

Facile Synthesis of PVP-MnO₂/CNT Composites as ORR Electrocatalyst for an Air-Cathode Microbial Fuel Cell

Huei Ruey Ong¹, Chee Wai Woon², Muhammad Sheraz Ahmad², Abu Yousuf³,
Chin Kui Cheng², Md. Maksudur Rahman Khan^{2,*}

¹ Faculty of Engineering and Technology, DRB-HICOM University of Automotive Malaysia, 26607 Pekan, Pahang, Malaysia.

² Faculty of Chemical and Natural Resources Engineering, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Kuantan, Pahang, Malaysia.

³ Department of Chemical Engineering and Polymer Science, Shahjalal University of Science and Technology, Sylhet-3114, Bangladesh

*E-mail: mrkhancep@yahoo.com

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The cathodic oxygen reduction reaction (ORR) is an influential step in fuel cells for the electrochemical energy conversion. Here we synthesized Polyvinylpyrrolidone incorporated carbon nanotube supported manganese dioxide (PVP-MnO₂/CNT) composite and used as ORR electrocatalyst for air-cathode microbial fuel cell (MFC). The physical and electrochemical characterization of PVP-MnO₂/CNT were performed by using Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray analysis (EDX), X-ray Diffraction analysis (XRD), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). The electrochemical characterization results showed that the PVP-MnO₂/CNT possessed the higher ORR catalytic activity with lower charge transfer resistance compared to MnO₂ and MnO₂/CNT. The performance of the electrocatalysts as cathode was evaluated in air-cathode MFC and it was found that the MFC with MnO₂-PVP/CNT electrocatalyst generated a maximum power density of 1365.30 mW/m³, which was higher than that of MFCs with MnO₂/CNT catalyst (1083.98 mW/m³), MnO₂ (540.91 mW/m³) and CNT (438.47 mW/m³). Therefore, the viable synthetic strategy and proposed application of PVP-MnO₂/CNT will broaden up the reality of MFC for power generation.

Keywords: PVP-MnO₂/CNT; Microbial Fuel Cell; Electrocatalyst; Oxygen reduction reaction

1. INTRODUCTION

Microbial fuel cell (MFC) has been considered as a superior sustainable energy system over the conventional fuel cells due to the usage of greener and renewable fuel and substrates [1]. Among the

MFC setups, the air-cathode MFC is commonly used due to its easy construction, high efficiency in power generation, and oxygen sustainability [2, 3]. However, the sluggish oxygen reduction reaction (ORR) rate and high overpotential losses, which typically results in 300-400 mV loss in the MFC voltage, hampers the overall performance [4]. Hence, electrocatalysts are needed to improve the kinetics of the ORR and thus does not limit the performance of air-cathode MFC. Pt and Pt based electrocatalysts are widely used as ORR catalysts [5]. However, high cost and low operational stability of Pt make it impractical for commercial use in air-cathode MFC [4-6]. Hence, huge impetus was given in past decades to develop Pt-free catalysts that can catalyse the ORR with comparable or superior rate [4, 7]. Manganese dioxide (MnO_2) in particular, can function as an alternative catalyst to Pt for ORR in air-cathode MFCs owing to its low cost and toxicity, environmental benignity and high chemical stability as well as possesses good electrocatalytic activity toward ORR [8, 9]. However, MnO_2 electrodes suffer for its poor electric conduction and deficient charge transfer [8, 10, 11]. To overcome these limitations, MnO_2 can be incorporated with supports, such as carbon nanotubes (CNT) possessing high surface area and good electrical conductivity [7, 10]. However, during the preparation of MnO_2/CNT , homogeneous dispersion of CNT in solution is crucial to achieve better distribution of MnO_2 on CNT which can be achieved by dispersing CNT in polymer solution [12]. Polyvinylpyrrolidone (PVP) has a high dielectric strength, low scattering loss, good charge storage capacity and dopant dependent electrical properties [13]. To our knowledge, there is no work on the nanostructured PVP- MnO_2/CNT composite as a cathode catalyst for ORR in air-cathode MFCs. In this paper, PVP- MnO_2/CNT was prepared by hydrothermal method. The as-prepared electrocatalyst was characterized through Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray analysis (EDX) and X-ray Diffraction analysis (XRD) and the evaluation on the ORR activity of the PVP- MnO_2/CNT nanocomposite was investigated through Cyclic Voltammograms (CV) and Electrochemical Impedance Spectroscopy (EIS). Finally, the performance of the catalyst was evaluated in air-cathode MFC.

2. EXPERIMENTAL

2.1. Catalyst preparation

PVP- MnO_2/CNT catalyst was prepared by hydrothermal method. Initially CNT was pre-treated with 5% nitric acid (HNO_3) for 2 h along with stirring. The treated CNT was filtered and washed with deionized (DI) water and dried in vacuum oven at 90 °C until a constant weight was achieved. Afterward, 0.8 g of PVP and 0.8 g of CNT were mixed and dispersed into 100 mL DI water for 12 h along with stirring. Then, 1 mL of acetic acid (CH_3COOH) was added into the mixture and stirred for another 30 min. Required amount (0.45 g) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was added into the mixture and stirred until its complete dissolution. The mixture was transferred to stainless steel hydrothermal reactor with Teflon vessel and placed into an oven at 180 °C for 24 h. The suspension was filtered and washed thoroughly with DI water. The black precipitate was denoted as PVP- MnO_2/CNT . For comparison MnO_2/CNT was prepared without PVP addition.

2.2 Physical Characterizations

The morphologies of the as-prepared electrocatalysts were characterized by using Field Emission Scanning Microscopy/Energy Dispersive X-ray Analysis (FESEM/EDX) (FESEM JSM-7800F, USA). The phase and crystallinity of the as-prepared PVP-MnO₂/CNT was identified by X-ray Diffraction (XRD) analysis by using RIGAKU, Miniflex II with Cu K α radiation (λ = 0.154056 nm).

2.3 Electrochemical Characterizations

The electrochemical experiments were carried out on an electrochemical workstation (PARSTAT 2273, USA) using a three-electrode system at room temperature. Ag/AgCl electrode and Pt wire were used as reference and counter electrode, respectively. During the working electrode preparation, 3.75 mg of the as-prepared PVP-MnO₂/CNT composite was mixed with 23 μ L of Nafion solution and 46 μ L of isopropanol and stirred overnight to form a homogenous slurry. The slurry was then brushed onto a strip of Toray carbon paper with the dimension of 1 cm x 1 cm. The carbon paper was then dried at 60 °C in a vacuum oven for overnight and denoted as the working electrode. The Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were employed to investigate the ORR catalytic activity and the electrochemical performance of the working electrode in a 0.1 M of aqueous Na₂SO₄ solution. The CV was carried out in the potential range of -1.6 to 0.1 V with the scan rate of 30 mV/s, meanwhile the EIS was carried out in the frequency range of 100 kHz to 10 mHz at open circuit potential. The Nyquist plot obtained from the EIS data was then fitted with a suitable equivalent circuit to investigate the electrochemical characteristics of the electrocatalysts such as charge transfer resistance, capacitance and Warburg impedance by using Zview software.

2.4 Electrode Preparation for MFC

Nafion 117 membrane with the dimension of 5 cm x 5 cm was pre-treated with 0.1 M of H₂SO₄ solution for 1 h at 100 °C and followed by DI water for another 1 h at 100 °C to remove the organic impurities in the membrane. The membrane was then washed several times and soaked overnight in DI water at room temperature before usage. Meanwhile, PACF with the dimension of 5 cm x 5 cm was cut. The catalyst ink was prepared by mixing the as-prepared electrocatalyst (26.50 mg), Nafion solution (162.61 μ L) and isopropanol (352.22 μ L). The catalyst ink was then brushed onto PACF surface in a circular shape with a diameter of 3 cm and area dispersion of 7.07 cm². The PACF surface coated with catalyst was used to attach the Nafion 117 membrane and then hot pressed at 100 °C for 2 min to form a membrane-electrode-assembly (MEA). A titanium wire was used to connect to the MEA with the external circuit to make an air-cathode.

2.5 Air-cathode MFC Set-up

The air-cathode single chamber MFC was built with a cubic plexi-glass which has a dimension of 5 cm x 5 cm (Shanghai Sunny Scientific, China) and a total working volume of 20 mL. Carbon

brush was directly used as anode electrode. The MEA was used as the air-cathode in MFC where the membrane surface side facing the anolyte while the PACF side facing the air.

POME and anaerobic sludge were collected from FELDA palm oil mill located at Panching, Pahang. The POME was diluted with distilled water in the ratio of 1:49 and used as the anolyte. The pH of the diluted POME was adjusted to 7 with NaOH solution. The POME was then sterilized with an autoclave. The anaerobic sludge enriched with microorganism was used as the inoculum. The ratio of inoculum to anolyte was 1:20.

2.6 COD Removal Efficiency

The COD of the anolyte was determined by using digestive solution (0-1500 mg/L range; Hach, USA) and measured using a COD reactor (HACH DRB 200, USA). The COD of the anolyte was taken just before the cell operated and referred as initial COD. The COD was then taken daily to investigate the COD removal efficiency of the air-cathode MFC by using different type of electrocatalysts. The COD removal efficiency of the cell was calculated with Eq. 1:

$$\text{COD removal efficiency} = \frac{\text{COD}_i - \text{COD}_f}{\text{COD}_i} \times 100\% \quad \text{Eq. 1}$$

Where COD_i = initial COD (mg/L) and COD_f = COD of the effluent (mg/L) in the anode chamber at any time.

3. RESULTS AND DISCUSSION

3.1 FESEM-EDX analysis

Morphologies of the PVP-MnO₂/CNT nanocomposite were characterized by FESEM as shown in Fig.1. It revealed that MnO₂ was present in the form of aggregates coated on CNT surface which is similar as reported by Woon, et al. [7].

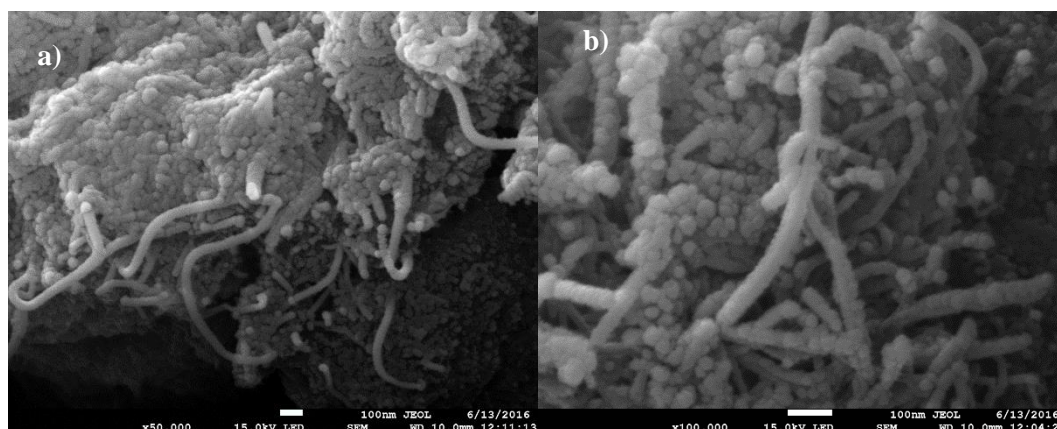


Figure 1. FESEM image of PVP-MnO₂/CNT at magnification of (a) 50k and (b) 100k

Energy Dispersive X-ray analysis (EDX) mapping was conducted to examine the elemental distribution of C, Mn, O and N in the as-prepared PVP-MnO₂/CNT and shown in Fig. 2. The mapping results indicate that the distribution of C, MnO and N elements is homogeneous throughout the catalyst, suggesting the presence of PVP in the composite.

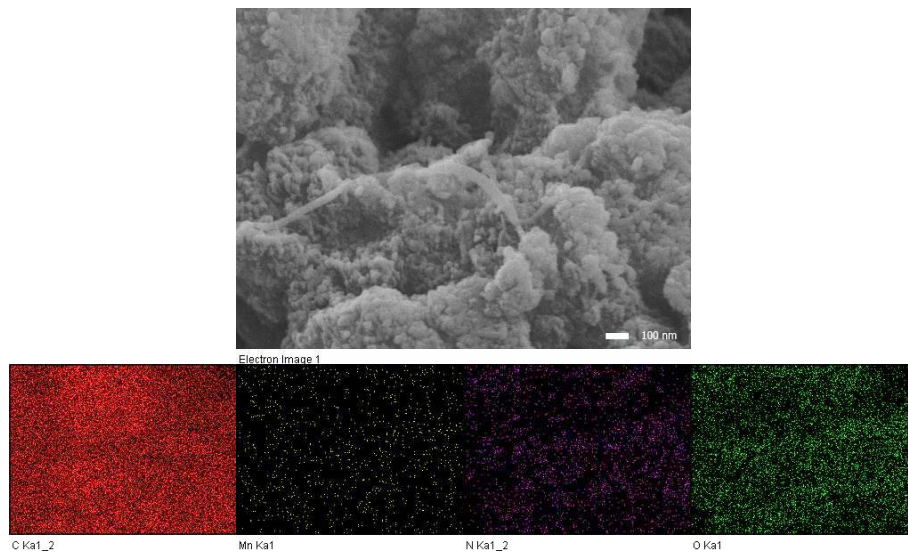


Figure 2. EDX elemental mapping of C, Mn, O and N for PVP-MnO₂/CNT

3.2 XRD analysis

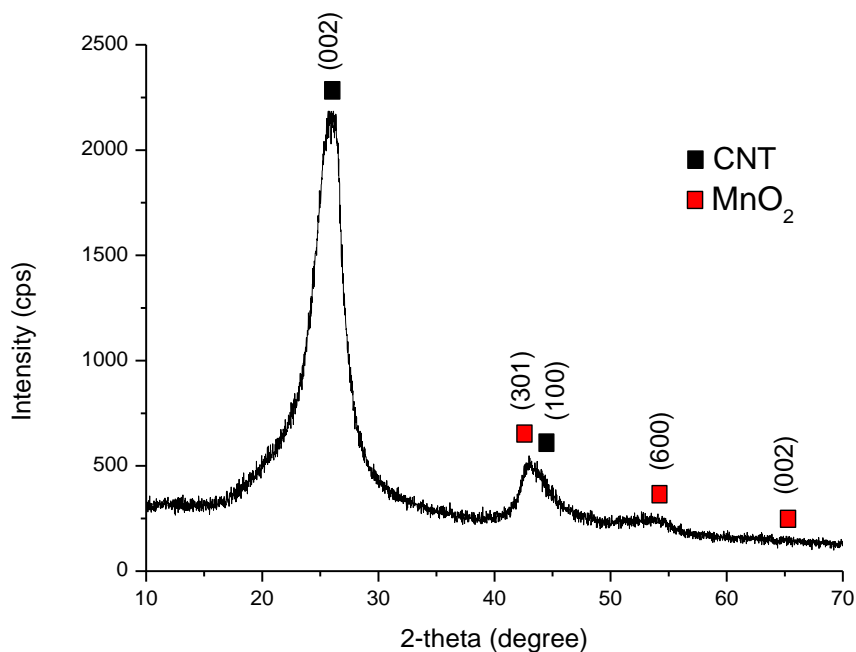
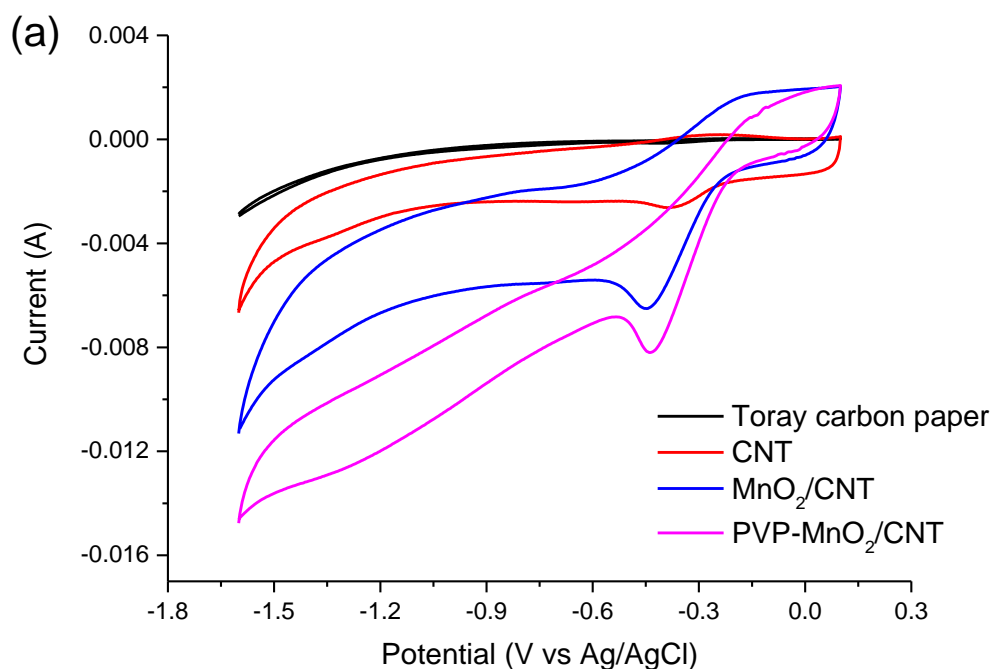


Figure 3. XRD patterns of MnO₂-PVP/CNT

X-ray Diffraction (XRD) analysis was done to identify the phase and crystallinity of the PVP-MnO₂/CNT and presented in Fig. 3. It can be seen that there are 2 carbon peaks; (0 0 2) and (1 0 0) at $2\theta = 25.65^\circ$ and 44° , respectively [14, 15]. Besides that, there are 3 peaks at $2\theta = 42.95^\circ$, 53.65° and 65.43° , corresponding to (3 0 1), (6 0 0) and (0 0 2), respectively. These peaks indicate the presence of α -MnO₂ in the composite [9, 11, 16]. The peak of MnO₂ was suppressed due to the presence of high amount of CNT in the PVP-MnO₂/CNT.

3.3 Electrochemical Characterizations

The ORR activity of the electrocatalysts (CNT, MnO₂/CNT and PVP-MnO₂/CNT) was investigated by using Cyclic Voltammetry (CV) as shown in Fig. 4(a). It revealed that there is no ORR activity in the Toray carbon paper which indicates that there is no electrochemical reaction occurred at the bare carbon paper electrode in the selected potential and scan rate [17]. The ORR peaks at the potential range between -0.2 and -0.4 V was observed for MnO₂/CNT and PVP-MnO₂/CNT catalysts which aligned with Zhang, et al. [9], Lu, et al. [18], Lu, et al. [19]. The oxygen reduction reactivity of the electrocatalysts are in order of PVP-MnO₂/CNT > MnO₂/CNT > CNT. The ORR activity was compared in term of area under the ORR peaks. It was found that PVP-MnO₂/CNT (4.57×10^{-4} VxA) has the highest ORR peak area and then followed by MnO₂/CNT (4.43×10^{-4} VxA), and CNT (9.17×10^{-5} VxA). This indicates that the as-prepared PVP-MnO₂/CNT is electrochemically active in ORR which could be applicable as an electrocatalyst in air-cathode MFC.



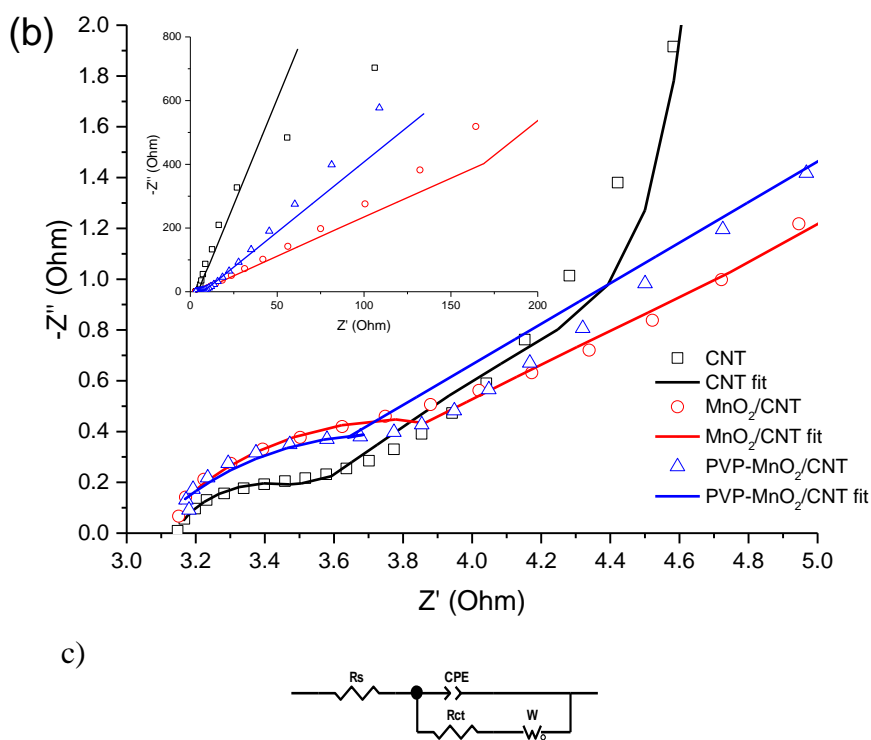


Figure 4. a) Cyclic voltammogram for the ORR of the as-prepared electrocatalysts in oxygenated 0.1 M of Na₂SO₄ aqueous solution (Potential range from -1.6 to 0.1 V; Scan rate = 30 mV/s) b) Nyquist plots and fitting of CNT, MnO₂, MnO₂/CNT and PVP-MnO₂/CNT; c) Equivalent circuit.

The electrochemical properties of the as-prepared electrocatalysts were further characterized by using electrochemical impedance spectroscopy (EIS) in 0.1 M of Na₂SO₄ aqueous solution at the frequency range of 100 kHz to 10 mHz with the AC signal amplitude of 10 mV. The Nyquist plots of the electrocatalysts were plotted in Fig. 4(b). It illustrates that all of the electrocatalysts have a semicircle at the high frequency range and increases at the low frequency range in the Nyquist plot. The Nyquist plots show one semi-circle at higher frequencies and a Warburg element at lower frequencies [20]. The equivalent circuit is shown in Fig. 4(c) consists of solution resistance (R_s), charge transfer resistance (R_{ct}), constant phase element (CPE) and Warburg element (W_o). The Warburg element represents the process of the diffusion of ions from the electrolyte to the interface which has three parts: diffusion resistance (W-R), capacitive part (W-T) and its exponent (W-P) [21]. CPE is often used to replace capacitor to compensate for non-homogeneity in the system [22]. The capacitance (C) can be estimated by using Eq. 2.

$$C = R \frac{1-n}{n} CPE \tag{Eq. 2}$$

where C is the capacitance, R is the parallel resistance, n is the empirical constant and CPE is the pseudo-capacitance [23].

Table 1. Fitting results of CNT, MnO₂, MnO₂/CNT and PVP-MnO₂/CNT with equivalent circuit

Elements	CNT	MnO ₂ /CNT	PVP-MnO ₂ /CNT
R _s , Ω	3.14	3.08	3.31
CPE-T (x10 ⁻³)	1.01	8.61	2.09
CPE-P	0.79	0.70	0.65
Capacitance, F (x10 ⁻⁵)	13.10	4.81	7.36
R _{ct} , Ω	0.56	1.47	1.40
W-R, Ω	3.51	5.91	5.81
W-T (x10 ⁻²)	5.64	2.11	4.05
W-P	0.48	0.38	0.42
R _T , Ω	7.20	10.46	10.51

According to Table 1 where the parameters are summarized, CNT has the lowest R_{ct} value (0.56 Ω) which increased in the MnO₂ based catalysts. The impregnation of PVP onto MnO₂/CNT enhanced the electrical conductivity of the electrocatalyst (lowering the charge transfer resistance about 5%). PVP has a high dielectric strength, low scattering loss, good charge storage capacity and dopant dependent electrical properties [13]. PVP is a good electrical conductivity polymer which could possibly enhance the electron transfer of the electrocatalysts.

3.4 MFC Performances

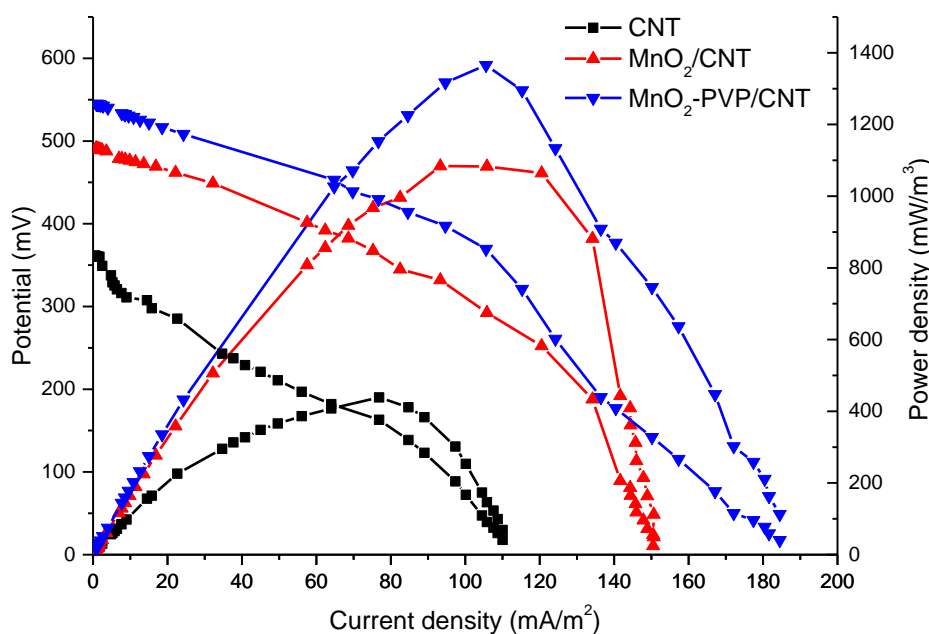


Figure 5. Polarization and power densities of different electrocatalyst materials for air-cathode MFC [Anolyte: POME, diluted with distilled water at the ratio of 1:49; pH of the anolyte = 7; Ratio (vol) of inoculum to anolyte was 1:20]

The synthesized catalysts were tested in the air-cathode MFC. Fig. 5 presents the power curves of air-cathode MFC where the following electrocatalyst were studied (CNT, MnO₂/CNT and MnO₂-PVP/CNT). The values of the power curves were obtained by varying the external resistance value (1000 kΩ to 100 Ω). The electrochemical properties of the catalysts and the performance of air-cathode MFC is summarized in Table 2. The addition of PVP into MnO₂/CNT has increased maximum power density about 21% (from 1083.98 to 1365.30 mW/m³). From Table 2, PVP-MnO₂/CNT has the highest OCP value (544.7 mV) followed by MnO₂/CNT (491.10 mV), and CNT (361.30 mV).

Table 2. Electrochemical properties of the catalysts and the performance of air-cathode MFC

Catalyst	CNT	MnO ₂ /CNT	PVP- MnO ₂ /CNT
ORR potential (V)	-0.36	-0.45	-0.43
ORR peak area (VxA) (x10 ⁻⁵)	9.17	44.30	45.70
R _{ct} (Ω)	3.35	3.38	3.31
Max. power density (mW/m ³)	438.47	1083.98	1365.30
Open circuit potential, OCP (mV)	361.30	491.10	544.7
COD removal eff. (%)	60.51	71.69	73.49

Table 3. Comparison of power densities generated in MFC with different electrocatalysts

Catalyst	Substrate	OCP (mV)	Max. power density (mW/m ³)	Ref.
MnO ₂ -PVP /CNT	POME	544.7	1365.3	This study
MnO ₂ /CNT	POME	582.0	215.57	[24]
MnO ₂	Acetate-laden synthetic waste-water	580.0	772.8	[25]
MnO ₂	POME	-	671.98	[26]
Pt	Glucose solution	627.0	726.0	[9]
MnO ₂		565.0	466.0	

Table 3 shows the comparison of power densities generated in MFC with different electrocatalysts. From this study, it can be concluded that PVP-MnO₂/CNT is a potential ORR electrocatalyst which can be used in the air-cathode MFC generating the maximum power density of 1365.30 mW/m³ with the OCP of 544.7 mV. POME was used in this study which could generate higher power density compared to those with other anolytes such as synthetic wastewater and glucose solution. The high COD value of POME could enhance the growth of microorganism due to the presence of amino acids, inorganic nutrients, nitrogenous compounds, free organic acids, and carbohydrates [27].

3.5 COD Removal Efficiency

The COD was measured every alternate days from first day until the seventh day. The COD removal efficiency of the air-cathode MFC is shown in Fig. 6. It can be seen that, PVP-MnO₂/CNT has the highest COD removal efficiency (73.49%) meanwhile CNT has the lowest COD removal efficiency (60.52%). In correlating with the power curve and COD removal efficiency, PVP-MnO₂/CNT is the most active ORR electrocatalyst which could generate the highest power density with the highest COD removal efficiency.

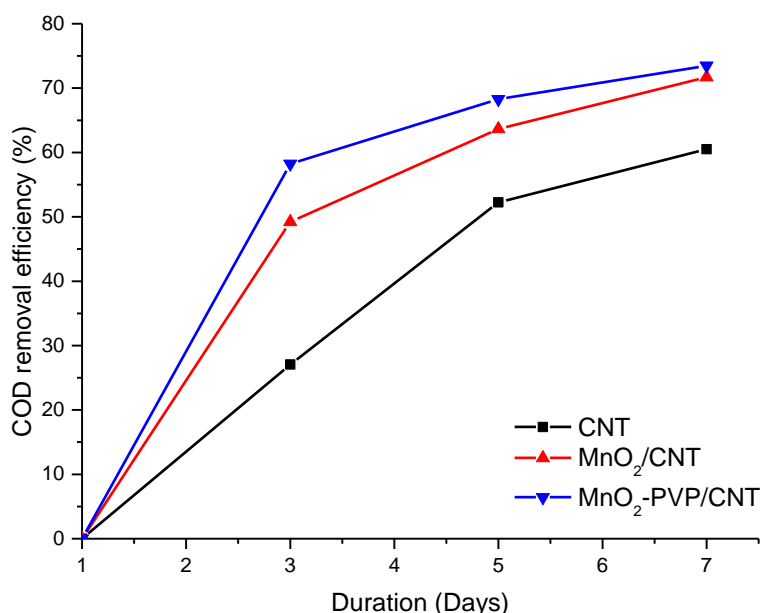


Figure 6. COD removal efficiency of the air-cathode MFC [Anolyte: POME, diluted with distilled water at the ratio of 1:49; pH of the anolyte = 7; Ratio (vol) of inoculum to anolyte was 1:20]

4. CONCLUSION

In summary, PVP-MnO₂/CNT catalyst was successfully synthesized and characterized. The ORR activity of the MnO₂-PVP/CNT catalyst was the highest with the ORR peak area of 4.57×10^{-4} A·V. The electrocatalysts were used in the cathode of the MFC operated with POME as anode substrate. MFC with MnO₂-PVP/CNT as air-cathode catalyst generates a maximum power density of 1365.30 mW/m³, which is higher than that of MFC with MnO₂/CNT (1083.98 mW/m³), and CNT (438.47 mW/m³). The PVP-MnO₂/CNT has the highest COD removal efficiency (73.49%). The results reveal that the cathode catalyst played the limiting role on the performance of MFC, hence highly active ORR catalyst could enhance the power generation in the MFC. In view of the terrific performance of the PVP-MnO₂/CNT catalyst, it has great promising potential in air-cathode MFCs.

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References

1. G. G. kumar, Z. Awan, K. S. Nahm, J. S. Xavier, *Biosens. Bioelectron.*, 53 (2014) 528
2. Z. Chen, K. Li, P. Zhang, L. Pu, X. Zhang, Z. Fu, *Chem. Eng. J.*, 259 (2015) 820
3. U. S. Hampannavar, N. V. Pradeep, *Int. J. Environ. Sci.*, 2 (2011) 114
4. M. T. Noori, M. M. Ghangrekar, C. K. Mukherjee, *Int. J. Hydrogen Energy*, 41 (2016) 3638
5. R. N. Singh, R. Awasthi, C. S. Sharma, *Int. J. Electrochem. Sci.*, 9 (2014) 5607
6. X. Zhang, J. Shi, P. Liang, J. Wei, X. Huang, C. Zhang, B. E. Logan, *Bioresour. Technol.*, 142 (2013) 109
7. C. W. Woon, M. A. Islam, B. Ethiraj, H. R. Ong, C. K. Cheng, K. F. Chong, G. Hedge, M. Khan, M. Rahman, *ChemistrySelect*, 2 (2017) 7637
8. Q. Wen, S. Wang, J. Yan, L. Cong, Z. Pan, Y. Ren, Z. Fan, *J. Power Sources*, 216 (2012) 187
9. L. Zhang, C. Liu, L. Zhuang, W. Li, S. Zhou, J. Zhang, *Biosens. Bioelectron.*, 24 (2009) 2825
10. Y. Lv, H. Li, Y. Xie, S. Li, J. Li, Y. Xing, Y. Song, *Particuology*, 15 (2014) 34
11. X. Xie, L. Gao, *Carbon*, 45 (2007) 2365
12. K. Gong, P. Yu, L. Su, S. Xiong, L. Mao, *J. Phys. Chem. C*, 111 (2007) 1882
13. M. Ravi, S. Bhavani, K. K. Kumar, V. V. R. N. Rao, *Solid State Sciences*, 19 (2013) 85
14. K. B. Liew, W. R. W. Daud, M. Ghasemi, K. S. Loh, M. Ismail, S. S. Lim, J. X. Leong, *Int. J. Hydrogen Energy*, (2015)
15. D. Xu, B. Li, C. Wei, Y.-B. He, H. Du, X. Chu, X. Qin, Q.-H. Yang, F. Kang, *Electrochim. Acta*, 133 (2014) 254
16. V. Subramanian, H. Zhu, B. Wei, *J. Power Sources*, 159 (2006) 361
17. M. Ghasemi, W. R. W. Daud, M. Rahimnejad, M. Rezayi, A. Fatemi, Y. Jafari, M. R. Somalu, A. Manzour, *Int. J. Hydrogen Energy*, 38 (2013) 9533
18. M. Lu, L. Guo, S. Kharkwal, H. Y. Ng, S. F. Y. Li, *J. Power Sources*, 221 (2013) 381
19. M. Lu, S. Kharkwal, H. Y. Ng, S. F. Y. Li, *Biosens. Bioelectron.*, 26 (2011) 4728
20. W. J. Basirun, M. Sookhakian, S. Baradaran, Z. Endut, M. R. Mahmoudian, M. Ebadi, R. Yousefi, H. Ghadimi, S. Ahmed, *Sci. Report.*, 5 (2015) 9108
21. Z. Jovanovic, G. Buică, V. Miskovicstankovic, E. Ungureanu, C. Amarandei, *UPB Scientific Bulletin, Series B*, 75 (2013) 125
22. W. A. Ang, N. Gupta, R. Prasanth, S. Madhavi, *ACS Appl. Mater. Interfaces*, 4 (2012) 7011
23. Q. Li, V. Thangadurai, *Fuel Cells*, 9 (2009) 684
24. C. W. Woon, H. R. Ong, K. F. Chong, K. M. Chan, M. M. R. Khan, *Procedia Chem.*, 16 (2015) 640
25. X.-W. Liu, X.-F. Sun, Y.-X. Huang, G.-P. Sheng, K. Zhou, R. J. Zeng, F. Dong, S.-G. Wang, A.-W. Xu, Z.-H. Tong, *Water Res.*, 44 (2010) 5298
26. C. W. Woon, J. H. Lim, H. R. Ong, M. R. Khan, *Int. J. Mater. Sci. Innov.*, 3 (2015) 33
27. E. Baranitharan, M. R. Khan, D. M. R. Prasad, J. B. Salihon, *Water, Air, Soil Pollut.*, 224 (2013) 1