The activation losses depend on the type of catalyst used: a better catalyst decreases the activation energy and hence causes lower activation losses. The catalysts that has been widely tested is Pt, which is reported to get polluted by bacterial suspensions. It has been reported that some success has been achieved by coating the electrode with a conducting layer that shield microbes from direct contact with the catalyst material [63]. Immobilization of catalysts such as neutral red (that also acts as a mediator) and manganese oxide on the electrode surface have shown to increase MFC power output [64].

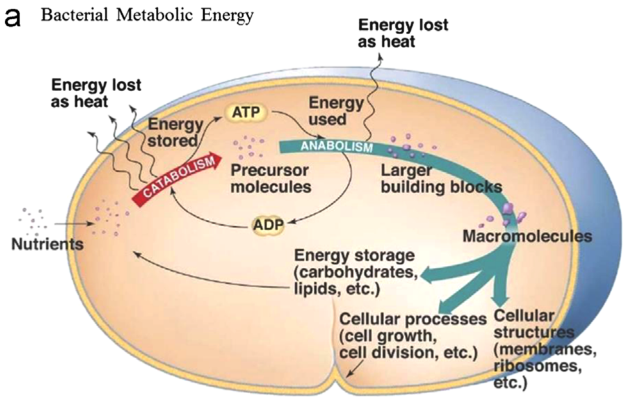
3.1.2. Bacterial metabolic losses

Loss of voltage can also occur due to catabolic and anabolic activities of the microbe while deriving energy from fuel oxidation (Fig. 3a). Bacterial metabolic energy is generated by transporting electrons from a substrate to a final electron acceptor, which in MECs, is the anode (Fig. 3b). In an MEC, the anode is the final electron acceptor and its potential determines the energy gain for the bacteria. The difference between the anode potential and the redox potential of the substrate will determine the metabolic energy gain for bacteria [65].

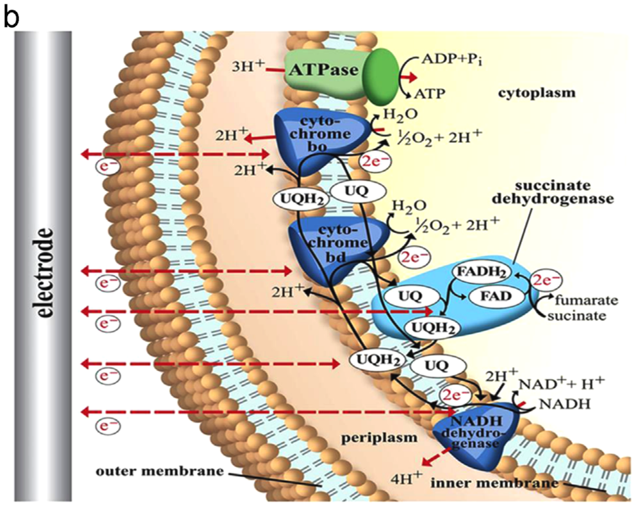
The higher the energy gain for bacteria the higher the voltage loss in the system. Extremely low anode potential can hinder electron transfer causing fermentation of fuel while producing high energy products, resulting in loss of electrons. Furthermore, this also leads to added electron losses by excessive buildup of anodophilic biomass. A number of factors such as type of microbes, community composition, anode-microbe interaction, rate of fuel degradation by the microbes, number of microbes actively degrading the fuel and mix up of fuel through the electrolyte between the electrodes can affect the microbial metabolic losses.

3.1.3. Mass transport or concentration losses

It is elated to mass transport limitations. Imbalance in rate of mass transfer of substrate and products to and from the anode respectively and the total current generated in the system may result in increase in anode potential and decrease in cathode potential or vice versa causing concentration (or mass transport) losses. These losses are most prominent at high current densities due to diffusion-limited mass transfer of fuel to the anode surface. Also, the accumulation of oxidized products and cations in the biofilm may change the redox conditions and alter the metabolic activities of the microbes. Hindrance in cation transport may further cause a pH gradient between the electrodes leading to a significant reduction in the current production.



Microbial Metabolism is composed of catabolic and anabolic reactions



Schematic image of electron transport chains in in a bioelectrochemical system

Fig. 3. (a) Microbial metabolism is composed of catabolic and anabolic reactions. (b) Schematic image of electron transport chains in in a bioelectrochemical system.

3.2. Ohmic losses

The ohmic overpotential or losses in MECs include voltage losses related to the resistance to the flow of electrons in electrodes and connections, and the resistance to the flow of ions in the electrolyte component and the membrane (if present), they are simply governed by Ohm's law:

$$\eta_{ohm} = IR_{ohm}$$

where I is the current (A) and R_{ohm} is the ohmic resistance (Ω) of the MEC. The ohmic resistance is a combination of both ionic, R_{ion}, and electronic, R_{elec}, resistances, and includes the resistance from the electrode, electrolytes and interconnections:

$$R_{ohm} = R_{ion} + R_{elec}$$

Internal resistance is usually dominated by the electrolyte resistance since the ionic conductivity is orders of magnitude lower than the electrical conductivity of the electrode materials [66]. The ohmic resistance of the electrolyte, R_{ion}, can be expressed by

$$R_{ion} = \frac{l}{AK}$$

where l is length of ionic transport path, normally thickness of electrolyte (cm) and A is the cross-sectional area (cm^2) over which the ionic conduction occurs or MEC reaction area, and K is the specific conductivity $(\Omega\,\mathrm{cm})^{-1}$ of the electrolyte materials.

Numerous factors affect internal resistance in MECs, increasing the conductivity of anode material, minimizing contact resistance and the total travel distance of electrons within the anode helps in limiting the ohmic losses. Use of highly conductive anode materials with 3D architecture (e.g. 3D graphite felt electrode) has shown to produce higher current generation by overcoming the ohmic losses [67]. The three dimensional structure not only offers a high surface to volume ratio but also an evident increase in the anode-microbe interaction, thus facilitating higher electron transport [68]. The anodic (electrical) resistance were reported to be negligible when graphite electrodes were used [69] and the contact resistance can also be significantly low as compared to the ionic resistance. Apart from this, when the space between the two electrodes is reduced, the protons have less distance to travel, and the ohmic resistance is lowered. Liu et al. [70] demonstrated that decreasing the spacing between the electrodes from 4 to 2 cm reduced the ohmic resistance and resulted in a 67% increase in the power output. The effect of electrode spacing on performance of MECs has also been verified in other studies [8]. Moreover, a using a low resistance membrane while improving the conductivity and buffer capacity of the electrolyte (tolerable by the microorganism) are concomitant strategies to improve ion transfer through the membrane [48,71]. The use of ionic exchange membranes in bioelectrochemical systems physically separates the anode and cathode, and therefore it separates oxidation and reduction products. However a configuration with membrane increases voltage losses. In fact, Rozendal et al. [71] estimated between 0.26 and 0.38 V the voltage loss associated with an ionic exchange membrane31. The removal of the membrane not only can simplify the construction, operation and maintenance of bioelectrochemical systems, but it also decreases the internal resistance and reduces the gradients of pH, theoretically increasing the output of the system. Increasing the membrane surface area reduces the ionic resistance associated with the membrane. Oh and Logan [72] reported that an increase in the membrane surface area from 3.5 to 30.6 cm^2, in a two-compartment MFC with fixed anode and cathode surface areas (22.5 cm^2), decreased the internal resistance (from 1110 to 89 Ω) and resulted in power output improvement from 45 to 190 mW/m^2.

4. Essential factors for improving MEC performance

Factors affecting the performance of MECs include the microbiological factor, Anode, cathode and catalyst, separator, substrate, MEC Architecture, and operational factors. To improve the hydrogen production yield of MECs and realize their practical application, the above performance factors must be investigated and optimized; in this section, factors affecting the performance of MECs are reviewed.

4.1. Biological factors

An MEC is an up-surging technology in the field of bioenergy generation along with wastewater treatment. It generates hydrogen with the help of microbes that make it a green future source of energy. The exoelectrogens play the key role in the MECs. A better understanding of microbial community in an MEC will aid in our efforts to increase hydrogen production required for our envisioned application of MECs.

4.1.1. Electro-active microorganisms or exoelectrogens in MECs

As it is well known, the key feature of MEC/MFC system is the bacteria-catalysed electron transfer from the substrate or organic matter to electrodes. exoelectrogens are essential for the anode or/and cathode reactions. Exoelectrogens/electrogens are microorganisms applied in anodes of MECs/MFCs that have the ability to transfer the electrons from substrate to extracellular electron acceptors (EEA) without an exogenous mediator [59,73–75].

Exoelectrogens are collectively known as electricigens [76], anode-respiring bacteria (ARB) [75,77–80], and electrochemically active bacteria (EAB) [81–83]. To date, the electrogenic microorganisms have been found in a wide variety of environments, such as domestic wastewater (DWW) [43,84–87], ocean and marine sediments [88,89], and anaerobic sewage sludge [90,91]. To date, an expansive diversity of exoelectrogenic microorganisms have been isolated and characterized. A list of electrogenic microorganisms is shown in Table 1 together with their substrates.

The isolated exoelectrogenic bacteria so far belong to diverse genetic groups, including α-Proteobacteria (*Rhodopseudomonas*, *Ochrobactrum* and *Acidiphilium*), β-Proteobacteria (*Rhodoferax*), γ-Proteobacteria (*Citrobacter*, *Shewanella*, *Klebsiella*, *Enterobacter*, *Aeromonas*), δ-Proteobacteria (*Geobacter*, *Geopsychrobacter*, *Desulfobulbus*), Actinobacteria (*Propionibacterium*), Epsilonproteobacteria (*Arcobacter*), Firmicutes (*Clostridium* and *Thermincola*), Acidobacteria (*Geothrix*). Electrogenic microorganisms can be affected by various external factors such as pH, buffer strength, temperature [116,117].

4.1.2. Extracellular electron transfer mechanisms in MEC

The performance of MECs is significantly influenced by the ability of exoelectrogens on the anode to facilitate the transfer of electrons from substrate to anode (electronic generation). Better understanding the mechanisms of microbial extracellular electron transfer (EET) is vital for enhancing the electron transfer rate from exoelectrogens to electrode. The experiments performed by Torres et al. [78] demonstrated that the most forms of respiration involve a soluble compound (e.g. oxygen, nitrate, and sulfate) as an electron acceptor; nevertheless, some microorganisms are able to respire solid electron acceptors (metal oxides, carbon, and metal electrodes) in order to obtain energy. EET, which refers to the transfer of electrons obtained from an electron donor to the anode electrode. It is not yet entirely certain the EET mechanisms. Currently, the most persuasive general explanation on the EET mechanisms are shown in Fig. 4. The first mechanism presents direct electron transfer between electron carriers in the bacteria and the solid electron acceptor [78]. The second mechanism occurs in the presence of a soluble electron shuttle, which is a compound (e.g. melanin, phenazines, flavins, and quinones) that carries electrons between the bacteria and the electrode by diffusive transport [118–120]. The third mechanism proposes a solid component (cellular pili as nanowires) that is part of the extracellular biofilm matrix and is conductive for electron transfer from the bacteria to the solid surface [59,121].

4.1.3. Microbial populations in MEC

The enhancement in the performance of mixed-culture MECs requires great understanding of the ecology in microbial communities of the MECs. Nevertheless, there are fewer studies of the microbial communities on the anodes of MECs than for MFCs. To the authors' best knowledge, only two studies by Liu et al. [122] and Wang et al. [123] found that *Shewanella, Geobacter, Pseudomonas, Desulfovibrio and Rhodopseudomonas* were present on the anode, consistent with some findings for MFCs [73]. Liu et al. [122] studied the microbial community analysis of an MEC and observed that *Pseudomonas spp*. and *Shewanella spp*. existed on the anode. Wang et al. [123] disclosed that *Pseudomonas* species are most abundant (43–57%) in MEC reactors, implying that they should play some role in MEC operation. However, these strains contribute insignificantly to hydrogen recovery in MEC reactors. Wang et al. [123] also presumed that the operation of MECs is under completely anaerobic conditions, and therefore promotes the growth of obligate anaerobic bacteria such as exoelectrogenic *Geobacter*, and other non-exoelectrogenic fermentative or methanogenic bacteria. Thus, microbial community in MECs may be different from those in MFCs. Apparently, methanogenesis could be a problem in MECs, because high concentrations of hydrogen gas favor the growth of hydrogenotrophic methanogens, which reduces hydrogen gas production and contaminates the gas with methane. Three methods can be applied to suppress the growth of methanogens, including: (1) lowering the environment pH by using a medium solution (pH 5.8) containing phosphate buffer, (2) exposing the cathode to air for 15 min when the methane content in the headspace was higher than 5%, (3) boiling the anodes from MFCs for 15 min before placing them in MECs [124]. A variety of mixed-culture sources enriched from DWW and anaerobic sewage sludge have been used as inoculum in the most MEC studies [42,43,45,46,87,124–127]. Other reports highlighted the interactions between species in mixed cultures that enable produce greater current densities and hydrogen production rates (HPRs) in MECs. In another report, it was demonstrated that metabolites generated by one species can be utilized by another species as a shuttle to transfer electrons [128], further research is required to elucidate metabolic patterns of niche-partitioning, interspecies communication.

It has been recently demonstrated that pure cultures can provide well-controlled systems and produce methane-free gases in MECs. *Shewanella oneidensis* MR-1 was examined in a single-chamber MEC, but it exhibited much lower HPR under the same operational conditions with mixed-culture [124]. While The *Geobacter sulfurreducens* PCA strain produced H_2 in MECs at rates and recoveries comparable to mixed cultures [127,129]. The *G.*

Table 1
The electrogenic microorganisms used in MFCs or MECs.

Electrogenic microorganisms	Substrate	Reference
Rhodopseudomonas palustris DX-1	Volatile acids, yeast extract, thiosulfate	[92]
Ochrobactrum anthropi YZ-1	Acetate, lactate, propionate, butyrate, glucose, sucrose, cellobiose, glycerol, ethanol	[93]
Acidiphilium sp. strain 3.2 Sup 5	Ferric iron Ferrous iron	[94]
Rhodoferax ferrireducens, Citrobacter sp. SX-1	Glucose; Citrate, glucose, lactose, sucrose, acetate, glycerol	[95,96]
Shewanella putrefaciens MR-1, IR-1, SR-21	Lactate, pyruvate, acetate, glucose	[97]
Shewanella oneidensis MR-1	Lactate	[98]
Klebsiella pneumoniae strain L17, *Enterobacter cloacae*	Glucose, starch; Cellulose	[99,100]
Aeromonas hydrophila KCTC 2358	Acetate	[101]
Aeromonas sp. strain ISO2-3, *Geobacteraceae*	Glucose; Acetate	[102,103]
Geobacter metallireducens, Geobacter sulfurreducens	Acetate	[104–107]
Desulfobulbus propionicus	Pyruvate, acetate	[108]
Propionibacterium freudenreichii ET-3	Acetate, lactate	[109]
Arcobacter butzleri strain ED-1	Sodium acetate	[110]
Clostridium beijerinckii, Clostridium butyricum EG3	Starch, glucose, lactate, molasses; Glucose	[111,112]
Firmicutes Thermincola sp. strain JR	Acetate	[113]
Geothrix fermentans, Gluconobacter oxydans	Acetate; Glucose	[114,115]

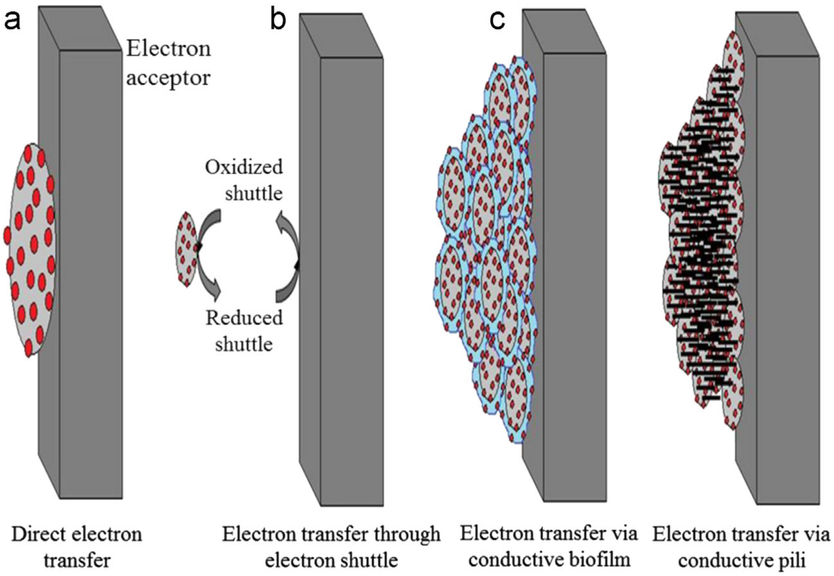


Fig. 4. Schematic diagram describing the EET mechanisms in an MEC anode: (A) Direct electron transfer: cell in direct contact with electron acceptor via surface c-type cytochromes, (B) Electron transfer through electron shuttle, (C) Electron transfer through conductive biofilm and conductive pili.

sulfurreducens PCA strain was discovered in a sample of soil contaminated by hydrocarbons in Norman, Oklahoma, Japan. The primary enrichment was performed three times. 10% inoculum transferred into the basal medium with sodium acetate (as the electron donor) and ferric PPi (as the electron acceptor) [105]. It is rod-shaped, gram-negative, nonmotile, with no spore formation, cells contain c-type cytochromes. The *G. sulfurreducens* PCA was originally considered to be a strict anaerobe [105], but it has been shown that the *G. sulfurreducens* PCA can grow under low dissolved oxygen (10% or less) conditions and it is inactivated [130] or killed at higher concentrations [131].

4.2. *Anode materials*

So far, electrode materials in MECs can be principally classified into three categories, namely anode, cathode, and membrane or separator. Carbon, low price metals, and anion exchange membrane are widely used materials for anode, cathode and membrane, respectively. It is important to note that anode of MECs is an indispensable component because exoelectrogens adhere to the surface of anodes to transfer electrons to the electrode. The anode material in MECs can be the same as anodes used in MFCs. It has been shown in the literature that an ideal anode material should have the following features [73]: (a) good electrical conductivity and low resistance; (b) strong biocompatibility; (c) chemical stability and anti-corrosion; (d) large surface area; and (e) appropriate mechanical strength and toughness. Within the last decade, numerous kinds of anode materials have blossomed.

4.2.1. *Traditional carbon anode materials*

It has been recently shown in the literature that almost all the research in MECs has utilized carbon-based materials for the anode, except for bio-cathode MECs because the microorganisms are grown on the cathode instead of anode. The carbon-based anodes are so popular because of their good conductivity, biocompatibility, versatility in morphologies, significantly low overpotentials and relatively low costs [48,82]. The carbon-based anode materials are chemically stable under the anaerobic anodic process in MECs. The common anode materials in laboratory scale MECs research include carbon cloth [42,132], carbon paper [43], graphite felt [45,58,60,133], graphite granules [46,134–136], carbon fiber [137], ammonia (NH_3) or heat treated (450 °C, 30 min) graphite brushes [125,138–143], carbon mesh [144]. When the graphite granules are used, a graphite rod is inserted into the bed of granules as a current collector. For a graphite brush, the two twisted wires of a conductive and noncorrosive metal such as titanium or stainless steel holding the cut carbon fibers form the anode [145]. For the other materials, the electrode is pressed or glued using epoxy to a connecting wire. Suppliers of carbon-based electrode materials include E-TEK (USA), Graphite Electrode Sales (USA), FMI Composites Ltd. (UK), National Electrical Carbon BV (Netherlands), and Alfa Aesar (Germany), Gaojieshi Graphite Products Co. Ltd. (China).

4.2.2. *Carbon nanotubes (CNTs)*

It should be noted that CNTs are well known for their eminent electrical and structural properties such as nanometer size, high surface area, ease of functionalization with different groups that simplify reactions, light weight, hardness, extraordinary electronic conductivity, and low material cost. PANI (Polyaniline) is an important conductive polymer due to its relatively facile properties, such as excellent environment stability, ease of synthesis and controllable conductivity by protonation and charge-transfer doping. A study carried out by Qiao et al. [146] illustrated that CNTs could amplify the electron transfer feasibility and electrode surface area with utilizing carbon nanotube/polyaniline nanostructure composite as anode materials. It has long been known that the nano-materials are extremely stable not only structurally but also have stable chemical and electrical properties. Au and Pd nanoparticle decorated graphite anode was developed and evaluated in a newly designed multi-anode MEC reactor [147].

4.2.3. *Pretreatment methods of anode materials*

To enhance performance of the anode materials, the carbon-based materials (anodes) are pre-treated with a high temperature NH_3 or N_2 gas process [148]. Alternatively, it was recently discovered that heat treatment of carbon based materials can improve the anode performance in MECs likely due to a cleaning effect of the electrode surface. Wang et al. [149] discovered that inexpensive heat-treated carbon mesh materials can be used as the anode in MFCs/MECs and providing a good performance. The advantages of this treatment are: (1) to a faster start-up, (2) higher current densities. Thus, the heat treatment (450 °C, 30 min) is a large scale alternative for high temperature ammonia gas treatment method.

4.3. Cathodes and catalysts

Similar to the anode, cathode is one of the most important parts of the MECs where H_2 as well as other value-added chemical compounds are produced. The hydrogen evolution reaction (HER) on plain carbon electrode is very slow and a high overpotential is needed to generate H_2 [150]. Expensive metal catalysts, such as platinum is usually used as the catalyst in MECs. A major drawback of using Pt cathode include its high cost and poisoning by chemicals such as sulfide (a common constituent of wastewater). To resolve this problem, several attempts have been made to search for Pt-free cathode materials for HER in MECs.

4.3.1. Stainless steel alloy (SS) cathodes

To date, considerable research efforts have been made to find out alternative for expensive Pt cathode. It was found that first row transition metals are very useful due to their stability, easy availability, low cost, low overpotentials and low toxicity to living organisms. The most promising materials investigated so far are SS (stainless steel) and nickel alloys [139]. Olivares-Ramírez et al. [151] worked on three different types of SS each with different metal composition. SS 304, SS 316 and SS 430 containing 9.25%, 12%, and 0.75% of nickel respectively were used for HER in the alkaline electrohydrolyzer (NaOH and KOH). The electrochemical analysis of the SS showed that the SS 316 was the best cathode material in alkaline medium, since the SS 316 has the highest nickel content. In a similar vein, Selembo et al. [139] studied different SS alloys 304, 316, 420, A286 and nickel alloys 201, 400, 625, HX. The experiments were carried out at either E_{ap}=0.6 V or 0.9 V at constant temperature of 30 °C and neutral pH condition. SS A 286 showed the best performance of all the alloys tested at E_{ap}=0.9 V. Call et al. [138] selected high nickel containing (8–11%) SS 304 to use in an MEC test. They compared the performance of high surface area SS brush with that of Pt contained carbon cloth (Pt/CC) cathode and also examined the effect of material composition on current production with SS brush and graphite brush cathode. The SS 304 woven and expanded meshes having composition of (0.08%) C, (2%) Mn, (1%) Si, (18-20%) Cr, and (8–11%) Ni were evaluated for their suitability as cathode in MECs. The results obtained on that study demonstrated that SS woven mesh performed better than expanded mesh for H_2 production in MEC [142]. It has recently been shown that the presence of phosphate species and some weak acids have a beneficial effect in MEC, because the charged species increase the electrolyte conductivity and also reduce the over-potential on Pt-carbon cathodes [152]. The study on microbial corrosion showed that the HER enhanced via deprotonation of phosphate species on SS cathodes [153,154]. Munoz et al. [155] reported that the high concentration of phosphate species used in combination with a SS cathode allowed high current density for hydrogen evolution and HPRs in saline solutions at pH=8. Ambler and Logan [141] reported that combination of bicarbonate buffer solution (BBS) and SS 304 cathode with mesh No. 60 showed good performance compared to MECs with Pt cathode and phosphate buffer solution (PBS). Su et al. [156] showed that a 3D macroporous stainless steel fiber felt (SSFF) with high electrochemical active surface area has an excellent catalytic activity for hydrogen generation, which is comparable to Pt/CC cathode and superior to stainless steel mesh (SSM) cathode in the single-chamber MEC. The SSFF cathode (mean filter rating 100 mm) produces hydrogen at a HPR of 3.66 ± 0.43 m^3 H_2/m^3 d with current density of 17.29 ± 1.68 A/m^2, a hydrogen recovery of $76.37 \pm 15.04\%$ and overall energy efficiency of $79.61 \pm 13.07\%$ at E_{ap}=0.9 V.

4.3.2. Nickel and Ni-based alloys

Efforts have also been made to explore suitability of Nickel and Ni-based alloy cathodes for hydrogen production in MECs. Selembo et al. [139] successfully developed nickel oxide catalysts for a single-chamber MEC reactor, which exhibited an improved volumetric HPR (0.08–0.76 m^3 H_2/m^3 d) and energy efficiency (31–137%). However, the diminished mechanical stability of this MEC reactor caused the performance of the nickel oxide cathodes to decrease over time. Meanwhile, Hu et al. [132] developed cathodes by electrodepositing NiMo and NiW onto a three-dimensional carbon-fiber weaved cloth material and were first evaluated at neutral pH in electrochemical cells. These electrodes were also examined for hydrogen production in single chamber tubular MECs with cloth electrode assemblies (CEA). Similar performances were observed in electrochemical cells, NiMo cathode exhibited better performances than NiW cathode in MECs and achieved a comparable performance to the Pt cathode in terms of the HPR. Hrapovic et al. [157] developed a low cost MEC cathode by Ni electrodeposition onto a porous carbon paper, and evaluated different Ni or Pt loadings. They found that at a Ni load of 0.2–0.4 mg cm^{-2} under acetate non-limiting conditions, hydrogen production could reach 5.4 L L^{-1} d^{-1} with a corresponding current density of 5.7 A/m^2. Manuel et al. [158] studied the impact of the catalyst load on HPR, and concluded that the chemical deposition of Ni can be successfully employed for continuous-flow production of hydrogen in a MEC. Ni foam was found to have high HER catalytic activity under alkaline condition [159,160], and low electrical resistivity than graphite or titanium [161], it is also cheap and easily available. Instead of using Ni as a deposited catalyst onto carbonaceous materials, Jeremiasse et al. [162] used Ni foam as cathode for producing high purity H_2 in dual-chamber continuous flow MEC reactor, which had a high specific surface area and a low HER overpotential. However, the performance of this MEC decreased after long-term operation. Jeremiasse et al. [133] investigated nickel–iron–molybdenum (NiFeMo) and cobalt-molybdenum (CoMo) alloys as possible HER cathode catalysts in MEC, around neutral and mild alkaline pH. Cu sheet cathodes coated with NiMo, NiFeMo or CoMo alloy showed a high catalytic activity for the HER compared to cathodes that consist of only Ni. In another report, a Ni-based gas diffusion cathode having Ni loading of 0.4 mg cm^{-2} was used to treat DWW in a continuous flow MEC [163]. The wastewater treatment efficiency observed was the maximum of 76% COD reduction at organic load of 441 mg L_a^{-1} $d^{-1}$and E_{ap}=0.75 V, this results comparable with the work of Cusick et al. [164] which was done with Pt cathode. The Ni-based nanomodified materials: Nickel–iron (NiFe), nickel–iron–phosphorous (NiFeP) and nickel–iron–cobalt–phosphorous (NiFeCoP) are promising electrocatalysts for HER in near neutral electrolytes and could be cused as cathodes in MECs [165]. Nickel foam (NF), SSW, platinum coated SS mesh, and molybdenum disulfide (MoS_2) coated SS mesh electrodes were used as catalysts for H_2 production under practical conditions of high pH and in un-buffered saline catholytes in two-chamber MEC [166]. A non-noble metal electroformed Ni mesh cathode alternatives to typical cathode material (Pt/CC) was intensively examined in a single-chamber membrane-free MEC [167], the MEC was operated in fed-batch mode and the performance of the Ni mesh cathode was compared with that of Pt/CC cathode in terms of C_E ($75 \pm 4\%$ vs. $72.7 \pm 1\%$), overall hydrogen recovery (R_{H2}) ($89.3 \pm 4\%$ vs. $90.9 \pm 3\%$), overall energy efficiency ($62.9 \pm 5\%$ vs. $69.1 \pm 2\%$), the maximum volumetric HPR (4.18 ± 1 m^3 H_2/m^3 d vs. 4.25 ± 1 m^3 H_2/m^3 d), volumetric current density (312 ± 9 A/m^3 vs. 314 ± 5 A/m^3). Farhangi et al. [168] investigated the use of commercial electrodes as cathodes in a single-chamber MEC. The cell was operated in sequencing batch mode and the performance of the electrodes was compared with carbon cloth containing 0.5 mg Pt/cm^2. The R_{H2} was 66.7 ± 1.4, 58.7 ± 1.1 and 55.5 ± 1.5% for Pt/CC, Ni and Ti mesh electrodes, respectively.

4.3.3. *Other metals and nanostructured materials*

Another option is to use nanostructured cathode materials. Recent years, extensive studies have been carried out on other metals and nanostructured materials for HER in MECs. Harnisch et al. [169] synthesized tungsten carbide powder via a carburization procedure and explored its electrocatalytic behavior in MECs by pasting the powder onto graphite disc with Nafion. Palladium is the most platinum like metal and with excellent catalytic property and high abundance. An experimental investigation was carried out by Huang et al. [170] revealed that the feasibility of using Pd nanoparticles for hydrogen evolution in MECs. The results demonstrated that utilization of the cathode with Pd nanoparticles could substantially reduce the costs of the cathode while maintaining the MEC system performance. Use of MoS_2 as a photocatalyst for hydrogen evolution photoelectrochemical cell is well-known but it was first used as a catalyst for HER in MECs [171]. A novel nitrogen-containing coreeshell-structured catalyst NeFe/Fe_3C@C was prepared and used to produce H_2 in MECs. The new catalyst consists of iron-based composite (Fe/Fe_3C) nanorods as the core and graphite carbon as the shell. The performance of H_2 production and catalyst stability were studied [172]. The main drawback of these nanostructured materials is their harmful effect on the biofilm, reducing the electrical performance of the MECs. Hou et al. [173] developed an MEC constructed with spiral wound electrode and to evaluate its effectiveness for wastewater treatment and methane (CH_4) production. The spiral wound design can provide more than 60 m^2/m^3 of specific surface area of the electrode and low internal resistance. The energy efficiency in the spiral-wound-electrode MEC could be 66%.

4.3.4. *Biocathodes*

More recently, many researchers have studied and explored several metabolic processes present in the cathode, stepping toward a possibility to develop a biocathode [174]. Compared with chemical catalysts, the use of microorganisms as cathode catalysts has the advantage of being low cost and self-generating without producing secondary pollution. It is wise to pay special attention to the biocathode MECs. Rozendal et al. [175] for the first time described the development of the bioelectrode or microbial biocathode for H_2 production from a naturally selected mixed-culture of EAB. An MEC half-cell with graphite felt electrodes was constructed with a biological anode and used acetate as fuel sources. The MEC operation initially started in a batch mode and latter shifted to continuous operation mode. To understand the difference of performance predicted from the electrochemical half-cell by Rozendal et al. [175]. Similarly, Jeremiasse et al. [176] carried out investigation of a full biological MEC, where both the anode as well as cathode reactions in MEC were catalyzed by bacteria (biocathode). The same experimental set up as with the previous study was used. In their work, cobalt was successfully recovered with simultaneous methane and acetate production in biocathode MECs. At an applied voltage of 0.2 V, 88.1% of Co(II) was reduced with concomitantly achieving yields of 0.266 ± 0.001 mol Co/mol COD, 0.113 ± 0.000 mol CH_4/mol COD, and 0.103 ± 0.003 mol acetate/mol COD [177].

Chen et al. [178] attempted to modify biocathodes with PANI (Polyaniline)/MWCNT (Multi-Walled Carbon Nanotube) composites to improve hydrogen production in single-chamber, membrane-free biocathode MECs. The results showed that the hydrogen production rates increased with an increase in applied voltage. At E_{ap}=0.9 V, the modified biocathode MECs achieved a HPR of 0.67 m^3 H_2/m^3 d, current density of 205 A/m^3, COD of 86.8%, C_E of 72%, cathodic hydrogen recovery (R_{CAT}) of 42%, and energy efficiency of 81% with respect to the electrical power input. Bio-cathodes are a welcome advancement in the quest to implement MECs for practical applications, such as wastewater treatment and sediment MECs because of potential cost savings, waste removal, and operational sustainability.

4.4. *Separator or membrane*

Conventionally, MECs have always included a membrane, which presumably is used to improve the purity of the produced hydrogen and to prevent microbial consumption of the hydrogen at anode. It also functions as a separator to avoid any short circuit. Various membranes have been used in MECs, the most common membrane is a proton exchange membrane (PEM) from Ion Power, Inc. called Nafion [45,139,179,180]. Other membranes have also been tested in MECs, including anion-exchange membranes (AEMs), such as AMI-7001 [46,58], nanofiber-reinforced composite proton exchange membrane (NFR-PEM) [181], forward osmosis membrane [182], bipolar membranes and charge-mosaic membranes [71].

As an instructive note, there are some drawbacks of using a membrane in MECs: substantial potential losses have been attributed to the inclusion of a membrane; A membrane causes a pH gradient across the membrane which can lead to lower pHs at the anode and higher pHs at the cathode. The pH gradient that develops can lead to performance losses in MECs, a unit change in pH contributes to a potential loss of 0.06 V. As an example, using a Nafion membrane in an MEC, Rozendal et al. [58] showed a pH increase of 6.4, which corresponded to a 0.38 V loss of the applied 1.0 V. Furthermore, membranes are expensive and add a significant cost to the MEC system [46,124].

4.5. *Substrates used in MEC*

Substrate is considered as one of the most crucial factors affecting H_2 generation in MECs. The type, concentration and feeding rate of substrate is vital to MEC as it determines the reaction process and H_2 yield [46]. A large variety of substrates can be used for H_2 production in MECs, ranging from pure compounds to complex mixtures of organic matters in wastewater. Fig. 5 illustrates a classification of substrates that have been used in MEC studies.

4.5.1. *Acetate and other fermentation end products*

Acetate (CH_3COONa) is the most widely used substrate in MECs, because it is a common end product of dark fermentation. The best MEC performances have been obtained using acetate as the substrate. Jeremiasse et al. [176] achieved the highest HPR of 50 m^3 H_2/m^3 d in a two chamber MEC at an applied voltage of 1 V. Hydrogen recoveries are also high using the acetate as fuel sources and have approached close to the theoretical limit of 4 mol H_2/mol acetate [125]. Cheng and Logan [46] tested different fermentable (glucose, cellulose) and non-fermentable substrates (VFA: acetic, butyric, lactic, propionic, and valeric) in a two-chamber MEC. They obtained lower results for fermentable substrates in terms of R_{H2}: 71% and 68% for glucose and cellulose instead of 91% for acetic and lactic acids. Overall energy efficiencies were 64–63% with glucose and cellulose, compared with 82% for acetic and lactic acids. Cellulose had the lowest HPR with 0.11 m^3 H_2/m^3 d compared with over 1.0 m^3 H_2/m^3 d for acetic acid, lactic acid and glucose.

Lu et al. [183] reported that additional H_2 can be produced from the effluent of an ethanol-type dark-fermentation reactor. The R_{H2} of 83 ± 4% was obtained using a buffered effluent (pH=6.7–7.0), with a HPR of 1.41 ± 0.08 m^3 H_2/m^3 d at E_{ap}=0.6 V. When the MEC was combined with the fermentation system, the overall hydrogen recovery was 96%, with a HPR of 2.11 m^3 H_2/m^3 d, corresponding

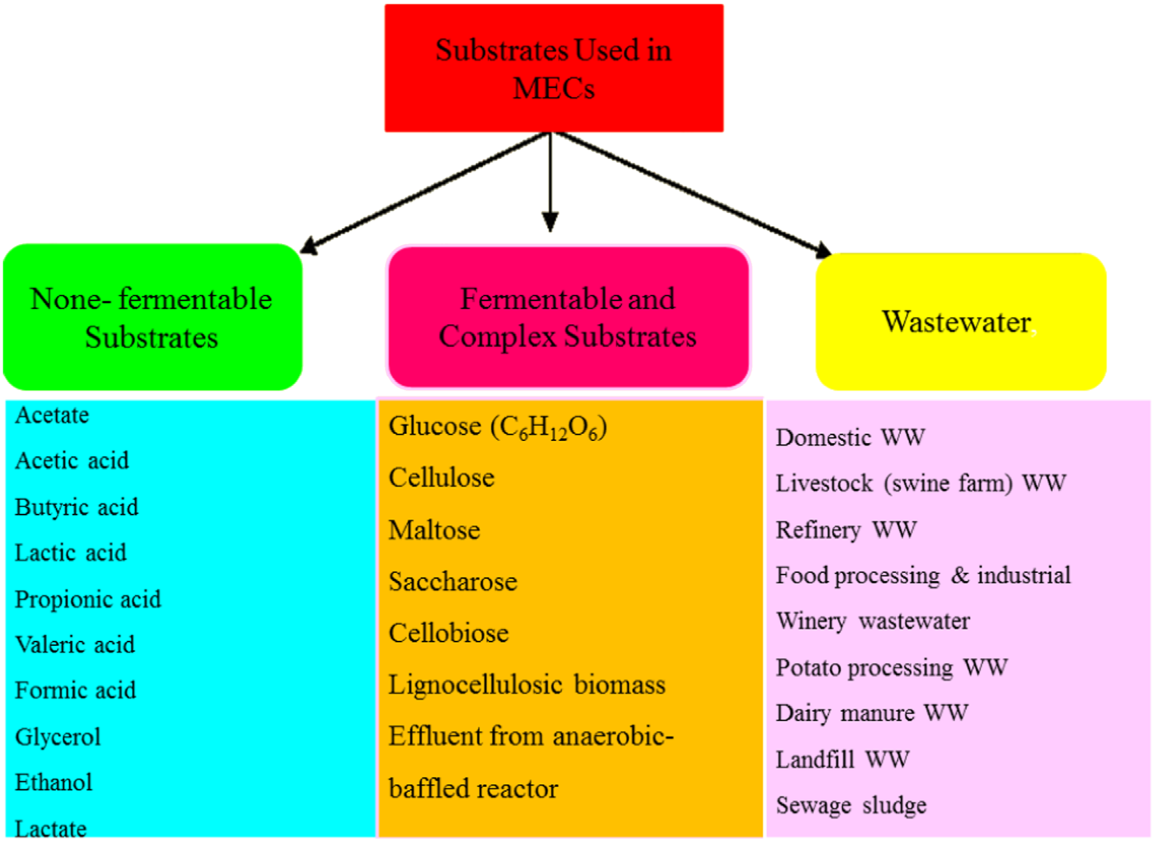


Fig. 5. Classification of different substrates used in microbial electrolysis cells (MECs).

to an electrical energy efficiency of 287%. High R_{CAT} ($70 \pm 5\%$ to $94 \pm 4\%$) were obtained at $E_{ap}=0.5$–0.8 V. Yang et al. [184] investigated the performance of MECs fed with three common fermentation products: acetate, butyrate, and propionate. The results showed high current densities for acetate, but low current densities for butyrate and propionate (the maximum values were 6.0 ± 0.28 A/m^2, 2.5 ± 0.06 A/m^2, 1.6 ± 0.14 A/m^2, respectively). Acetate also showed a higher C_E of $87 \pm 5.7\%$ compared to 72 ± 2.0 and $51 \pm 6.4\%$ for butyrate and propionate, respectively.

4.5.2. Glucose ($C_6H_{12}O_6$)

Glucose is a simple carbohydrate that can be converted to electrical current and H_2 in MFCs and MECs, respectively. It has recently been suggested that a few exoelectrogenic microorganisms can directly oxidize glucose (e.g. *Klebsiella pneumoniae*, *Rhodoferax ferrireducens*, and *Aeromonas hydrophila*) and transfer the electrons to anodes [185]. Previous studies implied that, when using glucose as a carbon source, the glucose is first oxidized to organic acids or H_2 by fermentation, followed by consumption of fermentation products by the exoelectrogens, which eliminates feedback inhibition of glucose fermentation [186]. Tartakovsky et al. [187] showed that glucose was fermented in the MEC by *acidogenic* bacteria to produce VFAs which were then used as substrate by the exoelectrogenic bacteria.

It has been long known that H_2 can be produced from glucose by fermentation process at mesophilic temperatures, typically between 20 °C and 45 °C. Lu et al. [188] demonstrated that hydrogen can also be obtained from glucose at low temperatures using MEC. Thus, overcomes the dark-fermentation bottleneck. H_2 was produced from glucose at 4 °C in single chamber MECs at a hydrogen yield (Y_{H_2}) of 6 mol-H_2/mol-glucose, and at HPR of 0.25 ± 0.03 m^3 H_2/m^3 d ($E_{ap}=0.6$ V), and 6.1 mol-H_2/mol-glucose, 0.37 ± 0.04 m^3 H_2/m^3 d ($E_{ap}=0.8$ V). These results are different from those in a previous MEC study, H_2 was produced from glucose at 30 °C in single chamber MECs at a (Y_{H_2}) of 6.4 mol-H_2/mol-glucose, and at HPR of 0.83 ± 0.3 m^3 H_2/m^3 d ($E_{ap}=0.5$ V), and 7.2 mol-H_2/mol-glucose, 1.87 ± 0.3 m^3 H_2/m^3 d ($E_{ap}=0.9$ V) [189].

4.5.3. Glycerol ($C_3H_8O_3$)

Glycerol is a common side product of biodiesel fuel production. It is a commodity chemical widely used by the pharmaceutical, food, and cleaning industries. However, it is being overproduced as a result of biodiesel fuel production. The production of 10 L of biodiesel fuel results in the production of 1 L of glycerol [190]. The glycerol byproduct (B-glycerol) from biodiesel was used in a two-chamber MEC with a mediator, the maximum hydrogen yield was 0.77 mol-H_2/mol-glycerol [191]. P-glycerol and B-glycerol were evaluated in a single-chamber mediator-less MEC, Y_{H_2} for P-glycerol at $E_{ap}=0.9$ V was reached 3.9 mol-H_2/mol-glycerol, while Y_{H_2} for B-glycerol was 1.8 mol-H_2/mol-glycerol [189]. Escapa et al. [192] demonstrated that H_2 production from glycerol in a membrane-less MEC with a gas-phase cathode, which was shown to improve the volumetric HPR in comparison with a PEM or liquid-phase cathode MECs. Speers et al. [193] developed an MEC driven by the synergistic metabolisms of the exoelectrogens *Geobacter sulfurreducens* and the bacterium *Clostridium cellobioparum*, which fermented glycerol into ethanol in the highest yield of 90% and produced fermentative byproducts that served as electron donors for *G. sulfurreducens*. Syntrophic cooperation stimulated $C_3H_8O_3$ consumption, ethanol production, and the conversion of fermentation byproducts into H_2 in the MEC. A two-chambered MEC fed with ultrapure glycerol obtained a comparable hydrogen production rate of 2.01 ± 0.41 m^3 H_2/m^3 d to that fed with glucose (1.87 ± 0.30 m^3 H_2/m^3 d), though the MEC fed with the glycerol by-product of biodiesel fuel achieved a much lower hydrogen production rate (0.41 ± 0.13 m^3 H_2/m^3 d) [189]. To achieve higher hydrogen conversion efficiency from glycerol, Chookaew et al. [194] integrated an MEC/MFC with a dark fermentation process.

4.5.4. Protein

Microorganisms can produce H_2 at high rates by fermentation of carbohydrates, but not from proteins. However, many studies reported that it is possible to produce H_2 at high rates and yields from proteins in MECs. The work of Lu et al. [47] suggested that MECs can be used to produce H_2 from proteins at a rate of 0.42 ± 0.07 m^3 H_2/m^3 d and it can also be used as a method for treatment of protein-containing wastewaters. Wastewaters from cellulosic fermentations (FWW) contain high concentrations of proteins, VFAs and alcohols. Nam et al. [195] examined hydrogen gas production from FWW in continuous flow MECs, with a focus on fate of the protein. The maximum HPR was 0.49 ± 0.05 m^3 H_2/m^3 d for the FWW, compared to 0.63 ± 0.02 m^3 H_2/m^3 d using a synthetic wastewater containing only acetate ($E_{ap} = 0.9$ V). The protein was completely removed using higher applied voltages ($E_{ap} = 1.0$ or 1.2 V).

4.5.5. Cellulose and complex substrates

As another potential source, lignocellulose has attracted attention as a promising feedstock for hydrogen production in MECs because of its abundance and renewability. Lignocellulosic biomass is rich in complex carbohydrates that can be used to feed microorganisms for the production of renewable energy sources, such as, H_2, ethanol, methane and electricity [196–198]. However, they cannot be directly utilized by electrochemically active microorganisms in MECs for H_2 generation. It has to be converted to monosaccharides or other low-molecular-weight compounds. Dark fermentation was used to convert lignocellulose into acetic, lactic, succinic, and formic acids and ethanol, which are significantly more easily degradable organic compounds by electrochemically active bacteria in MECs. In this context is noteworthy that an integration of two-stage dark-fermentation and MEC process was used to convert the recalcitrant lignocellulosic materials into H_2 at high yields and rates [22,183,199,200]. This process consists of a dark-fermentation process to optimize the conversion of pre-treated lignocellulosic biomass into H_2, CO_2, acetic, formic, succinic, and lactic acids, and ethanol, followed by electrohydrogenesis to convert the residual VFAs and alcohols into H_2. The hydrogen production from the effluent of lignocellulose and cellobiose fermentation was 1.0 ± 0.19 m^3 H_2/m^3 d and 0.96 ± 0.16 m^3 H_2/m^3 d in a two-stage MEC [22]. Catal [201] examined the direct production of H_2 from various carbohydrates of lignocellulosic biomass by using single-chamber MECs. H_2 was produced from all carbon sources used, including monosaccharides (glucose, galactose, mannose, xylose and arabinose) and disaccharides (maltose, saccharose and cellobiose). The HPR varied from 0.01 m^3 H_2/m^3 d (Arabinose) to 0.09 m^3 H_2/m^3 d (Cellobiose), while the maximum hydrogen yield ranged from 14% to 111%. Yan et al. [202] investigated electricity and hydrogen generation by bacteria *Geobacter sulfurreducens* in a dual-chamber MFC/MEC following the fermentation of hemicellulose by bacteria *Moorella thermoacetica*. Experimental results showed that 10 g l^{-1} xylose under 60 °C was appropriate for the fermentation of xylose by *M. thermoacetica* yielding 0.87 g-acetic acid per gram of xylose consumed. Lewis et al. [203] described a new approach to hydrogen production from switchgrass using an integrated pyrolysis–microbial electrolysis process. The Y_{H_2} ranged from $50 \pm 3.2\%$ to $76 \pm 0.5\%$ while C_E ranged from $54 \pm 6.5\%$ to $96 \pm 0.21\%$, respectively.

4.5.6. Variety of wastewaters

Wastewater often consists of a complex mixture of organics that must be removed before discharge into the environment. The production of a useful and valuable product during wastewater treatment, such as H_2, could help to reduce the treatment costs. Various types of wastewater have been examined as substrates for MECs, including DWW, livestock (swine farm) wastewater, refinery wastewaters, food processing and industrial wastewater, winery wastewater, potato processing wastewater, dairy manure wastewater, and landfill wastewater, but lower hydrogen production rates were obtained compared with acetate-fed MECs.

For instance, Ditzig et al. [43] reported hydrogen production using DWW as the substrate in the MECs process first time, and evaluated system performance in terms of hydrogen recovery C_E, and the effectiveness of treatment (such as BOD, COD, and DOC removal). In order to determine the possibilities of treating DWW in larger scale MECs, a 120 L of MEC was operated on site in Northern England, using raw DWW to produce H_2 for a period of over 3 months [86]. A 100 L of MEC was operated for 12 month period fed on raw DWW at temperatures ranging from 1 °C to 22 °C, producing an average of 0.6 L/day of H_2, with the C_E of 41.2% [87]. In addition, Ivanov et al. [204] developed simple quantitative methods for comparing the performance of different wastewaters in MECs operated under fed-batch operation mode. The MEC reactors were inoculated in several different ways using industrial wastewater (IW) and DWW.

It has been reported that in a single-chamber MEC with a graphite-fiber brush anode, H_2 was generated at 0.9–1.0 m^3 H_2/m^3 d using a full-strength or diluted swine wastewater. COD removals ranged from 8 to 29% in 20 h tests, and from 69% to 75% in longer tests of 184 h using full-strength wastewater [205]. The results revealed that the MEC is an effective method for hydrogen recovery from swine wastewater treatment. Although, the process needs to be further evaluated for reducing methane production, increasing the efficiency of converting the organic matter into current and increasing recovery of H_2 produced at the cathode. Refinery wastewaters were tested as fuels in MECs for the first time by Ren et al. [206]. The treatability of six different refinery wastewater samples collected at various points in the existing treatment processes at several different facilities. These results were similar to those obtained using DWW.

In other studies, Tenca et al. [207] examined two different types of wastewaters in MECs, a methanol rich industrial wastewater (IW) and a food processing (FP) wastewater. The FP wastewater contained high concentrations of complex carbohydrates (1940 ± 17 mg/L), and acetate, while the IW (from a specialty chemicals manufacturing facility) had a high concentration of methanol (1537.4 ± 48.6 mg/L) and a lower concentration of biodegradable organic matters. Substantially more biogas was recovered in MECs through cathodic process with the *Pt* cathode. Cusick et al. [164] investigated hydrogen production performance and economics of MECs fed with domestic wastewater and winery wastewater; the respective hydrogen production rates were 0.28 ± 0.04 m^3 H_2/m^3 d and 0.17 ± 0.09 m^3 H_2/m^3 d. The resulting hydrogen production costs were \$4.51/kg H_2 for winery wastewater and \$3.01/kg H_2 for domestic wastewater [164]. Based on these results, the first pilot-scale continuous flow MEC (1000 L) having 144 electrode pairs in 24 modules was constructed and tested for current generation and COD removal with winery wastewater [208]. Enrichment of an exoelectrogenic bio-film required ~60 days. The volumetric current density reached a maximum of 7.4 A/m^3 by the planned end of the test (after 100 days). HPR through cathodic process reached a maximum of 0.19 ± 0.04 L/L/day [208]. Kiely et al. [209] attempted to treat potato processing (PP) and dairy manure (DM) wastewater in MECs. PP wastewater was collected from the primary clarifier of the wastewater treatment system, and diluted with ultrapure water (Milli-Q system; Millipore Corp) in order to lower the organic loading rate. At $E_{ap} = 0.9$ V, the MECs fed PP wastewater produced 4.5 mA (0.64 mA/cm^2) of electrical current and HPR of

0.74 m^3-H_2/m^3-d. The biogas produced by PP wastewater MECs was on average 73% H_2, 13% CH_4, and 14% CO_2. The C_E was 80%, with a total COD removal of 79%. These results show that the MECs fed DM wastewater did not produce measurable quantities of biogas. The current production (I) was very low (<1 mA). It was concluded that PP wastewater was a suitable substrate for both MFCs and MECs.

Wang et al. [210] examined the MECs with Pt catalyzed and microbial catalyzed at cathodes for their hydrogen production performance at a low temperature of 9 °C using molasses wastewater as the fuel. In their work, the overall hydrogen recovery of 72.2% ($E_{ap}=0.6$ V) was obtained when the Pt catalyst was used. In contrast, when a cheaper catalyst (biocathode; $E_{ap}=0.6$ V) was used, hydrogen can still be produced but at a lower overall hydrogen recovery of 45.4%. Pre-fermentation of poorly biodegradable landfill leachate (BOD_5/COD ratio of 0.32) was evaluated for enhanced current density (I_V), Coulombic efficiency (C_E), Coulombic recovery (C_R), and removal of organics (BOD and COD) in MECs. Semi-continuously fermented leachate to the anode of an MEC significantly improved its performance: 83% BOD removal, 68% C_E, 17.3% C_R, and 23 A/m^3 I_V (or 16 mA/m^2), compared to 5.6% BOD removal, 56% C_E, 2.1% C_R, and 2.5 A/m^3 I_V (or 1.7 mA/m^2) for the raw leachate [211]. More recently, the use of synthetic wastewater containing carbon sources of different complexity (glycerol, milk and starch) was evaluated in single chamber MEC for hydrogen production. hydrogen production was only sustained with milk as a single substrate and with the simultaneous degradation of the three substrates. The later had the best results in terms of current intensity (150 A/m^3), HPR (0.94 m^3 H_2/m^3 d) and cathodic gas recovery (91%) at an $E_{ap}=0.8$ V [212]. Waste-activated sludge, which contains a large amount of carbohydrates undegradable by electrochemically active bacteria, has been tested as a substrate in MECs [213–215]. From the raw waste-activated sludge, very low hydrogen was produced (0.056 ± 0.008 m^3 H_2/m^3 d) in a two-chambered MEC, though with alkaline-pretreated waste-activated sludge, a larger amount of hydrogen was generated (0.91 ± 0.10 m^3 H_2/m^3 d) [213]. As with lignocellulose, a higher hydrogen production rate was achieved from waste-activated sludge in MECs by combining an MEC with a fermentation process [216]. Finally, an anaerobic-baffled reactor (ARB) was utilized to degrade complex organic compounds into volatile shortchain fatty acids and ethanol, with the ARB effluent then being supplied to MECs for hydrogen production [217].

An integrated dark fermentation and MEC process was evaluated for hydrogen production from sugar beet juice [218], the overall hydrogen production from the integrated biohydrogen process was 25% of initial COD (equivalent to 6 mol H_2/mol hexose added), and the energy recovery from sugar beet juice was 57% using the combined biohydrogen.

4.5.7. Urine

Kuntke et al. [219] demonstrated that the use of a MEC for the ammonium removal, COD removal and hydrogen production from five times diluted urine. During operation with a batch cathode, current density, HPR, ammonium removal rate, and COD removal rate were reported as of 23.07 ± 1.15 A/m^2, 48.6 ± 7.47 m^3 H_2/m^3 d, 173.4 ± 18.1 g N/m^2 d, and 171.0 ± 16.9 g COD/m^2 d, respectively. The stable operation period was prolonged by addition of new cathode media (HRT 6 h), but this resulted in a lower current density (14.64 ± 1.65 A/m^2), HPR (32.0 ± 0.89 m^3 H_2/m^3 d), ammonium removal rate (162.18 ± 10.37 g N/m^2 d) and COD removal rate (130.56 ± 4.45 g COD/m^2 d).

4.5.8. Spent yeast (SY)

Spent yeast (SY), a major challenge for the brewing industry, was treated using an MEC to recover energy [220]. Concentrations of SY from bench alcoholic fermentation and ethanol were tested, ranging from 750 to 1500 mg COD/L and 0 to 2400 mg COD/L respectively. COD removal efficiency (RE), coulombic efficiency (CE), coulombic recovery (CR), hydrogen production and current density were evaluated. The best treatment condition was 750 mg COD/L SY + 1200 mg COD/L ethanol giving higher COD RE, CE, CR (90 ± 1%, 90 ± 2% and 81 ± 1% respectively), as compared with 1500 mg COD/L SY (76 ± 2%, 63 ± 7% and 48 ± 4% respectively). Future work should focus on electron sinks, acclimation and optimizing SY breakdown.

4.6. MEC reactor designs and configurations

The MEC reactor design directly affects the current density and Y_{H_2} via internal resistance (R_{in}). In the past a few years, various configurations of MECs are being developed using wide variety of materials. Several different types of MEC reactor configurations have been proposed for lab-scale studies (Fig. 6), but they all share the same operating principles. They are operated under different conditions to enhance the performance, HPR and reduce the overall cost of MECs.

4.6.1. Two or dual-chamber MEC

Two-chamber MEC is the most widely used design consisting of two chambers with the anode and cathode compartments separated by an ion exchange membrane (Fig. 1). A various dual chamber MEC with two liquid chambers [42–46,175,221–223] were developed in recent years. The chambers can be bottle-type or dual chambered H-type [42], rectangular-shaped [175,221], cube or cylindrical type [43,46], disc-shaped [46,58]. Double-chamber MECs with one liquid chamber and one gas chamber [58,126] were also developed using GDE (gas diffusion electrode) either with a membrane electrode assembly (MEA) structure [58] or without a membrane [126]. However, double-chamber MECs are complex and pose practical problems when they need to be scaled up.

Early studies showed that there are some drawbacks of using a membrane in MECs: Firstly, substantial potential losses have been attributed to the inclusion of a membrane; a membrane causes a pH gradient across the membrane which can lead to lower pHs at the anode and higher pHs at the cathode. The pH gradient that develops can lead to performance losses in in both MFCs and MECs. A unit change in pH contributes to a potential loss of 0.06 V. As an example, Rozendal et al. [58] showed that a pH increase of 6.4, which corresponded to a 0.38 V loss of the applied 1.0 V. Furthermore, membranes are expensive and add a significant cost to the MEC system [46,124]. Lastly, the high membrane resistance; a Nafion membrane resistance up to 86% of total internal resistance was reported in a dual-chamber MFC [224]. To overcome abovementioned difficulties, a single-chamber MFC represents a real alternative, offering cost and operational savings among other advantages.

4.6.2. Single-chamber MEC

Since H_2 is relatively insoluble in water (0–1.5 mg/L at $T=25$ °C, $P_{H_2}=1$ atm) and if production rates are high enough, it is likely that microbial conversion of H_2 to CH_4 will be slow [125]. Also, since MECs are completely anaerobic as opposed to MFCs, removing the membrane will not introduce oxygen to the anode and thus should not negatively impact efficiency of MEC.

To overcome the disadvantages and difficulties in use of membrane in MECs, a number of single-chamber MECs were developed recently by removing membranes from two-chamber systems, Single chamber MECs, which consist of an anode and cathode in a shared electrolyte, the schematic diagram of a single-chamber MEC reactor is shown in Fig. 7.

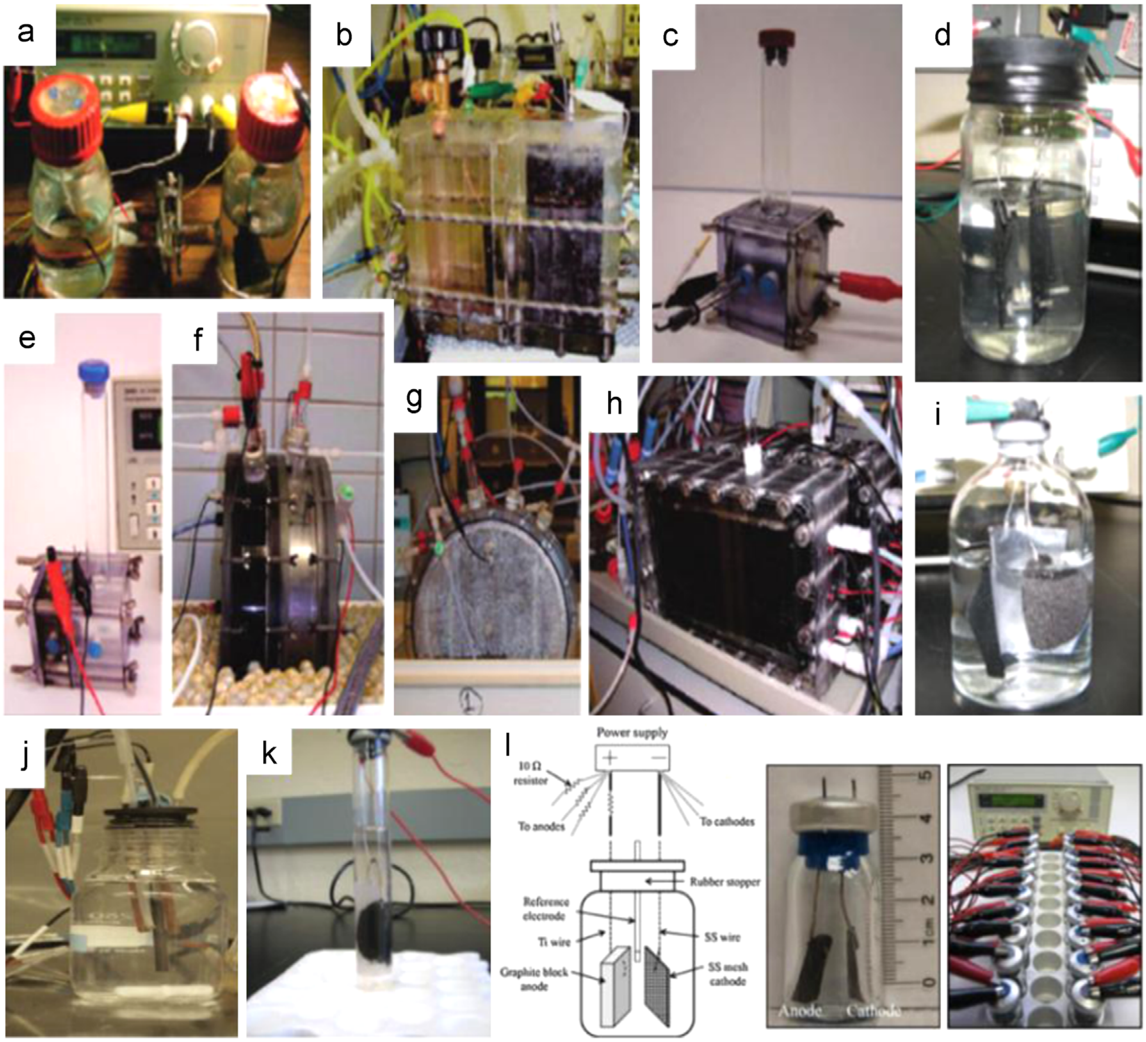


Fig. 6. Photos of various MEC designs: (A) an H-type two-chamber MEC (B) a large cube-type MEC (C) a cube-type MEC with a graphite brush anode (D, I, J) three bottle-type single-chamber MECs (E) a small cube-type MEC (F) a disc-shaped MEC (G) a disc-shaped MEC with membrane electrode assembly (H) a rectangular-shaped MEC with biocathode (K) a tube-type MEC with carbon cloth anode and cathode separated by cloth (L) a small clear glass serum bottle MEC.

The main bodies of MEC reactors can be made with commercially available materials. A plastic (polycarbonates) cube [125], a wide mouth glass bottle [124,225] or clear glass serum bottles [124,226], Plexiglass cylindrical chamber [91] and a glass tube [132]. With the goal of maximizing the HPR, an up-flow or cathode-on-top single-chamber MEC was developed and constructed by placing the cathode on the top of the anode [135,225].

Obviously, a great advantages of using single-chamber MECs are that the removal of membrane can avoid the potential loss caused by the membrane resistance, thereby increasing the current density and the HPR. Moreover, single chamber MEC easy to fabricate, also the problems related to membranes, such as fouling, clogging, biodegradation and high cost can be avoided in the single-chamber MEC system. A relatively simple setup is used for this design.

4.6.3. *Integrated MEC system*

4.6.3.1. An MEC-MFC coupled system. Sun et al. [227] demonstrated the possibility of using an MEC-MFC-coupled system for hydrogen production from acetate, in which hydrogen was produced in an MEC and the extra power was supplied by an MFC. In this coupled system, hydrogen was produced from acetate without external electric power supply. At 10 mM of phosphate buffer, the HPR reached 2.2 ± 0.2 mL L^{-1} d^{-1}, the R_{CAT} and overall systemic C_E were 88–96% and 28–33%, respectively, and the overall systemic (Y_{H2}) peaked at 1.21 mol-H_2 mol-acetate^{-1}. In order to improve the voltage supply, one or two additional MFCs were introduced into the MFC-MEC coupled system [228]. The hydrogen production was significantly enhanced by connecting MFCs in series.

4.6.3.2. Dark fermentation and MFC-MEC coupled system. Recently, combining dark fermentation with MECs seems to be very promising. The integrated hydrogen production system consisted of a dark fermentation reactor, one to three MFCs, and one MEC [199]. Cellulose was continuously fed to the fermentation reactor, with the effluent collected and used as described below for feeding the MFCs and MECs. Two MFCs (each 0.025 L) connected in series to an MEC (0.072 L) produced a maximum of 0.43 V using fermentation effluent as a feed, achieving a HPR from the MEC of 0.48 m^3 $H_2/m^3/d$, and a (Y_{H_2}) of 33.2 mmol H_2/g COD removed in the MEC [199]. Montpart et al. [212] obtained a group of microorganisms able to degrade a specific complex substrate (glycerol, milk and starch) by separately growing fermentative and ARB microbial communities in culture flasks and in an MFC respectively before combining both communities in a single chamber MEC. In this approach, they demonstrated that the growth of an anodic syntrophic consortium between fermentative bacteria and

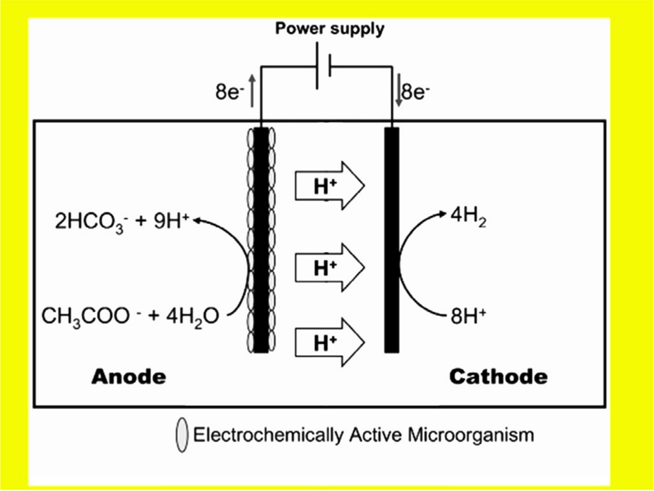


Fig. 7. Schematic diagram of a single-chamber MEC reactor.

ARB was operationally enhanced and increased the potential of these complex substrates to be treated [212].

4.6.4. Dye-sensitized solar cell (DSSC)-powered MEC

A dye sensitized solar cell (DSSC) has been used to provide an additional reductive power from light to an MEC. H-shaped two-chambered glass bottle MECs were run with the assistance of DSSCs as an external power source. An open circuit voltage of 0.6 V was produced by the DSSC and then supplied to the MEC. The whole system produced 400 mmol H_2 within 5 h with cathode recovery efficiency of 78% [180]. In order to further reduce the cost of this coupled system, the platinum catalyst-free cathode of MEC was developed [179]. The system with plain cathode produced almost the same level of hydrogen as that produced with Pt-loaded carbon felt electrodes when E_{ap} was higher than 0.7 V. Furthermore, significantly enhancement in hydrogen production was observed using carbon nanopowder-coated electrode without Pt [179]. Results of the present study indicated that through solar cell-MEC-coupled system, solar energy is converted to liquid or gas transportation fuels (i.e., hydrogen, methane, and ethanol) which can be stored for future use. To further improve the system performance, connecting several solar cells in series is needed in future work.

4.6.4.1. Bio-photo electrochemical cell (BPEC) and MFC-MEC coupled system. Wan et al. [229] successfully developed a new MEC system for H_2 generation that was composed of an MFC and a BPEC. The BPEC consisted of a photocathode and a microbially-catalyzed anode. In the new MEC system, H_2 was produced by the BPEC photocathode when it was illuminated with visible light, with the voltage for electrolysis supplied by the MFC. The electrons produced from the MFC anode were transferred to the BPEC photocathode through an external circuit and then photogenerated holes captured some of the electrons emitted by the MFC anode under visible light. This prevented the recombination of the photogenerated hole and electron pairs, leaving more photogenerated electrons available for HER. This also allowed the remaining electrons from the MFC anode to participate in HERs. Under visible light, H_2 was continuously produced from the new MEC system, with a maximum current density of 0.68 A/m^2 and an average HPR of 1.35 ± 0.15 mL/h.

4.6.4.2. Microbial reverse-electrodialysis electrolysis cells (MRECs). Kim and Logan [230] developed a unique method for H_2 production based on combing a small reverse electrodialysis stack (five membrane pairs) into a MEC, and renamed it as MREC [230]. In MREC, the energy for H_2 production is derived from microbial oxidation of organic matter in the anode and the salinity gradient between seawater and river water, and thus external power resources are not needed. The MREC, constructed with five pairs of seawater and river water cells, produced from 21 to 0.026 L of gas over each fed-batch cycle. A cubic Lexan block with a cylindrical chamber (0.03 L, 7 cm^2 in cross section) was used for an anode and cathode container, with a glass tube (0.02 L) glued to the top of the cathode chamber to collect H_2. Only five pairs of seawater and river water cells were sandwiched between an anode, containing exoelectrogenic bacteria, and a cathode, forming a MREC. Exoelectrogens added an electrical potential from acetate oxidation and reduced the anode overpotential, while the reverse electrodialysis stack contributed 0.5–0.6 V at a salinity ratio (sea-water:river-water) of 50. The HPR increased from 0.8 to 1.6 m^3 H_2/m^3/d for seawater and river water flow rates ranging from 0.1 to 0.8 mL/min. H_2 recovery, the ratio of electrons used for H_2 evolution to electrons released by substrate oxidation, ranged from 72% to 86%. Energy efficiencies, calculated from changes in salinities and the loss of organic matter were 58% to 64%. An MREC was used to produce hydrogen gas from fermentation wastewater without the need for additional electrical energy [9]. Hydrogen production using a fermentation wastewater (10 cell pairs, HRT = 8 h) reached 0.9 ± 0.1 L H_2/L$_{reactor}$/d (1.1 ± 0.1 L H_2/g-COD), with 58 ± 5% COD removal and C_E of 74 ± 5%.

4.6.4.3. Microbial electrodialysis cell (MEDC). MECs have been integrated with microbial desalination cell (MDC) to boost the desalination performance and energy recovery. Mehanna et al. [231] for the first time demonstrated the integration of MEC with MDC, and the new system was renamed as microbial electrodialysis cell (MEDC). In this experiment, two different initial NaCl concentrations of 5 g/L and 20 g/L were examined. Conductivity in the desalination chamber was reduced by up to 68 ± 3% in a single fed-batch cycle, with electrical energy efficiencies reaching 231 ± 59%, and the maximum HPR of 0.16 ± 0.05 m^3 H_2/m^3 d obtained at E_{ap} = 0.55 V. Compared to the former study, much higher HPR 1.5 m^3 H_2/m^3/d (1.6 mL/h) from cathode chamber was obtained due to the relatively higher voltage added (E_{ap} = 0.8 V). Correspondingly, 98.8% removal of the 10 g/L NaCl was observed [230].

4.6.4.4. Microbial saline-wastewater electrolysis cell (MSC). The MEDC was further modified by exchanging the position of AEM and CEM and renamed as MSC [230]. In an MSC, electroactive biofilm on the anode degrade organic maters in saline wastewater, and hydrogen is produced at the cathode as what is done in an MEDC or MEC. Unlike MEDC, MSC can simultaneously removal of organic matter and salt ions from saline wastewater. With E_{ap} = 1.2 V, up to 84% of salinity (initial conductivity 40 mS/cm) and 94% of chemical oxygen demand were removed at substrate concentration of 8 g/L [232].

4.6.4.5. Microbial electrolysis desalination and chemical production cell (MEDCC). By combining the microbial electrolysis cell and the microbial desalination cell (MDC), the microbial electrolysis desalination cell (MEDC) becomes a novel device to desalinate salty water. The desalination process in these systems results in large pH differences in anode (pH decrease) and cathode (pH increase) chambers [233]. The low pH (< 5) in the anode chamber is harmful to the microbial activities, while the high pH in the cathode lower the hydrogen production rate. Secondly, high levels of Cl^- accumulated in the anode chamber may also inhibit the microbial activities [231,234]. To solve these problems, Chen et al. [234] developed a microbial electrolysis desalination and chemical-production cell (MEDCC) with four chambers using a bipolar membrane. With applied voltages of 0.3–1.0 V, 62–97% of C_E was achieved from the MEDCC, which were 1.5–2.0 times of those from the MEDC. With 10 mL of 10 g/L NaCl in the desalination chamber, desalination rates of the MEDCC reached 46–86% within 18 h.

4.7. MEC operational factors

4.7.1. Inoculation

It is reported that the type and source of inoculum is the most important biological factors affecting the performance of MECs. Four methods are commonly used to inoculate MECs: (I) Operating MFCs till reaching stable power generation and then transferring the anodes to MECs [42,57,124,125]. This procedure ensures the enrichment of exoelectrogenic community on anodes and provides a rapid start-up for MEC operation; (II) Using the effluent from running MFCs/MECs or scraping biofilms from these anodes [46,48]; (III) Directly using wastewater or anaerobic sludge as seeds: generally, most wastewater contains high amounts of microorganisms which are very suitable for its biological treatment. That is why inoculum used in most MECs and MFCs works is taken from different microbial system [215,220], such as wastewater treatment plant [42,87,126,207]; and (IV) Using cultured pure bacterial species [124,167].

4.7.2. Applied voltage

The applied voltage is needed in MEC to obtain energy in form of hydrogen, which should affect the formation and evolvement of the microbial anode system. The most MECs were operated at applied voltages of 0.3–1.0 V [46,124,125]. $E_{ap} > 1.1$ V are not recommended because the electrical energy input is so large that the MEC becomes closer to a water electrolysis process [235]. In addition, a change in applied voltage has significant effect on growth and distribution of micro-organisms and further impacts microbial anode potential (MAP) [235,239] or methane generation [215,236–240]. Although hydrogen production was detected at $E_{ap} = 0.2$ V [46], applied voltages lower than 0.3 V may result in low HPR and erratic system performance [42,44,45]. The E_{ap} of ≥ 0.7 V is chosen because this ranges of applied voltage allowed for relatively fast cycle times compared to those obtained with lower applied voltages [226].

4.7.3. Electrolyte or ion strength

The conditions of electrolytes, such as pH and conductivity, are important factors that affect the performance of MECs; electrolyte pH can influence the activity of electrochemically active bacteria and be used to control the redox reaction potentials on the electrode [241,242]. However, the electrolyte conductivity can affect the internal resistance of MECs [152]. There have been several research works that explore the effect of electrolytes on the performance of MECs as described next. Merrill et al. [152] reported that specific electrolytes can increase the performance of MECs by reducing the cathode overpotential or solution resistance according to its pH; phosphate and acetate electrolytes can improve the performance of MECs by decreasing the overpotential at pH 5. However, at a higher pH (pH 9), carbonate electrolytes increased the performance of MECs by reducing the solution resistance. Munoz et al. [155] showed that for MECs equipped with a stainless steel cathode electrode, the existence of phosphate species in an electrolyte improved the current density for hydrogen production because of the cathodic deprotonation reaction. Yossan et al. [243] tested five groups of catholytes in MECs, including a phosphate buffer, NaCl solution, deionized water, tap water, and acidified water. The MEC containing a 100 mM phosphate catholyte exhibited the highest hydrogen production rate because of its high buffer capacity, followed 9 bioelectrochemical production of hydrogen from organic waste 263 by NaCl solution due to its high conductivity, and then acidified water as it provided extra protons for hydrogen production. Liu et al. [244] investigated the optimal anolyte pH in MECs and found that the optimal pH was 9 for a maximum HPR of 0.55 m^3 H_2/m^3 d.

4.7.4. Electrode physico-chemical properties

Various factors can affect the internal resistance in MEC, but this can be reduced by optimizing the electrode physico-chemical properties, such as surface area, activation resistance, conductivity, surface morphology, distance, electrode position. As examples, Call and Logan [125] improved the HPR by increasing the anodic surface area using graphite granules. Wang et al. [245] decreased the internal resistance in an MEC by shortening the distance between the anode and cathode electrodes from 14 to 4 cm. Cheng and Logan [8] and Kadier et al. [246] reported that the hydrogen production rate in an MEC can be increased by reducing the electrode spacing; the maximum hydrogen production rate they achieved in an MEC had a 2 cm electrode spacing [8]. Gil-Carrera et al. [241] investigated the optimum electrode size and arrangement in flat-plate MECs. They reported that the optimum electrode size and arrangement in flat-plate MECs was a two-layer carbon felt anode having a 10 mm thickness and a single gas diffusion cathode. Liang et al. [247] further showed that optimizing the anode arrangement effectively reduced the internal resistance. In their study, an MEC separately positioning two anode electrodes at either side of the cathode in parallel reached a higher current density of 621.3 ± 20.6 A/m^3 and HPR of 5.56 m^3 H_2/m^3 d than an MEC having two anodes at one side of the cathode (360 A/m^3 and 2.55 m^3 H_2/m^3 d).

4.7.5. Temperature

Temperature is important thermodynamic parameter. It can also affect the activity and selection of microorganisms in MECs. Omidi and Sathasivan [248] demonstrated, based on the COD removal rate and amount of biomass in MECs, that 31 °C was the optimum condition for MEC operation. In general, MEC tests are now conducted at a controlled temperature range of around 30 °C. However, hydrogen has been successfully generated in a single-chambered MEC enriched and operated at temperatures as low as 4 °C and 9 °C [249]. Under this psychrophilic condition, methane production by methanogen is effectively inhibited.

4.7.6. Hydraulic retention time (HRT) and organic loading rate

In addition to the aforementioned MEC operating factors, the effects of hydrodynamic force and dissolved oxygen on the MEC performance and anode biofilm have been evaluated as operational factors [250]. It was found that the hydrogen production in an MEC was markedly influenced by the hydrodynamic force, but not significantly affected by the anode biofilm exposure to dissolved oxygen. As final considerations in this subsection, it has been shown that the organic loading rate and hydraulic retention time can be crucial operational factors under the continuous-mode operation of MECs [251,252]. More hydrogen could be obtained by optimizing or studying these operational factors.

5. MEC for microbial production of value-added chemicals

The fast growing application possibilities of MECs offers this versatile technology promising perspectives. Apart from hydrogen generation, some other applications were developed recently in the MEC cathodes. Especially the recent invention of microbial electrosynthesis (MES) provides an innovative option for efficient and sustainable chemicals production. In the cathodic chamber of MESs have two pathways. One pathway is H_2O reduction, the other proton reduction. Basic principles in chemical production by MES are shown in Fig. 8.

The obvious and more important application of the MEC systems is the production of green hydrogen. Beside hydrogen gas, cathode reactions of MECs can also be used to produce a variety of valuable compounds. Table 2 shows some reported value-added products from MECs, including methane, acetate, H_2O_2, ethanol, and formic acid.

5.1. Methane (CH_4)

Methane is an excellent fuel and is being widely used all over the word. It is commonly detected in the MECs during hydrogen production due to the growth of methanogens. It is reported that the production of methane in the cathode of MECs frequently coexists with the production of H_2 [164]. This will reduce the commercial value of H_2 and increase the energy and economical cost for its purification [55]. A new perspective on this issue is to use MECs to produce methane as an alternative energy source. Cheng et al. [51] for the first time described the production of methane from carbon dioxide using a two-chamber MECs containing a methanogens-attached biocathode at a set cathode potential less than 0.7 V (vs. Ag/AgCl), methane production rate reached to 0.06 mmol/L/h at voltage of 1.2 V. Likewise, Villano et al. [256] measured a methane production ratio of 0.055 ± 0.002 mmol/D-mg VSS from carbon dioxide in a two-chamber MECs with a biocathode incubated with a hydrogenophilic menthanogenic culture at potentials more negative than 0.65 V (vs. SHE) (corresponding to 0.85 V vs. Ag/AgCl). It has been noted from the work of Chae et al. [257] that the methane production from MECs is varied with inoculum, substrate and reactor configuration. The appearance of methanogens is unexpected in hydrogen-producing MECs, as it lowers the hydrogen production. Several approaches have been employed to inhibit the growth of methanogens in MECs [125,149,258]. However, most of the methods are ineffective or energy intensive. Instead of inhibition of methanogens, direct production of methane in MECs holds several advantages compared to traditional anaerobic digestion processes. Firstly, organic matter oxidation and methane production are two separated processes in MECs which allow high methane content in biogas. Secondly, the process occurs at ambient temperature, i.e. heating is not required, thereby saving energy. Thirdly, methanogens can accept electrons directly from cathode, which may make the process more tolerant to toxic compounds such as ammonia [259]. Fourthly, MECs can use waste streams with low organic matter content, where anaerobic digestion cannot function [260]. At the early stage, methane production in the cathode of MECs was mediated by hydrogen with abiotic cathode. Clauwaert et al. [259] found that hydrogen produced from the cathode of MECs can be further converted to methane in an external anaerobic digester, where the process was not inhibited even at ammonium concentration of 5 g-N/L. The application of biocathode has greatly reduced the costs of electrode catalyst in MECs. To better understand the underlying mechanisms for methane bioelectrosynthesis, a two-chamber MECs containing a carbon biocathode was developed and studied [261]. Considerable methane yield was achieved at a poised potential of 0.9 V (vs. Ag/AgCl), reaching 2.30 ± 0.34 mL after 5 h of operation with a faradaic efficiency of 24.2 ± 4.7%. One key factor that governs electron exchange and methane formation efficiencies is the electrode material. To promote methane production, a biocathode via modifying plain carbon stick with a layer of graphite felt (GF) (hereafter referred as "hybrid GF-biocathode") was developed and evaluated in a two-chamber MEC [262]. Methane production with hybrid GF-biocathode reached 80.9 mL/L at the potential of −1.4 V after 24 h of incubation with C_E of 194.4%.

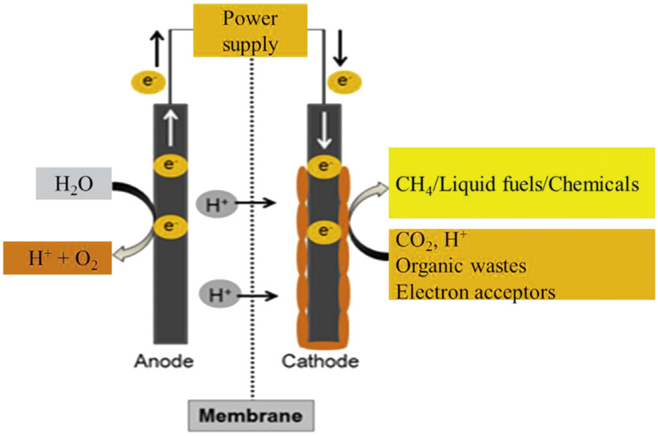


Fig. 8. Schematic overview of chemical production in a typical MES.

5.2. Acetate

Solar and wind as renewable sources of energy have gained tremendous attention in the past decade. However, the intermittent nature of these energy sources demands efficient storage technologies to store the unutilized electrical energy. Capture of electric energy in covalent chemical bonds is the first choice, since compounds can be readily stored and supplied on demand via existing infrastructures. Indeed, experiments conducted by Nevin et al. [253] demonstrated the possibility of reduction of carbon dioxide to acetate by acetogenic microorganism Sporomusa ovata with electrons delivered directly from a graphite electrode (Table 2). It has been found from the work of Nevin et al. [253] that *S. ovata* biofilms on the graphite cathode surfaces consumed electrons from electrode and converted carbon dioxide to acetate and small amounts of 2-oxobutyrate. 85% of supplied electrons were captured into these products. It is for the first time that the concept of microbial electrosynthesis has been proposed, which provides a highly attractive and novel route that might convert solar energy to valuable organic products more effectively than traditional approaches. As an entire new technology, the related mechanisms, foundation theory and process understanding are still on the way. Rabaey and Rozendal [263] elucidated the principles, challenges and opportunities of microbial electrosynthesis, gave important point of view on this exciting and new discipline at the nexus of microbiology and electrochemistry.

5.3. Hydrogen peroxide (H_2O_2)

Hydrogen peroxide as an important industrial chemical can also be produced by MECs. The feasibility of H_2O_2 production, based on the microbial oxidation of organic matter in the anode coupled to oxygen reduction in the cathode of MECs, has been recently demonstrated [52]. With E_{ap} = of 0.5 V, this system was capable of producing H_2O_2 at a rate of 1.17 mmol/L/h in the aerated cathode, resulting in an overall efficiency of 83% based on acetate oxidation [52]. Compared to conventional electrochemical method, the H_2O_2 production in MECs requires much lower energy, which was 0.93 kWh/kg H_2O_2 in the reported study. In principle, H_2O_2 can be produced in MFCs with simultaneous electricity production, which has been demonstrated by several studies [264,265]. However, the production rate of H_2O_2 in MFCs was much lower than that of MECs. H_2O_2 production has greatly expanded the application possibilities of MECs. The most attractive application is the combination of Fenton reaction with MECs, as the MECs can serve as the relatively cheap H_2O_2 source for the Fenton-reaction [266,267]. To become a mature technology, more

Table 2
Summary of the products from MECs platform.

Value-added chemicals	Input voltage (V)	MEC reactor	Cathode	Electron acceptor[a]	Production rate (mmol/L/h)[b]	References
Acetate ($C_2H_3O_2^-$)	0.4	Two-chamber	Graphite sticks	CO_2	–[e]	[253]
Methane (CH_4)	0.7–1.0	Single/two-chamber	Biocathode	CO_2	0.06	[51]
Hydrogen peroxide (H_2O_2)	0.5	Two-chamber	Carbon cloth gas diffusionelectrode	O_2	1.17	[52]
Ethanol (C_2H_6O)	−0.55[c]	Two-chamber	Biocathode	Acetate	0.00003	[254]
Formic acid (CH_2O_2)	1.13[d]	Two-chamber	Pb	CO_2	0.09	[255]

[a] Electron acceptor in the cathode chamber.
[b] Calculated based on total reactor volume with the available data.
[c] Cathode potential.
[d] The power source is MFC stack.
[e] Not stated.

efforts should be put on the improvement of H_2O_2 concentration. H_2O_2 concentration that can be achieved in MECs at present is only 0.13 wt% [52], which is still an order of magnitude lower than the expected level for practical industrial implications. A life-cycle analysis suggests that production of H_2O_2 in MECs is more sustainable than traditional manufacturing routes [264]. However, the technology is still limited by several challenges, among which H_2O_2 supply and presence of residual H_2O_2 after the Fenton reaction are two key issues [268,269]. An innovative Bioelectro-Fenton system capable of alternate switching between MEC and MFC mode of operation was developed to meet the challenges [270].

5.4. *Ethanol (C_2H_5OH)*

Recently, the feasibility of ethanol production by using electrode instead of hydrogen as electron donor in a biocathode MEC has been demonstrated (Table 2) [254]. In a two-chamber MEC, acetate was reduced to ethanol via the assistance of electron mediator such as methyl viologen (MV). When the cathode potential was set at 0.55 V, a maximum current density of 1.33 A/m^2 was obtained after MV addition, leading to 1.82 mM ethanol production. The ethanol production was mainly dependent on the MV concentrations, and the production stopped after 5 days when MV was depleted [254]. MECs platform provide a new way to overcome the limitation of traditional biological ethanol production. However, there are underlying challenges that need to be addressed. The mechanism of acetate reduction in the cathode is still unknown. Since hydrogen (0.0035 N m^3/m^2/d) was observed in the cathode, it could also be involved in acetate reduction. In addition, requirement of irreversibly electron acceptors will add the operation cost, which is a critical challenge for the practical application. Selection of electroactive microorganisms which can accept electrons directly from cathode rather than via mediator for ethanol production could be interesting in future work. In addition to above, the ethanol production rate and the final concentration achieved in the reported system are still low, which will require extensive energy for distillation. Further reduction in electrode overpotential, system internal resistance and energy losses could boost the ethanol production and make the technology industrial applicable.

5.5. *Formic acid (HCOOH)*

The production of formic acid, which is an important chemical used in pharmaceutical syntheses as well as in paper and pulp production, was achieved based on organic matter oxidation in the anode and CO_2 reduction in the cathode (Table 2) [255]. The electricity required for this process was supplied by a five seriesconnected MFCs units, which produced an open circuit voltage (OPC) of 2.73 V. Consequently, formic acid was produced at a rate of 0.09 mM/L/h, and a coulombic efficiency of 64.8% was achieved [255]. This technology will contribute to recover and recycle of the carbon dioxide released during wastewater or waste treatment without energy input, thereby promoting the greenhouse gas reduction. However, the production rate and the final obtained concentration of formic acid are still low at the current stage. The mass transfer and the cathode electrode are two most important factors to the conversion rate. Strategies such as gas diffusion through hollow fiber membrane could be adapted in future work to increase the dissolution of CO_2, and thereby promoting the mass transfer. In addition, the advances in the electrode materials of MECs such as nanofabrication of electrode surface could also bring benefit to lower the cathode overpotential in MECs.

6. Needs and challenges in the development of practical MEC technology

Hydrogen is believed to be the fuel of the future. Many scientific works have demonstrated that MECs are a promising green technology for hydrogen production from a variety of materials, such as natural organic matter, complex organic waste or renewable biomass, and can be advantageously combined with applications in wastewater treatment. In terms of the development of MECs during the last decade several intermittent, significant breakthroughs were discovered. However, MEC still face considerable challenges apart from low hydrogen production which needs considerable attention. Several of great challenges to be overcome in the development of practical MEC technology are discussed as below.

(1) *High capital cost:* Unarguably the most critical problem hindering the large scale application of MEC is its reducing capital cost, which mainly arises from the expensive construction materials. Reducing the capital cost can be achieved by using highly efficient, scalable and less-expensive anode, cathode and membrane materials. For the anode, one of the most promising electrode structures is a graphite fiber brush, which is made by incorporating graphite fibers into a non-corrosive metal core (certain stainlesssteels or titanium). Metals such as tungsten and stainless steel can also be used in brush form. However, much remains to be known about the distribution of microbes, and the proton and electron transfer mechanisms inside the anode chamber.
(2) *Cathode:* The cost of cathode materials is still a key factor limiting their practical application. Platinum (Pt) is the best

choice in respect of high catalysis activity and has been widely used in MECs studies. Generally, Pt is more suitable for foundation studies where a stable cathode activity is required. However, it is well accepted that Pt is not feasible for up-scaling application due to the high cost and negative environmental impacts [271]. The second issue associated with Pt is it can be poisoned by chemicals such as sulfide and thereby losing catalysis activities. Developing high performing, stable, and low-cost cathodes is paramount for practical application of MEC technology to be realized. To further lower the overpotential and the overall internal resistance, and cost of catalysts are a well-known strategies to improve the overall MECs performance. Biocathode is deemed as promising alternatives to noble metals as cathode catalyst due to its simple construction, low operating costs, not requiring a metal catalyst or an artificial electron mediator, good stability, and environmental friendly property. However, the effectiveness of biocathode in pilot-scale operation is still unknown. More effective and tolerant biofilms need to be investigated.

(3) *Scalable MEC reactor:* The rector design is also a key factor to up-scaling of MECs. Membrane-less single chamber MECs are widely used in lab studies. Though the construction cost is greatly reduced due to the removal of membrane, methane production is always observed due to the growth of methanogens, which make MECs inefficient for hydrogen production or other applications. This problem becomes more significant in pilot scale test. Cusick et al. [208] developed the first pilot-scale (1000 L) continuous flow membrane-less single chamber MEC for simultaneous hydrogen production and winery wastewater treatment. The purity of hydrogen and hydrogen losses due to methane formation are still the main challenges toward the practical application of membrane-less single chamber MECs. For the purpose of hydrogen production, better methods will be needed to suppress methanogenic growth and isolate hydrogen from other gas products (e.g., CO_2). Furthermore, the proliferation of the electrochemical active bacteria is to date the main weakness of this technology. Designing more efficient reactors that maintain performance during scale-up and evaluating the performance over the long-term is paramount to move MFC technology closer to practical application. Application oriented reactor design is necessary to lower both construction costs and energy losses. The MECs should be configured and designed such that they can be easily integrated with current infrastructure.

(4) *Long-term stability:* Increasing long-term stability is important for the energy balance and economic feasibility of the MEC system. A deteriorating performance of MECs during long term operation has been detected in many studies [163,272,273]. Reasons for this performance decline arise from many factors, such as the decrease of electrochemical activity of anodic biofilm, the deterioration of cathode performance, fouling and deformation of separator materials, and clogging of the system by excessive biomass and solid pollutants in wastewaters. Moreover, treatment of electrogenic microorganisms with antibiotics could be an alternative biotechnological approach for increased hydrogen generation in MECs inhibiting methanogenesis, and can be used in the enrichment of electroactive bacteria from mixed cultures specifically for long term MEC applications.

(5) *Operational mode:* Another aspect that limits the implementation of MEC for hydrogen production is operation mode of the MEC system. Scale-up of MECs from bench experiments to pilot-scale for hydrogen production has been recently reported. Though the electric energy recovery was above 70%, the Coulomb efficiency and hydrogen production rate are still much lower compared to the maximum value observed in lab scale studies, indicating the necessary of further optimization [274,275]. The MECs could be run in continuous-flow mode to facilitate scale-up in the future.

(6) *Application:* Other application possibilities of MECs such as chemicals synthesis, pollutants removal and metal recovery have not yet moved out from lab. A step-change improvement in performance is required for many applications. This includes much higher power densities and energy efficiencies. The application scopes of MECs could be further expanded e.g. for nutrients recovery. MECs can be an alternative and promising technology to store electrical energy generated from renewable energy sources such as wind and solar into biofuels as well as contribute to CO_2 mitigation. The integration of MECs with existing separation, convention and treatment processes (e.g. anaerobic digestion) is helpful for overcoming drawback and bringing benefits to each other, and thereby boosting the waste conversion and hydrogen production.

(7) *Power sources:* Renewable and sustainable power sources are needed to make the whole process more cost-effective and renewable. In return, MECs could be an alternative method to store the extra renewable energy (e.g. electricity from windmill).

From the above discussion it is inferred that in spite of the enduring challenges, if MEC keeps its pace in research and development, it is reasonable to believe that in the near future this platform technology will provide viable solutions to address many energy and environmental related issues.

7. Conclusions

MECs have gained attention as a novel alternative hydrogen production method because of their high hydrogen conversion efficiency, low energy requirement, and their applicability to many organic substrates. Despite the major technological breakthroughs and advances made in the past decade, many inherent problems still hinder the large scale and real-world applications of MECs. A comprehensive understanding of MEC and various critical factors that can regulate MFC performance has been depicted in the present review. Exoelectrogens is the key component that governs the overall MEC performance through their substrate metabolism and EET. In recent years, an expansive diversity of exoelectrogenic microorganisms have been isolated and characterized. Nevertheless, there is limited understanding of the mechanisms of microbial EET in MECs. Recently, several non-Pt catalysts are investigated in MEC including biocathode, Nickel (Ni) and Ni alloy, metal nanoparticles, and stainless steel (SS). Among these catalysts, SS is probably the most promising cathode material due to its low cost, commercially availability and good stability. Moreover, the type and nature of substrate significantly influences the system performance. In the initial years, simple substrates like acetate (sodium acetate) and glucose were commonly used in MECs, but in recent years researchers are using more unconventional substrates with an aim of utilizing renewable biomass or treating wastewater. Besides, substantial progress has recently been made in improving MEC reactor design using wide variety of materials. In addition, the several experimental evidences indicate that the performance of MFCs is affected by many operating conditions, including inoculation, applied voltage, electrolyte or ion strength, electrode physico-chemical properties, operating temperature, hydraulic retention time (HRT), and organic loading rate. More research will be needed to understand the effect of different operational parameters and optimize the hydrogen production from the MFC. With continuous improvements in MEC, it may be possible to increase

HPR and reduce production and operating cost of MECs. Thus, the combination of waste treatment along with hydrogen production may help in compensating the cost of wastewater treatment, making the MEC technology more sustainable.

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