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Review

Internal resistance of microfluidic microbial fuel cell: Challenges and potential opportunities

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HIGHLIGHTS

- There is growing interest in the development of microfluidic MFCs with μL volume.
- μMFCs are serving as a versatile platform for fundamental MFC studies.
- μMFCs are effective in screening of electrochemically microbes and electrodes.
- μMFCs generate lower volumetric power density due to the high internal resistance.
- Manipulation of μMFCs design elements contributes to lower internal resistance.

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ABSTRACT

The efficiency of microbial fuel cells (MFCs) is affected by several factors such as activation overpotentials, ohmic losses and concentration polarization. These factors are handled in micro-sized MFCs using special electrodes with physically or chemically modified surfaces constructed with specified materials. Most of the existing μLscale MFCs show great potential in rapid screening of electrochemically-active microbes and electrode performance; although they generate significantly lower volumetric power density compared with their mL counterparts because of their high internal resistance. This review presents the development of microfluidic MFCs, with summarization of their advantages and challenges, and focuses on the efforts done to minimize the adverse effects of internal resistance (ohmic and non-ohmic) on their performance.

1. Definitions and general remarks of MFC

Microbial fuel cells (MFCs) are bio-electrochemical systems that use bacterial metabolism to generate electrical current from a variety of organic substrates (Pant et al., 2012). The use of microorganisms eliminates the separation of individual enzymes, thus providing economical biocatalysts for biological fuel cells.

Classic MFCs are designed with cathode and anode chambers separated by a proton exchange membrane (PEM) (Fig. 1). Organic substrates are oxidized at the anode via bio-catalyzed reactions in which the released electrons are transferred to the cathode, to form the current, via an external electrical circuit that connects both electrodes. Suitable electrocatalysts (including some of biological origin) complete reduction reactions at the cathode, where the protons transported via the PEM are combined with electrons and oxygen to form water. It is now evidenced that electricity can be produced from any biodegradable substrate, ranging from pure fuels such as glucose, acetate, ethanol, cysteine and bovine serum albumin to complex mixtures of organic matter including domestic, animal, meat-packing and food-processing wastewaters (Pant et al., 2010). The driving force of a typical MFC using glucose as fuel can be articulated at anode and cathode, respectively, as follows (Grzebyk and Poźniak, 2005):

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$$
$$6O_2 + 24H^+ + 24e^- \rightarrow 12H_2O$$

Interaction between electrodes and microbes can occur via direct electron transfer (DET) or mediated electron transfer (MET). In DET, microbial enzymes are set in such a way that electronic states in the surface material and enzyme active center (or other conductive structures) overlap, increasing the probability of electron transfer across the interface. In MET, natural or artificial

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electron transferring agents can readily participate in redox reactions of biological components. Accessibility, suitable redox potentials, electrostatic interactions, pH and ionic strength are major factors that play a role in facilitating MET (Dominguez-Benetton et al., 2012).

MFCs have several advantages over the conventional technologies currently used for producing energy from organic matter. First, high conversion efficiency is enabled from the direct transformation of substrate energy (contained in chemical bonds) to electricity (Logan, 2007). Second, MFCs take advantage of general biochemical reaction, based on the physiology of microbial communities, without any extra energy input for aeration on the cathode. Third, an MFC does not require gas treatment because the off-gases of MFCs are mainly composed by carbon dioxide which does not have any useful energy content (as compared to e.g. methane from anaerobic biodigestion). Furthermore the redox products are usually CO_2 and H_2O, which are not considered contaminants. Fourth, MFCs can use a huge range of resources as their fuel because they do not need to be high quality. Wastes and wastewaters apply since they are generally full of organic compounds of which most are biodegradable (Rabaey and Verstraete, 2005). Fifth, MFCs have the potential for general application in sites lacking electrical infrastructures and also to inflate the diversity of fuels we use to fulfill our energy requirements (Logan, 2007).

2. Overpotentials: bottlenecks of MFC

There are several bottlenecks which limit the performance of large scale implementation of MFC technology, i.e. overpotential associated with preceding chemical or biochemical reactions (Bard and Faulkner, 2001). However, the direct flow of electrons from the bacteria to the electrode is hindered mainly by the transfer resistances which are known as overpotentials (Larminie and Dicks, 2000). These overpotentials minimize the potential achieved from the MFC and therefore decrease the energy efficiency. The losses can be mainly classified as activation overpotentials, concentration polarization and ohmic losses.

Electrochemical reactions at MFC electrode surfaces require certain activation energy, for charge transfer to either complete substrate oxidation at the anode (or for preceding biochemical electron transfer from a reducing equivalent) or reduce oxygen at the cathode (Larminie and Dicks, 2000). The activation overpotential could be decreased by increasing the operation temperature, up till certain extents, only for indirect systems. Also, it could be decreased by the addition of a catalyst to the electrode (Schroder et al., 2003). Increasing the roughness and specific surface of the electrode decrease the current density and hence the activation losses.

Concentration polarization occurs when compounds are being oxidized faster at the anode than they can be transported to the surface, and this could be due to the large oxidative force of the anode (Rabaey et al., 2005b). Concentration polarization would be a problem, in cases where diffusion is seriously hindered by, for example, a thick non-conductive biofilm, hydrodynamics and geometrical aspects of the cell design.

Ohmic losses are due to electrical resistances of the electrodes, membrane and electrolyte. However, the resistance over the MFC can increase rapidly by suboptimal contacts or limited conductivity and turbulence of the electrolyte. The structure of the anode should support free flow of influent and effluent, growth of a biofilm, conductivity and sufficient turbulence for adequate proton diffusion towards the membrane and cathode. The cathode resistance could be inclined by using effective materials or microorganisms as catalyst, increasing the specific surface area and the mass transport rate, or adapting the electrolyte solution (Sleutels et al., 2012). Furthermore, it has been observed that cathode resistance could be significantly reduced by increasing the size of the cathode compared to the anode (Fan et al., 2008).

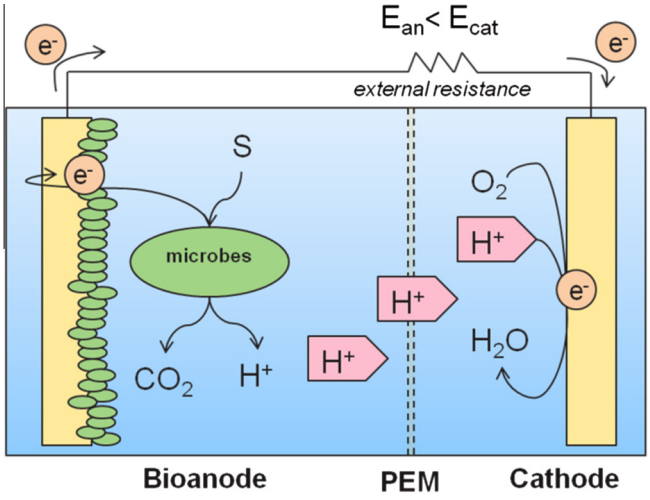

Fig. 1. Schematic diagram of typical two-chamber microbial fuel cell producing electricity through electron transfer to the anode.

The selection of a separating membrane between anode and cathode represents a choice between two disparate interests: high selectivity for protons and high stability in a bacterial colloidal and nutrient rich environment. Nafion™ has been widely used as proton exchange membrane (PEM) for fuel cells and MFCs (Bond and Lovley, 2003), and has the large advantage of being very selective for protons. This membrane type scores high for selectivity but low for stability. The limitation for applying membranes lies in the development of a pH gradient between anode and cathode which involves an additional energy loss. Alternatively, a high pH value at the cathode enables a lower cathodic resistance, in which some strategies were tested to decrease this pH gradient, i.e. CO_2 addition to the cathode (Sleutels et al., 2012). A second approach is the use of a more general cation exchange membrane (CEM), such as Ultrex™ (Rabaey et al., 2003). This type of membrane has a larger resistance and is less selective but generally shows larger stability. These membranes have been reported to perform adequately for over three months (Rabaey et al., 2005a). Several studies commonly reported MFC challenges caused by the membrane, which are pH gradient in the anode chamber, O_2 diffusion, H_2 loss, fluxes of carboxylates, and concentration overpotential across the membrane (Torres et al., 2008a).

On the other side, losses occur in the cathode compartment due to overpotentials. To decrease the activation overpotential, catalysts need to be added to the electrode, or a suitable mediator is needed to transfer the electrons from the cathode to oxygen. Generally, Pt is used as a catalyst in the electrode (Schroder et al., 2003), at concentrations up to 45% w/w, entailing a considerable cost. However, activated carbon (AC) air–cathodes are inexpensive and useful alternatives to Pt-catalyzed electrodes in MFCs in terms of cathode performance and cost (Zhang et al., 2011). Recently gas diffusion electrodes based on activated carbon have been proposed as an alternative to low-cost cathodes for MFCs (Pant et al., 2011).

3. Microfluidic MFC integrated research

The mL-scale devices serve as convenient tools for exploring the interplay between device architecture and electrochemically-active microbes, as well as fundamental problems in electron transfer at the microbial/anode interface. Indeed, owing to the flexibility in

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