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Review

Thermophiles for biohydrogen production in microbial electrolytic cells

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ABSTRACT

Thermophiles are promising options to use as electrocatalysts for bioelectrochemical applications including microbial electrolysis. They possess several interesting characteristics such as ability to catalyze a broad range of substrates at better rates and over a broad range of operating conditions, and better electrocatalysis/electrogenic activity over mesophiles. However, a very limited number of investigations have been carried out to explore the microbial reactions/pathways and the molecular mechanisms that contribute to better electrocatalysis/electrolysis in thermophiles. Here, we review the electroactive characteristics of thermophiles, their electron transfer mechanisms, and molecular insights behind the choice of thermophiles for bioelectrochemical/electrolytic processes.

1. Introduction

According to the predictions of the World Energy council, global demand for energy per capita is expected to peak in 2030 (Davis, 2016). For example, oil production is expected to reach its peak in 2030 at between 94 million barrels per day and 103 million barrels per day. Hydrogen is a promising source of energy to supplement the conventional energy sources and to meet the global energy demand to a certain extent. Hydrogen is a reliable, economical and ecofriendly source of energy. A recent report on "Hydrogen Generation Market" by Generation & Delivery Mode forecasts that the hydrogen generation market is expected to grow to USD 152 billion by 2021 from an estimated USD 118 billion in 2016 at a compound annual growth rate of 5.2% during the prediction period (Market, 2017). Hydrogen can be produced by different methods such as natural gas reforming, coal gasification, solar thermochemical process, photoelectrochemical process, electrolysis and biological processes such as dark fermentation, photo-fermentation and combined fermentation (Bibra et al., 2018; Christopher and Dimitrios, 2012; Ge et al., 2014; Hamedi et al., 2014; Kelly, 2014; Ngoh and Njomo, 2012). The use of microorganisms for hydrogen production has the major advantage that it can make use of the organic waste material as the substrate, thereby simultaneously helping in the bioremediation of wastes and cutting down the costs of bioprocess operation by using cheaper substrates. Similarly, hydrogen production using an electrolytic process has advantages such as simple installation/operation, low cost, environmental sustainability, ease of scale up and most importantly, unlike other processes, it does not produce any undesired products. Energy requirements and the high cost of electrocatalysts, such as noble metals, can be minimized by harnessing the electrocatalytic activity of the microorganisms using a microbial electrolysis cell.

Microbial electrolysis cells (MECs) are bioelectrochemical devices that make use of the electrocatalytic activity of the microorganisms to supplement energy for electrolysis thereby producing H_2. On the other hand, conventional processes for H_2 production make use of thermal, electrochemical or biological process. Microbial electrolysis is a modern hybrid strategy that combines the electrochemical potential offered by the microorganisms and from an external source for electrolytic reaction to produce H_2 in an economical and an efficient manner.

Microorganisms play a crucial role in any microbial systems/processes by mediating the biocatalytic reactions using its complex metabolic machinery. In the case of the microbial electrolytic process or any other bioelectrochemical systems, the microorganism should be electroactive and able to mediate the electrocatalytic reactions. The microorganism should be able to respire onto electrodes either by direct electron transfer using its inbuilt electron transfer machinery or should mediate the electron transfer onto electrodes using their self-produced electron shuttling compounds/electron mediators. Additional features, such as the ability to mediate oxidation/reduction at high rates and with a wide range of substrates (including recalcitrant materials), and the ability to operate at high temperatures, makes thermophiles a

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highly advantageous choice for bioelectrochemical applications. Several reports are documented in the literature on the use of thermophiles (Cerrillo et al., 2016b, 2017a; Lee et al., 2017) as electrocatalysts in MECs. MECs are promising strategies for biohydrogen production from wastes. Use of thermophiles that can metabolize a wide range of substrates including recalcitrant materials and mediate oxidation/reduction reactions with high electrogenic activity in MECs will be an added advantage to rapidly disposing the wastes as well as increasing the yield of biohydrogen in MECs.

The mechanism of operation of mesophilic and thermophilic MEC remains the same as standard MEC except for the use of mesophiles/thermophiles and the operating temperature. The use of thermophiles as electrocatalysts for mediating anodic and/or cathodic reactions enhances the electrocatalytic rates over the mesophiles leading to enhanced oxidation currents and biohydrogen yields. In addition, the use of thermophiles that can oxidize a wide range of substrates including lignocellulosic biomass/recalcitrant will help in converting the wastes to biohydrogen at higher yields when compared with the mesophilic processes. In addition to the microbial catalysis, the high temperature also helps in contributing to enhanced hydrolysis of lignocellulosic wastes. In the cathodic compartment, the use of thermophiles or thermophilic hydrogenases aid in increased reduction of protons for biohydrogen production. Fig. 1 depicts the various hydrogen production pathways using glucose and xylose.

In this article, the advantages of using thermophiles for MEC, their electrocatalytic activity, and their electron transfer characteristics will be discussed. This will be helpful in elucidating the gaps that hinder this technology from practical applications.

2. Operation of MEC

MECs are electrochemical devices that operate on the principles of bioelectrocatalysis (Cheng and Logan, 2007; Logan, 2008, 2004; Logan et al., 2008). In MECs, the microorganisms act as the electrocatalysts and accelerate the electrochemical reaction. The mechanism of MECs is often described as the reverse mechanism of a microbial fuel cell. In the microbial fuel cell, the microorganisms oxidize the substrate and generate a voltage which is used for producing electricity. In contrast, in a microbial electrolytic cell, an external voltage is applied in addition to the voltage produced by the microorganism, to produce hydrogen. But, this explanation of MEC is not entirely accurate. The unique aspect of MEC, when compared with other electrochemical systems, is that it mediates conversion of chemical energy to electrical energy in the anode and conversion of electrical energy to chemical energy in the cathode. It is unique in the sense that both conversion of chemical to electrical energy and electrical energy to chemical energy take place in a single electrochemical system. The reaction happening at the cathode is a good example of an electrosynthetic process. In a MEC, at the anode, the microorganisms oxidize the substrate (electron donor) and produce electrons and protons (H^+ ions) as observed in the case of microbial fuel cells. The electrons are received by the anode and they reach the cathode through an external circuit mediated by the electrolyte. The anaerobic cathodic reaction carries out the production of hydrogen by combining the H^+ ions using the microbial/non-enzymatic electrocatalysts (Logan, 2008). The energy produced by the bioelectrocatalytic reaction in the anode is insufficient to provide the reducing power required for the hydrogen evolution reaction (HER) at the cathodic site. Hence, a small amount of voltage that is deficient (normally 0.2 V–1.0 V) for the hydrogen evolution reaction is supplemented externally.

MEC requires a very small voltage when compared to the much higher voltage (> 1.2 V) in the case of conventional water electrolysis processes for hydrogen generation. MEC for biohydrogen production is an energy-efficient option. The use of efficient microbial electrocatalysts will help to mediate enhanced electrocatalysis and produce electrochemical potential that will lessen the amount of external voltage required for the electrolysis. Selecting optimal electrocatalysts for mediating the cathodic reaction will also aid in mediating the synthesis of hydrogen at a much lower voltage, thereby contributing to better yields, as well as to lower external energy requirements. Logan et al. (2008) reported that the energy requirement for hydrogen production in a microbial electrolytic process is only about 0.6 kWh m^{-3} (0.2 mol H_2 energy/mol-H_2 produced), whereas water electrolysis requires 4.5–5 kWh m^{-3} (1.5–1.7 mol H_2 energy/mol-H_2 produced) (Cheng and Logan, 2007; Logan et al., 2008). One of the most interesting features of the electrochemical system is that it can produce hydrogen from electrical energy and vice versa (electrical energy from hydrogen).

3. Choice of thermophiles for anodic reactions

Major bottlenecks in MECs lies in identifying the promising electrocatalysts for oxidation/reduction reaction. The anodic reaction in MEC is mediated by the electrocatalysis of an electron donor by the electroactive microorganisms. The MEC technology has emerged from the field of *Microbial* Fuel Cells (MFC). The anodic reaction in an MEC and MFC are similar (Liu et al., 2005; Rozendal et al., 2006). At the electrode-electrolyte interface, the electrogenic microorganisms mediate the anodic reaction. Both photosynthetic or non-photosynthetic organisms can serve as the electrocatalyst for mediating the oxidation reaction in the anodic compartment. The non-photosynthetic electrogenic microorganisms oxidize the substrate (electron donor) and release electrons and protons, thereby generating an electrochemical potential. The electrons produced are transferred across the electron transport chain, creating a proton gradient across the membrane which helps the microorganisms to generate ATP, the energy currency of the cell. The

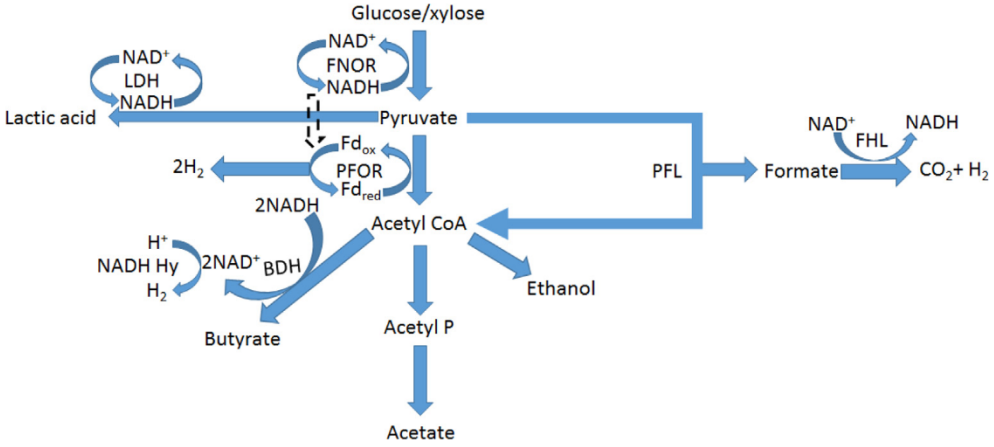

Fig. 1. Hydrogen production by various routes using glucose and xylose (LDH-lactate dehydrogenase, PFL-pyruvate formate lyase, FHL-Formate hydrogen lyase, NAD-nicotinamide adenine dinucleotide, NADH-nicotinamide adenine dinucleotide hydrogen, FNOR-ferredoxin NAD^+ oxidoreductase, FDH-formate dehydrogenase, PFOR-Pyruvate formate oxidoreductase).

voltage generated in the electrocatalytic reaction can be used for generating the required reduction potential for hydrogen production in the cathodic site of the MECs. The Gibbs free energy of oxidation at the anodic site of MEC provides the required energy for the survival, growth and metabolism of heterotrophic microorganisms. The microorganism can carry out the oxidation/reduction reaction with either a single enzyme or a complex series of enzymes. The enzyme involved in electrocatalysis could be either extracellular or intracellular production. These factors greatly influence the entire biochemical reaction as well as its electrocatalytic rates. Other major challenge lies in inhibiting the methanogenesis in MECs. Methane is produced in MECs with mixed cultures having acetoclastic methanogens or hydrogenotrophic methanogens. Acetoclastic methanogens such as *Methanosarcinaceae* and *Methanosaetaceae* converts acetate to methane in MECs. The presence of hydrogenotrophic methanogens such as *Methanobacteriales* and *Methanomicrobiales* helps to produce methane from carbon dioxide and hydrogen (Karthikeyan et al., 2018).

The use of thermophilic microorganisms for mediating the bioelectrocatalytic reactions at the anodic site of the MEC has several advantages over the mesophiles or non-enzymatic and enzymatic electrocatalysts. Thermophilic organisms such as *Bacillus licheniformis* (Choi et al., 2004), *Therminicola* (Parameswaran et al., 2013), have been shown to enhance the oxidation rate at the anodic sites in the MECs. Thermophiles used in Microbial Electrolysis Cells are shown in Table 1.

Faster growth rates of thermophiles when compared with the mesophiles is another major advantage for use in MECs. Faster growth rates of the thermophiles at higher temperatures will increase the reaction kinetics and lead to better oxidation rates, higher substrate utilization, and increased yield of current and biohydrogen. For instance, González et al. (1995) isolated the strain *Thermococcus peptonophilus* sp. nov., from deep-sea hydrothermal vents in the western Pacific ocean which is a fast-growing, extremely thermophilic archaebacterium.

4. Electrogenic activity of thermophiles

Many thermophilic strains are reported to have good electrogenic characteristics capable of mediating electron transfer at very fast rates at electrode-electrolyte interfaces (Aono et al., 1995; Jong et al., 2006; Marshall and May, 2009; Wrighton et al., 2008). This makes them suitable candidates for use as electrocatalysts in developing robust bioelectrochemical systems. In addition, use of high temperature in bioprocesses improves solubility of complex substrates, mass transfer rates, and limits the risk of contamination significantly (Turner et al., 2007).

Wrighton et al. (2011) reported the direct electron transfer by a thermophile, *Thermincola potens* strain JR, isolated from a microbial fuel cell. Pure cultures of *Thermincola potens* strain JR were grown at 60 °C. Electroanalytical investigations showing that transfer of the electrode biofilms to sterile anoxic MFCs did not affect the current production indicate that the electron shuttling compounds are not involved in mediating the electron transfer reactions. Electrolytes used for bioelectrochemical investigations, testing for the presence of electron shuttling compound, failed to reduce amorphous hydrous Fe(III) oxide which confirms that this thermophilic strain does not produce any electron shuttling compounds. Further, it was demonstrated that there was no correlation between biofilm thickness and power production, indicating that biofilms adhered onto the electrode surface were primarily responsible for electron transfer reaction. Formation of biofilm onto the electrode helps in mediating the direct electron transfer via conductive proteins from microorganisms to the electrode or vice versa thereby enhancing the electron transfer rates/electrocatalysis when compared to mediated electron transfer reactions. However, the investigations have shown that increasing the thickness will not linearly increase the electrocatalytic rates. Increasing the thickness of biofilm above a specific thickness will lead to increased mass transfer resistance leading to decreased oxidation of electron

Table 1
Thermophiles used in microbial electrolysis cells.

S. No	Organism	Substrate	Configuration, Temperature, and working volume	Hydrogen yield	Current density	Reference
1	Members of *Bacteroides* isolated from brine pools in red sea	Acetate	Single chamber, 70 °C, and 100 ml		6.8 ± 2.1 A/m^2	Shehab et al. (2017)
2	*Ferroglobus placidus* and *Geoglobus ahangari*	Hydrocarbons and aromatic compounds	Single chamber, 80 °C & 85 °C, and 5 ml		0.68 ± 0.11 A/m^2 & 0.57 ± 0.10 A/m^2	Yilmazel et al. (2018)
3	Activated sludge-based biofilm	Rice straw	dual-chamber, 50 °C, and 380 ml	2.1 mmol/L/D		Wang et al. (2017)
4	Anerobically digested sewage sludge	Acetate	two chamber, Upto 49.4 °C, and 326 ml	1.1 mol/mol acetate	1.6 mA	Kyazze et al. (2010)
5	*Thermincola ferriacetica and Thermincola pseudethanolicus*	Acetate	two chamber, 60 °C, and 350 ml		6.8 ± 1.1–11.2 ± 2.7 A m^{-1}	Lusk et al. (2016)
6	*Thermincola ferriacetica* DSM 14005	Acetate	two chamber, 60 °C, and 325 ml		7–8 A m^{-2}	Parameswaran et al. (2013)
7	Firmicutes with the *Thermoanaerobacter* and *Thermincola* genera	Cellulose	two chamber, 60 °C, and 350 ml		6.5 ± 0.2 A m^{-2}	Lusk et al. (2018)

donor as well as increased electron transfer resistance leading to decreased electrocatalysis. This study also demonstrated the presence of c-type cytochromes in mediating the charge transfer across the Gram-positive bacterial cell envelope.

Parameswaran et al. (2013) documented a detailed investigation of the extracellular electron transfer mechanisms in *Thermincola ferriacetica*. The biofilms of *T. ferriacetica* DSM 14005 were grown at 60 °C on graphite-rod anodes poised at −0.06 V (vs) SHE in MECs. The MEC with biofilms of *T. ferriacetica* DSM 14005 achieved a high current density of 7–8 A m^{-2} and an average Coulombic Efficiency (CE) of 93%. The cyclic voltammetric investigations of the bioelectrodes displayed a Nernst-Monod response with a half saturation potential (EKA) of −0.127 V (vs) SHE. The high current densities were observed as a result of a thick biofilm layer (~38 μm) produced by several layers of active cells. The Nernst-Monod behavior confirmed the extracellular electron transfer through a solid conductive matrix in this case. Yilmazel et al. (2018) reported the current generation in the MEC using hyperthermophilic two iron-reducing archaea *Ferroglobus placidus* and *Geoglobus ahangari* from the family Archaeoglobaceae. With an applied external voltage of 0.7 V, the developed MEC operated with *F. placidus* at 85 °C, produced a current density of 0.68 ± 0.11 A/m^2, and *G. ahangari* MECs at 80 °C produced a current density of 0.57 ± 0.10 A/m^2.

Although the electron transfer mechanisms of electroactive mesophiles at cellular and molecular levels are well-explored, the electrogenic activity of thermophiles and their electron transfer mechanisms are not well investigated. Aono et al. (1995) reported the effect of temperature on the redox activity of the ferredoxin purified from a thermophilic hydrogen oxidizing bacterium, *Bacillus schlegelii*. The results of this investigation showed that on increasing the temperature from 60 °C to 70 °C and 80 °C increased the reduction of cytochrome *c* by 20%. This indicates the thermostability of the electron transfer protein. The increase in the activity of the ferridoxin is mediated by the interconversion of the [4Fe-4S] cluster to the [3Fe-4S] cluster. Reports have also demonstrated that Plastocyanin isolated from *Phormidium laminosum* adsorbed onto a graphite electrode displayed redox activity at temperatures as high as 90 °C (Olloqui-Sariego et al., 2012). Hickey and Daniel (1979), investigated the thermostability of the electron transfer proteins of *Thermus* T351, isolated from the Rotorua thermal region of New Zealand. NADH and succinate oxidases had higher activity at 75 °C and it decreased to less than one-tenth at 40 °C. Lubberding and Schroten (1986) investigated the photosynthetic electron transfer in a thermophilic cyanobacterium *Synechococcus* 6716. Olloqui-Sariego et al. (2014) demonstrated the electron-transfer kinetics of the thermophilic protein Plastocyanin isolated from *Phormidium laminosum*. Studies on the temperature variations in thermophilic plastocyanin adsorbed on a 1,11-undecanedithiol self-assembled layers showed mechanistic changeover at 40 °C.

An acidophilic thermophile will offer greater potential to electrocatalysis research. Shehab et al. (2017), have tested the inoculum from three different brine pools in the Red Sea for use as electrocatalysts in MECs under thermophilic (70 °C) and hypersaline (25% salinity) conditions. Among the inoculum collected from three different sources, the inoculum from Valdivia brine pool displayed high electrocatalytic activity with a current of 6.8 ± 2.1 A/m^2 at an applied anode potential of +0.2 V vs Ag/AgCl for over 58 days. The MECs fed with the Atlantis II and Kebrit samples produced low current densities of 1.3 ± 0.08 A/m^2 and 0.05 A/m^2 respectively. Microbial community analysis revealed that the genus *Bacteroides* were dominant on the anode of the Valdivia MEC. This report also showed the microbial community in the wastewater is one major parameter that determines the performance of MEC. These extremophilic bioelectrochemical systems would be ideal for treating highly saline or thermophilic wastewaters which remain a major limitation with the conventional mesophilic systems. These systems will be promising for treating wastewaters that are highly saline and high temperature such as from oil and natural gas production (10% salinity, and 80–100 °C), dyeing units (3–15% salinity and 40–70 °C) and food processing (1.3–3.9% salinity) (Xiao and Roberts, 2010).

Yilmazel et al. (2018) investigated electrogenic activity of two iron-reducing archaea from the family Archaeoglobaceae, *Ferroglobus placidus* and *Geoglobus ahangari* at thermophilic (40–65 °C) and hyperthermophilic (80 °C) conditions for MEC applications. In addition with Fe(III) as an electron acceptor, *Ferroglobus placidus* were shown to utilize a wide range of electron donors, including hydrocarbons and aromatic compounds. Electroanalaytical investigations showed that these two strains displayed direct electron transfer at electrode-electrolyte interfaces. The presence of 30 genes coding for putative c-type cytochrome proteins in the *F. placidus* genome further confirms the direct electron transfer. Transcriptomic investigations of *F. placidus* grown in the presence of soluble Fe(III) citrate and insoluble Fe(III) oxide showed that the eight genes coding for multiheme c-type cytochromes were upregulated on growing *F. placidus* with insoluble Fe(III) oxide when compared to soluble Fe(III) citrate. These investigations confirmed that *F. placidus* also exhibit flagella mediated direct electron transfer. It is evident from the presence of numerous archaella (archaeal flagella) and upregulation of genes coding for two type IV pilin-like domain proteins in Fe(III) oxide-grown cells (Smith et al., 2015).

The electron transfer in microbial electrocatalysis becomes difficult if the electrocatalytic reactions occur deep within the cell. It is vital to understand if thermophiles have a different orientation of electron transfer proteins that confers better electron transfer characteristics in thermophiles. To mediate the anodic or cathodic reaction in MEC, the thermophile should contain these conductive proteins on the surface of the cell wall or be capable of producing electron shuttling compounds. Electron transfer characteristics of microorganisms are also vital to mediate the cathodic reaction for biohydrogen production.

Aono et al. (1995) reported the effect of increasing temperatures on the reduction of cytochrome *c* in *Azotobacter*-type 7Fe ferredoxin from *Bacillus schlegelii*. Investigations on the electroactivity of ferredoxin at 60, 80 and 90 °C showed that the activity increased by 10, 20 and 20% respectively. Increase in temperature resulted in increase in the interconversion of the [4Fe-4S] cluster to the [3Fe-4S] cluster which in turn contributes towards increased rates of catalysis. Hirano et al. (1981) demonstrated that the increase in temperature increases the membrane fluidity leading to enhanced electron transport. Investigations with a thermophilic blue-green alga, *Synechococcus* sp., showed that plastoquinone acts as a mobile electron carrier mediating electron transfer from the protein assembly of Photosystem II to that of Photosystem I. The electrons flow *through* the fluid hydrophobic matrix of the membranes and increase in temperature leads to enhanced phase changes in the membrane lipids.

5. Operating conditions for thermophilic MECs

Optimizing the operating conditions such as the temperature, electrolyte pH in MECs, electrolyte composition, MEC configuration, electrode materials, and interelectrode distance will aid in improving the performance of thermophilic MECs. Wang et al. (2017) investigated the effect of temperature and anolyte pH on hydrogen production through simultaneous saccharification and fermentation of lignocellulose in a dual chamber MEC. Activated sludge was used as a source of electroactive microorganisms and rice straw was used as the substrate. The system was tested at temperatures up to 50 °C and pH of 4.5–7.0. The results showed that the reducing sugars reached the maximal levels of 8011.69 mg/L at a culture temperature of 50 °C. The MEC operated at 40 °C, 45 °C, and 50 °C had the hydrogen yield of 2.1 mmol/L/D, 1.6 mmol/L/D, and 0.7 mmol/L/D. However, in this case, the moderate temperature was found to be optimal for the growth of microorganisms and production of hydrogen/organic acids, as the electroactive microorganisms obtained from activated sludge were not rich a source of extremophiles. Similarly, the investigations on the effect of pH showed that the hydrogen yields of the MEC was 0.4, 0.6, 1.0, 1.5, and

2.5 mmol/L/D at pH values of 4.5, 5.0, 5.5, 6.0, and 6.5 respectively. The acidic and high temperature conditions greatly contribute to hydrolysis of lignocellulosic biomass which in turn could contribute to better rates of electrocatalysis when suitable extremophiles are used as electrocatalysts. Kyazze et al. (2010), investigated the effect of the cathode pH and temperature on the hydrogen production from acetate in MEC. Carbon cloth coated with 0.5 mg/cm^2 Pt was used as the cathode in membrane electrode assembly. A cation exchange membrane (CMI 7000, Membranes International, NJ, USA) was used to separate the anodic and cathodic segments. The results showed that the highest hydrogen production rate was obtained at pH 5 at 850 mV which amounts to 200 cm^3_{stp}/I_{anode}/day. The coulombic efficiency and cathodic hydrogen recovery were found to be 60% and 45% respectively with H_2 yield of 1.1 mol/mol acetate converted and a COD reduction of 30.5%.

Lusk et al. (2016) investigated the effect of pH and buffer concentration on anode biofilms of *Thermincola ferriacetica* in MECs. The bioanodes were poised at a potential of −0.06 V vs. SHE in MECs at 60 °C. These thermophilic MECs were operated in the pH range of 5.2–8.3 with acetate as the electron donor, and it produced a highest current density at pH 8.3. The current density at pH 5.2 and at pH 7.0 were 8% and 14% lower than the current density at pH 8.3. Further investigations on the effect of increasing bicarbonate buffer concentrations from 10 mM to 100 mM showed that the current density increased from 6.8 ± 1.1 to 11.2 ± 2.7 A m^{-2}. *T. ferriacetica* biofilms were shown to have faster transport rates at higher temperature when compared with the mesophilic *Geobacter sulfurreducens* biofilms keeping other conditions constant. In addition, its ability to grow at relatively lower pH allowed the production of higher current densities at lower buffer concentrations.

6. Recalcitrant feedstocks in MECs

Having good oxidation ability, both in terms of oxidizing a wide range of electron donors and oxidizing at a very fast rates, would be advantageous for use in the anodic compartment of the MEC (Wang et al., 2018). Certain thermophiles were shown to produce several enzymes for degrading the recalcitrant materials such as the lignocellulosic biomass as well as offering better resistance to substrate and product inhibition. Thermophiles were shown to have higher yield of enzymes with higher activity and thermal stability. These in turn will enhance the rates of electrocatalysis in the anodic compartment of MECs. For example, Bhalla et al. (2014) reported a thermostable GH39 β-xylosidase from a *Geobacillus* sp. strain WSUCF1 with a very high specific activity of 133 U/mg when incubated with *p*-nitrophenyl xylopyranoside. The enzyme displayed very high thermostability and retained 50% activity at 70 °C after 9 days. The enzyme also had high tolerance to xylose and retained 70% of relative activity at 210 mM xylose concentration.

Lusk et al. (2018), reported an MEC with enriched mixed culture of thermophilic (60 °C) bacteria will cellulose as the source of carbon. Microbial community analysis revealed that the *Thermoanaerobacter* and *Thermincola* genera are in high relative abundance on the biofilm anode whereas *Tepidmicrobium* and *Moorella* genera were in high relative abundance in the MEC electrolyte. The developed thermophilic MEC produced a sustained current density of 6.4 A/m^2 with cellulose as the sole electron donor. MEC was steady for nearly 26 days and the coulombic efficiency and coulombic recovery were found to be 84% and 46%, respectively. The current produced by this thermophilic MEC was found to be much higher than cellulose-fed mesophilic MECs. Further, thermophilic MEC also had a higher chemical oxygen demand conversion rate of 0.05 g COD l^{-1} d^{-1}.

The potential of the extremophilic organisms to oxidize a wide range of substrates is one major reason for its use in MxCs including Microbial Electrolysis cells. Several thermophilic strains have been reported for the enhancing the anodic reaction for different electrochemical systems. Unlike the MECs operated with mesophiles, the use of thermophiles in MECs supports the use of more complex substrates including recalcitrant feedstocks which is one of the major bottlenecks in the mesophilic processes.

Cerrillo et al. (2017a) reported a thermophilic anaerobic digester coupled MEC for treatment of slurry and current generation. An anaerobic thermophilic 4 L lab-scale continuous stirred tank reactor was connected in series to the anodic compartment of a two-chambered MEC. The pig slurry was pretreated in the AD reactor and was fed to the anodic compartment of the MEC. The recirculation loop between the AD and the MEC helped to overcome the issues of high organic and nitrogen loading rate, leading to increased methane production from 0.03 to 0.55 m^3 d^{-1}. The maximum COD and ammonium removal efficiency of the developed thermophilic MEC was shown to be 29% and 34%, respectively. The thermophilic AD-MEC achieved an overall COD removal efficiency around 60%. Hydrogenotrophic methanogens (*Methanobacteriaceae*) were predominant in the AD biomass due to high ammonia concentrations in the reactor. *Desulfuromonadaceae* was dominant in the anodic biofilm of thermophilic MEC. The existence of the recirculation loop, and that this configuration is more tolerant to stress, helps in attaining the stability of its MEC consortium.

Cerrillo et al. (2017b) reported the use of electromethanogenic biocathodes in microbial electrolysis cells for increasing the yield of methane from carbon dioxide in anaerobic digestors. Mixture of biomass from the anode of a MEC and anaerobic granular sludge and biomass enriched in a methanol-fed upflow anaerobic sludge blanket reactor were used as source of inoculum. Hydrogenotrophic methanogenic archaea, belonging to *Methanobrevibacter* genus were found to be dominant in these sources. *Methanobrevibacter* genus based biocathodes had an average CH_4 production rate of 0.23 ± 0.01 L m^{-3} day^{-1}.

Thermophilic MECs also have other advantages as they help to overcome the organic and nitrogen overload in anaerobic digesters. Cerrillo et al. (2016a) reported a new strategy to overcome the organic and nitrogen overload in thermophilic anaerobic digestion of pig slurry by coupling with MEC (Cerrillo et al., 2016a). The AD-MEC-loop system helped to increase in methane production by 55%. The developed AD-MEC system had the COD removal rates of 46%.

7. Cathodic reaction in MECs

The reduction reactions in the cathode also have a crucial role in increasing the hydrogen production rates as well as lessening the energy requirement from external sources (Kadier et al., 2016). Investigations on the use of thermophilies for biocathode development are limited. Fu et al., (2015) reported a thermophilic biocathode composed of *Methanothermobacter*-related methanogen and *synergistetes*- and *thermotogae*-related bacteria for electromethanogenesis. The cathodic reaction was mediated with electromethanogenesis at a potential of −0.5 V vs SHE. The developed thermophilic biocathode displayed higher rates of CH_4 production (max. 1103 mmol m^{-2} day^{-1} at an applied voltage of 0.8 V) at 55 °C with current-capture efficiencies > 90%.

Materials such as platinum, stainless steel, and nickel are widely used as electrocatalysts for cathodic reaction in MECs (Call et al., 2009; Lee et al., 2009; Logan et al., 2008; Selembo et al., 2010). The low activation potential of Pt makes it a promising material for applications in electrochemical systems. However, the use of platinum as electrocatalysts makes these processes expensive. Pt is susceptible to poisoning by sulfur and carbon monoxide which limits the use of Pt although it greatly reduces the cathode overpotential (Chae et al., 2009). Selembo et al. (2009) developed cathodes for MEC by electrodepositing a nickel oxide layer onto the surface area of the sheet metal. It had a cathodic hydrogen recovery of 52% and maximum volumetric hydrogen production rate of 0.76 m^3 m^{-3} day^{-1} (Selembo et al., 2009). However, the performance of the surface engineered nickel oxide cathodes on hydrogen yields decreased with decrease in the mechanical stability of

Table 2
Hydrogen production by various thermophilic organisms with different substrates.

Organism and type	Temperature (°C) and pH	Cultivation & Method	Hydrogen yield	References
Thermotoga neapolitana (wild)	80 and 7.0	Continuous Stirred-Tank Reactor & Fermentative H_2 production	3.1 mmol/mmol sugar	Dreschke et al. (2018)
Thermophilic mixed culture (wild)	55 and 5.5	Upflow Anaerobic Sludge Blanket reactor & Fermentative H_2 production	1.68 mmol/mmol sugar	Kongjan et al. (2018)
Thermopolis hot spring consortium (wild)	60 and 7.0	Batch & Fermentative H_2 production	1.07 mmol/g prairie cord grass	Bibra et al. (2018)
Caldicellulosiruptor bescii strain DSM 6725 (wild)	78 and	Batch & Fermentative H_2 production	4.40 mmol/g volatile solids	Yilmazel et al. (2015)
Caloranaerobacter azorensis strain H53214 (wild)	60 and 7.7	Batch & Fermentative H_2 production	1.46 mmol/mmol glucose	Jiang et al. (2014a,b)
Thermoanaerobacterium thermosaccharolyticum TERI strain S7 (wild)	60 and 7.5	Batch & Fermentative H_2 production	2.5 mmol/mmol glucose	Singh et al. (2014)
Caldicellulosiruptor bescii (recombinant-*idh ΔpyrFA, ura-/5-FOA*^{R})	75 and 7.0	Batch & Fermentative H_2 production	5 mmol/g switch grass	Cha et al. (2013)
Caldicellulosiruptor saccharolyticus DSM 8903 (wild)	65 and 7.2	Batch & Fermentative H_2 production	11.2 mmol/ g switch grass	Talluri et al. (2013)
Thermoanerobacterium thermosaccharolyticum strain W16 (wild)	60 and 7.0	Batch & Fermentative H_2 production	10.8 mmol/g sugar equivalent	Ren et al. (2010)

the oxides with time. In some cases, the electrocatalysts are functionalized onto the surface of the electrodes. The binding agents that are required for modifying the electrodes with electrocatalysts are expensive and in most cases affect the ionic or electronic conductivity in the electrode (Ivanov et al., 2017).

Cai et al. (2016), reported the fabrication of 3D self-assembly nickel foam-graphene cathode using a facile hydrothermal approach. However, the developed cathode demands a higher applied voltage of 0.8 V to improve the hydrogen production rate (Cai et al., 2016). Wang et al. (2012) reported the use of carbon nanotubes as electrocatalysts in a cathode of MEC. However, the results showed that Pt/MWNT cathode had a much better electrocatalytic activity and hydrogen production rate when compared with the MWNT cathode (Wang et al., 2012). Reports are also documented in the literature on the development of nanomaterial composites such as carbon-nanotube-polyaniline composites and molybdenum disulfide (MoS_2) coated conductive carbon nanotubes for reduction reactions in the cathode of MEC (Jiang et al., 2014a,b; Yang et al., 2015; Yuan et al., 2014). However, the use of carbon nanotubes in MECs affects the microorganism in the anode as they are toxic to the microbial cells. It has been reported in the literature that membrane-free configurations of MEC provide much higher yield in terms of high hydrogen recoveries and production rates when compared with the configurations with membranes. The use of a membrane-free system also helps to avoid the potential losses and cuts down costs (Kadier et al., 2016; Logan et al., 2008). However, membrane-free systems demand that the materials used as electrocatalysts for reduction of protons be non-toxic to the microorganisms that mediate the anodic reactions.

The use of biocathodes in MECs will help to overcome the limitations of material catalysts. Several reports have been documented in the literature on the use of microorganisms or enzymes as electrocatalysts for MEC applications (Croese et al., 2011; Geelhoed and Stams, 2010; Pisciotta et al., 2012; Rozendal et al., 2007). The use of biocathodes will greatly help in cutting down the costs of MEC as they help in replacing the noble metal catalysts such as platinum. It has been reported that the cathode and metal catalyst contribute 47% of the total cost in bioelectrochemical systems (Rozendal et al., 2008). In addition to hydrogen production, the microorganisms in biocathodes help in production of other value-added products in MECs or coupled with bioremediation of wastes. The use of biocathodes also helps to overcome the issues of replenishment of the electron mediator. The electroactive microorganisms that are used for biocathode development will be capable of mediating direct electron transfer onto the electrode or producing electron shuttling compounds (He and Angenent, 2006). Most reports on MECs either uses microorganisms for anodic or cathodic reactions, but reports on using electroactive microorganisms to mediate both anodic and cathodic electrocatalytic reactions in MECs are scarce.

Jeremiasse et al. (2010) developed a MEC for the first time, wherein both oxidation and reduction reactions are carried out by microorganisms. The developed MECs produced a maximum current density of 1.4 A/m^2 at an applied cell voltage of 0.5 V. Half-cell studies on the developed biocathode showed that the MEC produced higher current density of 3.3 A/m^2 when compared with the control cathode (0.3 A/m^2, graphite felt without biofilm). The developed MEC process had a hydrogen yield of 0.11 L with cathodic hydrogen recovery of 21% (Jeremiasse et al., 2010).

The concept of using a photosynthetic organism in the anodic compartment is slightly different from non-photosynthetic electrocatalysts. In principle, the photosynthetic microorganisms behave as photovoltaics and they generate electrons upon irradiation with the photons. This is due to the presence of photosystems, pigments, and photosynthetic machinery of these organisms. Ochiai et al. (1980), demonstrated the biophotolysis of water and biohydrogen production using a thermophilic blue-green alga, *Mastigocladus laminosus* isolated from Matsue hot springs. *Mastigocladus laminosus* immobilized onto a calcium alginate functionalized SnO_2 optically transparent electrode

produced a steady current for 20 days or more upon continuous irradiation using fluorescent lamps at 2000 lux. This indicates the stability of the blue green algae immobilized electrode for mediating photoelectrocatalysis.

The thermophiles producing hydrogen at higher rates are promising for use as electrocatalysts in cathodic reactions. The biochemical production of H_2 is mainly carried by three pathways, namely formate pathway, acetone-butanol pathway, and NADH pathway. (Tanisho, 2001) Several thermophilic microorganisms belonging to genus *Clostridium, Thermoanaerobacter, Thermoanaerobacterium, Caldicellulosiruptor, Thermotoga, Caloranaerobacter* have been shown to produce hydrogen. The higher kinetic rates and versatile catabolism of the thermophiles offer advantages for hydrogen production (Kumar et al., 2015; Bibra et al., 2018). Table 2 shows the various thermophiles used for hydrogen production.

Dark fermentation is another promising strategy for biohydrogen production. However, reports are not available using dark fermentation strategy in thermophilic MECs. Lu et al. (2011), developed a single chambered MEC that operates at psychrophilic conditions. MECs were enriched successfully at 4 °C and 9 °C, and their hydrogen yields and bacterial community structures under these different initial temperatures were examined. The thermophilic MECs can be integrated with consolidated bioprocessing technologies such as the one-pot CRUDE (Conversion of Raw and Untreated Disposal into Ethanol) process that is reported in the literature for the conversion of undigested recalcitrant residues from anaerobic digestor for bioethanol production. Further the residues from MECs can be used for production of methane using thermophilic anaerobic digestion (TAD) process.

8. Conclusion and future prospects

Use of thermophiles offer serval advantages in increasing the yield of MECs as well as cutting down the costs of operations. This opens abundant opportunity for scaling up thermophilic MECs for practical applications. However, reactor configurations, including stability of the electrode materials, and membranes that operate at high temperatures, require investigation. Thermophilic bioanodes have been shown to be very promising for waste utilization and electrogenesis at accelerated rates but reports on biocathodes for reduction of protons to hydrogen in MECs are limited. Developing efficient biocathodes for MECs will help in replacing the expensive electrocatalysts for mediating the reduction reaction without compromising the performance of MECs. The major bottleneck for MECs is that both the oxidation and reduction catalyst should have the same optimal temperature: i.e., the optimal temperature of one electrocatalyst should not affect the performance of the other. In addition to oxidation/reduction reactions mediated by microbial electrocatalysis, coupling the reactions with the electrosynthesis process will be an added advantage to produce thermostable enzymes, biopolymers and other renewable chemicals.

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