

None-platinum electrode catalysts and membranes for highly efficient and inexpensive H₂ production in microbial electrolysis cells (MECs): A review

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ABSTRACT

Microbial electrolysis cell (MEC) is a gripping bio-electrochemical device producing H₂ gas from renewable biomass while at the same time treat wastewater. Through extensive global research efforts in the latest decade, the performance of MECs, including energy efficiency, hydrogen production rate (HPR), and hydrogen recovery have achieved significant breakthroughs. However, employing a low-cost, stable and high efficient cathode to replace platinum catalyzed cathode (Pt/C) is the greatest challenge for large-scale industrialization of MEC. Numerous studies have demonstrated that the performance of MEC directly depends on the kinetics of the anode and cathode reactions within the electrolysis cell, with the performance of the electrode catalyst highly affected by the materials they are made from. In a relatively short space of time, a wide range of electrode materials have been tested to amplify the performance of MECs, such as carbon-based electrode catalysts have emerged as promising electrode materials for both anode and cathode construction. Composite materials have also shown to have the potential to become materials of choice for electro-catalyst manufacture. More recently, various transition metal oxides and alloys have been extensively examined as alternatives to conventional expensive noble-metals like platinum for hydrogen evaluation reaction (HER) in MECs. Numerous studies have confirmed that stainless steel, Ni alloys, and Pd nanoparticle decorated cathode are worth mentioning and have very good efficiency. In the present article, we present a comprehensive review centered on the development of a low-cost and high efficient electrode materials and membrane to boost the performance of MECs, including anode, cathode, and membrane.

Keywords: Hydrogen production, Microbial electrolysis cell (MEC), Anode materials, Cathode catalysts, Stainless steel (SS), Hydrogen production rate (HPR), Biocathode.

1. Introduction

Fossil fuels are still widely used in our modern society. According to the International Energy Agency (IEA), at present, fossil fuels (FFs) such as oil, coal, and natural gas represent more than 86% of global energy

consumption and transport in particular depends 95% on oil [1,2]. However, the use of FFs has some major drawbacks. Firstly, the FFs are finite and they will eventually run out. FFs will be depleted shortly because of the decline in discoveries of major new reserve and the rapid rise in their continued use [3,4]. Moreover, the use of FFs raises serious environmental issues and concerns. The burning of FFs is directly

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linked to global warming as CO₂ is a primary greenhouse gas (GHG) [5,6]. GHGs are defined as water (H₂O), SO_x, CO₂, methane (CH₄), nitrous oxide (NO_x), chlorofluorocarbons (CFCs) and aerosols [7]. Scientists are concerned that the highest GHG emissions in the atmosphere of the earth are causing an increase in global mean temperatures, with potentially harmful consequences for the environment and human and animal health [8,9]. Based on the above considerations, actions will be needed to explore carbon-neutral energy sources to power our world with the most sustainable and cleanest way [10,11].

It should be noted that hydrogen gas provides exceptional value as an energy carrier and industrial feedstock. Compared to other alternative energy sources, H₂ has many advantages. Firstly, hydrogen is a green fuel that is almost free of CO₂ and other pollutant emissions, due to its oxidation product is only water [12-14]. Secondly, H₂ is high calorific value fuel. Compared to other gaseous fuels, H₂ has the highest energy density. The energy content of 120-142 MJ/kg for H₂, other possible biofuels CH₄: 50 MJ/kg or ethanol: 26.8 MJ/kg and 44 MJ/kg for gasoline [15-18]. Thirdly, H₂ can be derived from a wide variety of renewable feedstock and domestic waste materials. So, H₂ can be cost effective, clean, sustainable and renewable [19-21]. Fourthly, H₂ is an important feed stock to the chemical industry.

There are numerous renewable options available to produce hydrogen, such as water electrolysis, biophotolysis, photo-fermentation, dark fermentation (DF) [22-24]. Despite its great possibilities, H₂ production is not yet practical because of limitations inherent to each approach. In comparison to other options of producing H₂, DF 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 [25]. However, the thermodynamic limitations of DF process result in the lower conversion of the substrate [26,27]. Furthermore, DF leaves many hydrogen-containing components as end-products for example, acetic acid, butyric acid and ethanol [28,29], which cannot be further converted to H₂ without adding an external energy input [30].

Microbial electrolysis cells (MEC) is an innovative and promising bio-electrochemical route that can convert renewable biomass to H₂ and other value-added chemicals with only a small energy input [31-33]. MEC analogous to microbial fuel cells (MFCs), contrary to the MFCs, the cathode of MECs operates under anaerobic conditions [34,35]. In comparison

with other conventional technologies, the MEC has some important advantages. Firstly, the MECs theoretically offer the possibility to produce H₂ at relatively low energy inputs; 0.6 kWh/m³H₂ [42] and 1 kWh/m³H₂ [36], which are much lower than the typical energy requirement of 4.5–50.6 kWh/m³H₂ for water electrolysis [37]. Secondly, no precious metals were needed on the anode of MEC, because of self-sustaining microbial biocatalysts. 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 [10] reported an efficiency of 8.55 mol H₂/mol-glucose at 0.6 V compared with the typical 4 mol H₂/mol-glucose obtained by dark fermentation [31]. Fourthly, relatively pure hydrogen is produced in the cathode chamber and thus expensive gas purification processes are not required [38]. Lastly, the MEC using microbes as biocatalysts that produce other value added products such as CH₄ [39], H₂O₂ [40,41], C₂H₅OH (ethanol) [42], while using final electron acceptors like protons, CO₂ and acetate.

One of the key factors to MEC performance and application is the (cathode) catalyst for H₂ production. The past decade has witnessed great advances in the MEC technology, as an upshot of these efforts, numerous non-Pt catalysts are investigated to replace Pt in MECs, for instance, stainless steel (SS), Nickel (Ni) and Ni alloy, metal nanoparticles, and biocatalyst. Among these catalysts, SS is probably the most promising cathode material due to its low cost, commercial availability and good stability. In this review, the state-of-art the electrode material used by different research groups for H₂ generation are provided and results obtained with electrodes were discussed.

2. Microbial electrolysis cell (MEC)

2.1. H₂ production pathway in MECs

In principle, a typical MEC composed of three major components: anaerobic anode chamber, cathode chamber and separator or membrane. Fig. 1 shows the essential physical components of an MEC that consists of an anode, a cathode, a membrane, electrochemically active bacteria (EAB), and a power supply.

In an MEC, Electrochemically active bacteria (EAB) colonized on the anode surface and broke down the organic matter or wastes into CO₂, electrons (e⁻), and protons (H⁺) as a part of its metabolism.

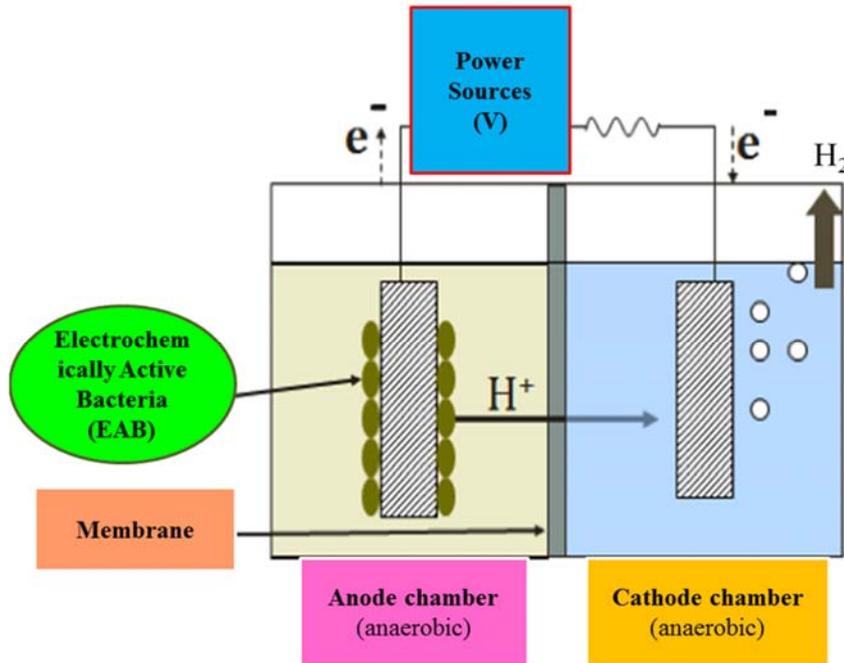
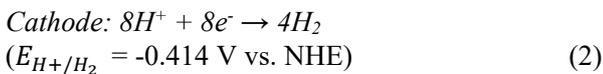
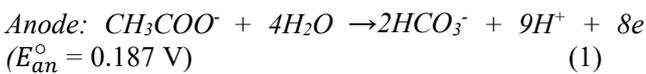


Fig. 1. Schematic representation of a typical two-chamber MEC reactor and its operation.

The bacteria transfer the produced electrons to a solid electrode (anode), while the protons are diffused directly into the MEC electrolyte solution to participate in the reduction reactions. In the meanwhile, the electrons then delivered continuously through an external circuit to a cathode with the help of power supply and combined with the free protons in the solution generate H_2 . If acetate is considered as a substrate, the process can be described in the following electrochemical reactions:



Note that the final reduction of protons to hydrogen ($8H^+ + 8e^- \rightarrow 4H_2$) is a thermodynamically non-spontaneous reaction. Hence it requires an external energy input or supplemental voltage [43-45].

2.2. Thermodynamics of MEC

In MECs, the theoretical reduction potential of each half cell reaction are written and calculated based on the Nernst equation. In case of $pH = 7$, for the cathode reaction, the theoretical reduction potential in MECs are written and calculated according to equation (4):

$$E_{cat} = E_{cat}^\circ - \frac{RT}{2F} \ln \frac{P_{H_2}}{[H^+]^2} = 0 - \frac{8.314 \times 298.15}{2 \times 96485} \ln \frac{1}{[10^{-7}]^2} = -0.414 \text{ V} \quad (4)$$

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 equation (5):

$$E_{an} = E_{an}^\circ - \frac{RT}{8F} \ln \frac{[CH_3COO^-]}{[HCO_3^-]^2 [H^+]^9} = 0.187 - \frac{8.314 \times 298.15}{8 \times 96485} \ln \frac{0.0169}{[0.005]^2 [10^{-7}]^9} = -0.3000 \text{ V} \quad (5)$$

Where E_{an}° (0.187 V) is the standard electrode potential for acetate oxidation, for a solution with $HCO_3^- = 0.005M$, $CH_3COO^- = 0.0169M$, $pH = 7$ [45]. Thus the cell voltage (E_{cell}) necessary for a MEC to produce H_2 at the cathode under these conditions is:

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

Equation (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 ($> 0.114 \text{ V}$) 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 [43,46]. Nevertheless, this voltage is much lower than the voltages required for water electrolysis (typically 1.23 – 2.0 V) [47].

2.3. Extracellular electron transfer (EET) pathways in MECs

EAB play a key role in hydrogen production in MECs. The performance of MECs is significantly influenced by the ability of EAB on the anode to facilitate the transfer of electrons from substrate to anode (electronic generation). A better understanding about the microbial extracellular electron transfer (EET) may promote the development of new strategies for engineering MECs. The experiments carried out by Torres et al. [48] 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. Although the mechanism of EET has not yet been fully elucidated, several possible pathways have been proposed. Currently, the most persuasive general explanations on the EET mechanisms are shown in Fig. 2. The first mechanism (A) represents direct electron transfer between electron carriers in the bacteria and the solid electron acceptor [48]. The second mechanism (B) 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 [49-51]. The third mechanism (C) 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 [52,53].

3. Electrode materials used in MECs for hydrogen evolution

Electrode materials are critical for MECs since they influence the construction and operational costs. So far, electrode materials in MECs can be principally classified into three categories, namely anode, cathode, and membrane or separator

3.1. Anode electrode catalyst or materials

EAB adhere to the surface of anodes to transfer electrons to the electrode. Thus, it is essential to select an appropriate anodic electrode material. It has been shown in the literature that an ideal anode material should have the following features [54]: (a) high 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. The anode material in MECs can be the same as anodes used in MFCs. Within the last decade, numerous kinds of anode materials have blossomed. The most common electrode materials used as anodes or cathodes in MECs are shown in Fig. 3.

3.1.1. Classic carbon-based anode materials

In many works, carbon-based materials have been frequently used as anode in MECs. The carbon-based anodes are so popular because of their high electric conductivity, biocompatibility, versatility in morphologies, vast surface area, chemical stability, significantly low over-potentials and relatively low-costs [36,55]. To date, the most common anodes used in laboratory scale MECs studies originated from carbon based materials such as carbon cloth [56,57], carbon paper [58], graphite felt [43,47,59,60], graphite granules [46, 61-63], carbon fiber [64], ammonia (NH_3) or heat treated (450°C , 30 min) graphite brushes [65,66-71], carbon mesh [72]. When the graphite granules are used, a graphite rod is inserted into the bed of granules as a current collector.

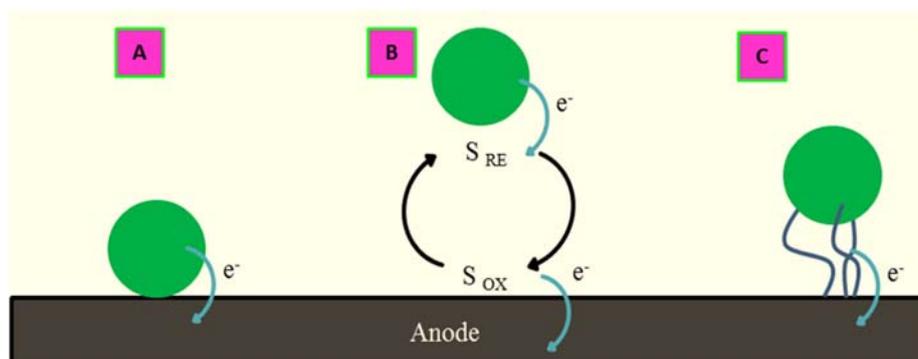


Fig. 2. Schematic diagram describing the EET mechanisms in an MEC anode.

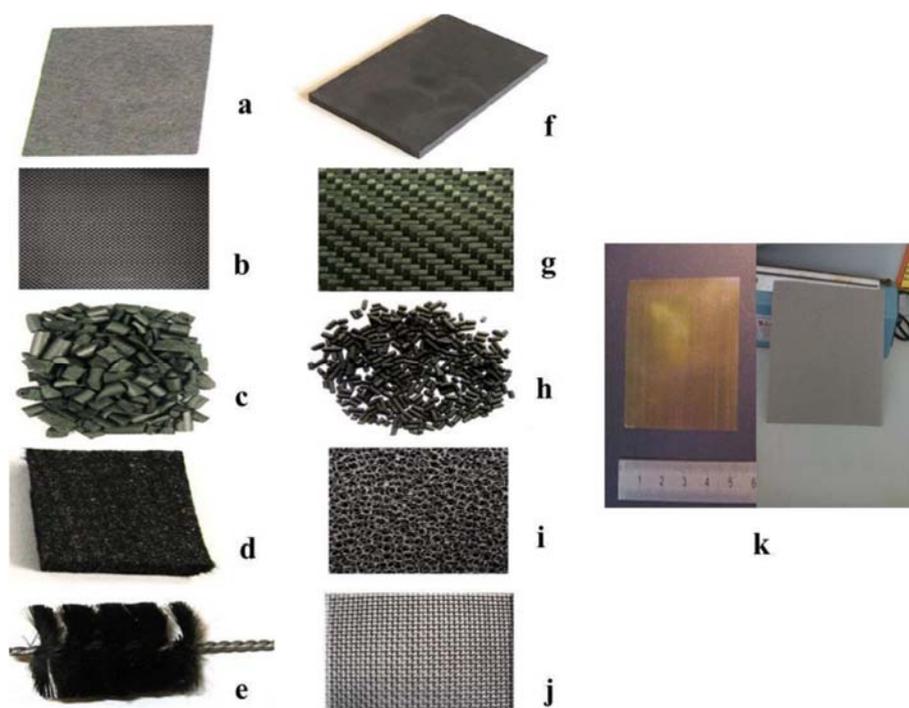


Fig. 3. Photographs of electrode catalyst or materials used for MEC: (a) carbon paper; (b) carbon cloth; (c) granular graphite; (d) carbon felt; (e) carbon brush; (f) graphite plate; (g) carbon mesh; (h) granular activated carbon; (i) reticulated vitrified carbon; (j) SS mesh; (k) electroformed Ni mesh.

Table 1. Summary of reported anode electrode materials used in MECs.

Electrode material (size)	HPR ($\text{m}^3 \text{H}_2/\text{m}^3 \text{d}$) or current density (A/m^2)	Ref.
Carbon cloth ^a	0.88 A/m^2	[56]
Carbon cloth ^b	2.5 $\text{m}^3 \text{H}_2/\text{m}^3 \text{d}$	[57]
Carbon paper ^a ($4.0 \times 4.0 \text{ cm}$)	0.015 $\text{m}^3 \text{H}_2/\text{m}^3 \text{d}$	[58]
Graphite felt ^a (0.65 cm thickness)	6.5 A/m^2	[59]
Carbon felt ^b	50 $\text{m}^3 \text{H}_2/\text{m}^3 \text{d}$	[60]
Graphite granule ^a	1.1 $\text{m}^3 \text{H}_2/\text{m}^3 \text{d}$	[46]
Carbon fiber brush ^b	1.5 $\text{m}^3 \text{H}_2/\text{m}^3 \text{d}$	[67]
Graphite brush ^b	292 A/m^3	[65]
carbon mesh	-	[72]
Carbon nanotube-reticulated vitreous carbon ($1.0 \times 1.0 \times 0.66 \text{ cm}$)	68 A/m^2	[74]
Graphite plate ^b ($1.5 \times 1.0 \text{ cm}$)	-	[75]
Graphite rod ^a	-	[76]
Oxidized stainless steel felt ^a	19.2 A/m^2	[77]
Stainless steel mesh + graphite granule ^a	2.8 A/m^2	[78]
Fe-NP-decorated ^a graphite disk (5.2 cm^2)	42.5 $\mu\text{A}/\text{cm}^2$	[79]
75 wt% (MnO_2) and HNTs (Haloysite nanotubes) on n carbon cloth	767.3 mW/m^2	[80]

^aSingle chamber.

^bTwo chamber.

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 [73]. For the other materials, the electrode is pressed or glued using epoxy to a connecting wire.

3.1.2. Carbon Nanotubes CNT/PANI composite anode

It is noteworthy 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. A study carried out by Qiao et al. [81] 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 [82]. Xu et al. [79] investigated the effects of Fe nanoparticle-modified graphite disks as anodes on the performance of *Shewanella oneidensis MR-1* in MECs. Their results demonstrated that MECs equipped with Fe nanoparticle-decorated graphite anodes achieved a 5.89-fold higher average current density than those equipped with plain graphite anodes.

3.1.3. Pretreatment methods of anode materials

Various surface treatments for anode materials in MECs have been undertaken specifically to boost the performance of MECs, and to reduce methanogens activity in single chamber MECs. In this regard, ammonia treatment has shown to be efficient method for anode treatment. Ammonia treatment increases the adhesiveness between the bacteria and the electrode surface by making the electrode surface more positively charged, bacteria are generally negatively charged [83]. The work of Cheng et al. [46] showed that the ammonia-treated electrode greatly increased the power density by 48 % and reduced the start-up time of the MFC from 150 to 60 h. Zhang et al. [84] modified the stainless steel mesh anode with graphene and observed a power density of 2668 mW/m², which was 18 times higher than a plain stainless steel mesh electrode [84]. Additionally, it was reported that heat treatment of carbon based materials could improve the anode performance in MECs likely due to a cleaning effect of the electrode surface. In work by Wang et al. [85] it was observed that inexpensive heat-treated carbon mesh materials could be used as the anode in MFCs/MECs and provide 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 minutes) is a large-scale alternative to high-temperature ammonia gas treatment method.

Moreover, when the electrode surface is treated with concentrated inorganic acids, it results in the protonation of functional groups over the electrode surface, as such increasing the number of positive charges over the surface of the electrode. Further, acid treatment leads to creation of cracks (roughness) in the material which also enhance the performance [86]. This treatment is very effective in combination with heat treatment. The results of a study carried out by Feng et al. [87] showed that by using a combination of heat and acid treatment, which result in an increase in power production by 25 % [87]. Recently, it has been illustrated that electrochemical oxidation treatment created new functional groups over the surface. The bacteria form peptide bonds with electrodes and therefore create a pathway for the effective transfer of electrons. It has been shown that the use of acid treatment can increase the power density by 57 % [88].

3.2. Cathode electrode materials and cathodic catalysts

Cathode is one of the most important parts in the MECs where H₂ is produced, the efficiency and economic feasibility of MECs are very closely related to the cathode. Rozendal et al. [36] reported that the cathode (including catalyst) could account for the greatest percentage (47%) of the total capital costs for MECs. As mentioned above, the properties requirements for cathode materials are similar to those of anode, however, in addition, a suitable cathode must have the following properties: large active surface area, good electro-catalytic activity, electrochemical stability, high electronic & ionic conductivity, low hydrogen over-potential [89], and a long electrode life is also desirable.

The HER on plain carbon electrode is insufficient or occurs very slow, therefore, it is necessary to coat it with a catalyst layer. In almost all cases, expensive metal catalysts, platinum (Pt) is the most successful catalyst for HER because of its high surface area and low over potential for HER. However, its high price, poisoning by chemicals such as alcohols, carbon monoxide and sulfides (a common constituent of wastewater) or phosphate anions [90], pH sensitivity, and non-sustainability hinders its application in real wastewater conditions. Therefore, a low-cost and high efficient cathode is urgent to be developed to substitutes for Pt cathode. Different cathode materials used in MECs are shown in Fig. 3 and Fig. 4.

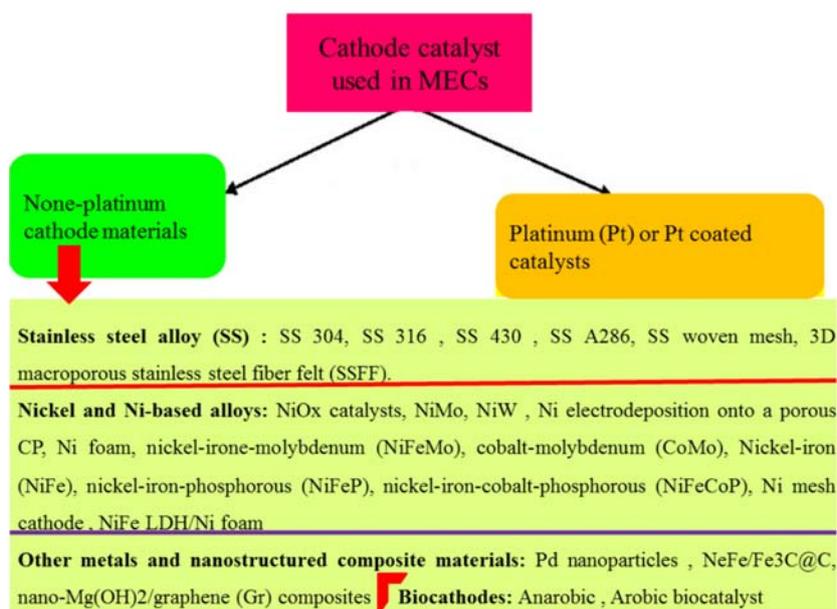


Fig. 4. The classification of the main cathode materials used in MECs

3.2.1. Stainless steel (SS) cathodes

To date, considerable research efforts have been made to find out alternative for expensive Pt cathode. It is well-established that first row transition metals are very useful due to their stability, easy availability, low cost, over-potentials, and toxicity to living organisms [67]. Several studies have aimed to use stainless steel (SS) as a cathode in MECs; Olivares-Ramírez et al. [91] 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. Based on previous work, Selembo et al. [67] examined several SS alloys, 304, 316, 420, A286 and nickel alloys 201, 400, 625, HX as cathode electrodes in an MEC. 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. According to their results, SS A 286 showed the best performance of all the alloys tested at $E_{ap} = 0.9$ V. Furthermore, Call et al. [66] selected high nickel containing (8-11%) SS 304 to use in an MEC test. They compared the performance of 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 investigated for

their suitability as cathode in MECs. The results obtained on that study demonstrated that SS woven mesh performed better than expanded mesh for H₂ production in MEC [92]. Notably, 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/CC [93]. The study on microbial corrosion showed that the HER enhanced via deprotonation of phosphate species on SS cathodes [94,95]. Munoz et al. [96] reported that the high concentration of phosphate species used in combination with a SS cathode allowed high current density for hydrogen evolution and hydrogen production rates (HPRs) in saline solutions at pH = 8. Additionally, Ambler and Logan [97] 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). Notably, Su et al. [98] 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 m³ H₂/m³ d with current density of 17.29 ± 1.68 A/m², hydrogen recovery of $76.37 \pm 15.04\%$ and overall energy efficiency of $79.61 \pm 13.07\%$ at $E_{ap} = 0.9$ V. These important findings suggest that SSFF can be a promising alternative for Pt catalytic cathode in MEC for HER.

3.2.2. Nickel and Ni-based alloys

Another frequently used alternative cathode is Nickel and Nickel alloys. Efforts have also been made to explore the suitability of these cathodes for hydrogen production in MECs. Selembo et al. [67] developed NiOx + SS cathode catalysts for a single-chamber MEC reactor through electro-deposition of NiSO₄ and (NH₄)₂SO₄ onto on a sheet metal, which exhibited an improved volumetric HPR (0.08-0.76 m³ H₂/m³ 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. [99] 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 H₂ 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 regarding the HPR. In one approach, Hrapovic et al. [100] have developed low-cost gas diffusion cathodes with electrodeposited nickel (Ni) particles and evaluated different Ni or Pt loadings. They found that at a Ni load of 0.2-0.4 mg/cm² under acetate non-limiting conditions, H₂ production could reach 5.4 L/L d with a corresponding current density of 5.7 A/m². Manuel et al. [101] investigated the impact of the catalyst load on HPR, and concluded that the chemical deposition of Ni could 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 [102,103], and low electrical resistivity than graphite or titanium [104], it is also cheap and easily available. Instead of using Ni as a deposited catalyst onto carbonaceous materials, Jeremiasse et al. [105] used Ni foam as a cathode for producing high purity H₂ 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. Another approach, Jeremiasse et al. [60] investigated NiFeMo and 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/cm² was used to treat domestic wastewater (DWW) in a continuous flow MEC [106].

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. [107] which was done with Pt cathode. The Ni-based nano modified materials: NiFe, NiFeP and NiFeCoP are promising electrocatalysts for HER in near neutral electrolytes and could be used as cathodes in MECs [108].

To maximize the electrode surface area, a brush-type Nickel foam (NF), SSW, platinum coated SS mesh, and molybdenum disulfide (MoS₂) coated SS mesh electrodes were used as catalysts for H₂ production under practical conditions of high pH and in un-buffered saline catholytes in two-chamber MEC [109]. A non-noble metal electroformed Ni mesh cathode alternatives to typical cathode material (Pt/CC) was intensively examined in a single-chamber MEC [110], the MEC was operated in fed-batch mode and the performance of the Ni mesh cathode was compared with that of Pt/CC cathode. The columbic efficiency (C_E) was $75 \pm 4\%$ and $72.7 \pm 1\%$ for Ni mesh cathode and Pt/CC cathode, respectively. Overall hydrogen recovery (R_{H_2}) was $89.3 \pm 4\%$ and $90.9 \pm 3\%$, for Ni mesh cathode and Pt/CC cathode, respectively. Overall energy efficiency (η_{E+S}) was $62.9 \pm 5\%$ and $69.1 \pm 2\%$ for Ni mesh cathode and Pt/CC cathode, respectively. The maximum volumetric HPR was 4.18 ± 1 m³H₂/m³d and 4.25 ± 1 m³H₂/m³d, for Ni mesh cathode and Pt/CC cathode, respectively. Volumetric current density was 312 ± 9 A/m³ and 314 ± 5 A/m³ for Ni mesh cathode and Pt/CC cathode, respectively.

Similarly one interesting article by Farhangi et al. [111] 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/cm². The R_{H_2} was 66.7 ± 1.4 , 58.7 ± 1.1 and 55.5 ± 1.5 % for Pt/CC, Ni and Ti mesh electrodes, respectively. A novel NiFe layered double hydroxide (NiFe LDH) electrocatalyst was directly grown on nickel foam for H₂ evolution from actual brewery wastewater and its fermentation effluent [112]. The NiFe LDH catalyst demonstrated comparable high HPR (2.01–2.12 m³-H₂/m³/d) with benchmark Pt catalyst but showed higher R_{H_2} of 76–80% , which is twice as much as the rate (55–66%) obtained from popular stainless steel mesh and bare nickel foam cathodes [112]. More interestingly, different from the Pt-coated cathode, the NiFe LDH/Ni foam cathode demonstrated very stable and even increased performance overtime when operated in real wastewater.

3.2.3. Other metals and nanostructured composite materials

Nanostructured cathode material is another promising candidate. Recent years, extensive studies have been carried out on other metals and nanostructured materials for HER in MECs. Harnisch et al. [113] synthesized tungsten carbide powder via a carburization procedure and explored its electro catalytic behavior in MECs by pasting the powder onto graphite disc with Nafion. On the other hand, 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. [114] revealed that the feasibility of using Pd nanoparticles for hydrogen evolution in MECs. The results demonstrated that the Pd nanoparticle electrode achieved a better HPR ($2.6 \pm 0.5 \text{ L/m}^2 \text{ d}$) than a Pt-coated electrode ($2.1 \pm 0.3 \text{ L/m}^2 \text{ d}$). In addition, Tokash et al. [115] used MoS_2 , a well-known photocatalyst for hydrogen evolution photoelectron-chemical cell, as cathodic catalyst for HER in MECs. The results showed that the MoS_2 cathode catalyst generated an analogous average current density of $10.7 \pm 1.2 \text{ A/m}^2$ [115]. In work of Xiao et al. [116], a novel nitrogen-containing core-shell-structured catalyst $\text{NiFe}/\text{Fe}_3\text{C}@\text{C}$ was prepared and used as cathode in MECs. The new catalyst consists of iron-based composite ($\text{Fe}/\text{Fe}_3\text{C}$) nanorods as the core and graphite carbon as the shell. The performance of H_2 production and catalyst stability were studied [116]. The main drawback of these nanostructured materials is their harmful effect on the biofilm, reducing the electrical performance of the MECs. Hou et al. [117] 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 $60 \text{ m}^2/\text{m}^3$ of specific surface area of the electrode and low internal resistance. The energy efficiency in the spiral-wound-electrode MEC could be 66% [110]. Dai et al. [118] synthesized a nano- $\text{Mg}(\text{OH})_2/\text{graphene}$ (Gr) composites via simple hydrothermal method using $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and graphene oxide (GO) as precursors, hydrazine hydrate as additive [118]. In the MEC tests, the nano- $\text{Mg}(\text{OH})_2/\text{Gr}$ cathodic catalyst was comparable with the Pt/CC cathode in terms of current densities and energy efficiency. The R_{H_2} , R_{CAT} and HPR obtained with nano- $\text{Mg}(\text{OH})_2/\text{Gr}$ MEC were $71 \pm 12\%$, $83 \pm 9\%$ and $0.63 \pm 0.11 \text{ m}^3\text{H}_2/\text{m}^3 \text{ d}$, slightly higher than those obtained with the Pt/CC cathode MEC. The nano- $\text{Mg}(\text{OH})_2/\text{Gr}$ cathode exhibited good stability, and it was inexpensive (less than 1.7% of the cost of the Pt/C cathode) [118]. CNTs have been

employed as catalysts and catalyst supporters to enhance hydrogen production in several MEC studies because of their nanometer size, high conductivity, high surface area, and relatively cheap price [119-121]. 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, which enables the synthesis of PANI/MWCNTs composites [119-121]. In addition, the modified electrode (Ni(II)-NClin/CPE) was used for studding the electrocatalytic oxidation of methanol in alkaline solution by cyclic voltammetry (CV) and chronoamperometry techniques [122]. Similarly, Mn(II)-NClin/CPE, Mn(II)-MClin/CPE [123], and Co(II)-NClin/CPE [124] were used in methanol oxidation reaction as a catalyst in strong basic pHs (pH 13). The results demonstrated that the catalytic rate constant for the oxidation of methanol by the proposed electrocatalysts. These modified nanoparticle electrodes could be simple, cheap and effective alternative electrode for MECs.

3.2.4. Biocathodes or Biocatalyst

A recent novel development is the use of EAB as cathode catalyst in MECs. It is wise to pay special attention to the biocathode MECs. 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. Recently, many researchers have studied and explored several metabolic processes present in the cathode, stepping toward a possibility to develop a biocathode [125]. Rozendal et al. [126] first attempted to replace Pt with a mixed culture of EAB through a three-phase startup procedure. 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. This work was promising however it did not report higher production using biocathode. To better understand the difference of performance predicted from the electrochemical half-cell by Rozendal et al. [126], Jeremiasse et al. [127] carried out investigation of a full biological MEC, where both the anode as well as cathode reactions in MEC were catalyzed by EAB. The same experimental set up as with the work of Rozendal et al. [126] was used. In their work, cobalt was successfully recovered with simultaneous methane and acetate production in biocathode MECs. At $E_{\text{ap}} = 0.2 \text{ V}$, 88.1% of Co(II) was reduced with concomitantly achieving yields of $0.266 \pm 0.001 \text{ mol Co/mol COD}$,

0.113 ± 0.000 mol CH₄/mol COD, and 0.103 ± 0.003 mol acetate/mol COD [128]. Very little is known about microbial community of biocathodes, Croese et al. [129] carried out for the first time a study on biocathodic microbial community. 16S rRNA and DGGE analysis showed that *Desulfovibrio*, *Firmicutes* and *Bacteroidetes* were dominant in biocathode [130]. In work of Fu et al. [130] a biocathode was firstly developed in a single-chamber MEC operated at 55°C and further analyzed in a two-chambered MEC. The results showed that at the potential of 0.8 V vs. standard hydrogen electrode (SHE), the thermophilic biocathode produced a current density of 1.28 and an HPR of 376.5 ± 73.42 mmol/d m², which was around 10 times higher than those of the non-inoculated electrode, with R_{CAT} of 70% [130].

Another interesting research proposed by Chen et al. [131] 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 HPR increased with an increase in applied voltage. At $E_{ap} = 0.9$ V, the modified biocathode MECs achieved a HPR of 0.67 m³ H₂/m³ d, current density of 205 A/m³, COD of 86.8%, C_E of 72%, R_{CAT} of 42%, and energy efficiency of 81% with respect to the electrical power input. More recently, in work of Chen et al. [133] enhanced Cd(II) removal with simultaneous hydrogen production was achieved in the biocathode MECs using carbon source of acetate or NaHCO₃, reaching 7.33 ± 0.37 mg/L/h

and 0.301 ± 0.005 m³ /m³ d (acetate), and 6.56 ± 0.38 mg/L/h and 0.127 ± 0.024 m³ /m³ d (NaHCO₃) at an initial Cd(II) of 50 mg/L [132].

3.3. Membrane or separator

A typical MEC design is a two-chambered reactor that consists of an anode, a cathode, and a separator. Separators or membranes play an important role in MECs. Membranes physically divide the anode and cathode chambers and theoretically prevent mass, transport of substrate, hydrogen gas, methane gas, and microorganisms, between the anode and cathode chambers, except for protons. It also functions as a separator to avoid any short circuit in MEC system. Various membranes have been used in MECs [133] (Table 2), among the membrane in used in MECs, proton exchange membrane (PEM) is the most common membrane, called Nafion [43,67,134]. Other membranes have also been tested in MECs, including anion-exchange membranes (AEMs), such as AMI-7001 [46,47], nanofiber-reinforced composite proton exchange membrane (NFR-PEM) [135], forward osmosis membrane [136], bipolar membranes and charge-mosaic membranes [137].

A striking discovery demonstrated that there are some drawbacks of using a membrane in MECs. One of the problems accompanying the inclusion of a membrane in MECs is substantial potential losses. A membrane causes a pH gradient across the membrane that can lead to lower pHs at the anode and higher pHs at the cathode.

Table 2. Summary of membrane or separators reported in previous MEC studies.

Separator	HPR (m ³ H ₂ /m ³ d)	Current density (A/m ³)	Ref.
Cation exchange membrane ^a (256 cm ²)	0.33	2.25	[47]
Anion exchange membrane ^a (256 cm ²)	0.31	2.37	[47]
Anion exchange membrane ^b (30 mm)	1.10	–	[46]
Cation exchange membrane ^b (Nafion)	About 0.5 mL/h	–	[138]
Anion exchange membrane ^b	2.0 mL/h	–	[138]
Cation exchange membrane ^a	1.22	1.8	[139]
Anion exchange membrane ^b	0.43	109 A/m ³	[140]
Cation exchange membrane ^b	0.36	92 A/m ³	[140]
Bipolar membrane ^b (8 cm ²)	0.018	–	[141]
Cation exchange membrane ^b (Nafion; 25 cm ²)	12.9 mL	–	[135]
Cation exchange membrane ^b (sulfonated polyether ether ketone based; 25 cm ²)	14.4 mL	–	[135]

^aSingle chamber.

^bTwo chamber.

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. [47] 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 [46,142,143].

4. Conclusions and future perspectives

There have been substantial improvement and technological advancement in the MFC electrode materials. Electrode materials have a great impact on the performance of MECs. Since anodes and cathodes have different characteristics, the materials and design for them also differ. In general, electrode materials are considered in terms of surface area, surface charge, electronic conductivity, chemical stability, cost and sustainability. In addition, an anode material should be biocompatible to allow microorganisms to grow. Materials with cell toxicity cannot be used regardless of their other properties. Carbon-based materials are widely used because of their high conductivity, biocompatibility, chemical stability, versatility as well as low cost. Furthermore, the surface treatment of the anode materials leads to a better performance of the MEC.

On the other hand, the cathode catalyst materials require enhanced catalytic properties due to the poor kinetics of hydrogen evaluation reaction on cathodes. Even though platinum is cathode catalyst material, research is ongoing to find alternative materials due to its high cost, making it unfeasible to implement in real world applications. Recently, several non-Pt cathodes are investigated in MEC including, stainless steel (SS), Nickel (Ni) and Ni e alloy, and carbon based metal nanoparticles. Among these catalysts, SS is probably the most promising cathode material due to its low cost, commercially availability and good stability. Due to a lack of sustainable catalytic materials, microorganisms such as EAB can also be used as cathode catalyst, which is termed as a biocathode. In the future, microorganisms can be manipulated to increase their endogenous mediators for improved electron transfer. As the final point, a better understanding of microorganism interactions with electrode surfaces will be helpful to optimize the performance of the MECs.

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