Review

Cathodic limitations in microbial fuel cells: An overview

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ABSTRACT

Microbial fuel cells (MFCs) are a promising technology for sustainable production of alternative energy and waste treatment. The performance of microbial fuel cells is severely affected by limitations based on irreversible reactions and processes in the anode and the cathode compartments. The purpose of this paper is to review the cathodic limitations MFCs and provide an overview on cathodic activation, ohmic and mass transport losses and substrate crossover. Recent studies that have addressed these limitations and explored approaches for improvement are also discussed. MFCs still face many challenges but with consistent advances, especially with respect to the cathode, performance can continue to improve.

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Contents

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1. Introduction

With the increasing concern for alternative energy sources, waste management, global climate change, and non-edible feedstocks, the search for novel technological solutions continues. Fuel cells are one alternative energy technology being studied for full-scale implementation [1]. These can be classified into three subgroups: catalytic, enzymatic, and microbial. Since the turn of the century, the research on microbial fuel cells (MFCs) has experienced rapid increases. MFCs are unique in their ability to utilize microorganisms, rather than an enzyme or inorganic molecule, as catalysts for converting the chemical energy of feedstock directly into electricity.

MFCs often consist of two compartments, the anode and cathode, which are often separated by a proton-exchange membrane (PEM) (Fig. 1). The anode chamber contains microorganisms that oxidize the available substrate (i.e., the electron donor). The anaerobic oxidation is coupled with liberation of electrons which are transported through the cellular respiratory chain ultimately to the anode. Substrates used in MFC research vary from sugars and organic acids such as glucose or acetate to complex polymers such as starch and cellulose. Domestic, industrial, and animal waste streams have been used as feedstock for generating electricity in MFCs. In this example, glucose is the electron donor:

$$Anode : C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \qquad (1)$$
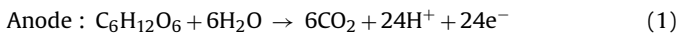
The anode acts as an artificial, external electron acceptor for the microorganisms. The electrons travel through a resistor or a device to be powered, generating electricity until reaching the cathode.

$$Cathode : 6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O \qquad (2)$$
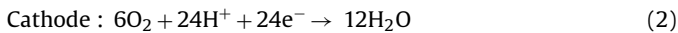
While the electrons travel through the circuit, the corresponding protons migrate to the cathodic compartment through a proton-exchange membrane to maintain charge neutrality. At the cathode an electron acceptor (e.g., oxygen) is reduced by the electrons via the circuit and the protons via the membrane. The electrochemical reactions in MFCs are comparable but the kinetics and coulombic efficiencies may vary depending on the physical, chemical and biological operating conditions.

The cathodic reduction can be classified into aerobic or anaerobic reactions depending on the source of the final electron acceptor available. In aerobic cathodes, oxygen is the terminal electron acceptor. The reduction of oxygen is the most dominant electro-

chemical reaction at the surface of cathode electrodes. Unlimited availability and high standard redox potential make oxygen an exceptional electron acceptor. Two processes can occur during cathodic oxygen reduction. The desired reaction is the production of water through a four-electron pathway:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (E'^0 = 0.816\,V) \qquad (3)$$
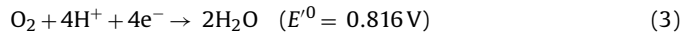
The other pathway consists of a two-electron reaction with the production of hydrogen peroxide:

$$2O_2 + 4H^+ + 4e^- \rightarrow 2H_2O_2 \quad (E'^0 = 0.295\,V) \qquad (4)$$
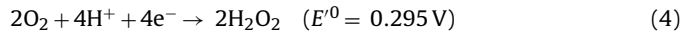
Incomplete reduction of oxygen leads to low energy conversion efficiency and produces reactive intermediates and free radical species which can be destructive. Permanganate has also been used as an alternative electron acceptor to oxygen to support the cathodic reduction reaction [2]. The cathode compartment can also be maintained under anaerobic conditions. In this case, microorganisms transfer the electrons from the cathode to the final electron acceptor (e.g., nitrate) [3,4].

An ideal MFC can produce current while sustaining a steady voltage as long as the substrate is supplied. The theoretical ideal voltage, E_{thermo} (V), attainable from an MFC can be thermodynamically predicted by the Nernst equation:

$$E_{thermo} = E^0 - \frac{RT}{nF} \ln \left(\prod \right) \qquad (5)$$

where E^0 is the standard cell potential (V), R is the ideal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), n is the number of electrons transferred in the reaction (dimensionless), F is the Faraday's constant (96,485 C mol^{-1}), and Π is the chemical activity of products divided by those of reactants (dimensionless).

In practice, the actual voltage output of an MFC is less than the predicted thermodynamic ideal voltage due to irreversible losses (i.e., overpotentials). The three major irreversibilities that affect MFC performance are: activation losses, ohmic losses, and mass transport losses. These losses are defined as the voltage required to compensate for the current lost due to electrochemical reactions, charge transport, and mass transfer processes that take place in both the anode and cathode compartments [5]. The extent of these losses varies from one system to another. The real operational voltage output (V_{op}) of an MFC can be determined by subtracting the voltage losses associated with each compartment from the thermodynamically predicted voltage as follows:

$$V_{op} = E_{thermo} - [(\eta_{act} + \eta_{ohmic} + \eta_{conc})_{cathode}$$
$$+ (\eta_{act} + \eta_{ohmic} + \eta_{conc})_{anode}] \qquad (6)$$

where E_{thermo} is the thermodynamically predicted voltage, η_{act} is the activation loss due to reaction kinetics, η_{ohmic} is the ohmic loss from ionic and electronic resistances, and η_{conc} is the concentration loss due to mass transport limitations. The above equation shows that cathode and anode overpotentials collectively limit the performance of MFCs and that the overall performance can be improved by optimizing both the anode and cathode.

The purpose of this paper is to review cathodic limitations in MFCs and recent studies that have addressed these problems and explored approaches for improvement. These limitations are based on irreversible reactions and processes in the cathode compartment that can severely affect the performance of MFCs. Many reviews are available on MFC technology and operations (Table 1) but to this point, no in-depth overview of cathodic limitations exists in the literature.
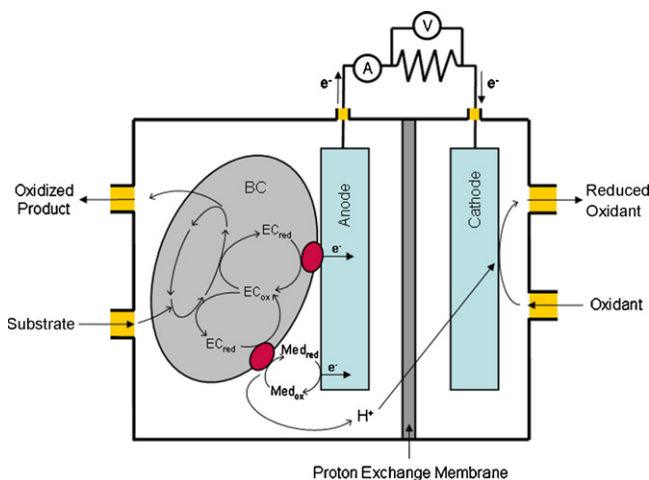

Fig. 1. A schematic of a microbial fuel cell containing a model bacterial cell (BC). Electron transport involves oxidized and reduced electron carriers (EC$_{red}$ and EC$_{ox}$), and mediators (Med$_{ox}$ and Med$_{red}$).

Table 1
Summary list of recent (2001–2007) review papers on MFCs

Title	Year	Citation
Extracellular electron transfer	2001	[6]
Production of bioenergy and biochemicals from industrial and agricultural wastewater	2004	[7]
Microbial fuel cells: novel biotechnology for energy generation	2005	[8]
Applications of bacterial biocathodes in microbial fuel cells	2006	[9]
Electricity-producing bacterial communities in microbial fuel cells	2006	[10]
Electrochemically active bacteria (EAB) and mediator-less microbial fuel cells	2006	[11]
Microbial fuel cells: novel microbial physiologies and engineering approaches	2006	[12]
Microbial fuel cells: challenges and applications	2006	[13]
Microbial fuel cells: methodology and technology	2006	[14]
Microbial fuel cells in relation to conventional anaerobic digestion technology	2006	[15]
Microbial fuel cells for wastewater treatment	2006	[16]
Anodic electron transfer mechanisms in microbial fuel cells and their energy efficiency	2007	[17]
A state of the art review on microbial fuel cells: a promising technology for wastewater treatment and bioenergy	2007	[18]
Extracellular respiration	2007	[19]
Microbial ecology meets electrochemistry: electricity-driven and driving communities	2007	[20]

2. Cathodic limitations

2.1. Activation losses

Current production in MFCs depends largely on the kinetics of the reduction that takes place at the cathode. The reaction kinetics is limited by an activation energy barrier which impedes the conversion of the oxidant into a reduced form (i.e., Eq. (1)). When current is drawn from a fuel cell, a portion of the cathode potential is then lost to overcome this activation barrier. The potential loss due to activation is called cathodic activation loss $(\eta_{act})_{cathode}$ (i.e., activation overpotential) [5].

Activation losses result in a characteristic, exponentially formed loss on the current–voltage curve at low current densities (Fig. 2). As more current is taken from the MFC, the activation loss increases and results in a lower cell potential [21]. As with chemical and biological fuel cells, the cathodic activation losses dominate the performance of MFCs [22]. The magnitude of cathodic activation overpotential depends on the reduction kinetics. Kinetic performance can be improved by decreasing the activation barrier and increasing the reaction interface area, temperature, or oxidant concentration.

2.2. Ohmic losses

MFC performance is also restricted by cathodic ohmic overpotentials, also known as internal resistances. This loss is the voltage that is required to drive the electron and proton transport processes. Since MFC conductors are not ideal, they have an intrinsic resistance to charge flow [21]. The ohmic overpotential (η_{ohmic}), therefore, represents the voltage which is lost in order to accomplish charge transport (i.e., electrons and protons). This loss generally follows the Ohm's law:

$$\eta_{ohmic} = i R_{ohmic} \tag{7}$$

where i is the current (A) and R_{ohmic} is the ohmic resistance (Ω) of the MFC. The cathodic ohmic resistance is a combination of both ionic, R_{ion}, and electronic, R_{elec}, resistances, and includes the resistance from the electrode, electrolytes and interconnections:

$$R_{ohmic} = R_{ion} + R_{elec} \tag{8}$$

Internal resistance is usually dominated by the electrolyte resistance since the ionic conductivity is orders of magnitude lower than the electrical conductivity of the electrode materials [5]. The ohmic resistance of the electrolyte, R_{ion}, can be expressed by

$$R_{ion} = \frac{l}{AK} \tag{9}$$

where l is the distance (cm) and A is the cross-sectional area (cm^2) over which the ionic conduction occurs, and K is the specific conductivity (Ω cm)$^{-1}$ of the electrolyte [21].

The cathodic ohmic loss is more pronounced at medium current densities and, following the Ohm's law, the operating voltage decreases linearly as current increases (Fig. 2). Reducing the cathodic ohmic losses is important for improving the performance of MFCs.

2.3. Mass transport losses

The process of supplying oxidants (i.e., O$_2$) and removing products (i.e., H$_2$O) at the cathode of an MFC is governed by mass
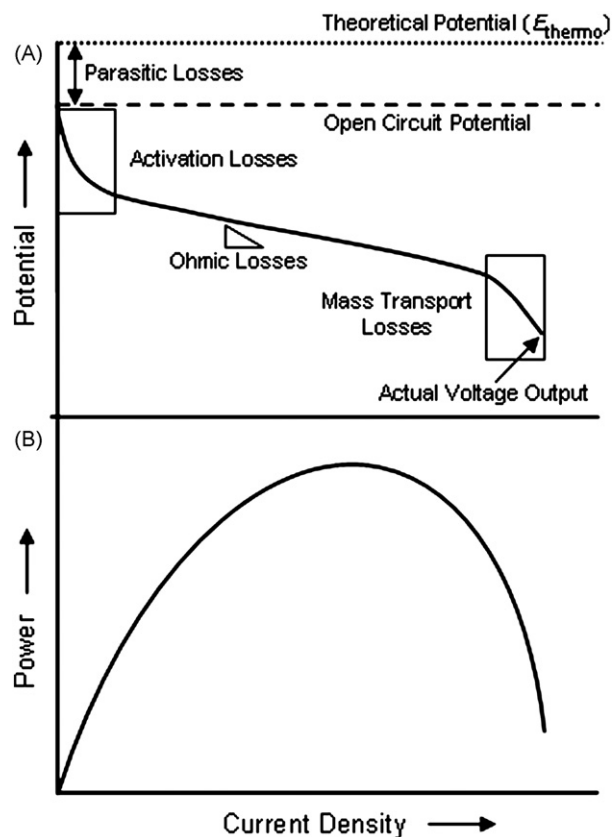

Fig. 2. (A) Schematic potential losses for a cathodic reaction displaying activation, ohmic, mass transport and parasitic regions. (B) A typical power–current curve.

transport. Insufficient mass transport causes reactant depletion or product accumulation. Reactant depletion affects both the Nernstian cell voltage and the reaction rates, leading to a performance loss. This loss is the voltage required to drive mass transport processes at the cathode and is referred to as cathodic concentration loss or mass transport loss $(\eta_{conc})_{cathode}$ [5]. Mass transport losses occur at high current density, and the magnitude increases with increasing current density (Fig. 2).

Mass transport limitations due to oxidant transport in the cathode compartment are typically much more severe than transport limitations in the anode compartment. Hence, when determining mass transport losses in fuel cell systems, only the limiting concentration for the oxidant is considered.
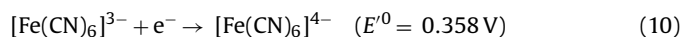
3. Reducing cathodic activation losses

Oxygen reduction is the most common cathodic reaction in MFCs. The slow rate of oxygen reduction on the surface of graphite/carbon electrodes leads to a high reduction overpotential, which is among the most limiting factors in the performance of MFCs [22]. Therefore, improved cathodic reaction rates impact the efficiency and power output of MFCs and represent a major challenge for research and development [23,24]. Different approaches have been explored in several studies to improve the performance of the cathode by lowering the cathodic overpotential for oxygen. These approaches include the use of mediators, electrode modification with catalysts, and optimizing operational conditions within the cathodic compartment.

3.1. Mediators

Mediators that undergo reversible redox reactions can reduce the cathodic overpotentials in MFCs. They act as electron shuttles and transfer electrons from the cathode electrode to the terminal electron acceptor. The rate of reduction of the mediator on the electrode surface is relatively faster than that of oxygen, thereby enhancing the kinetics of cathodic reactions. Despite the benefits, employing mediators is considered unsustainable due to the need for regular replacement and therefore not practical for long-term MFC applications [13].

The most common soluble mediator used for the cathodic reaction in MFCs is ferricyanide (hexacyanoferrate) (Fig. 3A). It has faster reduction kinetics than that of oxygen on the cathode and a relatively large redox potential. In contrast to oxygen, its concentration in the solution is not also limited by the solubility.

$$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-} \quad (E'^0 = 0.358\,V) \tag{10}$$

$$O_2 + 4[Fe(CN)_6]^{4-} + 4H^+ \rightarrow [Fe(CN)_6]^{3-} + 2H_2O \tag{11}$$

Due to the slow rate of re-oxidation by oxygen, ferricyanide functions however as an electron acceptor rather than a mediator [25]. Oh et al. [26] described a 50–80% increase in maximum power using ferricyanide in the cathode compartment as compared to an oxygen-saturated aqueous cathode or a platinum-coated air-cathode. The observed differences were attributed to high open circuit potential and a greater mass transfer efficiency of ferricyanide solution than that of dissolved oxygen. Similar results have also been reported by Oh and Logan [27], Ringeisen et al. [28], and Liu and Li [29]. Although widely used in laboratory experiments, ferricyanide is not a suitable choice for sustainable electricity generation in MFCs. It is potentially toxic, requires regular replenishing due to its low rate of regeneration by oxygen, and diffuses through the membrane over long-term operation which eventually reduces the overall performance of the MFCs [13].

Impregnating mediators into the cathode electrode materials has been demonstrated to eliminate the need for continuous addition or recycling of soluble mediators [30]. Metal oxides incorporated into the cathode electrode as electron transfer mediators have been shown to improve power output of MFCs due to

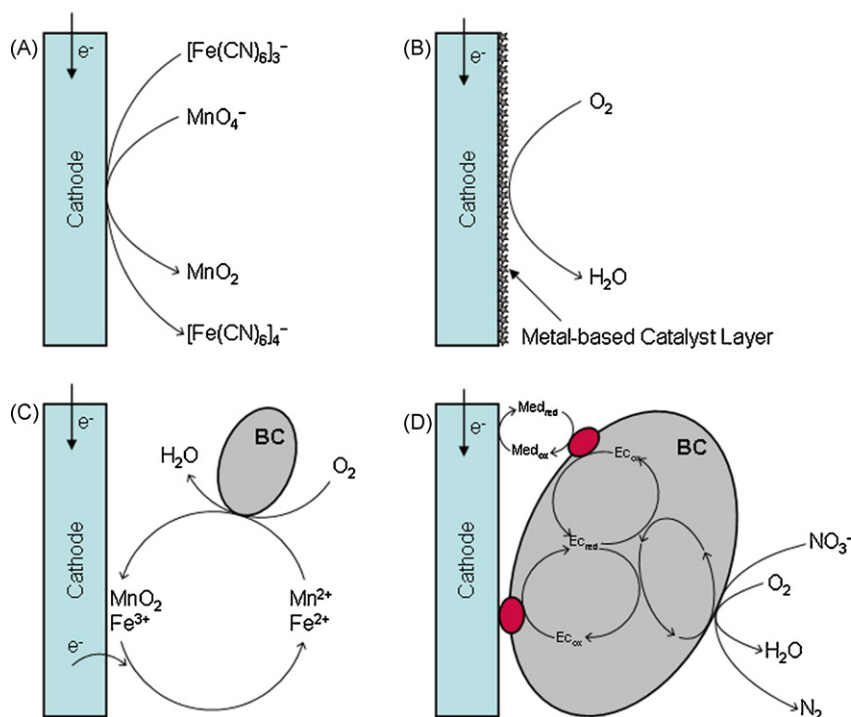**Fig. 3.** Different approaches to enhance cathodic kinetics in MFCs. (A) The use of mediators (e.g., ferricyanide) and strong oxidants (permanganate); (B) catalytic electrode; (C) bacteria (BC) catalyzing the oxidation of transition metals; and (D) bacteria (BC) catalyzing the reduction of the final oxidant (i.e., electron acceptor) through hypothetical direct and indirect electron transport mechanisms.

enhanced electron transfer kinetics [30]. The redox couple Fe^{3+}/Fe^{2+} has been used as an alternative mediator for cathodic oxygen reduction because of its fast redox reaction rate and relatively high standard potential ($E^0 = 0.77\,V$) [31]. This reversible electron transfer reaction was shown to considerably decrease the cathodic overpotential. However, the performance of a ferric iron reducing cathode is limited by the low solubility of ferric iron at pH values higher than 2.5. MFCs commonly contain catholyte with near neutral pHs. Furthermore, the transport of cation species other than protons through the PEM also raises the pH of catholyte [32]. Ter Heijne et al. [31] demonstrated that, by employing a bipolar membrane, the catholyte pH can be maintained sufficiently low to keep Fe^{3+} soluble.

The cathodic activation loss can also be minimized by using oxidants that have redox potentials higher than that of oxygen (Fig. 3A). Using permanganate as the cathodic electron acceptor (Eq. (12)) under acidic conditions in a two-compartment MFC, You et al. [2] reported 4.5 and 11 times higher power density as compared to ferricyanide and oxygen, respectively, as the cathodic oxidant.

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O \quad (E^0 = 1.70\,V, \text{ pH } 1.0) \quad (12)$$
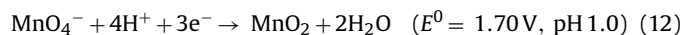
The increase in power output was attributed to the higher open circuit potential of the permanganate cathode, and it was found to be pH dependent. The performance of permanganate was less than that of oxygen under alkaline conditions. The practical application of a permanganate catholyte is, however, limited due to the need for replenishing the depleted permanganate solution and the acidic pH requirement for optimal operation [2].

3.2. Catalysts

The use of catalysts on the cathode surface can lower the cathodic activation overpotential and increase the current output of MFCs. Such catalysts considerably decrease the activation energy barrier and improve the kinetics of oxygen reduction at the electrode surface [5]. Different chemical and biological catalysts have been tested in efforts to improve MFC performance.

3.2.1. Metal-based catalysts

Platinum (Pt) has been widely used as the most common precious metal catalyst in cathode materials of MFCs because it has a favorably low overpotential for oxygen reduction. Logan et al. [33] reported one order of magnitude increases in the power output of two-compartment MFCs with a Pt-coated cathode as compared to a plain carbon electrode. Although Pt has excellent catalytic ability, its relatively high cost limits its application. Efforts have been made to address this problem by lowering the amount of Pt necessary to coat the cathode electrode. Cheng et al. [34] reduced the Pt loading to as little as $0.1\,mg\,cm^{-2}$ of the cathode surface area and reported no severe drop in MFC performance.

Gold (Au) has also been tested as a cathode catalyst in MFCs because of its low overpotential for oxygen reduction. Kargi and Eker [35] reported electricity generation in a two-compartment MFC with Au-coated copper as a cathode electrode. The authors did not however elaborate on the performance of such an electrode in comparison to that of commonly used electrodes in MFCs.

Non-precious metals have also been studied as catalysts for improving the kinetics of oxygen reduction in the cathode. The main distinction of using non-noble metals is the cost consideration for future potential large-scale applications of MFCs [23]. Morris et al. [24] compared the catalytic performance of lead dioxide (PbO_2) to Pt in two-compartment MFCs. Their results demonstrated up to four times improvement in the power output and 50% reduction in cost per unit of power with PbO_2-coated electrodes as compared to that obtained with Pt-cathodes. However, the possibility of lead

leaching from the cathode is a potential hazard that limits the use of PbO_2 as a cathode catalyst in MFCs. Such a limitation can be overcome by improving coating techniques and binding materials that would enhance stability of the catalyst. It has been shown that MFC performance can be affected by the binding material used to apply the catalyst to the electrode. Cheng et al. [34] compared MFC performance using Nafion and polytetrafluoroethylene (PTFE) as a Pt binder and reported 12 and 14% higher cathode potential and maximum power density, respectively, with Nafion.

Cobalt- and iron-based materials have also been investigated as alternative catalysts for oxygen reduction in MFCs. Zhao et al. [23,36] used pyrolyzed-Fe(II) phthalocyanine (pyr-FePc) and cobalt-tetramethylphenylporphyrin (CoTMPP) as cathode catalysts and reported performances similar to that of Pt. These results were also confirmed in other studies in which CoTMPP was tested in air-cathode MFCs [34], and used for catalytic tubular membrane cathodes [37].

Metal-based catalysts are generally susceptible to adverse environmental conditions that may occur in MFCs as a result of chemical reactions, biological activities, and changes in catholyte composition. For example, their catalytic activity is reduced in sulfide- or chloride-rich environments. Schmidt et al. [38] used a thin-film rotating disk Pt-electrode in a liquid electrolyte to demonstrate that adsorbed Cl^- ions act as site blocking species. This effect reduced the active area available for oxygen reduction and changed the reaction pathway toward the production of H_2O_2.

Metal-based catalysts are also sensitive to high cathodic pH values, a common phenomenon that occurs in MFCs due to crossover of cations through the membrane to the cathode compartment. Zhao et al. [23] studied the influence of catholyte composition on the performance of iron- and cobalt-based cathode catalysts for oxygen reduction. They demonstrated that lowering the concentration of a phosphate buffer catholyte (pH 3.3) from 500 to 50 mM reduced the performance of a pyr-FePc modified electrode by 40% (Fig. 4). An increase in the catholyte pH from 2.4 to 7 (500 mM phosphate) resulted in an 80% decrease in the rate of oxygen reduction by a CoTMPP-based electrode (Fig. 5). Increasing the catalyst load could partially compensate for the unfavorable neutral pH and low buffering capacity and thus improve the cathodic performance [23].

3.2.2. Biocatalysts

Microorganisms can also be used as catalysts and mediators in the cathode. Microbial growth is inevitable in the cathodic compartment because it is not feasible to operate it as a sterile unit. Several studies have demonstrated the capability of some
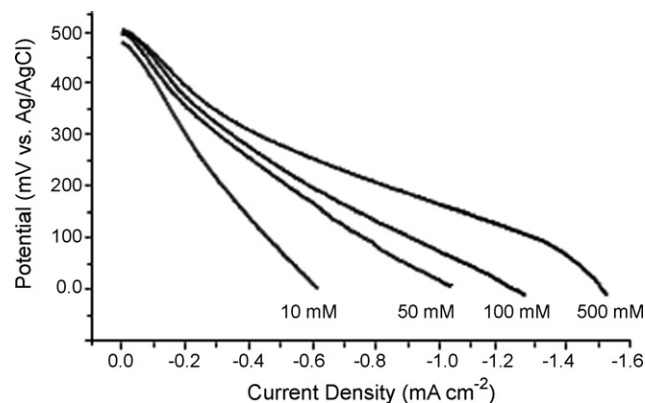

Fig. 4. Effect of phosphate buffer concentration (pH 3.3) used as catholyte on the galvanodynamic polarization properties of pyr-FePc modified cathode for oxygen reduction. Modified from Zhao et al. [23].
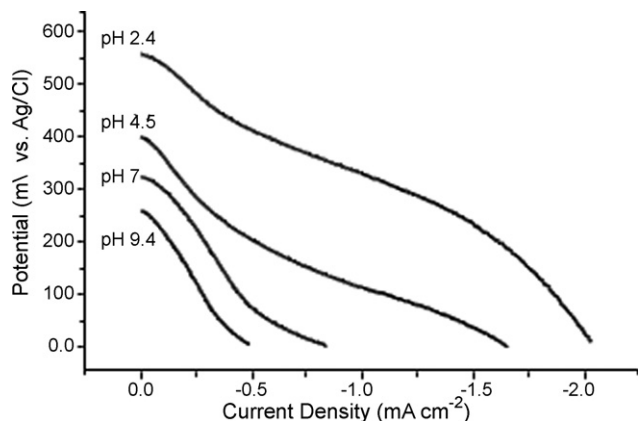
Fig. 5. Effect of catholyte pH (500 mM phosphate buffer) on the galvanodynamic polarization properties of CoTMPP modified cathode for oxygen reduction. Modified from Zhao et al. [23].

microorganisms to utilize the cathode as the sole source of electron donors. These biocatalysts retrieve electrons directly from the cathode (Fig. 3C), or from electron mediators impregnated into the cathode (Fig. 3D), using mechanisms that are not yet understood [9]. The electrons are then transferred to a final electron acceptor such as oxygen or an alternative oxidant such as nitrate [4,39,40]. Bergel et al. [41] found increased performance with a stainless steel cathode colonized by marine bacteria as compared to a clean cathode. Clauwaert et al. [42] reported electricity generation in MFCs, in which the cathode was exposed to air and inoculated with a consortium of sludge and sediment microorganisms. Although the underlying mechanisms were not explained, these two studies suggested that the oxygen reduction on the cathode was directly catalyzed by the biofilm.

Bacteria have also been used to catalyze the re-oxidation of redox couples incorporated into the cathode electrode as electron mediators. Rhoads et al. [40] used a manganese-oxidizing bacterium, *Leptothrix discophora*, as the biocatalyst in the cathode. The current output improved by two orders of magnitude in comparison to a plain graphite electrode. The cathodic reaction in this system involved the reduction of electrode-deposited MnO_2 to manganese ion (Mn^{2+}) by electrons at the cathode surface. The concurrent re-oxidation of Mn^{2+} to MnO_2 was then mediated by the Mn-oxidizing *Leptothrix*. Ter Heijne et al. [43] used an iron oxidizing bacterium, *Acidithiobacillus ferrooxidans*, for continuous ferrous iron oxidation on the cathode in a bipolar-membrane MFC. This biologically catalyzed Fe^{2+}/Fe^{3+} cathodic reaction produced a power output ($1.2\,W\,m^{-2}$) higher than that obtained with a similar cathodic reaction under abiotic conditions ($0.86\,W\,m^{-2}$) [31].

The research on using microorganisms as cathode catalysts is still in its infancy. The performance of biocatalysts is constrained by high cathodic activation overpotentials [4]. Appropriate comparisons between the performance of biocatalysts and metal-based catalysts in MFCs have yet to be reported. The dynamics of environmental conditions in MFCs can be inhibitory to biocatalysts. The accumulation of metabolites and ions crossed over through the membrane can hinder the bacterial activity. Metabolites can also compete against the cathode by acting as electron donors for bacteria, counteracting the biocatalyst effect and reducing the performance. Sustenance of bacteria in the cathode compartment requires a carbon source. It is not known whether bacteria acting as biocatalysts obtain electrons required for energy metabolism from the cathode or from the oxidation of the carbon sources. A potential benefit of using biocatalysts may be the reduction of pollutants such as nitrates or chloroorganics in the cathode compartment [9,12,43].

In addition, the cost and properties of biocatalysts and their compatibility with operating conditions, as compared to metal-based catalysts, may be more favorable for some future MFC applications.

3.3. Cathode surface area

The power output of MFCs is constrained by the surface area of the cathode electrode [26,37,44]. Increasing the cathode surface area provides more reaction sites available for oxidant reduction and improves the cathodic reaction rate. This provides, therefore, an approach for enhancing the power output of MFCs. Using two-compartment MFCs, Oh and Logan [27] demonstrated that increasing the cathode surface area by 11-fold (from 2 to 22.5 cm^2), at a fixed surface area for the anode (22.5 cm^2) and the PEM (30.6 cm^2), improved the maximum power density by one order of magnitude (Fig. 6). Similar results have also been reported by others [26,35,37,45].

The increase in the reactor volume required to accommodate electrodes with large surface areas remains a challenge, especially in large-scale applications [13]. Various electrode materials and design configurations have been investigated in attempts to increase the available reaction sites in the cathode compartment while maximizing the surface area per volume ratio, i.e., specific surface area. Since graphite plate and carbon paper electrodes have limited surface areas, woven graphite felt [22,30], woven graphite mat [46], granular graphite [44], and reticulated vitreous carbon [28,47,48] have been tested because they have a larger specific surface area than a graphite plate of identical dimensions. Tubular cathodes containing high surface area to volume ratios have also been investigated in MFCs [37,46–48]. The scalable characteristic of tubular cathodes makes them a promising architecture for developing large-scale MFCs [37].

3.4. Operational conditions

Increasing oxidant concentration at the cathode affects the performance of MFCs through both the Nernst equation and the kinetics of reduction reaction [49]. The concentration of reactants and products at the reactions sites determines the ideal thermodynamic voltage according to the Nernst equation (Eq. (5)). The thermodynamic gain from increasing the oxidant concentration is, however, small due to the logarithmic nature of the Nernst equation. In contrast, increasing the oxidant concentration substantially improves the cathodic kinetics by increasing the reaction rates in a
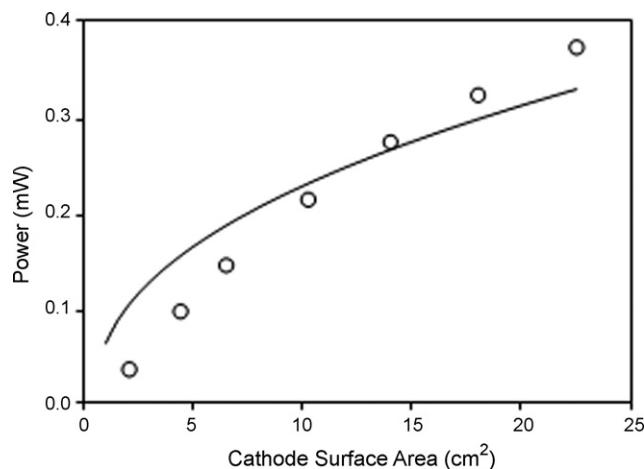

Fig. 6. Power output as a function of cathode surface area (2–22.5 cm^2) in a two-compartment MFC with fixed surface areas for anode (22.5 cm^2) and PEM (30.6 cm^2). Modified from Oh and Logan [27].

linear fashion [5]. For a general reduction;

$$aO + e^- \rightarrow bR \tag{13}$$

where O and R are the oxidant and reduced species, and a and b are the corresponding stoichiometric coefficients, the reaction rate (r) can be calculated by

$$r = k[O]^a \tag{14}$$

where [O] is the concentration of an oxidant and k is the rate constant.

The effect of reactant concentration also works in concert with concentration losses at high current densities and will be discussed further in the section on reducing mass transport limitations.

The operating temperature also controls the cathode performance by affecting the kinetics of oxidant reduction and mass and proton transfer [50]. Using a single-chamber membrane-less MFC, Liu et al. [51] reported a 9% increase in power output when the operating temperature increased from 20 to 32 °C. This improvement was shown to be mainly a result of increases in the cathodic potential.

The mesophilic temperature range (20–40 °C), at which many MFCs are operated, is suboptimal for cathodic reduction and performance of metal-based catalysts. Increasing the operating temperature of MFCs is, however, limited by the temperature tolerance of microorganisms employed as catalysts in the anode and cathode. Operation of MFCs at temperatures beyond this limit can adversely affect the MFC performance by inactivating the microorganisms. Thermophilic bacteria have been shown to generate electricity at elevated temperatures up to 60 °C [52,53]. The upper temperature limit for extreme thermophiles is in excess of 100 °C. While thermophilic operation reduces the activation, mass transport, and ohmic overpotentials, it requires a considerable amount of energy input to maintain the elevated temperatures. Thermophilic MFCs do not appear practical unless the resulting improvements compensate for the energy input requirement. There is no meaningful comparison of performance between mesophilic and thermophilic MFCs available in the literature at present.

4. Reducing cathodic ohmic losses

Cathodic ohmic losses can be minimized by increasing the conductivity of the electrolyte materials used as catholyte and proton-exchange membrane. Improvement can also be introduced by reducing the path distance between the cathode and anode electrodes.

4.1. Catholyte

Several catholyte characteristics have been found to restrict MFC performance due to high ohmic resistance. These elements include low proton concentrations at neutral pH values [54] and low ionic conductivity of the employed catholyte in most MFCs. Optimization of catholyte composition and concentration can, therefore, enhance the performance of MFCs [23].

Increasing the ionic strength of the catholyte improves the cathodic proton transfer rate and results in increased current output [22,54]. Liu and Logan [55] reported 85% increase in the power output of a single-chamber MFC when the ionic strength of the electrolyte was increased from 100 to 400 mM with NaCl. This effect was attributed to a decrease in the internal resistance. Increasing the conductivity of electrolyte from 10 to 60 mS cm^{-1} through the addition of 0.4 M KCl into a two-compartment MFC was shown to reduce the ohmic resistance by 42% (from 1087 to 625 Ω) [27]. Zhao et al. [23] demonstrated that increasing the concentration of phosphate buffer (pH 7.0), used as the catholyte, from 50 to 500 mM in a two-compartment MFC reduced the ohmic resistance by threefold, resulting in a 53% increase in the power output. Such improvements in the performance were due to a decrease in catholyte resistance to proton transfer. The cathodic ohmic resistance can also be minimized by active control of the bulk catholyte pH. Jang et al. [54] reported that acidification of the catholyte improved the current output of MFCs, suggesting that the H$^+$ availability in the cathode compartment was limiting MFC performance. The authors did not, however, elaborate on the actual pH values.

Extremes of ionic strength and pH of the catholyte can adversely affect cathodic performance by resulting in the inactivation of metal-based catalysts and biocatalysts. The inactivation effect is bound to vary from one type of catalyst to another. The tolerance of catalysts to ionic strength and pH has not been addressed in the MFC literature.

4.2. Membrane

The PEM functions as a solid electrolyte, permits the proton flux from the anode to the cathode, and is not conductive to electrons. The membrane has an inherent resistance to the transport of protons which contributes to the ohmic losses. The magnitude of this resistance can be mitigated by optimizing the physical properties and the type of membrane [5].

The thickness and surface area of the membrane affect its resistance to proton conduction. The effect of membrane thickness on the performance of MFCs has not so far been reported. Thinner membranes are expected to give a lower ohmic overpotential as a result of lower transfer resistance and faster flux. Thin membranes, however, tend to have a higher rate of substrate crossover [56].

Increasing the membrane surface area reduces the ionic resistance associated with the membrane. Oh and Logan [27] showed that an increase in the membrane surface area from 3.5 to 30.6 cm^2, in a two-compartment MFC with fixed anode and cathode surface areas (22.5 cm^2), decreased the internal resistance (from 1110 to 89 Ω) and resulted in power output improvement from 45 to 190 mW m^{-2}. The surface area of a membrane should be compatible with the extent of proton flux available from the anodic reaction. At a fixed PEM surface area (3.5 cm^2), an increase in the surface area of the anode (from 2 to 22.5 cm^2) resulted in a negligible change in the power output, suggesting that the proton transfer to the cathode was a limiting factor (Fig. 7). However, similar increases in the surface area of the anode when the membrane surface area was 30.6 cm^2 improved the power output by fourfold
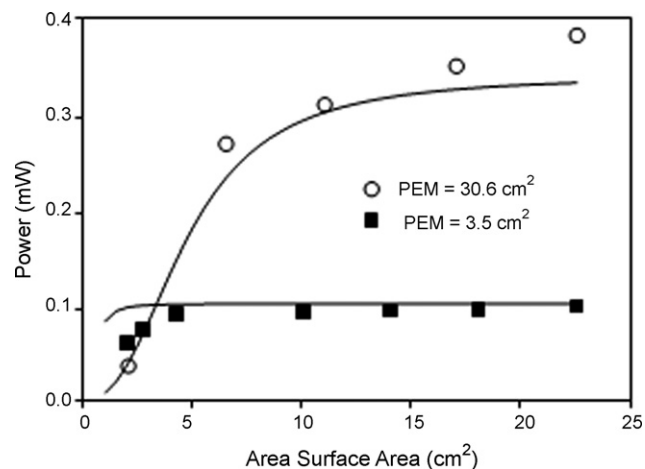
Fig. 7. Power output as a function of anode surface area (2–22.5 cm^2) in a two-compartment MFC with different PEM surface areas. Modified from Oh and Logan [27].
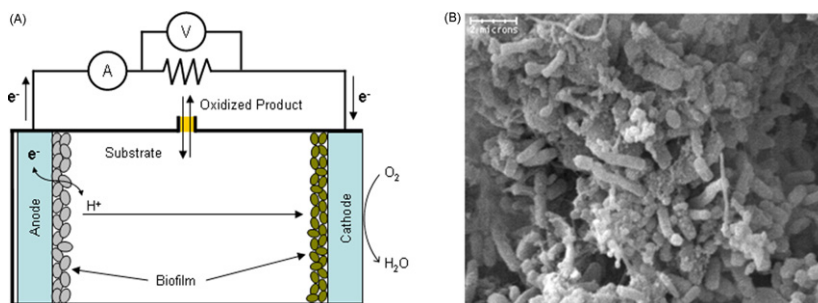
Fig. 8. (A) Schematic of a single-chamber membrane-less microbial fuel cell. The cathode is exposed to air on one side and to the anolyte containing the substrate on the other side. Biofilm is formed on the anode and the interior-side of the cathode. (B) SEM image of bacterial biofilm on the interior-surface of the cathode electrode in a membrane-less MFC [55]. Reprinted with permission from ACS.

(Fig. 7) [27]. Increasing the ratio of membrane surface area to the total MFC volume has also been shown to enhance the proton flux [46,47].

Because of its relatively high conductivity to cations, Nafion, a sulfonated tetrafluorethylene synthetic polymer (pore size <5 nm), has been extensively used as a PEM in MFCs. The transport of protons in the membrane is accompanied by transport of water through the formation of hydronium ion (H_3O^+). The long-term stability of Nafion in MFCs is unknown. The stability of Nafion can be compromised due to degradation by chemical and biological oxidative substances in the anode and cathode compartment. Operating conditions such as ambient temperature, neutral pH, and the presence of positively charged ions other than protons may repress the functionality of Nafion [57,58].

Efforts have been made to replace Nafion with other types of membranes that can function effectively under the operating conditions of MFCs [57,59,60]. Grzebyk and Pozniak [61] synthesized an interpolymer membrane from polyethylene/poly(styrene-co-divinylbenzene) and used it for electricity generation in MFCs. Comparison of the performance of the synthesized membrane vs. conventional membranes was not reported. While the operating conditions are conducive to the use of alternative membranes, they often have a relatively high proton transport resistivity as compared to Nafion. In an MFC with tubular membrane-cathode assembly design, the use of a hydrophilic polysulfone ultrafiltration membrane (50 kDa molecular weight cutoff) accounted for up to 64% of the ohmic resistance [37]. Kim et al. [60] compared the performance of cation exchange membrane (CEM), anion exchange membrane (AEM), and ultrafiltration membranes with that of Nafion in two-compartment MFCs. They showed that the internal resistance of MFCs with a CEM or an AEM was relatively similar to that with Nafion. However, the power outputs of MFCs were 6% lower with CEM, and 19% higher with AEM compared to that achieved by Nafion. The authors also reported more than one order of magnitude increase in the MFC internal resistance when an ultrafiltration membrane (0.5 kDa) was compared to Nafion. The MFCs with more

porous ultrafiltration membranes (1 and 3 kDa) had 10% more internal resistance and produced 10% less power output than MFCs with Nafion. Increased membrane porosity, however, enhances the crossover of oxygen and the substrate [60].

Biffinger et al. [57] demonstrated that nanoporous nylon and polycarbonate membranes (0.2 μm pore size) could replace Nafion in miniature MFCs (1.2 ml anode and cathode compartment volume). The application of these membranes resulted in power output and stability similar to that of Nafion. These membranes are, however, non-specific and permit considerable electrolyte and substrate crossover due to larger pore size as compared to Nafion. While this may not be a problem for miniature MFCs it could be detrimental to MFC performance at larger scales. Cellulose nitrate membrane was also tested in miniature MFCs and was found to be more susceptible to physical degradation, resulting in a lower performance as compared to Nafion [57].

MFC membranes allow diffusion of other cations in addition to protons from the anode to the cathode [32,58]. It has been reported that the diffused cations inhibit the transfer of protons through the Nafion membrane by occupying the sulfonate groups of Nafion [32,58]. Cations crossover also results in the formation of a pH gradient across the membrane, the cathodic side being more alkaline [32,58]. This condition has been shown to decrease the cathodic performance [23]. One reason for such an effect is reduced activity of the cathode catalysts at increasing pH values. Solutes from chemical reactions and biological activity as well as microbial adherence can foul the membrane and hinder the transfer of protons [58]. Exclusion of PEM from MFC designs has been tested as a way to address these problems and reduce the ohmic resistance [54,55,62]. The design requires air-cathode MFCs, which have a single chamber and the cathode is exposed to air on one side [63]. This design can be operated with or without a PEM. If present, the PEM is attached to the cathode side facing the anolyte.

Membrane-less MFCs (Fig. 8A) have relatively high maximum power densities but at the expense of a somewhat reduced overall coulombic efficiency [45,55,62]. The removal of membrane
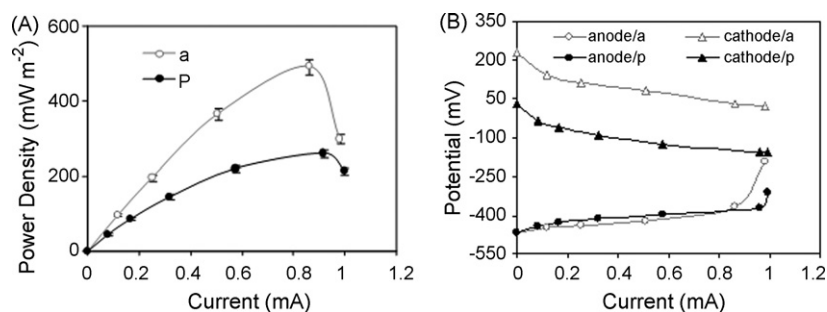

Fig. 9. (A) Power–current and (B) polarization properties of an air-cathode MFC in the presence (p) and absence (a) of a PEM. Modified from Liu and Logan [55].

increases the flux of protons, reducing the internal resistance and improving the power output of membrane-less MFCs [62]. The power output of an air-cathode MFC was improved by 88% when the PEM was omitted (Fig. 9A) [55]. In this case, the higher power output was also shown to be due to increased cathode potential (Fig. 9B). Biofilm formation on the cathode in membrane-less MFCs has been reported (Fig. 8B) [51,55]. Biofilm may become a diffusion barrier to the H+ transfer to the cathode and lead to biofouling problems over a long-term operation.

4.3. Electrode-spacing

The ohmic resistance in MFCs scales with the distance between the anode and cathode (Eq. (9)). Thus, if the space between the two electrodes is reduced, the protons have less distance to travel, and the ohmic resistance is lowered. Modification of electrode orientation has been, therefore, investigated as an effective approach to improve the performance of MFCs.

Using a membrane-less MFC, Liu et al. [51] demonstrated that decreasing the spacing between the electrodes from 4 to 2 cm reduced the ohmic resistance and resulted in a 67% increase in the power output (Fig. 10). The effect of electrode spacing on performance of MFCs has also been verified in other studies [45,54,60,64]. However, if the electrodes are spaced too close to each other in membrane-less MFCs, oxygen diffusion from the cathode to the anode increases. This can become inhibitory to anaerobic respiration and promote aerobic respiration, both of which reduce the coulombic efficiency.

Cheng et al. [62] used continuous advective flow through the anode toward the cathode and reported reduced oxygen diffusion and increased power output. Fan et al. [45] separated the anode and cathode using J-cloth in a membrane-less MFC with 1.7 cm electrode spacing. They reported about a twofold increase in coulombic efficiency (from 35 to 71%) as compared to the MFC without a J-cloth, which was attributed to reduced oxygen diffusion to the anode.

Relatively high power outputs have also been achieved in MFCs with a membrane-electrode assembly (MEA) design in which the electrodes are placed against either side of the PEM (Fig. 11A) [28,65,66]. The design minimizes the electrode spacing and reduces ohmic resistance. Liang et al. [67] compared
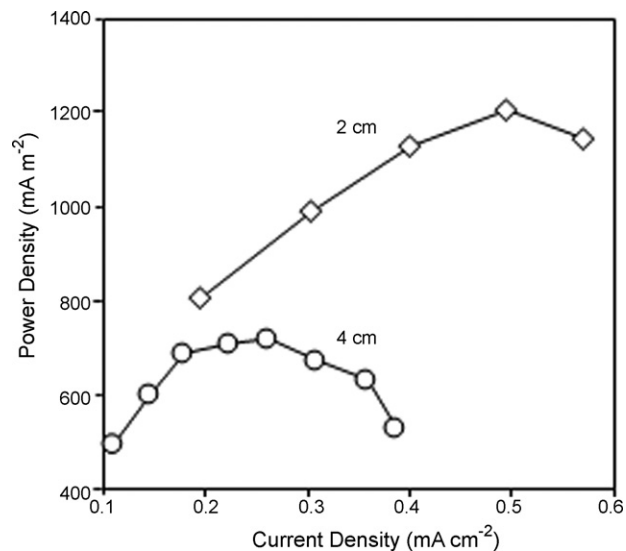

Fig. 10. Effect of electrode spacing (2 and 4 cm) on power output of a membrane-less MFC. Modified from Liu et al. [51].

the internal resistance of two air-cathode MFCs, one with an MEA design and the other one with a 4-cm electrode spacing. The authors showed that the cathodic internal resistance of the MFCs with MEA design (94 Ω) was 68% less than that of the MFCs with 4-cm distance between the anode and cathode (291 Ω), resulting in a more than threefold increase in maximum power output (1180 mW m−2 vs. 354 mW m−2) achieved by MEA-MFCs.

Using another MFC design with a tubular cathode, Zuo et al. [37] showed that the ohmic resistance was reduced by about 22% when the electrode spacing decreased from 3 to 5 cm, improving the cathode potential. He et al. [47] reported that inefficient proton transfer over a relatively large distance between the anode and cathode hindered the power output of an upflow MFC (Fig. 11B) by more than threefold from the theoretically predicted value. Optimization of the upflow MFC configuration by introducing an interior cathode (Fig. 11C) reduced the ohmic resistance by 80% and improved the power output by one order of magnitude [48].
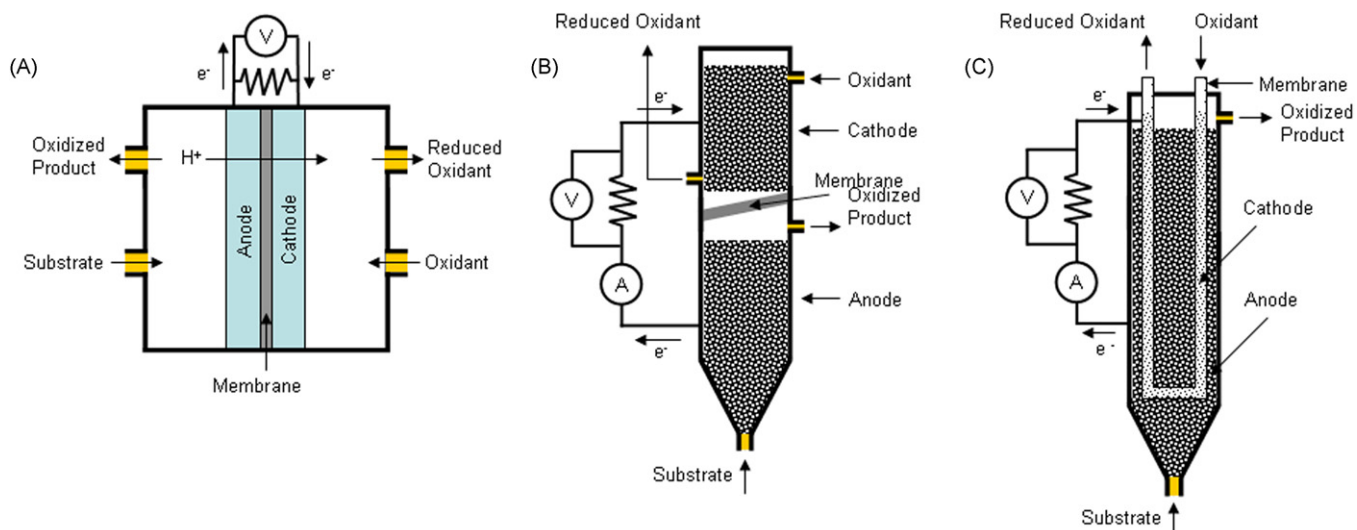

Fig. 11. Schematic of (A) a membrane-electrode assembly MFC, (B) an upflow MFC, and (C) an upflow MFC with an interior cathode.

5. Reducing cathodic mass transport losses

Mass transport in the cathode compartment depends on convection and diffusion. Mass transport in bulk catholyte is dominated by convection (i.e., macroscopic flow). In contrast, mass transport at the cathode surface is typically dominated by diffusive transport. Maintaining high bulk concentrations and an even distribution of oxidant (e.g., O_2) across the cathode compartment can reduce mass transport losses. In addition, optimization of MFC operating conditions, electrode material, and cathode compartment geometry can minimize mass transport limitations and performance losses.

5.1. Oxidant concentration

Power output has been shown to be proportional to the concentration of dissolved O_2 in the catholyte of two-compartment MFCs [22]. However, increasing the dissolved O_2 concentration is limited by its solubility in water. In general, stirring and flushing the catholyte with air or pure O_2 and recirculation of the catholyte have been tested in attempts to enhance the oxygen flux to the cathode. Using an upflow membrane-less MFC, Jang et al. [54] demonstrated that a fourfold increase in the rate of cathode aeration doubled the current output. Jong et al. [52] studied the effect of the retention time of air-saturated catholyte on the performance of a thermophilic MFC with continuous flow in the anode and the cathode compartments. They reported that the current output doubled when the retention time was reduced from 2.7 to 0.7 min. Further decreases in retention time, however, did not change the current output, suggesting that oxygen availability was no longer limiting the performance.

In a unique instance involving a bench-scale sediment MFC (Fig. 12) with exogenous supply of sucrose, He et al. [68] employed a rotating cathode to enhance the oxygen flux from the air to the underlying water column. The rotating cathode was 50% immersed in water and 50% exposed to air. The power output improved during cathode rotation because of increased cathodic potential, suggesting O_2 limitation of the cathodic reaction. However, the anodic potential also increased, perhaps because of O_2 diffusion to the anode.

Exogenous supply of oxygen to the cathode requires energy input and also increases the potential of oxygen diffusion to the anode. This may result in competition for electrons between the anode and dissolved O_2. The electron scavenging effect of O_2 in the anolyte reduces the current output and lowers the coulombic efficiency [25,55,57,68].

The effect of increasing the cathodic oxidant concentration on MFC performance has also been studied using reactants other than oxygen. For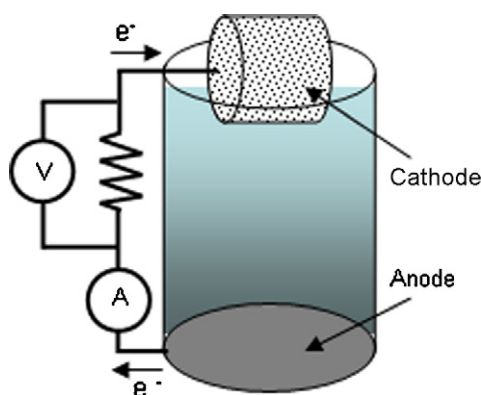 example, using an upflow two-compartment MFC, Tar-takovsky and Guiot [69] compared cathode oxygenation by air and hydrogen peroxide. Oxygenation with hydrogen peroxide resulted in a threefold increase in the power output as compared to aeration. The power output increased with loading rate of H_2O_2. Hydrogen peroxide is a strong oxidant that decomposes upon contact with organic compounds (including microbial biomass) and metals.

$$2H_2O_2 \rightarrow O_2 + 2H_2O \tag{15}$$

Clauwaret et al. [4] used an MFC in which a microbial consortium containing denitrifiers in the anaerobic cathode compartment reduced nitrate as the final electron acceptor. An increase in the loading rate of nitrate increased the cathodic potential and improved the power output (Fig. 13). You et al. [2] studied the effect of permanganate concentration, used as the cathodic electron acceptor, on the performance of MFCs. They reported a threefold increase in the current density when the permanganate concentration was increased from 0.02 to $0.2\,g\,L^{-1}$.

In contrast to dissolved O_2, the aqueous solubility of oxidants such as hydrogen peroxide and permanganate does not limit cathodic mass transport. The influence of oxidant concentration on the performance of MFCs depends on the current density. At high current output, the rate of oxidant depletion is higher than that at low current densities, aggravating the cathodic mass transport losses. Thus MFCs become more responsive to an increased supply of oxidant with an increase in current density.

5.2. Cathode electrode design

Research on optimizing electrode design and material selection in the MFC field and the resulting effect on mass transport processes has been rather limited and mainly focused on the anode. At the current status of technology, MFCs operate at relatively low current densities ($<5\,mA\,cm^{-2}$) making activation and ohmic overpotentials more pronounced than the mass transport losses. As those limitations are ameliorated, mass transport losses become a noticeable issue.

The design of the electrode to minimize cathodic mass transport losses in MFCs has not been addressed in the literature. Several design criteria should be considered including the thickness, porosity, composition, geometry, and high specific surface area of the electrode. Ideally these characteristics should improve hydrodynamic flow to facilitate the mass transport and prevent accumulation of water at the cathode.
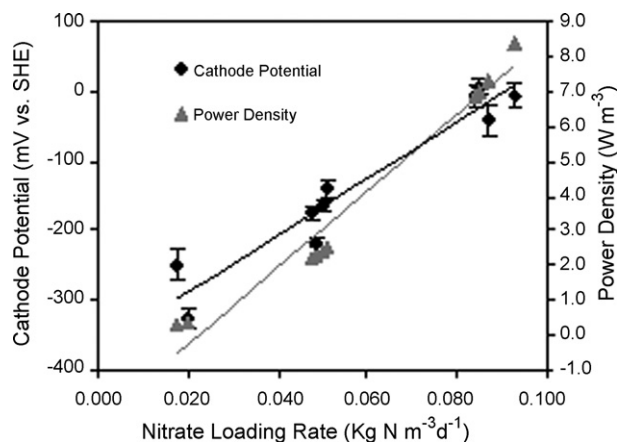

Fig. 12. Schematic of a sediment microbial fuel cell with a rotating cathode.

Fig. 13. Effect of nitrate loading rate on the cathode potential and power density normalized by the net volume of cathode compartment of an MFC with an anaerobic denitrifying cathode compartment. Modified from Clauwaert et al. [4].

5.3. Cathode compartment design

The cathodic mass transport overpotential is also a compartment configuration issue. In two-compartment MFCs with aqueous catholyte, the mass transport is limited by the lack of hydrodynamic flow and low oxidant solubility in the case of oxygen. Moreover, in this design biofilm formation on the cathode surface limits the oxidant transfer to the cathode. Such limitation increases as the thickness of the biofilm develops with time. Chemicals used to provide catholyte buffering capacity and ionic conductivity may also have adverse effects on the cathode performance by reducing the active electrode surface area and limiting the activity of catalysts in two-compartment MFCs with aqueous catholyte [65].

Air-cathode MFCs have been tested in efforts to overcome some of the problems associated with two-compartment MFCs [30,55,63,65]. In air-cathode MFCs, the mass transport loss is minimized due to direct oxygen supply from ambient air to the electrode. This alleviates the energy requirement for providing hydrodynamic flow in the catholyte. The design also makes the MFC structure relatively simple and compact, and eliminates the catholyte and the inherent problems associated with it.

Air-cathodes have been reported to form salt accumulation through the crossover of cations and anions through the membrane, possibly reducing the activity of cathode catalysts [65]. This problem has not yet been addressed in the literature. Air-cathodes are also prone to flooding. The accumulation of water is due to oxygen reduction at the cathode and crossover of water from the anode compartment. Cathode flooding slows down oxygen replenishment via diffusion, leading to mass transfer losses. This problem is particularly pronounced in membrane-less MFCs. The effect of cathode flooding on the MFC performance has not been investigated in detail. The accumulation of water at the cathode can be alleviated with forced air flow over the cathode, which has yet to be tested, and by employing physical barriers that decrease the crossover water flow. Coating the air-side of the cathode with polytetrafluoroethylene, a hydrophobic compound, has been shown to improve the MFC performance, presumably, by decreasing the water flooding of the cathode [70]. However, the thickness of hydrophobic coatings could hinder oxygen diffusion to the reaction site and adversely affect the performance at high current densities. With the increasing current densities being achieved by MFC technology, optimization of the coating material and thickness is required to balance adequate oxygen flux with minimized cathode flooding.

6. Other losses

Substrate crossover and unwanted side reactions in the cathode compartment, collectively called parasitic losses, affects the MFC performance negatively (Fig. 2). Substrate crossover through the membrane from the anode to the cathode has been reported in MFCs [37,55,57,58,60]. The membrane should ideally not allow the transport of reactants between the anode and cathode compartments. However, substrate crossover occurs commonly because of molecular diffusion and electro-osmosis [71]. Reactant crossover is particularly severe in membrane-less MFCs because there is no physical barrier to separate the contents of the anode compartment from that of the cathode compartment.

Substrate crossover influences the cathodic performance by lowering its potential below the thermodynamically predicted value. It also affects the coulombic efficiency because the substrate is utilized and/or transported away from the anode. Further, the substrate and its oxidation products may result in structural changes on the cathode surface and poisoning of the cathode catalyst.

The effects of reactant crossover on cathode overpotentials could depend on factors such as the material and thickness of the membrane, concentration of the reactants, electrode material and spacing, and the current output. Increasing the current density, reducing the substrate concentration, and improvements in membrane materials, cathode catalysts, and design of electrodes are possible approaches to decrease substrate crossover and minimize its associate effects. Substrate crossover has not been fully characterized in MFCs and remains a target for further study.

7. Concluding remarks

The unit current output is low in present-day MFC design, and a successful experimental approach to improve this limitation has yet to be reported. In this review, we have addressed the performance limiting factors associated with MFC cathodes and the recent progress in researching how to overcome these limitations. As summarized here, cathodic overpotentials are the main contributor to overall performance losses in MFCs. By elucidating the underlying mechanisms of the cathodic reaction, strategies for optimization can be better formulated. An effective strategy must address all of the cathodic overpotentials and their interactions: the reduction reaction (leading to activation losses), charge transfer (leading to ohmic losses), and mass transport processes (leading to mass transport losses).

Activation losses appear to be the dominant limitation in MFCs. Many approaches have been attempted to limit the loss through using more effective mediators and oxidants, catalysts and biocatalysts, and by optimizing the cathodic conditions. Materials with catalytic activity comparable to precious metal catalysts but with less sensitivity to operating conditions are needed. Catalysts must be made with material of high durability that can perform effectively under characteristic conditions of MFCs. The optimization of catalyst processing, electrode coating techniques, binder composition, and the catalyst/binder ratio remain a challenging target for further improvement.

Cathode ohmic limitations depend on the electrolyte conductivity and electrode spacing. An improved membrane should be developed with high ionic conductivity, selective permeability, and less susceptibility to biological and chemical fouling. This membrane should have sufficient mechanical and chemical integrity to prevent pores or cracks from developing during long-term operation and under varying cathodic conditions. Other possible ways to decrease ohmic losses include optimizing catholyte composition to reach increased ionic conductivity.

Mass transport limitations become more prominent with continued advancement of MFCs and thus must also be minimized to achieve the best performance. Oxidants should consistently be added and products removed. More research is needed to investigate active modes of oxygen transport to the cathode. For a point of reference, this has been extensively researched in chemical fuel cells. The cost for such active aeration must be compensated by increases in performance of MFCs.

The cost of the materials for construction of MFCs has been brought up in numerous articles but an overall economic analysis is premature at this stage because the designs and choice of materials continue to rapidly improve. Expensive materials (e.g., Pt and Au), although not feasible in large-scale, may give useful insight into reaction mechanisms. The suitability of less expensive materials has not been unequivocally examined. The research to date has been mostly empirical and only two papers [72,73] have been published on systematic optimization and modeling of MFCs. Modeling based on the published information poses a problem due to differences in design and operational conditions of the MFCs reported

in the literature. Although numerous applications for MFCs have been proposed, none has been scaled up to a demonstration scale. MFCs still face many challenges but with consistent advances in research and development, especially with respect to the cathode, performance can continue to improve.

Acknowledgements

References

[1] R.A. Bullen, T.C. Arnot, J.B. Lakeman, F.C. Walsh, Biosens. Bioelectron. 21 (2006) 2015–2045.
[2] S.J. You, Q.L. Zhao, J.N. Zhang, J.Q. Jiang, S.Q. Zhao, J. Power Sources 162 (2006) 1409–1415.
[3] H.I. Park, D.K. Kim, Y.J. Choi, D. Pak, Process Biochem. 40 (2005) 3383–3388.
[4] P. Clauwaert, K. Rabaey, P. Aelterman, L. De Schamphelaire, T.H. Ham, P. Boeckx, N. Boon, W. Verstraete, Environ. Sci. Technol. 41 (2007) 3354–3360.
[5] R. O'Hayre, S.-W. Cha, W. Colella, F.B. Prinz, Fuel Cell Fundamentals, John Wiley & Sons, New York, 2005, p. 409.
[6] M.E. Hernandez, D.K. Newman, Cell. Mol. Life Sci. 58 (2001) 1562–1571.
[7] L.T. Angenent, K. Karim, M.H. Al-Dahhan, R. Domiguez-Espinosa, Trends Biotechnol. 22 (2004) 477–485.
[8] K. Rabaey, W. Verstraete, Trends Biotechnol. 23 (2005) 291–298.
[9] Z. He, L.T. Angenent, Electroanalysis 18 (2006) 2009–2015.
[10] B.E. Logan, J.M. Regan, Trends Microbiol. 14 (2006) 512–518.
[11] I.S. Chang, H. Moon, O. Bretschger, J.K. Jang, H.I. Park, K.H. Nealson, B.H. Kim, J. Microbiol. Biotechnol. 16 (2006) 163–177.
[12] D.R. Lovley, Curr. Opin. Biotechnol. 17 (2006) 327–332.
[13] B.E. Logan, J.M. Regan, Environ. Sci. Technol. 40 (2006) 5172–5180.
[14] B.E. Logan, B. Hamelers, R. Rozendal, U. Schrorder, J. Keller, S. Freguia, P. Aelterman, W. Verstraete, K. Rabaey, Environ. Sci. Technol. 40 (2006) 5181–5192.
[15] T.H. Pham, K. Rabaey, P. Aelterman, P. Clauwaert, L. De Schamphelaire, N. Boon, W. Verstraete, Eng. Life Sci. 6 (2006) 285–292.
[16] P. Aelterman, K. Rabaey, P. Clauwaert, W. Verstraete, Water Sci. Technol. 54 (2006) 9–15.
[17] U. Schroder, Phys. Chem. Chem. Phys. 9 (2007) 2619–2629.
[18] Z.W. Du, H.R. Li, T.Y. Gu, Biotechnol. Adv. 25 (2007) 464–482.
[19] J.A. Gralnick, D.K. Newman, Mol. Microbiol. 65 (2007) 1–11.
[20] K. Rabaey, J. Rodriguez, L.L. Blackall, J. Keller, P. Gross, D. Batstone, W. Verstraete, K.H. Nealson, ISME J. 1 (2007) 9–18.
[21] J. Larminie, A. Dicks, Fuel Cell Systems Explained, 2nd ed., John Wiley & Sons, New York, 2003, p. 406.
[22] G.C. Gil, I.S. Chang, B.H. Kim, M. Kim, J.K. Jang, H.S. Park, H.J. Kim, Biosens. Bioelectron. 18 (2003) 327–334.
[23] F. Zhao, F. Harnisch, U. Schrorder, F. Scholz, P. Bogdanoff, I. Herrmann, Environ. Sci. Technol. 40 (2006) 5193–5199.
[24] J.M. Morris, S. Jin, J.Q. Wang, C.Z. Zhu, M.A. Urynowicz, Electrochem. Commun. 9 (2007) 1730–1734.
[25] T.H. Pham, J.K. Jang, I.S. Chang, B.H. Kim, J. Microbiol. Biotechnol. 14 (2004) 324–329.
[26] S. Oh, B. Min, B.E. Logan, Environ. Sci. Technol. 38 (2004) 4900–4904.
[27] S.E. Oh, B.E. Logan, Appl. Microbiol. Biotechnol. 70 (2006) 162–169.
[28] B.R. Ringeisen, E. Henderson, P.K. Wu, J. Pietron, R. Ray, B. Little, J.C. Biffinger, J.M. Jones-Meehan, Environ. Sci. Technol. 40 (2006) 2629–2634.
[29] Z.D. Liu, H.R. Li, Biochem. Eng. J. 36 (2007) 209–214.
[30] D.H. Park, J.G. Zeikus, Biotechnol. Bioeng. 81 (2003) 348–355.
[31] A. Ter Heijne, H.V.M. Hamelers, V. De Wilde, R.A. Rozendal, C.J.N. Buisman, Environ. Sci. Technol. 40 (2006) 5200–5205.
[32] R.A. Rozendal, H.V.M. Hamelers, C.J.N. Buisman, Environ. Sci. Technol. 40 (2006) 5206–5211.
[33] B.E. Logan, C. Murano, K. Scott, N.D. Gray, I.M. Head, Water Res. 39 (2005) 942–952.
[34] S. Cheng, H. Liu, B.E. Logan, Environ. Sci. Technol. 40 (2006) 364–369.
[35] F. Kargi, S. Eker, J. Chem. Technol. Biotechnol. 82 (2007) 658–662.
[36] F. Zhao, F. Harnisch, U. Schroder, F. Scholz, P. Bogdanoff, I. Herrmann, Electrochem. Commun. 7 (2005) 1405–1410.
[37] Y. Zuo, S. Cheng, D. Call, B.E. Logan, Environ. Sci. Technol. 41 (2007) 3347–3353.
[38] T.J. Schmidt, U.A. Paulus, H.A. Gasteiger, R.J. Behm, J. Electroanal. Chem. 508 (2001) 41–47.
[39] K.B. Gregory, D.R. Bond, D.R. Lovley, Environ. Microbiol. 6 (2004) 596–604.
[40] A. Rhoads, H. Beyenal, Z. Lewandowski, Environ. Sci. Technol. 39 (2005) 4666–4671.
[41] A. Bergel, D. Feron, A. Mollica, Electrochem. Commun. 7 (2005) 900–904.
[42] P. Clauwaert, D. Van der Ha, N. Boon, K. Verbeken, M. Verhaege, K. Rabaey, W. Verstraete, Environ. Sci. Technol. 41 (2007) 7564–7569.
[43] A. Ter Heijne, H.V.M. Hamelers, C.J.N. Buisman, Environ. Sci. Technol. 41 (2007) 4130–4134.
[44] S. Freguia, K. Rabaey, Z. Yuan, J. Keller, Electrochim. Acta 53 (2007) 598–603.
[45] Y.Z. Fan, H.Q. Hu, H. Liu, J. Power Sources 171 (2007) 348–354.
[46] K. Rabaey, P. Clauwaert, P. Aelterman, W. Verstraete, Environ. Sci. Technol. 39 (2005) 8077–8082.
[47] Z. He, S.D. Minteer, L.T. Angenent, Environ. Sci. Technol. 39 (2005) 5262–5267.
[48] Z. He, N. Wagner, S.D. Minteer, L.T. Angenent, Environ. Sci. Technol. 40 (2006) 5212–5217.
[49] S. Srinivasan, Fuel Cells: From Fundamentals to Applications, Springer, New York, 2006, p. 691.
[50] M. Amirinejad, S. Rowshanzamir, M.H. Eikanic, J. Power Sources 161 (2006) 872–875.
[51] H. Liu, S.A. Cheng, B.E. Logan, Environ. Sci. Technol. 39 (2005) 5488–5493.
[52] B.C. Jong, B.H. Kim, I.S. Chang, P.W.Y. Liew, Y.F. Choo, G.S. Kang, Environ. Sci. Technol. 40 (2006) 6449–6454.
[53] B. Mathis, C. Marshall, C. Milliken, R. Makkar, S. Creager, H. May, Appl. Microbiol. Biotechnol. 78 (2008) 147–155.
[54] J.K. Jang, T.H. Pham, I.S. Chang, K.H. Kang, H. Moon, K.S. Cho, B.H. Kim, Process Biochem. 39 (2004) 1007–1012.
[55] H. Liu, B.E. Logan, Environ. Sci. Technol. 38 (2004) 4040–4046.
[56] J.G. Liu, T.S. Zhao, Z.X. Liang, R. Chen, J. Power Sources 153 (2006) 61–67.
[57] J.C. Biffinger, R. Ray, B. Little, B.R. Ringeisen, Environ. Sci. Technol. 41 (2007) 1444–1449.
[58] K.J. Chae, M. Choi, F.F. Ajayi, W. Park, I.S. Chang, I.S. Kim, Energy Fuels 22 (2008) 169–176.
[59] B.K. Min, S.A. Cheng, B.E. Logan, Water Res. 39 (2005) 1675–1686.
[60] J.R. Kim, S. Cheng, S.E. Oh, B.E. Logan, Environ. Sci. Technol. 41 (2007) 1004–1009.
[61] M. Grzebyk, G. Pozniak, Sep. Purif. Technol. 41 (2005) 321–328.
[62] S. Cheng, H. Liu, B.E. Logan, Environ. Sci. Technol. 40 (2006) 2426–2432.
[63] H. Liu, R. Ramnarayanan, B.E. Logan, Environ. Sci. Technol. 38 (2004) 2281–2285.
[64] M.M. Ghangrekar, V.B. Shinde, Biores. Technol. 98 (2007) 2879–2885.
[65] T.H. Pham, J.K. Jang, H.S. Moon, I.S. Chang, B.H. Kim, J. Microbiol. Biotechnol. 15 (2005) 438–441.
[66] J.C. Biffinger, J. Pietron, R. Ray, B. Little, B.R. Ringeisen, Biosens. Bioelectron. 22 (2007) 1672–1679.
[67] P. Liang, X. Huang, M.Z. Fan, X.X. Cao, C. Wang, Appl. Microbiol. Biotechnol. 77 (2007) 551–558.
[68] Z. He, H.B. Shao, L.T. Angenent, Biosens. Bioelectron. 22 (2007) 3252–3255.
[69] B. Tartakovsky, S.R. Guiot, Biotechnol. Progr. 22 (2006) 241–246.
[70] S. Cheng, H. Liu, B.E. Logan, Electrochem. Commun. 8 (2006) 489–494.
[71] R.Z. Jiang, D.R. Chu, J. Electrochem. Soc. 151 (2004) A69–A76.
[72] A.K. Marcus, C.I. Torres, B.E. Rittmann, Biotechnol. Bioeng. 98 (2007) 1171–1182.
[73] C. Picioreanu, I.M. Head, K.P. Katuri, M.C.M. van Loosdrecht, K. Scott, Water Res. 41 (2007) 2921–2940.