The oxygen paradox in microbial fuel cells

A. S. Vishwanathan, S. Siva Sankara Sai and Govind Rao

Microbial fuel cells harness electrons from bacterial oxidation of substrates and have the potential to address two of the major sustainability issues that confront the globe – production of clean energy and wastewater treatment. Relentless multi-disciplinary efforts have opened up possibilities of enhancing efficiency of these systems in terms of performance and cost-effectiveness. Detailed studies on individual components provide fundamental insights for performance assessment. Oxygen, an integral component of bioelectrochemical systems, assumes contrasting inhibitory and supportive roles at the anode and cathode respectively.

Bacterial respiration

Catabolic biochemical processes, viz. glycolysis and the Krebs cycle, lead to an electron transport system by which bacteria obtain useful energy from varied sources of nutrition for carrying out cellular activity. The electron transport system, localized on the bacterial plasma membrane, is a chain of electron carriers – comprising membrane proteins, flavins, cytochromes, non-heme iron components, other smaller non-protein carriers as well as multiple cytochrome oxidases – that possess successively higher redox potentials to facilitate spontaneous transfer of electrons. The electron transfer process starts with the electron-rich reduced coenzyme NAD(P)H and culminates in a terminal electron acceptor via a series of reversible redox reactions. Electron transport is accompanied by translocation of protons across the membrane resulting in a proton gradient which forms the basis for ATP synthesis.

Versatility of bacteria

Oxygen, due to its ubiquity and the ability to spontaneously take up electrons from the bacterial membrane surface, is the default terminal electron acceptor for aerobic bacteria. Bacteria were present even before oxygen was available on the Earth's surface and hence are also capable of using other inorganic electron acceptors such as nitrates and sulphates, or even elemental sulphur and iron[1]. Anaerobic mode of respiration is seen in bacteria living in oxygen-deficient habitats. Obligate anaerobes can survive only in the absence of oxygen. Facultative anaerobes can switch to alternate electron acceptors when oxygen is unavailable. Due to the wide range of electron acceptors that can be utilized, bacterial electron transport chains are extensively branched[1]. *Shewanella oneidensis* MR-1 is a highly versatile anaerobic bacterium that is known for its ability to use up to 10 different electron acceptors[2]. In essence, the terminal electron acceptor serves as a sink for electrons coming down the electron transport system.

Microbial fuel cells

Microbial fuel cells (MFCs) and related technologies[3] exploit this versatility by channellizing electrons, resulting from microbial oxidation of organic substrates, through customized routes to a terminal electron acceptor. Practically any substrate capable of microbial degradation can serve as the electron source[4]. The microbes only need a compatible acceptor for depositing the electrons thus obtained and this role is readily taken up by the anode of the MFC. These electrons are diverted across an external load (resistor) to extract usable energy. The final step of the electron transport chain occurs at the cathode in the presence of a terminal electron acceptor. As shown in Figure 1, MFCs mimic the natural process of electron transport, albeit under engineered conditions.

Anodic electron transfer

Microbial electron transfer to the anode is direct or mediated by a shuttle. Anode-respiring bacteria[5] are capable of transferring electrons directly to the electrode while few others such as *Shewanella* and *Geobacter* are known to produce 'microbial nanowires'[6] which form a conduit for electrons to the electrode. Mediated transfer can occur by means of naturally synthesized primary or secondary metabolites or exogenous redox shuttles, as described by Schröder[7] in a comprehensive review on the mechanisms of anodic electron transfer in MFCs.

Anodic environment at anode

Barring obligate anaerobes, most other microbes preferentially transfer electrons to oxygen, if available, as it provides the maximum energetic advantage. Even a trace of oxygen at the anode would take away the electrons and impede their transfer to the electrode. In order to maximize harvest of electrons from the microbes, the anode is strictly maintained under anoxic conditions by sparging the anolyte with nitrogen or argon. While cysteine has been used as a scavenger in the anolyte[8] to limit the effects of oxygen, it would be worthwhile exploring newer microbe-friendly materials that can keep oxygen away and also enhance electron transfer to the anode. Qu *et al.*[9] report that a co-culture of non-exoelectrogenic bacteria in the anode of a MFC can scavenge low levels of dissolved oxygen to increase power production. Selection pressure in the anode chamber must be regulated to allow only specific microbial communities to develop so as to maximize electron transfer to the anode. Even the slightest irregularity in oxygen levels at the anode can significantly alter the microbial community and thereby the performance of the MFC.

Electron transfer at the cathode

The cathode of a MFC is the interface for the confluence of the terminal electron acceptor and charged ions (electron and protons) from the anode. It needs to provide a sufficiently large conducting

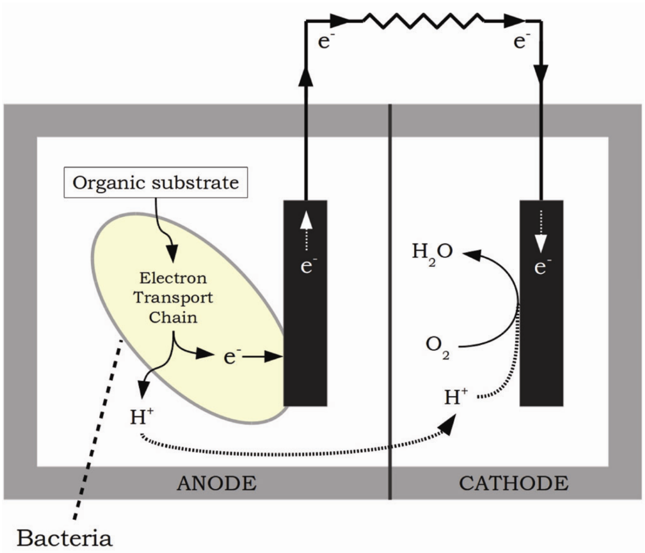

Figure 1. Schematic of the working of a two-chambered microbial fuel cell. Electrons and protons resulting from anaerobic breakdown of organic substrates at the anode are channelized to the cathode where they combine in the presence of oxygen to form water.

surface for the reduction reaction to occur. Since the final step of the electron transport chain has been spatially separated in a MFC, oxygen can be used as the terminal electron acceptor irrespective of the oxygen compatibility of the bacteria at the anode.

Aerobic environment at cathode

Oxygen is considered to be a near-perfect terminal electron acceptor due to its 'virtually inexhaustible availability'[10], high positive redox potential and propensity to get reduced to water. The only drawback is the high activation energy requirement for oxygen reduction often leading to poor kinetics of the reaction.

Although expensive, platinum is used as a catalyst to enhance the reaction. However, many low-cost alternatives such as manganese dioxide[10] have been successfully used in MFCs. Catholytes such as ferricyanide and permanganate have been used as terminal electron acceptors, but they are impractical and not sustainable because they lead to accumulation of reduced compounds and have to be regenerated continuously[6]. As a result, oxygen becomes the most preferred terminal electron acceptor in spite of its shortcoming. It has also been experimentally demonstrated[11] that the availability of oxygen at the cathode has a direct bearing on the performance of a MFC. If the level of oxygen at the cathode limits the flow of electrons, the current density is drastically hampered.

The oxygen paradox

Oxygen is a critical factor at both the reaction centres of a MFC. Enhanced impetus is being provided to scale up MFCs for practical applications[3]. This underlines the need to continuously track levels of oxygen. The manifold advantages of using a minimally invasive oxygen sensor compared to probe-based ones in MFCs have been described previously[11]. On-line monitoring of oxygen at multiple locations in the MFC would provide valuable inputs on the dynamics of oxygen for enabling mid-course intervention and correction to regulate oxygen levels at the cathode and to prevent losses due to fission of oxygen to the anode. Oxygen performs a paradoxical dual role – one by its absence and the other by its presence – and holds a key to the performance of a MFC.

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A. S. Vishwanathan is in the Department of Biosciences and S. Siva Sankara Sai is in the Department of Physics, Sri Sathya Sai Institute of Higher Learning, Prasanthi Nilayam, Puttaparthi 515 134, India and Govind Rao is in the Center for Advanced Sensor Technology, Department of Chemical, Biochemical and Environmental Engineering, University of Maryland, Baltimore County, Baltimore, Maryland 21250, USA.*
**e-mail: asvishwanathan@sssihl.edu.in*