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Review article

Microfluidic microbial fuel cells: from membrane to membrane free

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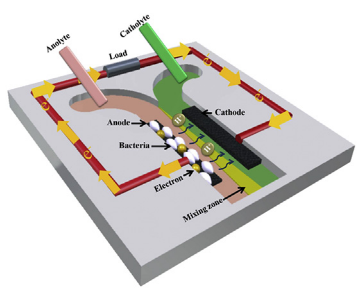
HIGHLIGHTS

- This paper reviews the development of laminar-flow controlled microbial fuel cells.
- Basic principles, issues and advantages of co-laminar MMFCs are fully analyzed.
- Major technological challenges and further applications are also discussed.

GRAPHICAL ABSTRACT



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ABSTRACT

Microfluidic microbial fuel cells (MMFCs) are small carbon-neutral devices that use self-organized bacteria to degrade organic substrates and harness energy from the waste water. Conventional MMFCs have made great strides in the past decade and have overcome some limitations, such as high capital costs and low energy output. A co-laminar flow MFC has been first proposed in 2011 with the potential to be an attractively power source to niche applications. Co-laminar MFCs typically operate without any physical membranes separating the reactants, and bacterial ecosystems can be easily manipulated by regulating the inlet conditions. This paper highlights recent accomplishments in the development of co-laminar MFCs, emphasizing basic principles, mass transport and fluid dynamics including boundary layer theory, entrance conditions and mixing zone issues. Furthermore, the development of current techniques, major challenges and the potential research directions are discussed.

1. Introduction

Microbial fuel cells (MFCs) represent an emerging technology that exploits bacteria to recover the energy from complex organic mixtures [1–3]. This new area relies on self-assembled bacteria, which are usually inoculated into the anode chamber to biocatalyze the substances to produce electrons, protons and other metabolic products. The protons diffuse to the cathode chamber and participate in the reduction reactions, while the electrons flow through the external circuit. Benefitting from mild operation conditions and easily accessible nutrients, MFCs have drawn much attentions in both scientific researches [4–7] and practical applications [8–12].

MFCs can be classified by their device size as macro, meso and micro sizes. A micro MFC, or microfluidic MFC (MMFC), is defined as a miniature MFC with a total cell volume in the range of 1–200 μL [13]. Electrodes, membranes, fluid delivery systems and other accessories are integrated into a microfluidic chamber and a bio-chip. Because of their small dimensions, microfluidic MFCs are

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compatible with some easy-microfabrication technologies, such as photolithography and soft-photolithography. Significantly, their small characteristic length offers great advantages over other size MFCs, including a high surface area-to-volume (*SAV*) ratio, quick response to reactants and precise manipulation [14,15]. On one hand, benefiting from an accelerated inoculation process and a decreased labor involvement, microfluidic MFCs have been used as a laboratory tool to guide the development of large-scale MFCs [16]. For example, some research groups have employed a micro MFC to study a new electrode material [17,18] and to validate its potential application in microbial fuel cells. Namely, research into microfluidic MFCs is partly in the service of macro MFCs development for waste water treatment. On the other hand, a significant amount of effort is being thrust into researching micro MFCs in their own right as biosensors [19–21] and micro power resources [22]. The driving force behind this research mainly stems from the common features of micro MFCs like short response time and an ability to meet a power demand on the μW-mW scale, and the current density has been improved significantly in the past decade.

However, most typical micro MFCs are simply downsized large-scale MFCs, and one of the major drawbacks is the poor cost effectiveness of the low power density [23–26], i.e., the operation costs are still high considered with the poor net power generation. High internal resistance is recognized as the major reason for the insufficient power output, which is mainly attributed to the limited bacterial colonization on the small size electrode [27]. Many well-defined methods including electrode surface modifications [17,22,28–30] and cell architecture optimization [31] have been demonstrated to improve power output. However, the existing methods sacrifice the fabrication cost and handling flexibility of the system. Further steps should be taken to minimize the capital costs and simplify the cell architectures.

Note that once the characteristic lengths of the microfluidic chamber are reduced to millimeter or submillimeter, the viscous effects and surface forces are crucial to the microfluidic flow [32,33]. The fluidic Reynolds (*Re*) number, which compares the inertial force to the viscous force, is relatively small [34]. Significantly, fluid flow with low *Re* number is typically laminar rather than turbulent [35]. Due to the nature of laminar flow, the mixing of multiple fluids is mainly constrained to a narrow interface, and determined by diffusion rather than convection. The mixing interface that develops would eliminate the membrane in the conventional micro fuel cells [36,37]. Based on this principle, the co-laminar MFC was first theorized by Lee et al. [38] and developed by Li et al. [39], and received increasing attention because it could provide platforms for fundamental researches and potentially powering portable electronics and biosensors. In addition to the advantages of other micro MFCs, co-laminar MFCs possess some unique advantages, such as simplified structures, low internal resistance and easy integration with on-chip technologies. With these advantages in mind, they have been successfully developed as a research tool to study bacterial power generation from the microfluidic perspective [39–41] and as a biosensor to detect some stimuli [42,43]. Meanwhile, in-depth investigations into the fundamental processes have been conducted to broaden our understandings of co-laminar MFCs [44,45].

Several review articles [13,23,24,26,38] on micro MFCs have published in past several years, however, they are mainly focused on the challenges and applications of conventional micro MFCs with separators. There has been no review article focusing on co-laminar MFCs development and fundamental understanding to this new bio-technology especially from the perspective of flow and mass transport. This critical review article briefly discusses the progress and reviews the substantial challenges of conventional microfluidic MFCs. In response to these problems, the concept of co-laminar MFCs is proposed and their related characteristics are described. Then, their development is summarized and some key issues are analyzed, mainly involving the mass transfer and fluidic manipulation. Finally, future opportunities in co-laminar MFCs applications are presented. It is hopefully recalibrated and identified this technology's role in future paradigm of microfluidic energy and microbial engineering.

2. Conventional microfluidic MFCs

2.1. Principles

Fig. 1 shows a schematic diagram of a conventional two-chamber MFC. The two chambers are separated by a physical separator through which hydrogen ions and other cations can be freely transferred. Exoelectrogens, typically the *Geobacter* and *Shewanella* species, or other mixed bacteria from sludge, are inoculated on the anode [46–51]. The oxidation of organic substrates in the anolyte is catalyzed through the metabolism of the microbial communities. The generated electrons can be donated from extracellular surface to the anode surface by three pathways, including direct transfer, conductive pili and electron shuttles [52–54]. Then, the electrons are delivered through an external resistance to the cathode. Protons and electrons transferred to cathode can be consumed by oxidants (*e.g.*, oxygen, ferricyanide, or permanganate). So far, microbial fuel cells have been well-demonstrated with reactor chamber volumes from several liters to liters [55–60]. To shed light on the interplay between microbial colonization and electricity generation on the visible scale, some researchers have started to downsize the chamber volume from liters to milliliters or sub-milliliters. Once all of the reaction components (*e.g.*, the membrane, electrodes, and the reactants delivery and removal systems) are confined to a micro-scale space, a new type of micro fuel cells is defined, called micro or microfluidic MFCs.

In these devices, bio-chemistry reactions are always accompanied by fluid flow and mainly depend on the type of microfluidic. At this dimension, fluid can be precisely controlled with a small volume of fL-μL. Microfluidics is a multi-disciplinary technique related to physics, chemistry, biotechnology and micro-fabricated technology [61,62]. With easy-fabrication and precise fluid manipulation, microfluidic MFCs can supply a visual platform to observe the growth of bacteria and monitor bio-electricity generation process.

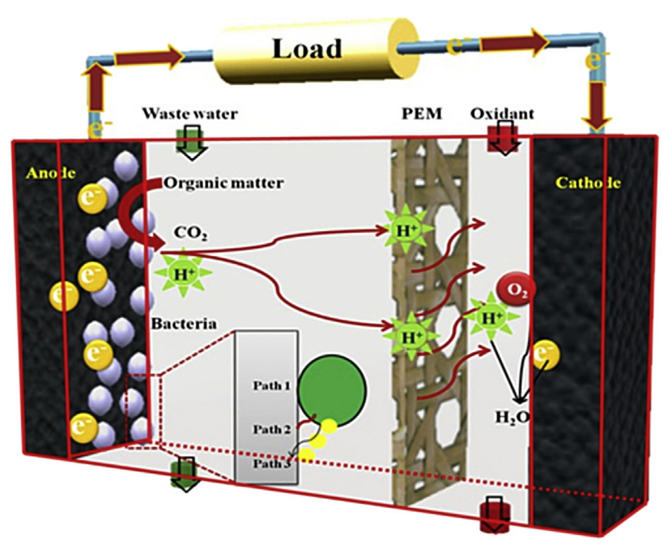

Fig. 1. Operational principles of a conventional two-chamber micro MFC.