Microbial fuel cells: From fundamentals to applications. A review

Carlo Santoro a, *, 1, Catia Arbizzani b, **, 1, Benjamin Erable c, ***, 1, Ioannis Ieropoulos d, ****, 1

a Department of Chemical and Biological Engineering, Center Micro-Engineered Materials (CMEM), University of New Mexico, 87106, Albuquerque, NM, USA
b Department of Chemistry “Giacomo Ciamician”, University of Bologna, Via Selmi 2, 40126, Bologna, Italy
c University of Toulouse, CNRS, Laboratoire de Génie Chimique, CAMPSAC INP — ENSIACET, 4 Allée Emile Monso, CS 84234, 31432, Toulouse Cedex 4, France
d Bristol BioEnergy Centre, Bristol Robotics Laboratory, T Block, University of the West of England, Frenshay Campus, Coldharbour Ln, Bristol, BS16 1QY, United Kingdom

HIGHLIGHTS

• The history of MFCs in the context of bioelectrochemical system is introduced.
• Electroactive biofilms and electron transfer mechanisms are described.
• Carbonaceous and metallic anode materials are presented.
• Cathode catalysts are presented and ORR mechanisms are described.
• Utilization of MFC energy output for practical applications is described.

ABSTRACT

In the past 10–15 years, the microbial fuel cell (MFC) technology has captured the attention of the scientific community for the possibility of transforming organic waste directly into electricity through microbially catalyzed anodic, and microbial/enzymatic/abiotic cathodic electrochemical reactions. In this review, several aspects of the technology are considered. Firstly, a brief history of abiotic to biological fuel cells and subsequently, microbial fuel cells is presented. Secondly, the development of the concept of microbial fuel cell into a wider range of derivative technologies, called bioelectrochemical systems, is described introducing briefly microbial electrolysis cells, microbial desalination cells and microbial electrosynthesis cells. The focus is then shifted to electroactive biofilms and electron transfer mechanisms involved with solid electrodes. Carbonaceous and metallic anode materials are then introduced, followed by an explanation of the electro catalysis of the oxygen reduction reaction and its behavior in neutral media, from recent studies. Cathode catalysts based on carbonaceous, platinum-group metal and platinum-group-metal-free materials are presented, along with membrane materials with a view to future directions. Finally, microbial fuel cell practical implementation, through the utilization of energy output for practical applications, is described.

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* Corresponding author.
** Corresponding author.
*** Corresponding author.
**** Corresponding author.
E-mail addresses: carlo.santoro830@gmail.com (C. Santoro), catia.arbizzani@unibo.it (C. Arbizzani), benjamin.erable@ensiacet.fr (B. Erable), ioannis.ieropoulos@brl.ac.uk (I. Ieropoulos).

1 All the authors have equally contributed to the manuscript.
1. Introduction

Microbial Fuel Cells (MFCs) (Fig. 1a and b) and more recently extended into various Bio-Electrochemical Systems (BESs) (Fig. 1c and d) are an interesting and constantly expanding field of science and technology that combines biological catalytic redox activity with classic abiotic electrochemical reactions and physics [1–4].

The addition of biological organisms responsible for catalyzing electrochemical reactions, gives these systems a level of complexity that is perhaps above that of already complex electrochemical systems (e.g., batteries, fuel cells and supercapacitors). The main differences of MFCs with the conventional low temperature fuel cells (direct methanol fuel cell or proton exchange membrane fuel cell) are: i) the electrocatalyst is biotic (electroactive bacteria or proteins) at the anode [5–7]; ii) the temperature can range between 15 °C and 45 °C, with close to ambient levels as optimum [8–10]; iii) neutral pH working conditions [11–14]; iv) utilization of complex biomass (often different types of waste or effluent) as anodic fuel [15,16]; v) a promising moderate environmental impact assessed through life cycle analysis [17,18].

The original idea of utilizing microbes to generate electricity was conceived and attributed to Potter in 1911 [19], even though the concept of “animal electricity” dates back to the 18th century, when Galvani was experimenting with frog legs [20]. Further concepts and practical developments were explored since, with Cohen’s 35-unit setup in 1931 [21], Karube et al. catalyst investigations in the 60’s [22] and more recently in the 80s-90s, with the work of Bennetto et al. on synthetic mediators, which resulted in the development of the so-called “analytical MFC” that is still in use to date [23]. From those early examples, significant progress on the understanding of electron transfer mechanisms, development of efficient bio-electrocatalytic interfaces and development of novel, low cost and durable electrode materials, has already been achieved but there is nevertheless ample room for improvement and work to be done, before reaching industrialization of MFCs [24,25].

Several BESs have been proposed and they are classified by applications (Fig. 1). The first one and the most studied, is MFC representing over 75% publications in 2016 according to the ISI OF WEB OF SCIENCE (Fig. 1a). This type of BES can extract chemical energy from complex organic substrates and convert it into useful electricity [1,26]. Other BESs have been developed that generate useful products (e.g. hydrogen [27–29], formate [30,31], acetate [32,33], methane [34–36], etc [37,38]) or desalinate water (e.g. microbial desalination cell [39], etc [40–42]).

Numerous challenges still remain unsolved in the MFC field for successful deployment in real environments, although some initiatives have been reported [43]. Starting from the anode, remarkable progress has been made with synthetic substrates and model microbial catalysts or microbial consortia developed in the laboratory. However research questions of implementation are inherently more complicated when it comes to working in more complex conditions such as real industrial effluents [15,16] or natural environments (sediments [44–48], marine environments [49–51], lagoons [52–55], etc.). As an example, several types of organic waste have been used as fuel for microbial anodes [15,16], but electroactive bacteria kinetics remains poor and the interaction between electrode and bacteria has still not been fully understood [56–58]. Moreover, interaction and/or coexistence in electron transfer mechanisms between bacteria and solid electrodes are not well described, especially in complex environments in which a multitude of microbial species (electroactive or not) can be found on the electrodes [59–63]. Finally, the attraction of microbial cells towards the electrodes [64], biofilm formation and development on anode surface [64,65], interaction and inter-species cooperation [60–63,66–69], as well as influence of environmental parameters on microbial colonization [4,25], remain unknown due to the difficulty of coupling the complicated processes of microbial electrochemistry and the existing imaging technology [70–74]. To a certain extent, the interaction of bacteria with electrode surfaces has been studied by varying the surface morphology and chemistry [75].

At the cathode, oxygen has primarily been used as the oxidant due to its abundance and high reduction potential [76,77]. Some studies showed also the possibility of utilizing metallic oxidants (e.g. U [78,79], Cd [80], Cr [81,82], Cu [83,84] etc.) that can be reduced to a less toxic oxidation state. The oxygen reduction reaction (ORR) remains one of the main bottlenecks of this technology, due to the high over-potentials and low kinetics that are encountered [76].

A further challenge is related with the low energy produced by MFCs, which is currently orders of magnitude lower compared to that of chemical fuel cells. The harvesting and management of the low power generated by MFCs has given rise to new hybrid systems that partially address this problem by coupling MFCs with external off-the-shelf harvesting systems based mainly on supercapacitors [85], with a number of applications reported (See Section 2.8).

Finally, several organic compounds coming from different municipal and industrial types of wastewater have been successfully investigated showing the feasibility of BES in generating power and simultaneously degrading pollutants, thus becoming an alternative technology for cleaning water with zero or positive energy budget [15,16].

In this review, the authors describe briefly the important steps that moved the electrochemical abiotic field towards the biological-electrochemical hybrid. The authors wish to communicate the level of progress achieved in: i) evolution of bioelectrochemical systems from MFC to MXC; ii) understanding of the microbiology of anode and the electron transfer mechanisms in electroactive microbial biofilm; iii) electrochemistry regarding the anode and cathode, iv) electrode materials research and development and v) practical applications involving MFCs.

2. Discussion

2.1. From abiotic fuel cell to biological and microbial fuel cell

Luigi Galvani, physician and professor at the University of Bologna, is historically considered to be the first electrochemist and bioelectricity pioneer [20]. In fact with his experiments in 1780, he discovered that the muscles of dead frog legs moved (or twitched) when struck by an electrical spark and coined the term “animal electricity” to describe the force that activated the muscles of his specimens as being generated by an electrical fluid that is carried to the muscles by the nerves. Alessandro Volta, a contemporary professor of experimental physics at the University of Pavia, checked Galvani’s experiments and believed that the contractions occurred due to the metal cable Galvani used to connect nerves and muscles in his experiments. The Galvani-Volta controversy grew fervent at the end of the 18th century and was the platform that led shortly to the invention of an early battery, resulting from Volta’s experiments [85]. Significant advancements dealing with electrochemical systems for power generation or energy storage have been carried out in several areas during the first few decades of the 19th century. It is important to cite, among the breakthroughs in electrochemical devices, the lead-acid battery that was invented in 1859 by the
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