Review

An overview of cathode material and catalysts suitable for generating hydrogen in microbial electrolysis cell

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Abstract

Bio-electrohydrogenesis through Microbial Electrolysis Cell (MEC) is one of the promising technologies for generating hydrogen from wastewater through degradation of organic waste by microbes. While microbial activity occurs at anode, hydrogen gas is evolved at the cathode. Identifying a highly efficient and low cost cathode is very important for practical implication of MEC. In this review, we have summarized the efforts of different research groups to develop different types of efficient and low cost cathodes or cathode catalysts for hydrogen generation. Among all the materials used, stainless steel, Ni alloys, Pd nanoparticle decorated cathode are worth mentioning and have very good efficiency. Industrial application of MEC should consider a balance of availability and efficiency of the cathode material.

1. Introduction

Energy is considered as the lifeline of modern era. Non-renewable energy sources like coal, oil and natural gas are excessively utilized to meet the world’s energy requirements. This has come out with an increased rate of depletion of the natural resources. This is a global concern as the future generations would definitely be at threat if the natural resource is depleted at this alarming rate. There are of course alternatives for non-renewable energies. Utilization of solar energy, wind, tidal, geothermal and bio energy, which in principle are renewable, are possible alternatives.

Bio-electrochemical system (BES) possesses a tremendous potential for energy generation and simultaneous treatment of wastewater containing organic substances. Microbes present in the anode degrade the organic substance and release electron to the solid anode surface which travel through the external circuit. There are two aspects of this BES. One in which electricity is produced known as MFC and another where hydrogen is produced known as Microbial Electrolysis Cell (MEC) [1]. Cathode is one of the most important parts of the MEC where hydrogen as well as different chemical compounds are produced. In recent time numbers of researches are directed toward development and application of a low cost cathode or cathode catalyst for practical utilization in MECs for hydrogen generation. In this article the material and catalyst used by different research groups for hydrogen generation and result obtained are discussed.

2. Hydrogen as fuel

Recently interest on hydrogen as a fuel has increased a lot mainly due to the reason that hydrogen has the highest
gravimetric energy density of any known fuel and is compatible with electrochemical and combustion processes for energy conversion without creating environmental pollution and contributing to climate change by producing carbon-based emissions. Hydrogen has a high energy density by weight yet when it is burnt in engines produces almost no pollution. An Otto cycle internal-combustion engine has a maximum efficiency of about 38%, 8% higher than a gasoline internal-combustion engine when the former is run on hydrogen [2]. Hydrogen is a colorless, odorless gas that accounts for almost 75 percent of the entire universe's mass. However it is available on Earth only in combination with other elements like oxygen, carbon and nitrogen and must be separated from these other elements to obtain pure hydrogen to be used. Although, hydrogen is not a primary source of energy like coal, rather it is an energy carrier like electricity. Hydrogen fuel cells and related hydrogen technologies provide the essential link between renewable energy sources and sustainable energy services. NASA has used liquid hydrogen as fuel for space shuttle and rockets since the 1970s [3,4]. Hydrogen is used there as fuel to power the electrical systems and as byproduct pure water is produced, used by the crew as drinking water. The market of hydrogen fuel is increasing and according to a market research company the total world production of hydrogen as a chemical constituent and as an energy source was valued at $120 billion in 2010. An expected increase at a 6.3% compound annual growth rate it may reach a value of $163 billion in 2015 [5]. This seems to be very promising not only for the business but also for the academicians because a chunk of this money will be invested in the R&D section where the researcher can research on novel technology to increase the power output and machineries to use the hydrogen as fuel at lesser cost. There are different types of processes for hydrogen production like steam reforming, partial oxidation, plasma reforming, water electrolysis, water thermolysis, photocatalytic water splitting, sulfur–iodine cycle. Biomass and waste streams can in principle be converted into bio-hydrogen with biomass gasification, steam reforming or biological conversion like biocatalysed electrolysis or fermentative hydrogen production. Fermentative hydrogen production is a well-known process. Besides dark and photo fermentation, bio-electrohydrogenesis (electrolysis using microbes) is another possibility. The biocatalysed electrolysis process is based on a biological anode where electrochemically active microorganisms transfer electrons from organic substrate directly to a solid surface and the get combined with $H^+$ ions at cathode in absence of oxygen.

Microbial electrohydrogenesis provides a completely new approach for hydrogen generation from biomass, such as bio-waste and wastewater, and accomplishing waste treatment at the same time.

3. MEC system

Microbial Electrolysis Cell (MEC) technology represents a new form of clean and green energy by generating electricity and hydrogen from what would otherwise be considered waste. In bio-electrochemical systems bacteria oxidize organic matter and release carbon dioxide and protons into solution and electrons to anode [6]. The electrons released in anode flows through an external electrical circuit to the cathode where they are used in reduction of oxygen. When oxygen is supplied to the cathode, current can be produced and the system is known as MFC. However, in absence of oxygen, and electrochemically enhancing the cathode potential in an MFC circuit it is possible to produce hydrogen (Fig. 1) directly by reduction of protons and electrons produced by the bacteria [3,7–9]. This approach greatly reduces the energy needed to make hydrogen directly from organic matter compared to that required for hydrogen production from water via electrolysis. In a typical MFC, the

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Please cite this article in press as: Kundu A, et al., An overview of cathode material and catalysts suitable for generating hydrogen in microbial electrolysis cell, International Journal of Hydrogen Energy (2012), http://dx.doi.org/10.1016/j.ijhydene.2012.11.031
open circuit potential of the anode is 0.30 V [10,11]. When hydrogen production occurred at the cathode, the half reactions occurring at the anode and cathode, with acetate oxidized at the anode, is as follows [7]:

Anode: \( \text{C}_2\text{H}_4\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 8\text{e}^- + 8\text{H}^+ \)  

Cathode: \( 8\text{H}^+ + 8\text{e}^- \rightarrow 4\text{H}_2 \)  

Producing hydrogen at the cathode requires a potential of at least \( E^\circ = 0.41 \text{ V (NHE)} \) at pH 7.0 [12], so hydrogen can theoretically be produced at the cathode by applying a circuit voltage greater than 0.11 V (i.e., 0.41–0.30 V). This voltage is substantially lower than that needed for hydrogen derived from the electrolysis of water, which is theoretically 1.21 V at neutral pH. In practice, 1.8–2.0 V is needed for water electrolysis under alkaline solution conditions due to overpotential at the electrodes [7].

Hence, thermodynamic analysis shows that, the addition of greater than 0.11 V to the power that generated by bacteria (0.3 V) will generate hydrogen gas at the cathode. However it is observed that voltages of 0.2 V are needed because of electrode over potentials. This hydrogen evolution process provides a route for extending bio-hydrogen production past the endothermic barrier imposed by the microbial formation of fermentation dead-end products, such as acetic acid and same exoelectrogenic bacteria can be used that was used in MFCs and not exposing the cathode to oxygen [7,10,13]. Although, some researchers [7–9,14] referred to the MEC as a biocatalyzed electrolysis cell (BEC) or a bio-electrochemically assisted microbial reactor (BEAMR) but Logan et al. [1] defined the process as electrohydrogenesis or microbial electrolysis to emphasize that in an MEC there is an electrically driven hydrogen evolution process that is distinct from fermentation.

4. Cathode material and catalyst used in MEC for hydrogen evolution

The hydrogen evaluation reaction (HER) reaction occurs at the cathode. MEC construction includes one anodic chamber with the anode; one cathodic chamber with cathode; or a single chamber with both anode and cathode [15]; an external electrical power source; and an electronic separator. Cathode acts as the primary electron donor in an MEC system [7,8,16].

A variety of parameters can limit current density in MECs, for example, distance between the anode and cathode, electrolyte resistivity (including the membrane), ARB (Anode-respiring bacteria) density on the anode, and the specific surface area of the electrodes, cathode material and catalyst [17–20]. The base material of cathode and the catalyst applied on it have significant effect on the performance of the MECs. The base material of the cathode may be graphite, titanium of other conductive materials. The hydrogen evolution reaction (HER) on plain carbon electrodes is very slow, requiring a high overpotential to drive hydrogen production. To reduce the over potential a catalyst is used on the cathodes [1].

4.1. Platinum as cathode catalyst

Platinum is commonly used as the catalyst due to its low overpotential (–0.05 V at 15 Am\(^{-2}\)) for the HER under optimized conditions (for phosphate buffer at pH 6.2, for ammonia it was at pH 9.0) of mass transport [21]. Platinum catalyzed electrodes are commercially available e.g., E-TEK, USA; Magneto Special Anodes, The Netherlands; Alfa Aesar, Germany but can easily be prepared in the laboratory [22,23] by mixing commercially available platinum (e.g., 10 wt% Pt/C, E-TEK) with a chemical binder (5% Nafion solution or 2% PTFE solution). Hydrogen production rates obtained 3.12 ± 0.02 m\(^3\) m\(^{-3}\) reactor liquid day\(^{-1}\) at \( E_{ap} = 0.8 \text{ V} \) with a cathodic hydrogen recovery \( \text{H}_2, \text{cat} = 96\% \) and an overall energy efficiency of \( \eta_{E,LS} = 75\% \) by using Pt catalyst on carbon cloth in a single chamber MEC of volume 28 ml [24]. Titanium mesh having surface area 400 cm\(^2\), thickness 1 mm, specific surface area 1.7 m\(^2\)m\(^{-2}\) with platinum catalyst were used by Rozendal et al. (2007) in two-chamber and one-chamber configurations, with hydrogen production rates up to 0.3 m\(^3\) m\(^{-3}\) reactor liquid day\(^{-1}\) at an applied voltage of 1.0 V [8,15]. Selenmo et al. (2010) applied platinum catalyst of particle size 0.002 \( \mu \text{m} \) mixing with 400 \( \mu \text{L} \) and 50 mg carbon black on carbon cloth using a brush to obtain hydrogen production rate 1.6 ± 0.0 m\(^3\) m\(^{-3}\) reactor liquid day\(^{-1}\), Columbic efficiency 85.0 ± 6.4% [25].

However, there are many disadvantages to using platinum, including the high cost and the negative environmental impacts incurred during mining/extraction [26]. Platinum can also be poisoned by chemicals such as sulfide, which is a common constituent of wastewater [1]. Therefore, finding out alternative of Pt catalyst for commercialization of the MEC system was very important. Different materials were tested as cathode in MECs. In the following sections different alternatives of platinum which has been used by different research groups has been discussed in detail.

4.2. Microbial biocathode

Concepts of a cathode where microorganism will act as the catalyst were first developed in the 1960s but no significant progress was made [27]. In the recent years researchers have studied and explored several metabolic processes present in the cathode, stepping toward a possibility to develop a cathode catalyzed by microorganisms or biocathode [28]. Microorganisms that can produce hydrogen are found in a large variety of environments [29] and contain hydrogenases that catalyze the reversible reaction given in Eq. (3).

\[ \text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2 \]  

Purified hydrogenases have been successfully used on carbon electrodes as a catalyst for hydrogen production [30–33].

Rozendal et al. [34] describes the development of a microbial biocathode for hydrogen production from a naturally selected mixed culture of electrochemically active microorganisms. An MEC half cell with carbon felt electrodes was constructed with a biological anode and fed with acetate and hydrogen at the initial phase. The operation started in a batch mode and latter shifted to continuous mode. Hexacyanoferate(III) was reduced
at the cathode. Once the anodic current was stable, the acetate and hydrogen supply was stopped, and the polarities of anode and cathode were reversed, resulting in a biocathode and chemical anode as schematically described in Fig. 2.

At a cathode potential of −0.7 V, the average current generation of the biocathode was about 1.2 Am⁻², average volumetric hydrogen production rate during the hydrogen yield tests was about 0.63 m³ H₂/m³ cathode liquid volume/day for the biocathode chamber and 0.08 m³ H₂/m⁻³ cathode liquid volume/day for the control electrode chamber. A carbon monoxide inhibition test was conducted to prove that the biocathode is microbial in origin and expected microbial bio-cathode behavior was observed.

Jeremiasse et al. [35] studied a full biological MEC where both the anodic as well as cathodic reactions were catalyzed by microorganisms to understand the difference of performance predicted from the electrochemical half cell by Rozendal et al. [34] using the same experimental set up. Two set ups (MEC1 and MEC2) were used in this 1600 h study. The cathode chamber was inoculated 600 h after the inoculation of anode chamber. During the 52-h yield test, MEC 1 had an average current density of 0.79 Am⁻² and produced 0.08 L of hydrogen; and MEC 2 had an average current density of 0.84 Am⁻² and produced 0.11 L of hydrogen. Hydrogen production rate was 0.03 Nm⁻³m⁻³ reactor liquid/day to 0.04 Nm⁻³m⁻³ reactor liquid/day. At an applied cell voltage of 0.8 V, both MECs had a current density of 3.3 Am⁻². According to the authors this result is compatible with the result of Tartakovskiy et al. (3.2 A m⁻² at 0.85 V) [36].

Jeremiasse et al. [37] further investigated for the faster start-up of microbial biocathode. Two attributes were studied, the effects of cathode potential and carbon source. The former attribute had no effect on the start-up time but the latter reduced the start-up time almost 2 folds. According to the researchers of this study higher biomass yield from acetate may have helped the faster start-up of the microbial biocathode which was supported by thermodynamic calculations. To increase the H₂ production rate, a flow through biocathode fed with acetate was investigated. This biocathode produced 2.2 m³ H₂ m⁻³ reactor day⁻¹ at a cathode potential of −0.7 V versus NHE. In Table 1 the experimental conditions used for biocathodes are tabulated.

### 4.3. Use of stainless steel as cathode

In the research to find out alternative for expensive Platinum catalyst it was found that first row transition metals are very useful due to their stability, abundance in nature, low cost, and low toxicity to living organisms. The most promising materials identified so far are nickel and stainless steel alloys for their low cost, easy availability, low overpotentials, and stability in highly alkaline solutions [39].

Olivares-Ramírez et al. [40] worked on three different type of stainless steel 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 hydrogen evaluation reaction (HER) in the alkaline electrohydrolyzer. From the cyclic voltametry experiments modification of active surface of the stainless steel and cyclic voltammograms well defined cathode and anode peaks corresponding to hydrogen and oxygen evolution zones in the cathodic (−1500 mV to −1350 mV/NHE) and anodic (400−500 mV/NHE) regions respectively were reported. The hydrogen evolution rate which was analyzed by means of the graphical mineral oil volume displacement as a function of time reveals that SS 316 is the best cathode electrode at various applied voltage among SS 304, SS 316 and SS 430 and it was attributed to its higher nickel content than the others used in the experiment.

Selembou et al. [39] studied different stainless steel alloys 304, 316, 420 and A286 and nickel alloys 201, 400, 625 and HX at neutral pH condition. The cathodes were made by cutting sheet metal in to 3.8 cm diameter disks. Sheet metal of flat surface was used to eliminate the influence of factors like catalyst particle size, binding efficiency etc. The experiments were conducted at either 0.6 V or 0.9 V at 30°C constant temperature. According to the results obtained SS A286 is the best alloy in terms of overall hydrogen recovery (H₂, COD = 62 ± 6%), cathodic hydrogen recovery (H₂, cat = 61 ± 3%), energy efficiency relative to electrical input (ηE = 107 ± 5%), overall energy recovery based both electric and substrate inputs (ηE-I = 46 ± 3%). Current density (I₀ = 222 ± 4 A m⁻²), hydrogen production rate (Q = 1.50 ± 0.04 m³ m⁻³ day⁻¹), and H₂ content (80 ± 2%) at 0.9 V. SS 304 also showed better result in comparison to platinum sheet metal. SS alloys A286 (21.2 ± 2.2 ml) and 304 produced

Fig. 2 – Three phase biocathode start-up procedure. A) Start-up of an acetate and hydrogen-oxidizing bioanode after inoculation with a mixed culture of electrochemically active microorganisms, B) adaptation to hydrogen oxidation only, C) polarity reversal to a hydrogen-producing biocathode and biocathode. Adopted from Ref. [34].
Experimental conditions for the testing of biocathode.

Table 1

<table>
<thead>
<tr>
<th>Type of electrode used</th>
<th>Type of electrolyte used</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Mode of operation</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>Anode</td>
<td>Standard microbial activated microbes on graphite felt</td>
<td>-</td>
<td>7</td>
<td>Initially fed-batch mode</td>
<td>[34]</td>
</tr>
<tr>
<td>Cathode</td>
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19.1 ± 1.1 ml hydrogen at an applied voltage of 0.9 V compared to Platinum sheet metal producing 18.9 ± 5.4 ml. Ni 625 performed better than the other metals in terms of total hydrogen gas production at 0.6 V applied voltage by producing 6.61 ml H₂. Performance of SS A268 and Ni 625 were enhanced when nickel oxide was electrodeposited on the surface of the sheet metal. Gas production increased from 9.4 to 25 ml for SS A286 and from 16.2 to 25 ml for Ni 625 at an applied voltage of 0.6 V. Energy recovery based on electrical input (ηE) increased from 3.1% (SS A286) and 31% (Ni 625) to 137% for SS A286 and Ni 625 both with nickel oxide coating. Volumetric hydrogen production rates (Q) also improved from 0.01 (SS A286) and 0.1 (Ni 625) to 0.76 m³ H₂ m⁻³ day⁻¹ for both nickel oxide modified metals at 0.6 V. Methane gas production was reduced from 6.8 to 4.1 ml for SS A286 and from 7.7 to 4.2 ml for Ni 625. These results are very promising in terms of good performance and at low cost which is an absolute requirement for large scale application.

Call et al. [41] selected high nickel containing SS 304 to use in an MEC. They compared the performance of high surface area SS brush with Pt-catalyzed carbon cloth (Pt/C) cathodes and also examined the effect of material composition on current production with SS brush and graphite brush cathode. Hydrogen production rates and overall energy recoveries obtained here for a reactor with 100% loaded SS brush oriented vertically above and parallel to the core of the anode was Q = 1.7 ± 0.1 m³ H₂ m⁻³ d⁻¹ and overall energy recovery was ηE,S = 78 ± 5%.

Stainless steel mesh SS 304 woven and expanded mesh having composition 0.08%C, 2%Mn, 1%Si, 18~20%Cr, and 8~11%Ni, was tested for their suitability as cathodes in MECs as cathode [42]. SS mesh has higher surface area as well as flat nature like flat sheet therefore closer space between anode and cathode can be arranged. Linear sweep voltammetry (LSV) result shows that -0.67 ± 0.01 V of voltage is required to generate substantial current and cyclic voltammetry (CV) tests results measured that electrochemically active areas for all mesh ranged from 12.23 to 23.26 cm². Matsuda’s equation (Eq. (4)) was applied to obtain the peak current, i_p (A) and effective surface area of the working electrodes:

\[ i_p = 0.4464 \times 10^{-3} \frac{n^3 F^2 D^2}{R T} \frac{1}{v} \frac{C_{Fe}}{c_{Fe}}^{1/2} \]  

(4)

where \( n = 1 \) is the number of electrons transferred, \( F = 96,487 \text{ C/mol e}^{-1} \) Faraday’s constant, \( R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \) the gas constant, \( T = 303 \text{ K} \) the temperature, \( C_{Fe} \) the initial ferrocyanide concentration, and \( v \) the scan rate.

SS mesh no 60 with a wire diameter of 0.019 cm and a pore size of 0.023 cm produced the highest current densities and hydrogen production rate (3.3 ± 0.4 m³ H₂ m⁻³ d⁻¹, 2.1 ± 0.3 m³ H₂ m⁻³ d⁻¹, and 0.8 ± 0.1 m³ H₂ m⁻³ d⁻¹) at the three different applied voltages of 1.2 V, 0.9 V, 0.6 V respectively with respect to other different meshes. When tested in MEC SS mesh no 60 was used the Coulombic efficiency obtained was 101 ± 1%. At applied voltage 0.9 V–1.2 V the cathodic hydrogen recoveries (ηH₂) was almost 100%. The energy recovery relative to electricity input (ηE,R) reached the highest value of 232 ± 9% at 0.6 V and the highest overall energy efficiency (ηH₂+ηE,R) of 74 ± 4% at 0.9 V. A similar overall efficiency of 72 ± 11% was reached at 0.6 V. The SS mesh showed good stability as the SEM-EDS measurement shows little variation the composition of the SS after 15 cycles at applied voltage of 0.9 V.
Study on microbial corrosion showed that hydrogen evolution reaction enhanced due to deprotonation of phosphate species on stainless steel [43,44]. When stainless steel was combined with phosphate species it was found that the cathodic deprotonation of phosphate identified in corrosion was combined with phosphate species it was found that the evolution rates of up to 4.9 L h\(^{-1}\) in saline solutions at pH 8.0, a relevant pH value for MEC operation [45]. The presence of phosphate species and other weak acids has recently been shown to have a beneficial effect in MEC, because the charged species increase the electrolyte conductivity and also reduce the overpotential on Pt-graphite cathodes [46]. The cathode was tested in an MEC that used a microbial anode formed from marine sediment and operated at high salinity. Combination of bicarbonate buffer and SS 304 cathodes with mesh no 60 provided good performance compared to MECs containing Pt catalysts or phosphate buffers [47]. The maximum volumetric hydrogen production rate of \(Q = 1.40 \pm 0.13 \, m^3 \cdot h^{-1} \), electrical energy efficiency of \(\eta_e = 155 \pm 8\%\), overall energy efficiency of \(\eta_{E,S} = 68 \pm 3\%\), and a Coulombic Efficiency (CE) = 87 ± 5% with MECs using SS cathodes and BBS were similar to values produced with either PBS or a PGM catalyst at \(E_{op} = 0.9 \, V\). Hence inexpensive SS catalysts and carbonate buffers can achieve performance similar to those achieved with Pt and phosphate buffers which are expensive as well as there is discharge limit of phosphate in the environment which make phosphate buffer unsuitable to be used for wastewater treatment. A comparison of the testing conditions of stainless steel as cathode is tabulated in Table 2.

4.4. Use of other metals and materials as cathode and cathode catalyst

Tungsten carbide (WC), in spite of performing less than platinum as catalyst, is considered as catalyst material since 1960s because of its low price and insensitivity toward catalyst poisons like \(H_2S\) and CO [48]. In a half cell experiment with conventional three electrode system maximum current density of –118 mA cm\(^{-2}\) at overpotential 760 mV and 26 mA cm\(^{-2}\) at overpotential 300 mV the electrocatalytic activity for tungsten carbide was observed. Interestingly when different composition of the tungsten carbide was tested a significant relation between WC content and HER current densities obtained [49].

Nickel and Ni-alloy for hydrogen production in MECs was tested for the development of efficient, stable and cost-effective cathodes by different research groups. Hu et al. [50] developed cathodes by electrodepositing NiMo and NiW onto a three-dimensional carbon-fiber-weaved cloth material and were evaluated at neutral pH using electrochemical cells. These electrodes were also examined for hydrogen production in single chamber tubular MECs with cloth electrode assemblies (CEA). While similar performances were observed in electrochemical cells, NiMo cathode exhibited better performances than NiW cathode in MECs. At an applied voltage of 0.6 V, the MECs with NiMo cathode accomplished a hydrogen production rate of 2.0 m\(^3\) m\(^{-3}\) reactor liquid day\(^{-1}\) at current density of 270 Am\(^{-2}\) (12 A m\(^{-2}\)), which was 33% higher than that of the NiW MECs producing 1.5 m\(^3\) m\(^{-3}\) reactor liquid day\(^{-1}\) and slightly lower than that of the MECs with Pt catalyst producing 2.3 m\(^3\) m\(^{-3}\) reactor liquid day\(^{-1}\). The overall hydrogen recoveries were 65%, 55% and 48% for the MECs with NiMo, NiW, and Pt catalysts, respectively at the applied voltage of 0.6 V. NiMo and NiW MECs ran for over 30 h and no methane was detected by the end of the batches.

The possible reason for higher HER activity may be attributed to the higher loading of the catalysts than the Pt catalyst [50]. According to the authors the uniform deposition of NiW or NiMo increase the surface area of catalyst coating and decrease cathodic over potential [51,52]. In a further study the research group has shown that the optimal condition for electrodeposition of NiMo on carbon cloth is Mo/Ni mass ratio of 0.65 in electrolyte bath, an applied current density of 50 mA cm\(^{-2}\) and electrodeposition duration of 10 min and under this condition, the NiMo catalyst has a formula of Ni\(_6\)MoO\(_2\) with a nodular morphology [53].

Commercially available Nickel and stainless steel powder with different sizes at different metal loadings were used on carbon cloth to construct cathodes by Selenbo et al. [25]. Two cathode namely Ni 210 with 60 mg Ni in 267 \(\mu\)L anion and Ni 210 + CB with 60 mg Ni in 400 \(\mu\)L. Nafion had the low over-potential of –0.500 V and –0.683 V at this current density range (–0.63 mAc m\(^{-2}\) = –3.2 log Acm\(^{-2}\)). Very similar current densities produced with these two materials over the complete range of applied voltages. These two metal powder and binder combinations were used as cathodes in MECs. Single chamber MECs made of Lexan were 4 cm long containing 3 cm diameter cylindrical-shaped chambers were used and anodes were ammonia treated graphite fibre brushes (25 mm diameter \(\times\) 25 mm length, 0.22 m\(^2\) surface area) made with a titanium wire twisted core. The maximum current increased for the two Ni cathodes over the first 6 cycles by as much as 4.7 mA for Ni 210 and 4.1 mA for Ni 210 + CB. The surfaces of the Ni 210-based cathodes maintained very similar structures before and after 12 MEC cycles [25]. Nickel powder was relatively stable with respect to corrosion when MECs were continuously maintained under anaerobic conditions but if exposed to air a nickel oxide layer is formed and can become hydroxylated, forming Ni(OH)\(_2\) in water, and may get dissolved. Different types of Ni alloy with different composition, chemically deposited on a GDL 25BC carbon paper was evaluated by Manuel et al. [54]. A stable \(H_2\) production at rates of 2.8–3.7 L L\(_{\text{r}}\) D\(^{-1}\) was obtained at a total catalyst load of 1 mg cm\(^{-2}\) containing Ni, Mo, Cr, and Fe on cathode. Only 5% methane was present in the gas stream. When Ni loading was of 0.6 mg cm\(^{-2}\) hydrogen production reached volumetric rate of 4.1 L L\(_{\text{r}}\) D\(^{-1}\).

An optimized composition of 150 mM NiSO\(_4\) \(\cdot\) 7H\(_2\)O, 25 mM NiCl\(_2\) \(\cdot\) 6H\(_2\)O, 500 mM H\(_3\)BO\(_3\), and 1 mM CTAB at pH 4.5 was used for Ni electrodeposition onto a porous carbon paper to develop a low cost cathode capable of prolonged hydrogen generation [55]. Hydrogen production as high as 5.4 L L\(_{\text{r}}\) D\(^{-1}\) with a corresponding current density of 5.7 A m\(^{-2}\) was achieved at a Ni load of 0.2–0.4 mg cm\(^{-2}\) under acetate non-limiting conditions. The optimized Ni load and high porosity of gas diffusion cathode providing higher surface area and
<table>
<thead>
<tr>
<th>MEC system</th>
<th>Type of electrode used</th>
<th>Type of electrolyte used</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Mode of operation</th>
<th>Reference</th>
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<td>Electrochemical half cell</td>
<td>Graphite felt</td>
<td>Electrochemically activated microbes on graphite felt</td>
<td>–</td>
<td>7</td>
<td>Initially fed-batch mode later continuous mode</td>
<td>[34]</td>
</tr>
<tr>
<td>Two chambered</td>
<td>Electrochemically activated microbes on graphite felt</td>
<td>Standard microbial nutrient solution* + 1.36 g L⁻¹ Na₃HPO₄ and 2.45 g L⁻¹ NaH₂PO₄·H₂O, 0.31 g L⁻¹ NH₄Cl, 0.13 g L⁻¹ KCl, and trace vitamins and minerals.</td>
<td>30</td>
<td>7</td>
<td>Continuous mode</td>
<td>[35]</td>
</tr>
<tr>
<td>Single chamber</td>
<td>Ammonia treated graphite brushes (25 mm diameter × 25 mm length, 0.22 m² surface area)</td>
<td>50-mM phosphate buffer solution (4.58 g L⁻¹ Na₃HPO₄ and 2.45 g L⁻¹ NaH₂PO₄·H₂O, 0.31 g L⁻¹ NH₄Cl, 0.13 g L⁻¹ KCl, and trace vitamins and minerals.</td>
<td>30</td>
<td>7</td>
<td>Fed-batch</td>
<td>[39]</td>
</tr>
<tr>
<td>Single chamber</td>
<td>Ammonia treated graphite brushes (grade 304 SS)</td>
<td>1 g L⁻¹ Sodium acetate in a 50 mM phosphate buffer medium (PBS; Na₂HPO₄ 4.58 g L⁻¹, and NaH₂PO₄·H₂O, 2.45 g L⁻¹) and nutrient solution (NH₄Cl, 0.31 g L⁻¹; KCl, 0.13 g L⁻¹; trace vitamins and minerals.</td>
<td>30</td>
<td>7</td>
<td>Fed-batch</td>
<td>[41]</td>
</tr>
<tr>
<td>Single chamber</td>
<td>Ammonia treated graphite brushes (25 mm diameter × 25 mm length, 0.22 m² surface area)</td>
<td>SS 304 woven and expanded mesh</td>
<td>1 g L⁻¹ of sodium acetate; 50 mM PBS phosphate buffer (4.58 g L⁻¹ Na₃HPO₄ and 2.45 g L⁻¹ NaH₂PO₄·H₂O, 0.31 g L⁻¹ NH₄Cl, 0.13 g L⁻¹ KCl, and trace vitamins and minerals.</td>
<td>30</td>
<td>7</td>
<td>Fed-batch</td>
</tr>
<tr>
<td>Double chamber</td>
<td>Cylindrical felt carbon anode (0.25 m² projected surface area)</td>
<td>254SMO stainless steel</td>
<td>Seawater at pH 7.5 added with marine sediments from the Atlantic Oce</td>
<td>Room temperature</td>
<td>Fed-batch</td>
<td>[45]</td>
</tr>
<tr>
<td>Single chamber</td>
<td>Ammonia treated graphite brushes (grade 304 SS)</td>
<td>The SS brush cathodes (grade 304 SS)</td>
<td>1 g L⁻¹ sodium acetate and Bicarbonate buffer (BBS, 80 mM; 6.71 g L⁻¹ NaHCO₃, 0.31 g L⁻¹ NH₄Cl, 0.05 g L⁻¹ Na₃HPO₄, 0.03 g L⁻¹ NaH₂PO₄·H₂O, pKa = 8.34, pH = 8.9 as prepared)</td>
<td>30</td>
<td>8.9</td>
<td>Fed-batch</td>
</tr>
</tbody>
</table>

* 0.74 g L⁻¹ KCl, 0.58 g L⁻¹ NaCl, 0.68 g L⁻¹ KH₂PO₄, 0.87 g L⁻¹ K₂HPO₄, 0.28 g L⁻¹ NH₄Cl, 0.1 g L⁻¹ MgSO₄·7H₂O, 0.1 g L⁻¹ CaCl₂·2H₂O, and 1 mL L⁻¹ of a trace element mixture [38].
<table>
<thead>
<tr>
<th>MEC system</th>
<th>Type of electrode used</th>
<th>Type of electrolyte used</th>
<th>Temperature (°C)</th>
<th>pH</th>
<th>Mode of operation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemical half cell</td>
<td>Platinum electrodes served as the counter electrodes</td>
<td>Tungsten carbide powder mixed with 5% Nafion® solution and hand-pressed onto the graphite disc.</td>
<td>100 mM H₂SO₄ and 100 mM sodium phosphate-buffer,</td>
<td>22–23</td>
<td>7</td>
<td>–</td>
</tr>
<tr>
<td>Single chamber</td>
<td>Carbon cloth type A</td>
<td>NiMo and NiW on carbon cloth</td>
<td>5 g l⁻¹ of sodium acetate trihydrate, 100 mM phosphate buffer and other nutrients.</td>
<td>30 ± 2</td>
<td>7</td>
<td>Fed-batch</td>
</tr>
<tr>
<td>Single chamber</td>
<td>Ammonia treated graphite brushes (25 mm diameter × 25 mm length, 0.22 m² surface area)</td>
<td>Nickel (2–10 μm), nickel oxide NiOx 87302 (&lt;74 μm), and stainless steel powder on carbon cloth (Nafion used as binder)</td>
<td>1 g L⁻¹ acetate and a 50 mM phosphate buffer nutrient medium</td>
<td>30</td>
<td>7</td>
<td>Fed-batch</td>
</tr>
<tr>
<td>Double chamber (membrane less)</td>
<td>Carbon felt measuring (10 cm × 5 cm and 5-mm thick)</td>
<td>Ni-alloy catalyst ink with 30% Nafion on GDL 25BC carbon paper</td>
<td>Sodium acetate (90.7 g L⁻¹), yeast extract (6.7 g L⁻¹), NH₄Cl (18.7 g L⁻¹), KCl (148.1 g L⁻¹), K₂HPO₄ (64.0 g L⁻¹), and KH₂PO₄ (40.7 g L⁻¹).</td>
<td>30</td>
<td>–</td>
<td>Continuous flow</td>
</tr>
<tr>
<td>Double chamber (membrane less)</td>
<td>Carbon felt measuring (10 cm × 5 cm and 5-mm thick)</td>
<td>Ni-salts electrodeposited on GDL 25BC carbon paper</td>
<td>Sodium acetate (90.7 g L⁻¹), yeast extract (6.7 g L⁻¹), NH₄Cl (18.7 g L⁻¹), KCl (148.1 g L⁻¹), K₂HPO₄ (64.0 g L⁻¹), and KH₂PO₄ (40.7 g L⁻¹).</td>
<td>30</td>
<td>–</td>
<td>Continuous flow</td>
</tr>
<tr>
<td>Double Chamber with anion exchange membrane</td>
<td>Graphite felt (10 × 10 × 0.25 cm)</td>
<td>Ni foam (10 × 10 × 0.2 cm, 1360 kg m⁻³)</td>
<td>2.72 g l⁻¹ NaCH₃COO·3H₂O, 0.68 g l⁻¹ KH₂PO₄, 0.87 g l⁻¹ K₂HPO₄, 0.74 g l⁻¹ KCl, 0.58 g l⁻¹ NaCl, 0.28 g l⁻¹ NH₄Cl, 0.1 g l⁻¹ CaCl₂·2H₂O, 0.01 g l⁻¹ MgSO₄·7H₂O and 0.1 mL⁻¹ of a trace element mixture</td>
<td>0.1 M KCl</td>
<td>30 ± 1</td>
<td>Not controlled</td>
</tr>
<tr>
<td>Double chamber with heterogeneous anion exchange membrane</td>
<td>Graphite felt of (10 × 10 × 0.25 cm)</td>
<td>Alloys with nickel–iron–molybdenum (NiFeMo) and cobalt–molybdenum (CoMo) electrodeposited on Cu sheet</td>
<td>2.72 g l⁻¹ NaCH₃COO·3H₂O, 0.68 g l⁻¹ KH₂PO₄, 0.87 g l⁻¹ K₂HPO₄, 0.74 g l⁻¹ KCl, 0.58 g l⁻¹ NaCl, 0.28 g l⁻¹ NH₄Cl, 0.1 g l⁻¹ CaCl₂·2H₂O, 0.01 g l⁻¹ MgSO₄·7H₂O and 0.1 mL⁻¹ of a trace element mixture</td>
<td>0.1 M KCl</td>
<td>30 ± 1</td>
<td>6</td>
</tr>
</tbody>
</table>
better transport of hydrogen improved the hydrogen production rate not allowing the microbial conversion of hydrogen to methane. The highly reproducible procedure of electrodeposition could be effectively used for manufacturing large scale cathodes for pilot scale and industrial scale MECs. The size and density of Ni particles could be easily controlled by electrodeposition time and/or the concentration of Ni salt. The authors made the observation that Ni nuclei of 200 nm formed nodular Ni structure of about 10 μm and after 45 days the characteristics were unchanged [55]. They attribute the stability of the electrode to the nodular structure of Ni deposition.

Jeremiasse et al. [56] used Ni foam as cathode for generating high purity hydrogen at high volumetric production rate. Ni foam was found to have high HER catalytic activity under alkaline condition [57,58] and low electrical resistivity than graphite or titanium [59]. It is also cheap and easily available. The pH was not controlled to observe the change in overpotential due to pH change if any. The performance of the MEC was found to be 50 m³ m⁻³ MEC d⁻¹ of hydrogen production at current density 22.8 ± 0.1 A m⁻² and electrical energy input of 2.6 kWh m⁻³ H₂ at applied cell voltage 1 V. The cathodic overpotential was found to be low and the authors suggested that this may be due to a large specific surface area of Ni foam (128 m² m⁻² projected area). The measured overpotential for Ni foam was −0.14 V at 10.5 A m⁻². Due to large surface area the true surface current density decreased and consequently the activation overpotential was lowered. It was found that the cathode overpotential increased during long term operation but the reason for that is unclear to the authors. This may be due to poisoning of active surface area of cathode, formation of Nickel hydride or due to hydrogen gas bubbles, clogging the pores but it needs further investigation.

Jeremiasse et al. [60] investigated with nickel—iron—molybdenum (NiFeMo) and cobalt—molybdenum (CoMo) range of alloys as possible HER catalysts in an MEC around neutral and mild alkaline pH although these alloys are known to have a high catalytic activity under strong alkaline conditions in water electrolysers [60–62]. The catalytic activity of these alloys was compared in a 0.1 M phosphate buffered electrolyte of pH 6. Near neutral 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. Mass transport limitation at near neutral pH becomes a hindrance for catalytic activity. Their catalytic activity is best exploited at alkaline pH where mass transport is not limiting. This was demonstrated in an MEC with CoMo coated Cu cathode and anion exchange membrane, which reached a production rate of 50 m³ H₂ m⁻³ MEC d⁻¹ (at STP) at an electricity input of 2.5 kWh m⁻³ H₂. A Ni-based gas diffusion cathode having Ni loading of 0.4 mg cm⁻² was used to treat domestic wastewater in a continuous flow microbial electrolysis cell. Wastewater treatment efficiency observed was maximum of 76% COD reduction at organic load 441 mg La⁻¹ d⁻¹ and applied voltage V_app = 0.75 V. The energy consumption at high organic loading of 3120 mg La⁻¹ d⁻¹ was 0.77 Wh g COD⁻¹ and at lowest organic load 243 mg La⁻¹ d⁻¹ it became 2.20 Wh g COD⁻¹ [63] which is comparable with the work of Cusick et al. which was done with Pt-based Microbial Electrolysis Cell [64].
Table 4 – Performance of different cathode materials and cathode catalysts used in MEC.

<table>
<thead>
<tr>
<th>Cathode materials and catalyst</th>
<th>Cathode potential (V)</th>
<th>H₂ yield (%)</th>
<th>Current generated (I) A m⁻³ (unless otherwise stated)</th>
<th>Q = hydrogen production rate m⁻³ m⁻³ reactor liquid day⁻¹ (unless otherwise stated)</th>
<th>Columbic efficiency (%)</th>
<th>Cathodic hydrogen recovery rH₂, cat (%)</th>
<th>Overall hydrogen recovery rH₂, COD (%)</th>
<th>Energy efficiency relative to electrical input ηₑ (%)</th>
<th>Overall energy recovery based both electric and substrate inputs ηₑ+S (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biocathode</td>
<td>−0.7</td>
<td>−</td>
<td>−1.2 Am⁻²</td>
<td>0.63</td>
<td>−</td>
<td>49</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>[34]</td>
</tr>
<tr>
<td>Biocathode</td>
<td>0.8</td>
<td>−</td>
<td>3.3 Am⁻²</td>
<td>0.03–0.04</td>
<td>−</td>
<td>17–21</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>[35]</td>
</tr>
<tr>
<td>Biocathode</td>
<td>−0.7</td>
<td>−</td>
<td>2.2</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>[37]</td>
</tr>
<tr>
<td>Stainless steel A286</td>
<td>0.9</td>
<td>80 ± 2</td>
<td>222 ± 4</td>
<td>1.50 ± 0.04</td>
<td>−</td>
<td>61 ± 3</td>
<td>62 ± 6</td>
<td>107 ± 5</td>
<td>46 ± 3</td>
<td>[39]</td>
</tr>
<tr>
<td>Stainless steel 304</td>
<td>0.9</td>
<td>77 ± 1</td>
<td>100 ± 4</td>
<td>0.59 ± 0.01</td>
<td>−</td>
<td>53 ± 1</td>
<td>49 ± 0</td>
<td>90 ± 2</td>
<td>38 ± 1</td>
<td>[39]</td>
</tr>
<tr>
<td>Ni 625</td>
<td>0.9</td>
<td>67 ± 9</td>
<td>160 ± 22</td>
<td>0.79 ± 0.27</td>
<td>−</td>
<td>43 ± 9</td>
<td>41 ± 13</td>
<td>75 ± 16</td>
<td>31 ± 8</td>
<td>[39]</td>
</tr>
<tr>
<td>SS A286 + NiOₓ</td>
<td>0.6</td>
<td>76 ± 2</td>
<td>130 ± 21</td>
<td>0.76 ± 0.16</td>
<td>−</td>
<td>52 ± 4</td>
<td>56 ± 2</td>
<td>137 ± 12</td>
<td>48 ± 3</td>
<td>[39]</td>
</tr>
<tr>
<td>Ni 625 + NiOₓ</td>
<td>0.6</td>
<td>76 ± 5</td>
<td>131 ± 7</td>
<td>0.76 ± 0.15</td>
<td>−</td>
<td>52 ± 9</td>
<td>56 ± 10</td>
<td>137 ± 24</td>
<td>48 ± 9</td>
<td>[39]</td>
</tr>
<tr>
<td>Stainless steel-brush</td>
<td>0.6</td>
<td>–</td>
<td>188</td>
<td>1.7</td>
<td>−</td>
<td>84</td>
<td>−</td>
<td>−</td>
<td>155 ± 8</td>
<td>[41]</td>
</tr>
<tr>
<td>Stainless Steel 304 mesh + bicarbonate buffer</td>
<td>0.9</td>
<td>–</td>
<td>–</td>
<td>1.40 ± 0.13</td>
<td>87 ± 5</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>155 ± 8</td>
<td>[47]</td>
</tr>
<tr>
<td>NiMo on carbon-fiber-weaved cloth</td>
<td>0.6</td>
<td>2.6 mol mol⁻¹</td>
<td>270</td>
<td>2.0</td>
<td>75</td>
<td>86</td>
<td>−</td>
<td>182</td>
<td>65</td>
<td>[50]</td>
</tr>
<tr>
<td>NiW on carbon-fiber-weaved cloth</td>
<td>0.6</td>
<td>2.2 mol mol⁻¹</td>
<td>200</td>
<td>1.5</td>
<td>73</td>
<td>−</td>
<td>−</td>
<td>114</td>
<td>55</td>
<td>[50]</td>
</tr>
<tr>
<td>Ni 210 (60 mg Ni in 267 μL Nafion on carbon cloth)</td>
<td>0.6</td>
<td>92 ± 0</td>
<td>160 ± 31</td>
<td>1.3 ± 0.3</td>
<td>92.7 ± 15.8</td>
<td>79 ± 10</td>
<td>73 ± 3</td>
<td>210 ± 40</td>
<td>65 ± 2</td>
<td>[25]</td>
</tr>
<tr>
<td>Ni 210 + CB (60 mg Ni in 400 μL Nafion on carbon cloth)</td>
<td>0.6</td>
<td>92 ± 1</td>
<td>139 ± 2</td>
<td>1.2 ± 0.1</td>
<td>83.8 ± 1.2</td>
<td>94 ± 5</td>
<td>79 ± 5</td>
<td>252 ± 12</td>
<td>73 ± 4</td>
<td>[25]</td>
</tr>
<tr>
<td>Ni (0.6 gm chemically deposited on a GDL 25BC carbon paper)</td>
<td>1.0</td>
<td>2.8 mol mol⁻¹</td>
<td>3.60 Am⁻²</td>
<td>4.14</td>
<td>68.0</td>
<td>103.3</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>[54]</td>
</tr>
<tr>
<td>Pd nanoparticle on carbon cloth</td>
<td>0.6</td>
<td>–</td>
<td>–</td>
<td>2.6 ± 0.5 L m⁻³ d⁻¹</td>
<td>56.0 ± 10.2</td>
<td>46.4 ± 8.5</td>
<td>26.0 ± 4.8</td>
<td>−</td>
<td>−</td>
<td>[66]</td>
</tr>
<tr>
<td>MoS₂ on carbon cloth</td>
<td>–</td>
<td>92 ± 3</td>
<td>10.7 ± 1.2 Am⁻²</td>
<td>−</td>
<td>−</td>
<td>90 ± 2</td>
<td>123 ± 7</td>
<td>57 ± 3</td>
<td>−</td>
<td>[72]</td>
</tr>
</tbody>
</table>
Recent extensive works in the field of nanofabrication provide a unique opportunity to develop efficient electrode materials due to the fact that nanomaterials are very stable not only structurally but also have stable electrical and chemical properties [65]. Palladium, being the most platinum like metal and with excellent catalytic property and high abundance, is of prime importance. Huang et al. [66] investigated the feasibility of using Pd nanoparticles for hydrogen evolution in MEC. Electrochemical deposition of Pd was conducted in 0.1 M NaCl solution containing 1.26 mM K2PdCl4 as the precursor on a carbon cloth with a maximum loading calculated as 0.17 mg, or 0.0106 mg cm⁻² assuming 100% electrodeposition. A low surface density of Pd nanoparticles with uniform shape was formed under the tested conditions. The Pd nanoparticles coated cathode performed better with coulombic efficiency of 56.0 ± 10.2% and hydrogen generation of 2.6 ± 0.5 L m⁻² d⁻¹ than the Pt catalyst used in this study with coulombic efficiency of 52.0 ± 7.4% and hydrogen production of 2.1 ± 0.3 L m⁻² d⁻¹. The catalytic efficiency of Pd was almost 50 times more than Pt. This much higher catalytic activity in MEC for hydrogen evolution may be due to the surface nano-sized morphology of Pd deposition and deposition condition [67].

The Ni-based nanomodified materials are promising electrocatalysts for HER in near neutral electrolytes and could be applied as cathodes in MECs [68]. The electrocatalytic properties of electrodeposited NiFe₅, NiFe₉ and NiFeCo₅ nanostructures onto carbon felt toward HER in neutral and weak acidic solutions show higher catalytic activity than bare carbon felt. The voltage needed to initiate hydrogen production and the current production rates were in the range of −0.60 and −0.75 V vs. Ag/AgCl as estimated from obtained linear voltammograms. The highest current production rate corresponding to 1.7 ± 0.1 m³ m⁻³ reactor liquid day⁻¹ was achieved with NiFeCo₅/Carbon felt electrodes. These nanostructure modification results in improvement of the corrosion resistance in neutral phosphate buffer and weak acidic (pH 5.5) acetate buffer solutions.

Research work on enzymes and quantum chemical simulations suggested that molybdenum disulfide (MoS₂) would have a small free energy difference for HER [69–71]. Use of MoS₂ as a photocatalyst for hydrogen evolution is well-known but it was used in electrochemical studies for HER by Tokash et al. [72]. Based on LSV study in sodium perchlorate and a phosphate buffer solution optimum MoS₂ loading was 54 mg MoS₂ and 60 mg carbon black, or 47 wt.% MoS₂, with a surface density of 45 g m⁻² but considering the cost with the performance of LSV and galvanostatic polarization tests the 33 wt.% MoS₂ composite cathode was chosen for tests in MECs. The performance was compared with a typical Pt catalyst on carbon cloth which maintained the same amount of carbon black and Nafion binder as used in the MoS₂ composite cathodes. At average current density of 10.0 ± 1.6 Am⁻² for Pt and 10.7 ± 1.2 Am⁻² for MoS₂, and the average fed-batch cycle time 14.7 ± 0.4 h the gas compositions were H₂ = 90 ± 6%, CH₄ = 1 ± 0.6%, and CO₂ = 8.7 ± 5.4% for the Pt cathodes, and H₂ = 92 ± 3%, CH₄ = 1 ± 0.8%, and CO₂ = 6.7 ± 2.3% for the MoS₂ cathodes. COD removals were 88 ± 2% for MECs with Pt-based cathodes and 90 ± 2% for the MECs with MoS₂ based cathodes. Electrical energy efficiency for cathodes was 123 ± 7% which is less than platinum-based cathodes (158 ± 14%). However, overall efficiency of MoS₂ cathodes was similar to platinum-based cathodes with 61 ± 5%. Considering the cost MoS₂ composite cathodes costs one fifth of the typical platinum cathode. Table 3 describes the experimental conditions for testing different material as cathode and cathode catalyst other than stainless steel or bio-cathode.

5. Summary
Cathode is one of the most important parts of the MEC system. Toward the practical implication of MEC system the cost of the cathode along with its higher efficiency are two very important parameters which are of immense importance. Cathode along with its catalyst may contribute almost 47%, which is a substantial amount toward the total cost of the MEC system [73]. Although it was well-known that platinum is a good catalyst for hydrogen generation its cost prevented it to be used in practical situation. In search of material having same or more efficiency at much lower cost it was found out that stainless steel or nickel alloys are good alternatives. Gas diffusion cathode prepared by chemical deposition of Ni alone can successfully be used for hydrogen production. Molybdenum disulfide, tungsten carbide, Ni alloys like NiMo, NiW, NiFeMo are successfully used by different research groups for hydrogen generation. Application of nanotechnology has shown a new area of research. Electrodeposited palladium nanoparticles as cathode catalyst for hydrogen generation was successfully operated. Ni-based nanomodified materials are also very promising electrocatalyst for hydrogen production. The comparison done in Table 4 disclose that among all the cathode materials stainless steel, MoS₂ and nickel foam are worth mentioning owing to their easy availability, low cost and comparative efficiency with platinum cathode catalyst. Stainless steel is probably the better material in terms of its durability, structural strength and easy adaptability to mass-manufacturing approaches. Although, pilot scale application of these cathodes and cathode catalysts are yet to be tested for their performance in real wastewater treatment, this development of different low cost material to be used as cathode or cathode catalyst has taken the possibility of MECs to be used more and more in practical purposes a step closer to be reality.

Acknowledgments
The authors are grateful to University of Malaya (Project no: UM.C/HIR/MOHE/ENG/20) for providing the fund for the research work.

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