Bioresource Technology 195 (2015) 170–179

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Review

Separators used in microbial electrochemical technologies: Current status and future prospects

Siti Mariam Daud [a], Byung Hong Kim [a,b,c,*], Mostafa Ghasemi [a], Wan Ramli Wan Daud [a,d]

[a] Fuel Cell Institute, 43600 UKM Bangi, Selangor Darul Ehsan, Malaysia
[b] Korea Institute of Science and Technology, Seoul 136-791, Republic of Korea
[c] State Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, China
[d] Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, University Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia

HIGHLIGHTS

- METs have not been commercialized due to various constraints including one associated with the separator.
- Many problems associated with the Nafion PEM such as high cost of membrane, significant oxygen and substrate crossovers, and transport of cations other than protons and biofouling.
- Porous materials enable non-ion selective charge transfer are better materials for MET separators.
- In organic separator such as earthenware and ceramic are promising materials for the purpose.

ARTICLE INFO

Article history:
Received 29 April 2015
Received in revised form 18 June 2015
Accepted 19 June 2015
Available online 25 June 2015

Keywords:
Microbial electrochemical technologies
Proton exchange membrane
Porous separator
Earthenware
Inorganic separator

ABSTRACT

Microbial electrochemical technologies (METs) are emerging green processes producing useful products from renewable sources without causing environmental pollution and treating wastes. The separator, an important part of METs that greatly affects the latter's performance, is commonly made of Nafion proton exchange membrane (PEM). However, many problems have been identified associated with the Nafion PEM such as high cost of membrane, significant oxygen and substrate crossovers, and transport of cations other than protons protons and biofouling. A variety of materials have been offered as alternative separators such as ion-exchange membranes, salt bridges, glass fibers, composite membranes and porous materials. It has been claimed that low cost porous materials perform better than PEM. These include J-cloth, nylon filter, glass fiber mat, non-woven cloth, earthen pot and ceramics that enable non-ion selective charge transfer. This paper provides an up-to-date review on porous separators and plots directions for future studies.

1. Introduction

Fossil fuel will be depleted in the near future because of the decline in discoveries of major new reserve and the rapid rise in their continued use. Renewable energy sources are greatly needed in the energy mix to continue sustaining the standard of living for future generations on this planet while reducing environmental issues caused by the use of fossil fuels such as global warming and climate change. One of the most promising renewable energy resources is biomass that could be converted readily to renewable energy by using a variety of conversion technologies. One of the most promising and emerging energy conversion technologies from biomass are microbial electrochemical technologies (METs), which include microbial fuel cell (MFCs) and microbial electrolysis cells (MECs) among others. Organic materials contained wastewaters can be used to generate electricity in MFCs and to produce hydrogen as an alternative energy carrier in MECs.

Abbreviations: METs, microbial electrochemical technologies; PEMs, proton exchange membranes; MFCs, microbial fuel cells; MEC, microbial electrolysis cell; EAB, electrochemically active bacteria; CE, Coulombic efficiency; IEM, ion-exchange membranes; CEM, cation exchange membrane; AEM, anion exchange membrane; PVDF, polyvinylidene fluoride; SPEEK, sulfonated poly-ether ether ketone; PSEBS, sulfonated polystyrene–ethylene–butylene–polystyrene; MFM, microfiltration membrane; UFM, ultrafiltration membrane; NWF, non-woven fabric filter; ABPBI, poly[2,5-benzimidazole]; COD, chemical oxygen demand.

* Corresponding author at: Fuel Cell Institute, 43600 UKM Bangi, Selangor Darul Ehsan, Malaysia. Tel.: +60 3 891108527.

E-mail address: bhkim@ukm.edu.my (B.H. Kim).

http://dx.doi.org/10.1016/j.biortech.2015.06.105
0960-8524/© 2015 Elsevier Ltd. All rights reserved.

EABs, known as exoelectrogens oxidize electron donors (or fuel/substrate) in the anode compartment and the resulting electrons are transferred to the cathode through the anode and the external circuit. The cathode catalyses reduction of electron acceptors such as oxygen and nitrate in MFCs and protons in MECs consuming electrons transferred from the anode compartment. For thermodynamic reasons, external energy in the form of electricity is supplied to reduce protons to hydrogen in MECs. Proton exchange membranes (PEMs) used as separators are one of the most important components in MET devices that influence their performances (Rahimnejad et al., 2014a; Xu et al., 2012).

Nafion is the best options used as PEM in the METs. However, problems associated with the Nafion PEM have been reported such as highly cost, oxygen and substrate crossovers, cation transfer rather than proton and biofouling (Chae et al., 2007; Li et al., 2011). The higly cost of Nafion is attributing the high construction cost of MET devices (Rozendal et al., 2008).

In addition, one of the major problems in METs using Nafion as PEM is the pH imbalance between the anode and the cathode chambers occurring gradually during the course of their operation that limits the performance of METs (Sivasankaran and Sangeetha, 2011). In order to maintain electrical neutrality, for each electron that is transferred to the cathode, an equivalent proton must be transported to the cathode through the separator membrane (Chung et al., 2011). The pH decrease in the anode chamber and its rise in the cathode chamber during METs' operation are caused by the slower transport of protons through the Nafion separator compared to both the proton production rate in the anode chamber and the proton consumption rate in the cathode chamber (Gil et al., 2003; Sivasankaran and Sangeetha, 2011). The pH imbalance also results in higher internal resistance because of concentration polarization loss (ElMekawy et al., 2013) high ohmic losses because of higher affinity for cation species than protons (Logan, 2008) and a significant reduction in MFC performance (Rozendal et al., 2008).

Various materials have been offered as alternative separators such as ion-exchange membranes, salt bridges, glass fibers, earthenware (Behera et al., 2010a,b) and composite membrane (Li et al., 2011) to replace the Nafion PEM in METs. The suitability of separators can be assessed by analysing the power density output of the METs using them. The criteria for assessing potential separators for commercial application of METs are low cost, low cross-over of substrate and oxygen (Li et al., 2011), good transport of ions other than just protons and minimum or no biofouling.

Nafion has been developed for electrochemical application where non-aqueous eletrolytes are used. Recently, porous materials that enable non-ion selective charge transfer have been reported that could help improve performance of the technologies at low cost. Winfield et al. (2013b) employed bi-directional polarization methods to show that porous materials perform better as separators in MFCs with lower internal resistance than CEMs.

In recent years, METs as new emerging renewable energy technologies, have been reviewed extensively (Atanassov et al., 2014; Liew et al., 2014; Ge et al., 2014; Jafary et al., 2015; Dhar and Lee, 2013) including reviews on separators used in METs (Kim et al., 2007; Kraytsberg and Ein-Eli, 2014; Leong et al., 2013; Rahimnejad et al., 2014a; Varcoe et al., 2014; Wang and Ren, 2013) but none of the reviews have considered inorganic separators as main topics of review such as ceramic and earthenware.

In the present paper, an overview of porous and non-porous separators that have been used, including their advantages and disadvantages are presented. The suitability of inorganic porous material for MFC separator application is also discussion highlighted and is main part of authors studied.

2. Separators used in MET studies

Good low-cost separators should have minimum crossover of substrate and oxygen and efficient transfer of protons and other ions present in the electrolyte. However, the performance of specific separators may also vary significantly depending on their material characteristics, thickness, surface conditions and configuration. Moreover, the operating conditions such as electrolyte composition and current discharge also affect the performance of the separator as well as of the MFCs as a whole (Harnisch and Schröder, 2009). It is therefore difficult to give a systematic comparison of their specific performance based only on published data that have been obtained using reactors of different design under different conditions.

One way to assess performance of the separators is to compare cost and ion and mass permeability (Kim et al., 2007). An ideal separator should increase both power density and Coulombic efficiency (CE). However, CEs measured for the different separators are inversely correlated with power density, demonstrating that materials which reduce the oxygen diffusion into the anode chamber also hinder proton transport to the cathode, reducing power production through higher internal resistance (Kim et al., 2007).

2.1. Ion-exchange membranes (IEM)

Ion-exchange membranes usually consist of polymer backbones containing charge carrying functional groups that facilitate transport of oppositely charged ions (Fig. 1). Sulphonates are the most common negatively charged group in cation exchange membrane, l-p = whilst positively charged tertiary amines ($-NH^{3+}$) constitutes the most common functional groups in anion exchange membrane.

2.1.1. Cation exchange membranes (CEMs)

2.1.1.1. Nafion membranes. Nafion membranes, used widely in METs, are the standard proton exchange membranes (PEMs) in chemical fuel cells. They are used in the latter as solid electrolytes to transport cations selectively and as effective internal separators between the anode and cathode chambers. Nafion is a sulphonated tetrafluoroethylene copolymer that consists of a hydrophobic fluorocarbon backbone ($-CF_2-CF_2-$) and hydrophilic sulphonate groups (SO_3^-) that are attached to this backbone (Choi et al., 2006). The high level of cation conductivity in Nafion membranes is due to the presence of the sulphonate groups. Nafion membranes are also durable and resistant to attacks by a variety of chemicals (Peighambardoust et al., 2010).

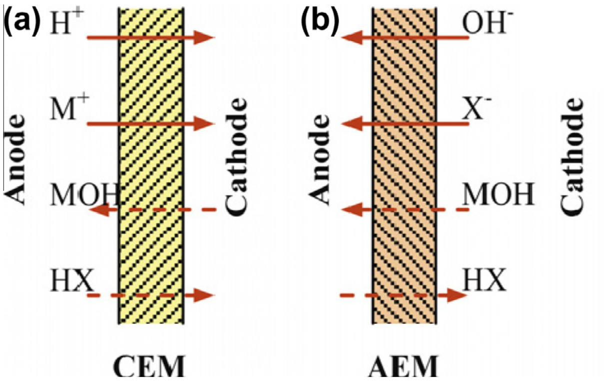

Fig. 1. Schematic of ion and mass transfer across: (a) cation; and (b) anion exchange membrane. MOH and HX represent undissociated base and acid, respectively (Harnisch and Schröder, 2009).

Nafions are highly selective for cations but are poorly selective for protons under MET operating conditions. Transport of electrons to the cathode chamber via an external circuit must be compensated by transport of an equal amount of positively charged ions to the cathode chamber through the separator in order to maintain electroneutrality (Rozendal et al., 2008). Theoretically, electronuetrality could be maintained by transport of protons through the separator (Werner et al., 2013). However, in practice cations from various inorganic salts that are used to support microbial growth, are transported faster than proton. A typical growth medium contains salts of Na^+, K^+, Ca^{2+}, Mg^{2+}, and NH^{4+}, whose concentrations are 10^5 times higher than that of protons at pH 7.0. The gradual build-up of cations in the cathode during MFC operation leads to a low pH in the anode chamber and a high pH in the cathode chamber, which increases the internal resistance and inhibits microbial activity (Rozendal et al., 2006). Furthermore, pH control in MEC could raise the energy efficiency with respect to the electrical energy input nearly nine fold (Ruiz et al., 2015).

2.1.1.2. Sulfonated poly-ether ether ketone (SPEEK). A cation exchange membrane could be made by sulfonating poly ether ether ketone (PEEK), a low-cost thermally and mechanically stable polymer (Vona et al., 2006) to form the sulfonated PEEK (SPEEK), whose degree of sulfonation (DS) can be controlled easily by varying the parameters of the sulfonation reaction (Yee et al., 2013). SPEEK has been shown to be a good alternative to Nafion in direct methanol fuel cell application (Ghasemi et al., 2011) because its negative fixed charge sulfonate ions (SO_3^-) allow only cations to pass through but reject the passage of anions (Zhao et al., 2006).

SPEEK shares a similar structure with Nafion, where ionic clusters co-exist with hydrophobic domains of the polymer backbone as shown in Fig. 3. In addition, SPEEK is stiffer than Nafion because the presence of aromatic groups in the polymer backbone greatly stiffens it (Rinaldi et al., 2008). MFCs with SPEEK membrane separator generates 20% less power than those with Nafion because of SPEEK's higher internal resistance, lower conductivity and higher activation loss (Ghasemi et al., 2013). The COD removal of MFCs with SPEEK membrane (88%) is about 18% higher than those with Nafion, but the energy generation of MFCs with Nafion (106.7 mW/m^2) is better by about 29% (Ghasemi et al., 2013). In terms of cost, SPEEK is two-thirds cheaper than Nafion (Ghasemi et al., 2013).

2.1.1.3. Sulfonated polystyrene–ethylene–butylene–polystyrene (PSEBS). Another important low cost cation exchange membrane used in MFCs is the sulfonated polystyrene–ethylene–butylene–p olystyrene (SPSEBS). It is synthesized by sulfonating polystyrene–ethylene–butylene–polystyrene tri-block polymer (PSEBS), which is a thermoplastic elastomer that consists of styrene blocks (thermoplastic phase) dispersed in an ethylene–butylene matrix (elastomeric phase) (Ayyaru et al., 2012). The ionomer is based on a hydrocarbon network with an aromatic nonfluorinated backbone, which is chemically, thermally and mechanically stable.

MFCs using SPSEBS membranes as separators produced twice as much maximum power density (600 $mW\ m^{-2}$) compared to MFCs using Nafion membranes while the pH difference between the anode and the cathode chambers in the former (pH 6.4–7.6) is also only a quarter of the pH difference in the latter (pH 4.4–10.3) due to the latter's poor transport of protons between the two chambers (Ayyaru et al., 2012). These superior properties of the SPSEBS membranes as MFC separators compared to Nafion are due to their higher proton conductivity and greater water swelling, which facilitate more efficient proton transport from the anode to the cathode chambers that consequently reduces pH difference (Mishra et al., 2012).

2.1.1.4. Other CEMs. Two other important CEMs that have been used in METs recently include Ultrex CMI 7000 made by Membranes Inc. USA) and Hyflon Ion made by Solvay-Solexis SPA. Ultrex CMI 7000 is a strong, acid polymer membrane with a gel polystyrene backbone structure cross-linked with divinyl benzene containing a large amount of sulphonate groups (Ismail and Jaeel, 2013). Although its cation conductivity and mechanical durability are comparable to Nafion, its performance in MFCs is poorer than Nafion (Sotres et al., 2014) because its ohmic resistance is quite high (Rahimnejad et al., 2014b).

Hyflon Ion is a copolymer of tetrafluoroethylene (TFE) and a short-side-chain (SSC) perfluorosulfonylfluoridevinyl ether (Arcella et al., 2003). It exhibits better chemical stability and higher cation conductivity than Nafion (Arico et al., 2006). MFCs using Hyflon Ion generated twice as much current and power densities compared to MFCs with Nafion (Ieropoulos et al., 2010).

2.1.2. Anion exchange membrane (AEM)

AEMs are polymer electrolytes that conduct anions, such as OH^- and Cl^-, since they contain positively charged cationic groups bound covalently to a polymer backbone (Varcoe et al., 2014). Although AEMs have not been as widely used in MET processes as CEMs, but there were reports that AEMs could function better than CEMs in MFCs.

An MFC with an AEM, AMI-7001 has been reported to generate 25% higher power density (610 mW/m^2) than that with a CEM (Kim et al., 2007). It is believed that protons are consumed neutralising OH^- that diffuses through the AEM without further pH reduction in the anode chamber. An MFC with a membrane cathode assembly using the same AEM generates almost twice as much power density (13.1 W/m^3) compared to that of a CEM cathode assembly (Zuo et al., 2008). The internal resistance of MFCs with AEM separators having different electrical resistance is related positively to the ion-exchange capacity of the separator used, and the MFC performance was inversely related to the ion-exchange capacity (Ji et al., 2011).

AEM functions better than CEM as a separator of METs probably because of the easier diffusion of OH^- through AEM than proton through CEM under MFC conditions (Piao et al., 2013). There are several hypotheses to explain better performance of MFCs with AEMs than those with CEM. AEMs have lower ion transport resistance and less membrane fouling and cathode resistance caused by the precipitation of transported cations (Piao et al., 2013). AEM has higher substrate permeability from the anode to cathode chamber which causes mixed potentials at the cathode and parasitic currents (Kim et al., 2007). Electrochemically active bacteria like most anaerobic respiratory bacteria except denitrifiers use fermentation products preferentially over complex substrate, and fermentation products include short chain fatty acids that are in deprotonated state under MET conditions (Varcoe et al., 2014). In addition, AEMs have been proved to be more liable to deformation than CEM in single chamber air cathode MFC (Zhang et al., 2009). This deformation would generate a void space between the membrane and cathode when they are closely placed, and lead to a high internal resistance.

2.1.3. Composite membrane

Composite membranes are made by combining different polymeric membranes together or polymeric membranes and other organic or inorganic materials, creating novel separators whose performance are better compared to Nafion or single PEMs (Ghasemi et al., 2013).

Nafion could be combined with other materials to improve its separator properties. MFCs using carbon nanofiber (CNF)/Nafion and activated CNF (ACNF)/Nafion nanocomposite membranes generate higher power density (57.6 mW/m^2) than those with Nafion (Ghasemi et al., 2011). The CE is better than Nafion because there is less pH gradient between the anode and cathode chamber because CNF and the ASCNF increases the conductivity of the composite membrane. MFCs using a Nafion/polyaniline (PANI) composite membranes as separators have higher current densities but less biofouling than MFCs with pure Nafion separators (Mokhtarian et al., 2013). The higher performance is due to the higher proton conductivity afforded by the PANI and the lower biofouling of the composite. In the same way, MFCs with polyvinylidene fluoride (PVDF)/Nafion composite membranes shows comparable performance to Nafion separators (Shahgaldi et al., 2014).

Composite membranes could also be made by combining two or more cation polymers other than Nafion but with mixed results. Separators made from 5% sulfonated poly(ether ether ketone) (SPEEK)/polyethersulfone (PES) composite membranes generate higher MFC power and current densities (150 mW/m^2) compared to Nafion and is cheaper than the latter (Lim et al., 2012). MFCs using undoped polyaniline (PANI) nanoparticles/polysulfone (PS) nanocomposites membranes generated 10% less power density than Nafion (Ghasemi et al., 2013). SPEEK/charged surface modifying molecule (cSMM) composite membranes used in MFCs generates 16.5% more power density (172.1 mW/m^2) and 21% higher CE (17.6%) compared to Nafion (Mayahi et al., 2015).

Organic–inorganic composite membranes could be produced by blending a polymer with conducting inorganic material. MFCs with a 15% Fe_3O_4 nanoparticle/PES composite membrane generates 29% higher power than Nafion (Rahimnejad et al., 2012). MFCs with Zirfon, a macro-porous organo-mineral material containing 85 wt% of hydrophilic ZrO_2 powder and 15 wt% polysulphone (Vermeiren et al., 2008) has a much lower specific resistance than Nafion, but its higher oxygen permeability is detrimental to anodic reactions (Pant et al., 2010a,b).

2.2. Salt bridge

A salt bridge is simpler and inexpensive compared to ion-exchange membranes. In a salt bridge MFC, ions are conducted between the two chambers via a salt bridge consisting of a glass tube filled with electrolytes (Min et al., 2005). Inert electrolytes such as saturated KCl solution and phosphate buffer solution are frequently used in salt bridge for ions conduction (Min et al., 2005). Agar is often added to prevent the intermixing of fluids. For example, a salt bridge consisting of a 2% KCl-containing agar (10%) layer sandwiched between two perforated plexi-glass plates has used as a separator in an MFC (Kargi and Eker, 2007). In addition, oxygen diffusion is almost undetectable in an agar salt bridge (Min et al., 2005). The low oxygen permeability of salt bridge ensures higher Coulomb efficiency compared with that of a MFC used CEM as a separator (Liu and Li, 2007).

However, the salt-bridge MFC resulted in a low power density due to a high internal resistance. A phosphate buffer solution salt bridge has been reported to yield a significantly higher internal resistance than the Nafion membrane under similar conditions (Min et al., 2005). Even a much lower peak voltage than that of a CEM–MFC has been reported in KCl-agar salt-bridge MFC (Liu and Li, 2007). Similar results were obtained in salt-bridge MFCs for the treatment of chocolate industry wastewater, where the maximum power density is lower compared with that of a CEM–MFC (Patil et al., 2009).

All these studies proved that the high internal resistance is a major challenge for MFCs using salt bridge as a separator. It is possible to reduce the internal resistance by appropriately selecting electrolyte composition and concentration (Li et al., 2011). In addition, increasing the surface area of salt bridge in contact with the anode and cathode chambers can also be an efficient approach to improve the power-generating performance of a salt-bridge MFC (Mohan et al., 2008). Close positioning of anode and cathode reduces the internal resistance by reducing the distance proton (or anion) to move (Mohan et al., 2008). Hence, the long distance of proton diffusion is probably the reason why MFCs with salt bridge shows high internal resistance.

3. Porous membrane

Porous separator materials that enable non-ion selective charge transfer have been used in METs. These include J-cloth (Fan et al., 2007), non-woven cloth (Xu et al., 2014; Choi et al., 2013), glass fiber (Zhang et al., 2010), earthen pot (Behera et al., 2010a), ceramic (Winfield et al., 2013b), biodegradable bag (Winfield et al., 2013b) and natural rubber (Winfield et al., 2013c). Porous separators can be generally divided into two categories based on their pore sizes. They are either microporous filtration membranes, such as microfiltration membrane (MFM) and ultrafiltration membrane (UFM) (Sun et al., 2009) or course-pore filter materials, such as fabrics, glass fiber, nylon mesh and cellulose filters (Li et al., 2011).

3.1. J-cloth, nylon and glass fiber filter

When glass fiber mats of different thicknesses were compared with J-cloth and CEM as separators in MFCs, both the 1.0 mm thick glass fiber mats and the J-cloth produce similar maximum power densities (790 mW/m^2) and perform much better than the CEM (Zhang et al., 2009). Coulombic efficiency (CE) of MFCs using the non-biodegradable glass fiber mats with 1.0 mm thicknesses (81%) is much higher than that of the J-cloth. Based on these results, it is evident that the proton transport properties of these different materials are similar but the oxygen transfer properties are different (Zhang et al., 2009). Increasing pore size of nylon mesh and filters used as MFC separators increases MFC power density significantly but increasing pore size in glass fiber filters does not cause similar significant rise in MFC power density because of the narrower range of pore size used in the latter (Zhang et al., 2010).

3.2. Non-woven cloth

Non-woven fabric filter (NWF) used in water purification and wastewater treatment processes could be used as a cheap separator in MFCs because its cost is only one 350th of Nafion's (Choi et al., 2013). MFCs with NWF shows lower internal resistance than that with Nafion 117 (Choi et al., 2013). The former also generates higher voltage and power density (97.0 mW/m^2) than the latter because of high water permeability in the former (Choi et al., 2013). Although oxygen crossover for both MFCs remains roughly the same, acetate diffusion is higher in Nafion 117 because the hydrophobic backbone of Nafion enhances the diffusion of undissociated form of acetic acid (Choi et al., 2013). The performance of an MFC with NWF is more stable over 300 days than that of the MFC with PEM, which decreases due to biofilm formation and chemical precipitation on the membrane surface (Choi et al., 2013).

NWFs also have larger pore sizes that facilitate greater overall chemical species transfer and a higher proton transfer capability compared to Nafion, thus contributing to the lower ohmic losses (Li et al., 2011). Furthermore, proton conductivity of NWF could be improved by applying a proton transfer conductor such as poly[2,5-benzimidazole] (ABPBI) on the NWF (Choi et al., 2013). The overall performance of the MFC with ABPBI applied NWF improves because of the enhanced ion conductivity and steric contact, producing almost twice the power of an MFC using a PEM as separator (Choi et al., 2013).

3.3. Earthen pot

Another separator that have been used in MFCs recently is the cheap earthen pot (Behera et al., 2010a; Winfield et al., 2013a). An MFC using an earthen pot separator with a stainless steel mesh cathode and $KMnO_4$ as the oxidant, generates four fold higher maximum power of 70.48 $W\,m^{-3}$ at two fold higher CE of 64.5% than another MFC with an earthen pot separator but with a graphite plate cathode (Behera et al., 2010a). These results show that proton diffusion is not the limiting factor for the power generation in the MFC with earthen pot separator, but the rate of electron consumption at the cathode.

In addition, following the same trend, an MFC using an earthen pot separator treating rice mill wastewater generates four fold higher power density of 2.3 $W\,m^{-3}$ at 4–6% higher removal efficiencies of 96.5% for chemical oxygen demand (COD), 84% for lignin and 81% for phenol compared to an MFC using a Nafion 117 separator (Behera et al., 2010b).

Although the more porous earthen pot separator in an air–cathode MFC tends to transfer anolytes faster compared to the denser terracotta separator in a similar MFC, the more porous and less iron-rich earthen pot is the better separator material for power production despite the MFC with the denser terracotta separator producing higher open circuit voltage (Winfield et al., 2013a).

A tubular-type up-flow MFC reactor using earthen pot separator generates 46% higher volumetric power density of 14.59 $W\,m^{-3}$ than that produced in a similar tubular MFC with a Nafion 117 separator (Jana et al., 2010). Similarly, MFCs using cylindrical earthen pot produce 75% higher current and 33% power (33%) than MFCs with terracotta separator (Winfield et al., 2013a). The higher power density is probably caused by the lower internal resistance of the MFC with earthen pot cylindrical separator compared with the MFC using Nafion and terracotta separators (Jana et al., 2010; Winfield et al., 2013a).

The thickness of the earthenware also affects its performance as the separator in MFCs (Behera and Ghangrekar, 2011). The reactor with the thinnest separator performed the best to achieve 60% higher power density of 24.32 $mW\,m^{-2}$, volumetric power of 1.04 $W\,m^{-3}$ and coulombic efficiencies of 7.7%. Although the volumetric power density is higher, but the Coulomb efficiency is much lower due to substrate consumption by anaerobic microbes such as methanogenic archaea or sulfate-reducing bacteria as observed elsewhere (He et al., 2005).

Although it is meaningless to compare performance of MFCs with different design because other factors like separator surface area (Oh and Logan, 2006) and reactor architecture also influence MFC performance (Vázquez-Larios et al., 2011), these results nonetheless clearly show that earthen pot can replace PEM in MFC application.

3.4. Porous ceramic

The power and current densities of porous ceramic and biodegradable bag (BioBag) used as MFC separators are compared with cation exchange membrane MFC separators using bi-directional polarization methods as shown in Fig. 2 (Winfield et al., 2013b). CEM has a power overshoot during the forward

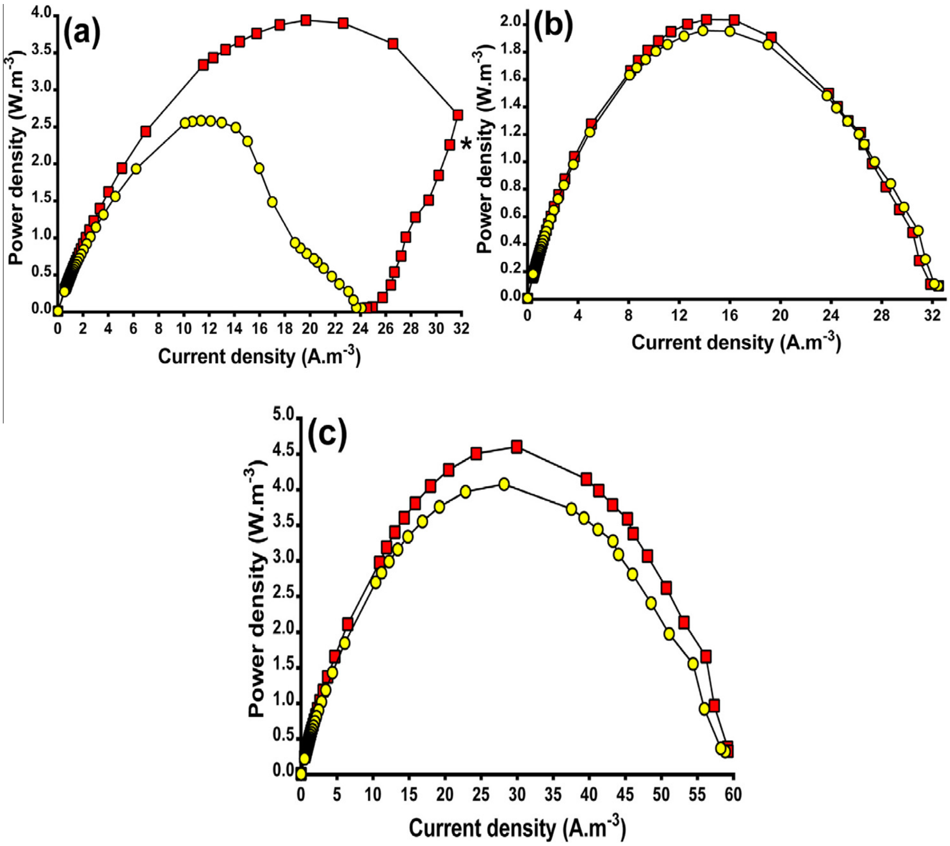

Fig. 2. Bi-directional power density curves for MFCs using (a) CEM, (b) compostable BioBag and (c) ceramic as membrane. 🟥 (square symbols) indicate the forward curve (OCV to short circuit) and 🟡 (closed circles) represent the reverse sweep (short circuit to OCV) (Winfield et al., 2013b).

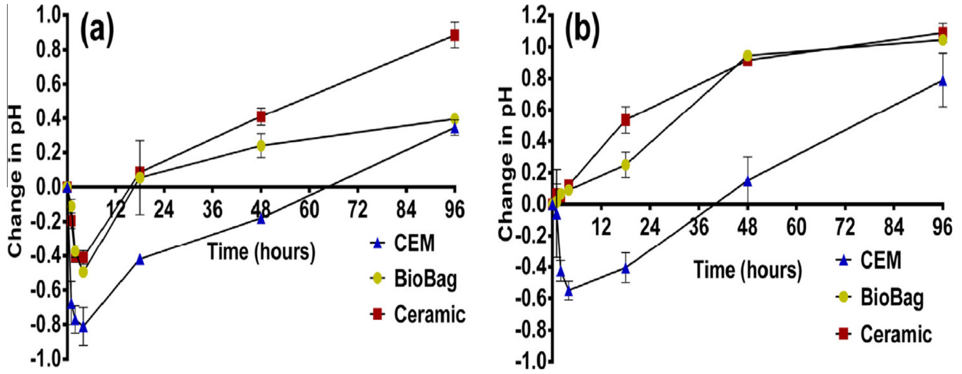

Fig. 3. The change of anolyte pH in anode chamber over time for MFCs loaded with; (a) external resistance: 100 Ω, (b) external resistance: 1000 Ω (Winfield et al., 2013b).

sweep followed by a significant 38% power decline over the reverse sweep. On the other hand, the porous membranes have no power overshoot and relatively smaller drops in power during the reverse sweep of about 8% for ceramic and 5.5% for BioBag. When the external resistance of an MFC with porous separators is changed from 100 Ω to 1000 Ω, the anolyte pH that is originally decreasing at the lower load, has now increased in MFC with porous separators as shown in Fig. 3. These results show that porous separators have higher proton conductivity than CEM and therefore ideal candidates for MFC separators in terms of cost and operational stability.

3.5. Bio-degraded separator

Biodegraded natural rubber has been used as a separator in MFCs (Winfield et al., 2013b). Pristine natural rubber membrane used as an MFC separator is initially impermeable to protons, but if the membrane is allowed to biodegrade in the MFC, a working voltage is gradually generated that improves with time. MFCs with natural rubber membrane out performs those with AEM, but are slightly below MFCs with CEM (Winfield et al., 2013b). When performance of MFCs with both AEM and CEM decline after 11 months, MFCs with biodegraded natural rubber continue to improve and generate higher power and current than MFC with CEM. Scanning electron microscopy images show the formation of micropores in biodegraded natural rubber samples that was used as an MFC separator for 9 months (Winfield et al., 2013b). The channels and micropores formed as a result of biodegradation provide increasing number of pathways for proton transfer as the rubber degrades, which is reflected by the steady increase in power generation over time (Winfield et al., 2013b).

3.6. Comparison of separators used in MFC

Even though direct comparison of published MET performance data is not feasible since the reactor architecture influences greatly MET performance (Vázquez-Larios et al., 2011), but the comparison can yield useful information. Table 1 summarizes performance data of MFCs with different separators. The salt bridge is the poorest separator in MET due to its limited surface area. Generally, porous materials are proven to be better MFC separators than ion-exchange membranes. Table 1 also shows more porous materials having better properties (Table 1).

Advantageous and disadvantageous properties of separators used in METs are summarized in Table 2. Most of the ion-exchange membranes have been developed for electrochemical application where non-aqueous electrolytes are used. In early stage of MET development, Nafion, a commercial cation exchange membrane, was used widely as the separator, but performance of ion-exchange membranes including Nafion is not as good as performance of porous materials as shown in Table 1.

4. Current status and future prospects for separator of microbial electrochemical technologies

The technical feasibility of microbial electrochemical technologies has been proven since Kim et al. (1999) published the first paper on electrochemically active bacterium leading to a large volume of research in the area. But these technologies have not been commercialized due to various constraints. One of them is problems associated with the membrane separating the anode from cathode. In early studies on these technology, CEMs were commonly used as the separator. They are expensive and proven to be poor proton conductors. They were believed to be good proton conductors as in chemical fuel cell application. Unlike chemical fuel cells METs employ aqueous electrolyte that contains inorganic salts to support microbial growth. The reason for poor proton conductance of CEMs is the use of salt solution as the electrolyte in METs. Various materials have been tested as a separator to show that porous materials are better separators than ion-exchange membranes under MET conditions.

Porous materials used in the studies include inorganic and organic materials, and the most of the organics are biodegradable that is not suitable for a long-term operation of the technologies. Among the inorganic materials used as separators, glass fiber may not be suitable to produce reproducible separators because its structure is not uniform. To obtain useful electricity, the voltage and current should be increased through stacking. Voltage reversal is a problem in stacking, and uneven performance of stacked reactors is the main cause of voltage reversal (Oh and Logan, 2007; Kim et al., 2012). For the reason earthenware and ceramic are promising candidates as good materials for MET separators.

Winfield et al. (2013a) reported that the more porous and less iron-rich earthenware is the better material for power production. It would be interesting to find if earthenware or ceramic can be produced with increased porosity, if their elementary composition can be controlled to render the inorganic materials with proton conductance (ABPBI) as in non-woven fabric (Choi et al., 2013).

Table 1
Parameters of MFC performance with different separator.

MFC reactor	Substrate used	External resistor (Ω)	Separator material	Voltage (mV)	Thickness (mm)	Porosity (μm)	Power density (mW/m^2)	Volumetric power density (mW/m^3)	Coulombic efficiency (%)	Internal resistance (Ω)	Cost ($)	References
Single chamber	Acetate	1000	Nylon	–	0.17	0.2	443 ± 27	–	70	84.6	–	Zhang et al. (2010)
			Nylon	–	0.17	0.45	650 ± 7	–	63	57.3	–	
			Nylon	–	0.045	10	769 ± 65	–	55	41.4	–	
			Nylon	–	0.05	60	816 ± 34	–	45	39.5	–	
			Nylon	–	0.08	100	908 ± 24	–	41	37.3	–	
			Nylon	–	0.1	160	941 ± 47	–	31	35.7	–	
			Glass fiber filter	–	0.38	0.7	732 ± 48	–	56	40.4	–	
			Glass fiber filter	–	0.72	1.0	716 ± 60	–	60	42.3	–	
			Glass fiber filter	–	0.38	2.0	779 ± 43	–	55	39.6	–	
Dual chamber	Acetate	1000	Nafion 117	551 ± 56	–	–	57.5 ± 3.9	609 ± 41	31	93 ± 2	1400 (m^2)	Choi et al. (2013)
			Non woven cloth	402 ± 56	0.13	2.01	–	432 ± 76	–	43 ± 2	2 (m^2)	
			Non woven cloth	531 ± 35	0.18	1.78	–	839 ± 69	–	53 ± 6	3 (m^2)	
			Non woven cloth	388 ± 21	0.25	1.81	–	664 ± 74	–	37 ± 1	4 (m^2)	
			Non woven cloth	545 ± 22	0.13	1.21	97.0 ± 7.5	1027 ± 79	20	51 ± 7.5	2 (m^2)	
Dual chamber	Acetate	1000	Eathen ware	191	3	–	–	1042.31	7.7	–	–	Behera and Ghangrekar (2011)
			Earthen ware	–	5	–	–	905.26	7.1	–	–	
			Eathen ware	–	7	–	–	896.53	6.8	–	–	
			Eathen ware	–	8.5	–	–	780.30	6.0	–	–	
Single chamber	Acetate	1000	Nafion 117	–	–	–	267 ± 22	14 ± 1	131.7 ± 8.4	–	–	Zhang et al. (2009)
			J-cloth	–	–	–	786 ± 23	46 ± 1	40.1 ± 0.4	–	–	
			Glass fiber				623 ± 4	40.1 ± 0.4	38.1 ± 0.1			
Cylindrical chamber	Tryptone	1000	Ceramic	–	4	–	1.12×10^{-2}	–	–	–	–	Winfield et al. (2013a)
			Ceramic	–	8	–	7.22×10^{-3}	–	–	–	–	
			Ceramic	–	18	–	8.04×10^{-3}	–	–	–	–	
			Terracotta	–	4	–	1.08×10^{-2}	–	–	–	–	
			Terracotta	–	8	–	8.06×10^{-3}	–	–	–	–	
			Terracotta	–	18	–	6.62×10^{-3}	–	–	–	–	
Single chamber	Acetate	1000	Nafion 117	–	–	–	514	–	46	84 ± 4	–	Kim et al. (2007)
			CMI-7000,CEM	–	–	–	480	–	54	84 ± 2	–	
			AMI-7001, AEM	–	–	–	610	–	72	88 ± 4	–	
Dual chamber	Glucose	1000	Nafion 117	–	–	–	106.7	–	29	727	120 (12 cm^2)	Ghasemi et al. (201)3
			SPEEK	–	–	–	77.30	–	18	811	45 (12 cm^2)	
Dual chamber	Glucose	1000	Nafion 117	640 ± 40	0.175	–	290 ± 7	–	51	125	1500 (m^2)	Ayyaru et al. (2012)
			SPSEBS	680 ± 30	0.18	–	600 ± 14	–	85	70	250 (m^2)	
Dual chamber	Acetate	1000	Nafion 117	293	–	–	38	–	55	1286	–	Min et al. (2005)
			Salt bridge	201	–	–	2.2	–	55	19,920	–	

Table 2
Advantage and disadvantage of separators.

Separator	Advantage	Disadvantage	References
Salt bridge	• Inexpensive • Easy to handle • Low oxygen diffusion	• Low power density • High internal resistance • Low input voltage	• Min et al. (2005) • Liu and Li (2007)
Ion-exchange membranes			
Nafion, CEM	• High level of proton conductivity • Durable and resistant to a variety of chemicals • Thermally stable	• Expensive, high cost • Low proton transport under MET conditions • Substrate and oxygen crossover • Biofouling	• Rozendal et al. (2006) • Piao et al. (2013) • Leong et al. (2013) • Peighambardoust et al. (2010)
CMI-7000, CEM	• Less expensive than Nafion • Highly selective for cations including proton	• Other cation has higher mobility into cathode chamber rather than proton • Much thicker and stiffer than Nafion • High ohmic resistance	• Varcoe et al., 2014 • Winfield et al., 2013a
AMI-7001, AEM	• Less expensive than Nafion • Reduce pH splitting by lowering pH in anode chamber • Power density higher than CEM • Reduce biofouling • Lower oxygen permeability • Lower ohmic loses	• High substrate crossover • Voltage losses over longer operational periods • Membrane deformation	• Kim et al. (2007) • Zuo et al. (2008) • Piao et al. (2013) • Varcoe et al. (2014)
Composite membranes			
SPEEK	• Less expensive than Nafion • Good hydrophilic and proton conductivity	• Low Coulombic efficiency • Low power density	• Ghasemi et al. (2013)
PBSEBS	• Less expensive than Nafion • Excellent mechanical, chemical and thermal stability • High power density	• Difficult to handle	• Ayyaru et al. (2012) • Mishra et al. (2012)
Porous materials			
J-cloth	• Low cost • Effective separator to favour transport of protons	• Biodegradable • Power density lower than CEM • Low CE • Higher flux of oxygen and substrate	• Zhang et al. (2010) • Li et al. (2011) • Fan et al. (2007)
Nylon filter	• Low cost • Highly porous • Low internal resistance	• Oxygen crossover increase give • Low CE	• Zhang et al. (2010)
Glass fiber filter	• Low cost • Larger pore size give higher power density • Less permeable to oxygen • Resistant to biomass growth • High CE	• Reduce cathode potential • Increase ohmic resistances • Alleviate pH splitting problem	• Zhang et al. (2010) • Li et al. (2011)
Non Woven Cloth	• Low cost • Low ohmic loses • Long term stability • Highly porous	• Higher internal resistance • Oxygen and substrate crossover	• Choi et al. (2013) • Li et al. (2011)
Earthen ware	• Low cost • High power density • Good proton transfer • Sustain the hydrostatic pressure and mechanical stress	• Brittle	• Behera et al. (2010a) • Behera et al. (2010b) • Behera and Ghangrekar (2011)
Ceramic	• Low cost • Short and long term stability • Suitable for structural MFC • Good proton transfer • Accelerate to scale-up MFC	• Brittle	• Winfield et al. (2013b)

5. Conclusion

Technically feasible METs have not been commercialized due to various constraints including one associated with the separator. A good separator should have certain properties such as low cost, low oxygen and fuel crossover, enable higher proton transfer than other cations and long term stability. Cation exchange membranes commonly used in chemical fuel cell are suitable in MET application where aqueous salt solution is used as the electrolyte. Porous materials are better materials for MET separators. Among them earthenware and ceramic are promising materials for the purpose. Challenges with them as MET separators are increase porosity, proton conductivity, and their brittleness.

Acknowledgements

The authors appreciate the financial support rendered by Universiti Kebangsaan Malaysia by researcher's grant (AP-2014-016, 03-01-02-SF0985 and DIP-2012-27) for this project.

References

Arcella, V., Ghielmi, A., Tommasi, G., 2003. High performance perfluoropolymer films and membranes. Adv. Membr. Technol. 984, 226–244.

Arico, A.S., Baglio, V., Blasi, A.D., Antonucci, V., Cirillo, L., Ghielmi, A., Arcella, V., 2006. Proton exchange membranes based on the short-side-chain perfluorinated ionomer for high temperature direct methanol fuel cells. Desalination 199, 271–273.

Atanassov, P., El-Naggar, M.Y., Cosnier, S., Schröder, U., 2014. Biological fuel cells: cardinal advances and critical challenges. ChemElectroChem 1 (11), 1702–1704.

Ayyaru, S., Letchoumanane, P., Dharmalingam, S., Stanislaus, A.R., 2012. Performance of sulfonated polystyrene–ethylene–butylene–polystyrene membrane in microbial fuel cell for bioelectricity production. J. Power Sources 217, 204–208.

Behera, M., Jana, P.S., Ghangrekar, M.M., 2010a. Performance evaluation of low cost microbial fuel cell fabricated using earthen pot with biotic and abiotic cathode. Bioresour. Technol. 101 (4), 1183–1189.

Behera, M., Jana, P.S., More, T.T., Grangrekar, M.M., 2010b. Rice mill wastewater treatment in microbial fuel cells fabricated using proton exchange membrane and earthen pot at different pH. Bioelectrochemistry 79 (2), 228–233.

Behera, M., Ghangrekar, M.M., 2011. Electricity generation in low cost microbial fuel cell made up of earthenware of different thickness. Water Sci. Technol. 64 (12), 2468–2473.

Chae, K.J., Choi, M., Ajayi, F.F., Park, W., Chang, I.S., Kim, I.S., 2007. Mass transport through a proton exchange membrane (Nafion) in microbial fuel cells. Fuels 22 (1), 169–176.

Choi, Y., Wang, G., Yau, S.T., 2006. Electronic composite of sulfonated tetrafluorethylene copolymer with potassium ferricyanide exhibiting room-temperature negative differential resistance. Appl. Phys. Lett. 89, 233116.

Choi, S., Kim, J.R., Cha, J., Kim, Y., Premier, G.C., Kim, C., 2013. Enhanced power production of a membrane electrode assembly microbial fuel cell (MFC) using a cost effective poly[2,5-benzimidazole] (ABPBI) impregnated non-woven fabric filter. Bioresour. Technol. 128, 14–21.

Chung, K., Fujiki, I., Okabe, S., 2011. Effect of formation of biofilms and chemical scale on the cathode electrode on the performance of a continuous two chamber microbial fuel cell. Bioresour. Technol. 102, 355–360.

Dhar, B.R., Lee, H.-S., 2013. Membranes for bioelectrochemical systems: challenges and research advances. Environ. Technol. 34 (13–14), 1751–1764.

ElMekawy, A., Hegab, H.M., Dominguez-Benetton, X., Pant, D., 2013. Internal resistance of microfluidic microbial fuel cell: challenges and potential opportunities. Bioresour. Technol. 142, 672–682.

Fan, Y.Z., Hu, H.Q., Liu, H., 2007. Sustainable power generation in microbial fuel cells using bicarbonate buffer and proton transfer mechanisms. Environ. Sci. Technol. 41, 8154–8158.

Ge, Z., Li, J., Xiao, L., Tong, Y., He, Z., 2014. Recovery of electrical energy in microbial fuel cells. Environ. Sci. Technol. Lett. 1 (2), 137–141.

Ghasemi, M., Shahgaldi, S., Ismail, M., Kim, B.H., Yaakob, Z., Daud, W.R.W., 2011. Activated carbon nanofibers as an alternative cathode catalyst to platinum in a two-chamber microbial fuel cell. Int. J. Hydrogen Energy 36, 13746–13752.

Ghasemi, M., Daud, W.R.W., Ismail, A.F., Jafari, Y., Ismail, M., Mayahi, A., Othman, J., 2013. Simultaneous wastewater treatment and electricity generation by microbial fuel cell: performance comparison and cost investigation of using Nafion 117 and SPEEK as separators. Desalination 325, 1–6.

Gil, G.C., Chang, I.S., Kim, B.H., Kim, M., Jang, J.K., Park, H.S., Kim, H.J., 2003. Operational parameters affecting the performance of a mediator-less microbial fuel cell. Biosens. Bioelectron. 18 (4), 327–334.

Harnisch, F., Schröder, U., 2009. From MFC to MXC: chemical and biological cathodes and their potential for microbial bioelectrochemical systems. Chem. Soc. Rev. 39, 4433–4448.

He, Z., Minteer, S.D., Angenent, L.T., 2005. Electricity generation from artificial wastewater using an upflow microbial fuel cell. Environ. Sci. Technol. 39 (14), 5262–5267.

Ieropoulos, I., Greenman, J., Melhuish, C., 2010. Improved energy output levels from small-scale Microbial Fuel Cells. Bioelectrochemistry 78 (1), 44–50.

Ismail, Z.Z., Jaeel, A.J., 2013. Sustainable Power Generation in Continuous Flow Microbial Fuel Cell Treating Actual Wastewater: Influence of Biocatalyst Type on Electricity Production. Hindawi Publisher. http://dx.doi.org/10.1155/2013/713515.

Jafary, T., Daud, W.R.W., Ghasemi, M., Kim, B.H., MdJahim, J., Ismail, M., Lim, S.S., 2015. Biocathode in microbial electrolysis cell; present status and future prospects. Renew. Sustain. Energy Rev. 47, 23–33.

Jana, P.S., Behera, M., Ghangrekar, M.M., 2010. Performance comparison of up-flow microbial fuel cells fabricated using proton exchange membrane and earthen cylinder. Int. J. Hydrogen Energy 35, 5681–5686.

Ji, E., Moon, H., Piao, J., Ha, P.T., An, J., Kim, D., Woo, J.-J., Lee, Y., Moon, S.-H., Rittmann, B.E., Chang, I.S., 2011. Interface resistances of anion exchange membranes in microbial fuel cells with low ionic strength. Biosens. Bioelectron. 26 (7), 3266–3271.

Kargi, F., Eker, S., 2007. Electricity generation with simultaneous wastewater treatment by a microbial fuel cell (MFC) with Cu and Cu–Au electrodes. J. Chem. Technol. Biotechnol. 82, 658–662.

Kim, B.H., Kim, H.J., Hyun, M.S., Park, D.H., 1999. Direct electrode reaction of an Fe(III)-reducing bacterium, *Shewanella putrefaciens*. J. Microbiol. Biotechnol. 9 (2), 127–131.

Kim, J., Cheng, S., Eunoh, S., Logan, B.E., 2007. Power generation using different cation, anion, and ultrafiltration membranes in microbial fuel cells. Environ. Sci. Technol. 41, 1004–1009.

Kim, D., An, J., Kim, B., Jang, J.K., Kim, B.H., Chang, I.S., 2012. Scaling-up microbial fuel cells: configuration and potential drop phenomenon at series connection of unit cells in shared anolyte. ChemSusChem 5 (6), 1086–1091.

Kraytsberg, A., Ein-Eli, Y., 2014. Review of advanced materials for proton exchange membrane fuel cells. Energy Fuels 28 (12), 7303–7330.

Leong, J.X., Daud, W.R.W., Ghasemi, M., Liew, K.B., Ismail, M., 2013. Ion exchange membranes as separators in microbial fuel cells for bioenergy conversion: a comprehensive review. Renew. Sustain. Energy Rev. 28, 575–587.

Li, W.W., Sheng, G.P., Liu, X.W., Yu, H.Q., 2011. Recent advances in the separators for microbial fuel cells. Bioresour. Technol. 102 (1), 244–252.

Liew, K.B., Daud, W.R.W., Ghasemi, M., Leong, J.X., Lim, S.S., Ismail, M., 2014. Non-Pt catalyst as oxygen reduction reaction in microbial fuel cells: a review. Int. J. Hydrogen Energy 39 (10), 4870–4883.

Lim, S.S., Daud, W.R.W., Jahim, J.M., Ghasemi, M., Chong, P.S., Ismail, M., 2012. Sulfonated poly(ether ether ketone)/poly(ether sulfone) composite membranes as an alternative proton exchange membrane in microbial fuel cells. Int. J. Hydrogen Energy 37, 11409–11424.

Liu, Z.D., Li, H.R., 2007. Effects of bio- and abio-factors on electricity production in a mediatorless microbial fuel cell. Biochem. Eng. J. 36, 209–214.

Logan, B.E., 2008. Exoelectrogenic bacteria that power microbial fuel cells. Nat. Rev. Microbiol. 7 (5), 375–381.

Mayahi, A., Ilbeygi, H., Ismail, A.F., Jaafar, J., Daud, W.R.W., Emadzadeh, D., Shamsaei, E., Martin, D., Sisakht, M.R., Ghasemi, M., Zaidi, J., 2015. SPEEK/cSMM membrane for simultaneous electricity generation and wastewater treatment in microbial fuel cell. Chem. Technol. Biotechnol. J. 90 (4), 641–647.

Min, B., Cheng, S., Logan, B.E., 2005. Electricity generation using membrane and salt bridge microbial fuel cells. Water Res. 39, 1675–1686.

Mishra, A.K., Bose, S., Kuila, T., Kim, N.H., Lee, J.H., 2012. Silicate-based polymer-nanocomposite membranes for polymerelectrolyte membrane fuel cells. Prog. Polym. Sci. 37, 842–869.

Mohan, Y., Kumar, S.M.M., Das, D., 2008. Electricity generation using microbial fuel cells. Int. J. Hydrogen Energy 33, 423–426.

Mokhtarian, N., Ghasemi, M., Daud, W.R.W., Ismail, M., Najafpour, G., Alam, J., 2013. Improvement of microbial fuel cell performance by using Nafion polyaniline composite membranes as a separator. J. Fuel Cell Sci. Technol. 10, 1–6.

Oh, S., Logan, B.E., 2006. Hydrogen and electricity production from a food processing wastewater using fermentation and microbial fuel cell technologies. Water Res. 39, 4673–4682.

Oh, S.E., Logan, B.E., 2007. Voltage reversal during microbial fuel cell stack operation. J. Power Sources 167, 11–17.

Pant, D., Van Bogaert, G., Diels, L., Vanbroekhoven, K., 2010a. A review of the substrates used in microbial fuel cells (MFCs) for sustainable energy production. Bioresour. Technol. 101, 1533–1543.

Pant, D., Van Bogaert, G., De Smet, M., Diels, L., Vanbroekhoven, K., 2010b. Use of novel permeable membrane and air cathodes in acetate microbial fuel cells. Electrochim. Acta 55 (26), 7710–7716.

Patil, S.A., Surakasi, V.P., Koul, S., Ijmulwar, S., Vivek, A., Shouche, Y.S., Kapadnis, B.P., 2009. Electricity generation using chocolate industry wastewater and its treatment in activated sludge based microbial fuel cell and analysis of developed microbial community in the anode chamber. Bioresour. Technol. 100, 5132–5139.

Peighambardoust, S.J., Rowshanzamir, S., Amjadi, M., 2010. Review of the proton exchange membranes for fuel cell applications. Int. J. Hydrogen Energy 35, 9349–9384.

Piao, Jingmei., An, J., Ha, P.T., Kim, T., Jang, J.K., Moon, H., Chang, I.S., 2013. Power density enhancement of anion-exchange membrane-installed microbial fuel cell under bicarbonate-buffered cathode condition. J. Microbiol. Biotechnol. 23 (1), 36–39.

Rahimnejad, M., Ghasemi, M., Najafpoura, G.D., Ismail, M., Mohammad, A.W., Ghoreyshia, A.A., Hassan, S.H.A., 2012. Synthesis, characterization and application studies of self-made Fe_3O_4/PES nanocomposite membranes in microbial fuel cell. Electrochim. Acta 85 (2012), 700–706.

Rahimnejad, M., Bakeri, G., Najafpour, G., Ghasemi, M., Oh, S.E., 2014a. A review on the effect of proton exchange membranes in microbial fuel cells. Biofuel 1, 7–15.

Rahimnejad, M., Bakeria, G., Ghasemi, M., Zirepour, A., 2014b. A review on the role of proton exchange membrane on the performance of microbial fuel cell. Polym. Adv. Technol. http://dx.doi.org/10.1002/pat.3383.

Rinaldi, A., Mecheri, B., Garavaglia, V., Licoccia, S., Nardoc, P.D., Traversa, E., 2008. Engineering materials and biology to boost performance of microbial fuel cells: a critical review. Energy Environ. Sci. 1, 417–429.

Rozendal, R.A., Hamelers, H.V., Buisman, C.J., 2006. Effects of membrane cation transport on pH and microbial fuel cell performance. Environ. Sci. Technol. 40 (17), 5206–5211.

Rozendal, R.A., Hamelers, H.V., Rabaey, K., Keller, J., Buisman, C.J.H., 2008. Towards practical implementation of bioelectrochemical wastewater treatment. Trends Biotechnol. 26 (8), 450–459.

Ruiz, Y., Baeza, J.A., Guisasola, A., 2015. Enhanced performance of bioelectrochemical hydrogen production using a pH control strategy. ChemSusChem 8 (2), 389–397.

Shahgaldi, S., Ghasemi, M., Daud, W.R.W., Yaakob, Z., Sedighi, M., Alam, J., Ismail, A.F., 2014. Performance enhancement of microbial fuel cell by PVDF/Nafion nanofibre composite proton exchange membrane. Fuel Process. Technol. J. 124, 290–295.

Sivasankaran, A., Sangeetha, D., 2011. Development of MFC using sulphonated polyether ether ketone (SPEEK) membrane for electricity generation from waste water. Bioresour. Technol. 102, 11167–11171.

Sotres, A., Díaz-Marcos, J., Guivernau, M., Illa, J., Magrí, A., Prenafeta-Boldú, F.X., Bonmatí, A., Viñas, M., 2014. Microbial community dynamics in two-chambered microbial fuel cells: effect of different ion exchange membranes. J. Chem. Technol. Biotechnol. http://dx.doi.org/10.1002/jctb.4465.

Sun, J., Hu, Yu., Bi, Z., Cao, Y., 2009. Improved performance of air-cathode single chamber microbial fuel cell for wastewater treatment using microfiltration membranes and multiple sludge inoculation. J. Power Source 187 (2), 471–479.

Varcoe, J.R., Atanassov, P., Dekel, D.R., Herring, A.M., Hickner, M.A., Kohl, P.A., Kucernak, A.R., Mustain, W.E., Nijmeijer, K., Scott, K., Xu, T., Zhuang, L., 2014. Anion-exchange membranes in electrochemical energy systems. Energy Environ. Sci. 7, 3135–3191.

Vázquez-Larios, A.L., Solorza-Feria, O., Vázquez-Huerta, G., Esparza-García, F., Rinderknecht-Seijas, N., Poggi-Varaldo, H.M., 2011. Effects of architectural changes and inoculum type on internal resistance of a microbial fuel cell designed for the treatment of leachates from the dark hydrogenogenic fermentation of organic solid wastes. Int. J. Hydrogen Energy 36 (10), 6199–6209.

Vermeiren, P., Leysen, R., Beckers, H., Moreels, J.P., Claes, A., 2008. The influence of manufacturing parameters on the properties of macroporous Zirfon separators. J. Porous Mater. 15, 259–264.

Vona, M.L.D., D'Epifanio, A., Marani, D., Trombett, M., Traversa, E., Licoccia, S., 2006. SPEEK/PPSU-based organic–inorganic membranes: proton conducting electrolytes in anhydrous and wet environments. J. Membr. Sci. 279, 186–191.

Wang, H., Ren, Z.J., 2013. A comprehensive review of microbial electrochemical systems as a platform technology. Biotechnol. Adv. 31 (8), 1796–1807.

Werner, C.W., Logan, B.E., Saikaly, P.E., Amy, G.L., 2013. Wastewater treatment, energy recovery and desalination using a forward osmosis membrane in an air-cathode microbial osmotic fuel cell. J. Membr. Sci. 428, 116–122.

Winfield, J., Greenman, J., Huson, D., Ieropoulos, I., 2013a. Comparing terracotta and earthenware for multiple functionalities in microbial fuel cells. Bioprocess Biosyst. Eng. 36 (12), 1913–1921.

Winfield, J., Chambers, L.D., Rossiter, J., Ieropoulos, I., 2013b. Comparing the short and long term stability of biodegradable, ceramic and cation exchange membranes in microbial fuel cells. Bioresour. Technol. 148, 480–486.

Winfield, J., Ieropoulos, I., Rossiter, J., Greenman, J., Patton, D., 2013c. Biodegradation and proton exchange using natural rubber in microbial fuel cells. Biodegradation 24 (6), 733–739.

Xu, J., Sheng, G.P., Luo, H.W., Li, W.W., Wang, L.F., Yu, H.Q., 2012. Fouling of proton exchange membrane (PEM) deteriorates the performance of microbial fuel cell. Water Res. http://dx.doi.org/10.1016/j.watres.2011.12.060.

Xu, G., Wang, Y., Sheng, G., Mu, Y., Yu, H., 2014. An MFC-based online monitoring and alert system for activated sludge process. Sci. Rep. 4, 6779. http://dx.doi.org/10.1038/srep06779.

Yee, R.S.L., Zhang, K., Ladewig, B.P., 2013. The effect of sulfonated Poly(ether ether Ketone) Ion Exchange Preparation Condition on membrane properties. Membranes 3, 182–195.

Zhang, X., Cheng, S., Wang, X., Huang, X., Logan, B.E., 2009. Separator characteristics for increasing performance of microbial fuel cells. Environ. Sci. Technol. 43 (21), 8456–8461.

Zhang, X., Cheng, S., Huang, X., Logan, B.E., 2010. The use of nylon and glass fiber filter separators with different pore sizes in air-cathode single-chamber microbial fuel cells. Energy Environ. Sci. 3, 659–664.

Zhao, C., Li, X., Wang, Z., Dou, Z., Zhong, S., Na, H., 2006. Synthesis of the block sulfonated poly(ether ether ketone)s (S-PEEKs) materials for proton exchange membrane. J. Membr. Sci. 280, 643–650.

Zuo, Y., Cheng, S., Logan, B.E., 2008. Ion exchange membrane cathodes for scalable microbial fuel cells. Environ. Sci. Technol. 42 (18), 6967–6972.