Role of membranes in bioelectrochemical systems

Bahareh Kokabian [a] and Veera Gnaneswar Gude[*]

Department of Civil and Environmental Engineering, Mississippi State University,
Mississippi State, MS 39762, USA

Abstract. This paper provides an overview of the role of membranes in bioelectrochemical systems (BESs). Bioelectrochemical systems harvest clean energy from waste organic sources by employing indigenous exoelectrogenic bacteria. This energy is extracted in the form of bioelectricity or valuable biofuels such as ethanol, methane, hydrogen, and hydrogen peroxide. Various types of membranes were applied in these systems, the most common membrane being the cation exchange membrane. In this paper, we discuss three major bioelectrochemical technology research areas namely microbial fuel cells (MFCs), microbial electrolysis cells (MECs) and microbial desalination cells (MDCs). The operation principles of these BESs, role of membranes in these systems and various factors that affect their performance and economics are discussed in detail. Among the three technologies, the MFCs may be functional with or without membranes as separators while the MECs and MDCs require membrane separators. The preliminary economic analysis shows that the capital and operational costs for BESs will significantly decrease in the future due mainly to differences in membrane costs. Currently, MECs appear to be cost-competitive and energy-yielding technology followed by MFCs. Future research endeavors should focus on maximizing the process benefits while simultaneously minimizing the membrane costs related to fouling, maintenance and replacement.

Keywords: membranes; bioelectrochemical systems; bioelectricity; biohydrogen; desalination

1. Introduction

Wastewater treatment continues to be the most basic sanitation need to protect the environment and the water resources that serve as potential drinking water reserves. Currently wastewater treatment systems are mostly based on the well-established activated sludge process in most parts of the world. While activated sludge process produces superior results within reasonable processing times, the process is chemical-, and energy-intensive requiring high capital and operation/maintenance costs (Sustarsic 2009). On the other hand, anaerobic treatment has been practiced for high strength wastewaters and various industrial wastewaters and excess sludge streams from the wastewater treatment plants. This technology has been developed over a century to treat wastewaters successfully while recovering valuable bioenergy (Visvanathan and Abeynayaka 2012). Wastewater treatment plants with an anaerobic digestion unit in place have

---

∗Corresponding author, Assistant Professor, E-mail: gude@cee.msstate.edu
a Ph.D. Candidate, E-mail: Kokabian.b@gmail.com

demonstrated the potential for energy savings through energy-rich biogas production.

The U.S. utilizes about 3-4% of the total energy to treat water and wastewater resources and for their collection/distribution (U.S. EPA 2012). Wastewater treatment requires about 0.5-2 kWh/m^3 depending on the wastewater characteristics and the treatment process and interestingly, it contains about 5 times the energy required to treat it (Gude 2015). Capturing this energy could result in a sustainable wastewater treatment solution. Energy locked in wastewater is mainly present in three forms: 1- organic matter (~1.79 kWh/m^3); 2- nutritional elements such as nitrogen, phosphorous (~0.7 kWh/m^3); and 3- thermal energy (~7 kWh/m^3) (McCarty *et al*. 2011). Chemical energy can be efficiently harvested while thermal heat may not be extracted except by use of a heat pump and subject to wastewater source temperature. By extracting this hidden chemical energy, wastewater treatment can be turned into an energy-yielding or energy-independent process rather than an energy consuming process while eliminating environmental pollution[1]. Conventionally, energy is extracted from wastewater though anaerobic digestion in the form of biogas, which requires further separation and purification steps. Direct conversion of waste into clean electricity or high value energy or chemical products was recognized as a better option to eliminate the excess sludge and energy issues (Logan 2008). Biological systems having potential to convert chemical energy (in the form of organic substance in wastewater) into electrical energy or other high energy-value products are known as bio-electrochemical systems (BESs) (Kiran kumar *et al*. 2012). These novel technologies depend on membranes for product separation and some other essential functions. This paper reviews three promising technologies (MFCs, MECs and (MDCs) in terms of their basic principles of operation, use of various membranes and their effects on the performance.

2. Bioelectrochemical systems

2.1 Microbial Fuel Cells (MFCs)

One of the most widely studied BESs is a microbial fuel cell. Fig. 1 shows three different BESs (Logan *et al*. 2006, Logan 2008). In MFCs, organic substrates are converted into carbon dioxide and water in the anodic compartment involving release of electrons which pass through an external load as electric current (Fig. 1(a)). The electric current will then combine with a cathode electron acceptor through electrocatalytic or biocatalytic reduction reactions (Rosenbaum *et al*. 2010). Examples of organic substrates (electron donors) are glucose, acetate, sucrose, and organic substrates present in domestic and industrial wastewaters. Few examples of electron acceptors are oxygen, nitrates, nitrites, and sulfates. Municipal wastewater contains a multitude of organic compounds that can fuel MFCs. Since the MFCs employ anaerobic or facultative bacteria, aeration is not necessary. The amount of power generated by MFCs (using anaerobic digestion supernatant) in the wastewater treatment process can significantly reduce the electricity needed for aeration in conventional treatment processes. MFCs yield significantly less biosolids (50-90% less) compared to other processes (Du *et al*. 2007). For instance, the cell yield of exoelectrogenic bacteria (0.07-0.16 gVSS/gCOD[2]) in MFCs is much less than the activated sludge process (0.35-0.45 gVSS/gCOD) (McCarty and Rittmann 2001, Huggins *et al*. 2013). MFCs can be employed to remove both carbon and nutrient compounds simultaneously from a variety of wastewaters

---

[1] Each kWh of electricity production involves release of 0.9 kgCO$_2$ emissions; For every 1000 tons of wastewater treated, 1500 tons of greenhouse gases are released (EIA 2009, Wang *et al*. 2010).
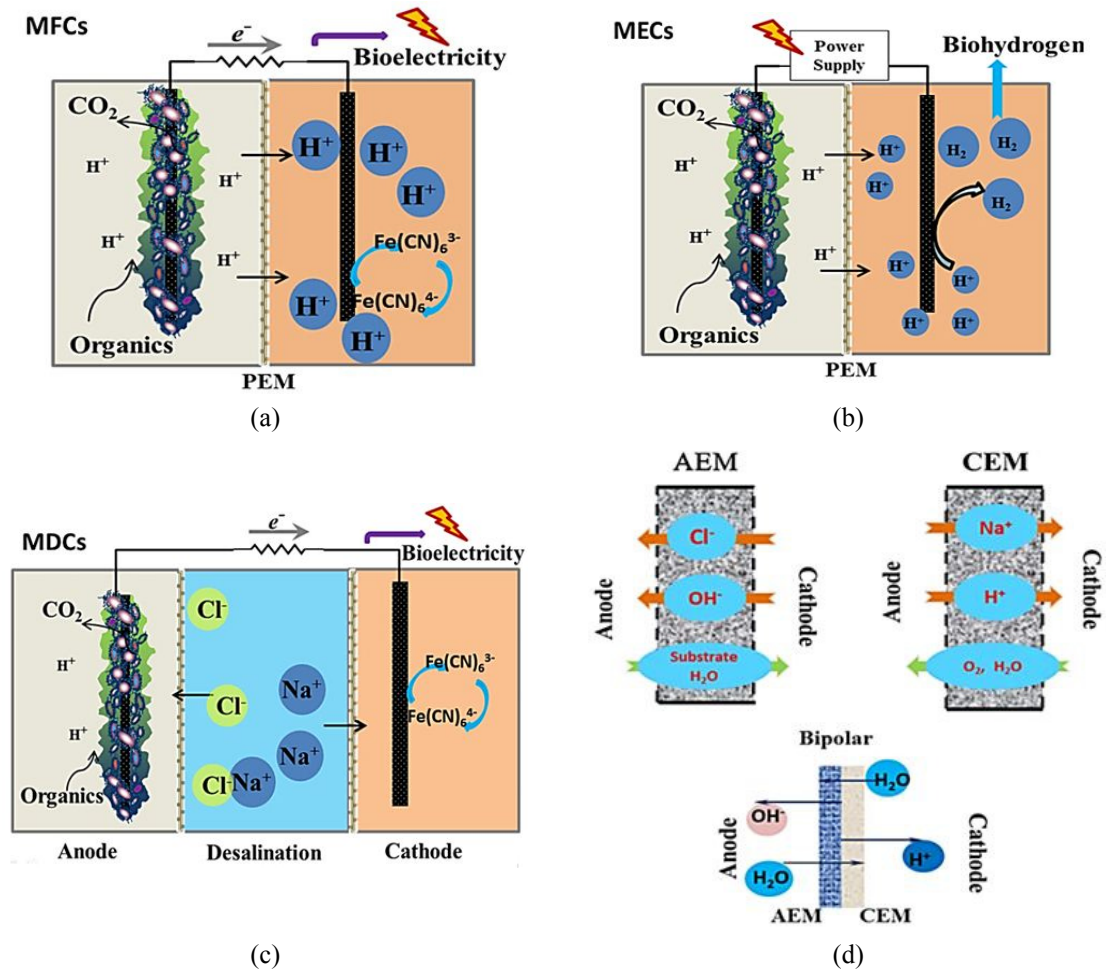[2] Volatile Suspended Solids/Chemical Oxygen Demand

Fig. 1 Bioelectrochemical Systems by Principle of Operation: (a) microbial fuel cells; (b) microbial electrolysis cells; ad (c) microbial desalination cells; and d) membrane functions (Logan 2008)

including domestic, industrial, and agricultural sources and yet produce electricity to satisfy the process energy requirements.

2.2 Microbial Electrolysis Cells (MECs)

Microbial electrolysis cells (MECs) produce high energy/value products such as hydrogen or methane or hydrogen peroxide instead of electricity. In MFCs, the potential of the biochemical reactions taking place between the anode and cathode chambers is adequate to drive the reaction forward to result in electricity production. However, in MECs, an external voltage needs to be applied to produce hydrogen, a high energy/value commodity (Fig. 1(b)) since the potential generated by substrate oxidation is not adequate to generate hydrogen (Kim and Logan 2011). The following examples describe the fundamental difference between the MFC and MEC principles of
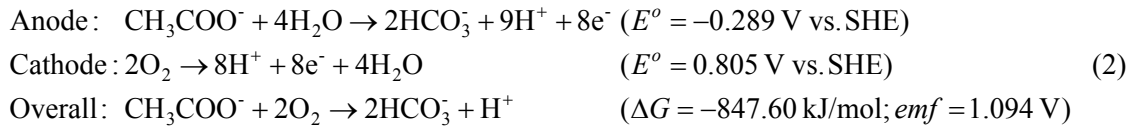
operation (Rozendal *et al.* 2008).

The difference between the MFC and MEC systems is the theoretical cell voltage or electromotive force (*emf*) of the overall reaction, which determines if the system is capable of electricity generation (MFC) or needs electricity to drive the reaction (MEC). The following equation shows how the electromotive force can be calculated from the Gibbs free energy of the overall reaction occurring in the system
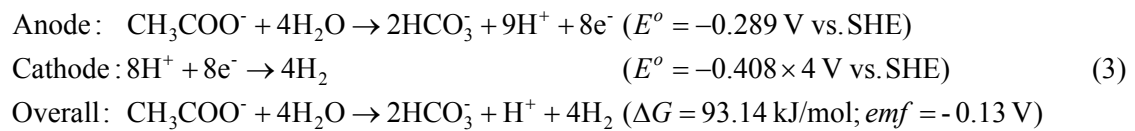
$$emf = -\frac{\Delta G}{nF} \tag{1}$$

where *emf* represents the electromotive force (in *V*), ΔG the Gibbs free energy of the reaction (in J/mol), *n* the amount of electrons involved in the reaction (in mol), and *F* Faraday's constant (96485.3 C/mol). The Gibbs free energy of a reaction measures the maximum amount of useful work that can be obtained from a reaction of thermodynamic system.

In a MFC, the Gibbs free energy of the reaction is negative and so the *emf* is positive, indicating that electricity can be generated from the reaction. For example, if acetate is used as the organic substrate ($[CH_3COO^-] = [HCO_3^-]$ = 10 mM, pH 7, 298.15 K, pO_2 = 0.2 bar), and with oxygen reduction, the anode-cathode (red-ox) reactions will be

$$
\begin{aligned}
&\text{Anode:} \quad CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \;(E^o = -0.289\,V\,vs.\,SHE) \\
&\text{Cathode:} \; 2O_2 \rightarrow 8H^+ + 8e^- + 4H_2O \qquad\qquad (E^o = 0.805\,V\,vs.\,SHE) \\
&\text{Overall:} \quad CH_3COO^- + 2O_2 \rightarrow 2HCO_3^- + H^+ \qquad (\Delta G = -847.60\,kJ/mol;\,emf = 1.094\,V)
\end{aligned} \tag{2}
$$

In an MEC, however, the Gibbs free energy of the reaction is positive and the *emf* is negative showing that in order to run the reaction, the electricity needs to be invested. If acetate is used as the organic substrate and hydrogen is produced ($[CH_3COO^-] = [HCO_3^-]$ = 10 mM, pH 7, 298.15 K, pH 2 = 1 bar)

$$
\begin{aligned}
&\text{Anode:} \quad CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \;(E^o = -0.289\,V\,vs.\,SHE) \\
&\text{Cathode:} \; 8H^+ + 8e^- \rightarrow 4H_2 \qquad\qquad\qquad (E^o = -0.408 \times 4\,V\,vs.\,SHE) \\
&\text{Overall:} \quad CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + H^+ + 4H_2 \;(\Delta G = 93.14\,kJ/mol;\,emf = -0.13\,V)
\end{aligned} \tag{3}
$$

In MFCs, the value of *emf* is the maximum cell voltage that can be generated in the system, while in MECs it is the minimum required voltage that is needed to drive MEC; however, due to the various electrochemical losses such as electrode potential losses and ohmic losses, less voltage will be generated in MFCs and more electrical energy is required in MECs. Efficient BES designs therefore need to focus on reducing electrochemical losses as much as possible (Rozendal *et al.* 2008).

2.3 Microbial Desalination Cells (*MDCs*)

Microbial desalination cells (MDCs) were discovered recently which provide an additional benefit of recovering saline or high hardness groundwater (Cao *et al.* 2009). The principle of operation is very similar to the MFCs except an additional desalination chamber is introduced

between the anode and cathode chambers with anion and cation exchange membranes to facilitate ionic transport between different chambers. A desalination cell is sandwiched between the anode and cathode chambers of an MFC, and the anolyte and catholyte are isolated with anion exchange membrane (AEM) and cation exchange membrane (CEM) respectively (Fig. 1(c)). Desalination of salt water is achieved by the transfer of negative and positive ions across AEM and CEM respectively. In order to preserve electroneutrality condition due to discharge of electric current from the bioelectrochemical oxidation of organic matter in the anode, the negatively charged ions from the desalination cell (such as Cl^-, NO_3^- and SO_4^{2-}) migrate to the anode. Similarly, in the cathode, the terminal electron acceptors (for example oxygen) receive electrons to form reduced compounds, and in turn, positively charged ions from the desalination chamber (such as Na^+, Ca^{2+} and Mg^{2+}) pass through the cation exchange membrane to the cathode chamber (Cao *et al*. 2009). In other words, the transport of cations and anions are restricted in the anode and cathode compartments respectively. The working principles and operational details have been described in Kim and Logan (2013). The overall effect of bio-electro-chemical processes in MDCs results in simultaneous power generation and water desalination. This feature has the potential to enhance the electricity production due to increase in ionic and electron transport within the anode/cathode and desalination chambers as reported previously (Luo *et al*. 2012a). Valuable products such as acid and alkali solutions (such as hydrochloric acid) can be generated in MDCs by employing bipolar membranes as shown in Fig. 1(d) (Gude *et al*. 2013).

3. Membranes in bioelectrochemical systems

Membranes provide a separation structure to isolate different bulk liquids on the anode and cathode chambers. They also facilitate transfer of ionic species from one chamber to another. The ionic transport through the membrane may occur due to migration which is caused by the electric field that builds up as the result of anodic and cathodic reactions. Some diffusion (undesirable) of substrates and other compounds (oxidants) may occur as well across the membrane due to the concentration polarization effect. Loss of desirable products such as hydrogen and their contamination with other less valuable products (for ex: methane or carbon dioxide) is eliminated by placing membranes. Membranes in microbial electrolysis cells separate the anode and cathode chambers similar to microbial fuel cells. The membrane reduces the hydrogen losses to the microbes in the anode chamber and prevents mixing of the hydrogen product gas with the carbon dioxide. Anion and cation exchange membranes which are used in microbial desalination cells help facilitate ionic transport primarily Na^+ and Cl^- across the membrane. Some water transport across the membrane is also possible in MDCs which depends on the osmotic pressure of the liquids on either side of the membranes. Fig. 1(d) shows the potential migrational and diffusional transport of ionic species and other compounds through the anion, cation and bipolar membranes.

The most commonly used proton exchange membrane in microbial fuel cells is Nafion membrane. DuPont developed the perfluorinated ion exchange membrane Nafion in the early 1960s during work with General Electric on a fuelcell. The major application of Nafion has been as a separating membrane in electrolytic cells used to produce chlorine and sodium hydroxide and as a solid polymer electrolyte in fuel cells and batteries (Grzebyk and Pozniak 2005). The purpose of membranes and potential products from the bioelectrochemical systems are shown in Table 1.

PEMs are often used in MFCs to separate the liquids in the anode and cathode chambers while allowing protons to pass between the chambers. Since Nafion has low proton transfer capability,

Table 1 Membrane use in bioelectrochemical systems

Technology	Membranes used	Purpose	Energy consumption	Form of energy produced
Microbial fuel cells	Cation exchange membrane (CEM or PEM*)	Proton transfer, eliminate substrate and oxygen transport	~0.1 (kWh/kg COD) for process flow	Electricity
Microbial electrolysis cells	Cation exchange membrane (CEM or PEM)	Proton transfer, eliminate substrate transport, hydrogen losses	0.5-2.4 (kWh/kg COD)	H_2, CH_4
Microbial desalination cells	Ion exchange membranes (AEM and CEM)	Cation / anion transfer, charge balance, desalination	~0.1 (kWh/kg COD) for process flow	Electricity

*Proton exchange membranes

ion exchange membranes were introduced in MFCs. AEMs have produced higher power density and coulombic efficiencies compared to the commonly used Nafion membranes. Both PEMs and CEMs help to reduce oxygen diffusion into the anode chamber. Later, ultrafiltration membranes were also tested. The results obtained from these tests varied significantly from each other. Cation exchange membranes are less expensive than Nafion and will be discussed in a later section.

MDC technology can be described as membrane-dependent technology since it requires both anion and cation exchange membranes to facilitate a desalination chamber in the center. Ion exchange membranes play a major role in Microbial desalination cells. AEM is inserted next to the anode and CEM next to the cathode (Fig. 1(c)). Due to the electric field caused by the bacteria (with proton release), anions move to the anode and cations move towards the cathode chamber resulting in water desalination in the middle chamber without any extra electrical energy or water pressure (Cao *et al*. 2009, Kim and Logan 2013). Anion exchange membranes have been widely used in three chamber MDCs. Most of commercial AEMs for electrodialysis have a styrene-*co*-divinylbenzene based matrix which have a drawback of difficult controlling of membrane structure while production and high manufacturing cost (Jikihara *et al*. 2013). However, recent AEMs have overcome this problem by applying water soluble polymers like poly (vinyl alcohol) (PVA) and then cross-linking the base polymer. The ion exchange capacity of these membranes depends on the polymer ratio of water-swollen base polymer to polyelectrolyte, the volume fraction of water in the polymer membrane, and the chemical nature of the polymer (Jikihara *et al*. 2013, Geise *et al*. 2013). CEMs used in MFCs can be applied in MDCs as well (Leong *et al*. 2013) with Ultrex CMI7000 made from divinylbenzene cross-linked poly (styrene) being the most used CEM in MDCs. Most of MDC studies have the regular three chamber configuration with AEM next to the anode and CEM next to the cathode. However, new configurations and designs have been developed in MDCs. One of these configurations that increases desalination rate is stacked MDC (SMDC) which contains multiple desalination chambers with alternating AEMs and CEMs (Kim and Logan 2013). Table 2 shows the applications of different membranes in bioelectrochemical systems and their performances.

Table 2 Materials and performances of MFC/MEC/MDC studies

			Microbial fuel cells					
System design	Exchange membrane	Anodematerial	Cathodematerial	Culture/Inoculum	Coulombic efficiency (%)	Current density	Power density	Ref.
Single chamber	None	Carbon cloth non-wet proof	Air Cathode Carboncloth non-wet proof coated carbon and PTFE	Wastewater	32	1.05 A/m^2	766 mW/m^2 19.1 W/m^3	Cheng et al. (2006)
Dual chambered stacked cell	Nafion 117	Reticulated vitreous carbon (RVC)	RVC 50 mM FeCN	Shewanella oneidensis strain DSP10	8.3	0.044 A/m^2	3 W/m^2 500 W/m^3	Ringeisen et al. (2006)
Dual chambered H-cell	Nafion 117	Solid graphite	Solid graphite with 50 mM FeCN	Geobacter sulfurreducens	95	0.0654 A/m^2	13.1 mW/m^2 0.36 W/m^3	Bond and Lovley (2003)
Upflow chamber	Ultrex	RVC	RVC	Anaerobic digestor sludge	8.1	0.516 A/m^2	170 mW/m^2 8.7 W/m^3	He et al. (2005)
Dual chambered stacked cell	Ultrex	Solid graphite	Graphite 100 mM FeCN	Anaerobic digestor sludge enrichment	65–89	6 A/m^2	3.6 W/m^2 216 W/m^3	Rabaey et al. (2003)

Table 2 Continued

	Microbial electrolysis cells							
Anion exchange membrane (Manufacturer)	Cation exchange membrane (Manufacturer)	Anode	Cathode (catalyst)	Anode medium	Cathodic efficiency (%)	Current density	Hydrogen production	Ref.
(Fumasep FAA, FuMa-Tech GmbH, Germany)		graphite felt	platinum coated titanium mesh	synthetic wastewater	83 ± 13	5.3 ± 0.5 A/m²	2.1 ± 0.5 m³ H₂/m³ – d	Sleutels *et al.* (2009)
	(Fumasep FKE, FuMa-Tech GmbH, Germany)	graphite felt	platinum coated titanium mesh	synthetic wastewater	47 ± 6	2.3 ± 0.3 A/m²	0.4 ± 0.1 m³ H₂/m³ – d	Sleutels *et al.* (2009)
Membrane-less; separated by a layer of J-Cloth (4 × 4 cm, First Brands Corporation, USA)		type A carbon cloth (without wet-proofing; E-Tek,USA)	type B carbon cloth (30% wet-proofing; E-Tek, USA)	Shewanella oneidensis MR-1, acetate	73 (CE)	14 A/m²	0.69 m³ H₂/m³ – d	Hu *et al.* (2008)
Membrane-less		graphite brush	wet-proofed (30%) carbon cloth (type B; E-TEK)	1 g/L sodium Acetate with mixed culture	78 ± 1% – 96 ± 1%	292 ± 1 A/m³	3.12 (0.02 m³ H₂/m³)	Call and Logan (2008)
Membrane-less; nonwoven cloth (Liplisse 3, Libeltex, Belgium)		graphite granules	graphite granules	1 g sodium Acetate per feeding cycle	36 ± 2% – 87 ± 5%	66 ± 2 to 156 ± 1 A/ m³	methane	Clauwaert and Verstrate (2008)

Table 2 Continued

				Microbial desalination cells						
Anion exchange membrane (Manufacturer)	Cation exchange membrane (Manufacturer)	Anode	Cathode (catalyst)	Anode (Acetate/ xylose, g/L)	Desalination g/L [NaCl]	Cathode medium	Desali-nation	COD removal	Power density	Ref.
AMI-7001, Membranes International Inc, R-5500, Solvay Advanced Polymers	CMI-7000, Membranes International	Ammonia-treated 14 carbon cloth (BASF, NJ)	Carbon cloth (platinum)	1.2	5-20	50 mM PBS	43-67%	77%	480 mW/m²	Mehanna et al. (2010a)
AMI-7001,	CMI-7000,	Graphite granules	Carbon cloth + Pt	4	30		99%		30.8 W/m³	Jacobson et al. (2011a)
AMI-7001,	CMI-7000,	Carbon brush	Carbon cloth + Pt	3	35 (artificial sea water)		94.3%; 73.8%	92%	28.9, 11.1 W/m³	Jacobson et al. (2011b)
AR204-SZRA-412	CR67-HMR-412 (Ionics, USA)	Heat treated graphite brush	Carbon cloth (PTFE)	WW	50 mM (Na$^+$, 50 mM Mg^{2+}, 50 mM Ca^{2+}, 50 mM Cl$^-$, 50 mM Br$^-$, 50 mM SO$_4^{2-}$)	100 mM PBS	13-29%	25%	660 mA/m²	Luo et al. (2012b)
AMI 7001	CMI 7000	heated graphite	Carbon cloth	WW	5.85	Ferricyanide	66%		8.01 W/m³	Luo et al. (2012a)
DF120, Tianwei	CMI7000,	carbon graphite fiber brushes	Carbon cloth	1 xylose	20	25 mM or 50 mM PBS	39%,		931 mW/m²	Qu et al. (2012)
AMI-7001,	CMI-7000,	graphite fiber granules	carbon cloth	1	35	Synthetic sea water	98%		800-1140 mW/m²	Kim and Logan (2011)
DF120, Tianwei membrane	CMI 7000,	carbon felt	carbon cloth (platinum)	1.64	20	PBS	99%			Chen et al. (2011)

3.1 Membrane vs. membrane-less bioelectrochemical systems

It was originally thought that a membrane barrier is a must to separate the contents of the anode and cathode compartments of BESs (especially in MFCs and MECs) for the aforementioned reasons. However, the use of membranes as barriers in bioelectrochemical systems has also resulted in some serious operational issues. One major issue is that the proton transfer from the anode chamber to the cathode chamber is significantly retarded resulting in accumulation of protons in the anode chamber and similarly accumulation of negatively charged ions in the cathode chamber which ultimately leads to low and high pH conditions in anode and cathode chambers respectively. It was shown that cations in the MFC medium(such as Na^+, K^+, Ca^{2+},and others), typically present at 10^5 higher concentrations than protons, are primarily responsible for the transport of positive charge across Nafion membranes. The transfer of these species, as opposed to protons, results in increased pH at cathode and reduced voltages (Rozendal *et al*. 2006, Kim *et al*. 2007). The presence of proton exchange membrane also increases the internal resistance of the MFC resulting in poor performance and operational instability (Li *et al*. 2011). Further, the use of membranes increases the overall cost of the bioelectrochemical systems.

Demonstrations with membrane-less reactors have reported interesting results in both MFCs and MECs.In a comparative study by Liu and Logan (2004) a single-chamber MFC was operated in the presence and absence of a Nafion 117 membrane. They observed a reduced power output when Nafion was present (262 ± 10 vs. 494 ± 21 mW/m^2). Potential measurements showed that the anode potential was identical in the presence and absence of a Nafion 117, but that the cathode potential was 0.177 ± 0.012 V lower when Nafion was present. It was shown that the internal resistance was reduced by eliminating the membrane which resulted in higher power production. But elimination of membrane will promote oxygen diffusion into the anode chamber causing operational instability or consume some of the protons to form water. Table 2 shows some examples of MFCs and MECs performances which lack a membrane. Similarly, in MECs, high cathodic hydrogen recoveries ($78 \pm 1\%$ to $96 \pm 1\%$) were achieved in an MEC despite the absence of a membrane between the electrodes (applied voltages of $0.3 < E_{ap} < 0.8$ V; 7.5 mS/cm solution conductivity). Through the use of a membrane-less system, a graphite fiber brush anode, and close electrode spacing, hydrogen production rates reached a maximum of 3.12 (0.02 m^3 H$_2$/m^3 reactor per day (292 ± 1 A/m^3) at an applied voltage of $E_{ap} = 0.8$ V. This production rate is more than double that obtained in previous MEC studies using membranes (Call and Logan 2008). Clauwaert and Verstraete (2009) demonstrated that membrane-less MECs can be operated for methane production without pH adjustment and that the ohmic cell resistance could be lowered by about 50% by removing the cation exchange membrane. They showed that the current production increased from 66 ± 2 to 156 ± 1 A/m^3 MEC by removing the membrane with an applied voltage of -0.8 V. Methane was the main energetic product despite continuous operation under carbonate-limited and slightly acidified conditions (pH 6.1-6.2). These results suggest that continuous production of hydrogen in membrane-less MECs will be challenging since methane production might not be avoided easily.

3.2 Membranes in microbial desalination cells

Various configurations of MDCs were developed recently which include three chamber MDCs, microbial desalination-electrolysis cells (MECs), bipolar MDCs for acid-alkali production, and osmotic MDCs (MODCs) (Cao *et al*. 2009, Chen *et al*. 2011, Kim and Logan 2011, Luo *et al*.

2011, Mehanna *et al*., 2010b, Zhang and He 2012). The desalting capacity of MDCs can be increased by stacking more than one membrane pair between anode and cathode. The body of scientific literature includes detailed reports on the desalination capacity and efficiency of both unit MDCs and stacked MDCs (Gude *et al*. 2013). Upflow MDC reactors have been developed to demonstrate the feasibility of microbial desalination at liter-scale flow rate capacity, and promote its potential for large scale application (Jacobson *et al*. 2011a, b).

MDCs face more severe membrane fouling and performance issues compared to the other two BESs due to the different types of membranes that will be used in its operation. As water desalinates through ion exchange membranes, the conductivity of the solution decreases leading to an increase in ohmic resistance of cell (Cao *et al*. 2009, Luo *et al*. 2011). This could be overcome by increasing the ion exchange capacity in the middle chamber by using ion exchange resins (IER). MDC studies applied mixed IERs in dilution chamber to obtain higher desalination rates with higher current efficiency compared to classic MDCs (Morel *et al*. 2012, Zhang *et al*. 2012a, Zuo *et al*. 2013). Since, resins' conductivity is much higher than bulk solution, ion transfer and solution conductivity are improved in R-MDCs. Morel *et al*. (2012) used a mixture of strong base resin as anion resin with strong acid resin as cation resin in the middle chamber of a MDC, and observed 1.5-8 times higher desalination rate with lower stabilized ohmic resistance, compared to the regular MDC. Zhang *et al*. (2012a) showed that resin packed MDCs improve desalination rate especially at lower initial salt concentration. It has been proved that resins applied in MDC can remove anions better than cations suggesting the use of this technology for desalination of water with lower hardness (Zuo *et al*. 2013).

In osmotic MDCs, water in the anode chamber transfers through a forward osmosis (FO) membrane to the desalination chamber due to the osmotic pressure gradient across the membrane, while cations still move through CEM from middle chamber to the cathode chamber. The benefits of using FO membranes instead of AEMs are the acceleration of desalination and water recovery due to the water transport from anode chamber to the middle chamber (Zhang and He 2012). However, one limitation of these MDCs is that the FO membrane prevents transfer of anions through the membrane, which makes the system unable to separate anions selectively resulting in reduction of current efficiency (Kim and Logan 2013). Zhang and He (2012) found out that reduction in salinity with the low initial salt concentrations occurs mostly due to the salt removal by electricity while for higher initial concentrations, transfer of water from anode to middle chamber is the main reason for salinity reduction. Thus the authors suggest the use of Osmotic Microbial Desalination Cell (OsMDC) for treatment of high salinity water. According to this study, the capital cost of FO membrane is less than AEM membranes, making BES systems using FO membranes more economical. It should be also noted that the internal resistance of BESs may increase by replacing the AEM with FO membranes with higher salt rejections. Thus more studies are recommended regarding use of FO membranes in MDC systems and its effect on power generation (Kim and Logan 2013).

4. Membrane types and issues in BESs

4.1 Membrane types and characteristics

Various types of membranes were used in MFCs, MECs and MDCs. The first MFCs and MECs used cation exchange membrane (CEM) known as Nafion. Nafion, a sulfonated tetrafluorethylene

Table 3 Physical properties of some CEMs (Yaroslavtsev and Nikonenko 2009)

Membrane	Manufacturer	Membrane type	Ion-exchange capacity, mg-eq/g	Swelling, %	Ion conductivity, Ω
Nafion-117	Du Pont, USA	homogeneous	0.9–1.0	< 20	0.012 (0.5 M NaCl), 0.03 (0.5 M HCl)
MF-4SK	Plastopolymer, Russia	homogeneous	0.9–2.0	20	0.008 (0.5 M NaCl)
Ralex CM	Mega, Czech Republic	heterogeneous	2.2	< 50	> 0.0062 [www.mega.cz]
MK-40	Shchekinoazot, Russia	heterogeneous	2.2	30 ± 5	0.007 (0.5 M HCl)

copolymer, consists of a hydrophobic fluorocarbon backbone ($-CF_2-CF_2-$) to which hydrophilic sulfonate groups (SO_3^-) are attached. The presence of negatively charged sulfonate groups in the membrane explains the high level of proton conductivity of Nafion, while also showing a significant undesirable affinity for other cations rather than protons (Chae *et al*. 2008). Table 3 shows basic characteristics of some cation exchange membranes (CEMs). MECs typically used Fumasep FKE (FuMA-Tech GmbH, Germany) membrane. Other types of membranes examined include anion exchange membranes (AEMs; Fumasep FAB, FuMA-TechGmbH,Germany; AMI, Membranes International, Glen Rock, NJ), a bipolar membrane (BPM; FumaSep FBM, FuMA-Tech GmbH, Germany), and a charge mosaic membrane (CMM; Dainichiseika Color & Chemicals, Co. Ltd., Japan) (Logan *et al*. 2008). Physical and chemical properties of these membranes are shown in Table 4. The use of an AEM was found to substantially increase MEC performance, as it allows for the transport of negatively charged chemical buffers, such as phosphate and bicarbonate alkalinity, across the membrane. This transport helps to buffer pH changes in the two chambers (Logan *et al*. 2008).

4.2 Oxygen-substrate transfer and internal resistances

Kim *et al*. (2007) investigated the effect of different types of membranes on the performance of MFCs. Nafion, AEM, CEM and three different ultrafiltration (UF) membranes with molecular weight cut offs of 0.5 K,1 K, and 3 K Daltons were used in different types of MFCs. They found that the AEM produced the highest power density (up to 610 mW/m^2) and Coulombic efficiency (72%) in comparison with other CEM or Nafion membranes. The increased performance of the AEM was attributed to proton charge transfer facilitated by phosphate anions and low internal resistance. They reported that the type of membrane affected maximum power densities in two-chamber, air-cathode MFCs with low internal resistance (84-91 Ω for all membranes except UF-0.5 K) but not in two-chamber aqueous cathode bottle MFCs (B-MFCs) due to their higher internal resistances (1230-1272 Ω except UF-0.5K). The UF-0.5 K membrane produced very high internal resistances(6009 Ω, B-MFC; 1814 Ω, C-MFC) and was the least permeable to both oxygen (mass transfer coefficient of $k_O = 0.19 * 10^{-4}$ cm/s) and acetate ($k_A= 0.89 *10^{-8}$ cm/s). It was concluded that Nafion was the most permeable membrane to oxygen ($k_O = 1.3*10^{-4}$ cm/s), and

the UF-3K membrane was the most permeable to acetate ($k_A = 7.2 * 10^{-8}$ cm/s). Only a small percent of substrate was unaccounted for based on measured Coulombic efficiencies and estimates of biomass production and substrate losses using Nafion, CEM, and AEM membranes (4-8%), while a substantial portion of substrate was lost to unidentified processes for the UF membranes (40-89%). A comparison of the mass transfer coefficients and diffusivities of oxygen and acetate are shown in Table 5. Similar results were reported by Chae *et al.* (2008). They estimated an oxygen mass transfer coefficient (K_O) and the oxygen diffusion coefficient (D_O) for Nafion as $K_O = 2.80 \times 10^{-4}$ cm/s and $D_O = 5.35 \times 10^{-6}$ cm^2/s, respectively when a 50 mM phosphate buffer was used as the catholyte. The MFC with distilled water instead of phosphate buffer showed similar values ($K_O = 2.77 \times 10^{-4}$ cm/s, $D_O = 5.27 \times 10^{-6}$ cm^2/s), indicating that the catholyte shows no significant effects on oxygen diffusion. Nafion was also found to be permeable to acetate, but this seemed negligible according to the authors.

Table 4 Physical and chemical properties of ion exchange membranes (Fumatech.com)

	Type	Reinforcement	Thickness μm[a]	IEC meq/g	Selectivity %[b]	Specific area resistance Ωcm^{2}[c]	Stability pH
FAS	Stability	none	30-50	1	> 97	< 1	1-14
FKS	cation	none	30-50	1.4	> 98	< 1	1-14
FAS	anion	PET	90-100	1	> 95	< 3	1-9
FKS	cation	PET	90-100	1.4	> 98	< 4	1-9
FAM	anion	PET/GF	90-100	1.6	> 92	< 3	1-9
FKM	cation	PP	90-100	1.9	> 95	< 1.7	1-9
Membranes for electrodialysis with bipolar membranes							
FAB	anion	PEEK	100-120	-	> 96	< 5	1-14
FKB	cation	PEEK	100-120	1.3	> 98	< 5	1-14
FBM	bipolar	PEEK	180-200	-	-	-	1-14
Special grade membranes							
FAD	anion	PET	80-100	1.5	> 93	< 0.8	1-9
FKD	cation	PEEK	80-100	1.3	> 95	< 1.8	1-14
FAP	anion	PEEK/PTFE	140-160	-	> 95	< 6.5	1-6
FAA	anion	PEEK	100-120	1.5	> 95	<1.5	1-14
FKL	cation	PEEK	100-120	1	> 98	<5	1-14
FKE	cation	none	50	1.3	> 98	<1.5	1-14
Ultrex™ membranes							
AMI-7001	anion	PP	500	1.3	> 96	25-30	1-10
CMI-7000	cation	PP	450	1.6	> 97	25-30	1-10

(a) reference membrane dried over P_2O_5 in vacum.;
(b) determined from membrane potential measurement in a concentration cell 0,1/0,5 M KCl @ 25°C;
(c) in Na+-/Cl$^-$ form at T = 25°C in H_2O
PET = polyester; PP = polypropylene; GF = glassfiber; PEEK = polyetheretherketone;
PTFE = polytetrafluoroethylene

Table 5 A comparison of the mass transfer coefficients and diffusivities of oxygen and acetate

Membrane property	Nafion[1]	Nafion[2]	CEM[1]	AEM[1]	UF-0.5K[1]	UF-1K[1]	UF-3K[1]
Thickness[a] (cm)	0.019	NR	0.046	0.046	0.0265[a]	0.0265[a]	0.0265[a]
k_O ($\times 10^{-4}$ cm/s)	1.3	2.8	0.94	0.94	0.19	0.41	0.42
D_O ($\times 10^{-6}$ cm^2/s)	2.4	5.35	4.3	4.3	0.51	1.1	1.1
k_A ($\times 10^{-8}$ cm/s)	4.3	NR	1.4	5.5	0.89	16	27
D_A ($\times 10^{-9}$ cm^2/s)	0.82	NR	0.66	2.6	0.24	4.2	7.2

[1] Kim *et al.* 2007; [2] Chae *et al.* 2008; [a] Average, based on the range of 0.018-0.035 cm provided by the manufacturer; NR = not reported

4.3 Membrane area

Membrane surface area available for proton transfer has a significant effect on the power production in microbial desalination cells. Oh and Logan (2006) studied the effect of membrane surface area and their ratios with respect to electrode surface areas using a proton exchange membrane (Nafion 117 by Du Pont). Three different membrane areas (A_{PEM} = 3.5, 6.2, or 30.6 cm^2) were tested and their corresponding power densities are shown in Fig. 2(a). They showed that for a fixed anode and cathode area, the power density increased with increase in the PEM area. The maximum power densities were determined by scaling the anode, cathode and PEM surface areas in the ratio $2A_{Cat} = A_{PEM} = 2A_{An}$. A mathematical equation representing the correlation between the power density and the anode, cathode and PEM areas was developed in this study. Fig. 2(b) shows the power production from MFCs within the anode and cathode areas of 0 to 500 cm^2 and PEM areas of 0 to 1000 cm^2.

$$P = \frac{A_{PEM}}{10,000} \times \frac{126.6 \times \left(\frac{A_{Cat}}{A_{PEM}}\right)^{0.439}}{1 + \left[0.155 \times \left(\frac{A_{PEM}}{A_{An}}\right)^{2.45}\right]} \tag{4}$$
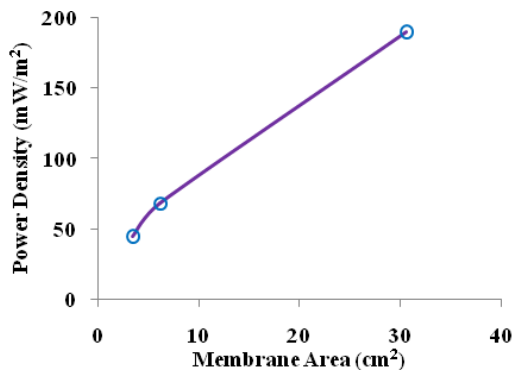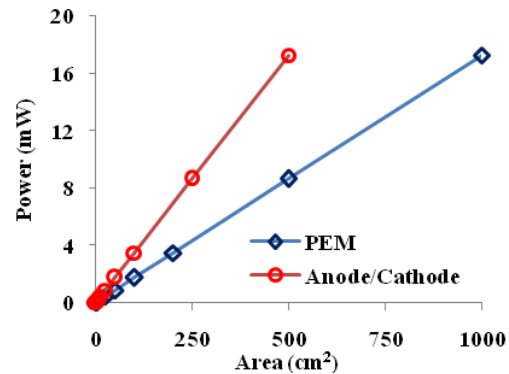
(a) Effect of membrane area on power density   (b) Electrode/membrane area vs. Power

Fig. 2 Effect of membrane area on power density and power production (Oh and Logan 2006)

In microbial desalination cells, the amount of salt removal that can be achieved depends on the membrane surface area. Also, the water transport in the osmotic MDCs will also decrease/increase with the available membrane surface area. In regular MDC configurations, the osmotic water transport needs to be reduced to avoid the water losses in the desalination chamber. Reducing the membrane area also increases the electrical resistance and eventually increasing the electrical potential losses. However, optimized membrane area will reduce the capital costs for MDCs since the ion exchange membranes cost about $150/m^2 (Yee *et al*. 2012).

4.4 Membrane fouling and other issues

Often poor performances in all three technologies (such as lower power density and lower Coulombic efficiencies) were attributed to electrode biofilm performance (Nevin *et al*. 2008, Yang *et al*. 2009) and variation of microbial communities (Kiely *et al*. 2011a). But this may not entirely be the case for the studies involving long term operation. Similar to other membrane processes (such as reverse osmosis, ultrafiltration, microfiltration and nanofiltration and membrane distillation), membranes in bioelectrochemical systems are also pone to biological and chemical fouling. A biofilm may form on the AEM or CEM (for biocathode) over time which may affect the performance of these systems. For instance, in microbial desalination cells, the AEM next to the anode chamber has high chances of suffering from biofouling due to the growth of exoelectrogenic bacteria (Kim and Logan 2013). Membrane fouling in MDCs was investigated through an eight-month operation by Ping *et al*. (2013). Multiple MDCs were set up by using cation (CEM), anion (AEM), and/or proton (Nafion) membranes. The MDCs exhibited relatively constant reduction of conductivity of artificial seawater during the testing period ($46.3 \pm 6.3\%$ in the CEM-MDC and $78.7 \pm 0.8\%$ in the Nafion-MDC in an operating cycle). However, the current generation decreased from 99 to 56 A/m^3 in the CEM-MDC after 250 days, and from 97 to 46 A/m^3 in the Nafion-MDC after 130 days, indicating the presence of membrane fouling. It was observed that the AEM contained significant biofouling, resulting from wastewater and microbial growth and organic compounds migrating across the membrane, while the CEM had substantial inorganic scaling, mainly consisting of calcium and magnesium. The membrane resistance of the CEM increased more significantly than that of the AEM, indicating that CEM needs more maintenance during MDC operation. (Ping *et al*. 2013).

The authors (Kokabian and Gude 2013) investigated the performance of photosynthetic microbial desalination cells (PMDCs) with algae as biocathode. Fig. 3 shows scanning electron microscopic (SEM) images of anion and cation exchange membranes used in the PMDCs after 45 days of operation (Kokabian and Gude 2015). Figs. 3(a) and (c) show clean anion and cation exchange membranes while Figs. 3(b) and (d) show the biofouling on the anion and cation exchange membranes respectively. Both inorganic and biofouling (similar to exoelectrogenic bacteria) can be found on the AEM (Fig. 3(b)) which can be attributed to high concentrations of buffer and other wastewater constituents and deposition of algal cells and slight contamination with other bacteria on the CEM (Fig. 3(d)).

Formation of biofilm on the AEM and CEM may also depend on the operational environment of the BESs. Both external and internal environments may influence the biofilm formation. For example, in MFCs the exoelectrogenic bacteria produce electricity in absence of oxygen whereas in MECs hydrogen is produced under anoxic conditions. MECs are generally developed by converting MFCs into MECs (Call and Logan 2008). This change in operational environment may affect the microbial community populations and their diversity (Kiely *et al*. 2011b). In Chae *et al*.

(2008), MFC and MEC anodic communities in a two chamber configuration supplied with acetic acid as substrate showed a reduced species diversity when changed to an MEC (Chae *et al*. 2008). The different conditions of the MFC and MEC are reflected by other changes in the microbial communities, as there is usually an increase in methanogenesis in MECs compared to MFCs, especially at low external Voltages or high organic loading (Call *et al*. 2009). External factors that may have an effect on the systems performance can be operating temperature (Ahn and Logan 2010) and the voltage/resistance applied.

In MDCs, the removal of ionic species from the middle chamber results in high internal resistance with continued operation. This may become a major drawback for the technology. For example, Cao *et al*. (2009) mentioned that when the salt was removed by 88% at an initial salt concentration of 5g/L, the ohmic resistance of the MDC increased by 40 times from 25 Ω to 970 Ω at the end of the cycle, which was due to the conductivity decrease in desalination chamber and interface resistance of bulk solution and membrane. Similarly, as demonstrated by Luo *et al*. (2012c), 98.8% salt was removed from initial 10 g/L NaCl in microbial electrolysis and desalination cell with simultaneous hydrogen production. But as the internal resistance increased from 70-250
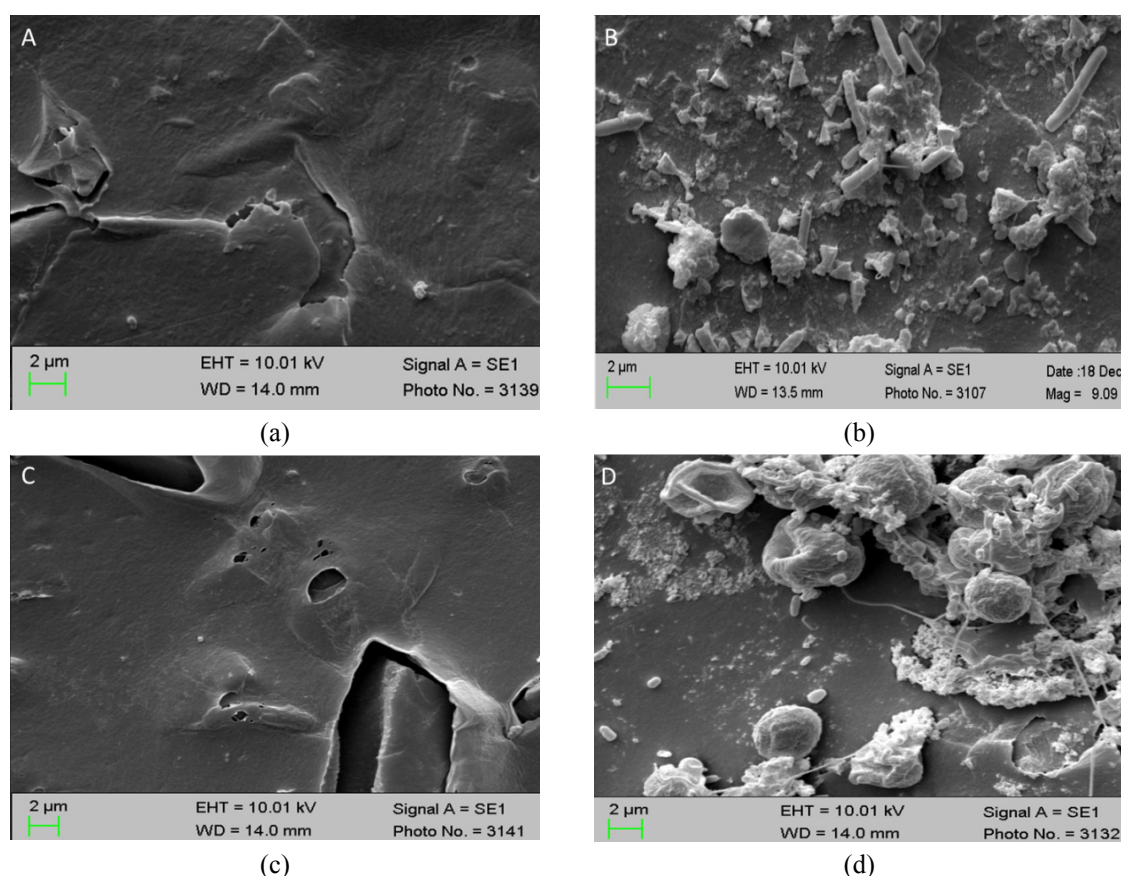

Fig. 3 Membrane fouling in photosynthetic MDCs – (a) anion exchange membrane (before); (b) anion exchange membrane (after 45 days of operation); (c) cation exchange membrane (before); and (d) cation exchange membrane (after)

to 850-1100 Ω, both hydrogen production rate and desalination rate were reduced. To avoid this drawback, Mehanna *et al*. (2010a) proposed MDC as a pre-desalination process for reverse osmosis, in which, the salt concentration was reduced to10 g/L, about 50% of the initial concentration. Another issue is high concentration of Cl$^-$ from desalination chamber which could inhibit the activity of microbial community at anodic chamber; requiring large quantities of anode solution exchange to sustain high performance of MDC and MDC running at low salt concentration could avoid the inhibition effect from Cl$^-$ (Zhang *et al*. 2012a).

4.5 Membrane costs and comparison with other technologies

Among the three different bioelectrochemical systems discussed here, MFCs produce more electricity than MDCs while MECs produce other valuable chemical compounds containing higher forms of energy. MFCs produce much lower power densities than other types of fuel cells, but their most promising application in the near future is perceived to be as a process for wastewater treatment. Increasing the maximum power densities per electrode area in an MFC is another important factor for its cost-effectiveness. MFC developments between the years 1999 and 2006 have shown an increase of six orders of magnitude of power production reaching as high as 1.54 W/m^2 (Logan 2009). Various *Shewanella* strains and mixed cultures produced less than 1 mW per m^{2}before the year 2000, but now routinely these systems extract>2 W per m^2 with these inocula owing to improved MFC design and architecture.

Microbial fuel cell construction essentially requires carbon or graphite electrodes, catalyst on the cathode electrode and may be a proton exchange membrane. Each of these key elements of construction is expensive. Reducing the cost of these materials for MFCs construction is essential for building an economical treatment system. Carbon paper or cloth is commonly used in MFCs as electrode materials, with platinum (Pt) as a catalyst on the cathode. While these materials are effective at producing higher power, they are expensive. Carbon cloth, for example, costs $1000/m^{2}with $140-$700/m^2 for the Pt catalyst (0.1-0.5 mg Pt/cm^2) (Zuo *et al*. 2008). While alternatives to Pt have been sought, none have approached the performance of Pt in MFCs. Pt is used on the cathode in air-cathode MFCs, so minimizing or eliminating the need for Pt can reduce the system capital costs (Cheng *et al*. 2006).

A few studies have shown that the proton exchange membrane can be eliminated in MFCs and that removing it actually increases maximum power densities. However, this needs to be demonstrated at a larger scale to confirm its viability. Meanwhile, to explore alternatives to the expensive PEM, the relatively low-cost materials such as ultrafiltration membrane, ion exchange membrane (Kim *et al*. 2007), and porous materials such as J-cloth (Fan *et al*. 2007) and nanoporous polymerfilters (Biffinger *et al*. 2007) were employed in MFCs and have been demonstrated to be feasible substitutes for PEM in laboratory systems. Similarly, the inexpensive alternatives to Pt like Co-tetra-methyl phenylporphyrin (CoTMPP), iron phthalocyanine (FePc) (Zhao *et al*. 2005, Cheng *et al*. 2006, Yu *et al*. 2007) and manganese dioxides (Zhang *et al*. 2009) have been demonstrated to be effective in catalyzing oxygen reduction.

Integrating membranes with electrode materials might help reduce the costs of the BESs. Zuo *et al*. (2007, 2008) produced membrane cathodes by coating graphite paint and CoTMPP onto the surface of ultrafiltration orion exchange membranes, which can produce comparable power density to MFCs using carbon paper/cloth and Pt-catalyst. Due to the replacement of carbon cloth with graphite paint, the cost was appreciably reduced. However, the use of these membranes significantly increased the internal resistance of MFC. In an attempt to reduce the internal

resistance, Zuo *et al*. (2008) used a stainless steel mesh pressed against the coated side of the membrane cathode as a current collector, which contributed a 38% reduction in internal resistance and improved the cathode performance. Apparently, the current collector would increase the cost and the difficulty of construction and operation, so it is not feasible for scalable MFC architecture. Also, the physical properties of UF and ion exchange membranes are not ideal for MFC applications since UF membrane is mechanically friable and ion exchange membranes tend to swell easily in aqueous solution, resulting in cracks on the coating. To address these concerns, membrane-less cloth cathode assembly was developed by Zhuang *et al*. (2009). These were constructed by coating the cloth with conductive paint (nickel-based or graphite-based) and non-precious metal catalyst (MnO_2). A comparison between membrane cathode assembly and cloth-cathode assembly (membrane-less) has shown that cloth cathode assembly would cost $623 per W electricity produced while membrane cathode assembly would cost $1048-1145 per W electricity (Zhuang *et al*. 2009). These numbers are three orders of magnitude higher than the electricity production from well-established solar photovoltaic technology which has an installed cost of $1-6 per W (Barbose *et al*. 2013). However, it should be noted that these calculations were based on power density 96 mW/m^2 for cloth cathode assembly, which are 2-3 orders of magnitude lower than those reported by Logan (2009). This shows that there is a strong potential for this technology to be cost-effective with future developments. For example, reducing the distance between the electrodes and doubling the cathode surface area to match the anode potential have improved the power production (Zuo *et al*. 2008).

It was reported that energy efficiency as high as 400% was obtained in MECs when the electricity production is considered which is much higher than the energy efficiency of water electrolyzers in the range of 56-73%. In comparison with typical fermentation processes that use glucose as substrate the conversion efficiencies are 18-38%, but the MECs yielded an efficiency of 72-93%. The costs for MECs were estimated as $0.62/kg H_2 whereas the costs for water electrolysis were $3.80/kg H_2. This comparison shows the competitiveness of the MEC technology and its potential for future applications (Call and Logan 2008).

Rozendal *et al*. (2008) have reported on the capital costs for the BESs and their composition (Fig. 4) for current and future scenarios assuming an $11/kg COD removed. A future comparison was made based on an assumption of $0.55/kg COD. The distribution of the capital costs includes membrane, electrode, current collector and other materials. For the present scenario, it can be noted that the membrane cost contributes to about 38% of the total capital cost which is expected to reduce to 20% in the future. The details of the estimates can be found elsewhere (Rozendal *et al*. 2008). Further, a comparison of the wastewater treatment economics using different technologies was reported (Table 6). The technologies compared were activated sludge (AS), anaerobic

Table 6 Comparison of estimated capital costs and product revenues among bioelectrochemical wastewater treatment (Rozendal *et al*.2008)

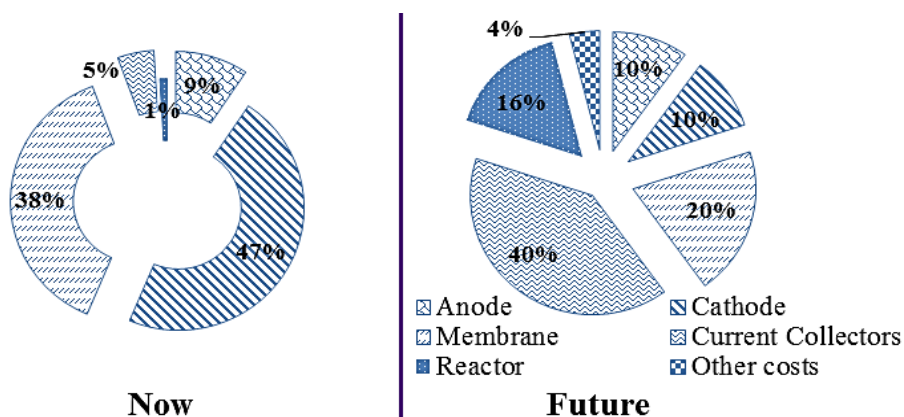| System	Product	Capital costs ($/kg COD)	Product revenue ($/kg COD)	Offset (product revenue minus capital costs) ($/kg COD)
AS	N/A	0.125	- 0.375	- 0.5
AD	CH_4	0.0125	0.125	0.125
MFCs	Electricity	8/0.4	0.25	- 0.25
MECs	H_2	8/0.4	0.75	0.25

Fig. 4 Estimated capital costs for bioelectrochemical systems: a) current; b) future*

* Estimated capital costs of BESs (single cell design; current density: 1000 A/m^3 reactor volume). The costs were either estimated based on materials currently used in laboratory systems (a) or on predicted future capital costs assuming less expensive substitute materials (b). The following cost assumptions were used: laboratory anode (graphite felt), 136$/m^2; laboratory platinum catalysed cathode, 680 $/m^2; laboratory membrane, 544$/m^2; laboratory current collectors, 34$/m^2; future substitute electrodes (graphite), 7$/m^2; future substitute membrane, 14 $/m^2; future substitute current collectors, 14 $/m^2; reactor, 5442$/m^3 reactor volume; other costs, 1360$/m^3 reactor volume. Lifetime assumptions: electrodes, membranes and current collectors, 5 yr; reactors and other materials, 25 yr. (euros converted using 2013-$ conversion factor)

digestion (AD), MFCs and MECs. It is expected that the AS does not produce any valuable form of energy, while AD, MFCs and MECs produce energy-rich biogas, bioelectricity, and high value hydrogen gas respectively. This comparison shows that AD and MECs have net positive revenues while MFCs have negative revenues indicating the need for further process development in terms of construction materials and product output rate. The economics of MDCs could even be worse since the technology has just been introduced. Further validation of the process technology at a higher scale is required to study its economic feasibility.

5. Conclusions

Bioelectrochemical systems hold great promise for the future as sustainable technologies to produce high energy/value products from waste streams originating from different sources. Recent advances and breakthroughs in scientific knowledge and research development in these technologies have been very encouraging and affirm their potential for their near future environmental remediation applications. MFCs have seen six orders of magnitude increase in power densities while the MECs were proven to produce a net energy gain of 2-3 times the energy input. In comparison, MDCs need to be developed alongside within near future since they are relatively new and further demonstrations are warranted to improve the energy generation and desalination capacities in these systems.

While none of these technologies are limited by the ability of the microorganisms to degrade the waste organic matter to produce valuable energy products, current capital and operating and maintenance costs for these technologies seem to be prohibitive (based on current economic analysis), indicating further developments and demonstrations in low cost membrane manufacturing or membrane-less operations, and further reduction in electrode costs to reduce the capital costs that make these systems affordable for domestic wastewater or high strength industrial wastewater treatment.

Acknowledgments

References

Ahn, Y. and Logan, B.E. (2010), "Effectiveness of domestic wastewater treatment using microbial fuel cells at ambient and mesophilic temperatures", *Bioresource Technol*., **101**(2), 469-475.

Barbose, G., Darghouth, N., Weaver, S. and Wiser, R. (2013), "Tracking the Sun VI: The Installed Price of Photovoltaics in the United States from 1998 to 2012", LBNL-6350E.

Biffinger, J.C., Ray, R., Little, B. and Ringeisen, B.R. (2007), "Diversifying biological fuel cell designs by use of nanoporous filters", *Environ*. *Sci*. *Technol*., **41**(4), 1444-1449.

Call, D. and Logan, B.E. (2008), "Hydrogen production in a single chamber microbial electrolysis cell lacking a membrane", *Environ*. *Sci*. *Technol*., **42**(9), 3401-3406.

Call, D.F., Wagner, R.C. and Logan, B.E. (2009), "Hydrogen production by Geobacter species and a mixed consortium in a microbial electrolysis cell", *Appl*. *Environ*. *Microb*., **75**(24), 7579-7587.

Cao, X., Huang, X., Liang, P., Xiao, K., Zhou, Y., Zhang, X. and Logan, B.E. (2009), "A new method for water desalination using microbial desalination cells", *Environ*. *Sci*. *Technol*., **43**(18), 7148-7152.

Chae, K., Choi, M., Ajayi, F., Park, W., Chang, I. and Kim, I. (2008), "Mass transport through a proton exchange membrane (Nafion) in microbial fuel cells", *Energ*. *Fuel*., **22**(1), 169-176.

Chen, X., Xia, X., Liang, P., Cao, X.X., Sun, H.T. and Huang, X. (2011), "Stacked microbial desalination cells to enhance water desalination efficiency", *Environ*. *Sci*. *Technol*., **45**, 2465-2470.

Cheng, S., Liu, H. and Logan, B.E. (2006), "Power densities using different cathode catalysts (Pt and CoTMPP) and polymer binders (Nafion and PTFE) in single chamber microbial fuel cells", *Environ*. *Sci*. *Technol*., **40**(1), 364-369.

Clauwaert, P. and Verstraete, W. (2009), "Methanogenesis in membraneless microbial electrolysis cells", *Appl*. *Microbiol*. *Biotechnol*., **82**(5), 829-836.

Du, Z., Li, H. and Gu, T. (2007), "A state of the art review on microbial fuel cells: A promising technology for wastewater treatment and bioenergy", *Biotechnol*. *Adv*., **25**(5), 464-482.

EIA 2009 (2009), CO_2 Emissions per Kilowatt Hour of Electricity Production (Retrieved on July 24, 2014). http://www.eia.doe.gov/cneaf/electricity/page/co2_report/co2report.html#electric2000

Fan, Y.Y., Hu, H.H. and Liu, H.H. (2007), "Enhanced coulombic efficiency and power density of air-cathode microbial fuel cells with an improved cell configuration", *J. Power Sources*, **171**(2), 348-354.

Fumatech (2013), Accessed online on December 28, 2013. http://www.fumatech.com/NR/rdonlyres/0FF1EDB0-DE8F-4601-AD33F7F1D37444/0/FuMaTech_fumasepMembranes.pdf

Geise, G., Hickner, M. and Logan, B. (2013), "Ionic resistance and permselectivity tradeoffs in anion exchange membranes", *ACS Appl*. *Mater*. *Interfaces*, **5**(20), 10294-10301.

Grzebyk, M. and Pozniak, G. (2005), "Microbial fuel cells (MFCs) with interpolymer cation exchange membranes", *Sep. Purif. Technol.*, **41**(3), 321-328.

Gude, V.G. (2015), "Energy and water autarky of wastewater treatment and power generation systems", *Renew. Sust. Energ. Rev.* DOI: 10.1016/j.rser.2015.01.055

Gude, V.G., Kokabian, B. and Gadhamshetty, V. (2013), "Beneficial bioelectrochemical systems for energy, water, and biomass production", *J. Microb. Biochem. Technol.*, **S6**, 005.

Hu, H., Fan, Y. and Liu, H. (2008), "Hydrogen production using single-chamber membrane-free microbial electrolysis cells", *Water Res.*, **42**(15), 4172-4178.

Huggins, T., Fallgren, P.H., Jin, S. and Ren, Z. (2013), "Energy and performance comparison of microbial fuel cell and conventional aeration treating of wastewater", *J. Microb. Biochem. Technol.*, **S6**, 002.

Jacobson, K.S., Drew, D.M. and He, Z. (2011a), "Use of a liter-scale microbial desalination cell as a platform to study bioelectrochemical desalination with salt solution or artificial seawater", *Environ. Sci. Technol.*, **45**(10), 4652-4657.

Jacobson, K.S., Drew, D.M. and He, Z. (2011b), "Efficient salt removal in a continuously operated upflow microbial desalination cell with an air cathode", *Bioresource Technol.*, **102**(1), 376-380.

Jikihara, A., Ohashi, R., Kakihana, Y., Higa, M. and Kobayashi, K. (2013), "Electrodialytic Transport Properties of Anion-Exchange Membranes Prepared from Poly(vinyl alcohol) and Poly(vinyl alcohol-co-methacryloyl aminopropyl trimethyl ammonium chloride)", *Membranes*, **3**(1), 1-15.

Kiely, P.D., Rader, G., Regan, J.M. and Logan, B.E. (2011a), "Long-term cathode performance and the microbial communities that developin microbial fuel cells fed different fermentation endproducts", *Bioresource Technol.*, **102**(1), 361-366.

Kiely, P.D., Cusick, R., Call, D.F., Selembo, P.A., Regan, J.M. and Logan, B.E. (2011b), "Anode microbial communities produced by changing from microbial fuel cell to microbial electrolysis cell operation using two different wastewaters", *Bioresource Technol.*, **102**(1), 388-394.

Kim, Y. and Logan, B.E. (2011), "Series assembly of microbial desalination cells containing stacked electrodialysis cells for partial or complete seawater desalination", *Environ. Sci. Technol.*, **45**(13), 5840-5845.

Kim, Y. and Logan, B.E. (2013), "Microbial desalination cells for energy production and desalination", *Desalination*, **308**, 122-130.

Kim, J.R., Cheng, S., Oh, S.E. and Logan, B.E. (2007), "Power generation using different cation, anion, and ultrafiltration membranes in microbial fuel cells", *Environ. Sci. Technol.*, **41**(3), 1004-1009.

Kiran Kumar, A., Venkateswar Reddy, M., Chandrasekhar, K., Srikanth, S. and Venkata Mohan, S. (2012), "Endocrine disruptive estrogens role in electron transfer: Bio-electrochemical remediation with microbial mediated electrogenesis", *Bioresource Technol.*, **104**, 547-556.

Kokabian, B. and Gude, V.G. (2013), "Photosynthetic microbial desalination cells (PMDCs) for clean energy, water and biomass production", *Environ. Sci. Process. Impact.*, **15**(12), 2178-2185.

Kokabian, B. and Gude, V.G. (2015), "Sustainable photosynthetic biocathode in microbial desalination cells", *Chem. Eng. J.*, **262**, 958-965.

Lawrence Berkeley National Laboratory (2013), Accessed online on December 30, 2013. http://newscenter.lbl.gov/news-releases/2013/08/12/installed-price-of-solar-photovoltaic-systems-in-the-u-s-continues-to-decline-at-a-rapid-pace/

Leong, J., Daud, W., Ghasemi, M., Liew, K. and Ismail, M. (2013), "Ion exchange membranes as separators in microbial fuel cells for bioenergy conversion: A comprehensive review", *Renew. Sust. Energ. Rev.*, **28**, 575-587.

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

Liu, H. and Logan, B.E. (2004), "Electricity generation using an air-cathode single chamber microbial fuel cell in the presenceand absence of a proton exchange membrane", *Environ. Sci. Technol.*, **38**(14), 4040-4046.

Logan, B.E. (2008), *Microbial Fuel Cells*, Wiley Publishers, Hoboken, NJ, USA.

Logan, B.E. (2009), "Exoelectrogenic bacteria that power microbial fuel cells", *Nat. Rev. Microbiol.*, **7**,

    375-381.

Logan, B.E., Hamelers, H.V.M., Rozendal, R., Schroder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W. and Rabaey, K. (2006), "Microbial fuel cells: Methodology and technology", *Environ. Sci. Technol.*, **40**(17), 5181-5192.

Logan, B.E., Call, D., Cheng, S., Hamelers, H.V., Sleutels, T.H., Jeremiasse, A.W. and Rozendal, R.A. (2008), "Microbial electrolysis cells for high yield hydrogen gas production from organic matter", *Environ. Sci. Technol.*, **42**(23), 8630-8640.

Luo, H., Ren, Z. and Jenkins, P. (2011), "Concurrent desalination and hydrogen generation using microbial electrolysis and desalination cells", *Environ. Sci. Technol.*, **45**(1), 340-344.

Luo, H., Xu, P., Roane, T.M., Jenkins, P.E. and Ren, Z. (2012a), "Microbial desalination cells for improved performance in wastewater treatment, electricity production, and desalination", *Bioresour. Technol.*, **105**, 60-66.

Luo, H., Xu, P., Jenkins, P.E. and Ren, Z. (2012b), "Ionic composition and transport mechanisms in microbial desalination cells", *J. Membr. Sci.*, **409-410**, 16-23.

Luo, H., Ren, Z. and Xu, P. (2012c), "Long-term performance and characterization of microbial desalination cells in treating domestic wastewater", *Bioresource Technol.*, **120**, 187-193.

McCarty, P.L. and Rittmann, B.E. (2001), *Environmental Biotechnology: Principles and Applications*, McGraw-Hill, New York, NY, USA.

McCarty, P.L., Bae, J. and Kim, J. (2011), "Domestic wastewater treatment as a net energy producer – Can this be achieved?", *Environ. Sci. Technol.*, **45**, 7100-7106.

Mehanna, M., Saito, T., Yan, J., Hickner, M., Cao, X., Huang, X. and Logan, B.E. (2010a), "Using microbial desalination cells to reduce water salinity prior to reverse osmosis", *Energy Environ. Sci.*, **3**(), 1114-1120.

Mehanna, M., Kiely, P.D., Call, D.F. and Logan, B.E. (2010b), "Microbial electrodialysis cell for simultaneous water desalination and hydrogen gas production", *Environ. Sci. Technol.*, **44**, 9578-9583.

Morel, A., Zuo, K., Xia, X., Wei, J., Luo, X., Liang, P. and Huang, X. (2012), "Microbial desalination cells packed with ion-exchange resin to enhance water desalination rate", *Bioresource Technol.*, **118**, 43-48.

Nevin, K.P., Richter, H., Covalla, S.F., Johnson, J.P., Woodard, T.L., Orloff, A.L., Jia, H., Zhang, M. and Lovley, D.R. (2008), "Power output and columbic efficiencies from biofilms of Geobacter sulfurreducens comparable to mixed community microbial fuel cells", *Environ. Microbial.*, **10**(10), 2505-2514.

Oh, S.E. and Logan, B.E. (2006), "Proton exchange membrane and electrode surface areas as factors that affect power generation in microbial fuel cells", *Appl. Microbiol. Biotechnol.*, **70**(2), 162-169.

Ping, Q., He, Z., Cohen, B. and Dosoretz, C. (2013), "Long-term investigation of fouling of cation and anion exchange membranes in microbial desalination cells", *Desalination*, **325**, 48-55.

Qu, Y., Feng, Y., Wang, X., Liu, J., He, W. and Logan, B.E. (2012), "Simultaneous water desalination and electricity generation in a microbial desalination cell with electrolyte recirculation for pH control", *Bioresour. Technol*, **106**, 89-94.

Ringeisen, B.R., Henderson, E., Wu, P.K., Pietron, J., Ray, R., Little, B., Biffinger, J.C. and Jones-Meehan, J.M. (2006), "High power density from a miniature microbial fuel cell using Shewanella oneidensis DSP10", *Environ. Sci. Technol.*, **40**(8), 2629-2634.

Rosenbaum, M., He, Z. and Angenent, L.T. (2010), "Light energy to bioelectricity: photosynthetic microbial fuel cells", *Curr. Opin. Chem. Biol.*, **21**(3), 259-264.

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

Sleutels, T.H., Hamelers, H.V., Rozendal, R.A. and Buisman, C.J. (2009), "Ion transport resistance in microbial electrolysis cells with anion and cation exchange membranes", *Int. J. Hydrogen Energy*, **34**(9), 3612-3620.

Sustarsic, M. (2009), "Wastewater treatment: Understanding the activated sludge process", CEP, 26-29.

U.S. EPA (2012), State and Local Climate and Energy Program: Water/Wastewater, Accessed: on January

01, 2014, Available at: http://www.epa.gov/statelocalclimate/local/topics/water.html

Visvanathan, C. and Abeynayaka, A. (2012), "Developments and future potentials of anaerobic membrane bioreactors (AnMBRs)", *Membr. Water Treat., Int. J.*, **3**(1), 1-23.

Wang, X., Feng, Y., Liu, J., Lee, H., Li, C., Li, N. and Ren, N. (2010), "Sequestration of CO_2 discharged from anode by algal cathode in microbial carbon capture cells (MCCs)", *Biosens and Bioelectron.*, **25**(12), 2639-2643.

Yang, S., Jia, B. and Liu, H. (2009), "Effects of the Pt loading side and cathode biofilm onthe performance of a membrane-less and single-chamber microbial fuel cell", *Bioresour. Technol.*, **100**, 1197-1202.

Yaroslavtsev, A.B. and Nikonenko, V.V. (2009), "Ion-exchange membrane materials: Properties, modification, and practical application", *Nanotechnol. Russia*, **4**(3-4), 137-159.

Yee, R.S.L., Rozendal, R.A., Zhang, K. and Ladewig, B.P. (2012), "Cost effective cationexchange membranes: A review", *Chem. Eng. Res. Des.*, **90**(7), 950-959.

Yu, E.H., Cheng, S., Scott, K. and Logan, B.E. (2007), "Microbial fuel cell performance with non-Pt cathode catalysts", *J. Power Sources*, **171**(2), 275-281.

Zhang, B. and He, Z. (2012), "Integrated salinity reduction and water recovery in an osmotic microbial desalination cell", *RSC Adv.*, **2**(8), 3265-3269.

Zhang, L., Liu, C., Zhuang, L., Li, W., Zhou, S. and Zhang, J. (2009), "Manganese dioxide as an alternative cathodic catalyst to platinum in microbial fuel cells", *Biosens. Bioelectron*, **24**(9), 2825-2829.

Zhang, F.F., Chen, M.M., Zhang, Y.Y. and Zeng, R.J. (2012), "Microbial desalination cells with ion exchange resin packed to enhance desalination at low salt concentration", *J. Membr. Sci.*, **417-418**, 28-33.

Zhao, F., Harnisch, F., Schröder, U., Scholz, F., Bogdanoff, P. and Herrmann, I. (2005), "Application of pyrolysed iron (II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells", *Electrochem. Commun.*, **7**(12), 1405-1410.

Zhuang, L., Zhou, S., Wang, Y., Liu, C. and Geng, S. (2009), "Membrane-less cloth cathode assembly (CCA) for scalable microbial fuel cells", *Biosens. Bioelectron.*, **24**(12), 3652-3656

Zuo, Y., Cheng, S., Call, D. and Logan, B.E. (2007), "Tubular membrane cathodes for scalable power generation in microbial fuel cells", *Environ. Sci. Technol.*, **41**(9), 3347-3353.

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

Zuo, K.K., Yuan, L.L., Wei, J.J., Liang, P.P. and Huang, X.X. (2013), "Competitive migration behaviors of multiple ions and their impacts on ion-exchange resin packed microbial desalination cell", *Bioresource Technol.*, **146**, 637-642.