



# Phasic availability of terminal electron acceptor on oxygen reduction reaction in microbial fuel cell



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## HIGHLIGHTS

- Phase of availability of TEA has influenced ORR kinetics.
- High performance of MFC-DC (PD-769 mW/m<sup>2</sup>) than MFC-SC (PD-684 mW/m<sup>2</sup>).
- Rapid neutralization of redox equivalents with DO as TEA.
- Benefit of higher bioelectricity generation along with wastewater treatment.

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## ABSTRACT

Oxygen-reduction reactions (ORR) plays a pivotal role in determining microbial fuel cells (MFC) performance. In this study, an attempt to determine the influence of the phasic availability of terminal electron acceptor (TEA) on ORR was made. Two MFCs operated with dissolved oxygen (MFC-DC) and air (MFC-SC) as TEA were constructed and analyzed in continuous mode under open and closed circuit conditions. The bio-electrochemical analysis showed a marked influence of dissolved oxygen resulting in a maximum power density with MFC-DC (769 mW/m<sup>2</sup>) compared to MFC-SC (684 mW/m<sup>2</sup>). The availability of O<sub>2</sub> in dissolved phase has lowered the activation losses during the MFC operation as a result of effective ORR. The cyclic voltammetry analysis revealed the TEA dependent biocatalyst activity of NADH and cytochrome complex which enabled electron transfer kinetics and improved substrate utilization. Finally, the study evidenced the critical role of TEA phasic availability to regulate the bio-electrogenic and substrate degradation potential in MFC.

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## 1. Introduction

Microbial fuel cell (MFC) is a sustainable source for generating green energy. MFC as hybrid microbial electrochemical system is finding diverse applications with the potential to lower carbon footprint along with harnessing bioelectricity and wastewater treatment (Ozkaya et al., 2013; Venkata Mohan et al., 2014a,b). Low productivity is a major concern pertaining to MFC that needs to be addressed. The limiting factors include, the electrochemical losses, partial substrate utilization, biocatalyst activity, reactor configurations, etc., Also the availability of TEA in different phases play a critical role in determining the MFC performance. The electron accepting potential varies under liquid and gaseous phases which also influences the other governing factors of MFC like electrode potentials, redox mediators, electron kinetics, power produc-

tion, etc. To regulate the electrochemical behavior of MFC towards higher power output and heighten the transfer kinetics at anode, it can be made possible through the optimization of circuitries and the varying phase of TEA available. The controlled electron flow through the circuit for recovering maximum power densities is dependent on the proton movement across the proton exchange membrane which is further interdependent on the terminal electron acceptor (TEA). To overcome the limitation of low H<sup>+</sup> mobility, the availability of an effective TEA is essential in the cathode chamber that enhances the driving force for drawing the electrons towards higher reduction (Sun et al., 2016). TEAs such as oxygen, nitrate, sulfate, iron, metals, etc., could act as effective TEAs owing to their high reducing capacity (Oh et al., 2004; Srikanth and Venkata Mohan, 2012; Fan et al., 2007; Butti et al., 2016).

Oxygen is considered an ideal TEA due to its ubiquity, inexhaustibility and high redox potential for MFC (Xia et al., 2013). Most bacteria are preferentially inclined towards transferring electrons to available oxygen compared to other TEAs since it provides the

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maximum energy harvest. But, to maintain the maximal harvest of electrons from the bacteria, the cathode surface area should be in optimal contact with sufficient oxygen for conducting and offering maximum ORR (Sun et al., 2016; Venkata Mohan et al., 2014b). In this study, different phases of oxygen as TEA in two identical MFC setups (MFC-double chamber (MFC-DC) and MFC-single chamber (MFC-SC)) with dissolved oxygen and air oxygen were evaluated in continuous mode operation for enhancing the MFC performance. The relative variation in the power densities (PD), electron transfer rates ( $K_{app}$ ), cyclic voltammetry (CV), oxidative and reductive tafel slopes, cathode ( $E_{ce}$ ) and anode potentials ( $E_{we}$ ), polarization profiles and substrate utilization demonstrated the regulatory role of an effective TEA. The bioelectrogenic performance was discussed with varying TEA phase.

## 2. Materials and methods

### 2.1. MFC setup

Two identical dual-chambered microbial fuel cells (MFC) [double chamber (MFC-DC); single chamber (MFC-SC)] were constructed using polycarbonate blocks (total/working volume-0.05 L), clamped together and fitted with two rubber gaskets that provide a water seal between the chambers. The identical design of MFC with separate blocks acting as anode and cathode, help in maintaining uniform anodic operation and negate the variations in cell performance induced by anodic activity and can help to evaluate the performance based on the cathodic variations only. Each chamber was designed for continuous mode of operation having specific inlet and outlet ports. Carbon cloth was used as electrodes in both anode and cathode chambers with a projected surface area of 7 cm<sup>2</sup>. The electrodes were pre-treated in 1% ammonium chloride (NH<sub>4</sub>Cl) by sonicating for 10 min and transferred to water bath maintained at 70 °C for 1 h which enhances their conductivity. The N-group of NH<sub>4</sub>Cl interferes with the electrode surface and compacts the porosity for higher electron percolation and thereby increasing the conductivity (Kondaveeti and Min, 2013; Moon et al., 2014). The distance between electrodes was approximately 4 cm. Proton exchange membrane (PEM) (Nafion117, Membrane Inc.) (4 cm × 4 cm) was used as separator between the two blocks, after it was pre-treated sequentially by boiling in deionized water (DIW) followed by hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (30% V/V) and 0.5 M H<sub>2</sub>SO<sub>4</sub> for 1 h each with an intermittent step of boiling in DIW for 1 h, later stored in DIW for use. Copper wires were used as connectors to maintain electrical contact with the electrodes and connect the external resistance ( $R_E$ ).

### 2.2. Biocatalyst

Mixed consortium from an operating laboratory scale anaerobic suspended growth reactor treating industrial wastewater was used as parent inoculum to start the MFC. Prior to inoculation, inoculum was washed thrice in saline buffer and enriched in design synthetic wastewater (DSW g/l: Glucose-3, NH<sub>4</sub>Cl-0.5, KH<sub>2</sub>PO<sub>4</sub>-0.25, K<sub>2</sub>HPO<sub>4</sub>-0.25, MgCl<sub>2</sub>-0.3, CoCl<sub>2</sub>-0.025, FeCl<sub>3</sub>-0.025, ZnCl<sub>2</sub>-0.0115, NiSO<sub>4</sub>-0.050, CuCl<sub>2</sub>-0.0105, CaCl<sub>2</sub>-0.005, MnCl<sub>2</sub>-0.015) under anaerobic conditions for 48 h at room temperature (28 ± 2 °C) with continuous N<sub>2</sub> sparging. The sludge was then re-filtered using a small porous metal mesh to collect the finest part of sludge and was subjected to pre-treatment (Pasupuleti et al., 2014). This inoculum was pre-treated by a combined pre-treatment strategy which includes subjecting it to heat treatment (80 °C for 1 h), acid pre-treatment (adjusting the pH to 3 with *ortho*-phosphoric acid (88%) and left for overnight) and finally by bromoethane sulfonic acid (BESA) treatment (0.2 g/l with constant mixing for 1 h) performed sequentially

to enrich the growth of electroactive bacteria by suppressing the methanogenic bacteria (Venkata Mohan et al., 2008a; Vamshi Krishna and Venkata Mohan, 2016; Mohanakrishna et al., 2017). The pretreated inoculum (10% V/V; volatile suspended solids (VSS) – 2.0 g/l) was enriched with DSW and used as biocatalyst in the anodic chamber of both MFC-DC and MFC-SC.

### 2.3. Operation of MFC

MFC-DC and MFC-SC were operated in continuous mode with a hydraulic retention time (HRT) of 12 h at room temperature (28 ± 2 °C). On attaining stable performances based on the stable open circuit voltages, both the MFC's were operated in closed circuit with the  $R_E$  (1 K $\Omega$ ) derived from the polarization profiles. Post the stabilization phase the modified DSW with varying salt concentrations (K<sub>2</sub>HPO<sub>4</sub> – 4.33 g/l, KH<sub>2</sub>PO<sub>4</sub> – 2.69 g/l, KCl – 0.65 g/l, NH<sub>4</sub>Cl – 1.55 g/l) and by replacing glucose with acetate (6 g/l) as a carbon source (pH-7) was given as anolyte to both the reactors. The anolyte was fed into the reactor in an up-flow mode at a flow rate of 0.05 ml/min using a peristaltic pump (Eyela) to prevent biofilm wash-off and to maintain continuous contact with electrodes. The effluent was discharged from the top and collected in a separate container for analysis. The catholyte for MFC-DC was oxygenated water (pH 7; DO, 4 ± 0.4 mg/l), continuously recirculated using peristaltic pump and in the case of MFC-SC air was sparged using an aerator into the cathodic chamber. The anolyte and catholyte were held independently in two reservoir bottles (Borosil) with continuous stirring at 200 rpm and were maintained at sterile conditions to prevent contamination during the operations. Silicone tubes with an inner diameter of 0.1 cm were used for circulation and withdrawing periodic samples for analysis. The anolyte and catholyte were replenished after every 72 h. Constant voltage and power outputs along with substrate removal efficiency were considered as indicators to assess the stabilized performance of MFCs.

### 2.4. Analysis

Selected physicochemical process parameters viz., pH, electrical conductivity (EC) and chemical oxygen demand (COD) were monitored at regular time intervals, for understanding the system performance (APHA, 1998). Bio-electrochemical analysis were performed to determine the influence of phasic availability of O<sub>2</sub> on the MFC performance based on open circuit voltage (OCV), current (I), electron discharge rates ( $K_{app}$ ), tafel analysis, power (P) and cyclic voltammetry (CV). Power (P) and power density (PD) were calculated using the equations  $P = V^2/R$ , where, R ( $\Omega$ ) represents resistance. Power density (PD) was calculated as  $PD = V^2/RS$ , where, S is the projected surface area of the electrode. Polarization curves were plotted with the function of current density (CD) against V and PD measured at different  $R_E$  (30–0.05 k $\Omega$ ) using a variable resistance box (100 k $\Omega$ –50  $\Omega$ ), for both the experimental variations. Anodic oxidation potential ( $E_{we}$ ) and cathodic reductive potential ( $E_{ce}$ ) were measured across various resistances (30–0.05 k $\Omega$ ) and the stabilized values were noted down after at least 10 min of stable output (±0.05 mV). Changes in the bioelectrocatalytic behavior of the anode was studied *in situ* through cyclic voltammetry (CV) using a three-electrode experimental setup with a potentiostat (Bio-Logic-VMP<sub>3</sub>), during the stabilized phase of operation. A potential ramp was applied with different scan rates from 100 to 0.5 mV/s (–1.0 to +1.0 V vs. Ag/AgCl (3.5 M KCl)). Prior to startup the initial CV's were recorded with distill water in both the chambers to neutralize the charges deposited on the electrodes developed by the presence of chemical species. The presence of very low faraday currents ( $i_f$ ) determines the absence of charges on the electrode. First order derivative and the electron discharge rates ( $K_{app}$ ) were analyzed using the cyclic voltammograms. The

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