

Minimizing losses in bio-electrochemical systems: the road to applications

Peter Clauwaert · Peter Aelterman · The Hai Pham ·
Liesje De Schampelaire · Marta Carballa ·
Korneel Rabaey · Willy Verstraete

Received: 13 March 2008 / Revised: 24 April 2008 / Accepted: 24 April 2008
© Springer-Verlag 2008

Abstract Bio-electrochemical systems (BESs) enable microbial catalysis of electrochemical reactions. Plain electrical power production combined with wastewater treatment by microbial fuel cells (MFCs) has been the primary application purpose for BESs. However, large-scale power production and a high chemical oxygen demand conversion rates must be achieved at a benchmark cost to make MFCs economical competitive in this context. Recently, a number of valuable oxidation or reduction reactions demonstrating the versatility of BESs have been described. Indeed, BESs can produce hydrogen, bring about denitrification, or reductive dehalogenation. Moreover, BESs also appear to be promising in the field of online biosensors. To effectively apply BESs in practice, both biological and electrochemical losses need to be further minimized. At present, the costs of reactor materials have to be decreased, and the volumetric biocatalyst activity in the systems has to be increased substantially. Furthermore, both the ohmic cell resistance and the pH gradients need to be minimized. In this review, these losses and constraints are discussed from an electrochemical viewpoint. Finally, an overview of potential applications and innovative research lines is given for BESs.

Keywords Biofuel cell · Bioenergy ·
Biocatalyzed electrolysis · Overpotentials · Biocatalysts ·
Ohmic resistance

Introduction

In bio-electrochemical systems (BESs), at least one of the anodic or cathodic reactions is microbially catalyzed (Rabaey et al. 2007). If a BES is producing electrical energy, the term microbial fuel cell (MFC) is used whereas a microbial electrolysis cell (MEC) indicates that a BES is consuming electrical energy to drive the electrochemical reactions (Rozendal et al. 2006b; Fig. 1). In the early BESs, electron mediation between microorganisms and an electrode was established by means of adding mediators (Allen and Bennetto 1993, Blake et al. 1994, Park et al. 1999). Only recently, electron transfer in both anodes and cathodes has been described without the external addition of artificial electron mediators (Bond and Lovley 2003, Clauwaert et al. 2007b, Gregory et al. 2004, Rabaey et al. 2004).

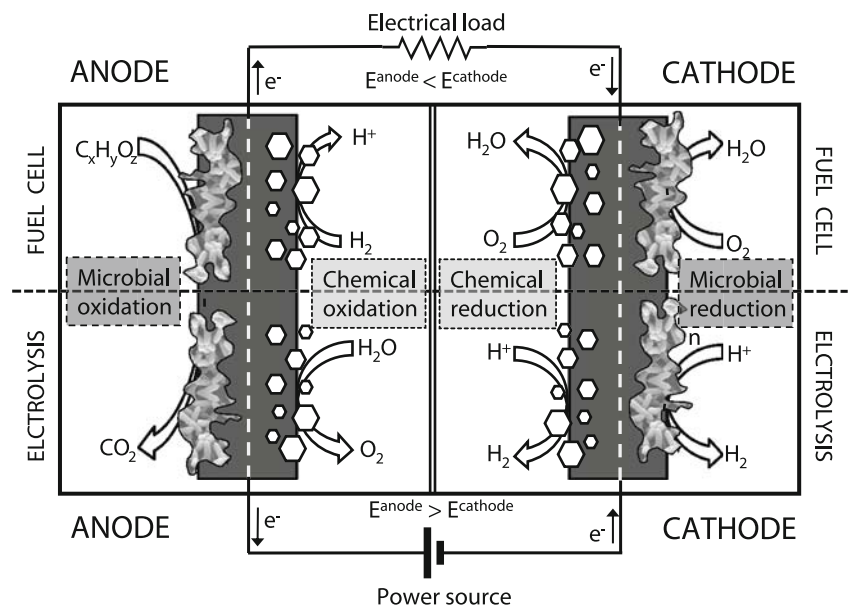
The primary focus of MFCs has been the production of plain electrical power; however, maximum power outputs achieved thus far are in the order of 100 W m^{-3} MFC (Table 1), which is rather low in terms of investment costs compared to anaerobic digesters that produce electrical power up to $1,000 \text{ W m}^{-3}$ (Pham et al. 2006). Recently, more emphasis is being given to added value purposes for BESs, such as hydrogen production (Liu et al. 2005b, Rozendal et al. 2006b), water purification (Clauwaert et al. 2007a, Rabaey et al. 2005b), and the use of BESs as biosensors (Kim et al. 2003).

Before bench-scale reactors can be upgraded to economically feasible applications, a number of hurdles that limit the overall performance need to be overcome. In this

P. Clauwaert · P. Aelterman · T. H. Pham · L. De Schampelaire ·
M. Carballa · W. Verstraete (✉)
Laboratory of Microbial Ecology and Technology (LabMET),
Ghent University,
Coupure Links 653,
9000 Ghent, Belgium
e-mail: Willy.Verstraete@UGent.be
URL: <http://labmet.UGent.be>

K. Rabaey
Advanced Water Management Centre, University of Queensland,
Brisbane, Queensland 4072, Australia

Fig. 1 Schematic overview of the possible combinations of microbial and chemical catalysis in BESs. Energy is harvested in MFCs ($E^{\text{anode}} < E^{\text{cathode}}$) and energy is consumed in MECs ($E^{\text{anode}} > E^{\text{cathode}}$)



review, an overview of limiting factors of BESs is given in an electrochemical context linking performance with physical and biological constraints. In addition, several research approaches resulting in potential applications for BESs are proposed.

Losses in bioelectrochemical systems

The cell voltage (ΔE [V]) in a BES is determined by the open circuit voltage (OCV) lowered with losses that occur as current is produced. The OCV is the difference between the cathodic and anodic equilibrium potential (E_e^{cathode} and E_e^{anode} [V vs standard hydrogen electrode (vs SHE)]). The losses that occur in BESs are the overpotentials of the anode and the cathode ($\Delta E_\eta = \Sigma \eta^{\text{cathode}} - \Sigma \eta^{\text{anode}}$ [V]) and the ohmic voltage losses of the system ($\Delta E_\Omega = I \cdot \Sigma R_\Omega$, [V]; I , [A]; ΣR_Ω , [Ω]):

$$\begin{aligned} \Delta E = \text{OCV} - \Delta E_\eta - \Delta E_\Omega &= (E_e^{\text{cathode}} - E_e^{\text{anode}}) \\ &- (\Sigma \eta^{\text{anode}} - \Sigma \eta^{\text{cathode}}) \\ &- I \cdot \Sigma R_\Omega. \end{aligned}$$

Plotting the cell voltage and electrode potentials in function of the current density produced, which is called a polarization curve, is one of the most revealing methods to express the cell performance (Fig. 2; Aelterman et al. 2006b; Cheng and Logan 2007a; Rozendal et al. 2006b). The total overpotential of an electrode (both activation and concentration overpotentials) is generally calculated as the difference between the electrode potential under consideration (E [V vs SHE]) and the equilibrium potential (E_e [V vs SHE]; Freguia et al. 2007, Rozendal et al. 2007b): $\eta = E -$

E_e . It is important that the distance between the reference electrode and the electrode is minimized to at least a few millimeters to minimize the ohmic voltage bias. In this section, all losses (ohmic voltage losses, activation overpotentials, concentration overpotentials, and coulombic losses) are discussed.

Ohmic voltage losses

In BESs, there are two types of charge transfer that give rise to ohmic voltage losses: electron transfer through the electrodes and ion transfer through the electrolyte. The ohmic voltage loss will thus be determined by the resistivity of the different conductors (electrodes, current collectors, wires, membranes, and electrolyte) on the one hand and cell configuration on the other hand. As the resistance of the system (ΣR_Ω [Ω]) is current-independent according to Ohm's law, the sum of all ohmic voltage losses (ΔE_Ω [V]) for a given current is obtained by multiplying the current produced (I [A]) with the resistance.

The ohmic resistance can be experimentally determined with the current interrupt method (Aelterman et al. 2006b) or electrochemical impedance spectroscopy (He et al. 2006; Rozendal et al. 2007b). The ohmic voltage loss over the membrane can be determined by measuring the voltage difference between two reference electrodes at both sides of the membrane, corrected for ohmic electrolyte voltage losses (Terheijne et al. 2006). When the increase of the overpotentials is negligible with increasing current densities, the slope of the cell voltage of the linear ohmic part of the voltage–current plot can be used as an equivalent for the ohmic resistance of the cell. However, if the overpotentials tend to increase with increasing current densities, the value

Table 1 Overview of various types of BESs: the maximum current production (I_{\max}) and power production (P_{\max}) for MFCs or the maximum current production and voltage applied (V_{applied}) for MECs in relation to the reactor size, electrode and membrane types, and operational conditions

I_{\max} (A m ⁻³ MFC)	P_{\max} (W m ⁻³ MFC)	V_{applied} (V)	Membrane		Anode		Cathode		Reference				
			Type	(m ² m ⁻³)	Substrate	Material	b/c	PBS (mM)		CBS (mM)	Substrate	Material	
36	13	0.028	a	a	Glu (BC)	C-paper	b	53		O ₂ /H ⁺	C-paper (Pt)	Liu and Logan (2004)	
100	18	0.029	a	a	Glu (BC)	G-brush (NH ₃)	b	200		O ₂ /H ⁺	UFT (CoTMPP)	Zuo et al. (2007)	
205	115	0.028	a	a	Ac (BC)	C-cloth (NH ₃)	b	213		O ₂ /H ⁺	C-cloth (Pt)	Cheng and Logan (2007a)	
237	56	0.026	a	a	Ac (BC)	G-brush (NH ₃)	b	200		O ₂ /H ⁺	KJB (FePe)	Yu et al. (2007)	
310	73	0.026	a	a	Ac (BC)	G-brush (NH ₃)	b	200		O ₂ /H ⁺	C-cloth (Pt)	Logan et al. (2007)	
100	30	0.036	CEM	44	Ac (BC)	C-paper	b	2	30		O ₂ /H ⁺	C-paper (Pt)	Liang et al. (2007)
251	83	0.184	CEM	69	Ac (BC)	G-granules	b	52	24		O ₂ /H ⁺ (BC)	G-felt	Clauwaert et al. (2007b)
29	7	0.500	CEM	1	H ₂ (BP)	Pt (FPA)	b	71	119		O ₂ /H ⁺	C-cloth (FePe)	Zhao et al. (2005)
33	7	0.500	CEM	1	H ₂ (BP)	Pt (FPA)	b	71	119		O ₂ /H ⁺	C-cloth (CoTMPP)	Zhao et al. (2005)
96	30	0.531	CEM	69	Ac (BC)	G-granules	b	52	24		O ₂ /H ⁺ (BC)	G-felt	Clauwaert et al. (2007b)
90	32	0.699	CEM	43	Ac (BC)	G-granules	b	52	24		O ₂ /H ⁺ (BC)	G-felt	Clauwaert et al. (2007b)
188	65	0.184	CEM	69	Ac (BC)	G-granules	c	52	24		O ₂ /H ⁺ (BC)	G-felt	Clauwaert et al. (2007b)
110	50	0.312	CEM	33	Ac (BC)	G-granules	c	64			FerricN	G-granules	Aelterman et al. (2006b)
68	25	0.482	CEM	60	Ac (BC)	G-granules	c	64			FerricN	G-felt	Rabaey et al. (2005b)
56	10	0.620	CEM	30	Suc (BC)	AC-granules	c	45–178			FerricN	AC-granules	He et al. (2006)
31	7	0.700	CEM	n.a.	Ac (BC)	G-granules	c	72			O ₂ /H ⁺	G-granules	Freguia et al. (2007)
103	28	1.240	BM	29	Ac (BC)	G-felt	c	20–30			O ₂ /H ⁺ (BC ^b)	G-felt	Ter Heijne et al. (2007)
176		0.850	CEM	25	Ac (BC)	C-cloth	b	50			H ⁺	C-paper (Pt)	Liu et al. (2005b)
145		0.800	CEM ^c	22	Ac (BC)	G-granules	b	52	24		H ⁺	G-cloth (Pt)	Clauwaert et al. (2008)
3		0.850	CEM	1	Ac (BC)	C-cloth	b	50			H ⁺	C-paper (Pt)	Liu et al. (2005b)
29		1.000	CEM	8	Ac (BC)	G-felt	c	10			H ⁺	MEA + CC (Pt)	Rozenal et al. (2007b)
36		0.825	CEM	n.a.	FerroCN	G-felt	b	10			H ⁺ (BC)	G-felt	Rozenal et al. (2008)

The reactor volume is here by convention the sum of the electrode volume, the membrane, and all the electrolyte in the reactor.

V Volume, T temperature, CEM cation selective membrane, BM bipolar membrane, Glu glucose, Ac acetate, Suc sucrose, BC biocatalyzed, BP biologically produced, C carbon, G graphite, AC activated carbon, NH_3 thermal ammonia treated, FPA fluorinated polyamine coated, b/c batch or continuous operated, PBS phosphate buffer strength, CBS carbonate buffer strength, $FerricN$ ferricyanide, $FerroCN$ ferrocyanide, $CoTMPP$ cobalt tetramethoxyphenylporphyrin, $FePe$ iron(II) phthalocyanine, UFT two ultrafiltration tubes with carbon paste, KJB Ketjenblack carbon, MEA membrane electrode assembly, CC current collector, $n.a.$ not available

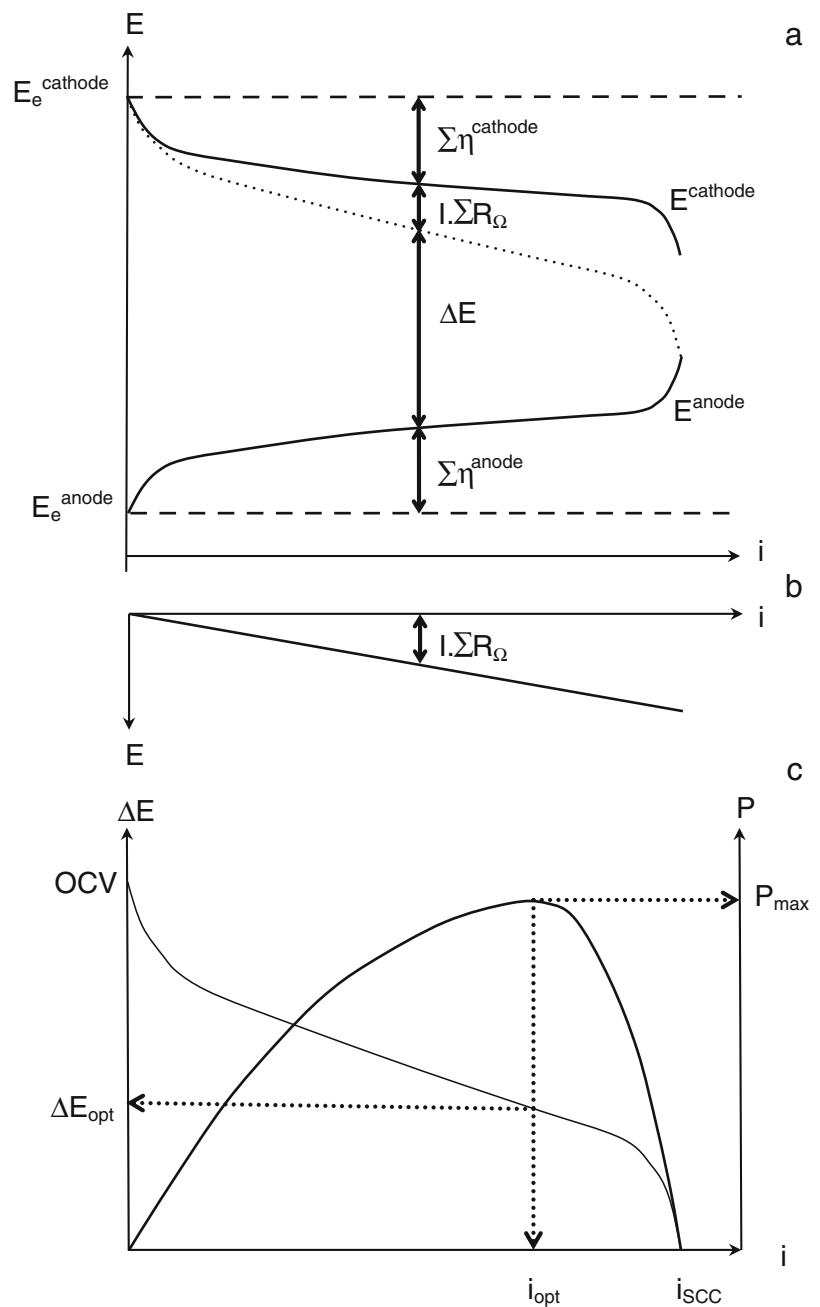
^a Not present

^b Fe^{2+}/Fe^{3+} was the electronshuttle for *Acidithiobacillus ferrooxidans*

^c Sliced membrane to minimize pH gradient for H₂/CH₄ production

^d Poised cathodic potential of -0.700 V vs SHE

Fig. 2 **a** Schematic overview of the anodic and cathodic overpotentials ($\Sigma\eta^{\text{anode}}$ and $\Sigma\eta^{\text{cathode}}$) in function of the current density (i) for MFCs (With a reference electrode in the anode: E^{anode} , the anode potential and $E^{\text{cathode}} = E^{\text{anode}} + \Delta E + I \cdot \Sigma R_{\Omega}$ = the cathode potential; $\text{OCV} = E_e^{\text{cathode}} - E_e^{\text{anode}}$ = the open circuit voltage). **b** Schematic overview of the ohmic voltage loss ($I \cdot \Sigma R_{\Omega}$) in function of the current density. **c** The cell voltage (ΔE) and the power density (P) in function of the current density ($R_{\text{opt}} = \Delta E_{\text{opt}} / i_{\text{opt}}$; i_{sc} = the short circuit current)



of the slope is not current-independent, and as a result, it cannot be expressed in ohms.

It is useful to relate the ohmic resistance with the reactor size, as the ohmic resistance is dependent on the reactor size and the spatial configuration. Expressing the ohmic resistance of the cell in $\Omega \cdot \text{m}^3$ BES by multiplying the ohmic resistance with the reactor volume allows a relative comparison between different types of cells (Fig. 3). Using volume instead of surface area is especially useful when the exact active surface area cannot be determined. The plain BES reactor volume is, here by convention, the sum of the electrode volume, the membrane, and all the electrolyte in

the reactor. When a maximal cell voltage of an acetate-driven open air MFC of, e.g., 0.930 V (Clauwaert et al. 2007b), is considered (assuming no other losses), it can be calculated that the ohmic resistance of a cell designed to convert maximally $10 \text{ kg COD m}^{-3} \text{ MFC day}^{-1}$ at near zero volts (or $i_{\text{sc}} = 1,396 \text{ A m}^{-3} \text{ MFC}$) should not exceed $0.66 \text{ m}\Omega \cdot \text{m}^3 \text{ MFC}$. For a lab scale system of 200 ml MFC, this would mean that a maximal ohmic resistance of 3.3Ω is acceptable to convert $10 \text{ kg COD m}^{-3} \text{ MFC day}^{-1}$ near the short circuit point operation (assuming no other losses). Ohmic resistance expressed in $\text{m}\Omega \cdot \text{m}^3 \text{ BES}$ appears to increase with increasing reactor size in present reactor types

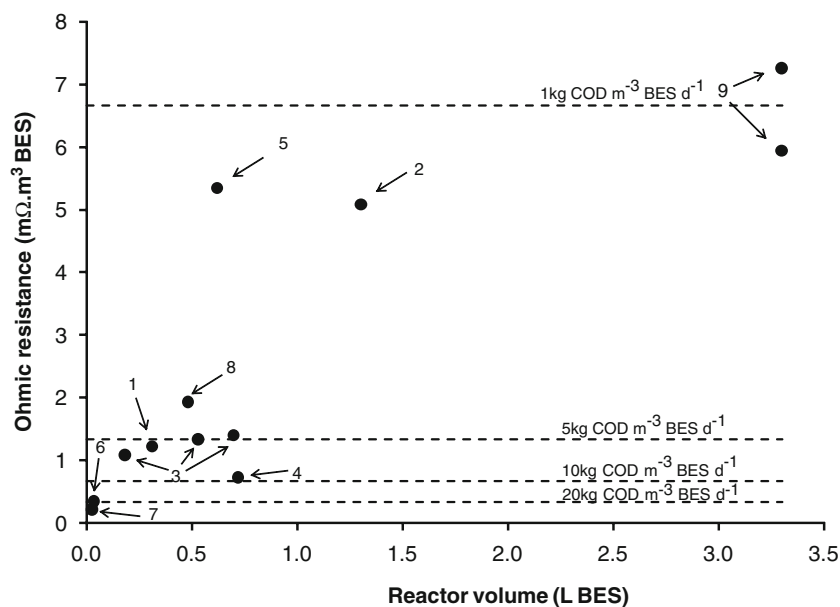


Fig. 3 The ohmic resistance ($\text{m}\Omega\cdot\text{m}^3 \text{ BES}$) in function of the reactor volume (1 BES). The *dashed lines* indicate the calculated theoretical volumetric COD conversion rates if the ohmic resistance would be the only voltage loss (assumptions to enable comparison: 0.930 V OCV for MFCs and current production at short circuit conditions and 1.100 V applied for MECs, of which 0.170 V equilibrium voltage;

1 kg $\text{COD m}^{-3} \text{ BES day}^{-1}=140 \text{ A m}^{-3} \text{ BES}$; calculated values from / Aelterman et al. (2006b), 2 Clauwaert et al. (2007a), 3 Clauwaert et al. (2007b), 4 Freguia et al. (2007), 5 He et al. (2006), 6 Liang et al. (2007), 7 Logan et al. (2007), 8 Rabaey et al. 2005b, 9 Rozendal et al. 2007b

(Fig. 3). Thus, one of the major challenges when BESs are scaled up is to maintain the same volumetric ohmic resistance at a reasonable cost. Besides minimizing the inactive reactor volume, a significant lowering of the electrode and membrane resistance is needed.

Activation overpotentials

The kinetic slowness of the redox reactions is accompanied by activation overpotentials. If concentration polarization is not taken into account, which is however never the case in reality, the Tafel equations can be used to calculate the exchange current and the symmetry factor. The higher the exchange current density, the lower the activation overpotential is (Freguia et al. 2007). The Tafel equations demonstrate that there is a linear correlation between the activation overpotential and the logarithmic value of the current. Thus, activation overpotentials are the most dominant overpotentials in the low current density range, and the activation overpotentials increase slower with increasing current densities (Fig. 2a).

The current density is typically expressed per total electrode surface. However, the electrochemical reactions only occur at specific reactive catalyst sites. In the case of a chemical catalyst, the catalyst loading will determine the number of reactive sites. Increasing the number of reactive sites lowers the associate activation losses (Cheng et al. 2006). Catalyst poisoning inactivates reactive sites and

further increases electrode overpotentials (Niessen et al. 2004).

Also for biological catalyzed reactions, energy is needed to onset electricity production. The amount of biocatalyzing microorganisms in relation to the available surface area, the intrinsic electron transfer rate of the rate determining enzyme/redox system, and the biological activity of the microbial consortium will determine the magnitude of the overpotentials. This biocatalytic activity is dependent on the environmental conditions (mineral composition, temperature, toxic compounds, electrode properties, and electrode potential) and biological competition within the microbial consortium (Cheng and Logan 2007a; Clauwaert et al. 2007b; Liu et al. 2005a; Rabaey et al. 2005b; Rabaey and Verstraete 2005). The maximum current production or the boundaries for the biocatalytic electron transfer rate in axenic and mixed cultured have not yet been determined, as BES reactor design and operation have been suboptimal until now.

Concentration overpotentials

Concentration overpotentials are associated with the concentration gradient of reagents and products in the proximity of the electrode. Inefficient mass transfer through diffusion and convection of substrate or removal of products may limit the maximal current production at an electrode. This is observed in the polarization curve as a

sharp decrease of the cathodic electrode potential or a sharp increase of the anodic electrode potential in the proximity of the short circuit current (i_{sc} ; Fig. 2a). However, if, for example, the anodic biocatalytic activity becomes limited due to local acidification at higher currents, the same polarization profile can be observed. Further research is needed to measure the contribution of different overpotentials in combination with the energy-consuming nature of the biocatalysts, as it is difficult to make a clear distinction at this moment.

Coulombic losses

The coulombic efficiency indicates the ratio between coulombs recovered as current over the total amount of coulombs from the electron donor added (e.g., eight electrons per mole acetate). On the one hand, there is incomplete substrate removal in the effluent, and on the other hand, there is occurrence of alternative reactions that do not result in current production. For a biocatalyzed anode, this means that, first, fermentation or anaerobic respiration of organic compounds in the anode can occur in a way that some products (e.g., gaseous compounds like methane) are not converted into electrical current production. If these anaerobic products, like acetate or H_2S , can be completely recovered as current, the coulombic efficiency is not affected; however, the energy liberated in these processes is lost (Rabaey et al. 2006). Secondly, the build-up of biomass gives rise to a lower coulombic efficiency. Thirdly, crossover of substrate or mixing of anodic and cathodic reagents can give rise to a low coulombic efficiency. In membraneless MFCs, a high influx of oxygen in the anode gives rise to aerobic conversion of the organic substrate with a low coulombic efficiency as a result (Liu and Logan 2004).

Strategies to minimize losses in BESs

To boost the performance of BESs, the losses described previously need to be minimized. Besides reactor configuration, also optimization of the operational parameters such as the electrode potentials, substrate loading rate, and hydraulic retention time enable BES operators to optimize the cell performance (Du et al. 2007). Engineering of the microbial consortium and the biofilm structure might also render useful tools in the development of better-performing BESs.

BES resistance and membrane use

To minimize ohmic voltage losses in BESs, the selection of highly conductive electrodes for electron transport is crucial. The resistivity of metals toward electron transfer

is in the order of 10^{-7} – 10^{-8} $\Omega\cdot\text{m}$ at 20°C , while the resistivity of carbon towards π -electrons is in the order $3.5 \cdot 10^{-5}$ $\Omega\cdot\text{m}$ (Serway and Beichner 2000). However, metals are generally more expensive than carbon and might be more subject to corrosion. Therefore, the combination of carbon fibers with a high specific surface area for microbial colonization combined with a limited amount of stainless steel as a current collector has been proposed (Logan et al. 2007; Rabaey et al. 2008). In addition, transition of charges between different conductors can give rise to a higher ohmic cell resistance in the case of bad contacts (Rozendal et al. 2007b).

For ionic charge transport in electrolytes, the resistance toward ion transfer is dependent on the concentration and mobility of the different ions. The resistivity of wastewater toward ion transfer at room temperature is typically between 20 $\Omega\cdot\text{m}$ (0.5 mS cm^{-1} , drinking water) and 0.2 $\Omega\cdot\text{m}$ (50 mS cm^{-1} , seawater). As a result, small BESs with an electrolyte with a high conductivity will perform better because of a lower ohmic voltage loss (Harnisch et al. 2008; Liu et al. 2005a). Generally, the electrolyte composition of wastewater cannot be altered; therefore, the distance between anode and cathode needs to be minimized (Liu et al. 2005a). The use of so called H-type reactors (Logan et al. 2006) needs to be avoided for this reason, unless only one electrode with potentiostatic electrode potential control is of interest.

The use of membranes increases the ohmic voltage loss in BESs (in the order of 5 to 14 $\Omega\cdot\text{m}$ or 9 to 45 $\text{m}\Omega\cdot\text{cm}^2$ at pH 7 with a 50 mM phosphate buffer; Harnisch et al. 2008; Liu and Logan 2004). It also results in the build-up of a pH gradient of several units across the membrane (Rozendal et al. 2006a). Such a pH gradient across the membrane is accompanied, according to the Nernst equation (0.059 V per pH unit), by a higher anodic equilibrium potential and/or a lower cathodic equilibrium potential, which lowers the attainable cell voltage in MFCs or increases the voltage needed to drive the MECs. These losses might turn out to be significant, as e.g., a pH difference across the membrane of 6.4 resulted in an additional voltage loss of 0.380 V (Rozendal et al. 2007b). Different types of membranes have been investigated; however, none of the membranes tested could solve these problems in a satisfactory way (Rozendal et al. 2007a; Ter Heijne et al. 2007). Introducing the anode effluent in the cathode has been proposed to obtain a pH neutral balance (Freguia et al. 2008).

Furthermore, a low-buffer capacity (Zhao et al. 2006) in combination with a slow proton transfer to the bulk solution and through a cation exchange membrane (Rozendal et al. 2006a) results in a rapid acidification of the anodic biofilm, thus decreasing its electro-catalytic activity (Harnisch et al. 2008). This imposes constraints to treat wastewater with a low pH-buffer capacity. The same constraints hold for

biocatalyzed cathodes, where an optimal pH is needed to ensure sufficient activity of cathodic microorganisms (Clauwaert et al. 2007b). Membraneless systems are only useful if mixing of the anodic and the cathodic reagents [e.g., acetate and oxygen (Liu and Logan 2004) or carbon dioxide and hydrogen gas (Rozendal et al. 2008)] is not giving rise to a low conversion efficiency.

BES configuration

To increase the overall voltage generation of MFCs for a set current generation, several authors have reported the connection of multiple MFCs in series (Aelterman et al. 2006b, Oh and Logan 2007, Shin et al. 2006). When MFCs are connected in series, the voltage of the different MFCs is added, while the current is determined by the average catalytic activity of the complete system. As the current is flowing through the complete system, the use of conductive but impermeable bipolar plates is needed to keep the ohmic voltage loss in the electrodes as low as possible. In addition, the biological and operational characteristics of the stacked MFCs need to be uniform to avoid cell reversal. During cell reversal, a MFC with a low catalytic activity or hampered influent flow will switch polarity and, on the long term, will fail (Aelterman et al. 2006b). Care should be taken to prevent this when MFCs are constructed in series (Oh and Logan 2007). Connecting several MFCs in parallel enables the generation of electricity at increased currents for a set voltage (Aelterman et al. 2006b).

BES operation

To maximize the power production per volumetric unit of MFC, one needs to apply the optimal external resistance (R_{opt}) as determined during polarization (Fig. 2c). Operating a MFC without external resistance will result in the short circuit current production (i_{sc}); however, as the cell voltage is zero, no energy is harvested. At external resistances higher than R_{opt} , the energetic efficiency increases; however, the volumetric current and power production decrease. For MECs, the applied voltage will determine the current production and thus the conversion rate.

To achieve a high volumetric conversion rate at a high conversion efficiency, it is necessary to select the appropriate hydraulic retention time for a given substrate concentration or volumetric substrate loading rate. For continuous biocatalyzed acetate oxidizing anode systems, the hydraulic retention times reported are typically in the order of 2.6 to 8.9 h for volumetric loading rates between 0.3 and 1.5 kg COD m^{-3} MFC day^{-1} achieving coulombic efficiencies between 65% and 96% (Aelterman et al. 2006b, 2008a; Clauwaert et al. 2007b; Freguia et al. 2007; Rabaey et al. 2005b). The substrate affinity constant (K_s) of the microbial

consortium under different operational conditions is a poorly investigated parameter for biocatalyzed reactions. For batch-fed acetate oxidizing MFCs, the K_s value was 9 mg acetate l^{-1} with an external resistance of 140 $m\Omega.m^3$ MFC vs 141 mg acetate l^{-1} for an external resistance of 6 $m\Omega.m^3$ MFC).

Electrode surface properties

Besides the specific electrode surface, the selection of a catalyst, its concentration, and the application of the catalyst on an electrode carrier have been described to highly affect the catalytic activity of the electrode in BESs (Yu et al. 2007; Zhao et al. 2006). Platinum has been widely used, both in anodes and cathodes, as it is highly reactive with hydrogen gas and oxygen, respectively. Protective coatings have been introduced to prevent the poisoning of platinum in microbial electrolytes (Niessen et al. 2004). Other metallic catalysts have been proposed as cheaper alternatives for oxygen reduction in the cathode (Cheng et al. 2006; Zhao et al. 2005). Furthermore, the combination of a chemical and microbial catalysis (Rhoads et al. 2005; Ter Heijne et al. 2007) or completely biological cathodes (Bergel et al. 2005; Clauwaert et al. 2007a,b; He and Angenent 2006; Rozendal et al. 2008) can be a sustainable and cost-effective alternative to lower cathodic overpotentials. Changing the electrode properties has been described to shorten the start-up of bioanodes and biocathodes with 30–50% (Cheng and Logan 2007a; Clauwaert et al. 2007b). The use of biodeposited metals on the cell wall of microorganisms as a way to increase the reactive surface area has successfully been applied to increase the rate of catalytic dechlorination (De Windt et al. 2005). This strategy could be applied in BESs to deposit reactive metallic catalysts more efficiently on a microbial-colonized electrode to enhance the catalytic activity of the electrode. Direct oxidation of organic molecules at an electrode or enzymatic catalyzed reactions might be an alternative approach to lower the overpotentials (Rosenbaum et al. 2006).

A strategy to lower the overpotentials is to lower the actual current density for a given current by a high specific electrode surface area in the order $10^6 m^2 m^{-3}$ (Freguia et al. 2007). This also increases the surface for enhanced substrate and product exchange between the electrode interface and the bulk solution, which can avoid limited current production due to concentration polarization. Especially for biological oxidations or reductions, it is difficult to know the exact electrochemical active surface area. It is not evident to verify if the complete electrode is covered with microorganisms and if every part of the electrode is equally colonized. The unknown fraction of electrochemically active microorganisms on the electrode in

combination with the possibility of an electrochemically active multilayer biofilm makes the online determination of the active surface area very difficult. While unsatisfactory for firm electrochemical conclusions, the expression of volumetric current density ($A\ m^{-3}$ BES) enables better comparison between different systems in a process engineering context (Table 1).

Selection for optimal microbial community functionality

Although the term biocatalyst is commonly used to address the microorganisms in BESs, strictly speaking, as the microorganisms consume part of the energy of the substrate for maintenance and growth, they are no real catalysts (Schroder 2007). At present, it is unknown to which extent the energy used for biomass growth and maintenance contribute to the overpotentials at a biocatalyzed electrode. Acetate-oxidizing microorganisms, which were operated at an anode potential of $-0.200\ V$ vs SHE, had a biomass concentration that was approximately 25% lower compared to an anode poised at 0.000 or $0.200\ V$ vs SHE after 30 days of operation. However, the specific biomass activity was in the order of $3.2\ g\ COD.g\ VSS^{-1}.day^{-1}$ (based on the current generation and biomass concentration) for the microbial consortium operating in the narrow redox range ($-0.200\ V$ vs SHE), whereas specific biomass activity in the order of 2.8 and $2.3\ g\ COD.g\ VSS^{-1}.day^{-1}$ for anodes operated at 0.000 and $0.200\ V$ vs SHE, respectively (Aelterman et al. 2008a). It seems that anodic microorganisms operated in a narrow redox range compensated a lower energy yield per mole electrons transferred by a higher activity. Because the electrode potential in an acetate-oxidizing anode is typically in this range, we hypothesize that microorganisms with electron transfer mechanisms that are highly active at low-anode potentials (or high for a

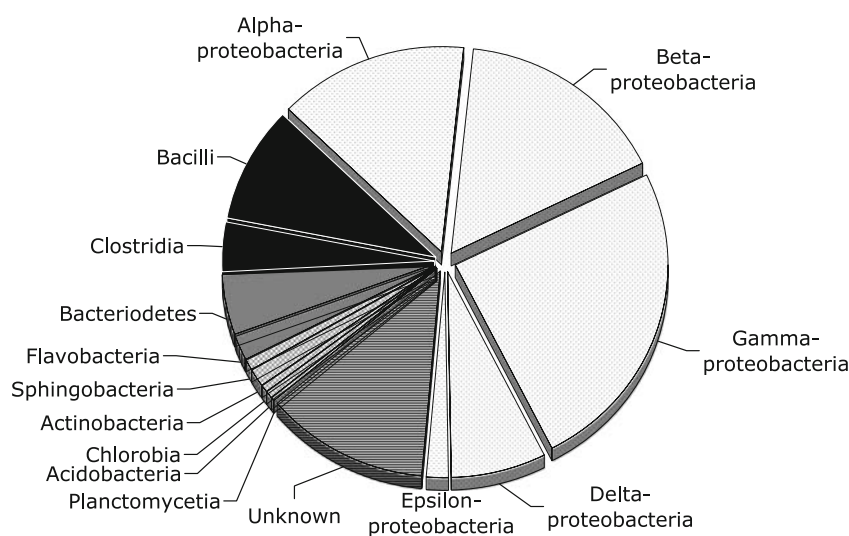
biocatalyzed cathode) might be able to out-compete other electroactive species, that are not able to respire at such redox conditions, by changing the electrode potential.

Microorganisms that use an inert electrode for direct respiration need a strategy to mediate the electrons between their respiratory electron transfer chain and the electrode. The effectiveness of this electron mediation will have an influence on the magnitude of the overpotentials and thus the attainable electron transfer rate. Two mechanisms have been proposed for anodic electron transfer: direct electron transfer with outer membrane cytochromes or nanowires (Bond and Lovley 2003; Gorby et al. 2006; Reguera et al. 2005, 2006) and the use of organic or inorganic electron shuttles between microorganisms and the electrode (Pham et al. 2008; Rabaey et al. 2004, 2005a). The mechanisms for cathodic biocatalyzed reactions without the use of electron-shuttling molecules remain unknown (Clauwaert et al. 2007b; Gregory et al. 2004).

Different anodic and cathodic microbial communities have been associated with a similar BES performance (Aelterman et al. 2008b; Clauwaert et al. 2007b; Rabaey et al. 2008). No typical MFC community was found while comparing eight different anode communities, although several genera were frequently reported (Fig. 4; Aelterman et al. 2008b). Clearly, a wide variety of microorganisms is capable of respiring with the help of an electrode. No electroactive communities have been reported to evolve to a quasi-axenic culture, even when fed with the same substrate for prolonged periods of time under the same conditions (Aelterman et al. 2006b).

It has been reported that, on an acetate-oxidizing anode, some dominant Gram-negative bacteria (*Pseudomonas* sp.) can produce metabolites such as pyocyanin and/or phenazine-1-carboxamide, which can function as electron shuttles (mediators), not only for the bacteria themselves but

Fig. 4 Overview of the different taxonomic classes in anodes of MFCs, examined by clone libraries and sequencing in eight different setups (Aelterman et al. 2006b; Back et al. 2004; Kim et al. 2004, 2006; Lee et al. 2003; Logan et al. 2005; Phung et al. 2004; Rabaey et al. 2004). The different phyla are represented by different patterns. The relative amount of the different phyla is given between brackets: Proteobacteria (64%), Firmicutes (13%), Bacteroides (7%), other phyla (3%), non-classified sequences (13%) (Aelterman et al. 2008b, with permission)



also for other species to transfer electrons to the anode (Rabaey et al. 2005a). *Brevibacillus* sp. was dominant in a microbial community of an acetate-oxidizing anode, but when operated as a single strain, it showed a poor performance and could only achieve significant electricity generation if phenazine-1-carboxamide was supplied into its anodic medium, together with a certain amount of rhamnolipid biosurfactant (Pham et al. 2008). It is therefore reasonable to conclude that exploiting microbial interactions, in ways that optimize the bacteria–electrode electron transfer could be an approach to enhance the overall performance of a BES.

Another approach to improve biocatalysis in a BES is to engineer the structure of the biofilms in the BES. Little is known about biocatalytic biofilm formation, which is unique in the way that microorganisms have to stay in touch with both sides of the biofilm: the bulk solution and the electrode. An open, ‘coral-like’ biofilm structure with a high-specific surface is likely to supply more electrochemical active species with substrate and to remove products, thus increasing the distance between the microorganisms and the electrode. Stimulation of microorganisms developing an electronic network of nanowires might enable this long-range electron transfer in a thick biofilm. This was suggested for a biocatalyzed anode, where an increase in the thickness of the biofilm up to 50 μm of *Geobacter sulfurreducens*, which produced electrically conductive pili, did not result in a decrease in the efficiency of the current production (calculated maximum current 27 A m^{-3} MFC) (Reguera et al. 2006). Strategies to promote such nanowire networks have not become available yet. On the other hand, compact and dense biofilms appear interesting in terms of short-distance electron transfer but might suffer from steeper substrate and product concentration gradients. Applying high shear ($>100 \text{ s}^{-1}$) has been described to promote stronger aggregation and attachment of microbes and hence more compact and denser biofilms in many microbial systems (van Loosdrecht et al. 2002).

Another strategy to increase the biomass density in an electrode, besides increasing biofilm thickness or density, is to increase the specific surface area of the electrode. With a mono-layer biofilm of 40 mg VSS m^{-2} [1 μm thick, 40 mg VSS/ml (Rittmann and McCarty 2001)] and an activity as described for an acetate oxidizing anode (2.3 $\text{g COD.g}^{-1} \text{VSS.day}^{-1}$), 10 kg COD m^{-3} electrode compartment per day can be converted if the specific surface area of the electrode is in the order of $1.1 \times 10^5 \text{ m}^2 \text{ m}^{-3}$. Granular graphite [$7.11 \times 10^4 \text{ m}^2 \text{ m}^{-3}$ available for colonization (Freguia et al. 2008)] should thus be able to convert 6.5 kg COD m^{-3} electrode day^{-1} when only a monolayer would be active. Taken into account that multi-layers of biocatalytic microorganisms can be active when electron mediators (Rabaey et al. 2004), or possibly nanowires

(Reguera et al. 2006), are present, also other electrode materials, like graphite brushes [$7.7 \times 10^3 \text{ m}^2 \text{ m}^{-3}$ (Zuo et al. 2007)], should sustain these conversion rates.

Application possibilities

Energy and chemical conversion processes

BESs are considered as environmentally friendly conversion technologies (Rabaey and Verstraete 2005). Typically, the chemical energy contained in an organic substrate is directly converted into electrical power, hydrogen gas, or methane in BESs (Cheng and Logan 2007b; Clauwaert et al. 2008; Liu et al. 2005b; Rabaey and Verstraete 2005; Rozendal et al. 2006b). However, to be competitive with anaerobic digestion, MFCs should be able to produce at least 400 W m^{-3} MFC on a cubic meter scale (Pham et al. 2006), whereas the highest power outputs at present are in the order of $10\text{--}100 \text{ W m}^{-3}$ MFC. For microbial electrolysis, Rozendal et al. (2006b) estimated that a production rate of $10 \text{ m}^3 \text{ H}_2 \text{ m}^{-3}$ MEC at an applied voltage of 0.3–0.4 V is only possible with low cathodic overpotentials ($|\eta_{\text{cathode}}| < 0.1 \text{ V}$). The highest volumetric hydrogen production reported at present is in the order of $1.2 \text{ m}^3 \text{ H}_2 \text{ m}^{-3}$ MEC (Cheng and Logan 2007b). Both MFCs and MECs have only been demonstrated on (sub)liter scale and without economical optimization of the materials.

Until BESs become more competitive compared to conventional technologies for energy production or conversion, the application field of BESs will have to be orientated toward specialized value-added applications [e.g., providing power to wireless sensors (Shantaram et al. 2005) or using biocatalyzed anodes for cathodic protection against corrosion (Orfei et al. 2006)]. Producing industrial chemicals from waste products in BES that have an economic added value might be another strategy. Besides cathodic hydrogen production (Liu et al. 2005b), the principle of cathodic ethanol production has also been demonstrated (Steinbush and Hamelers, unpublished results). Further research might demonstrate whether a wide variety of inorganic or organic compounds can be produced by either oxidation or reduction through biocatalyzed processes in BESs. However, purification costs and competition with existing technologies might render such processes economically difficult.

Water treatment

Removal of organic compounds from wastewater by anodic oxidation has been proposed as an energy-efficient treatment technology (Aelterman et al. 2006a). On the one hand, no energy is consumed for aeration (1 kWh kg

COD⁻¹ for conventional aeration), and on the other hand, energy can be recovered from the substrate [theoretical maximum: 3.8 kWh (kg COD)⁻¹]. In addition, a lower sludge production yield for anodic oxidation [0.02–0.05 g biomass-C (g substrate-C)⁻¹ used for acetate (Aelterman et al. 2008a); 0.07–0.22 g biomass-COD (g substrate-COD)⁻¹ used for glucose (Rabaey et al. 2003)] has been described in comparison to conventional aerobic wastewater treatment [0.53 g biomass-COD (g substrate-COD)⁻¹ (Verstraete and van Vaerenbergh 1986)]. Another interesting feature of BESs is the online activity measurement of the biological conversions by direct and easy monitoring of the current production and the electrode potential. In that way, a wastewater treatment operator can more rapidly adjust operational parameters. Nevertheless, high conversion rates with raw wastewater have not been demonstrated until now [<0.2 kg COD as current m⁻³ MFC day⁻¹ (Rabaey et al. 2005b)]. As long as conversion rates of organic compounds in wastewater are not in the order of 5–10 kg COD m⁻³ BES day⁻¹ at a cost of approximately 0.3 € m⁻³ wastewater, it is unlikely that BESs will out-compete conventional wastewater treatment technologies, unless wastewater treatment is accompanied with high value added features.

The development of novel contaminant removal technologies in BESs, not necessarily in combination with COD removal, is a first strategy. Sulfide oxidation in the anode (Rabaey et al. 2006), denitrification by a biocatalyzed cathode (Clauwaert et al. 2007a), perchlorate reduction (Thrash et al. 2007), and reduction of chlorinated organic compounds by biocatalyzed cathodes (Aulenta et al. 2007) might give extra added value to BESs. Furthermore, pre-emptive colonization of reverse osmosis filtrate by autotrophic microorganisms on a biocathode might prevent heterotrophic pathogens become dominant in these filtrates. In this context, BESs might have a bacteriostatic effect, as an anodic electrode can be used as an acidifying environment and a cathode to obtain local high pH values. In addition, cathodic hydrogen peroxide production can be combined with anodic COD removal for a combined disinfection and pollutant removal. In wetlands, sediments, or rice paddies, an enhanced oxidation of organics would not only result in a better water quality but also in a lower methane emissions. In fish ponds, BESs might be useful as a way to prevent methylmercury formation by redox balancing (De Schamphelaire et al. 2008). As biocatalyzed redox reactions has been described in seawater conditions (Bergel et al. 2005), COD removal and denitrification in highly conductive waste streams and brines (>5 mS cm⁻¹) could be an interesting niche application of BESs.

Another strategy to create added value is the combination of BESs with existing water treatment technologies. Combining anaerobic digestion with BESs has been

proposed for polishing sulfides and residual volatile fatty acids out of digester effluents (Aelterman et al. 2006a; Pham et al. 2006; Rabaey et al. 2006). Filter beds, commonly used in water treatment (Hammes et al. 2008; Kim and Kang 2008), could obtain extra oxidative or reductive properties when operated as bioelectrochemical systems. This can possibly enable polar and apolar substrate removal in the order of micrograms per liter when operated under optimal conditions.

Biosensors

MFCs have been proposed as BOD sensors, as the current production can be related to the BOD concentration in a solution (Kim et al. 2003). In addition, for biocatalyzed cathodic processes like nitrate or oxygen reduction, the current production might be a useful online concentration measurement (Clauwaert et al. 2007a,b). The inhibition of electrical current, on the other hand, can be a good indicator for toxic pulses. Introduction of an electrode in liquid streams containing biodegradable organic compounds can be a way to detect microbial contamination if current production is monitored. An extra advantage of harvesting electrical power is the possibility to use it for powering other sensors or data transmission systems (Shantaram et al. 2005).

Conclusions

Losses of a BES need to be characterized to minimize the global voltage loss (the sum of ohmic, overpotential, and pH gradient voltage losses) to values that allow current densities in the order of 1,400 A m⁻³ BES (10 kg COD m⁻³ BES day⁻¹). For MFCs, 400 W m⁻³ MFC should be taken as an objective, while 10 m³ H₂ m⁻³ MEC at an applied voltage of 0.3–0.4 V should be the goal for MECs. Improving the reactor configuration and operation and decreasing the costs of material use are the main abiotic challenges. In case of wastewater treatment, the benchmark cost of 0.3 € m⁻³ wastewater should be taken into account. Engineering electron transfer functionality within the microbial community and biofilm structure optimization appear to be the most challenging microbial parameters. Scaling BESs up will be difficult and, although useful strategies have already been brought forward, technological innovation is still needed to obtain economically feasible large-scale BESs, as the postulated performance has not been achieved yet on a liter scale.

Although COD oxidation rates are already in a competitive order of magnitude of 2 kg COD m⁻³ day⁻¹ (Table 1), it is doubtful whether the power production of MFCs or hydrogen production of MECs alone will render BESs

economically feasible. Therefore, further research should not only focus on optimization of cost-effective materials and optimizing microbial functionality but also on creating extra added value for bioelectrochemical systems. There might be several opportunities for small scale and more specialized applications. Cost calculations and life-cycle assessments will be necessary to convince policy makers and industries of the environmental and economical assets of versatile and controllable BESSs.

Acknowledgments The useful comments of Nico Boon are kindly acknowledged. This research was funded by a PhD grant (IWT grant 53305) of the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT-Vlaanderen), a postdoctoral grant (EX2006-0963) from the Spanish Ministry of Education and Science and the Flanders Research Foundation (FWO project G.0172.05).

References

- Aelterman P, Rabaey K, Clauwaert P, Verstraete W (2006a) Microbial fuel cells for wastewater treatment. *Water Sci Technol* 54:9–15
- Aelterman P, Rabaey K, Pham HT, Boon N, Verstraete W (2006b) Continuous electricity generation at high voltages and currents using stacked microbial fuel cells. *Environ Sci Technol* 40:3388–3394
- Aelterman P, Freguia S, Keller J, Verstraete W, Rabaey K (2008a) The anode potential regulates bacterial activity in microbial fuel cells. *Appl Microbiol Biotechnol* 78:409–418
- Aelterman P, Rabaey K, De Schamphelaire L, Clauwaert P, Boon N, Verstraete W (2008b) Microbial fuel cells as an engineered ecosystem. In: Wall J, Harwood CS, Demain AL (eds) *Bioenergy*. ASM, Washington, DC, USA, pp 307–320
- Allen RM, Bennetto HP (1993) Microbial fuel-cells-electricity production from carbohydrates. *Appl Biochem Biotechnol* 39:27–40
- Aulenta F, Catervi A, Majone M, Panero S, Reale P, Rossetti S (2007) Electron transfer from a solid-state electrode assisted by methyl viologen sustains efficient microbial reductive dechlorination of TCE. *Environ Sci Technol* 41:2554–2559
- Back JH, Kim MS, Cho H, Chang IS, Lee JY, Kim KS, Kim BH, Park YI, Han YS (2004) Construction of bacterial artificial chromosome library from electrochemical microorganisms. *FEMS Microbiol Lett* 238:65–70
- Bergel A, Feron D, Mollica A (2005) Catalysis of oxygen reduction in PEM fuel cell by seawater biofilm. *Electrochem Commun* 7:900–904
- Blake RC, Howard GT, McGinness S (1994) Enhanced yields of iron-oxidizing bacteria by in-situ electrochemical reduction of soluble iron in the growth-medium. *Appl Environ Microbiol* 60:2704–2710
- Bond DR, Lovley DR (2003) Electricity production by *Geobacter sulfurreducens* attached to electrodes. *Appl Environ Microbiol* 69:1548–1555
- Cheng S, Logan BE (2007a) Ammonia treatment of carbon cloth anodes to enhance power generation of microbial fuel cells. *Electrochem Commun* 9:492–496
- Cheng S, Logan BE (2007b) Sustainable and efficient biohydrogen production via electrohydrogenesis. *PNAS* 104:18871–18873
- Cheng S, Liu H, Logan BE (2006) Power densities using different cathode catalysts (Pt and CoTMP) and polymer binders (Nafion and PTFE) in single chamber microbial fuel cells. *Environ Sci Technol* 40:364–369
- Clauwaert P, Rabaey K, Aelterman P, DeSchamphelaire L, Pham TH, Boeckx P, Boon N, Verstraete W (2007a) Biological denitrification in microbial fuel cells. *Environ Sci Technol* 41:3354–3360
- Clauwaert P, Van der Ha D, Boon N, Verbeken K, Verhaege M, Rabaey K, Verstraete W (2007b) Open air biocathode enables effective electricity generation with microbial fuel cells. *Environ Sci Technol* 41:7564–7569
- Clauwaert P, Tolédo R, Van der Ha D, Crab R, Verstraete W, Hu H, Udert KM, Rabaey K (2008) Combining biocatalyzed electrolysis with anaerobic digestion. *Water Sci Technol* 57:575–579
- De Schamphelaire L, Van den Bossche K, Dang HS, Hofte M, Boon N, Rabaey K, Verstraete W (2008) Microbial fuel cells generating electricity from rhizodeposits of rice plants. *Environ Sci Technol* 42:3053–3058
- De Windt W, Aelterman P, Verstraete W (2005) Bioreductive deposition of palladium (0) nanoparticles on *Shewanella oneidensis* with catalytic activity towards reductive dechlorination of polychlorinated biphenyls. *Environ Microbiol* 7:314–325
- Du ZW, Li HR, Gu TY (2007) A state of the art review on microbial fuel cells: a promising technology for wastewater treatment and bioenergy. *Biotechnol Adv* 25:464–482
- Freguia S, Rabaey K, Yuan Z, Keller J (2007) Non-catalyzed cathodic oxygen reduction at graphite granules in microbial fuel cells. *Electrochim Acta* 53:598–603
- Freguia S, Rabaey K, Yuan ZG, Keller J (2008) Sequential anode-cathode configuration improves cathodic oxygen reduction and effluent quality of microbial fuel cells. *Water Res* 42:1387–1396
- Gorby YA, Yanina S, McLean JS, Rosso KM, Moyles D, Dohnalkova A, Beveridge TJ, Chang IS, Kim BH, Kim KS (2006) Electrically conductive bacterial nanowires produced by *Shewanella oneidensis* strain MR-1 and other microorganisms. *Proc Natl Acad Sci U S A* 103:11358–11363
- Gregory KB, Bond DR, Lovley DR (2004) Graphite electrodes as electron donors for anaerobic respiration. *Environ Microbiol* 6:596–604
- Hammes F, Berney M, Wang YY, Vital M, Koster O, Egli T (2008) Flow-cytometric total bacterial cell counts as a descriptive microbiological parameter for drinking water treatment processes. *Water Res* 42:269–277
- Harnisch F, Schröder U, Scholz F (2008) The suitability of monopolar and bipolar ion exchange membranes as separators for biological fuel cells. *Environ Sci Technol* 42:1740–1746
- He Z, Angenent LT (2006) Application of bacterial biocathodes in microbial fuel cells. *Electroanalysis* 18:2009–2015
- He Z, Wagner N, Minteer SD, Angenent LT (2006) An upflow microbial fuel cell with an interior cathode: assessment of the internal resistance by impedance spectroscopy. *Environ Sci Technol* 41:5212–5217
- Kim J, Kang B (2008) DBPs removal in GAC filter-adsorber. *Water Res* 42:145–152
- Kim BH, Chang IS, Gil GC, Park HS, Kim HJ (2003) Novel BOD (biological oxygen demand) sensor using mediator-less microbial fuel cell. *Biotechnol Lett* 25:541–545
- Kim BH, Park HS, Kim HJ, Kim GT, Chang IS, Lee J, Phung NT (2004) Enrichment of microbial community generating electricity using a fuel cell type electrochemical cell. *Appl Microbiol Biotechnol* 63:672–681
- Kim GT, Webster G, Wimpenny JWT, Kim BH, Kim HJ, Weightman AJ (2006) Bacterial community structure, compartmentalization and activity in a microbial fuel cell. *J Appl Microbiol* 101:698–710
- Lee JY, Phung NT, Chang IS, Kim BH, Sung HC (2003) Use of acetate for enrichment of electrochemically active microorganisms and their 16S rDNA analyses. *FEMS Microbiol Lett* 223:185–191

- Liang P, Huang X, Fan MZ, Cao XX, Wang C (2007) Composition and distribution of internal resistance in three types of microbial fuel cells. *Appl Microbiol Biotechnol* 77:551–558
- Liu H, Logan BE (2004) Electricity generation using an air-cathode single chamber microbial fuel cell in the presence and absence of a proton exchange membrane. *Environ Sci Technol* 38:4040–4046
- Liu H, Cheng SA, Logan BE (2005a) Power generation in fed-batch microbial fuel cells as a function of ionic strength, temperature, and reactor configuration. *Environ Sci Technol* 39:5488–5493
- Liu H, Grot S, Logan BE (2005b) Electrochemically assisted microbial production of hydrogen from acetate. *Environ Sci Technol* 39:4317–4320
- Logan BE, Murano C, Scott K, Gray ND, Head IM (2005) Electricity generation from cysteine in a microbial fuel cell. *Water Res* 39:942–952
- Logan BE, Hamelers B, Rozendal R, Schroder U, Keller J, Freguia S, Aelterman P, Verstraete W, Rabaey K (2006) Microbial fuel cells: methodology and technology. *Environ Sci Technol* 40:5181–5192
- Logan BE, Cheng S, Watson V, Estadt G (2007) Graphite fiber brush anodes for increased power production in air-cathode microbial fuel cells. *Environ Sci Technol* 41:3341–3346
- Niessen J, Schroder U, Rosenbaum M, Scholz F (2004) Fluorinated polyanilines as superior materials for electrocatalytic anodes in bacterial fuel cells. *Electrochem Commun* 6:571–575
- Oh SE, Logan BE (2007) Voltage reversal during microbial fuel cell stack operation. *J Power Sources* 167:11–17
- Orfei LH, Simison S, Busalmen JP (2006) Stainless steels can be cathodically protected using energy stored at the marine sediment/seawater interface. *Environ Sci Technol* 40:6473–6478
- Park DH, Laivenieks M, Guettler MV, Jain MK, Zeikus JG (1999) Microbial utilization of electrically reduced neutral red as the sole electron donor for growth and metabolite production. *Appl Environ Microbiol* 65:2912–2917
- Pham TH, Rabaey K, Aelterman P, Clauwaert P, De Schampelaire L, Boon N, Verstraete W (2006) Microbial fuel cells in relation to conventional anaerobic digestion technology. *Eng Life Sci* 6:285–292
- Pham TH, Boon N, Aelterman P, Clauwaert P, De Schampelaire L, Vanhaecke L, De Maeyer K, Hofte M, Verstraete W, Rabaey K (2008) Metabolites produced by *Pseudomonas* sp enable a Gram-positive bacterium to achieve extracellular electron transfer. *Appl Microbiol Biotechnol* 77:1119–1129
- Phung NT, Lee J, Kang KH, Chang IS, Gadd GM, Kim BH (2004) Analysis of microbial diversity in oligotrophic microbial fuel cells using 16S rDNA sequences. *FEMS Microbiol Lett* 233:77–82
- Rabaey K, Verstraete W (2005) Microbial fuel cells: novel biotechnology for energy generation. *Trends Biotechnol* 23:291–298
- Rabaey K, Lissens G, Siciliano SD, Verstraete W (2003) A microbial fuel cell capable of converting glucose to electricity at high rate and efficiency. *Biotechnol Lett* 25:1531–1535
- Rabaey K, Boon N, Siciliano SD, Verhaege M, Verstraete W (2004) Biofuel cells select for microbial consortia that self-mediate electron transfer. *Appl Environ Microbiol* 70:5373–5382
- Rabaey K, Boon N, Hofte M, Verstraete W (2005a) Microbial phenazine production enhances electron transfer in biofuel cells. *Environ Sci Technol* 39:3401–3408
- Rabaey K, Clauwaert P, Aelterman P, Verstraete W (2005b) Tubular microbial fuel cells for efficient electricity generation. *Environ Sci Technol* 39:8077–8082
- Rabaey K, Vandesompele K, Maignien L, Boon N, Aelterman P, Clauwaert P, De Schampelaire L, Pham HT, Vermeulen J, Verhaege M, Lens P, Verstraete W (2006) Microbial fuel cells for sulfide removal. *Environ Sci Technol* 40:5218–5224
- Rabaey K, Rodríguez J, Blackall LL, Keller J, Gross P, Batstone D, Verstraete W, Neals KH (2007) Microbial ecology meets electrochemistry: electricity-driven and driving communities. *ISME J* 1:9–18
- Rabaey K, Read S, Clauwaert P, Freguia S, Bond PL, Blackall LL, Keller J (2008) Cathodic oxygen reduction catalyzed by bacteria in microbial fuel cells. *ISME J* 2:519–527.
- Reguera G, McCarthy KD, Mehta T, Nicoll JS, Tuominen MT, Lovley DR (2005) Extracellular electron transfer via microbial nanowires. *Nature* 435:1098–1101
- Reguera G, Nevin KP, Nicoll JS, Covalla SF, Woodard TL, Lovley DR (2006) Biofilm and nanowire production leads to increased current in *Geobacter sulfurreducens* fuel cells. *Appl Environ Microbiol* 72:7345–7348
- Rhoads A, Beyenal H, Lewandowski Z (2005) Microbial fuel cell using anaerobic respiration as an anodic reaction and biomineralized manganese as a cathodic reactant. *Environ Sci Technol* 39:4666–4671
- Rittmann BE, McCarty PL (2001) Environmental biotechnology: principles and applications. McGraw-Hill, New York, USA, pp 434–437
- Rosenbaum M, Schroder U, Scholz F (2006) Investigation of the electrocatalytic oxidation of formate and ethanol at platinum black under microbial fuel cell conditions. *J Solid State Electrochem* 10:872–878
- Rozendal RA, Hamelers HVM, Buisman CJN (2006a) Effects of membrane cation transport on pH and microbial fuel cell performance. *Environ Sci Technol* 40:5206–5211
- Rozendal RA, Hamelers HVM, Euverink GJW, Metz SJ, Buisman CJN (2006b) Principle and perspectives of hydrogen production through biocatalyzed electrolysis. *Int J Hydrogen Energy* 31:1632–1640
- Rozendal R, Sleutels THJA, Hamelers HVM, Buisman CJN (2007a) Effect of the type of ion exchange membrane on performance, ion transport, and pH in biocatalyzed electrolysis of wastewater. In: Proceedings of the 11th IWA World Congress on Anaerobic Digestion: Bioenergy for Our Future. PP3A.3, IWA, Brisbane, Australia
- Rozendal RA, Hamelers HVM, Molenkamp RJ, Buisman JN (2007b) Performance of single chamber biocatalyzed electrolysis with different types of ion exchange membranes. *Water Res* 41:1984–1994
- Rozendal RA, Jeremiassen AW, Hamelers HVM, Buisman CJN (2008) Hydrogen production with a microbial biocathode. *Environ Sci Technol* 42:629–634
- Schroder U (2007) Anodic electron transfer mechanisms in microbial fuel cells and their energy efficiency. *Phys Chem Chem Phys* 9:2619–2629
- Serway RA, Beichner RJ (2000) Physics for scientists and engineers with modern physics. Saunders College Publishing, Philadelphia, USA, pp 846–848
- Shantaram A, Beyenal H, Raajan R, Veluchamy A, Lewandowski Z (2005) Wireless sensors powered by microbial fuel cells. *Environ Sci Technol* 39:5037–5042
- Shin SH, Choi YJ, Na SH, Jung SH, Kim S (2006) Development of bipolar plate stack type microbial fuel cells. *Bull Korean Chem Soc* 27:281–285
- Ter Heijne A, Hamelers HVM, Buisman CJN (2007) Microbial fuel cell operation with continuous biological ferrous iron oxidation of the catholyte. *Environ Sci Technol* 41:4130–4134

- Terheijne A, Hamelers HVM, De Wilde V, Rozendal RA, Buisman CJN (2006) A bipolar membrane combined with ferric iron reduction as an efficient cathode system in microbial fuel cells. *Environ Sci Technol* 40:5200–5205
- Thrash JC, Van Trump JI, Weber KA, Miller E, Achenbach LA, Coates JD (2007) Electrochemical stimulation of microbial perchlorate reduction. *Environ Sci Technol* 41:1740–1746
- van Loosdrecht MCM, Heijnen JJ, Eberl H, Kreft J, Picioreanu C (2002) Mathematical modelling of biofilm structures. *Antonie Van Leeuwenhoek Int J Gen Molec Microbiol* 81:245–256
- Verstraete W, van Vaerenbergh E (1986) Aerobic activated sludge. In: Rehm HJ, Reed G (eds) *Biotechnology*, vol. 8. VCH, Weinheim, Germany, pp 43–112
- Yu EH, Chang K, Scott K, Logan BE (2007) Microbial fuel cell performance with non-Pt cathode catalysts. *J Power Sources* 171:275–281
- Zhao F, Harnisch F, Schroder U, Scholz F, Bogdanoff P, Herrmann I (2005) Application of pyrolysed iron(II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells. *Electrochem Commun* 7:1405–1410
- Zhao F, Harnisch F, Schröder U, Scholz F, Bogdanoff P, Herrmann I (2006) Challenges and constraints of using oxygen cathodes in microbial fuel cells. *Environ Sci Technol* 40:5193–5199
- Zuo Y, Cheng S, Call D, Logan BE (2007) Tubular membrane cathodes for scalable power generation in microbial fuel cells. *Environ Sci Technol* 41:3347–3353