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Performance of Microbial Fuel Cell using different loadings of Polydimethylsiloxane (PDMS) as Catalyst Binder in Cathode

Niralee Verma[1], Md. T. Noori[2], M. M. Ghangrekar*

[1]*Department of Civil Engineering, Government Engineering College, Raipur, Chhattisgarh,(India)*

[2,3] *Department of Civil Engineering, Indian Institute Of Technology, Kharagpur, (India)*

ABSTRACT

The effects of the polydimethyl siloxane (PDMS) binder on the electrochemical performance of carbon cathodes in MFC are investigated. It is found that increasing the PDMS content up to 6.5 mg/cm^2 leads to improve electrochemical performance of the cathode and exhibited highest maximum power density of 52 mW/m^2 corresponding to the maximum current density of 1.06 A/m^2 and a low charge transfer resistance of 5.8 Ω. Power density using this cathode in MFC was noted 37% higher than that obtained with minimum binder loading of 2.5 mg/cm^2. The power density was, however found to be decreased by 16% (43.83 mW/m^2) with further increase in binder loading to 7.5 mg/cm2. The improved cathode performance with optimum binder loading can be attributed to higher oxygen affinity of PDMS, which enhanced oxygen reduction reaction (ORR); however at higher loading rate of binder, hydrophobicity of PDMS limited proton transfer thereby reducing the power density.

Keywords- Air-cathode; Binder; Electrochemical impedance spectroscopy; Linear sweep voltammetry; Microbial fuel cell

I. INTRODUCTION (*HEADING 1*)

Microbial fuel cell (MFC) is a promising technology that treats wastewater with simultaneous electricity production (Noori et al., 2016). Though there have been lot of research on MFC in the last decade, but for it to become practically applicable renewable energy source while treating wastewater, several factors need to be improved (Noori et al., 2017; Tiwari et al., 2017). MFC configuration such as anode and cathode materials, surface area of anode and cathode, separator etc. plays an important role in the performance of MFC. Among these components cathode plays a critical role. Cathode should have a high surface area per unit volume, it should allow high oxygen and proton mass transfer to the reaction site for improved oxygen reduction, and it should be low cost, mechanically stable and offer resistance against fouling for long term stable operation.

To reduce the overpotential of oxygen reduction, often catalysts are used on cathode (Noori et al., 2017; Tiwari et al., 2017). To apply catalyst properly on the electrode surface area binder is required. The binder must allow oxygen and ion transport to the active reaction sites and help in maintaining electrical contact of the catalyst with the current collector. Nafion is the most commonly used binder due to its high proton conductivity (Cheng et al., 2006; Zhang et al., 2012). Nonetheless the high cost of Nafion ($1500/m^2) (Ghasemi et al., 2013) and its property to hinder proton migration (Gong et al., 2014) limits its potential for large scale MFC applications.

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Thus, less expensive polymer binders like polytetrafluoroethylene (PTFE) (Cheng et al., 2006), polyvinyl alcohol (PVA) (Chatterjee and Ghangrekar, 2014), polyvinylidene fluoride (PVDF) (Qiu et al., 2015; Zhang et al., 2009), ethylene diamine tetra acetic acid (EDTA) (Gong et al., 2014), polydimethyl siloxane (PDMS) (Zhang et al., 2012), that can achieve high cathode performance are required to construct low-cost MFCs.

Along with good oxygen and ion transport properties a cathode should be anti-flooding in nature. Flooding reduces performance of cathode in two separate ways: by covering electrochemically active sites with liquid water, and by hindering oxygen transport to the reaction sites. Zhang et al. (2012) examined hydrophobic polydimethylsiloxane (PDMS) as an anti-flooding catalyst binder in MFC cathodes and observed that although PDMS binders used as alternatives to Nafion initially had a lower performance, they had almost equivalent performance after long-term use. Long term stability of PDMS to its anti-flooding and possible antifouling property have been attributed (Zhang et al., 2012). In addition, use of PDMS drastically reduces the production cost of MFC (Zhang et al., 2012). Even though the availability of a range of different polymer binders has allowed some improvement in the electrochemical performance of cathodes, it is still valuable to conduct detailed studies on PDMS loading in order to improve the cathode performance.

To measure the effects of binder loading on performance of MFC, cathodes with PDMS binders having different loading of 2.5 mg/cm^2, 4.5 mg/cm^2, 6.5 mg/cm^2 to 7.5 mg/cm^2 were fabricated and their electrochemical performances were measured using linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). These cathodes were used in single chamber air-cathode MFCs and performance was evaluated. Thus attempt is being made to systematically understand the impact of binder loading on the basic performance of cathodes in an air cathode MFC.

II. MATERIALS AND METHODS

A. MFC construction and operation

Four single-chambered MFCs (Figure 1) were fabricated using ceramic cylinder of 140 ml anodic chamber volume. The ceramic material acted as a proton exchange membrane (PEM) (Behera et al., 2010). Anode was made of graphite felt having projected surface area of 150 cm^2. Air cathodes were fabricated by coating the air-exposed side of the cylinder by high pressure sprayer with a solution containing 0.5 mg/cm^2 carbon (Vulcan XC, Cabot Corporation, MA), known loading of PDMSx binder (where, x = 2.5 mg/cm^2, 4.5 mg/cm^2, 6.5 mg/cm^2 and 7.5 mg/cm^2 for MFC-1, MFC-2, MFC-3 and MFC-4, respectively) and 20 ml of acetone. Stainless steel (SS) wires were used as electrode current collector and the electrodes were connected through concealed copper wire coupled with a 100 Ω external resistance.

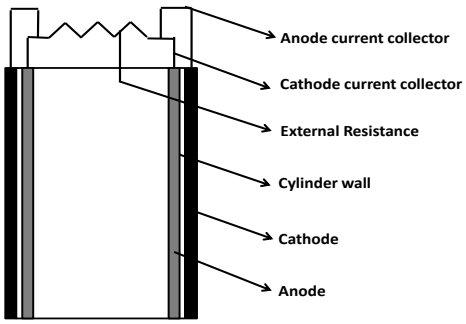

Figure 1: MFC used to determine optimum binder loading

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Each MFC was inoculated with 30 ml of heat treated anaerobic sludge collected from the bottom of a septic tank. Feed solution containing sodium acetate as a source of carbon having COD of 3000 mg/L was used. The acetate medium also contained (per gram of COD) $NaHCO_3$, 1500 mg; NH_4Cl, 318 mg; $CaCl_2.2H_2O$, 250 mg; $MgSO_4.7H_2O$, 64 mg; K_2HPO_4, 27 mg; and KH_2PO_4, 9 mg. Trace metals were added as $FeSO_4.6H_2O$, 10.00 mg/L; $MnSO_4$, 0.526 mg/L; $ZnSO_4.7H_2O$, 0.106 mg/L; H_3BO_3, 0.106 mg/L; and $CuSO_4.5H_2O$, 4.5 µg/L, $CoCl_2$, 105.2 µg/L, $(NH_4)_6Mo_7O_{24}.4H_2O$, 105.2 µg/L (Behera et al., 2010). The MFCs were operated in fed batch mode for 60 days with a feeding frequency of 3 days.

B. Electrochemical characterization of cathode

The template is used to format your paper and style the text. All margins, column widths, line spaces, and text fonts are prescribed; please do not alter them. You may note peculiarities. For example, the head margin in this template measures proportionately more than is customary. This measurement and others are deliberate, using specifications that anticipate your paper as one part of the entire proceedings, and not as an independent document. Please do not revise any of the current designations. Oxidation reduction property of the cathode was studied using EIS and LSV test for all the four MFCs using AUTOLAB AUT58696, Metrohm (The Netherlands) and NOVA 1.9 software. Scanning rate for LSV was kept at 10 mV/sec. 1M KCl solution was used as the electrolyte for performing the above tests. Three electrode method was used for the electrochemical analysis in an electrochemical cell, where the cathode acted as the working electrode, Ag/AgCl electrode (+197 mV vs. standard hydrogen electrode) was used as reference electrode and a platinum wire was used as the counter electrode. Nyquist plot was plotted to depict the imaginary impedance, which is indicative of the capacitive and inductive characteristics of the cell, versus the real impedance of the cell. In Nyquist plots activation-controlled processes with distinct time-constants show up as unique impedance arcs and the shape of the curve provides insight into possible mechanism or governing phenomena.

C. Analysis and Calculations

COD and pH of the influent and effluent wastewater were measured in each cycle. COD of the samples were measured by closed reflux colorimetric method. Electrode of water quality bench meter (Thermo scientific Co., USA) was used to measure pH. Operating voltage and open circuit voltage was measured daily. The Voltage (V) and current (I) were measured using a digital multimeter with data acquisition unit (Agilent Technologies, Malaysia). Power was calculated from these data according to the formula P = IV, where P = Power in mW, I = Current in A and V = Voltage in mV. Power density was calculated by normalizing power to projected surface area of anode. Polarization studies were carried out by varying the external resistances from 10000 Ω to 1 Ω. Internal resistance of the MFC was measured from the slope of the plot of voltage versus current (Behera et al., 2010) generated during polarization. Anode potentials were measured using Ag/AgCl reference electrode.

The Coulombic efficiency (CE) is defined as the ratio of total Coulombs actually transferred to the anode from the substrate, to maximum possible Coulombs if all substrate removed contributed to production of current. The total Coulombs obtained is determined by integrating the current over time, so that the Coulombic efficiency for a MFC run in fed-batch mode, evaluated over a period of time t, is calculated as (Logan et al., 2006):

$$CE = \frac{M \int_0^{tb} Idt}{Fbv_{An} \Delta COD} \qquad (1)$$

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Where, M = 32, the molecular weight of oxygen, I, is the current generated, F is Faraday's constant, b = 4, is the number of electrons exchanged per mole of oxygen, vAn is the volume of liquid in the anode compartment, and ΔCOD is the change in COD over time t.

III. RESULTS AND DISCUSSION

D. Electrochemical performance

LSV was conducted on MFCs between voltages ranging from 0.3 V to - 0.2 V. Current densities during LSV for the MFCs with binder loadings of 2.5 mg/cm^2, 4.5 mg/cm^2, 6.5 mg/cm^2 and 7.5 mg/cm^2 were found to be 0.926 A/m^2, 0.972 A/m^2, 1.06 A/m^2 and 0.972 A/m^2, respectively (Figure 2). Higher current response of the MFC having binder loading of 6.5 mg/cm$_2$ shows that it had better electrochemical activity compared to the other cells (Chung et al., 2012). This result supports the role PDMS plays in ORR. It is due to higher oxygen affinity of PDMS which enhances ORR at higher loading rate of binder. PDMS has a unique semiorganic structure, with a flexible inorganic Si-O backbone and very low rotation barrier of electrons within the Si-O bond, which enhances electron conductivity of PDMS. This distinct characteristic of PDMS enhances oxygen affinity to the electrode as a result ORR increases and current production is enhanced (Zhang et al., 2012). However, at higher loading of the binder hydrophobicity of PDMS limits proton migration through membrane, thus making anode more positive and eventually interferes with movement of electrons through the external circuit. This resulted in a lower current density of the MFC with PDMS loading higher than 6.5 mg/cm^2. LSV results supported that the cathodes made with PDMS binder were indeed electrically active and these agreed well with the performance observed for MFC.

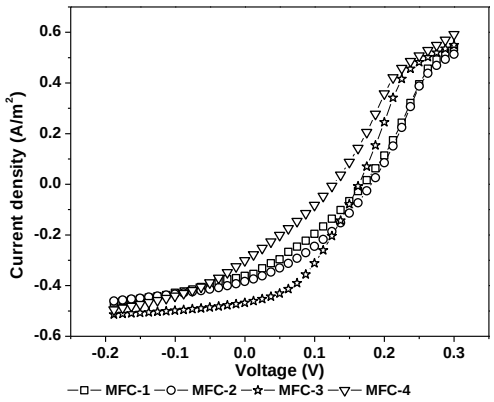

Figure 2: LSV of cathode with different PDMS binder loading of 2.5 mg/cm^2 (MFC-1), 4.5 mg/cm^2 (MFC-2), 6.5 mg/cm^2 (MFC-3) and 7.5 mg/cm^2 (MFC-4)

Interfacial charge transfer behaviour of the electrodes was investigated using EIS. The EIS spectra (Nyquist plot) were fitted to an equivalent circuit to identify the individual components of internal resistance of cathode. Charge transfer resistance (Rct) can be calculated by the extent of the diameter of the semicircle of the Nyquist plot (Wen et al., 2012). The Rct values for the cathodes having binder loading of 2.5 mg/cm^2, 4.5 mg/cm^2, 6.5 mg/cm^2 and 7.5 mg/cm^2 were found to be 10.47 Ω, 6.43 Ω, 5.89 Ω and 4.62 Ω, respectively (Figure 3). The results indicated that charge transfer resistance decreased and reaction rate increased with increase in PDMS binder loading which is in agreement with LSV analysis. A lower charge transfer rate indicates a faster rate of interfacial electron transfer (Liu et al., 2015; Wen et al., 2012). In case of 7.5 mg/cm^2 binder loading, lowest charge transfer

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resistance was observed among all due to a reasonably high electron conductivity of PDMS at high binder loading rate. The contradictory results of EIS and LSV evidenced that ORR not only depends on Rct but on proton transfer also. Liang et al. (2007) reported the effect of interfacial proton availability on cell resistance in MFC using Nafion as a membrane. They reported that cell resistance decreased from 0.48 Ω/cm^2 to 0.35 Ω/cm^2 as proton conductivity increased by hot-pressing of Nafion membrane. In the present study at higher binder loading rate (7.5 mg/cm^2) although Rct was low but due to reduced proton transfer the overall ORR decreased. The charge transfer resistances as obtained with PDMS loadings of 4.5 mg/cm^2, 6.5 mg/cm^2 and 7.5 mg/cm^2 were found to be less than that reported using Nafion as catalyst binder by Gong et al. (2014).

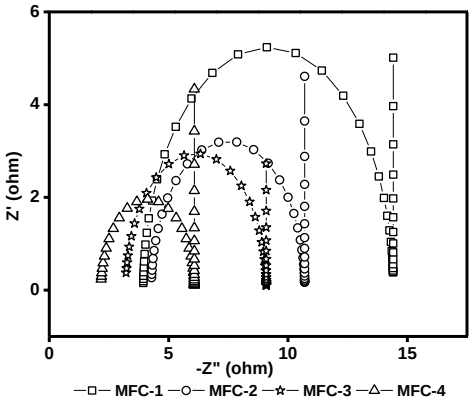

Figure 3: Nyquist plots of EIS spectra for different MFCs

E. **Electricity generation**

All the MFCs were started simultaneously. MFC-1, MFC-2, MFC-3 and MFC-4 generated stable average operating voltage (OV) with 100 Ω external resistance of 141 ± 3 mV, 153 ± 5 mV, 182 ± 4 mV and 145 ± 4 mV, respectively; with the average open circuit voltage (OCV) being 412 ± 5 mV, 443 ± 3 mV, 541 ± 4 mV and 403 ± 2 mV, respectively, after 7 days of operation (Figure 4). Maximum operating voltage of 182 mV was obtained for MFC-3 having a binder loading of 6.5 mg/cm2 and minimum operating voltage of 141 mV was observed for MFC-1 and MFC-4. The performance result of MFCs showed similar trend as LSV analysis as discussed in section 3.1. Increased voltage in MFCs with higher binder loading was because of higher ORR activity due to high oxygen affinity that enhances cathode performance and thus increases overall voltage generation from the MFC.

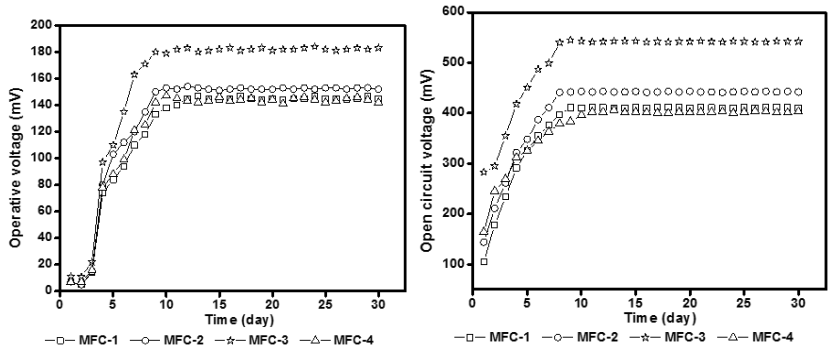

Figure 4: Variation of (a) operating voltage and (b) open circuit voltage with different binder loadings of 2.5 mg/cm^2 (MFC-1), 4.5 mg/cm^2 (MFC-2), 6.5 mg/cm^2 (MFC-3), and 7.5 mg/cm^2 (MFC-4)

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*F. **Electrode potentials***

The anode potential of MFC-1, MFC-2 and MFC-3 were found to be almost similar (Figure 5) but anode potential of MFC-4 was found to be higher than that of the other three MFCs. At higher binder loading due to low proton transfer, proton got accumulated in the anodic chamber that caused decrease in pH which inhibited the activity of anodic biofilm (Franks et al., 2008). The highest operating cathode potential of 33 ± 4 mV was obtained in the MFC having a binder loading of 6.5 mg/cm^2 (Figure 5). Again the results support LSV data that is best cathode performance was with the binder loading of 6.5 mg/cm^2 due to increased ORR.

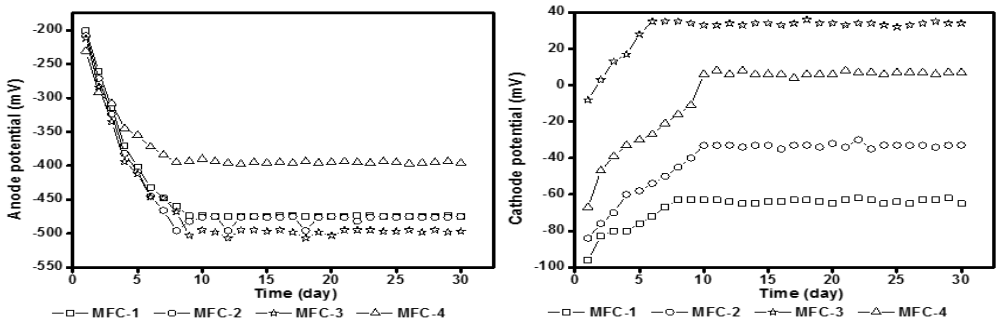

Figure 5: (a) Anode and (b) Cathode potential of the four MFCs

*G. **Polarization***

The polarization curves (Figure 6) of the MFCs were obtained by varying the external resistance from 10000 Ω to 1 Ω. The maximum power densities obtained from polarization study were 38 mW/m^2, 40.83 mW/m^2, 52 mW/m^2 and 43.83 mW/m^2 for MFC-1, MFC-2, MFC-3 and MFC-4, respectively. The maximum power density increased with increasing PDMS binder loading up to 6.5 mg/cm^2 with the power density around 37% higher than that obtained with minimum binder loading (2.5 mg/cm^2). The power density was however found to decrease with further increase in binder loading, and at binder loading of 7.5 mg/cm^2 the power density was 16% lower than the maximum power density. It is confirmed from LSV data that current generation was maximum for binder loading of 6.5 mg/cm^2; which shows higher ORR activity due to high oxygen affinity that enhances cathode performance and thus increases overall power generation from the MFC. Decrease in power production with further increase in binder loading was observed, which is due to increased hydrophobicity and lower proton transfer. The power density obtained in the MFC with binder loading of 2.5 mg/cm^2 is same as that obtained by Zhang et al. (2009) while using PVDF binder in an MFC without catalyst. However, power densities obtained after increasing binder loading was significantly higher than that obtained by Zhang et al. (2009).

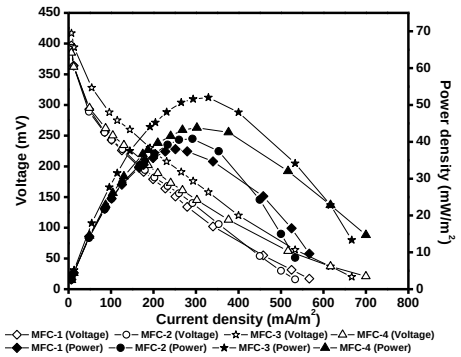

Figure 6: Polarization curves for the MFCs

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H. ***Wastewater treatment and Coulombic efficiency***

The COD concentration in the wastewater was used as a parameter to understand wastewater treatment efficiency of the MFCs. The supernatant from the anode chamber was collected and COD was measured to get an idea of COD removal in every feed cycle. The average COD removal efficiencies were 79.5 ± 2.51%, 79.43 ± 3.27%, 78.63 ± 3.71% and 70.29 ± 1.40% in MFC-1, MFC-2, MFC-3 and MFC-4, respectively (Figure 7). The COD removal of MFC-1, MFC-2 and MFC-3 were almost similar, whereas COD removal was slightly lower for MFC-4. The pH of anolyte was found in range of 7.04 to 8.13 for MFC-1, MFC-2 and MFC-3; whereas for MFC-4, pH ranged from 6.02 to 7.08. Decrease in pH was due to lower proton transfer towards cathode at higher loading of PDMS, which increased proton concentration in the anodic chamber of MFC. Acidic pH due to accumulation of proton inhibits activity of anodic biofilm, thus hampering the wastewater treatment efficiency of the MFC.

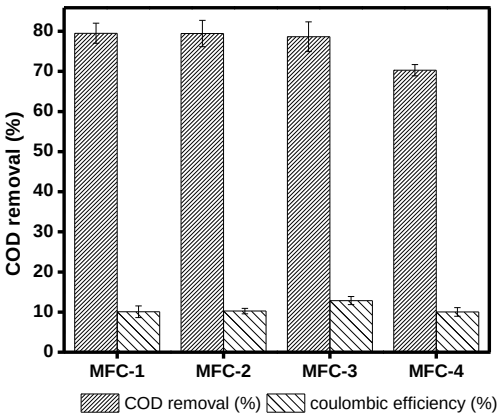

Figure 7: COD removal efficiency of MFCs

Coulombic efficiency of MFC-1, MFC-2, MFC-3 and MFC-4 was calculated as 10.09 ± 1.45%, 10.26 ± 0.67%, and 12.86 ± 1.01% and 10.04 ± 1.07%, respectively. The CEs of the MFCs were also found to increase with increased binder loading up to 6.5 mg/cm2 and it reduced with further increase in binder loading. Increased binder loading in the MFCs acted as a gas diffusion layer which is applied to reduce oxygen diffusion into the anodic chamber and also to reduce water loss (Wei et al., 2011). PDMS binder used is hydrophobic in nature and reduces water loss (Zhang et al., 2012). Reduced oxygen diffusion into the anodic chamber increased the CE; but increased binder loading hinders the four electron transfer pathway due to lower proton availability at the cathode that reduces electricity generation, thereby reducing CE. These CE values are comparable to that obtained by Cheng et al. (2006) using more established PTFE or Nafion as binder indicating suitability of cheaper PDMS as an alternative binder.

IV. CONCLUSION

MFC with PDMS binder loading of 6.5 mg/cm^2 showed highest maximum power density of 52 mW/m^2 among all the MFCs. Improvement in MFC performance with optimum binder loading is due to high oxygen mass transfer of PDMS used as binder. On the other hand, although charge transfer resistance was minimum for MFC with binder loading of 7.5 mg/cm^2, due to low proton conductivity of PDMS at this loading a 16% decrease in

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power density was observed as compared to the MFC with cathode binder loading of 6.5 mg/cm^2. Hence, PDMS binder loading of 6.5 mg/cm^2 can be considered as optimum binder loading for use in MFC. All the MFCs showed stable performance throughout the entire run which is due to anti-flooding and possibly antifouling property of PDMS. The cost of PDMS is quite low, which makes it a very promising low-cost alternative to costly binders in MFC cathodes for large scale applications.\

V. ACKNOWLEDGMENT

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