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Abstract

This study aims to investigate the potential of porous Co₃O₄ nanorods as the cathode catalyst for oxygen reduction reaction (ORR) in aqueous air cathode microbial fuel cells (MFCs). The porous Co₃O₄ nanorods were synthesized by a facile and cost-effective hydrothermal method. Three different concentrations (0.5 mg/cm², 1 mg/cm², and 2 mg/cm²) of Co₃O₄ nanorods coated on graphite electrodes were used to test its performance in MFCs. The results showed that the addition of porous Co₃O₄ nanorods enhanced the electrocatalytic activity and ORR kinetics significantly and the overall resistance of the system was greatly reduced. Moreover, the MFC with a higher concentration of the catalyst achieved a maximum power density of 503 ± 16 mW/m², which was approximately five times higher than the bare graphite electrode. The improved catalytic activity of the cathodes could be due to the porous properties of Co₃O₄ nanorods that provided the higher number of active sites for oxygen.

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Potential of porous Co₃O₄ nanorods as cathode catalyst for oxygen reduction reaction in microbial fuel cells

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Abstract

This study aims to investigate the potential of porous Co₃O₄ nanorods as the cathode catalyst for oxygen reduction reaction (ORR) in aqueous air cathode microbial fuel cells (MFCs). The porous Co₃O₄ nanorods were synthesized by a facile and cost-effective hydrothermal method. Three different concentrations (0.5mg/cm², 1 mg/cm², and 2 mg/cm²) of Co₃O₄ nanorods coated on graphite electrodes were used to test its performance in MFCs. The results showed that the addition of porous Co₃O₄ nanorods enhanced the electrocatalytic activity and ORR kinetics significantly and the overall resistance of the system was greatly reduced. Moreover, the MFC with a higher concentration of the catalyst achieved a maximum power density of 503 ±16 mW/m², which was approximately five times higher than the bare graphite electrode. The improved catalytic activity of the cathodes could be due to the porous properties of Co₃O₄ nanorods that provided the higher number of active sites for oxygen.

Keywords: microbial fuel cell, Co₃O₄ nanorods, oxygen reduction reaction

1. Introduction

Microbial fuel cell (MFC) technology has drawn a mounting consideration for a decade, since it demonstrates the incredible potential to produce electrical energy from organic materials (Hou et al., 2016; Huang et al., 2015b; Kumar et al., 2016; Liu et al., 2016). However, some constraints such as high cost of materials required in manufacturing the MFCs are discouraging the use of MFC technology for commercial-scale applications. Moreover, the total electric output also remains low and highly expensive when the investment is taken into consideration for an MFC system. The cost for the preparation of the cathode (including the catalyst) accounts for ca. 60% of the overall expense of an MFC (Gong et al., 2014). An air-cathode has been broadly acknowledged as the cathode of MFC because of the accessibility of abundant oxygen in air utilized as a free electron acceptor (Hou et al., 2016; Huang et al., 2015; Huggins et al., 2015; Kumar et al., 2015). An electrochemically active catalyst is generally required for oxygen reduction reaction (ORR) at the cathode (Huggins et al., 2015; Yazdi et al., 2016; Winfield et al., 2016). Besides, it is quite evident that the higher ORR rate is also one of the vital factors for enhanced power generation (Ghasemi et al., 2013; Huang et al., 2015a; Yang et al., 2015). Therefore, development of an efficient and cost-effective cathode catalyst could be an asset for improved MFC applications.

Cobalt or cobalt oxide has been successfully used as the cathode catalyst for improved ORR kinetics in MFCs (Hou et al., 2016; Li et al., 2016; Liu et al., 2014; Song et al., 2015; Xu et al., 2012; Yang et al., 2016). In a study, Co_3O_4 micro-particles were directly grown on stainless steel mesh by using an ammonia-evaporation-induced method. The cathode used in a double chamber MFC produced a maximum power of 17.8 W/m^3 , which was manifolds higher than the bare stainless steel mesh (Gong et al., 2014). Moreover, in an

alternative demonstration, Co_3O_4 nanosheets decorated on activated carbon was used as the air cathode that generated the maximum power density of ca. 1420 mW/m^2 and exhibited an exchange current density 2.6 times higher than the control (Liu et al., 2016). Cobalt has also been used in many composite catalysts for ORR with a variety of morphologies. For example, nitrogen-doped graphene/CoNi alloy encased within bamboo-like carbon nanotube hybrids (N-G@CoNi/BCNT) was developed as cathode catalyst, which exhibited a high ORR activity and analogous exchange current density as compared to commercial available Pt/C (Hou et al., 2016). The catalysts with unique morphology or structure may also exhibit additional active sites for oxygen, which might be responsible for higher ORR activity. For example, recently, mesoporous nano urchin-like NiCo_2O_4 was successfully synthesized by hydrothermal method. The mesoporous NiCo_2O_4 provided more active sites for oxygen, improving the electrocatalytic activity significantly. The cathode showed a maximum exchange current density of 25.49 A/cm^2 and a maximum power density of ca. 1730 mW/m^2 , which was 2.28 times higher than the control (Ge et al., 2016). Hence, it is quite evident that catalysts with porous structure show higher ORR activity and could be a substantial alternative for costly platinum in MFCs.

Cobalt oxide is recognized as a promising ORR catalyst in MFCs and its ORR catalytic activity can be further ameliorated by developing its different morphologies. The porous Co_3O_4 nanorods have not been used in the MFCs to the date. Therefore, in this study, the potential of porous Co_3O_4 nanorods as ORR catalyst has been demonstrated in a double chamber aqueous air cathode MFC. The Co_3O_4 nanorods were synthesized by using a facile and cost-effective hydrothermal method and further characterized by X-ray diffraction (XRD) and electron microscopic techniques. The catalyst ink of Co_3O_4 nanorods of varying concentration was prepared and coated on graphite electrodes, which were characterized by electrochemical techniques such as cyclic voltammetry (CV), linear sweep voltammetry

(LSV), and Tafel plot. Moreover, the effect of catalyst concentration on MFC performance has been also investigated. The porous structure of Co_3O_4 nanorods is expected to increase the ORR activity of the cathode and hence the MFC performance.

2. Experimental

2.1. Synthesis of Co_3O_4 nanorods

The chemicals used in all the experiments were of analytical grade and were purchased from Sigma-Aldrich. Porous cobalt oxide nanorods were synthesized using a simple and cost-effective hydrothermal method, earlier used by Wang et al. (2009). In a typical method, 3 gm of cobalt chloride (CoCl_2) and 150 mg of urea ($\text{CO}(\text{NH}_2)_2$) were mixed in distilled water to make a homogenous solution with a final volume of 100 ml. The solution was transferred to a 100 ml Teflon-lined autoclave and kept in an oven for 6 h at 105 °C. The autoclave was allowed to cool at the room temperature. The resulting solution was centrifuged at 9590 x 'g' for 20 min to isolate the pink precipitates, which were further washed with distilled water and ethanol for several times, respectively. The washed precipitates were dried in a vacuum oven overnight. The dried product was further calcined at 300 °C for 3.5 h. A black powder was obtained as the final product.

2. 2. Preparation of aqueous air cathodes

Graphite sheets were used as the supporting carbon/electrode material as they are highly conductive and also commercially available. Three different concentrations of porous Co_3O_4 nanorods that are 0.5 mg/cm², 1 mg/cm², and 2 mg/cm² were coated on the graphite electrodes to prepare three samples of aqueous air cathodes for the study, named as CON-1, CON-2, and CON-3, respectively. Earlier, the graphite sheets (with a projected surface area of 15 m²) were treated with a sand paper to make the electrode surface rough.

This was followed by 24 h successive treatments with 1M HCl and 1M NaOH (Patil et al., 2009). Finally, the electrodes were washed with distilled water.

A catalyst ink was prepared for each sample. The catalyst ink contains, for 1 mg catalyst, 1 μ l (water), 7 μ l (5 % polyvinylidene difluoride), and 2 μ l (isopropyl alcohol) were mixed and stirred for 24 h to make a homogenous solution. The prepared ink was coated uniformly on the treated electrode with a paint brush on each side of the sample electrode. Further, the electrodes were dried in an oven at 65 °C for 24 h and then stored in distilled water.

2. 3. Microbial fuel cell construction and operation

The double chamber MFC was constructed with a cylindrical Plexiglas chamber, with a total working volume of 240 ml. Graphite sheets were used as the anode, which were also treated as mentioned in Section 2.2. The prepared sample electrodes with different concentrations of porous cobalt oxide were employed as the cathode. The distance between the anode and the cathode was 6 cm. A proton exchange membrane, Nafion 117 with a projected surface area of 10.5 cm² was placed between the two chambers. The anode and the cathode were connected with a titanium wire. 100 mM phosphate-buffered saline (PBS) (pH = 7) was used as the catholyte. The PBS contained: Na₂HPO₄, 9.125 g/L; NaH₂PO₄, 4.904 g/L; NH₄Cl, 0.31g/L; KCl, 0.13 g/L. The 100 mM PBS was added with trace elements (12.5 ml/L), vitamins (12.5 ml/L) and sodium acetate (2 g/L), was used as the anolyte (Guo et al., 2015). Anaerobic sludge was used as the inoculum for all the MFCs and the inoculum: anolyte ratio was 1:3. The inoculum exhibits high chemical oxygen demand and biochemical oxygen demand i.e. 56,500 mg/l and 3500 mg/l, respectively. It predominantly contains the microorganisms such as *Pseudomonas aeruginosa*, *Azospira oryzae*, *Acetobacter peroxydans* and *Solimonas variicoloris*, as suggested by Baranitharan et al. (2015). The

anode chamber was sparged with pure nitrogen gas for 30 min to ensure the anaerobic conditions in the chamber. In the cathode chamber, air was continuously sparged with an air pump to maintain a sustained concentration of oxygen during the MFC operation. All the MFCs were operated at the room temperature, 28 ± 2 °C.

2. 4. Electrochemical analysis

The open circuit voltage of the MFCs was measured using a digital multimeter (Fluke 17B⁺) and the power density was calculated from the polarization curves by varying the external resistance from 1000 to 10000 Ω , as previously suggested by (Yang et al., 2015). Each resistor was tested for about 20 min to ensure a stable voltage.

The prepared Co₃O₄ nanorods were characterized by XRD. The XRD patterns were acquired on Miniflex II (Rigaku, Japan) X-ray diffractometer employing CuK α radiation ($\lambda = 1.5406$ Å) and Ni-filter. Further, the morphologies of the nanorods were examined using a JSM-7800F (JEOL, Japan) Field Emission Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM) (FEI, USA). The Brunauer-Emmett-Teller (BET) surface area of the nanomaterial was measured using gas adsorption studies employing a Micromeritics (Tristar 3000, USA) instrument in a nitrogen atmosphere.

The LSV for all the cathodes was tested by a potentiostat (Gamry interface 1000, USA) by sweeping the potential from -0.6V to 0.4V with a scan rate of 10 mV/s in the 100 mM PBS (pH = 7). A three-electrode system was used containing an Ag/AgCl electrode as the reference electrode, the platinum wire as the counter electrode and the prepared cathode as the working electrode. Similarly, the CV was performed by sweeping the potential from -0.8V to 0.8V at a scan rate of 100 mV/s.

Moreover, electrochemical impedance spectroscopy (EIS) of all cathodes was measured over a frequency range of 1-100000 Hz at the initial open circuit potential with a sinusoidal perturbation of 10 mV amplitude. The EIS data were fitted to an equivalent electrical circuit to calculate the activation resistance (R_{act}) and ohmic resistance (R_{ohm}) by using a software (Gamry Echem Analyst, USA).

Tafel plots were prepared for all the cathodes to calculate the exchange current density, were recorded by sweeping the overpotential from 20 to 100 mV at 1 mV/s (Liu et al., 2014), versus Ag/AgCl as the reference electrode. The exchange current density was calculated by using the following equation:

$$\lg i = \lg i_0 - \frac{\beta n F \eta}{2.303 RT} \quad (1)$$

All the electrochemical tests were performed using a potentiostat (Gamry interface 1000, USA) using 100 mM PBS (pH = 7) at room temperature 28 ± 2 °C in the similar MFC reactor which was further used in the experiments.

3. Results and Discussion

3.1. Morphological and physical characterization of Co_3O_4 nanorods

The Co_3O_4 nanorods synthesized using a simple hydrothermal method are assumed to be formed in two steps. In the first step of the hydrothermal process, an intermediate product $Co^{II}(OH)_a(CO_3)_b Cl_{(2-a-2b)} \cdot nH_2O$ could be formed. The crystalline structure of this intermediate product contains Co-OH layers and counteranions between the Co-OH layers (Hosono et al., 2005). In the subsequent calcination step, the Co-OH layers were converted into Co_3O_4 nanoparticles through dehydration and pyrolysis of counteranions into gases (Hosono et al., 2005). The spaces between the counteranions and -OH were

converted into pores, resulting porous Co_3O_4 nanorods as the end product. The crystalline structure of Co_3O_4 nanorods was investigated by XRD analysis. The X-ray diffraction patterns of Co_3O_4 nanorods are presented in Fig. S1, which are consistent with the peak positions determined earlier (PDF card No. 653103). The XRD pattern of Co_3O_4 nanorods showed diffraction peaks corresponds to $\text{Fd}3\text{m}: 2$ space group. Moreover, no impurity peaks were observed in the XRD pattern, suggesting the pure form of Co_3O_4 . The morphology of the nanorods was analyzed by FESEM and TEM technology. Fig. S2 shows FESEM images of Co_3O_4 nanorods. The results of FESEM and TEM confirmed that shape of the final product obtained by the hydrothermal method was rod shaped.

The BET surface area of Co_3O_4 nanorods was $\sim 15.55 \text{ m}^2/\text{g}$. In addition, the nanorods exhibited a micropore surface area of $1.0372 \text{ m}^2/\text{g}$ with a pore volume of $0.11 \text{ cm}^3/\text{g}$. The average width of a pore in the nanorods was $\sim 19.74 \text{ nm}$. Thus it can be suggested that the obtained product was nanoporous Co_3O_4 nanorods. Moreover, the mesoporous volume of Co_3O_4 nanorods was $0.985 \text{ cm}^3/\text{g}$ and micropore volume was $0.975 \text{ cm}^3/\text{g}$, which was higher than the catalysts $\text{Co}_3\text{O}_4/\text{AC}$ and $\text{Co}(\text{OH})_2/\text{AC}$ used in the recent study (Liu et al., 2016). The higher pore volume of Co_3O_4 nanorods could provide the higher number of pores on the catalyst surface and consequently, more active sites for oxygen molecules. Moreover, cobalt oxide has high affinity towards oxygen molecules, which makes it more favorable for chemisorptions of oxygen molecules onto the catalyst surface and hence, enhances the ORR activity (Winfield et al., 2016).

3.2. Electrochemical characterization

All the cathodes coated with varying concentration of Co_3O_4 nanorods were characterized by CV and LSV analysis to further evaluate the ORR performance of the cathodes in 100 mM PBS saturated with oxygen. The CV of all the cathodes were recorded

by sweeping the potential from -0.8V to 0.8V (V vs. Ag/AgCl) at the scan rate of 100 mV/s. The cyclic voltammograms of all the cathodes are shown in Fig. S3. The results demonstrated that the cathode with 2 mg/cm² Co₃O₄ nanorods (CON-3) showed a sharp cathodic peak at the potential 0.339V vs. Ag/AgCl, which was most positive than the other cathodes i.e. 1 mg/cm² Co₃O₄ (CON-2), 0.5 mg/cm² Co₃O₄ (CON-1), and bare cathode. The improved ORR activity can be attributed to the availability of abundant pores on the electrode surface that provided more active sites for oxygen molecules. Therefore, the electrode with the maximum concentration of Co₃O₄ nanorods obviously have the higher number of active sites for the electron acceptor (oxygen) and thus showed the best catalytic activity for ORR among the other cathodes.

Fig. 1 shows the results of LSV for the bare cathode and cathodes with different concentrations of Co₃O₄ nanorods, which demonstrates that the cathodes with increasing concentration of Co₃O₄ nanorods showed the current density accordingly. In other words, the cathode with CON-3 exhibited the highest current density and the bare cathode showed the least. The LSV results suggested that at the potential of -0.4V, CON-3 showed a current density of 0.453 mA/m², which was manifolds higher than the bare electrode. The current density achieved by CON-2 and CON-1 at the similar potential was 0.109 mA/m² (~7 times higher than the bare electrode) and 0.161 mA/m² (~11 times higher than the bare electrode), respectively. In addition, the results indicated that the current density increased with a rise in the concentration of Co₃O₄ nanorods, consequently, CON-3 showed better catalytic activity than the cathodes with the lower amount of catalyst and no catalyst. Xu et al. demonstrated that the ORR is usually carried out at the active sites which are associated with Co³⁺ ions on the surface of cobalt oxide nanorods. Moreover, the presence of these cations is largely dependent on the availability and the size of pore structures (Xu et al., 2012). Therefore, it can be also assumed that the abundance of pores on the surface of Co₃O₄ nanorods

represented more active sites or the reduction sites for the ORR, resulting in the enhanced catalytic activity of the cathodes. The results for CV and LSV are consistent with Tafel study and polarization curves.

3.3. Measurement of resistance by Electrochemical Impedance Spectroscopy

The EIS technique was used to determine the resistance of cathodic reaction for all the cathode samples using three electrode system containing an Ag/AgCl electrode as the reference electrode, the platinum wire as the counter electrode and the prepared cathode as working electrode. Furthermore, an equivalent circuit model was prepared by using a software (Gamry Echem Analyst, USA). The equivalent circuit model is given in Fig. S4. The Nyquist plots (Fig. 2) obtained for the different cathodes were fitted in the equivalent circuit model to determine the value of each parameter. The ohmic resistance that includes the ionic resistance of the electrolyte, the intrinsic resistance of active materials, and the contact resistance is valued as R_{ohm} and the activation resistance that shows charge transfer resistance is valued as R_{act} in the equivalent circuit model. The Warburg resistance and capacitance are denoted as W and C, respectively. The results indicated that there was a substantial decrease in the resistance in the MFC system after the addition of porous Co_3O_4 nanorods as the cathode catalyst. The bare electrode showed higher values for both R_{ohm} and R_{act} as compared to CON-1, CON-2, and CON-3. The values of R_{ohm} and R_{act} for bare electrode were 134.2 Ω and 26.51 Ω , respectively. The R_{ohm} and R_{act} for all the cathodes exhibited a similar trend as: CON-3 < CON-2 < CON-1 < bare electrode. The R_{ohm} achieved for CON-3 was 11.27 Ω , which was ~12 times less than the bare electrode, and ~4.5 and 2.2 times lower than CON-1 and CON-2, respectively. The decrease in ohmic resistance indicates that addition of Co_3O_4 nanorods increased the conductivity of the electrode surface and enhanced the charge transfer processes. Besides, there was a

substantial reduction in R_{act} for Co_3O_4 nanorods coated cathodes. The CON-3 exhibited R_{act} of $4.55\ \Omega$, which was ~ 5 times less than as compared to the bare electrode. The R_{act} achieved by CON-3 in this demonstration can be compared with other cathode catalysts. For example, in a recent study, R_{act} obtained by platinum was $\sim 5\ \Omega$, which is $\sim 10\%$ higher than CON-3 (Hou et al., 2016). Moreover, CON-3 exhibited ~ 2 times lesser R_{act} as compared to N-G@CoNi/BCNT (Hou et al., 2016). The CON-2 and CON-1 also showed lower values for R_{act} , which were approximately 4 times and 1.3 times less than the bare electrode, respectively. This substantial reduction in the resistance could be also attributed to the porous Co_3O_4 nanorods on the cathode surface, which are assumed to provide extra active sites for oxygen molecules that consequently, lead to the better electrocatalytic activity of the cathode for ORR in MFCs. As a result, the reduction in overall resistance of the MFC system allowed the increase in power density by manifolds.

3.4. Analysis of Oxygen reduction reaction by Tafel study

The ORR catalytic activity of all the cathode samples was further analyzed by plotting the Tafel plots. The exchange current density for ORR can be easily calculated from the Tafel plots, which provides a potential parameter to evaluate the electron transfer rate of a catalyst. The exchange current densities calculated for all the cathodes are given in Table 1. Generally, the magnitude of the exchange current density is directly proportional to the electron transfer rate of ORR and thus for the electrocatalytic activity of a catalyst for ORR. Fig. 3A and Fig. 3B show the Tafel plots for all the electrodes. The results suggested that CON-3 achieved the highest exchange current density i.e. 6.553 mA/cm^2 , which was >3 times higher than the bare electrode. This could be ascribed to the existence of maximum concentration of Co_3O_4 nanorods in CON-3, providing the cathode with the highest active sites to reduce the oxygen molecules. The bare electrode obtained an exchange current density of 2.072

mA/cm^2 that was 2 times less than CON-1 and 3 times less than CON-2. The results of Tafel plots obtained in this study can be compared with a recent study by He et al. (2016). A cathode, nitrogen doped-carbon nanotubes-carbon cloth was used in their study. The exchange current density reported was $5.13 \text{ mA}/\text{cm}^2$, which was moderately lesser as compared to the exchange current density achieved by CON-3 in this study (He et al., 2016). In addition, CON-3 showed a higher exchange current density than copper/activated carbon ($1.03 \text{ mA}/\text{cm}^2$) (Zhang et al., 2015). Therefore, the results suggest that Co_3O_4 nanorods showed a faster electron transfer kinetics and will be an efficient ORR catalyst for MFC applications. Furthermore, it can also be concluded that the lower resistance and higher electrocatalytic activity promoted the faster electron transfer between the electrode interfaces and this consequently, improved ORR kinetics of the cathodes. The Tafel results are consistent with EIS, CV and LSV.

3.5. Performance of Co_3O_4 nanorods-aqueous air cathodes

All the prepared cathodes were deployed in double chamber MFCs. Power density was taken as the key parameter to compare performances of all the MFCs for electricity generation. Therefore, polarization curves were measured after five days of operation to determine the maximum power density achieved by each MFC and are shown in Fig. 4A. The results demonstrated that the addition in Co_3O_4 nanorods improved the power generation significantly. Moreover, it was also found that the power density increased with increase in Co_3O_4 concentration. Expectedly, the MFC with CON-3 generated a maximum power density of $503 \pm 16 \text{ mW}/\text{m}^2$, which was ~ 5 times higher than the bare electrode ($108 \pm 5 \text{ mW}/\text{m}^2$). The enhanced power generation was mainly due to the faster ORR kinetics on the cathode, as confirmed by the varying cathode potentials. The anode potentials were almost similar in all the MFCs (Fig. 4B). Moreover, the results were consistent with LSV and Tafel plots.

Besides, the lesser internal resistance in the MFC also contributed in enhanced power generation. The maximum power density achieved in this study was higher than the previously reported value i.e. 135 mW/m^2 (nitrogen doped-carbon nanotubes-carbon cloth as a cathode) and also from carbon nanotubes/Pt composites that produced a power density of 139 mW/m^2 (He et al., 2016). Furthermore, CON-3 generated more power density than platinum, which was ca. five times higher than platinum (120 mW/m^2) and approximately equally higher than copper-phthalocyanine (118 mW/m^2) (Ghasemi et al., 2013). In addition to this, Co-naphthalocyanine was used as the cathode catalyst in a demonstration but could produce a maximum power density of 64.7 mW/m^2 (Kim et al., 2011), which is manifolds lesser than the power density achieved by CON-3 in this study. It further strengthens the fact that porous nanomaterials act as more efficient cathode catalyst as compared to other catalysts. Another noticeable point is that the MFC with a catalyst concentration of 0.5 mg/cm^2 (CON-1) and 1 mg/cm^2 (CON-2) produced ~ 3 times and ~ 4 times more power density than the bare electrode, respectively. But a further increase in the catalyst concentration i.e. 2 mg/cm^2 (CON-3) merely improved the power generation by one time. This possibly suggests that the oxygen molecules could only access the active sites that were present on upper layers of the catalyst or might be the multiple layers of Co_3O_4 nanorods decreased the availability of pores/active sites in the lower layers of the catalyst present on the cathode surface, indicating that an optimum catalyst concentration is preferred for substantial electricity generation.

3.6. Cost study

Finally, the porous Co_3O_4 nanorods are significantly advantageous over platinum in terms of material cost. The demonstration shows that 1 g of Co_3O_4 nanorods can be produced from 15 g of CoCl_2 and 0.75 g of urea with the hydrothermal method. Therefore, the cost of 1

gm Co_3O_4 nanorods is estimated ~\$ 0.7, which is ~78 times less expensive than using 10% Pt/C (\$ 55 for 1 g). Hence, Co_3O_4 nanorods can be preferred over platinum in large-scale MFC applications that can reduce the overall cost of the MFC setup.

4. Conclusion

In this work, porous Co_3O_4 nanorods with varying concentration were used as cathode catalyst to facilitate ORR in aqueous air cathode MFCs. The MFC with the higher catalyst concentration achieved a maximum power density of $503 \pm 16 \text{ mW/m}^2$. The electrochemical results and Tafel plots indicated that Co_3O_4 nanorods improved the ORR kinetics of the cathode, which could be attributed to the porous property of the nanomaterial that provided increased number of active sites for oxygen. The integration of such catalyst with other highly active ORR catalysts could be a significant alternative to platinum in MFC applications.

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Figure legends

Figure 1. TEM images of porous Co_3O_4 nanorods.

Figure 2. LSVs of different aqueous air cathodes at a scan rate of 10 mV/s.

Figure 3. Nyquist plot of different electrodes measured by EIS technology over a frequency range of 1 Hz-100000 Hz at the initial open circuit potential with a sinusoidal perturbation of 10 mV amplitude.

Figure 4. (A) Tafel plots of different electrodes with varying concentration of Co_3O_4 nanorods by sweeping the overpotential from 20 mV to 100 mV at 1 mVs⁻¹ and (B) the linear fit for the Tafel plots of overpotential from 60 to 80 mV.

Figure 5. (A) Polarization and power density curves of MFCs and (B) electrode potentials, using different concentration of porous Co_3O_4 nanorods on graphite electrode as aqueous air cathodes.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Table 1. Exchange current density (i_0) calculated from Tafel plots.

Cathode	Linear fitting equation (R^2)	i_0 (mA/cm ²)
Bare electrode	$y = -7.6223 + 2.7447x$ (0.9953)	2.07
CON-1	$y = -6.9967 + 4.9820x$ (0.9962)	4.40
CON-2	$y = -9.9273 + 3.0458x$ (0.9994)	6.01
CON-3	$y = -9.6104 + 2.4964x$ (0.9971)	6.55