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Electron acceptors for energy generation in microbial fuel cells fed with wastewaters: A mini-review

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HIGHLIGHTS

- This review summarized various electron acceptors adopted in microbial fuel cells.
- Merits and drawbacks of various electron acceptors were identified.
- Possible future research directions were discussed particularly from cathode aspect.

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ABSTRACT

Microbial fuel cells (MFCs) have gained tremendous global interest over the last decades as a device that uses bacteria to oxidize organic and inorganic matters in the anode with bioelectricity generation and even for purpose of bioremediation. However, this prospective technology has not yet been carried out in field in particular because of its low power yields and target compounds removal which can be largely influenced by electron acceptors contributing to overcome the potential losses existing on the cathode. This mini review summarizes various electron acceptors used in recent years in the categories of inorganic and organic compounds, identifies their merits and drawbacks, and compares their influences on performance of MFCs, as well as briefly discusses possible future research directions particularly from cathode aspect.

1. Introduction

Microbial fuel cells (MFCs), the device that uses bacteria as the catalysts to oxidize organic and inorganic matter with current generation, has obtained tremendous global notice over the last decades (Logan et al., 2006). MFC has a number of attractive characteristics such as direct electricity generation, high efficiency, and operation in ambient temperatures (Ren et al., 2012). Particularly, MFC can accomplish wastewater treatment simultaneously as well as reduce the amount of sludge production (Pant et al., 2010b).

The electron acceptor contributes to overcome the potential losses existing on the cathode, thus it is one of the major factors influencing power generation in MFCs. The conditions of being a good electron acceptor comprise possessing high redox potential, presenting fast kinetics, being economically valuable, and preferably have sustainability and easy availability (Lu and Li, 2012). Oxygen is one of most promising electron acceptors in MFCs (Logan et al., 2006). However, with the rapid progress of MFC technology as well as a better understanding of its principle, there is a broad awareness that the cathode process is far more than just oxygen reduction reaction (ORR). Various alternative electron acceptors, such as nitrate (NO_3^-), metal ions, perchlorate, nitrobenzene, and azo dyes, have been intensively explored to achieve bioremediation in MFCs (Liu et al., 2014).

So far, several reviews have focused on the cathode processes in MFCs especially in terms of fundamentals and application (He and Angenent, 2006; Harnisch and Schroeder, 2010; Lu and Li, 2012; Liu et al., 2014). He and Angenent (2006) for the first time addressed the development and experimental progress of biocathodes in MFCs. Harnisch and Schroeder (2010) presented the first primary comparative analysis on ORR in the cathode of MFCs. More recently, Liu et al. (2014) provided a panoramic picture of various cathodic catalysts applied in MFCs and gave an insight into their catalytic characteristics, mechanisms and limitations. However, a comprehensive review on the various electron acceptors which have been used in MFCs is still lacking.

Therefore, this mini review aimed at summarizing various electron acceptors used in recent years in the categories of inorganic and organic compounds. Moreover, the merits and drawbacks of

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different electron acceptors were identified and their influences on performance of MFCs were also compared. In addition, possible future research directions were briefly discussed in this mini review particularly from cathode aspect.

2. Fundamentals of MFCs

The operating principle of a MFC is illustrated in Fig. 1, for which a detailed description can be found elsewhere (Rozendal et al., 2008). In brief, electrons are produced by oxidizing substrates via microbial metabolism in anodic chamber of MFCs, and then transmitted to the cathode through external circuit for power generation or for further cathode applications. The overpotentials of the electrodes in an MFC can roughly be categorized as activation losses, concentration losses and bacterial metabolic losses (Logan et al., 2006). A lot of efforts have been directed to reduce these losses through decreasing electrode spacing, increasing electrode surface area and/or solution conductivity, using metal catalysts and establishment of an enriched biofilm on the electrodes (Logan et al., 2006).

Particularly, it is worthwhile to mention that biocathodes with microorganisms as catalyst have been demonstrated as one of the promising approaches to reduce activation losses occurring in the cathode of MFCs (He and Angenent, 2006). Although the biochemical mechanisms involved in microbial electron uptake from a cathode are still very unclear and thus need a further investigation, several possible extracellular electron transfer paths have been suggested, including (a) direct electron transfer using active centre of the membrane enzyme in microbe, such as cytochromes; (b) direct electron transfer via biological and fibrous protein structure nanowires; (c) mediated electron transfer using self-secreted shuttles; (d) long-distance electron transfer via a conductive biofilm matrix occupying "nanowire grid" and cytochromes related to matrix (Rosenbaum et al., 2011).

3. Inorganic electron acceptors

3.1. Oxygen

So far, the most sustainable and suitable electron acceptor known for MFCs is oxygen, because of its availability in the environment, low cost and high redox potential (Freguia et al., 2007). In order to increase the oxygen reduction kinetics and reduce cathodic activation overpotential, different kinds of catalysts have been used in the cathode (Erable et al., 2012). Platinum offers the highest catalytic performance with increased oxygen affinity and reduced activation loss, and is the most commonly used catalyst for ORR (Lu and Li, 2012). Logan et al. (2005) demonstrated that Pt-based MFC could achieve 5-fold increase in power output compared to the MFC with a plain carbon cathode. For cheaper and more sustainable, other catalysts such as lead dioxide (Morris et al., 2007), Fe/Fe_2O_3 (Zhuang et al., 2010), cobalt (Lefebvre et al., 2009), manganese dioxide (Lu and Li, 2012) or even activated charcoal (Pant et al., 2010a) have also been explored for oxygen reduction reactions at the cathode of MFCs.

Biocathodes with enzymes or microorganisms have been intensively applied for ORR in MFCs (He and Angenent, 2006). Some redox enzymes, mainly laccases and bilirubin oxidases, were applied to catalyze ORR (He and Angenent, 2006). Compared with the controlled Pt-based MFCs, the MFC with laccase generated 10-fold increase of the maximum power density (Schaetzle et al., 2009). However, enzymes have various drawbacks as the cathode catalyst for ORR, such as being sensitive to toxicants, full of complications to be immobilized on electrode surfaces, and short-life time (Erable et al., 2012). Microorganisms have been the most popular choice of biocatalyst for ORR in MFCs, due to many advantages compared to chemical and enzymatic catalysts (Lu and Li, 2012). Clauwaert et al. (2007) for the first time developed a biocathode with mixed microorganisms as biocatalysts for oxygen reduction in MFCs. Following this, mixed cultures were inoculated with various inoculums as the biocathodes for ORR in MFCs (Freguia et al., 2007; Rabaey et al., 2008). Although several pure strains were also adopted to be catalytics for ORR, the results have suggested that the MFC performance in terms of current density and power output was unable to reach to the similar levels demonstrated by the mixed population (Rabaey et al., 2008).

3.2. Nitrogen-containing compounds

Due to NO_3^- owing competitive redox potential to oxygen, denitrification process has drawn considerable attentions in MFCs with both electricity generation and wastewater treatment (Clauwaert

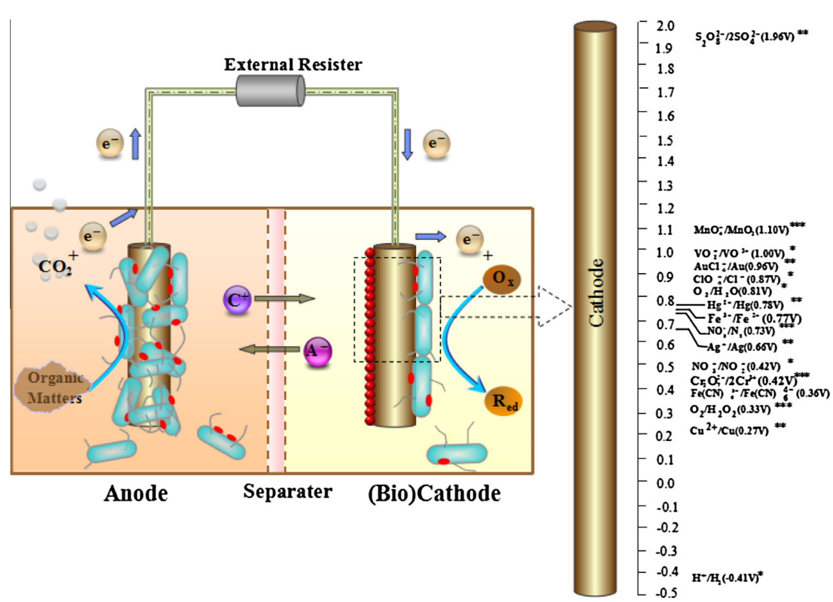

Fig. 1. Fundamental configuration of a MFC with the redox potential vs. SHE (Standard Hydrogen Electrode) of various electron acceptors (based on information from Lu and Li (2012) and He and Angenent (2006); *at pH = 7; **the molarity of ions were 5 mM; ***the molarity of ions were 5 mM at pH = 7).