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Need for optimizing catalyst loading for achieving affordable microbial fuel cells

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HIGHLIGHTS

- Catalysts loading play an important role is deciding MFC performance.
- MFC performs best only under optimal catalyst loading concentration.
- MnO_2-activated carbon nano-composite act as effective cathode catalyst.
- 18 times increase in power density is obtained by using the composite catalyst.

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ABSTRACT

Microbial fuel cell (MFC) technology is a promising technology for electricity production together with simultaneous water treatment. Catalysts play an important role in deciding the MFC performance. In most reports, effect of catalyst – both type and quantity is not optimized. In this paper, synthesis of nanorods of MnO_2-catalyst particles for application in Pt-free MFCs is reported. The effect of catalyst loading i.e., weight ratio, with respect to conducting element and binder has been optimized by employing large number of combinations. Using simple theoretical model, it is shown that too high (or low) concentration of catalysts result in loss of MFC performance. The operation of MFC has been investigated using domestic wastewater as source of bio-waste for obtaining real world situation. Maximum power density of ~61 mW/m^2 was obtained when weight ratio of catalyst and conducting species was 1:1. Suitable reasons are given to explain the outcomes.

1. Introduction

Microbial fuel cell (MFC) is a fascinating technology for simultaneous application as renewable energy source and wastewater treatment (Zhao et al., 2008). MFCs mostly consist of anode, cathode and an ion exchange membrane (Logan et al., 2006). To address the issue of high cost, membrane free MFCs with promising characteristics have also been recently proposed (Ghangrekar and Shinde, 2007). In a working MFC, electrons produced during reduction of biomass by bacteria travels through an external load to reach the terminal acceptor i.e., cathode. On the other hand, protons travel across an ion exchange membrane. This ion exchange membrane also acts as a separator between anodic and cathodic chambers (Khera and Chandra, 2012). Electron and ion recombination occurs at the cathodic surface in presence of catalyst. The efficiency of this recombination process has a direct consequence on MFCs power output. It has been observed that cathodic over-potentials due to slower kinetics of oxygen reduction reaction (ORR) significantly limits voltage and power production of MFC (Li et al., 2010). Therefore, type and quality of catalyst used to reduce activation energy needed for ORR becomes a critical parameter. Large number of catalysts ranging from metal oxides, noble metals, metal alloys, phthalocyanines, and recently developed graphene composites have been proposed for improving MFC performance (Cheng et al., 2006; Liu et al., 2010; Wen et al., 2012; Yang et al., 2011; Yuan et al., 2011; Zhang et al., 2011a, 2012).

The two important factors which are considered while using a catalyst in MFCs are: (a) loading i.e., amount of catalyst used at cathode and (b) conducting element to be used for supporting the catalyst (Ahmed et al., 2012). Catalyst loading controls device performance, cost and longevity while conducting element helps in charge conduction. For example, loading rate of Pt as a catalyst in MFC has been studied from 0.1 mg/cm^2 to 2 mg/cm^2 (Cheng et al., 2006). This study showed that, even by lowering of Pt loading by a factor of 5, similar MFC performance can be obtained. Few more studies using activated carbon (AC) have been recently reported (Ghasemi et al., 2011; Wei et al., 2012). It can be seen from literature that no report deals with systematic study to understand the need for optimizing the ratio of catalyst and conducting element. This can have appreciable effect on the final cost of the device. Table 1 lists the different catalysts used in MFCs with

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corresponding weight and power density achieved. In most of these studies, ratio of conducting element and catalyst has been kept fixed. But the reason for this choice of ratio remains unexplained.

In the present study, it is shown that changing the weight ratio of catalyst to conducting element significantly affects the performance of MFCs. Experimental results clearly show that too high (or low) values of ratio has detrimental effect on MFC performance. A simple theoretically conceptualized model is also used to explain experimental observations. The nature of catalyst itself will also have appreciable control on overall performance of the device. For the present study, a Pt-free catalyst was chosen to maintain economics of affordable MFCs. Recently, use of one dimensional nanostructures of MnO_2 catalyst particles has been found to significantly enhance MFC performance. The performance of MnO_2 catalytic particles depends on the particle size, shape and crystal structure (Debart et al., 2008). In this paper, synthesis of MnO_2 nanorods using hydrothermal route is also reported. Such tubular shaped particles are found to show high catalytic activity which contribute in achieving high performance in MFCs. Throughout the present study, AC was used as the conducting element.

2. Experimental

2.1. Materials used

Manganese (II) sulphate monohydrate purified ($MnSO_4{\cdot}H_2O$, $\geqslant$99%, M_w: 169.02 g/mol), Potassium permanganate GR ($KMnO_4$, $\geqslant$99%, M_w: 158.04 g/mol), sodium chloride crystalline pure (NaCl, $\geqslant$99%, M_w: 58.44 g/mol), charcoal activated, tryptone (pancreatic digest of casein) and yeast extract powder were purchased from Merck, India. Potassium hydroxide (KOH, 85%, M_w: 56.11 g/mol) was purchased from Fisher Scientific, India. Poly vinylidene fluoride-co-hexafluoropropylene (PVDF–HFP) GR (M_w: 130000 g/mol) pellets were purchased from Sigma-Aldrich. Domestic wastewater was collected from wastewater treatment plant at Indian Institute of Technology Kharagpur, India. Wastewater was used as inoculum for the MFC reactor. Mixed microbial cultures which are indigenous to domestic wastewater were grown in lysogeny-broth media (LB media) as a nutrient medium or organic source. LB media was prepared by stirring together tryptone (10 g/L), yeast extract powder (5 g/L) and sodium chloride (10 g/L).

2.2. Synthesis of MnO_2 nanorods

For hydrothermal synthesis of α-MnO_2, $KMnO_4$ and $MnSO_4$ were taken in 2.5:1 M ratio and dissolved in de-ionized water. This mixture was stirred to form a homogeneous solution before being transferred to a stainless steel Teflon lined autoclave. Autoclave was heated up to temperature of 140 °C for 24 h. The resultant brownish precipitate was filtered and washed repeatedly with de-ionized water and ethanol to remove the byproducts. The obtained powders were dried at 80 °C for 12 h. Phase formation was confirmed by the analysis of X-ray diffraction data. Scanning and transmission electron micrographs were analyzed to understand the particle morphologies.

2.3. Electrode preparation

Electrodes were prepared using different weight ratios of MnO_2 nanorods and AC. Weight ratio of PVDF binder was kept fixed at 20% for uniformity. First, PVDF was dissolved in N-methyl-2-pyrrolidone (NMP) by continuous stirring at 80 °C followed by addition of requisite ratio of MnO_2 and AC. This slurry was then

Table 1
List of various catalysts used in MFC with the ratio or amount of their conducting element support and corresponding power densities.

Catalyst	Conducting element support	Weight ratio or amount	Power densities obtained	Reference
Cobalt oxide and iron phthalocyanine (FePC)	Carbon particles	200 mg C-$CoO_x$with 20 mg FePC	654 ± 32 mW/m^2	Ahmed et al. (2012)
Fe, FePC and Pt	Carbon Vulcan, ketjen black and carbon	0.2 wt% and 0.4 wt% Fe in carbon vulcan, 0.2–1 wt% FePC in ketjen black, 46 and 30 wt% Pt in C	588 ± 6 mW/m^2 with FePc/ketjen black (0.8 wt% Fe) and 643 ± 20 with 30 wt% Pt/C	Birry et al. (2011)
Metal phthalocyanine's (FePC, CoPC, MnPC, FeCuPC) and Pt	Carbon nanoparticles (Ketjen Black and Vulcan) and Carbon	20 wt% Pt with carbon (commercial), for others weight ratio is not reported	634 mW/m^2 with FePC, 593 mW/m^2 with Pt, 353 mW/m^2 with MnPC	HaoYu et al. (2007)
Napthalocyanine (NPC) and cobalt naphthalocyanine (CoNPC)	Carbon black	0.4 g carbon black during catalyst synthesis and dispersed in carbon powders for electrode preparation	64.7 mW/m^2 with CoNPC and 9.3 mW/m^2 with NPC	Kim et al. (2011)
α-, β- and γ-MnO_2	Graphite powder and CNTs	For β-MnO_2:CNT: PVDF:: 8:2:2	97.8 mW/m^2 with β- MnO_2, 22.1 with α-MnO_2 mW/m^2, 82.6 mW/m^2 with γ- MnO_2	Lu et al. (2011)
Manganese cobalt oxide	Carbon vulcan	6.25 mg catalyst with 16.66 mg of carbon vulcan with binder and solvent	113 mW/m^2 with Mn/Co atomic ratio of 2	Mahmoud et al. (2011)
Iron ethylenediaminetetraacetic acid	Carbon black	0.5 g of carbon black during synthesis	1122 mW/m^2	Wang et al. (2011)
MnO_2/Graphene nano sheets	AC	86 wt% AC, 12 wt% PTFE, 2 wt% acetylene black with catalyst	2083 mW/m^2	Wen et al. (2012)
Iron phthalocyanine (FePC)	Polyaniline and carbon black (PANI/C)	7 mg of PANI/C in 7 mg of FePc	630.5 mW/m^2	Yuan et al. (2011)
Pt–Fe alloy	Carbon powders	10 wt% of catalyst in carbon	1097.6 ± 51.2 mW/m^2 with C/Pt–Fe	Zhang et al. (2011a)
α-, β- and γ-MnO_2	Graphite powder	MnO_2, graphite powder and PVDF in 65:20:15 weight ratio	125 ± 11 with α- MnO_2, 172 ± 7 with β- MnO_2, 88 ± 8 with γ-MnO_2	Zhang et al. (2009)
Iron pthalocyanine (FePC) and cobalt tetra-methoxyphenyl porphyrin (CoTMPP)	Carbon nanoparticles (Vulcan)	2 g FePc with 2 g vulcan	13.88 mW/L with FePC and 14.32 mW/L with CoTMPP	Zhao et al. (2005)