Anaerobes in Bioelectrochemical Systems

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Abstract

In bioelectrochemical systems (BES), the catalytic activity of anaerobic microorganisms generates electrons at the anode that can be used, for example, for the production of electricity or chemical compounds. BES can be used for various purposes, including wastewater treatment, production of electricity, fuels and chemicals, biosensors, bioremediation and desalination. Electrochemically active microorganisms are widely present in the environment and they can be found, i.e., from sediment, soil, compost, wastewaters and their treatment plants. Exoelectrogens are microorganisms capable of donating/accepting electrons to/from the anode electrode and are mainly responsible for current generation/use in BES. However, current generation from fermentable substrates often requires also the presence of electrochemically inactive microorganisms that breakdown the complex substrates into metabolites that can be further utilized by exoelectrogens. The growth and electron transfer efficiency of anaerobes depend on several parameters, such as system architecture, electrode material and porosity, electrode potential and external resistance, pH, temperature, substrate concentration, organic loading rate and ionic strength. In this chapter, the principles, microbiology and selective factors of bioelectrochemical systems are reviewed. The anaerobic microorganisms and their electron transfer mechanisms at the anode and cathode are described and future aspects are briefly discussed.

Keywords: Bioelectrochemical system, Anaerobe, Exoelectrogen

Abbreviations

BES	Bioelectrochemical system
BOD	Biological oxygen demand
CE	Coulombic efficiency
MDC	Microbial desalination cell
MEC	Microbial electrolysis cell
MES	Microbial electrosynthesis
MFC	Microbial fuel cell
OLR	Organic loading rate
VFA	Volatile fatty acid

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1. Introduction

Bioelectrochemical systems (BES) have gained increasing attention in the past decade. They can be used for various purposes, including production of electricity, fuels and chemicals, wastewater treatment, biosensors, bioremediation and desalination. In BES, the catalytic activity of anaerobic microorganisms is used at the anode to generate current. At the cathode, electrons can be accepted either by anaerobic microorganisms that utilize them, e.g., for the reduction of protons to hydrogen or abiotically by, e.g., oxygen. Aerobic microorganisms (He and Angenent 2006, Rosenbaum et al. 2011) and enzymes (Rubenwolf et al. 2011, Lapinsonniére et al. 2012) can also be used as biocatalysts at the cathode but are not in the scope of this chapter and thus, will not be further discussed. There are two main type of BES, microbial fuel cells (MFC) in which the anaerobic oxidation of organic matter is used for the production of electricity and microbial electrolysis cells (MEC) where applied electricity is required to overcome thermodynamically unfavorable biotic or abiotic reactions at the cathode.

Electrochemically active microorganisms are widely present in the environment and they can be found, for example, from sediment, soil, compost, wastewaters and their treatment plants. The most studied electrochemically active pure cultures are *Geobacter* and *Shewanella* species.

Microorganisms capable of generating and transferring electrons outside of the cell to the anode are called exoelectrogens (Logan and Regan 2006) and are mainly responsible for current generation in BES. These anaerobic bacteria can use the anode electrode as electron acceptor either through direct contact via c-type cytochromes or nanowires or via electron shuttling compounds called mediators. However, the current generation from fermentable substrates, such as glucose or wastewaters, often requires also the presence of electrochemically inactive microorganisms that breakdown the complex substrates into organic acids or alcohols that can be more readily utilized for current production by exoelectrogens. Anaerobes have also been shown to be capable of accepting electrons from the cathode electrode. Although the electron accepting mechanisms at the cathode are still fairly unknown, it has been shown that enzymes like c-type cytochromes and hydrogenases are involved in the process. The growth of anaerobes and their electron transfer efficiencies depend on several parameters, including system architecture, electrode material and porosity, electrode potential and external resistance, pH, temperature, substrate concentration, organic loading rate and ionic strength.

Bioelectrochemical systems are an attractive approach to capture the chemical energy stored in waste streams containing easily degradable organics and to convert this energy into valuable products. BES has many advantages over traditional wastewater treatment systems, including energy savings due to lack of aeration, simultaneous production of electricity and less sludge production. In addition, MECs can be used for the production of valuable chemicals, bioremediation and CO_2 fixation. Current densities of laboratory-scale BES approach values that would be suitable for practical implementation for wastewater treatment. Still, more studies with real wastewaters are required to develop strategies for improving the degradation of complex substrates, controlling the microbial reactions and optimizing the performance of full-scale BES (Rozendal et al. 2008).

In this chapter, the principles, microbiology and selective factors of bioelectrochemical systems are reviewed. The anaerobic microorganisms and their electron transfer mechanisms at the anode and cathode are described, and future aspects are briefly discussed.

2. Bioelectrochemical Systems

2.1 Principles of Bioelectrochemical Systems

There are various applications of bioelectrochemical systems, where anaerobes are used as biocatalysts for the production of electrons from biodegradable materials at the anode and/or for the utilization of electrons at the cathode (Table 1). BES traditionally consists of anode and cathode chambers separated with a selective membrane or separator. At the anode, microorganisms anaerobically oxidize organic or inorganic materials producing electrons that generate current when transferred from anode to cathode electrode through an external load. Simultaneously, produced protons are transferred through the separator to the cathode. At the cathode, electrons and protons react with electron acceptor either chemically or biologically. The generated current can be directly utilized in the form of electricity, in which case the bioelectrochemical systems are called microbial fuel cells. Although MFCs often have abiotic cathode where, e.g., oxygen reduction completes the

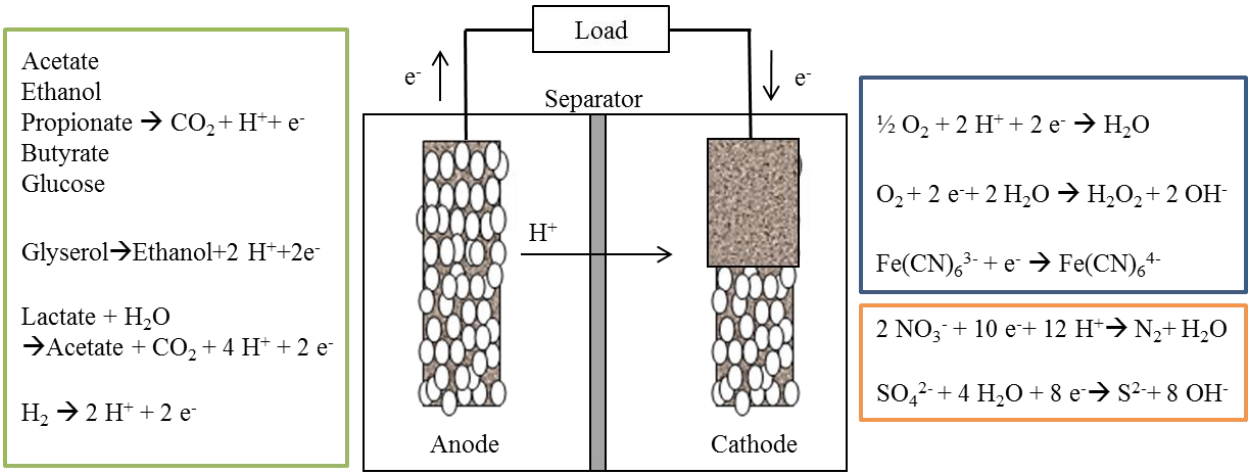
electron transfer, also biological anaerobic cathodes can be utilized (Figure 1.A). One example of anaerobic biocathode is the denitrification of nitrate into nitrite (Park et al. 2005) or directly to nitrogen (Clauwaert et al. 2007).

Table 1 Different applications of bioelectrochemical systems with anaerobic microorganisms at the anode and/or at the cathode.

BES	Function / Purpose	Reference
Microbial fuel cell (MFC)	Electricity production	Rabaey et al. 2003
	Electricity production and denitrification at the cathode	Clauwaert et al. 2007, Lefebvre et al. 2008
	Biological oxygen demand (BOD) sensor	Chang et al. 2004
Microbial desalination cell (MDC)	NaCl removal from saline waters and simultaneous electricity production	Cao et al. 2009
Microbial electrolysis cell (MEC)	H_2 or CH_4 production at the cathode with applied voltage	Rozendal et al. 2008, Chae et al. 2010
Microbial electrosynthesis (MES)	Production of organics at the cathode with applied voltage	Nevin et al. 2010, Steinbusch et al. 2010
Pollutants removal	Bioremediation of organic / inorganic compounds with or without applied voltage	Aulenta et al. 2007, Butler et al. 2010
Resource recovery	Recovery of metals at abiotic cathode with or without applied voltage	ter Heijne et al. 2010, Modin et al. 2012

Instead of producing electricity, current can be applied for the system to produce different compounds at the cathode. By adding current, thermodynamic limitations are overcome and the otherwise unfavorable biological reactions are supported energetically (Zhang and Angelidaki 2014). In microbial electrolysis cells (MEC, Figure 1.B), protons combine at the cathode with electrons or CO_2 to produce hydrogen or methane, respectively. The reactions can be abiotic (Liu et al. 2005a) or biotic (Rozendal et al. 2008, Cheng et al. 2009). One form of MEC are microbial electrosynthesis cells (MES; Rabaey et al. 2011), where CO_2 or other carbon sources are reduced to, e.g. acetate or ethanol (Nevin et al. 2010, Steinbusch et al. 2010, Sharma et al. 2013).

A



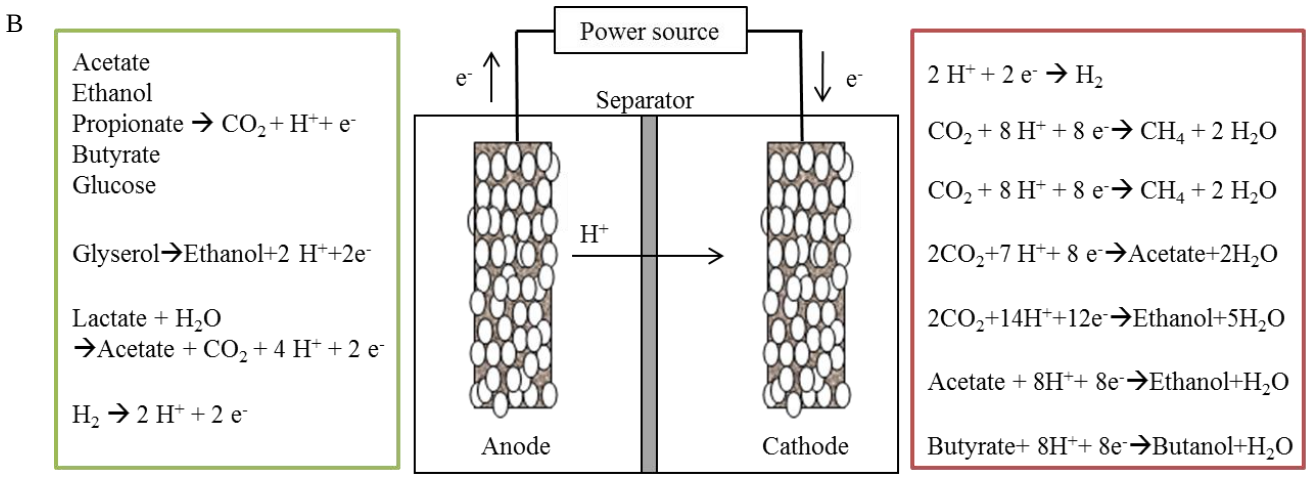


Fig. 1 Schematic diagrams of A) two-chamber microbial fuel cell with abiotic (blue) or biotic (orange) cathode, and B) production and synthesis of chemicals in microbial electrochemical cells or through microbial electrosynthesis at the cathode.

2.2 Bioelectrochemical Calculations

In bioelectrochemical systems, oxidation-reduction reactions and their biological standard potentials (Figure 2) at the anode and cathode determine whether the whole cell potential is positive, i.e. electricity production, or negative when applied voltage is required to drive the reactions. Gibbs free energy of reaction in standard conditions ($\Delta G^{0'}_r$) (available in Heijnen 1999) can be used to calculate the electrode potentials at standard conditions by using Nernst equation (Eq. 1), where $E^0_{an/cat}$ is the standard reduction potential (Eq. 2), R the universal gas constant (8.31447 J/mol K), T the temperature (K), n the number of electrons per reaction mol, F the Faraday's constant (96 485 C/mol), and [P] and [S] the concentrations of products and substrates, respectively.

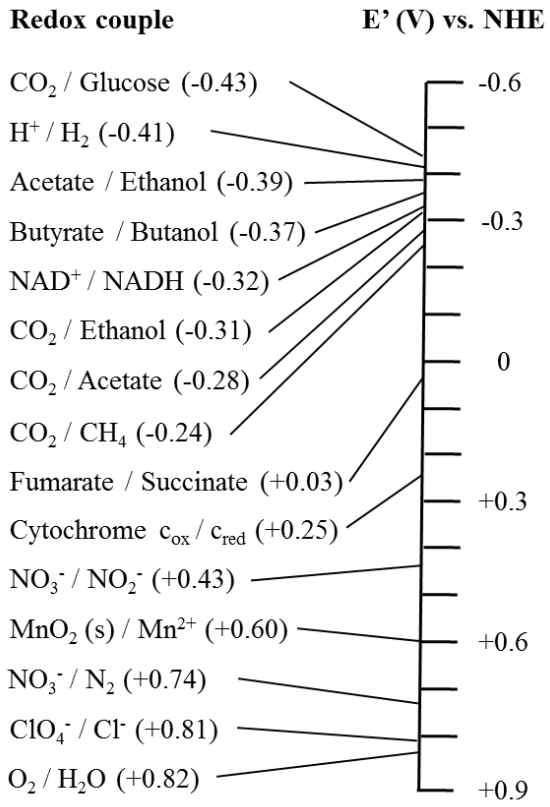


Fig. 2 Biological redox tower of electron donors and acceptors at pH 7.

The whole cell voltage (E_{eq}) is determined by the difference between the anodic (E_{an}) and cathodic (E_{cat}) redox potentials (Eq. 3). Thus, the higher the cathodic redox potential and the lower the anodic redox potential, the higher the whole cell voltage (MFC). If the redox potential at the cathode is lower than at the anode, voltage has to be applied to the system (MEC). The performance of the BES is often informed as the current (I) flowing through the system. This can be further converted into current density calculated based on the area of the anode electrode (I_{an}) or cell volume (I_v). One way to analyze the performance of BES is to calculate Coulombic efficiency (CE, Eq. 4) that gives the ratio of total electrons derived from the oxidized substrate for current production to maximum electrons present in the added substrate. In Eq. 4, C_p is calculated by integrating the current over time ($\int I\,dt$) and C_t according to $C_t = n \cdot F \cdot c \cdot V$, where c is the concentration of substrate (mol/L) and V the liquid volume at the anode (L).

$$E = E^{0}_{an/cat} - \frac{RT}{nF} ln\left(\frac{[P]^{x}}{[S]^{y}}\right) \quad (1)$$

$$E^{o}_{an/cat} = \frac{-\Delta G^{o'}_{r}}{nF} \quad (2)$$

$$E_{eq} = E_{cat} - E_{an} \quad (3)$$

$$CE = \frac{C_p}{C_t} \cdot 100\% \quad (4)$$

Theoretically, all the biochemical energy in the substrate can be converted into electricity. In practice, however, losses occur due to microbial growth and BES configuration. Electrons can be lost due to activation, ohmic, and mass transport losses. Activation losses occur due to the activation barrier present in the substrate or electron acceptor (Logan et al. 2006). These losses can be decreased by enhancing the biofilm thickness (Rabaey et al. 2007) or by increasing the electrode surface areas, temperature or substrate concentration (Rismani-Yazdi et al. 2008), which enhances the electron transfer between anaerobes and the electrode (Pham et al. 2009). Ohmic losses are associated with the electron and proton flows through the electrodes, electrolytes and interconnections (such as separators) (Clauwaert et al. 2008a, Rismani-Yazdi et al. 2008). Ohmic losses can be minimized by selecting highly conductive electrodes, improving contacts, decreasing the distance between anode and cathode electrodes, or by increasing solution conductivity (Liu et al. 2005a, Logan et al. 2006, Clauwaert et al. 2008b). Substrate diffusion or product removal close to the electrodes causes mass transport losses (Clauwaert et al. 2008a). For example, a thick biofilm may prevent diffusion at the electrode (Behera et al. 2010). Mass transport losses can be decreased by optimizing the operating conditions and geometry of BES or by choosing more efficient electrode materials (Rismani-Yazdi et al. 2008).

3. Anaerobic Microorganisms at the Anode

The current at the anode of bioelectrochemical systems is produced by anaerobic bacteria called exoelectrogens that are able to transfer electrons outside the cell to insoluble electron acceptor, such as anode electrode. Exoelectrogens have been shown to convert, e.g., H_2 (Bond and Lovley 2003), acetate (Zuo et al. 2008), lactate (Ringeisen et al. 2006), ethanol (Zuo et al. 2008) and glucose (Chaudhuri and Lovley 2003, Chung and Okabe 2009a) directly to current. However, direct conversion of more complex substrates, such as wastewater, into current is not possible and even the oxidation of glucose or lactate to current often requires syntrophic interaction of different bacterial species (Freguia et al. 2008, Miller and Oremland 2008, Xing et al. 2009). The fermentable substrates are first oxidized into soluble metabolites, volatile fatty acids (VFAs) and alcohols that are further converted to electrons, protons and CO_2 by exoelectrogens. In addition to producing current, the utilization of metabolites by exoelectrogens decreases feedback inhibition to fermentative bacteria (Kiely et al. 2011). To optimize current production, the competing anaerobic biological reactions have to be avoided. These include methanogens and homoacetogens, fermentative bacteria (if not leading to products amenable to exoelectrogens), nitrate reducers, aerobic microorganisms (if oxygen is present), and sulfate reducers that do not directly compete with current production but require carbon for their growth (Borole et al. 2011).

When bacteria oxidize organic or inorganic materials (Table 2), they have to dispose the produced electrons. In aerobic conditions, electrons are donated to oxygen that has the highest redox potential of electron acceptors (Figure 2). In anaerobic conditions, possible electron acceptors include nitrate, sulfate, carbon dioxide, ferric iron, fumarate as well as anode electrode. In BES, the competing electron acceptors are removed so that the anode electrode is the sole means for bacteria to complete respiration. The electron transfer mechanisms of exoelectrogens originate from nature, where e.g.

solid iron or manganese oxides can be used as electron acceptors by metal-reducing bacteria (El-Naggar et al. 2008, Lovley 2011). For example, metal-reducing bacteria *Geobacter sulfurreducens* (Bond and Lovley 2003) and *Shewanella putrefaciens* (Kim et al. 1999) have been shown to donate electrons directly to anode electrode.

Table 2 Possible electron donors at the bioanode.

Electron donor	Reaction	Reference
Hydrogen	$H_2 \rightarrow 2\ H+ + 2\ e-$	Bond and Lovley 2003
Acetic acid	$CH_3COOH + 4\ H_2O \rightarrow 2\ HCO_3^- + 10\ H^+ + 8\ e^-$	Zuo et al. 2008
Lactic acid	$C_2H_5OCOOH + 6\ H_2O \rightarrow 3\ HCO_3^- + 15\ H^+ + 12\ e^-$	Kim et al. 2002
Butyric acid	$C_3H_7COOH + 10\ H_2O \rightarrow 4\ HCO_3^- + 24\ H^+ + 20\ e^-$	Liu et al. 2005a
Propionic acid	$C_2H_5COOH + 7\ H_2O \rightarrow 3\ HCO_3^- + 17\ H^+ + 14\ e^-$	Chae et al. 2009
Xylose	$C_5H_{10}O_5 + 10\ H_2O \rightarrow 5\ HCO_3^- + 25\ H^+ + 20\ e^-$	Mäkinen et al. 2013
Glucose	$C_6H_{12}O_6 + 12\ H_2O \rightarrow 6\ HCO_3^- + 30\ H^+ + 24\ e^-$	Rabaey et al. 2003
Sulfur compounds	$H_2S \rightarrow S^0 + 2\ H^+ + 2\ e^-$ $HS^- \rightarrow S^0 + 2\ H^+ + 2\ e^-$	Zhao et al. 2009

The selection of efficient exoelectrogenic communities is crucial since the anaerobic metabolism and the rate and nature of electron transfer determine the anode performance (Schröder 2007). Thus, the anaerobic culture affects the biofilm formation on the electrode, internal resistance of the BES and the overall current generation (Sun et al. 2009, Jiang et al. 2010). Both pure and mixed cultures can be used for current production in BES. Exoelectrogenic pure cultures are usually capable of utilizing only certain substrates (Catal et al. 2008). Mixed cultures are often preferred over pure cultures since they (i) are more suitable for wastewater treatment, (ii) allow wider substrate versatility due to presence of both acidophilic and exoelectrogenic microorganisms, (iii) have higher resistance against process disturbances, (iv) often give higher current outputs, and (v) obligate aerobes present minimize the effects of oxygen diffusion through separator (Angenent et al. 2004, Chang et al. 2006, Du et al. 2007). However, pure culture studies are required to understand in detail electron transfer mechanisms and metabolism of microorganisms in BES and to evaluate how dominant strains evolve in mixed cultures in order to optimize BES performance (Han et al. 2010).

3.1 Pure Cultures

Direct electron transfer by bacteria attached to the anode electrode was first reported in the late 1990s by Kim et al. (1999) with a pure culture of *Shewanella putrefaciens*. Exoelectrogens are found from many bacterial groups including metal-reducing bacteria, such as *G. sulfurreducens* (Bond and Lovely 2003) and *S. putrefaciens* (Kim et al. 1999), sulfate-reducing bacteria, such as *Desulfobulbus propionicus* (Holmes et al. 2004a), and denitrifying bacteria, e.g. *Orchobactrum anthropic* (Zuo et al. 2008) and *Comamonas denitrificans* (Xing et al. 2010). Known pure exoelectrogenic cultures and their currently known electron transfer mechanisms and substrates used for current generation are listed in Table 3. Most known exoelectrogens are gram-negative bacteria but a few electrochemically active gram-positive bacteria have also been recognized. First evidences on direct electron transfer by gram-positive bacteria *Thermincola* sp. and *Thermincola ferriacetica* were reported by Wrighton et al. (2008) and Marshall and May (2009), respectively. Direct metabolism of carbohydrates into electricity is rare (Choi et al. 2004, Rezaei et al. 2009). For example, in addition to current *Lactococcus lactis* produced lactate and smaller amounts of acetate and pyruvate from glucose

(Freguia et al. 2009), while current production from cellulose by *Enterobacter cloacae* resulted in accumulation of many VFAs and alcohols with acetate as the main by-product (Rezaei et al. 2009).

Table 3 Pure cultures of exoelectrogenic bacteria cultures, their substrate versatility and proposed electron transfer mechanisms (without added external mediators).

Bacterium	Substrate(s)	Electron transfer mechanism	Reference
Aeromonas hydrophila	Yeast extract	c-type cytochromes[a]	Pham et al. 2006
Bacillus selenitireducens	Lactate	nr	Miller and Oremland 2008
Clostridium butyricum	Glucose	nr	Park et al. 2001
Comamonas denitrificans	Acetate	nr	Xing et al. 2010
Deltasulfuromonas acetoxidans	Acetate	nr	Bond et al. 2002
Desulfobulbus propionicus	Lactate, propionate, puryvate, H_2	Direct	Holmes et al. 2004a
Enterobacter cloacea	Sucrose, glycerol, glucose, cellulose	nr	Rezaei et al. 2009
Geobacter sulfurreducens	H_2, Acetate	c-type cytochromes, nanowires	Bond and Lovley 2003, Reguera et al. 2005, Holmes et al. 2006
Geothrix fermentas	Acetate, propionate, malate, lactate, succinate	Excreted electron shuttle	Bond and Lovley 2005
Geopsychrobacter electrodiphilus	Acetate, malate, fumarate, citrate	c-type cytochromes	Holmes et al. 2004b
Haloferax volcanii	Yeast extract + peptone	nr	Abrevaya et al. 2011
Klebsiella pneumoniae	Starch, glucose	Direct[a]	Zhang et al. 2008
Lactococcus lactis	Glucose	Excreted electron shuttle, soluble quinone	Freguia et al. 2009
Natrialba magadii	Yeast extract	nr	Abrevaya et al. 2011
Ochrobactrum anthropic	Acetate, lactate, propionate, butyrate, glucose, sucrose, cellobiose, glycerol, ethanol	nr	Zuo et al. 2008
Pseudomonas sp.	Tryptone and yeast extract	Excreted electron shuttle, phenazine-1-carboxamide	Pham et al. 2008
Rhodoferax ferrireducens	Glucose	nr	Liu and Li 2007
Rhodopseudomonas palustris	Acetate, lactate, ethanol, yeast extract, valerate, fumarate, glycerol, butyrate, propionate, thiosulfate	Direct[a]	Xing et a. 2008
Shewanella japoinica	Sucrose	Excreted electron shuttles	Biffinger et al. 2011
Shewanella marisflavi	Lactate	nr	Huang et al. 2010
Shewanella oneidensis	Lactate	Nanowire	Gorby et al. 2006, Ringeisen et al. 2006
Shewanella putrefaciens	Lactate	Outer membrane cytochromes	Kim et al. 1999, Kim et al. 2002
Thermincola sp.	Acetate	Direct[a]	Wrighton et al. 2008
Thermincola ferriacetica	Acetate	Direct[a]	Marshall and May 2009

[a] suggested, nr = nor reported

3.1.2 Mixed Cultures

Current producing microbial communities can be enriched and isolated from different natural and industrial environments, including anaerobic sludge from wastewater treatment plant (Oh and Logan 2005, You et al. 2006) and reactor treating brewery waste (Jong et al. 2006), domestic wastewater (Liu and Logan 2004, Jiang et al. 2010, Zhang et al. 2011), paper recycling wastewater (Huang and Logan 2008), compost (Carver et al. 2011, Nercessian et al. 2012, Mäkinen et al. 2013), cow rumen, (Rismani-Yazdi et al. 2007), soil (He and Angenent 2006, Ishii et al. 2008), sediment (Mathis et al. 2008, Huang et al. 2010), and river water (Phung et al. 2004). During the enrichment of exoelectrogenic cultures, the inhibition of methanogens is crucial since they compete from the same organic substrate with exoelectrogens and are the most critical cause decreasing Coulombic efficiency in BES (Chae et al. 2010). Methanogens can be inhibited, e.g., by initial selection of pH and buffer concentrations (Zhu and Béland 2006), periodic aeration (Freguia et al. 2008), and controlled substrate loading due to increase in the number of methanogens at higher substrate loadings (He et al. 2005). Rismani-Yazdi et al. (2013) showed that methanogenesis in MFCs stopped over time and performance of MFC improved without any need of methanogenic inhibition.

The microbial communities in MFCs usually contain *Proteobacteria* and *Firmicutes* (Rismani-Yazdi et al. 2007, Chung and Okabe 2009b). The bacterial composition depends on the original culture and substrate used for enrichment. With fermentable substrates more diverse cultures are enriched than with non-fermentable substrates, which enhances the fermentation of sugars and more complex substrates (Jung and Regan 2007, Rismani-Yazdi et al. 2007). These diverse cultures contain fermentative bacterial genera including *Clostridium* (Cheng et al. 2011), *Rhodopseudomonas* (Xing et al. 2009) and *Escherichia* and *Bacteroides* (Mäkinen et al. 2013) when fed with cellulose, glucose and xylose, respectively. Gram-negative bacteria, such as *G. sulfurreducens* (Kiely et al. 2011), often dominate the exoelectrogenic communities (Chang et al. 2006) and generally result in higher current production than Gram-positive bacteria (Borole et al. 2011). Although Gram-negative bacteria are most often associated with current generation, also Gram-positive bacteria have been shown to transfer electrons to the anode electrode (Wrighton et al. 2008).

3.2 Electron Transfer Mechanisms

For current to be produced in BES, electrons have to be transferred from inside of the cell membrane to its outside and further to the anode electrode. The intercellular electron transfer can occur through physical transfer with reduced compounds or via electron hopping across the cell membrane using membrane bound redox enzymes (Schröder 2007). Figure 3 shows examples of proposed intercellular electron transfer mechanisms that start from NADH derived from substrate oxidation. The disposal of electrons by *G. sulfurreducens* is proposed to occur via different cytochromes (OmcS, OmcB, Ppca, MacA) (Lovley 2008). In *S. oneidensis*, outer surface cytochromes (OmcA, MtrC) as well as other proteins are involved in intercellular electron transfer (Geelhoed et al. 2010). Electron transfer to the anode electrode occurs only if other electron acceptors, e.g. oxygen, sulfate, nitrate or fumarate are not present.

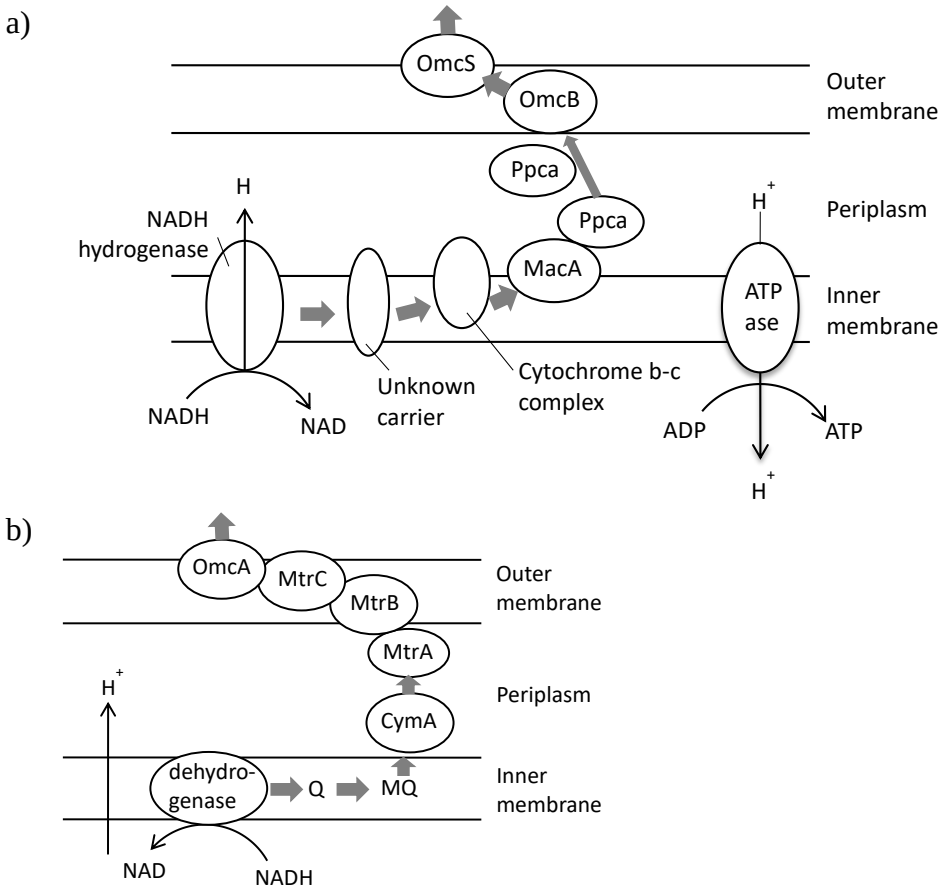


Fig. 3 Proposed intercellular electron transport system in a) *G. sulfurreducens* (Lovley 2008) and b) *S. oneidensis* (Geelhoed et al. 2010).

Several electron transfer mechanisms from bacterial cell to the electrode have been proposed (Figure 4). In direct electron transfer, exoelectrogens have to be in close contact with the electrode and thus, form a monolayered or multilayered biofilm on the anode. Direct electron transfer requires either the utilization of electrically active membrane-bound enzymes, such as c-type cytochromes (Lies et al. 2005, Holmes et al. 2006), or nanowires that can transfer electrons also from longer distances (Reguera et al. 2005). In addition to current generation, nanowires also play a structural role in biofilm formation (Reguera et al. 2007). Electrons from planktonic microorganisms as well as inside biofilm can be transferred to the anode with endogenous or exogenous electron shuttles called mediators (Marsili et al. 2008, Srikanth et al. 2008, Marsili et al. 2010). Exogenous, i.e. added mediators, include humic acids, thionine, viologens, methylene blue, and sulfur species (Chang et al. 2006, Stams et al. 2006). However, synthetic mediators are often expensive and even toxic, which limits their use in BES (Gil et al. 2003). Some bacteria can secret electron shuttles (i.e. endogenous mediators). For example, *Shewanella* sp. can produce riboflavins (Reguera et al. 2006), *L. lactis* quinones (Freguia et al. 2009), and *Pseudomonas* sp. phenazines (Pham et al. 2008). The production of electron shuttles can be thermodynamically unfavorable (Childers et al. 2002), although they have also been observed in continuous flow MFCs (Aelterman et al. 2006).

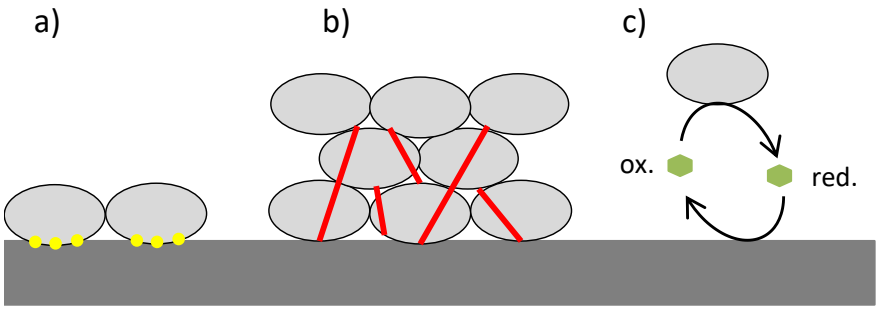


Fig. 4 Electron transfer mechanisms in BES anode: direct electron transfer with a) outer membrane cytochromes (yellow circles) or b) nanowires (red sticks), and c) mediated electron transfer with electron shuttling compound (green cycle). Ox.: oxidized, red.: reduced.

The electron transfer mechanisms of pure cultures of *G. sulfurreducens* and *S. odeinensis* have been widely studied. *G. sulfurreducens* has been reported to transfer electrons in direct contact with the electrode via c-type cytochromes (Bond and Lovley 2003, Holmes et al. 2006) or through nanowires (Reguera et al. 2006). The electron transfer mechanisms of *S. oneidensis* are more diverse. *S. oneidensis* can use both direct electron transfer mechanism through outer membrane cytochromes (Bretshger et al. 2007, Meitl et al. 2009) and nanowires (Gorby et al. 2006). Furthermore, *S. oneidensis* can excrete flavins to mediate electron transfer (Coursolle et al. 2010).

4. Anaerobic Microorganisms at the Cathode

Anaerobic microbes can be used at biological cathodes of MFCs and MECs for wastewater treatment (e.g. denitrification), production of chemicals, CO_2 fixation and bioremediation (Table 4). In biocathodes, electrons for the reduction reactions are provided by the oxidation reactions at the anode. An external power source is used in MECs to overcome cathodic reaction overpotentials (Rosenbaum et al. 2011) and thermodynamic limitations (Zhang and Angelidaki 2014). The use of anaerobes at the cathode has many advantages (He and Angenent 2006). They replace the expensive catalysts otherwise required at the cathode electrodes, which decreases the construction and operation costs. Further, the use of anaerobic cathodes eliminates the diffusion of oxygen to the anode, which could result in aerobic respiration by facultative exoelectrogens or by other bacteria (Logan and Regan 2006). In addition, a life cycle assessment showed that MECs producing hydrogen result in larger environmental benefits when compared to electricity generation in MFCs, if current densities of 1000 A/m^3 can be obtained (Foley et al. 2010). Aerobic biocathodes can also be used, for example, for the reduction of oxygen, Fe^{2+} or Mn^{2+} (e.g., He and Angenent 2006) but are not in the scope of this chapter.

Table 4 Possible biologically catalyzed cathodic reactions without (MFC) or with (MEC) applied voltage.

Purpose (MFC/MEC)	Reaction	Reference
Nitrate reduction (MFC)	$NO_3^{2-} + 2\ H^+ + 2\ e^- \rightarrow NO_2^- + H_2O$ $2\ NO_3^{2-} + 12\ H^+ + 10\ e^- \rightarrow N_2 + 6\ H_2O$	Clauwaert et al. 2007 Lefebvre et al. 2008
Sulfate reduction (MFC)	$2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ $SO_4^{2-} + 4\ H_2 \rightarrow S^{2-} + 4\ H_2O$ $SO_4^{2-} + 4\ H_2O + 8\ e^- \rightarrow S^{2-} + 8\ OH^-$	Coma et al. 2013
Hydrogen production (MEC)	$2\ H^+ + 2\ e^- \rightarrow H_2$	Rozendal et al. 2008
Methane production (MEC)	$CO_2 + 8\ H^+ + 8\ e^- \rightarrow CH_4 + 2\ H_2O$	Chae et al. 2010
Acetate synthesis from CO_2 (MEC/MES)	$CO_2 + 7\ H^+ + 8\ e^- \rightarrow$ Acetate $+ 2\ H_2O$	Nevin et al. 2010
Acetate synthesis to ethanol (MEC/MES)	Acetate $+ 5\ H^+ + 4\ e^- \rightarrow$ Ethanol $+ H_2O$	Steinbusch et al. 2010
Fumarate reduction to succinate (MEC)	Fumarate + 2 H+ + 2 e- → Succinate	Park et al. 1999
Trichloroethane (TCE) reduction to ethane or ethene (MEC)	TCE → Ethane	Aulenta et al. 2007
Perchlorate reduction to chloride (MEC)	$ClO_4^- \rightarrow Cl^-$	Butler et al. 2010

Electrochemically active anaerobic microorganisms used at the cathode include pure cultures, such as *G. sulfurreducens* (Dumas et al. 2008), *G. metallireducens* (Gregory et al. 2004) and *Methanobacterium palustre* (Cheng et al. 2009), as well as mixed cultures. Anaerobes can form electrochemically active biofilms on the cathode electrodes, although the extracellular electron transfer mechanisms at the cathodes are still poorly known (Borole et al. 2011). In nature, some bacteria are known to accept electrons from solid electron donors. For example, chemolithotrophic iron and sulfur oxidizers can accept electrons from Fe^{2+}, S^0 or S^{2-} in oxic/anoxic interfaces where oxygen is used as electron acceptor (Rosenbaum et al. 2011). In BES biocathodes, the electrode serves as the only electron donor for the bacteria, while for carbon source a small amount of CO_2 or other carbon has to be added.

4.1 Pure Cultures

Pure electrochemically active cultures have been shown to accept electrons from the cathode electrode for various different purposes, including denitrification and reduction of protons, CO_2 and environmental contaminants (Table 5). Some bacteria are able to both donate and accept electrons to/from electrode, respectively. *G. sulfurreducens* can act as biocatalyst both at the anode to oxidize acetate (Reguera et al. 2005) and at the cathode to reduce fumarate (Dumas et al. 2008) or uranium (Gregory and Lovley 2005).

Table 5 Anaerobic pure and mixed exoelectrogenic cultures in biological cathodes with or without mediators.

Culture	Reduction reaction	Electron transfer mechanism	Reference
Pure culture			
Actinobacillus succinogenes	Fumarate / Succinate	Exogenous NR mediator	Park and Zeikus 1999
Azospira suillum	ClO_4^- / Cl^-	Exogenous AQDS mediator	Thrash et al. 2007
Dechloromonas agitata	ClO_4^- / Cl^-	Exogenous AQDS mediator	Thrash et al. 2007
Desulfovibrio vulgaris	H^+ / H_2	Exogenous MVmediator	Lojou et al. 2002
Geobacter lovleyi	PCE / cis-DCE	Direct[a]	Strycharz et al. 2008
Geobacter metallireducens	NO_3^- / NO_2^-	Direct[a]	Gregory et al. 2004
Geobacter sulfurreducens	Fumarate / Succinate	Direct[a]	Gregory et al. 2004
Geobacter sulfurreducens	Fumarate / Succinate	Direct[a]	Dumas et al. 2008
Geobacter sulfurreducens	U(VI) / U(IV)	nr (mediatorless)	Gregory and Lovley 2005
Methanobacterium palustre	CO_2 / CH_4	Direct[a]	Cheng et al. 2009
Sporomusa ovate	CO_2 / Acetate	Direct[a]	Nevin et al. 2010
Mixed culture			
Anaerobic sludge	NO_3^- / N_2	nr	Zhang et al. 2005
Anaerobic sludge	NO_3^- / N_2	nr	Clauwaert et al. 2007
Hydrogenophilic mixed culture	H^+ / H_2	nr	Rozendal et al. 2008
Hydrogenophilic mixed culture	H^+ / H_2	nr	Jeremiasse et al. 2010
Hydrogenophilic methanogenis culture	H^+ / H_2, CO_2 / CH_4	Exogenous MV mediator/ Direct[a]	Villano et al. 2010
Anaerobic sludge	Acetate / Ethanol	Exogenous MV mediator	Steinbusch et al. 2010
Sulfate-reducing bacteria	Acetate/Ethanol Butyrate/Butanol	Direct[a]	Sharma et al. 2013
Hydrogenophilic dechlorinating culture	TCE / cis-DCE (VC / Ethane)	Endogenous mediator	Aulenta et al. 2010
Anaerobic digester effluent	Cr(VI) / Cr(III)	nr	Tandukar et al. 2009

[a] suggested, AQDS: anthraquinone-2,6-disulfonate, MV: methyl viologen, NR: neutral red, nr: not reported

4.2 Mixed Cultures

Mixed cultures used at biocathodes are listed in Table 5. Not many microbial communities from biocathodes have been characterized. Croese et al. (2011) produced hydrogen at a biocathode of an MEC and reported that *Proteobacteria* dominated at the biocathode. *Methanobacterium* spp. was a dominant anaerobe at an MEC biocathode producing methane (Cheng et al. 2009). Similar to bioanodes, the growth of methanogens in one-chamber MECs (MEC where anode and cathode electrodes are in the same chamber) producing hydrogen should be prevented. Methanogens disturb the process by decreasing CE, utilizing produced H_2 and by reducing the purity of the produced gas (Logan et al. 2008). For example Wang et al. (2009) reported that hydrogenotrophic methanogens (that produce methane from H_2 and CO_2) were responsible for methane production in one-chamber MEC. Easiest way to decrease methane production is to use two-chamber MEC, where methanogens may occur at the anode but are separated from the produced H_2 by a separator. Also, using higher applied voltages of >0.6 V have been reported to reduce methane production in one-chamber MECs (Wang et al. 2009).

4.3 Electron Transfer Mechanisms

At the cathode, anaerobes can accept electrons directly or with mediators. However, the precise electron transfer mechanisms of direct electron transfer are not yet known. Electrode has served as direct electron source, for example, for the following cultures: *S. ovata* for CO_2 reduction to acetate (Nevin et al. 2010), *G. metallireducens* to reduce nitrate to nitrite, *G. sulfurreducens* to reduce fumarate to succinate (Gregory et al. 2004), and for methanogens (Clauwaert et al. 2008a). Rosenbaum et al. (2011) suggested that c-type cytochromes and hydrogenases would play a role in cathodic electron transfer. Strycharz et al. (2011) and Rosenbaum et al. (2011) reported that the electron transfer mechanisms between the anode and cathode differed significantly despite of the similar gene expression. This was due to the different redox potentials of the electron transfer components (Rosenbaum et al. 2011). Geelhoed et al. (2010) suggested a mechanism for biological hydrogen production and preceding electron transfer at the cathode of an MEC (Figure 5).

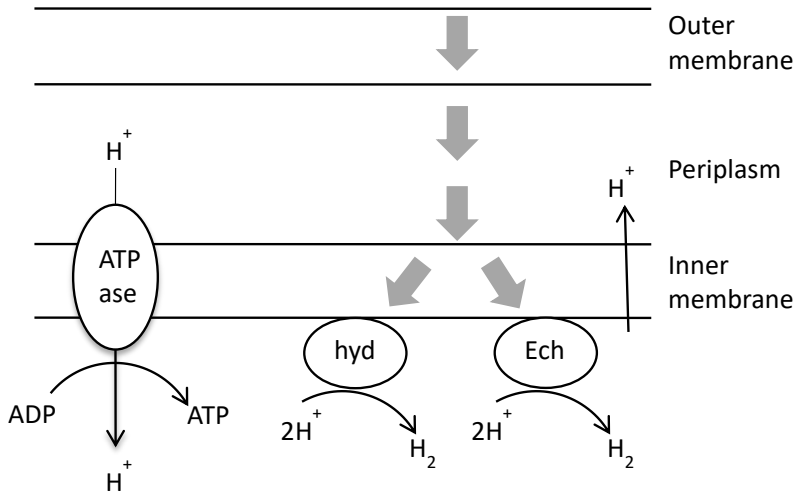


Fig. 5 Hydrogen production mechanism coupled to proton transport at biocathode as suggested by Geelhoed et al. (2010). Hydrogen is produced either with hydrogenase (hyd) or energy-conserving hydrogenase (Ech).

Exogenous mediators used for cathodic reduction reactions include methyl viologen, anthraquinone-2,6-disulfonate (AQDS) and neutral red. Methyl viologen has been used as mediator, e.g., for the reduction of protons to hydrogen (Lojou et al. 2002, Villano et al. 2010), acetate to ethanol (Steinbusch et al. 2010), or for the reduction of trichloroethane (TCE) to ethane or ethane (Aulenta et al. 2007). Thrash et al. (2007) reported perchlorate reduction with an exogenous AQDS mediator. However, perchlorate was also reduced in a mediatorless BES with a novel strain isolated from a natural culture (Thrash et al. 2007). Neutral red was used for fumarate reduction by Park and Zeikus (1999). Aulenta et al. (2010) reported that a mixed hydrogenophilic dechlorinating culture produced unknown endogenous mediators when reducing TCE at an anaerobic biocathode.

5. Factors Affecting the Growth of Electroactive Anaerobic Bacteria

In addition to the type of inoculum, operational parameters affect the growth of anaerobic electroactive communities. The structure and activity of the exoelectrogenic cultures are affected by various physical and chemical parameters, including pH, temperature, substrates concentration and loading rate, conductivity, shear stress, external resistance, electrode potential, and materials for electrodes and separators. This chapter presents a short introduction into these different parameters. Due to low number of studies on the effects of operational parameters on biocathodes, most of the chapters deal mainly with bioanodes.

5.1 Temperature

Current production in BES is easily affected by temperature changes since anaerobes are sensitive to the operating temperature. Most BES studies are conducted with mesophilic bacteria, while few studies have investigated the BES performance at higher temperatures (above 50ºC) (Choi et al. 2004, Mathis et al. 2008, Carver et al. 2011) mainly due to limitations in reactor design. Elevated temperatures make bioprocesses less sensitive to contamination, favor the kinetics and stoichiometry of chemical, electrochemical and enzymatic reactions, and increase conductivity according to Arrhenius laws (Zumdahl 1998, van Groenestijn et al. 2002). Increasing temperature, thus, enhances microbial growth that helps microbial attachment to an electrode (Min et al. 2008). For example, Patil et al. (2010) reported that increasing temperature from 15 to 35ºC increased the current densities and reduced lag times. The main drawbacks of elevated temperatures are lower cell densities, complex nutrient requirements and energy required for process heating (van Groenestijn et al. 2002, Hallenbeck 2005). However, high temperature waste streams may enable the use of higher temperatures.

5.2 pH

Neutral anodic pH has been used in several MFC studies (Bond and Lovley 2003, Rismani-Yazdi et al. 2007, Borole et al. 2009). In BES, cathodic pH tends to rise and anodic pH to decrease due to poor proton transfer through the separator. The resulting pH difference between the anode and cathode leads to increased internal resistance and reduces the whole cell voltage by 0.06 V per pH unit (Logan et al. 2008). Further, low pH can dramatically decrease bacterial activity at the anode (Biffinger et al. 2008) and may set some limitations to materials and chemicals used. There are few studies utilizing lower pH at the anode and/or the cathode. For example, Borole et al. (2008) oxidized glucose at pH below 4 and Sulonen et al. (2015) oxidized tetrathionate at pH below 2.5. Substrate oxidation or reduction at the biofilms can also lead to pH gradients across the biofilm and result, e.g., in lower pH values close to the anode electrode surface. The local pH changes reduce the performance of microorganisms and introduce a higher stress level to the anaerobes (Torres et al. 2008, Franks et al. 2009).

5.3 Anodic Substrate, Substrate Concentration and Organic Loading Rate

The BES performance is greatly affected by the type, concentration and feeding rate of substrate (Du et al. 2007). Electricity production from many different substrates have been investigated varying from simple organic acids, such as acetate (Zuo et al. 2008, Borole et al. 2009) and butyrate (Liu et al. 2005a), to more complex substrates, including sugars (Rabaey et al. 2003, Catal et al. 2008), cellulose (Ren et al. 2007) and real waste materials. Real wastewaters used for current production include domestic (Liu and Logan 2004), brewery (Wang et al. 2008), paper recycling (Huang and Logan 2008) and food processing (Oh and Logan 2005) wastewaters. In addition, biological sulfide oxidation to sulfate with simultaneous current production was reported by Sun et al. (2009).

Substrate influences the bacterial community composition, CE and current density of the BES. The more complex the substrate, the more diverse microbial community develops due to syntrophic bacterial species required for substrate degradation and electricity generation (Chae et al. 2009, Rodrigo et al. 2009, Velasquez-Orta et al. 2011). Using fermentable instead of non-fermentable substrates often results in decreased CEs, since proportion of the electrons are directed to production of soluble metabolites instead of electricity (Lee et al. 2008, Huang and Logan 2008). Wastewaters may also contain some inorganic or non-biodegradable compounds that interfere with electricity production and decrease current densities and CEs (Nam et al. 2010). The goal is, however, to utilize wastewaters or other complex substrates in BES to make them competitive with other renewable energy technologies. For example, wastewaters from food-processing industries, breweries and animal confinements contain high levels of easily degradable organic material and have high water content and thus, are especially suitable for BES (Angenent et al. 2004).

Substrate concentration and organic loading rate (OLR) also affect the current generation in BES. Substrate concentration controls the current production according to Monod relationship (Eq. 5, Torres et al. 2007), where j is current density (A/m^2), $j_{max,app}$ the maximum current density, S substrate concentration (e.g. g COD/m^3), and $K_{S,app}$ the half-maximum concentration (g COD/m^3). Increased substrate concentrations and OLR increase the current (Behera and Ghangrekar 2009) but only up to a certain limit (Aelterman et al. 2008a). High substrate concentrations in MFCs may lead to enhanced formation of fermentation products that decrease anodic pH lowering the bacterial activity (Sharma and Li 2010). At higher substrate concentrations more substrate is used for bacterial growth or alternative reactions, such as methanogenesis, lowering the CE (Sharma and Li 2010). In general, substrate removal efficiency decreases at high substrate concentrations (Sleutels et al. 2011). Also substrate concentrations may form gradients across the biofilm, which decreases the activity and performance of electroactive anaerobes close to the anode electrode (Lee et al. 2009).

$$j = j_{max,app}\left(\frac{S}{K_{S,app}+S}\right) \quad (5)$$

OLR has an effect on current density and substrate degradation (Mohan et al. 2007). It has been reported that only with small external resistance, increase in OLR results in enhanced electricity generation (Aelterman et al. 2008a). Martin et al. (2010) reported that increased portion of substrate was used for methane production at increasing OLR.

5.4 Ionic Strength

Ionic strength of an electrolyte in BES increases the solution conductivity and current production (Huang and Logan 2008) and decreases the internal resistance. However, there are only few microbial strains that can produce electricity at a very high ionic strength (Huang et al. 2010). Liu et al. (2005b) reported that power production was enhanced from 720 to 1330 mW/m^2 by increasing ionic strength from 0.1 to 0.4 M, respectively. Furthermore, halophilic bacteria *Shewanella marisflavi* and halophilic archaea *Haloferax volcanii* and *Natrialba magadii* have been reported to produce electricity at very high ionic strengths of 1.1 M (9.6 mW/m^2), 2.7 M (119 mW/m^2) and 3.6 M (46 mW/m^2), respectively (Huang et al. 2010, Abrevaya et al. 2011). Thus, BES can be effective for treatment of saline industrial wastewaters (Bond et al. 2002).

5.5 External Resistance and Anode Potential

External resistance regulates the anode availability as electron acceptor and electron flux through the circuit (Jung and Regan 2011). External resistance (R_{ext}) controls the ratio between the current (I) generation and cell voltage (U) according to Ohm's law (Eq. 6). In general, the lower the external resistance, the higher the current and coulombic efficiency (Aelterman et al. 2008b, Rismani-Yazdi et al. 2011, Jung and Regan 2011). Up to certain point, lower external resistance may select exoelectrogens that can meet their metabolic energy requirements with small potential gradient between the redox potential of their electron donor and the anode (Jung and Regan 2011). Thus, external resistance can be used in the enrichment of exoelectrogens since low external resistance facilitates electron transfer and favors the enrichment of exoelectrogens (Lefebvre et al. 2011).

$$U = IR_{ext} \quad (6)$$

Anode potential, on the other hand, regulates the activity of bacterial community in BES. Theoretically, microbes gain more energy by reducing a terminal electron acceptor with a more positive potential (Schröder 2007) according to Gibb's free energy ($\Delta G^{0\prime}$, Eq. 7), where n is the number of electrons transferred, F Faradays constant (96 485 C/mol), and $\Delta E^{0\prime}$ the difference in the potentials between the electron donor and electron acceptor, e.g. outer membrane cytocrome and anode electrode. More positive anode potential should increase the growth rate of bacteria resulting in higher biocatalyst density, respiration rates, faster start-up of electricity production and higher current generation (Aelterman et al. 2008b, Bond 2010). However, microbes must have metabolic pathways capable of capturing the available energy and maximize their energy gain for a given anode potential (Finkelstein et al. 2006, Wagner et al. 2010). For example, *Geobacter* sp. that use only a small portion of their net electron flow to ATP production dominated microbial communities at low anode potentials (Bond 2010).

$$\Delta G^{0\prime} = -nF\Delta E^{0\prime} \quad (7)$$

Although more positive anode potentials theoretically result in higher energy gain for bacteria, Wagner et al. (2010) proposed that it is primarily the potential of the terminal respiratory proteins used by certain exoelectrogenic bacteria, rather than the anode potential, that determines the optimal growth conditions in the reactor. This is supported by the studies of Finkelstein et al. (2006) and Wei et al. (2010), who reported that anode potential selected for exoelectrogens whose terminal respiratory proteins had redox potentials just negative of the anode potential. Theoretically, in order to maximize current flow in BES anode potential should be as negative as possible (Eq. 3). However, experimental results about the effects of anode potentials on current production remain contradictory. E.g., Torres et al. (2009) reported increased current production at lower anode potentials, while Wei et al. (2010) and Sun et al. (2012) obtained higher current densities at higher anode potentials.

5.6 Electrode and Separator Materials

Several electrode materials are applicable in BES and their main requirements include conductivity, biocompatibility, high surface area, chemical stability, high mechanical strength and low cost (Logan et al. 2006, Li et al. 2010). The electrode material affects the growth and electrochemical activity of the anaerobic culture (Aelterman et al. 2008a, Liu et al. 2010). Electrode materials used in BES include graphite plates and rods, carbon cloths and papers, graphite fiber brushes, activated carbon, carbon mesh, graphite foam, carbon nanotubes, tungsten and stainless steel (Logan et al. 2007, Logan 2010, Wei et al. 2011, Mohanakrishna et al. 2012). High surface area minimizes activation and ohmic losses and provides more space for the growth of anaerobes (Gnana Kumar et al. 2013). For example, Liu et al. (2010) reported 40% higher current densities with electrodes having higher surface area (carbon fiber or carbon paper) than graphite rod. For example, graphite fiber brushes, activated carbon cloth electrodes and carbon nanotube-base materials have high surface areas.

Separators are used in two-chamber BES and often in one-chamber BES. Separator is used, e.g., to physically separate anode and cathode chambers, reduce oxygen diffusion to the anode, to increase CE and to allow closer electrode spacing. Further, in MECs the use of separator reduces H_2 losses due to methanogenesis and increases the purity of gases (Logan et al. 2008). Separators used include salt bridges, proton exchange membranes, cation exchange membranes, anion exchange membranes, bipolar membranes, porous fabrics and glass fibers (Wei et al. 2011). Although the use of membrane is often compulsory, its use has many problems. It increases the BES construction costs and the internal resistance and may result in pH gradient across the membrane (Logan et al. 2008). Further, the membrane surface can meet fouling, which affects the performance of separator (Zhang et al. 2009).

6. Future Directions

Anaerobes are used in various BES applications both at the anode and cathode chambers. Further studies using different electrochemically active pure cultures are needed to better understand the

electron transfer mechanisms to and from the electrode. Oxidation of simple synthetic compounds has produced a fundamental mechanistic understanding during the past 15 years. However, more research is required on the oxidation of real wastewaters in the anode chamber and their possible inhibitory effects on exoelectrogens and current generation.

The utilization of electrochemically active anaerobes at the cathode is a rather new area of research. In recent years, it has been shown that many pure and mixed cultures accept electrons from the cathode for the reduction of various different compounds. Of these processes, biological production of H_2 and CH_4 are the most widely studied. More knowledge is required on the anaerobic cultures catalyzing reduction reactions at the cathode electrodes. These include electron transfer mechanisms, reaction routes and the effects of operational parameters on the reduction reactions.

In the future, BES may not be applicable solely for electricity production and/or wastewater treatment (Rozendal et al. 2008). Bioelectrochemical systems are more likely to become viable sooner, when combined with other valuable processes, such as bioremediation, denitrification or hydrogen production at the cathode (Jia et al. 2008, Lovley and Nevin 2011). Prior to commercialization BES have to be scaled-up. Few studies on the up-scaling of MFCs (Jiang et al. 2011) and MECs (Cusick et al. 2011) have reported various problems that require further attention. Challenges that need to be solved include the development of lower cost and more efficient electrode and separator materials, scaling-up by maintaining the current densities obtained at laboratory scale and minimizing the losses in BES.

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