

New applications and performance of bioelectrochemical systems

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Abstract Bioelectrochemical systems (BESs) are emerging technologies which use microorganisms to catalyze the reactions at the anode and/or cathode. BES research is advancing rapidly, and a whole range of applications using different electron donors and acceptors has already been developed. In this mini review, we focus on technological aspects of the expanding application of BESs. We will analyze the anode and cathode half-reactions in terms of their standard and actual potential and report the overpotentials of these half-reactions by comparing the reported potentials with their theoretical potentials. When combining anodes with cathodes in a BES, new bottlenecks and opportunities arise. For application of BESs, it is crucial to lower the internal energy losses and increase productivity at the same time. Membranes are a crucial element to obtain high efficiencies and pure products but increase the internal resistance of BESs. The comparison between production of fuels and chemicals in BESs and in present production

processes should gain more attention in future BES research. By making this comparison, it will become clear if the scope of BESs can and should be further developed into the field of biorefineries.

Keywords Bioelectrochemical system · Microbial fuel cell · Microbial electrolysis cell · Overpotential · Coulombic efficiency

Introduction

Bioelectrochemical systems (BESs) are emerging technologies which use microorganisms attached to one or both bioelectrode(s) to catalyze the oxidation reaction in case of a bioanode and/or reduction reaction in case of a biocathode (Rabaey et al. 2009). A BES is called a microbial fuel cell (MFC) if electrical power is harvested and is called a microbial electrolysis cell (MEC) if electrical energy is supplied to drive an otherwise nonspontaneous reaction. Historical breakthroughs toward the current BESs are the first discovery of electricity generation by microorganism *Escherichia coli* (Potter 1912), mediatorless direct electron transfer and oxidation of lactate by *Shewanella putrefaciens* (Kim et al. 2002), and mediatorless carbohydrate oxidation by *Rhodospirillum rubrum* in an MFC (Chaudhuri and Lovley 2003). These results provide the fundamental groundwork of numerous BES applications like wastewater treatment and electricity generation by microorganisms, since toxic soluble mediators were not needed any more (Logan 2005). The popularity of research on BESs is increasing rapidly as illustrated by the amount of peer reviewed papers on BESs like the MFCs which doubled over the year 2007 to 2008 (Scopus 2009). Over 100 research groups have attended the 2nd Microbial Fuel Cell

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Conference in South Korea, investigating BESs from fundamentals toward new applications (Chang et al. 2009).

To facilitate BES operation, a primary electron donor must be supplied to the anode and a final electron acceptor to the cathode. The advantage of BESs when using two compartments is that they not solely convert compounds but also separate oxidation and reduction products, which makes it possible to extract useful products out of wastes. Nowadays, BES with bioanodes uses electron donors derived from wastes (e.g., wastewaters; Logan 2005), sediments (Reimers et al. 2001), processed energy crops (as cellulose; Niessen et al. 2005; Ren et al. 2007; Rezaei et al. 2009), photosynthetic microorganisms (Strik et al. 2008b; Chiao et al. 2006; Fu et al. 2009), or in situ photosynthesized plant rhizodeposits (Strik et al. 2008a; De Schampelaire et al. 2008). BESs, like MFCs treating wastewater, combine energy harvesting with necessary wastewater cleaning. In case of solar powered or photosynthetic MFCs, the challenge is to produce net electricity (De Schampelaire and Verstraete 2009; Strik et al. 2008a, b). BESs with microorganisms at the bioanode or biocathode generally may be combined with any other known bio or chemical half-reaction at the other electrode (Rozendal et al. 2009). Recently, MFCs were developed with mediatorless biocathodes using various final electron acceptors like oxygen (Bergel et al. 2005), nitrate (Clauwaert et al. 2007a), or CO_2 (Cao et al. 2009). The last years, BES research has also moved in the direction from producing electricity in MFCs to MEC applications using microorganisms as novel biocatalysts that produce all kinds of value added products like H_2 (Rozendal et al. 2006b), CH_4 (Cheng et al. 2009), H_2O_2 (Rozendal et al. 2009), or ethanol (Steinbusch et al. 2009), while using final electron acceptors like protons, CO_2 , and acetate.

Summarized, BESs are in fashion, advancing rapidly, and a whole range of applications using different electron donors and acceptors have already been developed. Figure 1 illustrates existing and recent new BES applications with achieved in- and outputs which may evolve to large scale BESs. It shows the versatility of BES and the combined possible advantages like wastewater cleaning (Logan 2004), nutrient removal (Clauwaert et al. 2007a; Viridis et al. 2008), production of added value products, net power production, plant horticulture and energy landscape design (Strik et al. 2008a; Strik 2009), CO_2 capture (Cheng et al. 2009), microbial biomass production (Strik et al. 2008b), and biowaste treatment (Rozendal et al. 2008a; Selembo et al. 2009b).

In this mini review, we focus on technological aspects of the expanding application of BES. First, we will investigate four groups of typical compounds for the anode: (1) standard wastewater compounds: acetate and glucose; (2) a waste product in biodiesel production: glycerol; (3)

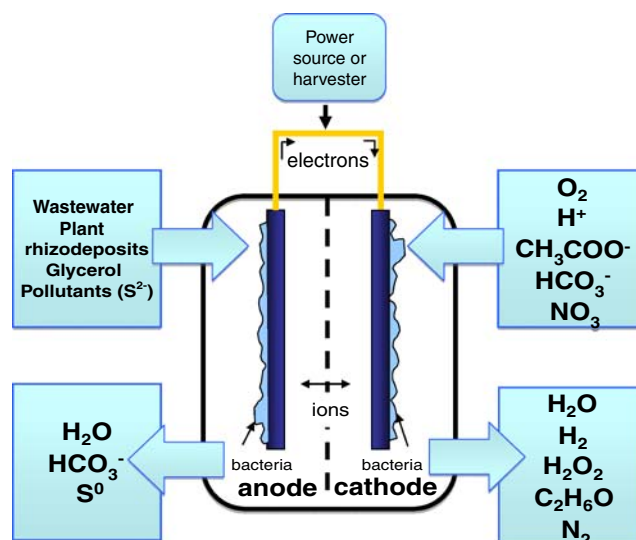


Fig. 1 Overview of inputs and outputs in BESs. Anode and cathode chambers are separated by a membrane. This membrane, however, needs not always be present: a water layer can already be a sufficient separator

typical plant rhizodeposits: malate, citrate, glycine, and serine; and (4) a pollutant: sulfur. For the cathode, we focus on (1) the reduction of oxygen to both water and hydrogen peroxide; (2) the production of fuels and chemicals: hydrogen, methane, and ethanol; and (3) the removal of pollutants: nitrogen.

The efficiency of a BES is determined to a large extent by the energy losses of the reactions, expressed as overpotentials, and the extent to which the produced electrons end up in the desired product, expressed as coulombic efficiency. We will analyze the anode and cathode half-reactions in terms of their standard and actual potential and report the overpotentials of these half-reactions by comparing the reported potentials with their theoretical potentials. In principle, any anodic reaction can be combined with any cathodic reaction to form a BES. Such a combination gives rise to new bottlenecks and opportunities that will be explored in the final paragraph.

Thermodynamics of BESs

The amount of energy of the electrons is expressed in the anode and cathode potential and is determined by thermodynamics of the anode and cathode reaction (Table 1). To calculate these potentials, the Gibb's free energy (kJ/mol) of the reaction needs to be determined. This Gibb's free energy under standard conditions can then be converted into a standard potential E^0 (V vs normal hydrogen electrode (NHE), where NHE is by definition zero). These calculations were performed as extensively described in (Logan et al. 2006). All values for Gibb's free energy were

Table 1 Overview of reactions with standard potential (E^0) and actual potential (E)

		E^0 (V vs NHE)	E (V vs NHE)
<i>Anodic oxidation reaction</i>			
Acetate	$C_2H_3O_2^- + 4 H_2O \rightarrow 2 HCO_3^- + 9 H^+ + 8 e^-$	0.187	-0.289
Glucose	$C_6H_{12}O_6 + 12 H_2O \rightarrow 6 HCO_3^- + 30 H^+ + 24 e^-$	0.104	-0.429
Glycerol	$C_3H_8O_3 + 6 H_2O \rightarrow 3 HCO_3^- + 17 H^+ + 14 e^-$	0.118	-0.396
Malate	$C_4H_5O_5^- + 7 H_2O \rightarrow 4 H_2CO_3 + 11 H^+ + 12 e^-$	0.01	-0.274
Citrate	$C_6H_5O_7^{3-} + 11 H_2O \rightarrow 6 H_2CO_3 + 15 H^+ + 18 e^-$	0.022	-0.242
Glycine	$C_2H_5NO_2 + 4 H_2O \rightarrow 2 HCO_3^- + 7 H^+ + 1 NH_4^+ + 6 e^-$	0.131	-0.24
Serine	$C_3H_7NO_3 + 6 H_2O \rightarrow 3 HCO_3^- + 12 H^+ + 1 NH_4^+ + 10 e^-$	0.105	-0.273
Sulfur	$HS^- \rightarrow S^0 + H^+ + 2e^-$	-0.062	-0.23
<i>Cathodic reduction reaction</i>			
Oxygen to water	$O_2 + 4 H^+ + 4 e^- \rightarrow 2 H_2O$	1.229	0.805
Oxygen to hydrogen peroxide	$O_2 + 2 H^+ + 2 e^- \rightarrow H_2O_2$	0.694	0.269
Protons to hydrogen	$2 H^+ + 2 e^- \rightarrow H_2$	0	-0.414
Bicarbonate to methane	$HCO_3^- + 9 H^+ + 8 e^- \rightarrow CH_4 + 3 H_2O$	0.227	-0.248
Acetate to ethanol	$C_2H_3O_2^- + 5 H^+ + 4 e^- \rightarrow C_2H_6O + H_2O$	0.128	-0.408
Nitrate to nitrogen gas	$2 NO_3^- + 12 H^+ + 10 e^- \rightarrow N_2 + 6 H_2O$	1.246	0.734

Conditions used to calculate actual potential:

$[HCO_3^-]$, $[H_2CO_3]=0.05$ M

Acetate, glucose, glycerol, bisulfide=0.05 M

Malate, citrate, glycine, serine=0.005 M

$[NH_4^+]=0.005$ M

$[S^0]=1$ M

$[H_2O]=1$ M

$[H^+]$: pH neutral= 10^{-7} M, for malate, citrate, glycine, and serine= 10^{-5} M

$pO_2=0.2$ bar

All product concentrations except $H_2O_2=1$ M

$[H_2O_2]=0.5$ M

$[NO_3^-]=0.05$ M

T=298 K

taken from Amend and Shock (2001). From these standard potentials, the actual potentials were calculated using actual concentrations that are typical for BESSs. For the typical plant rhizodeposits malate, citrate, glycine, and serine, the potentials are calculated at pH=5 as this is the actual pH in a plant MFC. All actual concentrations are indicated in Table 1.

The many different reactions in a BES occur at their own specific potential. Only when combining an oxidation and

reduction reaction, it becomes clear if the reaction is thermodynamically favorable, i.e., energy is produced, or if energy needs to be added to the system to let the reactions proceed. Table 2 gives an overview of the energy output and input when combining acetate oxidation as a typical anode reaction with the cathode reactions. We see that most reactions are thermodynamically favorable, while only the production of hydrogen and ethanol are electricity consuming reactions.

Table 2 The voltage that is gained or needs to be applied when linking acetate as the anode reaction to the different cathode reactions

	Oxygen to water	Oxygen to hydrogen peroxide	Protons to hydrogen	Bicarbonate to methane	Acetate to ethanol	Nitrate to nitrogen gas
Acetate	1.094	0.558	-0.125	0.041	-0.119	1.023

Metrics for electrode performance

The performance of an electrode can be characterized by two important metrics: the overpotential and the coulombic efficiency. The first metric, the overpotential, indicates the amount of energy lost at the electrode. As an example, we will discuss the anode overpotential here. The anode overpotential is defined as the difference between the anode potential and the theoretical anode potential. The theoretical anode potentials as calculated in Table 1 describe a situation in which the anode is in equilibrium with the electron donor, i.e., the energy level of the electrons in the anode equals that of the electron donor. When anode potential is increased from the equilibrium situation, a current may flow from the electron donor to the anode due to the presence of a potential difference. This electron flow will occur only in the presence of a suitable catalyst. The overpotential is then both a measure of the energy lost in the electron-transfer reaction and a measure of the driving force of the reaction. The same principle holds for the cathode. Now, when current is produced, the anode potential will increase and the cathode potential will decrease. The amount of energy lost at the electrode, i.e., the overpotential, is dependent on the current produced and the charge-transfer resistance: the higher the current, the more energy is lost and the higher the overpotential is.

The theoretical anode potential is in practice comparable to the open cell potential (OCP). The OCP is the potential of an electrode when no current is produced. In that case, no load is applied to the system, and the energy losses at the electrodes should be zero. In a strict sense, the anode potential is determined by the electron-exchange component, either soluble (mediator) or part of the microorganisms, e.g., an outer membrane cytochrome. When no current flows, the potential of the electron-exchange component is given by the Nernst equation: $E_{an} = E^0 + \frac{RT}{F} \ln \frac{[Ox]}{[Red]}$. When we disconnect the load, the biochemical catalyst will still supply electrons to the electron-exchange component. This will lead to further reduction of the oxidized form of the electron-exchange component to the reduced form, leading to a decrease of the potential. Therefore, if the biochemical catalyst is reversible and the reaction is indeed as presented in Table 1, anode potential will stop decreasing only when anode potential is in equilibrium with the potential of the electron donor. In this case, the values for the OCP should be comparable to the theoretical values (Table 1).

The second metric is the coulombic efficiency, indicating the extent to which the produced electrons end up in the desired product. In the following chapters, we will compare the reported potentials to the theoretical values, compare coulombic efficiencies, and discuss the implications for design when combining anodes and cathodes in BESs.

Anode performance

Overpotentials for acetate oxidation

In experimental stage BESs, often acetate is used as substrate for oxidation. Acetate is the end product of fermentation, and without an additional energy input, acetate cannot be converted further to useful products other than methane. Because of this, the use of acetate does not compete with feed or food production since it is a waste product (Steinbusch et al. 2008). Reported OCPs for acetate oxidation are typically close to the theoretical values reported in Table 1, for example ranging between -0.250 V vs NHE (Ter Heijne et al. 2006, 2008) in an MFC and -0.200 V vs NHE (Rozendal et al. 2007) in an MEC. The anode potentials found when current is produced, however, are often higher than the theoretical values. For example, anode potentials of -0.200 V vs NHE (Ter Heijne et al. 2006; Ter Heijne et al. 2008) were found for acetate oxidation at a current density of 1 A/m² while the theoretical potential is -0.289 V vs NHE (Table 1). Similar values for anode potentials have been found (Fan et al. 2007) for the oxidation of acetate at higher current densities.

Overpotentials for oxidation of glucose, glycerol, and plant rhizodeposits

For acetate, the reported values for the anode potential are close to the thermodynamical value as shown in the previous paragraph. When using MFCs with mixed cultures and more complex substrates such as wastewaters, the found OCP values turn out also to be close to the thermodynamical potential of acetate instead of approaching the theoretical value for the complex substrate in question. Plant rhizodeposits consist of actively or passively released low molecular weight molecules like sugars and organic acids, and dead plant material like sloughed-off root caps, and roots. Using *Glyceria maxima* rhizodeposits as substrate, anode potentials of -0.050 V at OCP to -0.075 V vs NHE were recorded during polarization (Strik et al. 2008a). This is considerably higher than the calculated actual potentials (Table 1). Using domestic wastewater as substrate, an OCP of -0.200 V vs NHE has been reported (Min and Logan 2004), and at a current density of 20 mA/m², the anode potential increased to $+0.150$ V vs NHE. The reason for these relatively high potential values compared to the theoretical values may be that these complex substrates are fermented via intermediates to acetate before being oxidized at the anode. For example, it was shown that direct oxidation of glucose to electrons plays a minor role in current generation (Freguia et al. 2008b). Glucose is first fermented to acetate and hydrogen which are then both used to produce current. So finally, the produced acetate is

used by the electrochemically active microorganisms to produce electrons. Furthermore, it was shown that 1,3-propanediol was the main intermediate in glycerol oxidation while also acetate and propionate were detected (Selembo et al. 2009b). This implies that not all the available energy from, i.e., glucose, but only the amount of energy that is available from acetate is transferred to the electrode. This lowers the voltage efficiency and therefore also the energy efficiency of the system drastically and is therefore an important feature to take into account when operating MFCs with more complex substrates.

The observation that when using mixed cultures, sugars and other complex substrates are not used directly to produce electricity but are first fermented to acetate, can also be explained from a thermodynamic perspective. In Fig. 2, we see that glucose is oxidized at an energy level of -0.429 V vs NHE. If the electrons would be released to the electrode at a value higher than the oxidation of acetate (-0.289 V vs NHE), so in the gray area, the microorganisms would get less energy from the production of electricity than from fermenting the glucose to acetate. Therefore, it is expected that they will first convert the glucose to acetate. Only when the potential of the electrode is equal or lower than the potential for acetate (dark gray area), it becomes thermodynamically more favorable to donate the electrons to the electrode.

Overpotentials for sulfide oxidation

Sulfur is present in wastewater mainly in the form of sulfates. The mechanism in which sulfur can be removed is as follows. By introducing sulfate reducers to the anodic compartment, sulfate is reduced to hydrogen sulfide using

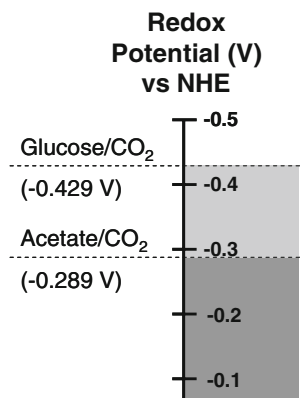


Fig. 2 The light gray area depicts the energy level at which it is thermodynamically more favorable for the microorganisms to produce acetate than electricity from glucose. Only when the anode potential is higher than -0.289 V, the microorganisms will produce electricity

the available organic electron donor (Zhao et al. 2008). Hydrogen sulfide is then abiotically oxidized to elemental sulfur and precipitates at the anode (Rabaey et al. 2006; Dutta et al. 2008). In theory, the oxidation of hydrogen sulfide to elemental sulfur occurs at a potential of -0.23 V vs NHE (Table 1). Open circuit anode potentials for sulfide oxidation have been reported to be close to this theoretical potential, namely -0.25 V vs NHE (Zhao et al. 2009a), and in an MFC in which the anode potential was controlled at -0.2 V vs NHE; also, sulfide was still found to be oxidized (Rabaey et al. 2006).

The removal of sulfur compounds in the anode seems a promising process as it occurs at low potentials and low overpotentials. It can therefore well be combined with other reactions at the cathode. This process, however, leads to an appreciable drop in coulombic efficiency, as of the eight electrons used to reduce sulfate, only two are recovered in the oxidation to elemental sulfur. Besides, more research is needed on the long-term operation as this might among others be limited by sulfur precipitation on the anode.

Decreasing anode overpotentials

Above, we have analyzed the OCPs and overpotentials of different anode reactions. These overpotentials represent the amount of energy that is lost in the oxidation reaction. These energetic losses that occur at the anode include: activation energy, microbial energy for growth and maintenance, and ohmic losses (Clauwaert et al. 2008a). Some of these losses are influenced by the design of the system and the materials used (Hamelers et al. 2009), while other energetic losses, like microbial growth and maintenance, are necessary losses to get a well-developed and viable biofilm to produce as much current as possible (Schröder 2007).

One way to reduce the anode overpotential is to guarantee sufficient mass transfer in the anode. This includes both the mass transfer of substrate toward the biofilm and of products (protons) away from the biofilm. This can be either done by sufficient mixing of the anolyte or, in case of protons, sufficient buffer capacity of the anolyte in combination with mixing (Sleutels et al. 2009b). The oxidation reaction at the anode is an acid-producing reaction where for every produced electron also a proton is produced. When insufficient buffer is available near the biofilm surface to take up the produced protons because of a low buffer concentration or because of limited mixing of the anolyte, the biofilm will acidify. Acidification will lead to a decrease in the performance of the biofilm, and furthermore, it will also lead to higher anode potentials as can be calculated from the Nernst equation (Torres et al. 2008).

Coulombic efficiency

The coulombic efficiency for anodes is lower than 100% when the substrate (1) is not converted to electrons but to other organic molecules, (2) is oxidized by oxygen coming from the cathode or by other electron acceptors present in the anode medium, e.g., sulfate, or (3) is used for growth of the microorganisms (Freguia et al. 2007). Since the anodes in BESs are anaerobic, the main competing process is methanogenesis in which methane is produced from the organic material. For complex substrates such as wastewaters, reported coulombic efficiencies range from 5% (Min and Logan 2004) to 38% (Wang et al. 2008b). So far, coulombic efficiencies of rhizodeposits in plant-MFC have not been determined (De Schampelaire et al. 2008; Strik et al. 2008a). It was estimated that a sediment MFC with rice plants had a coulombic efficiency of 31% based on an average of 3% of net assimilated carbon rice rhizodeposition (De Schampelaire et al. 2008). However, this value is only indicative, as rhizodeposition is depending on plant species, age, and environmental conditions and can reach values of 60%. In laboratory studies, often artificial wastewaters with a single substrate are used. These wastewaters usually contain less complex molecules like acetate and are therefore easier to oxidize by the electrochemical active microorganisms. For wastewaters containing acetate as the carbon source, coulombic efficiency values of 100% have been reported (Aelterman et al. 2008). Furthermore, the coulombic efficiencies in batch systems are usually higher than the coulombic efficiencies in continuous systems. This can be explained by the fact that anaerobic organisms like methanogens have a low growth rate. Because in batch systems the cycle time is usually too short for the methanogens to develop, the substrate can be completely used by electrochemically active microorganisms, resulting in a high coulombic efficiency. Continuous systems, however, are sometimes run for several months giving the methanogens sufficient time to develop.

Increasing the coulombic efficiency is one of the most important challenges in BESs, since as many as possible of the available electrons from the organic substrate have to be transferred to the product to create an economically feasible process. To increase the coulombic efficiency, the flow of electrons to other products should be limited, e.g., by placing an effective oxygen barrier like a membrane between anode and cathode. Also, biomass growth of the electrochemically active microorganisms themselves, and of other microorganisms that can compete for the substrate, should be minimized. Growth of methanogens can be limited by controlling the retention time of the anolyte. Since the methanogens have a long doubling time and are not dependent of a solid surface like the electrochemical

active organisms, lowering the retention time might wash out these methanogens. Furthermore, creating an anode potential that is favorable for the electrochemically active organisms might make them able to win the competition for substrate with the methanogens

Cathode performance

Depending on the nature of the reduction reaction taking place at the cathode, a BES can be used for a wide range of applications. The process is in theory spontaneous, and electricity is produced when the cathode potential is higher than the anode potential, for example, in case of oxygen reduction and the removal of nitrogen. If the cathode potential is lower than the anode potential, the process needs energy input to create added value products, like fuels and chemicals. In this paragraph, we discuss the reduction of oxygen to water and hydrogen peroxide, the production of the fuels hydrogen, ethanol, and methane, and the reduction of pollutants.

Overpotentials for oxygen reduction

The oxygen reduction reaction is the most commonly used cathodic reaction in MFCs. Oxygen is an attractive oxidant because of its availability, its thermodynamic high redox potential of 0.805 V vs NHE at actual MFC conditions (Table 1), and because the cathodic reaction product is clean water. Emissions like NO_x and SO₂ are prevented because of the low temperature at which the BES operates. The oxygen reduction reaction can follow two overall pathways: (1) the direct four-electron pathway in which oxygen is reduced to water or hydroxide and (2) the peroxide pathway (Yeager 1983). The oxygen reduction reactions via the two pathways are:

1. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
2. $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$

Note that in both cases, the oxygen reduction rate and the potential at which oxygen is reduced is strongly dependent on the solution pH. This is important because in MFCs and MECs, the catholyte pH generally increases in time as a result of cation transport through the cation-exchange membrane (Rozendal et al. 2006a).

In practice, the reduction of oxygen in MFCs turns out to be slow and to occur at much lower potentials than the thermodynamic potential, because a large part of the energy at the cathode is lost to drive the oxygen reduction at the desired rate. Open circuit potentials for uncatalyzed carbon materials are typically around +0.2 V vs NHE (Logan et al.

2006). This potential is close to the theoretical potential for hydrogen peroxide instead of oxygen reduction to water. Because carbon materials are good catalysts for the reduction of oxygen to hydrogen peroxide (Zhao et al. 2009b), hydrogen peroxide may be produced instead of water.

When a current is flowing, the cathode potential usually shows a steep drop, and overpotentials increase even further (e.g., (Yu et al. 2009)).

To improve the reaction rate for oxygen reduction, many studies have been devoted to the development of metal and nonmetal catalysts to reduce overpotentials for oxygen reduction. Metal catalysts other than platinum that have been examined are for example Fe(II) and Co-based catalysts (Lefebvre et al. 2009; Yu et al. 2009). Recently, more and more attention is paid to the development of biological catalysts on the cathode. These biocathodes can be either indirect via a mediating compound or direct. Examples of indirect biocathodes are (1) the use of *Acidithiobacillus ferrooxidans*, which oxidizes Fe(II) to Fe(III) while reducing oxygen. The formed Fe(III) is reduced at the (noncatalyzed) cathode at higher rate than oxygen (Ter Heijne et al. 2006, 2007) and (2) the reduction of MnO_2 to Mn^{2+} at the electrode, with simultaneous oxidation of Mn^{2+} to MnO_2 by manganese oxidizing bacteria (Rhoads et al. 2005). Direct biocathodes can be based on enzymes (Topcagic and Minteer 2006; Schaeztle et al. 2009) or contain microorganisms that are attached to the cathode and that accept electrons from the electrode while reducing oxygen. This last type of biocathodes has been studied in salt water as well as in freshwater (Bergel et al. 2005; Clauwaert et al. 2007b). Although (bio)catalyzed cathodes have been shown to catalyze oxygen reduction compared to the plain material, the open circuit potentials are still low: in the range of 0.4–0.5 V vs NHE or sometimes higher, 0.65 V vs NHE (Clauwaert et al. 2007b).

As carbon is commonly used as a cathode material in MFCs, its catalytic action for peroxide production may be the reason for the low cathode potentials measured in MFCs. Theoretically, the cathode potential for reduction of oxygen to hydrogen peroxide is 0.269 V vs NHE, which is considerably lower than 0.805 V vs NHE for reduction of oxygen to water (Table 1) and which is close to the typical open circuit cathode potentials measured for oxygen reduction in other studies as described above. One could take advantage of the fact that hydrogen peroxide is produced when considering hydrogen peroxide as an added value product. In an MFC, it should theoretically be possible to produce hydrogen peroxide and electricity at the same time, at a cell voltage of 0.56 V with a bioanode fed with acetate (Table 2). Hydrogen peroxide was indeed shown to be produced under MFC conditions (Rozendal et al. 2009), however, only at low rates. Therefore, a voltage

of 0.5 V was applied, resulting in a hydrogen peroxide production rate of 1.9 kg $\text{H}_2\text{O}_2/\text{m}^3/\text{day}$.

Although progress has been made, high overpotentials still occur for oxygen reduction, compared to the overpotentials found for bioanodes. This holds for both the reduction to water and to hydrogen peroxide. The challenge is to find cheap and renewable catalysts to further decrease the energy losses at the cathode.

Production of fuels and chemicals

Bioelectrochemical systems can be applied for the production of fuels and chemicals. Until now, production of hydrogen peroxide (above), hydrogen, methane, and ethanol in BESs have been described. Hydrogen is produced in a MEC (Logan et al. 2008). Methane is often regarded as an unwanted reaction that occurs in an MEC. However, if methane production is coupled to carbon dioxide capture, this may offer perspectives for industry to reduce their greenhouse gas emissions. The production of bioethanol from organic waste materials is interesting because it does not compete with food and feed production and does not release greenhouse gas (Steinbusch et al. 2008). As fuels are materials with a high energy density, it is no surprise that for the production of fuels, an applied voltage must be used. The energy content of the fuel in a BES originates partly from the organic material oxidized at the anode and partly from the energy supplied via the applied voltage.

Hydrogen

In an MEC, the hydrogen evolution reaction (HER; Table 1) proceeds at the cathode. From the Nernst equation follows that the HER is strongly pH dependent. Because the cathode is ionically connected to the bioanode, the HER proceeds typically at pH 7 or higher, resulting in an HER equilibrium potential of -0.42 V vs NHE or lower (Table 1). In practice, the HER potential is lower than the equilibrium potential. For example, a potential of -0.71 V vs NHE at pH 7 and a current density of 0.47 A/m^2 was measured (Rozendal et al. 2006b). The extrapotential, or overpotential, is largely dependent on current density, cathode material, and mass transport conditions.

Due to slow kinetics of the HER on carbon electrodes, a catalyst such as platinum has often been used to decrease the HER overpotential (Logan et al. 2008). Under optimized conditions of mass transport (Jeremiasse et al. 2009b), platinum shows a low overpotential (-0.05 V at 15 A/m^2) for the HER. However, its high costs make its application in MECs less suitable. Therefore, both chemical and biological alternatives for platinum-coated cathodes in MECs have been investigated.

Chemical alternatives that have been investigated are tungsten carbide (Harnisch et al. 2009) and various stainless steel and nickel alloys (Call et al. 2009; Selembo et al. 2009a; Hu et al. 2009). For example, the overpotential of a 304-stainless steel brush (-0.29 V) was similar to the overpotential of a platinum-coated (0.5 mg/cm²) carbon cathode (-0.3 V) operating at pH 7 and a current density of ~ 13 A/m² (current density based on a volumetric current density of 188 A/m³, an MEC volume of 48 mL, and a surface area of 7 cm² of the platinum-coated cathode; Call et al. 2009). At an applied voltage of 0.6 V, the MEC with stainless steel brush produced 1.7 m³ H₂ m⁻³ reactor day⁻¹ and had a cathodic hydrogen recovery of 84% .

Next to chemical cathodes, a microbial biocathode that catalyzed hydrogen production has been developed (Rozendal et al. 2008b; Jeremiasse et al. 2009a). The biocathode was tested in an MEC and showed an overpotential of -0.28 V at pH 7 and a current density of 1.9 – 3.3 A/m² (Jeremiasse et al. 2009a). At an applied voltage of 0.5 V, the MEC with biocathode produced maximally 0.04 Nm³ H₂ m⁻³ day⁻¹ and had a cathodic hydrogen recovery of maximally 21% . The low cathodic hydrogen recovery was attributed to diffusional losses through membrane and tubing and methanogenesis. For a possible application of the biocathode, the operating current density needs to be increased, while the overpotential needs to be reduced. Furthermore, strategies to prevent methanogenesis and scaling need to be developed (Jeremiasse et al. 2009a). Nevertheless, the low costs of a microbial biocathode justify its further exploration.

Besides using a suitable cathode material, previous studies (Jeremiasse et al. 2009b; Merrill and Logan 2009) have shown that for minimizing the cathode overpotential, mass transport needs to be optimized for the HER in an MEC. Mass transport is optimized if buffer p*K*_a, buffer concentration, linear flow speed, and current density are well balanced with the expected operational pH (Jeremiasse et al. 2009b).

Methane

The electrochemical reduction of carbon dioxide to methane (Table 1) is a complex reaction with only reasonable cathodic methane recovery on copper. The cathodic methane recovery depends on various conditions such as cathode potential, carbon dioxide concentration, and temperature (Gattrell et al. 2006). Low cathode potentials are required compared to the equilibrium potential of -0.25 V vs NHE (Table 1) to reduce carbon dioxide to methane. For example, in one study with an electrochemical cell that was galvanostatically controlled at a current density of 50 A/m², the potential of the copper cathode was -1.41 V vs NHE, at pH 6.8, [HCO₃⁻]= 0.1 M, p*C*O₂= 1 atm, and T= 19° C.

Compared with an equilibrium potential of -0.223 V vs NHE, this is an overpotential of -1.19 V. The cathodic methane recovery was 29.4% . The rest of the current was converted in ethylene, ethanol, formate, hydrogen, and some other products (Hori et al. 1989). The high overpotential and low cathodic methane recovery make the electrochemical reduction of carbon dioxide to methane an energy-inefficient process.

Biological methane production has often been observed in BESs, especially in membraneless MECs (Call and Logan 2008; Clauwaert et al. 2008b; Clauwaert and Verstraete 2009; Wang et al. 2009). Both acetoclastic methanogens that convert acetate into methane and hydrogenotrophic methanogens that convert produced hydrogen and carbon dioxide into methane were held responsible for this methane production. Recently, a BES with a biocathode was described that is capable of converting electrical current and carbon dioxide into methane (Cheng et al. 2009). At a biocathode potential of -0.8 V vs NHE, they observed a current density of 1.8 A/m². Compared with an equilibrium potential of -0.244 V vs NHE (assuming [HCO₃⁻]= 0.01 M), this means an overpotential of -0.56 V. The cathodic methane recovery was 96% , resulting in a methane production rate of ~ 0.012 Nm³ m⁻³ day⁻¹. The relatively low overpotential and high cathodic recovery make the biocatalyzed reduction of carbon dioxide to methane a much more energy-efficient process than the electrochemical process.

The conversion of captured carbon dioxide into methane at a biocathode is a new process. Based on experience with bioanodes, it can be expected that the performance of the biocathode will be improved, i.e., the methane production rate will be increased while the overpotential will be reduced. This may be partly achieved by further enrichment of the right microorganisms on the biocathode. Moreover, it is likely that mass transport plays an important role in reducing the overpotential because like the HER, the production of methane from carbon dioxide is a strongly pH dependent reaction.

Ethanol

Ethanol has been found as a byproduct in the electrochemical reductions of inorganics such as carbon monoxide (Hori et al. 1987). To our knowledge, the purely electrochemical reduction of organics to ethanol has not been described in literature. Bioelectrochemical reductions of organics to ethanol, however, have been described (Peguín et al. 1994; Shin et al. 2002; Steinbusch et al. 2009). Recently, Steinbusch et al. (2009) found that acetate could be reduced to ethanol by mixed cultures in presence of a redox mediator such as methyl viologen. At pH 6 and a cathode potential of -0.55 V vs NHE, they observed a

maximum current density of 1.32 A/m^2 . The theoretical potential for the reduction of acetate to ethanol under the applied conditions (pH 6, 40 mM acetate, 0.1 mM ethanol) is -0.28 V . The cathode overpotential in their BES was thus -0.27 V . The cathodic ethanol recovery was maximally 49%, resulting in an ethanol production rate of $0.656 \text{ mmol m}^{-3} \text{ reactor day}^{-1}$ (Steinbusch et al. 2009). Other products were also formed, such as methane, hydrogen, butyrate, and others, and it was not clear via which mechanisms ethanol was formed.

Also for ethanol production, mass transport plays an important role in the overpotential because the reaction is dependent on transport of protons, acetate, and ethanol. The ethanol-producing cathode (Steinbusch et al. 2009) has two disadvantages: (1) the formed ethanol could be lost to the anode through the membrane and (2) loss of the mediator decreased the cathode performance. It was suggested that immobilization of the mediator possibly solves this last problem.

Removal of pollutants

Besides electricity production, BESs can be used to remove pollutants from wastewater streams, possibly with simultaneous electricity production. In this review, we focus on biologically catalyzed denitrification and reduction of Cr^{6+} . The mechanism by which nitrogen can be removed from the waste stream is as follows. Nitrogen is present in wastewaters mainly in the form of ammonium. In the aerobic cathode, the ammonium is oxidized to nitrite or nitrate, which is reduced at the anaerobic cathode to nitrogen gas. This last denitrification reaction is catalyzed by microorganisms (Clauwaert et al. 2007a). A treatment system has been proposed (Viridis et al. 2008) where the effluent of the anode is brought to the cathode via an external aerobic nitrification reactor. In the nitrification reactor, the ammonium is oxidized to nitrate and nitrite, which are both reduced to nitrogen gas in the cathode of the MFC.

In theory, the potential at which reduction of nitrate to nitrogen takes place is 0.734 V vs NHE. Reported cathode potentials, however, are ranging between -0.3 and 0 V vs NHE (Clauwaert et al. 2007a) and between -0.2 and 0.15 V vs NHE (Viridis et al. 2008) for both nitrate and nitrite reduction, so the measured potentials are considerably lower than the theoretical potentials. This could be an effect of mixed potentials, which are measured when part of the current is converted into other products (Vetter 1967).

Besides removal of nitrogen, also the removal of Cr(VI) has been studied. It was shown that in an MFC, Cr(VI) was removed and detoxified at a cathode potential of $\sim 0.6 \text{ V}$ vs NHE (Wang et al. 2008a), compared to a thermodynamic potential of $+1.33 \text{ V}$ vs NHE, while electricity was

produced. Another study (Li et al. 2009) showed OCPs of up to 0.8 V vs NHE for a Cr(VI) reducing cathode.

Implications for design

A BES is a combination of an anodic compartment and a cathodic compartment. So far, the overpotentials and coulombic efficiencies of separate anode and cathode reactions have been discussed. Although the anodic and cathodic reactions take place in separate compartments, additional processes arise when combining anodes and cathodes. These additional processes also determine the performance of BESs. Anodes and cathodes are linked in two ways: ionically via the conducting solution and electronically via the external circuit.

The ionic connection between the anode and cathode chamber introduces new losses, in addition to the already described overpotentials. An important issue in this respect is the use of a membrane. The advantage of using a membrane is that the anode compartment and cathode compartment do not readily mix. This has the advantages that (1) products are cleaner, e.g., the carbon dioxide produced at the anode will not mix with the hydrogen produced at the cathode in an MEC; (2) coulombic efficiency is higher, as less oxidant can pass from the cathodic to the anodic compartment, e.g., oxygen passing to the anode leads to unwanted oxidation of the substrate; and (3) cathodic recovery is higher, as unwanted reactions of the desired product with components in the anolyte is lowered, e.g., the conversion of hydrogen to methane with bicarbonate originating from the anodic substrate oxidation. A major disadvantage of using a membrane is that a pH gradient develops between the anode and cathode compartment (Rozendal et al. 2006a). This pH gradient gives an additional overpotential at the electrodes as can be calculated using the Nernst equation.

A way to prevent this pH gradient is either to take out the membrane (Call and Logan 2008; Liu and Logan 2004) or to pump the anolyte to the cathode to guarantee mixing (Freguia et al. 2008a). Although it has been shown that both methods prevent the pH gradient to develop, it also causes substrate/product crossover giving unwanted side reactions and products. Especially in the case of fuel production, these side reactions lead to impure products and will increase costs because of an extra required purification step.

When a membrane is applied, not only a pH gradient will develop but also the membrane itself will increase the resistance of the system resulting in a lower voltage or higher required energy input (Sleutels et al. 2009a). Depending on membrane properties like charge (negative or positive) and charge density, different species of ions and amounts of ions will be transported. For example anion

exchange membranes have been shown to give a better performance than the frequently applied cation exchange membranes because of these different properties (Rozendal et al. 2008c; Cheng et al. 2009; Sleutels et al. 2009a; Kim et al. 2007).

Another important issue that arises when the anode and cathode are connected is the conductivity of the electrolytes. Often waste streams are used as substrate, while these typically have a low conductivity of 1–2 mS/cm (Rozendal et al. 2008a). It has been shown that at these low conductivities, a limited anode compartment thickness is allowed to achieve high current densities. In lab scale setups, often large amounts of salts and buffer are added to increase the conductivity. In full scale BES, however, this is not possible because of economical issues and discharge regulations.

The electrical connection is of importance as it allows the control of the current flowing through the BES. The electrical connection will make the cathodic and anodic current equal. The current can be controlled by either changing the load or the applied voltage. The current that can flow through the BES is limited by either the anode or the cathode current density. Control of the current is needed as it strongly determines the productivity and energy efficiency of the BES.

The energy efficiency of BESs can be straightforwardly defined as the energy output of the BES over the energy input. Energy can be present in the form of electrical energy and chemical energy, e.g., in the form of substrates and fuels. For instance with hydrogen production, the energy input is a combination of chemical energy in the substrate for the anode and electrical energy via a power supply. This total energy input results in the production of hydrogen, which can be used as a fuel. In this case, the energy content of the produced hydrogen can be compared to the total energy input, resulting in certain energy efficiency.

Care should be taken, however, when comparing different BESs on the merit of solely energy efficiency. Hydrogen can be used as a fuel but is more often used as a chemical. When hydrogen is used as a chemical, it is more meaningful to compare the hydrogen producing BES to alternative hydrogen production processes like steam reforming. Moreover, the product specifications are not captured completely in energy efficiency. Besides energy efficiency, it is also important to investigate both the purity of the product and the final product concentration that is desired. A high product concentration will result in a higher overpotential, resulting in lower energy efficiency. For comparing chemicals, it is therefore more meaningful to compare the amount of energy used or lost in producing one unit of the chemical at certain specifications.

Whatever metric is used, efficiency or specific energy use, both are strongly determined by the total energy loss in

the BES. As overpotentials, ohmic voltage drop and transport voltage drop all increase with increasing current density; the energy loss will increase with increasing current density in a BES. To have an energy-efficient process, the current should therefore be limited. Decreasing the current, however, also reduces the productivity of the BES, while a high productivity is preferred from an application perspective, as it decreases capital cost and reduces the footprint of the BES. There is thus a trade-off between the volumetric conversion rate and the specific energy input.

The only way to combine the demands of high efficiency and high productivity is to lower losses of BESs. Therefore, a thorough analysis of the internal losses is a prerequisite (Sleutels et al. 2009a). Based on this analysis, an efficient BES can be designed. It is important that these designs are scalable (Zuo et al. 2007), and they should prove itself on larger scale because new phenomena may arise when scaling up (Dekker et al. 2009).

Summarizing, we can define the following key-points in BES application and performance:

- The field of potential BES applications is widening from electricity via fuels to chemicals.
- Charge-transfer resistances seem to be higher for cathodes than for anodes, although there is not yet sufficient information on charge-transfer resistances of the different cathode reactions to make a detailed comparison with charge-transfer resistances of anodes.
- For application of BESs, it is crucial to lower the internal energy losses and increase productivity at the same time.
- Membrane application and the related losses are important research items as membranes will be needed to prevent mixing of anolyte with catholyte. This is especially true for products that remain dissolved in the solution but introduces an extra energy loss.
- The comparison between production of fuels and chemicals in BESs and in present production processes has so far not been investigated and should gain more attention in future BES research as it is an important asset for the feasibility and applicability of BESs. By making this comparison, it will become clear if the scope of BESs can and should be further developed into the field of biorefineries.

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