

Development of a metal oxide cathode catalyst for air-cathode microbial fuel cells

Ravinder Kumar

Faculty of Technology, Universiti Malaysia Pahang (UMP), Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

Lakhveer Singh*

Faculty of Technology, Universiti Malaysia Pahang (UMP), Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

Zularisam A. Wahid

Faculty of Technology, Universiti Malaysia Pahang (UMP), Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

Abstract— Microbial fuel cell (MFC) converts the organic compounds to electricity. The higher cost of the cathode catalyst for oxygen reduction reaction (ORR) is one of the major limitations in the technology. Therefore, the study endeavored to introduce a novel cathode catalyst i.e. porous Co_3O_4 flakes for ORR in MFCs. The flakes exhibited the micropore surface area of $1.0372 \text{ m}^2/\text{g}$. The MFC with cobalt oxide flakes as the cathode catalyst produced a maximum voltage of 670 mV, which was ca. 1.5 times higher than the bare electrode. In addition, the ohmic resistance was reduced ca. 3 times than the control MFC. The flakes showed a higher kinetics ($6.69 \text{ A}/\text{m}^2$) than the bare electrode ($4.49 \text{ A}/\text{m}^2$). The improved activity of the cobalt oxide flakes can be attributed to its porous surface that provided more active sites for the oxygen, consequently, resulted the faster ORR kinetics.

Index Terms— microbial fuel cell, oxygen reduction reaction, Co_3O_4 flakes, electricity generation

I. INTRODUCTION

Microbial fuel cell (MFC) technology has become the most attractive technology for renewable energy production. It converts the organic compounds to electricity using microorganisms as biocatalysts [1]. Oxygen is the most abundant and the cheapest electron acceptor used in the MFCs. However, the slow kinetics for oxygen reduction reaction (ORR) affects the performance of the MFC, consequently, decreases the power output. Moreover, the higher cost of the cathode catalyst (e.g., platinum) for oxygen reduction reaction (ORR) is one of the major limitations of the technology. Some nonprecious metal oxides such as cobalt oxide, manganese oxide, nickel oxide etc. have shown the potential to replace the precious platinum in MFCs [2], [3], [4]. The efficiency of these metal oxides for ORR can be increased by creating more active sites for oxygen on their surface, by developing different porous morphologies. Therefore, the study endeavoured to synthesize a novel, cheap cathode catalyst i.e. microporous cobalt oxide flakes and studied its application for ORR in MFCs. Platinum is the most widely used cathode catalyst for ORR in MFCs. But its rare availability and high cost limit its use at pilot scale applications. However, some fruitful attempts have been already made to replace the platinum that have shown the similar potential to the platinum [3], [4]. In a study, porous carbon nanosheets codoped with nitrogen and sulfur (N/S-CNS) was used as the cathode catalyst in air-cathode MFC. The catalyst showed an exchange current density of $6.6 \text{ A}/\text{m}^2$, which was approximately similar to that obtained with platinum [5]. Moreover, mesoporous nitrogen rich carbon materials as cathode catalyst studied for ORR produced a maximum power density of $979 \text{ mW}/\text{m}^2$, which was only 14 % less than the platinum catalyst [6]. Hence the literature suggests that the efficiency of the cathode catalyst can be further improved to obtain the higher power output in MFCs by developing different porous morphologies.

II. MATERIALS AND METHODS

A. Synthesis of Co_3O_4 flakes and electrochemical characterization

The Co_3O_4 flakes were synthesized by an easy and cost-effective hydrothermal method [7]. The flakes were further characterized by X-ray diffraction (XRD), Field emission scanning electron microscopy (FESEM). The synthesized Co_3O_4 flakes were coated on graphite sheet that was used as the cathode. A digital multimeter (Fluke 17B+) was used to measure the voltage and the current. All the electrochemical studies that is cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) were performed by a potentiostat (Gamry Interface 1000, USA). The ORR kinetics was studied by using Tafel analysis [8].

B. Configuration of MFC

In the study, two MFCs were used for the comparative evaluation of electricity generation. The electrode material used was graphite and employed for both anode and cathode chambers. In both MFCs, same size of electrodes was used. Electrodes were installed at the opposite ends of each other at 7.3 cm apart. The electrode at cathode was coated with 0.5 mg cm^{-2} Co_3O_4 flakes as a catalyst to increase the reduction of oxygen. The culture medium (100 ml) in anodic chamber was 50 mM PBS, added with sodium acetate of 2g/L and further supplemented with small amount of vitamin and minerals. The cathode chamber was filled with only 50 mM PBS (100 ml), was continuously air sparged by aquarium pump. Proton exchange membrane (Nafion 117) was used as connector between anode and cathode containers.

III. RESULTS AND DISCUSSION

The synthesized Co_3O_4 flakes was confirmed by XRD pattern as shown is Fig. 1 (A). The X-ray diffraction patterns of Co_3O_4 nanorods are presented in Fig.1, 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 Fd3m: 2 space group. Moreover, no impurity peaks were observed in the XRD pattern, suggesting the pure form of Co_3O_4 . FESEM images are depicted in Fig. 1 (B). The micropore surface area of the material was evaluated by BET, which was $1.0372 \text{ m}^2/\text{g}$. While the BET surface area was measured $3.1505 \text{ m}^2/\text{g}$. Further, the Co_3O_4 flakes were coated on the graphite sheet and was used the cathode electrode. The MFC performance in this study was evaluated in terms of open circuit voltage (OCV). The OCV was measured with a digital multimeter (Fluke 17 B⁺) after every 30 minutes. The results are shown in the Figure 3. The results showed that the MFC with bare electrode could produce a maximum OCV of 260 mV while the MFC with Co_3O_4 flakes ($0.5 \text{ mg}/\text{cm}^2$) generated a maximum OCV of 670 mV, which was approximately 1.5 times higher than the bare electrode. The enhanced OCV can be attributed to the addition of Co_3O_4 flakes that improved ORR kinetics at the cathode surface.

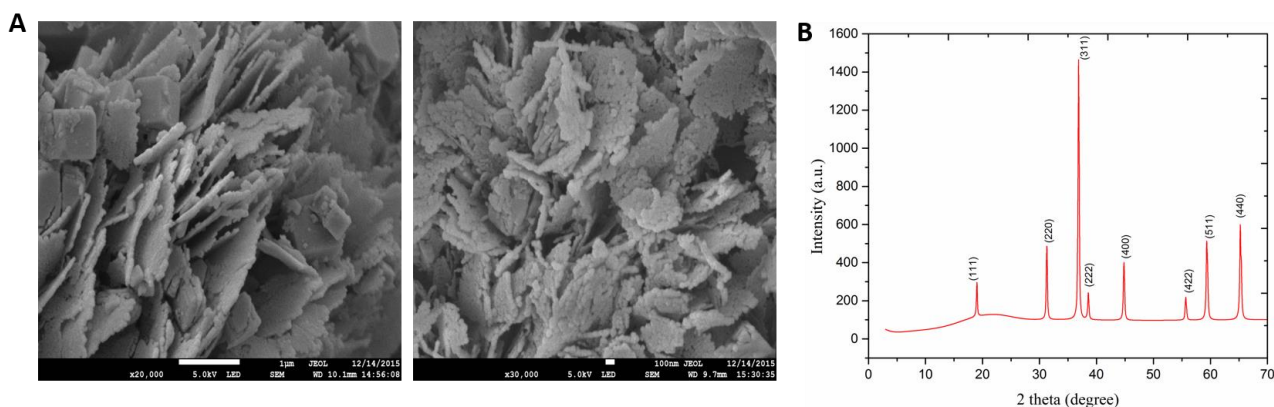


Figure 1. (A) FESEM images of cobalt oxide flakes, (B) XRD pattern of cobalt oxide.

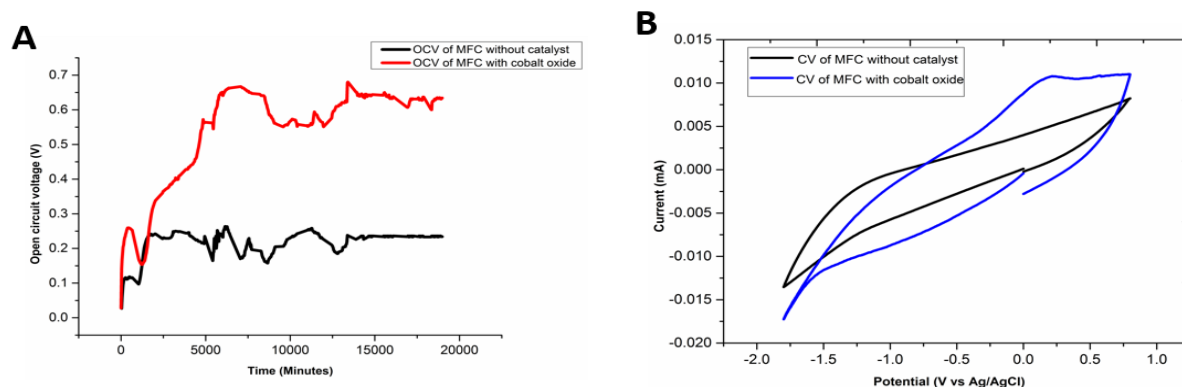


Figure 2. (A) Voltage Production, (B) CV characterization

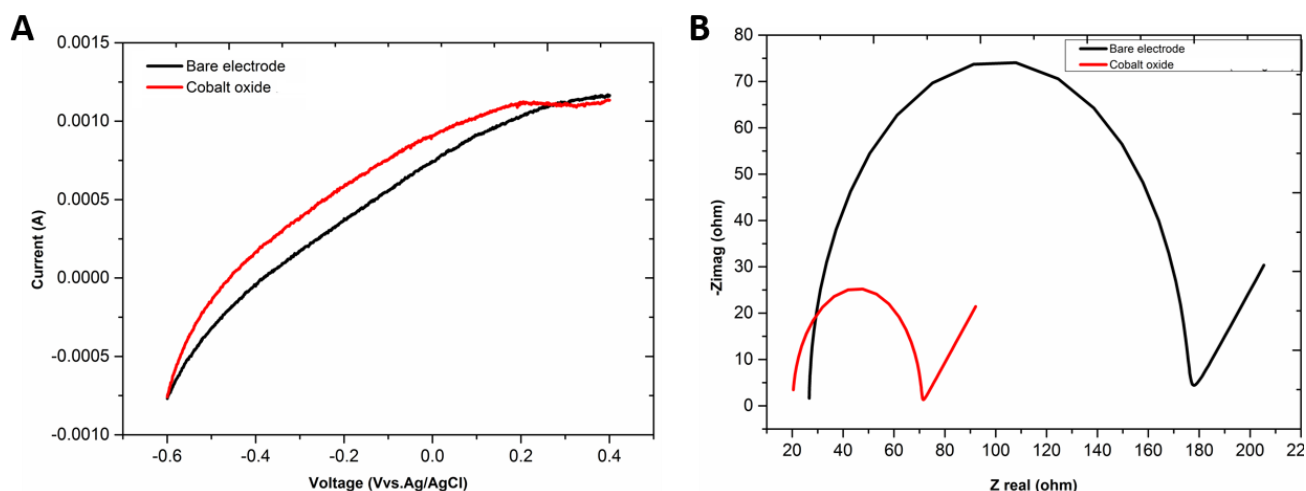


Figure 3. (A) LSV analysis, (B) EIS analysis

Electrochemical impedance spectroscopy (EIS) was used to determine the resistance of the cathode reaction. By fitting the data of the Nyquist plots, the value of each parameter was obtained, as shown in Fig. 3 (B). The addition of Co_3O_4 flakes in the cathode also reduced the ohmic resistance of the MFC from 148.4Ω to 50.2Ω , which was nearly 3 times less than the control MFC. The flakes showed a higher kinetics (6.69 A/m^2) than the bare electrode (4.49 A/m^2), which was also higher than the N/S-CNS that was used in the previous study [9]. The results of Tafel study are depicted in Figure 4. CV analysis was performed to further evaluate the ORR performance of the two cathodes in 50 mM PBS saturated with oxygen. The cyclic voltammetry and linear sweep voltammetry also showed the higher current density for the Co_3O_4 flakes, indicating the enhanced activity of the cathode, as shown in Fig. 2 (B) and Fig. 3 (A) respectively. The improved activity of the cobalt oxide flakes can be attributed to its porous surface that provided more active sites for the oxygen, consequently, resulted the faster ORR kinetics and hence the higher voltage. Therefore, the high efficiency and low price of microporous Co_3O_4 flakes indicate that it can be a competitive catalyst for applications of MFCs.

IV. CONCLUSION

The MFC with cobalt oxide flakes as the cathode catalyst produced a maximum voltage of 670 mV, which was ca. 1.5 times higher than the bare electrode. Moreover, the ohmic resistance was reduced ca. 3 times than the control MFC. The flakes showed a higher kinetics (6.69 A/m^2) than the bare electrode (4.49 A/m^2). The improved activity of the cobalt oxide flakes can be attributed to its porous surface that provided more active sites for the oxygen, consequently, resulted the faster ORR kinetics.

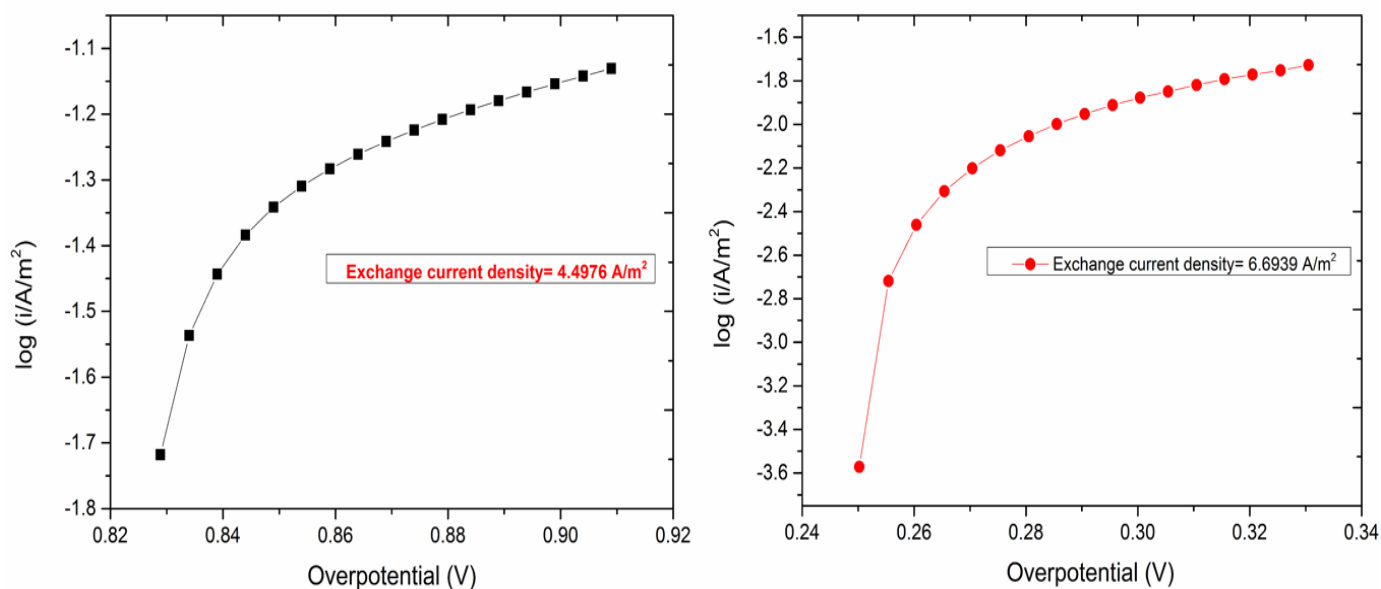


Figure 4. Tafel plot analysis.

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