



Research review paper

Microbial fuel cell (MFC) power performance improvement through enhanced microbial electrogenicity

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ABSTRACT

Within the past 5 years, tremendous advances have been made to maximize the performance of microbial fuel cells (MFCs) for both “clean” bioenergy production and bioremediation. Most research efforts have focused on parameters including (i) optimizing reactor configuration, (ii) electrode construction, (iii) addition of redox-active, electron donating mediators, (iv) biofilm acclimation and feed nutrient adjustment, as well as (v) other parameters that contribute to enhanced MFC performance. To date, tremendous advances have been made, but further improvements are needed for MFCs to be economically practical. In this review, the diversity of electrogenic microorganisms and microbial community changes in mixed cultures are discussed. More importantly, different approaches including chemical/genetic modifications and gene regulation of exoelectrogens, synthetic biology approaches and bacterial community cooperation are reviewed. Advances in recent years in metagenomics and microbiomes have allowed researchers to improve bacterial electrogenicity of robust biofilms in MFCs using novel, unconventional approaches. Taken together, this review provides some important and timely information to researchers who are examining additional means to enhance power production of MFCs.

1. Introduction

Due, in part, to increased concerns over depleting fossil fuel energy, climate change and environmental pollution, researchers around the world have made significant and impactful efforts to exploit new sustainable and environmentally-friendly energy resources. Bioelectrochemical systems, notably microbial fuel cells (MFCs) that can harvest energy from organic wastes through microbial metabolism, have attracted attentions in recent decades as a potential method for clean energy production coupled with the added benefits of bioremediation (Lovley, 2006a; Zhou et al., 2014; Wang et al., 2015b; Santoro et al., 2017).

Put simply, MFCs use microorganisms as biocatalysts to oxidize organic matter and transfer electrons via substrate oxidation to the anodic surface for bioelectricity production (Du et al., 2007; Logan, 2009; Wang et al., 2015a). A variety of organic compounds such as starch, cellulose, simple carbohydrates, organic acids, proteins/amino acids, chitin as well as toxic waste chemicals such as phenol, *p*-

nitrophenol, nitrobenzene, polycyclic aromatic hydrocarbons, indole, ethanolamine, and sulfide have been used as oxidizable substrates to power MFCs (Xia et al., 2015; Hao et al., 2016; Yang et al., 2013; Li et al., 2010; Sherafatmand and Ng, 2015; Shin et al., 2015). Municipal, paper mill, food industry wastewaters as well as metal contaminated wastewater, swine wastewater, brewery/distillery waste and marine sediments have also been successfully used in laboratory MFC devices for bioelectricity generation (Nimje et al., 2012; Kim et al., 2016; Bond et al., 2002; Wang and Ren, 2013; Wang and Ren, 2014) and for production of biomaterials (Zhou et al., 2013b).

In a typical MFC setup (Fig. 1), electrons released by anodic biofilm bacteria after oxidation of an electron donor (typically an organic substrate) are first transferred to the anode under anoxic condition (see Reaction 1 using acetate as substrate). This indicates that the anode is used by the electrogenic biofilm bacteria as the electron acceptor for anaerobic respiration. Protons generated from the oxidation process migrate to the cathode usually through a proton exchange membrane (PEM) that prevents diffusion of oxygen into the anodic chamber.

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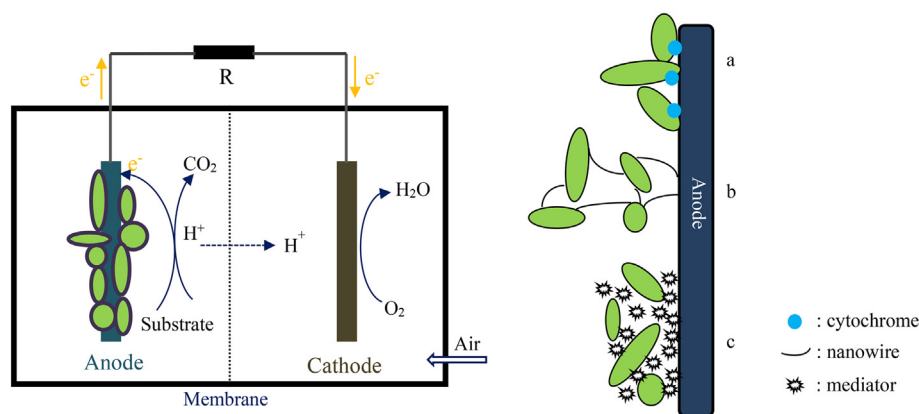
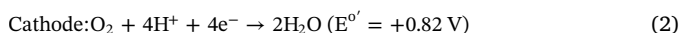
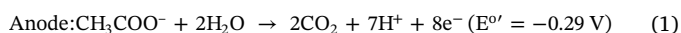


Fig. 1. Schematic illustration of MFC and the extracellular electron transfer through (a) outer-membrane bound cytochromes, (b) conductive nanowires (pili), (c) redox mediators.

Electrons reach the cathode via an external circuit with an applied resistance load. These electrons, protons and the dissolved oxygen in the catholyte react on the cathode surface to form water as shown in Reaction 2 (Lovley, 2006b; Zhang et al., 2016; Rabaey and Verstraete, 2005; Wang et al., 2015b).



The standard reduction potentials adjusted for pH 7 ($E^{\circ'}$) above indicate that the redox reaction combining Reactions 1 and 2 has a cell potential of +1.11 V at pH 7, which means that the reaction is thermodynamically favorable (i.e., energy is released).

In 1911, Potter (1911) observed that bacteria could generate electric current when a platinum electrode was inserted into a liquid suspension of yeast and *Escherichia coli*. This discovery was the advent of MFC research and ensuing technological development. Early progress in MFC research was very slow due to either naïve skepticism, a lack of interest or a myriad of unexpected technical difficulties. Until the 1980s, redox-active mediators were widely used in MFCs to improve power performance. The addition of these electron-donating mediators accelerated the rate of electron transfer from the microorganisms to the anode, thereby significantly enhancing the current and power density output of MFCs (Rabaey and Verstraete, 2005). However, this was too costly and impractical for further applications.

In subsequent studies, researchers discovered that microbes could transfer electrons to an external electrode directly by surface contact without an exogenous electron mediator (e.g., in a mediatorless MFC). These microbes include but are not limited to members of the genera *Geobacter* (Bond et al., 2002; Reguera et al., 2006), *Shewanella* (Kim et al., 1999; Kim et al., 2002), *Clostridium* (Park et al., 2001), and *Pseudomonas* (Rabaey et al., 2004) that are all well-established exoelectrogens. Thus, many researchers have focused on extracellular electron transfer mechanisms from exoelectrogens to an electrode (Reguera et al., 2005; Li et al., 2017a). The mechanisms by which microorganisms transfer electrons to electrodes have been classified into three categories (Fig. 1): (a) direct electron transfer through redox-active proteins on the outer membrane of microorganisms, such as c-type cytochromes, (b) direct electron transfer via type IV pili (proteinaceous appendages that have often been referred to as electrically conductive “nanowires”), and (c) mediator-based electron transfer utilizing exogenous or endogenous electron mediators (Logan, 2009; Yang et al., 2012; Lovley, 2008; Yu et al., 2015). Exogenous electron mediators are usually ruled out for practical applications due to their high cost, short lifetime and discharge problems (Yong et al., 2014b). In a cooperative, synergistic biofilm community, electrogenic and non-electrogenic microbes could “share” the secreted electron mediators to improve extracellular electron transfer (Rabaey et al., 2005; Pham et al., 2008; Von

Canstein et al., 2008). MFCs that do not rely on mediated extracellular electron transfer is known as mediator-less MFCs (MFCs). In recent years, MFCs have been widely used in laboratory investigations for wastewater treatment resulting in some very encouraging results (Gude, 2016; Zhang et al., 2016). Accordingly, the use of wastewater as a substrate in MFCs to generate bioelectricity is considered “environmentally friendly” (Pandey et al., 2016).

There has been no successful pilot-study to date using MFCs for what would be considered “practical” power generation (Zhou et al., 2013a). The MFC power output is still too low for applications other than powering sensor devices (Yang et al., 2015). Improving the power performance of MFCs remains the key focus of current research, with the hope of moving MFCs toward eventual practical applications. MFC reactor configurations, electrode materials, electrochemically active microbes, internal resistance, proton exchange membrane (PEM) bio-fouling and reactor operating conditions are some of the main factors that impact power performances of MFCs. Generally speaking, substrate degradation, electron transfer from the microorganisms to the anode, and proton migration from anode to cathode through liquid media, cathodic reduction reaction rate are key steps involved in MFC performance (Logan and Regan, 2006; Zhou et al., 2011). To increase the power performance of MFCs, some researchers (Richter et al., 2009; Yong et al., 2014a) have focused on microbiological aspects (e.g., extracellular electron transfer mechanisms of microbes, exoelectrogen modifications), or non-microbiological aspects (e.g., MFC reactor configurations, electrode materials, presence vs. absence of a PEM) (Li et al., 2017b; Xie et al., 2017). In this review, we have elected to focus on the electrogenic microorganisms currently used in MFCs and how to optimize them for improved MFC power generation. It should be noted that apart from the electron transfer (also known as charge transfer) bottleneck, mass transfer of substrate and proton migration from the anodic chamber to the cathode can also be rate-limiting (Gil et al., 2003; Liu et al., 2005; Yang et al., 2016). Those topics have been addressed in other reviews (Rabaey and Verstraete, 2005; Li and Yu, 2015; Oliot et al., 2016). As advances in the improvements of charge transfer are made through improved electrogenicity as discussed in this work, mass transfer effects will become more pronounced. Additional efforts to improve mass transfer will still be required.

2. Diversity of electrogenic microorganisms

Many types of microbes have proven to be useful in MFCs. They include bacteria, archaea (e.g., methanogens) and fungi (e.g., biodegradation fungal species) (Logan, 2009; McCormick et al., 2015; Hubenova and Mitov, 2015). A mixed-culture biofilm community is typically and ideally a synergistic community with each species playing specific roles in a “nutrient cycle ecosystem.” For example, some of

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