Mesoporous $\text{Co}_3\text{O}_4$ nanoflakes as an efficient and non-precious cathode catalyst for oxygen reduction reaction in air-cathode microbial fuel cells

Ravinder Kumar, Lakhveer Singh∗, A.W. Zularisam
Faculty of Engineering Technology, Universiti Malaysia Pahang, 26300 Kuantan, Malaysia

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A B S T R A C T
Cobalt oxide is well known for its excellent oxygen reduction reaction (ORR) activity, however, its ORR activity can be further improved by synthesizing its porous architecture. Therefore, mesoporous $\text{Co}_3\text{O}_4$ nanoflakes were prepared by a two-step hydrothermal method and were employed as the cathode catalyst in a double-chamber microbial fuel cell (MFC) to explore its ORR activity for electricity generation. The electrochemical tests suggested that addition of $\text{Co}_3\text{O}_4$ nanoflakes enhanced the electrocatalytic activity of the cathode significantly. Besides, the cathode with a higher concentration of $\text{Co}_3\text{O}_4$ nanoflakes (COF-2) showed faster ORR kinetics as compared to the bare cathode. Evidently, COF-2 achieved an exchange current density of 4.18 mA/cm², which was 3.2 times higher as compared to the bare cathode. Consequently, this improved ORR activity increased the power output in MFC. COF-2 obtained a maximum power density of $347 \pm 7 \text{ mW/m}^2$, which was approximately 8 times higher than the bare cathode. The enhanced ORR activity and improved electric output in the MFC can be attributed to the mesoporous nature of $\text{Co}_3\text{O}_4$ nanoflakes that exposed a higher number of ORR active sites at the cathode surface. Overall, mesoporous $\text{Co}_3\text{O}_4$ nanoflakes proved to be highly efficient and ca. 30 times cheaper than platinum, therefore, can be preferred in large-scale MFC applications over other expensive cathode catalysts.

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1. Introduction

Microbial fuel cell (MFC) is a promising technology that produces electricity from various organic substrates using microorganisms as the biocatalyst [1–3]. However, the technology is facing numerous challenges for its commercialization. One of these challenges is to replace the expensive platinum catalyst by an efficient and cost-effective cathode catalyst for oxygen reduction reaction (ORR) in air-cathode MFCs [4,5]. Platinum is a highly expensive and a rare element on the earth, so its use makes the MFC technology uneconomical and will not be feasible to upscale the technology. Therefore, it is a need of the hour to find a competitive alternative to platinum for commercialization of MFC technology. In this approach, a plethora of non-platinum cathode catalysts (e.g. MnCo$_2$O$_4$ nanoparticles, Spinel (Mn-Co) oxide, MnO$_2$–CNT, Co$_3$O$_4$–CNT) has been experimented for ORR in MFCs that have shown promising results comparable to platinum [6–14]. However, the literature shows that cobalt/cobalt oxide containing cathodes have shown higher ORR activity as compared to other catalysts [15,16], suggesting its significant electrocatalytic properties for oxygen reduction, which could be due to its higher affinity towards oxygen molecules that makes it more favorable for chemisorptions of oxygen molecules onto the catalyst surface [17–19]. Due to this advanced electrocatalytic activity, cobalt or cobalt containing composites have achieved comparable power output to platinum in air-cathode MFCs. For example, an MFC employed with $\text{Co}_3\text{O}_4$/carbon nanotubes as a cathode produced a maximum power density of 469 mW/m², which was competitive with the cathode containing carbon cloth/platinum (603 mW/m²) [20]. Moreover, in an alternative study, nano cobalt oxide anchored on nitrogen-doped graphene was used as cathode catalyst in a single-chambered MFC that generated a maximum power output of 713 mW/m², which was ∼25% more than platinum [6]. The other approach that is widely used to improve the ORR activity of the catalysts is synthesizing the porous structure of metals/metal oxides. The porous nanomaterial provides numerous extra active sites for oxygen reduction that play a key role in enhancing the ORR kinetics of the catalyst [18]. Evidently, such porous catalysts have shown faster ORR rate as compared to other conventional cathode catalysts. For example, recently, porous ortho-hexagon nano spinel $\text{Co}_3\text{O}_4$ showed a maximum exchange current density of 18.86 ($10^{-4} \text{ A/m}^2$), which was ∼2.2 times higher than the non-porous commercial $\text{Co}_3\text{O}_4$ [21].

∗ Corresponding author.
E-mail addresses: lakhveer@ump.edu.my, lucki.chem09@gmail.com (L. Singh).

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