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Electron transfer mechanisms, new applications, and performance of biocathode microbial fuel cells

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ABSTRACT

Broad application of microbial fuel cells (MFCs) requires low cost and high operational sustainability. Microbial-cathode MFCs, or cathodes using only bacterial catalysts (biocathodes), can satisfy these demands and have gained considerable attention in recent years. Achievements with biocathodes over the past 3–4 years have been particularly impressive not only with respect to the biological aspects but also the system-wide considerations related to electrode materials and solution chemistry. The versatility of biocathodes enables us to use not only oxygen but also contaminants as possible electron acceptors, allowing nutrient removal and bioremediation in conjunction with electricity generation. Moreover, biocathodes create opportunities to convert electrical current into microbially generated reduced products. While many new experimental results with biocathodes have been reported, we are still in the infancy of their engineering development. This review highlights the opportunities, limits, and challenges of biocathodes.

1. Introduction

Microbial fuel cells (MFCs) extracting energy from wastes or powering remote devices from sediments have attracted considerable research and public attention during the past decade. With crucial advances in understanding the biological reactions in these systems and substantial progress on the engineering side such as cell architecture, materials, and solution chemistry, considerable improvements in MFC performance have been achieved (Logan, 2009; Rinaldi et al., 2008). Just over a decade of intensive study has yielded a 5 to 6 order of magnitude increase in power production, with newer designs producing over 1 kW/m^3 (Aelterman et al., 2008; Logan 2010; Pant et al., 2010). While this power level allows MFC scale up and deployment for wastewater treatment, the cost of cathode materials incorporating precious metals such as Pt is prohibitive to wide-scale implementation, and the unsustainable use of ferricyanide as a catalyst-independent cathode electrolyte is not an option despite its positive effect on power density (Logan, 2010; Rismani-Yazdi et al., 2008). Although numerous non-precious catalysts and chemical modifications to air cathodes have been explored, cathode stabilization and power production still need to be improved (Duteanu et al., 2010; Rismani-Yazdi et al., 2008).

The microbial cathode, which uses bacteria as biocatalysts to accept electrons from the cathode substratum, provides a different path that avoids the use of noble or non-noble catalysts for oxygen reduction, thereby enhancing the economic viability and environmentally sustainability of MFC systems. Moreover, biocathodes enable the use of alternate electron acceptors that can broaden the utility of MFCs and present potential opportunities for the microbially catalyzed conversion of electrical current into various value-added products. He and Angenent (2006) proposed several possible biological cathodic processes for MFC systems that have been achieved at laboratory scale during the last few years, while some new processes have also been developed since that review was published. In an effort to minimize overlap, the present review will summarize these new experimental results on biocathode MFCs and emphasize the developments of four aspects, namely electron transfer mechanisms, biofilms, electrodes, and solution chemistry. Enzymatic biofuel cells (enzymatic biocathodes) have been reviewed elsewhere (Bullen et al., 2006; Cooney et al., 2008; Moehlenbrock and Minteer, 2008) and will not be addressed here.

2. Electron transfer mechanisms

While numerous investigations about electron transfer mechanisms have been performed in bioanode MFCs, only limited information is available on the electron transfer mechanisms in biocathode MFCs (Lovley, 2008). To date, two main mechanisms

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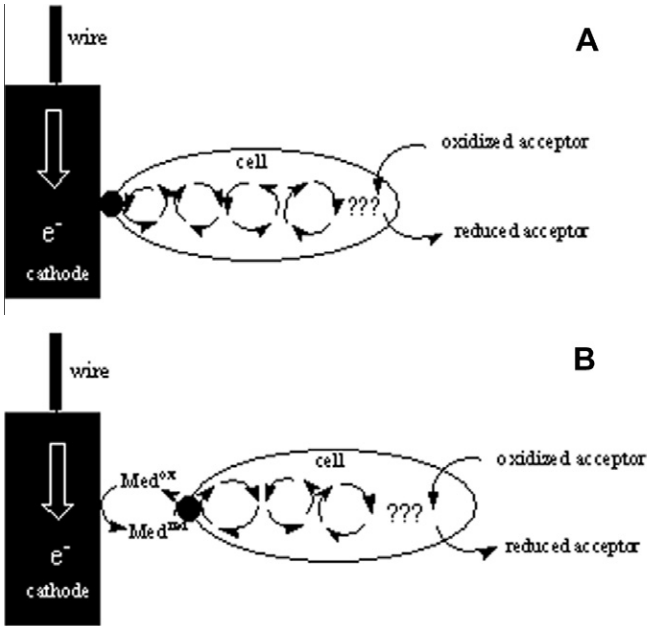

Fig. 1. Schematics of direct electron transfer mechanism via membrane bound cytochromes (A) and indirect electron transfer mechanism via added (exogenous) or secreted (endogenous) mediators (B).

have been reported, namely direct and indirect electron transfer (Fig. 1A and B, respectively). Direct electron transfer requires a physical contact between the bacterial cell membrane and the cathode electrode surface, and electrons from the electrode are directly received by the outer membrane redox macromolecules such as cytochromes (Fig. 1A). This electron transfer mechanism was reported with *Geobacter* species or mixed cultures using fumarate, nitrate, tetrachloroethene, CO_2, O_2, Cr(VI), or U(VI) as an electron acceptor (Table 1) (Cao et al., 2009; Dumas et al., 2008; Gregory and Lovley, 2005; Strycharz et al., 2008; Tandukar et al., 2009). *Shewanella putrefaciens*, which is versatile in anodic extracellular electron transfer mechanisms such as excreted flavins and menaquinone-related redox mediators as well as outer membrane cytochromes (Fredrickson et al., 2008; Kim et al., 1999; Newman and Kolter, 2000), can utilize an outer membrane-bound redox compound for electron transfer in microbially cathodic oxygen reduction. Also, this as yet unidentified compound may be released into the surrounding medium to carry out indirect electron transfer (Freguia et al., 2010). It is still unknown whether this electron transfer mechanism from cathode electrodes to *S. putrefaciens* is similar to that from *S. putrefaciens* to anode electrodes. For *Geobacter sulfurreducens*, however, it was found that electron transfer to *G. sulfurreducens* proceeds via a different mechanism than electron transfer to electrodes (Dumas et al., 2008). While most of the electrochemically active bacteria in biocathodes have been reported to be Gram-negative, some Gram-positive bacteria including *Micrococcus luteus*, *Bacillus subtilis*, and *Staphylococcus carnosus* were analyzed by a transitory electrochemical technique (cyclic voltammetry) and also shown to perform direct electron transfer, showing a potentially widespread capability among bacteria (Cournet et al., 2010). A better understanding of electron flow in biocathodes may be derived from the study of purified proteins that are potential candidates for the electrical contact between the outer cell surface and the electrodes (Eggleston et al., 2008; Voordeckers et al., 2010).

Besides pure-culture systems, direct electron transfer has also been demonstrated in mixed-culture biocathodes. This was suggested by the observation of an apparent reduction peak from cyclic voltammetry analysis on biocathodes using nitrate or carbon dioxide as an electron acceptor, as well as a rapid increase in power after the cathodic solution was replaced with fresh medium (Cao et al., 2009; Clauwaert et al., 2007a). Also, a short yet vigorous magnetic stirring of the liquid phase in a trichloroethene-reducing biocathodic chamber to transfer/dilute any redox-active components initially localized at the biofilm-electrode interface conclusively demonstrated direct electron transfer in this mixed culture (Aulenta et al., 2010).

While some bacteria perform direct electron transfer, some microorganisms can excrete redox-active compounds to carry out indirect electron transfer with electrodes. This mechanism does not need a physical contact between the bacterial cell membrane and the cathode electrode surface (Fig. 1B). *Acinetobacter calcoaceticus* was prevalent in a mixed-culture microbial cathode (Rabaey et al., 2008). This bacterium appeared to exploit a self-excreted redox compound with redox characteristics matching those of pyrroloquinoline quinine, a previously reported electron shuttle between a soluble enzyme and an electrode (Laurinavicius et al., 2004), for extracellular electron transfer in microbially cathodic oxygen reduction (Freguia et al., 2010). It has been suggested that in MFCs with naturally occurring microbial communities, extracellular substances are always involved in the electron transfer between microbes and electrodes (Watanabe et al., 2009). In such cases, it is thus important to understand the properties of the electron mediators present in biocathode MFCs (e.g. chemical structures, midpoint potentials, water solubility, stability, and toxicity), since cathodic electrode materials can be optimized to increase process efficiencies based on such information.

Besides the self-excreted redox-active compounds, microorganisms can also accept electrons from a solid-state electrode via the cathodic production of hydrogen or the reduction of various exogenously added mediators (Table 1). via the former mechanism, a natural microbial community together with the isolated strain VDY, closely related to the known dissimilatory perchlorate-reducing bacterium *Dechlorospirillum anomalous* strain WD, were shown to indirectly accept electrons from the electrode (poised at −0.5 V vs Ag/AgCl) to reduce perchlorate (Thrash et al., 2007). Similarly, by the reduction of the exogenously added mediator anthraquinone-2,6-disulfonate, an electrode poised at −0.45 V vs Ag/AgCl can indirectly donate electrons to perchlorate-reducing bacteria like *Dechloromonas agitata*, *D. aromatica*, and *Azospira suillum* for the microbially catalyzed reduction of perchlorate (Thrash et al., 2007). Also, dechlorinating bacteria can accept reducing equivalents directly from the surface of a methyl viologen-modified and polarized electrode for the dechlorination of trichloroethene (Aulenta et al., 2007). While the addition of exogenous mediators may be beneficial for the electron transfer between cathode electrode and microorganisms, in view of operation, it contributes additional cost and many of these mediators are toxic, short-lived, and unsustainable (Huang and Angelidaki, 2008). These drawbacks constitute a major obstacle for possible future application of biocathode MFCs using added mediators for extracellular electron transfer. Similar with these exogenously added mediators, the cycle of Mn(IV) reduction and subsequent reoxidation of Mn(II) coupled with oxygen reduction was observed in a biocathode (Clauwaert et al., 2007b; Nguyen et al., 2007; Rhoads et al., 2005). MnO_2 on a solid-state cathode was first reduced to MnOOH via electrons from the cathode, releasing Mn^{2+} into solution. Exploiting the catalysis of manganese-oxidizing bacteria, Mn^{2+} was oxidized back to MnO_2 with the reduction of oxygen (Nguyen et al., 2007; Rhoads et al., 2005). In comparison with an abiotic cathode, current was increased by two orders of magnitude with this catalysis of manganese-oxidizing bacteria on the cathode (Rhoads et al., 2005). Biological Mn(II) oxidation was also employed in the cathode of a sediment MFC to power wireless sensors (Shantaram et al., 2005), showing a potentially promising application for manga-