

Review

Application of Bacterial Biocathodes in Microbial Fuel Cells

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Abstract

This review addresses the development and experimental progress of biocathodes in microbial fuel cells (MFCs). Conventional MFCs consist of biological anodes and abiotic cathodes. The abiotic cathode usually requires a catalyst or an electron mediator to achieve high electron transfer, increasing the cost and lowering the operational sustainability. Such disadvantages can be overcome by biocathodes, which use microorganisms to assist cathodic reactions. Biocathodes are feasible in potentiostat-poised half cells, but only very few studies have investigated them in complete MFCs. The classification of biocathodes is based on which terminal electron acceptor is available. For aerobic biocathodes with oxygen as the terminal electron acceptor, electron mediators, such as iron and manganese, are first reduced by the cathode (abiotically) and then reoxidized by bacteria. Anaerobic biocathodes directly reduce terminal electron acceptors, such as nitrate and sulfate, by accepting electrons from a cathode electrode through microbial metabolism. Biocathodes are promising in MFCs, and we anticipate a successful application after several breakthroughs are made.

Keywords: Microbial fuel cell, Biofuel cell, Biocathode, Potentiostat-poised half cell, Terminal electron acceptor

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1. Introduction

Among electrochemical cells, microbial fuel cells (MFCs) are special types of biofuel cells, producing electric power by utilizing microorganisms, instead of isolated enzymes, to assist redox reactions [1]. The conventional MFC is a two-chamber system, consisting of anode and cathode chambers that are separated by a proton exchange membrane (PEM) (Fig. 1). This system has been half biological, because only the anode side contains electrochemically-active microorganisms, while the cathode is abiotic. The microorganisms function as biocatalysts, motivating the degradation of organic materials to produce electrons, which travel to the cathode side via an electric circuit. The presence of free electrons on the cathode of MFCs initiates a reduction reaction of oxygen to produce water [2]. Proton transport is plausible, because MFCs work in a similar manner as hydrogen fuel cells. However, recent studies have found that cation transport may play a more important role than proton transport in the completion of cathodic reactions [3, 4].

The first experimental evidence of bioelectricity was found in the late eighteenth century by Luigi Galvani, who observed electric response by connecting frog legs to a metallic conductor [5]. To further explore the potential of bioelectricity, Michael C. Potter built the first MFC in 1911. He demonstrated a current flow between two electrodes emerged in a bacterial culture and in sterile medium [6]. In 1931, Barnett Cohen [7] operated a potentiostat-poised half cell and obtained a current of 0.2 mA by applying +0.5 V.

He found that the capacity of this device could be improved by introducing potassium ferricyanide or benzoquinone as artificial electron mediators in the anode. During the 1960s, research on MFCs became popular due to the increased interest in converting organic waste into electric energy. Scientists were not able, however, to develop a MFC that could produce electricity at a consistent rate [6, 8, 9]. In the 1980s, British researcher H. Peter Bennetto succeeded in

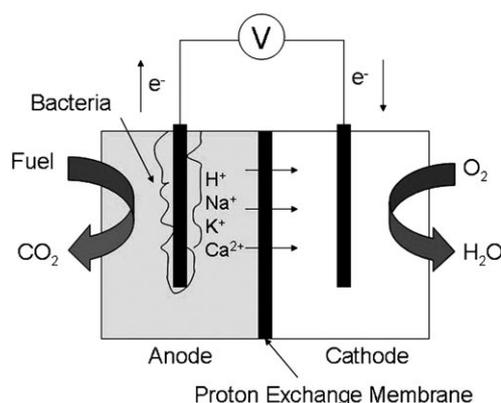


Fig. 1. Schematic and principles of a conventional MFC. For MFCs treating wastewater with a high content of ions, electro-neutrality may be maintained by transportation of cations from the anode to the cathode rather than protons. It is currently not clear if proton movement is critical to electricity generation in such fuel cells [3, 4].

extracting electric power from MFCs by employing pure cultures of bacteria to catalyze the oxidation of organics and utilizing artificial electron mediators to facilitate electron transfer in the anode [10–13]. Meanwhile, Japanese researchers focused on using photoautotrophic bacteria as energy converters in a potentiostat-poised half cell or the anode of a MFC [14–17].

In the past 10 years, MFC research has attracted greater attention from both academics and the public due to the urgent global demand of alternative energy sources [18–21]. To simplify the operation and promote the potential application of MFCs, researchers have now successfully operated MFCs without artificial electron mediators and have increased the power output by several orders of magnitude [20, 22–24]. Furthermore, researchers have focused on understanding the electron transfer process from bacteria to the electrode. The bacteria utilize either soluble electron mediators or cell membrane proteins (insoluble electron mediators) to aid electron transfer [25–27]. Recent studies revealed that bacteria may also use nanowires, a conductive protein structure, to electrically connect bacterial cells to each other or to the electrode [28, 29].

A plethora of research papers have focused on bioanodes with either pure or mixed bacterial cultures. The growth of microorganisms in the cathode chamber, however, is hard to avoid. We have consistently observed the formation of biofilms on the cathode electrode in lab-scale conventional MFCs. Others have also found biofilms on cathode electrodes, especially when PEM was absent, such as for MFCs with the anode in the anaerobic sediment and the cathode in the aerobic water column (i.e., sediment MFCs) [24, 30, 31]. Rather than preventing microbes from establishing themselves on cathode electrodes, bacteria could be used as biocatalysts to accept electrons from the cathode electrode [32]. An attempt to build a biocathode was made in the 1960s, but no practical progress was achieved [6]. In recent years, researchers explored several metabolic processes present in the cathode, reopening the door for biocathode studies. The purpose of this review is to summarize previous abiotic cathode and biocathode studies, and investigate the feasibility of biocathodes in MFCs. This review focuses on MFCs that contain bacteria as biocatalysts. Thus, enzymatic biofuel cells will not be addressed (enzymatic biocathodes have been reviewed in several publications [1, 33, 34]). The potential terminal electron acceptors for cathode (metabolic) processes are various; however, this review will focus on the ones that have been presented in studies related to MFCs.

2. Abiotic Cathodes

Abiotic cathodes can transfer electrons to oxygen as the terminal electron acceptor. Hydrogen peroxide, an intermediate product obtained during oxygen reduction, has also been used as a cathode oxidant [35, 36]. Due to slow oxygen reduction rates on the surface of carbon/graphite electrodes

catalysts or artificial electron mediators are generally required [9]. Platinum is the most popular catalyst for oxygen reduction in MFCs due to its excellent catalytic ability [37–39]. Platinum application, however, is limited because of the excessive cost and possible poisoning by components in the substrate solution [40]. In addition, pH increases, which are common in the cathode of MFCs, reduce the catalytic activity of platinum [4].

Transition metals, such as iron and cobalt, are suitable electron mediators between the cathode and the oxygen, because of their high reaction rate between their changeable redox states. Park and Zeikus [41, 42] impregnated Fe(III) compounds in the cathode electrode, where Fe(III) was reduced to Fe(II) by electrons generated from the anode reaction, and Fe(II) was, subsequently, reoxidized to Fe(III) by oxygen. In this way, electrons were transferred from the cathode electrode to the terminal electron acceptor (oxygen) with iron compounds as the electron mediators. The Fe(III)-cathode dramatically improved the power output of MFCs compared to woven graphite cathode, and showed a greater potential for commercial application. A cobalt based material, CoTMPP, has been tested by two research groups. Both groups concluded that the use of CoTMPP resulted in a similar performance as a platinum cathode [43, 44]. In addition, Zhao et al. [43] compared pyrolyzed iron(II) phthalocyanine and CoTMPP and found that CoTMPP was slightly better than iron compounds, probably due to a stronger back binding between oxygen and cobalt. Other compounds, such as cobalt oxide and molybdenum/vanadium, have also been employed to improve the reaction rates on active carbon or titanium cathodes of a MFC [45].

Ferricyanide is a commonly-used artificial electron mediator with transitional iron as the functional component [46–48]. Different than the electron mediators mentioned above, ferricyanide is a ‘theoretic’ electron mediator: it actually acts as a terminal electron acceptor, because the oxidation rate of $[\text{Fe}(\text{CN})_6]^{4-}$ by oxygen is considerably lower than the reduction rate of $[\text{Fe}(\text{CN})_6]^{3-}$ [39, 49]. As a result, the electric current generation from a MFC will depend on the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ instead of oxygen. The addition of ferricyanide to carbon/graphite electrodes greatly improves the electron transfer with a performance comparable to platinum [38, 39]. The highest power output of MFCs thus far obtained is 258 W/m^3 using a ferricyanide cathode [50]. Despite its excellent performance in MFCs, ferricyanide is not considered a sustainable chemical, because it requires continuous replacement after consumption.

3. Biocathodes

Biocathodes may be advantageous over abiotic cathodes for several reasons. First, the cost of construction and operation of MFCs may be lowered. Metal catalysts or artificial electron mediators could be made superfluous in MFCs with biocathodes, because microorganisms can function as catalysts to assist the electron transfer. In addition, under some special conditions, microorganisms, such as algae, can

produce oxygen through photosynthetic reactions, omitting the cost for an external oxygen supply (Sec. 3.1.3). Second, biocathodes may improve MFC sustainability, because problems with sulfur poisoning of platinum or consumption and replenishment of electron mediator will be eliminated. Third, the microbial metabolism in biocathodes may be utilized to produce useful products or remove unwanted compounds. For example, the microbial reduction of Fe(III) and Mn(IV), which can function as terminal electron acceptors in the cathode, is an alternative method to extract those metals from minerals [51]. Biocathodes can also be involved in the nitrogen removal process during wastewater treatment by reducing nitrate compounds (i.e., denitrification). By using denitrification in MFCs, electrons from organic waste oxidation can be used, rather than external electron donors, such as ethanol, methanol, or hydrogen gas, which are commonly added to denitrification bioreactors.

3.1. Aerobic Biocathodes

In general, biocathodes can be classified as aerobic and anaerobic biocathodes, depending on the terminal electron acceptors adopted in the cathode. Oxygen is the most popular terminal electron acceptor for the cathode reaction in MFCs, because of its high redox potential (Fig. 2) and abundance in the air, as well as relatively low cost to supply. Several studies utilized microorganisms to assist the oxidation of transition metal compounds, such as Mn(II) or Fe(II), for electron delivery to oxygen. In addition, bacteria in the cathode benefited the reaction by supplying oxygen. Finally, the positive effect of aerobic biofilms on electric power generation in sediment MFCs is discussed.

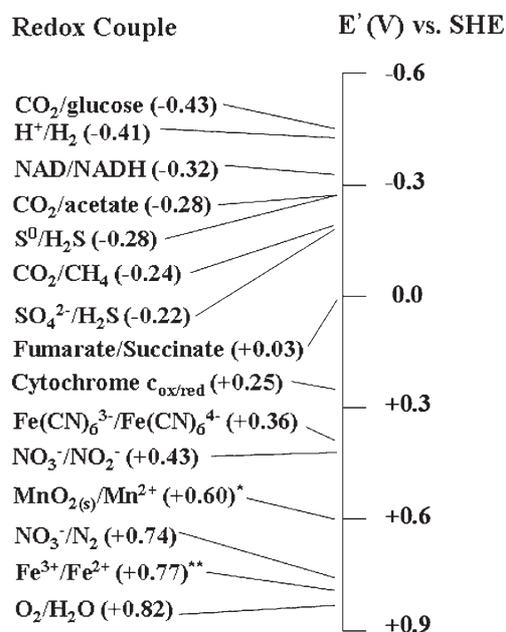


Fig. 2. Biological redox tower of electron donors and acceptors at pH 7 (based on information in [55, 76, 77]); * at pH 7.2; ** at pH 2.

3.1.1. Biological Mn(II) Oxidation

Manganese is an abundant metal that can be easily transformed between its oxidation states [52]. Both reduction of Mn(IV) and oxidation of Mn(II) can be accomplished through microbial activity at a high rate [51, 53, 54]. Rhoads et al. [55] employed the cycle of Mn(IV) reduction and subsequent reoxidation of Mn(II) in the cathode of a MFC and observed a consistent production of electricity. The first step in the cycle is abiotic in which MnO₂ is reduced to an intermediate product, MnOOH, by accepting one electron from the cathode electrode. This is followed by a further reduction of MnOOH to Mn²⁺ through the acceptance of another electron (Fig. 3; overall reaction shown in Table 1, reaction A). The second step is accomplished by manganese oxidizing bacteria (MOB), such as *Leptothrix discophora*, which oxidizes Mn²⁺ to MnO₂ by releasing two electrons to oxygen. The anode of this MFC contained *Klebsiella pneumoniae* as a biocatalyst to oxidize glucose with the aid of the electron mediators 2-hydroxy-1,4-naphthoquinone. The authors found that by adding the cycle of manganese reduction/oxidation to an aerated cathode, the maximum power output increased by more than 40 times [55]. To our knowledge, this work is the first to demonstrate a biocathode in a complete MFC.

To further explore the feasibility of such a biocathode in practice, researchers used biological Mn(II) oxidation in the

Table 1. Biocathode reactions.

Reaction	References
A	MnO _{2(s)} + 4H ⁺ + 3e ⁻ → Mn ²⁺ + 2H ₂ O [55]
B	Fe ²⁺ → Fe ³⁺ + e ⁻ [59]
C	C ₆ H ₆ O ₅ $\xrightarrow{h\nu}$ H ₂ + CO ₂ + other products [60]
	CO ₂ + H ₂ O $\xrightarrow{h\nu}$ (CH ₂ O) _x + O ₂
D	NO ₃ ⁻ + 2H ⁺ + 2e ⁻ → NO ₂ ⁻ + H ₂ O [70]
E	2H ₂ O + 2e ⁻ → H ₂ + 2OH ⁻ [78]
	SO ₄ ²⁻ + 4H ₂ → S ₂ ²⁻ + 4H ₂ O
	SO ₄ ²⁻ + 4H ₂ O + 8e ⁻ → S ²⁻ + 8OH ⁻
F	CO ₂ + 8H ⁺ + 8e ⁻ → CH ₄ + 2H ₂ O [66]
	Fumarate + 2H ⁺ + 2e ⁻ → Succinate

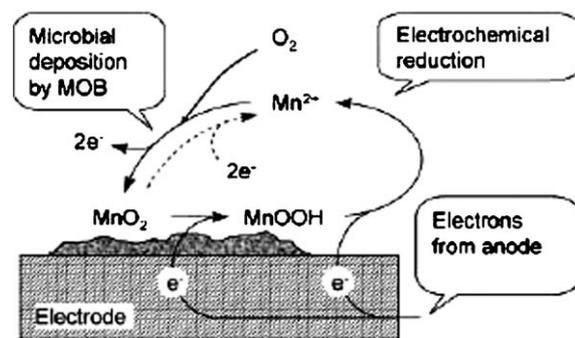


Fig. 3. Biological manganese deposition and reoxidation in a biocathode reaction process [55].

cathode of a sediment MFC to power wireless sensors [56]. This MFC is different from a conventional MFC because it used magnesium alloy as a sacrificial anode, instead of the microbial oxidation of organic fuel. Thus, the anode metal has to be replaced after consumption, limiting the lifetime of the MFC. This MFC produced a maximum voltage of 2.1 V, because of the high redox potential of magnesium oxidation. The voltage was further amplified to 3.3 V, which was sufficient to power a wireless sensor in the environment. The low-temperature environment (Roskie Creek in Bozeman, MT), where the MFC was installed, affected the microbial activity of the cathode, limiting the power output of this MFC. The study demonstrated, for the first time, the application of MFCs to power small electronic sensors in the environment and manganese compounds as promising biocathodes for sediment MFCs.

3.1.2. Biological Fe(II) Oxidation

Similar to manganese compounds, iron compounds are also popular transition metals, with an additional advantage that iron is 5–10 times more abundant than manganese [52]. The study of biocathodes using iron compounds is still in its infancy, although iron compounds have been used as electron mediators in abiotic cathodes (Sec. 2). Previous studies have revealed that Fe(II) is oxidized to Fe(III) through microbial activity by *Thiobacillus ferrooxidans* [57], for example, during mining or acid rock drainage. Iron compounds can be biologically recycled by accepting electrons from electrodes via electrochemical reactions and releasing electrons to the terminal electron acceptor (e.g., oxygen) [58]. Researchers have adopted this process to oxidize organics in an electrolytic cell in which electrical energy is converted into chemical energy, requiring an external voltage supply [59]. In the cathode chamber of this reactor, *T. ferrooxidans* was grown to regenerate the ferric irons by obtaining energy from the reaction (Table 1, reaction B); while in the anode, methanol was oxidized. The experiment with the electrolytic cell presents the feasibility of Fe(II) compounds as cathodic reactants. Further studies are required to examine if Fe(II) compounds can be oxidized by *T. ferrooxidans* with the electrons originating from an anodic bioreaction rather than an external power supply.

3.1.3. Biological Oxygen Production

The direct production of oxygen on the cathode has been shown by applying algae [6]. A MFC with blue-green marine algae on the cathode and *Rhodospirillum rubrum* on the anode delivered a maximum open potential of 0.96 V and a short-circuit current of 750 mA/m² [60]. The electricity generation from this MFC required illumination on both the anode to oxidize malate and the cathode to produce oxygen (Table 1, reaction C). Therefore, this MFC actually utilized microorganisms to convert light energy and chemical energy into electric energy. The efficiency of this MFC was only 0.1 to 0.2%, which is much lower compared to conventional

solar cells. No following studies have been reported. Illumination on the cathode is not practical for the use of MFCs to treat wastewater. However, in situ oxygen production could be valuable when MFCs are installed in natural systems, such as marine and river sediment, where oxygen concentration is low or oxygen supply is difficult.

3.1.4. Marine Biofilms

Marine sediment MFCs have been studied for their application as a potential long-term energy supply in remote areas [61–63]. Biofilm growth on the cathode of such MFCs can not be avoided, because the cathodes are exposed in an aqueous environment containing a diverse microbial community [31]. During a long-term project with an abiotic seawater fuel cell, consisting of a magnesium alloy anode and a carbon fiber cathode, Hasvold et al. [30] found that a biofilm on the cathode improved the oxygen reduction rates, indicating that the cathode biofilm functioned as a biocatalyst. Recently, Bergel et al. [64] tested a sea-water fuel cell with an abiotic Pt anode and stainless steel cathode with a biofilm separated by a PEM, and observed that the maximum power density decreased from 270 to 2.8 mW/m² after the biofilm was removed from the cathode (Fig. 4). The authors believed that the microorganisms in the biofilm were responsible for catalyzing the oxygen reduction. Through molecular analysis, Reimers et al. [65] found that the dominant species attached to the cathode of a MFC installed on the ocean floor was *Pseudomonas fluorescens*. Additionally, considering an equilibrium cathodic potential

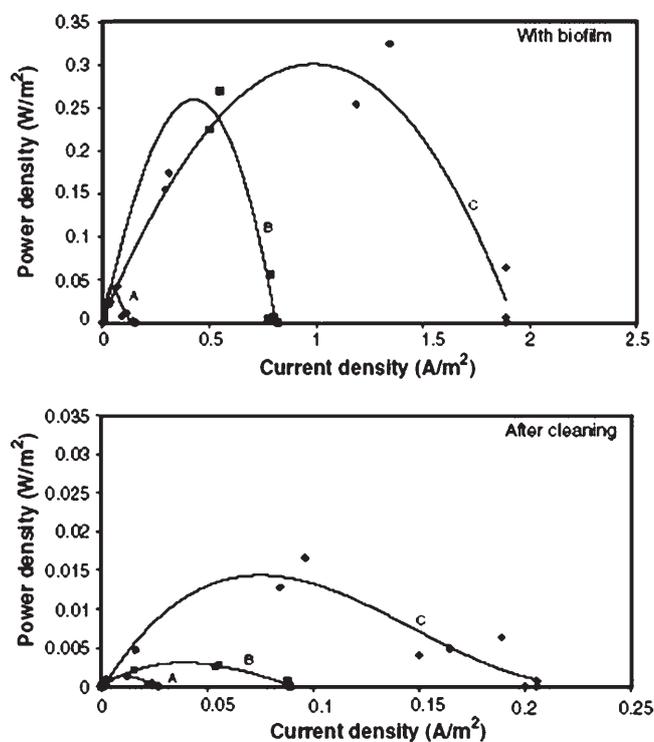


Fig. 4. Power density with a sea-water fuel cell before and after cleaning the cathodic biofilm [64].

of 0.384 V vs. Ag/AgCl, the authors suggested that manganese oxides, oxyhydroxides, and/or phenazines might be critical to the cathodic reaction in a low-oxygen environment. The mechanism of biofilm-driven catalysis of oxygen reduction is unknown, but biocatalytic processes, such as those discussed early, may be involved.

3.2. Anaerobic Biocathodes

In the absence of oxygen, other compounds, such as nitrate, sulfate, iron, manganese, selenate, arsenate, urinate, fumarate and carbon dioxide can function as terminal electron acceptors (note here that iron and manganese do not function as electron mediators under anaerobic conditions) [66, 67]. Among commonly found compounds, nitrate, iron, and manganese have a relative metabolic activity close to oxygen, while sulfate has a much lower relative activity (Table 2). Regarding their redox potentials, the cathodic potential with nitrate, manganese, and iron as terminal electron acceptors is comparable to oxygen (Fig. 2). On the other hand, sulfate has a negative potential, eliminating a favorable energy generation. Thus, based on metabolic activity and their electrochemical property, nitrate, iron, and manganese are promising as terminal electron acceptors in an anaerobic cathode. To our knowledge, only nitrate and sulfate have been studied as possible terminal electron acceptors in biocathodes of MFCs, including potentiostat-poised half cells. Studies on iron and manganese compounds as terminal electron acceptors in the cathodes of MFCs are lacking. An advantage of using an anaerobic biocathode instead of an aerobic biocathode is the elimination of oxygen diffusion into the anode via the PEM, preventing the loss of electrons to oxygen rather than the electrode. Several studies with anaerobic biocathodes in electrolytic cells with external power supply have appeared in the literature [68, 69]. We have reviewed only several of these studies here to indicate the feasibility of biocathodes in MFCs.

3.2.1. Nitrate Reduction

A biocathode using denitrifying bacteria to reduce nitrate to nitrogen gas was proposed 40 years ago [6]. Only recently, however, was this concept verified with experiments. Holmes et al. [31] found that the microorganisms on the cathode of a sediment MFC participated in biological reactions, such as ammonia oxidation and denitrification,

Table 2. The relative metabolic activity rate of electron acceptors to oxygen (modified from [79]).

Terminal electron acceptor	Metabolic activity rate
Oxygen	100
Nitrate	93
Manganese	87
Iron	84
Sulfate	6

and suggested the presence of nitrogen cycling at the cathode. Gregory et al. [70] showed that electrodes served as sole electron donors for nitrate reduction to nitrite in a potentiostat-poised half cell (Table 1, reaction D). In their study, nitrate was only reduced with the presence of *G. metallireducens* or an adapted enrichment culture, indicating the involvement of bacteria in nitrate reduction (Fig. 5). This result was confirmed by another group of researchers, who also observed biological nitrate reduction by accepting electrons from the cathode electrode in a potentiostat-poised half cell [71]. In their study, nitrate was reduced completely to nitrogen gas, and the reactions occurred in the absence of any organic substrates (electron donors). To exclude the possibility of hydrogen donating electrons to nitrate reduction, the authors examined the electrochemical hydrogen production and found its rate was 100-fold lower than the rate of nitrate reduction. This showed that hydrogen was an unlikely key electron donor for nitrate reduction, and that the cathode electrode directly delivered electrons to denitrifying bacteria. Geol and Flora [72] operated an electrolytic cell to perform nitrification in the anode and denitrification in the cathode. Their study used electrical power to promote these biological reactions, and showed that bacteria in the cathode can use the electrode as a sole electron donor. These studies were all conducted with an external supply of current. It is, therefore, still questionable if denitrification in the cathode can be sustained with electrons produced from an anodic bioreaction.

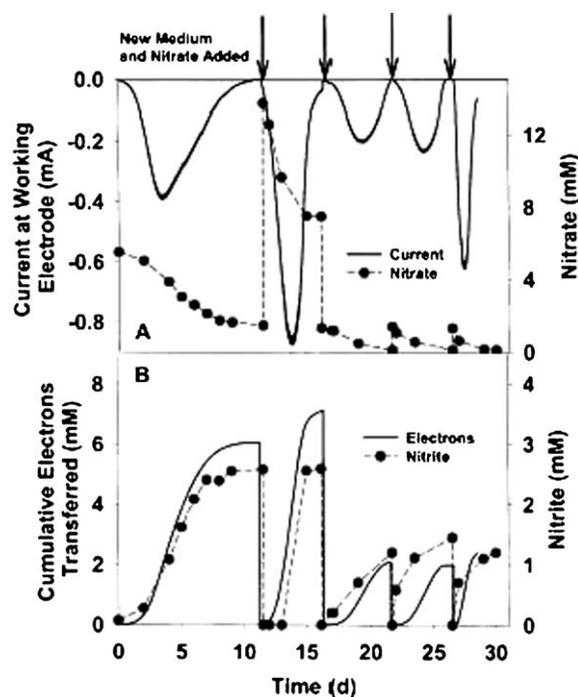


Fig. 5. Nitrate reduction with the electrode as a sole electron donor: A) electric current and nitrate concentration; B) cumulative electron flow and nitrite concentration [70].

3.2.2. Sulfate Reduction

Although sulfate is the least promising electron acceptor of the ones discussed, researchers have considered sulfate reduction as a possible cathode process. In a sea-water fuel cell with a sacrificial magnesium anode, the power output was higher when the cathode was colonized by sulfate-reducing bacteria [6]. Goldner et al. [73] investigated the nutrient requirement of sulfate-reducing bacteria when they were applied to biocathodes in a MFC with an active metal anode. Their results demonstrated that hydrogen oxidation was accomplished by an enriched culture of *D. desulfuricans* in sea water, containing a small amount of yeast extract and ammonium ions. Cord-Ruwisch and Widdel [74] suggested that the anaerobic corrosion of iron functioned as a hydrogen source for sulfate reduction. Generally, in such a biocathode, sulfate does not directly accept electrons from the cathode electrode (Table 1E).

3.2.3. Carbon Dioxide or Fumarate Reduction

Two other compounds with low redox potentials have also been examined as terminal electron acceptors. In a potentiostat-poised cathode, Park et al. [66, 75] supplied carbon dioxide and fumarate to methanogenic granules and *Actinobacillus succinogenes*, respectively. By consuming electrons from the cathode electrode with neutral red as an artificial electron mediator, microbes reduced carbon dioxide to methane and fumarate to succinate (Table 1F). This study demonstrated the biocathode concept, however, the redox potentials of CO₂/CH₄ and fumarate/succinate (−0.24 V and +0.03 V vs. SHE, pH 7, [Fig. 2]), are not favorable for electricity generation in MFCs.

4. Conclusions and Perspectives

This review has addressed the development of bacterial biocathodes. So far, few studies have described biocathodes in complete MFCs. Results from potentiostat-poised half cells and electrolytic cells, on the other hand, showed that biocathodes are promising substitutions for abiotic cathodes in MFCs. Biocathodes are a welcome advancement in the quest to implement MFCs for practical applications, such as wastewater treatment and sediment MFCs, because of potential cost savings, waste removal, and operational sustainability. We anticipate a successful application of biocathodes in MFCs after several accomplishments are made.

First, the bacterial electron-transfer mechanisms in the cathode must be fully understood. This is required to ascertain the limitations of electron transfer from cathode to microorganism, and to subsequently reduce the biological overpotentials.

Second, several successful implementations of biocathodes must be demonstrated without external power supplies. The current advances with biocathodes in potentiostat-poised half cells cannot automatically guarantee the

same results in complete MFCs, because an applied potential overcomes many limitations occurring in MFCs, such as anodic charge – and anolyte – resistances.

Third, a competitive advantage of electrochemically-active bacteria over other bacteria in the cathode must be sustainable, especially in natural systems or when wastewater is used as the catholyte. The presence of other electron donors than the electrode could disturb the cathodic electron flow, and therefore the electric current in MFCs.

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