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Performance of electron acceptors in catholyte of a two-chambered microbial fuel cell using anion exchange membrane

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ABSTRACT

The performance of the cathodic electron acceptors (CEA) used in the two-chambered microbial fuel cell (MFC) was in the following order: potassium permanganate (1.11 V; 116.2 mW/m^2) > potassium persulfate (1.10 V; 101.7 mW/m^2) > potassium dichromate, $K_2Cr_2O_7$ (0.76 V; 45.9 mW/m^2) > potassium ferricyanide (0.78 V; 40.6 mW/m^2). Different operational parameters were considered to find out the performance of the MFC like initial pH in aqueous solutions, concentrations of the electron acceptors, phosphate buffer and aeration. Potassium persulfate was found to be more suitable out of the four electron acceptors which had a higher open circuit potential (OCP) but sustained the voltage for a much longer period than permanganate. Chemical oxygen demand (COD) reduction of 59% was achieved using 10 mM persulfate in a batch process. RALEX™ AEM-PES, an anion exchange membrane (AEM), performed better in terms of power density and OCP in comparison to Nafion®117 Cation Exchange Membrane (CEM).

1. Introduction

Microbial fuel cells (MFCs) can utilize organic substrates and subsequently convert their chemical energy to electricity using microorganisms. MFC represents an upcoming method for the sustainable production of energy, in the form of direct electricity from biodegradable compounds present in the wastewater, achieving simultaneous wastewater treatment (Thurston et al., 1985; Rabaey et al., 2003; Chaudhuri and Lovley, 2003; Logan and Regan, 2006). Microorganisms such as members of the Geobacter family (Bond and Lovley, 2003), *Shewanella putrefaciens* (Kim et al., 2002), *Shewanella oneidensis* (Ringeisen et al., 2005), *Rhodoferax ferrireducens* (Chaudhuri and Lovley, 2003), *Pseudomonas aeruginosa* (Rabaey et al., 2004), *Clostridium butyricum* (Park et al., 2001) and *Aeromonas hydrophila* (Pham et al., 2003) have been reported to oxidize the organic matter by donating electrons to the anode to complete their metabolic process.

In spite of being a promising technology, MFC has some bottlenecks such as low power density, high cost etc. The factors which influence the performance of an MFC are substrate conversion rate, overpotentials at the anode and cathode, the ion exchange membrane performance, operational parameters, cell configuration and the electrode surface properties (Jadhav and Ghangrekar, 2009).

The use of a suitable ion exchange membrane is essential for improving the efficiency of the MFC, Cation Exchange Membrane (CEM) are prevalently used in the MFC. The transport of cations other than protons through PEMs or CEMs leads to a decrease in the pH of the anodic chamber causing impairing of microbial activity, while increasing the pH in the cathode chamber leads to reduction of the cathode potential as well (Gil et al., 2003; Rozendal et al., 2006; Stenina et al., 2004). Moreover, Mo et al. (2009) and Liang et al. (2007) showed that the transferred cation precipitates on the surface of the cathode catalysts in a single-chamber MFC thereby increasing their internal resistance. On the other hand, use of an anion exchange membrane (AEM) results in improvement of the performance of the MFC compared to the traditional PEM/CEM (Kim et al., 2007; Mo et al., 2009; Rozendal et al., 2007; Zuo et al., 2008). Improved control for maintaining low pH gradient across the membrane can be achieved by using AEMs.

The current production in MFCs is largely dependent on the reduction kinetics at the cathode. Hence in recent times lot of effort is being made to optimize and understand the reduction of the electron acceptor on the cathode surface (Li et al., 2009). Despite being cheap, abundant and having high redox potential, the use of oxygen as the terminal electron acceptor is limited by its slow reduction on the surface of the graphite/carbon electrodes (Gil et al., 2003). The power outputs of two-chamber MFCs using dissolved oxygen has been shown to be proportional to the concentration of the dissolved oxygen in the catholyte, which is limited in itself by the solubility of oxygen in water as also by the extraneous

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energy requirement for exogenous supply of oxygen (Rismani-Yazdi et al., 2008). In spite of a variety of MFC design modifications (flat plate, single chamber, air cathode, UASB, tubular MFCs), few of them surpass 1.0 V cell voltage due to the use of oxygen (maximum theoretical redox potential 0.8 V, seldom achieved in MFC) as a cathodic electron acceptor, with further reduction in cell voltage is caused by overpotential between the two electrodes (You et al., 2006). Substituting oxygen with other electron acceptors, with relatively faster rates of reduction and higher theoretical redox potential may be an option. Permanganate (You et al., 2006), persulfate (Li et al., 2009), ferricyanide or hexacyanoferrate (Park and Zeikus, 2000; Rabaey et al., 2003; Thurston et al., 1985) have been studied as electron acceptors in cathode using CEM. Dichromate, having chromium in a higher oxidation state, has been suggested as a potential electron acceptor (Li et al., 2009).

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}; \quad E^0 = 0.36\ V \tag{1}$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3-} + 7H_2O; \quad E^0 = 1.33\ V \tag{2}$$

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O; \quad E^0 = 1.68\ V \tag{3}$$

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}; \quad E^0 = 2.01\ V \tag{4}$$

In the absence of any buffer, the pH of the catholyte increases from 7 to 9.5, resulting in a lower power generation (Gil et al., 2003) as well as a reduction in the cathode potential at the rate of 59 mV/pH as predicted using Nernst equation. Use of buffer solutions can stabilize pH of the solution, increase solution conductivity, facilitate proton transfer as also reduce the internal resistance in MFCs, especially on using AEMs (Fan et al., 2007).

Comparison of permanganate, ferricyanide, dissolved oxygen (Kong et al., 2010; You et al., 2006), persulfate and ferricyanide (Li et al., 2009) have been reported previously using CEM. In the present study, RALEX™ AEM-PES (Mega Inc., Czechoslovakia) was introduced as a new membrane in MFC configuration. The performances of the aqueous solutions of electron acceptors viz. potassium dichromate, potassium ferricyanide, potassium permanganate and potassium persulfate were investigated to determine the most suitable electron acceptor in terms of the open circuit potential (OCP) and power density. The sustainability of voltage generation, especially at low pH of the catholyte as well as the feasibility of using phosphate buffer along with the electron acceptors, especially to maintain the acidic environments were also investigated. Results of comparative study of RALEX™ AEM and Nafion®117 (DuPont, USA) in acidic media of MFC have been reported. The effect of additional aeration along with the electron acceptors was also investigated. Finally, the effectiveness of MFCs with electron acceptors for COD removal in closed circuit mode was studied.

2. Methods

2.1. Microbial strain, media and growth conditions

S. putrefaciens (ATCC® BAA1097™) was used as biocatalyst in the anode chamber. Colonies of *S. putrefaciens* were grown on LB agar [composition: 10 g/L casein enzymic hydrolysate, 5 g/L yeast extract, 10 g/L NaCl, 15 g/L agar, final pH 7.5 ± 0.2] (HiMedia Laboratories Pvt. Ltd., India) at 37 °C for 24 h. Single colonies were inoculated in 50 mL LB broth [composition: 10 g/L tryptone, 5 g/L yeast extract, and 10 g/L NaCl final pH 7.5 ± 0.2] (HiMedia Laboratories Pvt. Ltd., India) in 100 mL conical flask and incubated aerobically in an incubator shaker at 180 rpm for 24 h. About 10 mL of the culture (0.41 ± 0.02 g dry cell weight/litre) was used as inoculum for each MFC set-up.

2.2. MFC assembly

The MFC setup comprised of two box-type chambers of transparent polyacrylic material of outer dimensions 9 × 8 × 5.5 cm with 110 mL capacity (Table 1). The anode and cathode chambers had two ports at the top, one for electrode terminal and the other for reference electrode (Ag/AgCl, saturated KCl; +197 mV, Equiptronics, India) and sampling. The cathode chamber was also configured in a similar fashion with a lid on top to prevent evaporation of the catholyte. The anode chamber and the cathode chamber were

Table 1
Design specifications and operational conditions of the two-chambered MFC.

Bacteria		
Species	*Shewanella putrefaciens*	
Inoculum age	16 h	
Inoculum concentration	0.41 ± 0.02 g dry cell weight/L	
Growth conditions	37 °C, 180 rpm, aerobic	
	Anode chamber	Cathode chamber
Dimensions ($L \times B \times H$)	3 cm × 6 cm × 7.5 cm	3 cm × 6 cm × 7.5 cm
Working volume	110 mL	110 mL
Operating mode	Anaerobic	Aerobic
Stirring conditions	None	Aeration
Gas, flow rate	None	Air, 2 L/min
Initial pH	7.5	Dependant on experiment
Electrodes	Anode	Cathode
Material	SS304	Pure graphite block
Projected surface area	31.5 cm^2	31.5 cm^2
Pretreatment		Sandpaper scrubbing
Electrode spacing	4 cm (Anode to cathode)	4 cm (Anode to cathode)
Wiring material	Copper rod	Copper wire
Membrane		
Type	RALEX™ AEM-PES	
Material	Polyester with polyethylene binder	
Thickness	0.45 mM (Dry), 0.75 mM (swelled)	
Dimensions	4.5 cm × 3.5 cm	
Pre-treatment	Washed in 1% w/v NaOH for an hour and rinsed with de-ionized water.	