Innovative Cost-Effective Nano-NiCo$_2$O$_4$ Cathode Catalysts for Oxygen Reduction in Air–Cathode Microbial Electrochemical Systems

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Abstract: Microbial electrochemical systems (MESs) can harvest bioelectricity from varieties of organic matter in wastewater through electroactive microorganisms. Oxygen reduction reaction (ORR) in a cathode plays an important role in guaranteeing high power generation, which can be enhanced by cathode catalysts. Herein, the tiny crystalline grain nanocrystal NiCo$_2$O$_4$ is prepared via the economic method and utilized as an effective catalyst in air–cathode MESs. The linear sweep voltammetry results indicate that the current density of 2% nano-NiCo$_2$O$_4$/AC cathode (5.05 A/m$^2$) at 0 V increases by 20% compared to the control (4.21 A/m$^2$). The cyclic voltammetries (CVs) and the electrochemical impedance spectroscopy (EIS) showed that the addition of nano-NiCo$_2$O$_4$ (2%) is efficient in boosting the redox activity. The polarization curves showed that the MESs with 2% nano-NiCo$_2$O$_4$/AC achieved the highest maximum power density (1661 ± 28 mW/m$^2$), which was 1.11 and 1.22 times as much as that of AC and 5% nano-NiCo$_2$O$_4$. Moreover, the adulteration of nano-NiCo$_2$O$_4$ with a content of 2% can not only enable the electrical activity of the electrode to be more stable, but also reduce the cost for the same power generation in MESs. The synthetic nano-NiCo$_2$O$_4$ undoubtedly has great benefits for large-scale MESs in wastewater treatment.

Keywords: advanced green material; nano-NiCo$_2$O$_4$; wastewater treatment; oxygen reduction; green energy conversion

1. Introduction

Microbial electrochemical systems (MESs) are one of the promising green energy conversion technologies that can convert the organic substrates (e.g., organic compounds, organic waste) in wastewater into electrical energy [1]. In MESs, electroactive microorganisms (EAMs) oxidize organic substrates to generate electrons and protons, then the electrons move to the cathode through an external circuit and combine with electron acceptors [2]. Meanwhile, the protons are transported through the membrane and react with oxygen to form a water molecule [3]. In recent years, air–cathode MESs have been widely used because this configuration can gain more electrical energy from oxygen in the air as the electron acceptor without aeration [4]. However, the performance of MESs is significantly limited by poor cathode oxygen reduction reaction (ORR) and high oxygen mass transfer resistance [5]. The electrode materials play an essential role in overcoming these problems [6,7]. Therefore, the research on materials of air–cathode becomes dominant in improving the performance of MESs. Generally, carbon materials such as carbon cloth [8], carbon nanofiber [9], and active carbon (AC) [10] are used as the cathode. Among these, AC is reported to have the advantage of a large surface area (1.2 × 10$^5$ m$^2$/m$^2$ of projected surface area, 0.0026 USD/g) with higher porosity than graphite [11]. Unfortunately, the electrocatalytic activity of these cathodes made of pure carbonaceous materials is still poor when compared with other catalyst-loaded materials, and it cannot satisfy the requirement.
of the four-electron pathway for high power output \cite{12}. Therefore, it is necessary to find a material which can be doped with an activated carbon electrode to generate the similar power of MESs at a similar or lower cost.

Platinum (Pt)-based catalysts are considered the most effective catalysts in MESs because of their high ORR kinetics, but their high cost hinders their practical applications \cite{13}. Thus, it is urgent to find low-cost and durable catalysts with high performance to replace Pt. Some of the catalysts shown in Table S1 have been reported as efficient and active, including transition metal oxides \cite{14}, non-platinum metals \cite{15}, non-metallic elements \cite{16}, and conductive polymers \cite{17}. Among these materials, transition metal compounds have attracted attention because of their excellent catalytic activity toward the ORR. Lv et al. used broccoli-like Co-Ni$_2$P as an ORR catalyst with AC \cite{18}. The maximum power density (MPD) with Co-Ni$_2$P/AC reached 1814 mW/m$^2$, which increased by 98\% compared with the control. Ortiz-Martinez et al. used NiMn$_2$O$_4$ as catalysts, and the power output increased by 80\% \cite{19}. Compared with these transition metal oxides, NiCo$_2$O$_4$ possessed much better electrical conductivity and excellent ORR catalytic activity (Table 1). For example, Ge et al. constructed a NiCo$_2$O$_4$-modified AC air–cathode MFC. MPD of the MFC (1730 ± 14 mW/m$^2$) was 2.28 times that of the bare AC cathode and was similar to the commercial Pt/C because of improvement to the ORR with reduced charger transfer resistance \cite{20}. Although the addition of NiCo$_2$O$_4$ is effective in improving the power generation performance of MES, the amount of NiCo$_2$O$_4$ added in the process of fabricating electrodes has still not been thoroughly investigated, and it is unknown whether an excessive amount of NiCo$_2$O$_4$ will lead to a decrease in the economic efficiency. The cost of the cathode with 15 wt.\% (45.62 mW/USD) NiCo$_2$O$_4$ is 1.2 times higher than that of the cathode with 10 wt.\% NiCo$_2$O$_4$ (55.27 mW/USD). As the addition amount of NiCo$_2$O$_4$ increases, energy consumption and material costs may become negative for large-scale applications. Therefore, it is necessary to determine the ratio of NiCo$_2$O$_4$ to ensure MPD while keeping the cost as low as possible.

Table 1. The published data of the NiCo$_2$O$_4$-modified cathode.

| Configuration | Application          | Cathode Materials                                      | Synthesis Methods       | Power Density (mW/m$^2$) | Ref. |
|---------------|----------------------|--------------------------------------------------------|--------------------------|--------------------------|------|
| Single-chamber MFC | Power generation | Active carbon and nano urchin-like NiCo$_2$O$_4$ | Rolling–press           | 1730                     | [20] |
| Dual-chamber MFC | Power generation | Active carbon and Co$_3$O$_4$ and NiCo$_2$O$_4$ | Electrophoretic deposition | 72                       | [21] |
| Dual-chamber MEC | Biohydrogen production | Nickel foam and NiCo$_2$O$_4$-graphene nanocomposites | Polymer binder           | /                        | [22] |
| Single-chamber MFC | Power generation | Active carbon and Co$_3$O$_4$ and NiCo$_2$O$_4$ | Rolling–press           | 1810                     | [23] |
| Single-chamber MFC | Power generation | Active carbon and NiCo$_2$O$_4$ | Hydrothermal            | 1676                     | [24] |
| Single-chamber MFC | Power generation | Carbon cloth and NiCo$_2$O$_4$ | Electrophoretic deposition | 645                      | [25] |
| Dual-chamber MFC | Power generation | Acetylene black and NiCo$_2$O$_4$ | Hydrothermal and coating | 1250                     | [26] |

In this work, a method with the ultimate goal of economic efficiency was reported to fabricate nanocrystalline NiCo$_2$O$_4$ (<5 nm in diameter), and it was applied as a cathode catalyst in an air–cathode MES. Different concentrations (0, 2%, and 5\%) of nano-NiCo$_2$O$_4$/AC composites were synthesized to optimize cathodes with the high electron transfer and ORR properties. The surface morphology and distribution of nano-NiCo$_2$O$_4$ catalysts were characterized with scanning electron microscopy (SEM) and X-ray diffraction (XRD). The catalytic performance of the synthesized cathodes was investigated by comprehensive electrochemical measurements in bioanode MESs. Finally, the production of the power density per dollar was evaluated.
2. Material and Methods

2.1. Synthesis of nano-NiCo$_2$O$_4$

NiCo$_2$O$_4$ was synthesized in three steps, as described [27]. First, 100 mg of CoCl$_2$•6H$_2$O and 61 mg of Ni(NO$_3$)$_2$•6H$_2$O were dissolved in 20 mL of tertiary butanol, and the solution was added to 20 mL of tertiary butanol containing 250 mg of KOH and ultrasonically dispersed for 2 h. Secondly, the resulting solution was transferred into a 50 mL autoclave and heated at 95 °C for 3 h. After that, the autoclave was cooled to room temperature. Thirdly, the obtained precipitate was centrifuged and washed with water and ethanol. Then, the precipitate was dried at 50 °C overnight. Finally, the above dry product was ground with an agate mortar. Then, the precipitate was calcined in a tube furnace at 300 °C for 3 h under an argon atmosphere, and the final product, nano-NiCo$_2$O$_4$, was obtained.

2.2. Cathode Preparation

The air–cathode, consisting of a 0.5 mm catalysis layer (CL), an electron collector (stainless steel mesh, Type 304N, 60 meshes, Detiannuo Commercial Trade Co. Ltd., Tianjin, China), and a 0.5 mm gas diffusion layer (GDL), was prepared according to the rolling-press procedure reported by our group [28]. The CL was composed of AC (Xinsen Carbon Co. Ltd., Fujian, China) and polytetrafluoroethylene (PTFE) suspension (60 wt.%, Hesen, Shanghai, China) with an AC/PTFE ratio of 6. The GDL was made by rolling a mixture of carbon black (Jinquishi Chemical Co. Ltd., Tianjin, China) and PTFE with a mass ratio of 3:7. For the nano-NiCo$_2$O$_4$-modified cathode, different mass ratios (0, 2 wt.%, 5 wt.%) of nano-NiCo$_2$O$_4$ were added during the stirring of AC and PTFE at 80 °C in a water bath in the preparation of CL. The cathodes were named control, 2% nano-NiCo$_2$O$_4$/AC, and 5% nano-NiCo$_2$O$_4$/AC, respectively.

2.3. MES Construction and Operation

The experiments were performed on dual-chamber reactors (each cylinder chamber was 3 cm in diameter and 4 cm in length, with a net volume of 28 mL and cross-section area of 7 cm$^2$) equipped with different NiCo$_2$O$_4$ proportioned air–cathodes [29]. All reactors were constructed by tightly bolting two cubes made of polymethyl methacrylate together. In addition, the chamber was separated by a cation exchange membrane (Ultrex CMI-7000, Membranes International Inc., Glen Rock, NJ, USA) which had been pretreated in electrolyte overnight before installment. Anodes were made of carbon fiber brushes (3 cm in diameter and 2 cm in length) pretreated with acetone and ethanol and then washed in deionized water [30].

All MESs were inoculated with the effluent from MESs operated for more than two years in our laboratory. The medium contained acetate (1.0 g/L), 50 mM phosphate buffer solution (PBS; NH$_4$Cl 0.31 g/L, KCl 0.13 g/L, NaH$_2$PO$_4$ 2.13 g/L, Na$_2$HPO$_4$ 4.576 g/L), trace mineral (12.5 mL/L), and vitamin solution (5 mL/L) [31]. The medium was continuously bubbled with nitrogen/carbon dioxide gas (V:V, 4:1) for 20 min to remove dissolved oxygen before filling the reactors. All solutions were refreshed when cell voltages were less than 50 mV. Reactors were operated at 25 ± 1 °C in a constant temperature incubator in the air atmosphere, and all experiments were carried out in duplicate.

2.4. Sample Characterization and Electrochemical Measurements

The topography of the sample was examined with a scanning electron microscope (SEM, Shimadzu SS-550, Japan). X-ray diffraction (XRD, D/Max2000, Rigaku, Tokyo, Japan) was used to analyze the synthesized nano-NiCo$_2$O$_4$ powder.

The voltages (V) across the 1000 Ω external resistance were recorded automatically every minute, and the average voltage was collected every 30 min using a data acquisition system (PISO-813, ICP DAS Co., Ltd., China). Cyclic voltammetry (CV) of bioanodes was performed at the scan rate of 1 mV/s over the potential from 0.2 to −0.6 V (stabilization period of 300 s). Linear sweep voltammetry (LSV) was performed in 50 mM fresh PBS at the scan rate of 0.1 mV/s (stabilization period of 300 s) over the potential from 0.3 to −0.2 V.
vs. Ag/AgCl, as described previously [32]. Electrochemical impedance spectroscopy (EIS) was measured at open circuit potential (OCP) over a frequency range of 100 kHz to 0.1 Hz with a sinusoidal excitation signal of 10 mV. All CV, LSV, and EIS analyses were performed using a three-electrode system which was composed of a working electrode (WE), a counter electrode (CE, 1 cm² Pt), and a Ag/AgCl (4.0 M KCl) reference electrode (RE, +198 mV vs. the standard hydrogen electrode). All electrodes were purchased from Aida Hengsheng Technology Co., Ltd., Tianjin, China, and connected to a potentiostat (Autolab PGSTAT 302N, Metrohm, Herisau, Switzerland). The difference was that the WE of CV and EIS was the bioanode, while the WE of LSV was the cathode. Polarization curves were performed with the external resistance varying from 1000 to 50 Ω in MESs as previously described [33].

3. Results and Discussion

3.1. Characterization of NiCo₂O₄ Nanoparticles and Improvement to Cathodes

The XRD technique was used to determine the phase, crystalline, and purity of the samples. The crystal structure of nano-NiCo₂O₄ was observed with XRD measurements within the range of 20°–80°, as shown in Figure 1. The main diffraction peaks could be clearly observed at 2 Theta of 31.1°, 36.7°, 44.6°, 59.1°, 65.0°, and 77.3°, corresponding to the (220), (311), (400), (511), (440), and (533) peaks, respectively, which are similar to the XRD pattern of the cubic spinel NiCo₂O₄ (JCPDS Card: 20-0781) [34,35]. Additionally, no peaks of other compounds were detectable, indicating the pure crystalline grain nanocrystal NiCo₂O₄ was successfully formed.

![Figure 1. X-ray diffraction patterns of NiCo₂O₄.](image)

SEM images were provided to investigate the surface morphology and the distribution of the synthesized catalysts on the electrode. Figure 2a,b show the SEM images of nanocrystal NiCo₂O₄ on the AC air–cathode. The NiCo₂O₄ nanoparticles were uniformly deposited on the surface of the cathode (Figure 2a). These nano-sized composites were reported as efficient in providing more electrochemical activity sites for oxygen access and accelerating the ORR of the electrode [36]. Figure 2c,d provide the SEM images of the AC air–cathode without NiCo₂O₄. In this cathode, AC provided more active sites for the redox reaction of NiCo₂O₄ by increasing the transport properties of ORR-relevant species [24].
The linear sweep voltammetry curves were utilized to evaluate the electrochemical performance and ORR activity of the AC air–cathode with different proportions of NiCo$_2$O$_4$ catalysts. As shown in Figure S1, the NiCo$_2$O$_4$/AC air–cathodes developed a higher current density than the control during the whole scan range. At a potential of 0 V, the current density produced by 5% NiCo$_2$O$_4$/AC (5.08 A/m$^2$) was similar to that produced by 2% NiCo$_2$O$_4$/AC (5.05 A/m$^2$), which showed an increase of 20% compared to the control (4.21 A/m$^2$). These results indicated that the NiCo$_2$O$_4$ modification promoted the ORR of the cathode. In addition, the open circuit potential (OCP) of air–cathodes was in the order of 5% NiCo$_2$O$_4$/AC (0.262 V) > 2% NiCo$_2$O$_4$/AC (0.249 V) > Control (0.225 V). The higher OCP indicated a higher electrochemical activity towards the ORR, indicating the effectiveness of the catalysts [23].

### 3.2. Power Generation Performance of MESs

The bare AC air–cathode, 2% NiCo$_2$O$_4$/AC air–cathode, and 5% NiCo$_2$O$_4$/AC air–cathode were used to assess the performance of power production in MESs. Therefore, it was obvious that the proper introduction of transition metal oxides into the AC cathode were used to assess the performance of power production in MESs. As presented in Figure 3, the formation of biofilm attached to the anode with the increase in voltage during 0–50 h. Although the three MESs with different cathodes did not appear to dramatically affect the time taken for power generation, the values of generated voltage are significantly different. The voltage of the MES with 2% NiCo$_2$O$_4$/AC air–cathode at 50 h was 0.32 V, which was two times that of the control. After 50 h, the biofilm gradually reached maturity with the different voltage outputs. Here, the maximum voltages of AC, 2% NiCo$_2$O$_4$/AC, and 5% NiCo$_2$O$_4$/AC were obtained in all MESs around 225 h with values of 0.57 V, 0.69 V, and 0.58 V, respectively. Compared with bare AC air–cathode MESs, the maximum voltage of the MES with 2% NiCo$_2$O$_4$ increased by 19%. The average voltages of AC, 2% NiCo$_2$O$_4$/AC, and 5% NiCo$_2$O$_4$/AC air–cathode MESs during 5 cycles reached 0.48 ± 0.02 V, 0.61 ± 0.04 V, and 0.40 ± 0.05 V, respectively. It could be observed that the maximum voltage and the average voltages values of AC air–cathode MESs were similar to 5% NiCo$_2$O$_4$/AC air–cathode MESs and significantly lower than 2% NiCo$_2$O$_4$/AC air–cathode MESs.
air–cathode MESs. Therefore, it was obvious that the proper introduction of transition metal oxides into AC cathodes greatly increased the maximum voltages. This phenomenon preliminarily confirmed that the NiCo2O4 as the cathode catalyst improved electrochemical performance and ORR activity to a certain extent compared to bare AC. Although NiCo2O4 had good redox activity, the conductivity of this synthesized material may be lower than AC. Thus, 5% NiCo2O4 in air–cathodes conversely affected the conductive performance and hindered the electron transfer process of MESs, thereby affecting the voltage output.

![Graph](image)

**Figure 3.** The output voltage of MESs with different cathodes.

### 3.3. Electrochemical Characterization of MESs

The cyclic voltammetries (CVs) were performed to provide kinetic information for the heterogeneous electron-transfer reactions [37]. Here, CV analysis was carried out to investigate the performance of EAMs, which could be affected by the ORR activity of the electrodes. Sigmoidal catalytic waves and oxygen reduction peaks were observed in all CVs (Figures 4 and S2), revealing the occurrence of redox processes on the anode. Although the CVs of all the MESs with different cathodes exhibited a similar reduction peak at ~0.267 ± 0.009 V, the reduction current changed with the different NiCo2O4 proportions. The cathode with 2% NiCo2O4 had a higher electroactivity towards the ORR, which could improve the performance of the bioanode. The MES with a 2% NiCo2O4 cathode had the highest maximum current (~8.54 mA), which was 1.16 and 1.30 times that of 5% NiCo2O4 (~7.34 mA) and the control (~6.59 mA). Moreover, at the potential of 0 V, the currents of the MESs with 2% NiCo2O4/AC, 5% NiCo2O4/AC, and control were 5.42 mA, 3.61 mA, and 4.78 mA, respectively, meaning that the proper addition of NiCo2O4 was efficient to boost ORR activity and thus improve the performance of MESs [38]. The addition of NiCo2O4 increased the activity sites for oxygen and accelerated electron transfer at the interface of electrodes [26].

To better investigate the impact of the catalyst on the charge transport of cathodes, the electrochemical impedance spectroscopy (EIS) experiments were conducted after one hour with OCP. Nyquist plots and the corresponding equivalent circuits are shown in Figure 5. The EIS was almost similarly shaped among these three MESs, with a well-defined single semicircle over the high-frequency range. There were few changes in ohmic resistance (R_0) with the value of 13.8 ± 0.2 Ω due to the use of the same reactor, fixed RE, and PBS solution in EIS tests. Differences in total resistance were mainly contributed by the charge transfer resistance (R_p). R_p usually represents the resistance of electrochemical reactions on the electrode [39]. As reported, the smaller the R_p, the faster the rate of electron transfer, which is beneficial to ORR activity [35]. R_p of 5% NiCo2O4/AC was 4.58 Ω, which was 1.7
and 1.8 times as much as that of the control (2.69 Ω), and 2% NiCo₂O₄/AC (2.55 Ω). It has been demonstrated that the smaller the charge transfer resistance (Rₚ), the faster the rate of electron transfer from microorganisms to the anode, which is beneficial to ORR activity, and therefore results in the improvement of current densities [35]. Therefore, the MES with a high proportion of NiCo₂O₄ (5%) could not improve the ORR activity. 

To better investigate the impact of the catalyst on the charge transport of cathodes, the polarization curves were measured. The power density and the polarization curves for the MESs with different cathodic catalysts are illustrated in Figure 6. As shown in Figure 6a, the cathode with bare AC produced an MPD of 1499 ± 36 mW/m², which was close to the former report [32,40], while the MES with 2% NiCo₂O₄/AC obtained the highest MPD (1661 ± 28 mW/m²), 1.11 times as much as that of bare AC. However, the MPD of MESs with 5% NiCo₂O₄/AC was 1364 ± 25 mW/m². The high MPD was related to both anode microbial activity and cathode catalysts with the operation of MESs. The voltage values decreased in all MESs with the increase in the current density. Therefore, the internal resistance of the MESs could be estimated by calculating the slope of the curves. From the linear fitting results, the slopes...
of the different MESs in this study were almost the same (-23.50 ± 1.37) and showed a similar trend in EIS; this could be explained as the cathode with 2% NiCo$_2$O$_4$ enabled more active sites and conductive channels to electron transfer in contact with the electrolyte [26].

![Figure 5](image)

**Figure 5.** Nyquist plots and the equivalent circuit of the control (a), 2% NiCo$_2$O$_4$/AC (b), and 5% NiCo$_2$O$_4$/AC (c).

The individual polarization curve of cathodes and anodes during the operation is shown in Figure 6b. The cathode potentials of 2% NiCo$_2$O$_4$/AC were significantly higher than that of the control, indicating the 2% NiCo$_2$O$_4$/AC exhibited a better catalytic performance and ORR activities in MESs. For example, at a current density of 1.3 A/m$^2$, the cathode potential of 2% NiCo$_2$O$_4$/AC (21.89 mV) was 6.10 times that of the control (3.59 mV). In addition, the anode potentials exhibited almost the same trend, which provided further evidence that the improved performance of MESs was mainly caused by the new cathode.

4. Cost–Benefit Analysis

The low cost plays a determining factor in the application of MESs from lab-scale to large-scale, though some mid-scale MESs are operated [41]. Therefore, the cost–benefit of an MES can be improved using low-cost materials that do not significantly sacrifice performance. Due to the low cost, natural abundance, better electrochemical activity, and
higher conductivity compared with nickel and cobalt oxide, NiCo$_2$O$_4$ has been accepted as a catalyst for electrode modification. Here, the 2% nano-NiCo$_2$O$_4$/AC air-cathodes showed superior electrochemical activities and promising performance. Considering the cost of necessary chemicals and energy (October 2020), 2% nano-NiCo$_2$O$_4$ air-cathodes cost 31 USD/m$^2$, while bare ACs cost 30 USD/m$^2$ [42]. Although the total costs are similar, significant differences are found in power generated per unit cost. The cost of power generation of 2% nano-NiCo$_2$O$_4$ air-cathodes was 106.85 mW/USD, which was 1.11 times as much as that (96.31 mW/USD) of AC air-cathodes. These results indicate that a 2% nano-NiCo$_2$O$_4$/AC air-cathode could be the better alternative for large-scale applications.

5. Conclusions
The highly efficient nanocrystal NiCo$_2$O$_4$ (with a diameter lower than 5 µm) as superior ORR catalysts for air–cathode MESs were synthesized via the economic method. The MPD of the MES with the optimal modifying ratio (2%) of nano-NiCo$_2$O$_4$ was found to be 1.11 and 1.22 times as much as that of bare AC air–cathode MESs and 5% nano-NiCo$_2$O$_4$/AC MESs. The enhancement is mainly attributed to the promotion of electron transfer and reduction in activation energy for the ORR. However, the higher NiCo$_2$O$_4$ addition may hinder the availability of the terminal electron acceptor-oxygen and increase the cost. These results indicate that the new nano-NiCo$_2$O$_4$ catalyst is an affordable and easily prepared cathode catalyst. Meanwhile, the amount of nano-NiCo$_2$O$_4$ catalyst addition needs to be considered comprehensively in preparing electrodes, which is important to reduce the cost and improve the power generation of large-scale MESs.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ijerph191811609/s1. References [12,15,43–52] are cited in the supplementary materials. Figure S1. The linear sweep voltammetry of the cathodes with 0, 2%, and 5% NiCo$_2$O$_4$. Figure S2. Cyclic voltammetry of the cathodes with 0, 2%, 5% NiCo$_2$O$_4$ under 10 mV/s. Table S1. The published data of different photocatalysts and their performance.

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References
1. Wang, X.; Cai, Z.; Zhou, Q.; Zhang, Z.; Chen, C. Bioelectrochemical stimulation of petroleum hydrocarbon degradation in saline soil using U-tube microbial fuel cells. Biotechnol. Bioeng. 2012, 109, 426–433. [CrossRef] [PubMed]
2. Logan, B.E. Exoelectrogenic bacteria that power microbial fuel cells. Nat. Rev. Microbiol. 2009, 7, 375–381. [CrossRef] [PubMed]
3. Rabaey, K.; Verstraete, W. Microbial fuel cells: Novel biotechnology for energy generation. Trends Biotechnol. 2005, 23, 291–298. [CrossRef]
4. Wang, Z.J.; Mahadevan, G.D.; Wu, Y.C.; Zhao, F. Progress of air-breathing cathode in microbial fuel cells. J. Power Sources 2017, 356, 245–255. [CrossRef]
5. Rismani-Yazdi, H.; Carver, S.M.; Christy, A.D.; Tuovinen, I.H. Cathodic limitations in microbial fuel cells: An overview. J. Power Sources 2008, 180, 683–694. [CrossRef]
6. Zhou, M.H.; Chi, M.L.; Luo, J.M.; He, H.H.; Jin, T. An overview of electrode materials in microbial fuel cells. J. Power Sources 2011, 196, 4427–4435. [CrossRef]
7. Tang, J.; Wang, Y.; Zhao, W.; Ye, W.; Zhou, S. Porous hollow carbon tube derived from kapok fibres as efficient metal-free oxygen reduction catalysts. Sci. China-Technol. Sci. 2019, 62, 1710–1718. [CrossRef]
8. Liu, X.; Niu, Y.; Wang, L.; Guo, Q. Treatment of m-Cresol Wastewater in an Anaerobic Fluidized Bed Microbial Fuel Cell Equipped with Different Modified Carbon Cloth Cathodes. Energy Fuels 2020, 34, 10059–10066. [CrossRef]

9. Bosch-Jimenez, F.; Martinez-Crespiera, S.; Amantia, D.; Della Pirriera, M.; Forns, I.; Shechter, R.; Borras, E. Non-precious metal doped carbon nanofiber air-cathode for Microbial Fuel Cells application: Oxygen reduction reaction characterization and long-term validation. Electrochim. Acta 2017, 228, 380–388. [CrossRef]

10. Ren, C.; Li, K.X.; Lv, C.C.; Zhao, Y.; Wang, J.J.; Guo, S. Nanorod CoFe₂O₄ modified activated carbon as an efficient electrocatalyst to improve the performance of air cathode microbial fuel cell. J. Electroanal. Chem. 2019, 840, 134–143. [CrossRef]

11. Zhang, F.; Pant, D.; Logan, B.E. Long-term performance of activated carbon air cathodes with different diffusion layer porosities in microbial fuel cells. Biosens. Bioelectron. 2011, 30, 49–55. [CrossRef]

12. Xin, S.S.; Shen, J.G.; Liu, G.C.; Chen, Q.H.; Xiao, Z.; Zhang, G.D.; Xin, Y.J. Electricity generation and microbial community of single-chamber microbial fuel cells in response to Cu₂O nanoparticles/reduced graphene oxide as cathode catalyst. Chem. Eng. J. 2020, 380, 9. [CrossRef]

13. Ben Liew, K.; Daoud, W.R.W.; Ghasemi, M.; Leong, J.X.; Lim, W.S.; Ismail, M. Non-Pt catalyst as oxygen reduction reaction in microbial fuel cells: A review. Int. J. Hydrog. Energy 2014, 39, 4870–4883. [CrossRef]

14. Zhao, Y.F.; Chen, S.Q.; Sun, B.; Su, D.W.; Huang, X.D.; Liu, H.; Yan, Y.M.; Sun, K.N.; Wang, G.X. Graphene-Co₃O₄ nanocomposite as electrocatalyst with high performance for oxygen evolution reaction. Sci Rep. 2015, 5, 7. [CrossRef] [PubMed]

15. Tiwari, A.K.; Jain, S.; Mungray, A.A.; Mungray, A.K. SnO₂/PANI modified cathode for performance enhancement of air-cathode microbial fuel cell. J. Environ. Chem. Eng. 2020, 8, 8. [CrossRef]

16. Song, Y.E.; Lee, S.; Kim, M.; Na, J.G.; Lee, J.; Lee, J.; Kim, J.R. Metal-free cathodic catalyst with nitrogen- and phosphorus-doped ordered mesoporous carbon (NPOMC) for microbial fuel cells. J. Power Sources 2020, 451, 8. [CrossRef]

17. Papiya, F.; Pattanayak, P.; Kumar, V.; Das, S.; Kundu, P.P. Sulfonated graphene oxide and titanium dioxide coated with nanostructured polyaniline nanocomposites as an efficient cathode catalyst in microbial fuel cells. Mater. Sci. Eng. C Mater. Biol. Appl. 2020, 108, 13. [CrossRef]

18. Lv, C.; Guo, S.; Yang, T.; Li, K. Improvement of oxygen reduction capacity by activated carbon doped with broccoli-like Co-Ni₂P in microbial fuel cells. Chem. Eng. J. 2020, 399, 125601. [CrossRef]

19. Ortiz-Martinez, VM; Touati, K.; Salar-Garcia, M.J.; Hernandez-Fernandez, F.J.; de los Ríos, A.P. Mixed transition metal-manganese oxides as catalysts in MFCs for bioenergy generation from industrial wastewater. Biochem. Eng. J. 2019, 151, 9. [CrossRef]

20. Ge, B.; Li, K.; Fu, Z.; Pu, L.; Zhang, X.; Liu, Z.; Huang, K. The performance of nano urchin-like NiCo₂O₄ modified activated carbon as air cathode for microbial fuel cell. J. Power Sources 2016, 303, 325–332. [CrossRef]

21. Tajid Khajeh, R.; Aber, S.; Zarei, M. Comparison of NiCo₂O₄, CoNiAl-LDH, and CoNiAl-LDH@NiCo₂O₄ performances as ORR catalysts in MFC cathode. Renew. Energy 2020, 154, 1263–1271. [CrossRef]

22. Jayabalan, T.; Manickam, M.; Naina Mohamed, S. NiCo₂O₄-graphene nanocomposites in sugar industry wastewater fed microbial electrolysis cell for enhanced biohydrogen production. Renew. Energy 2020, 154, 1144–1152. [CrossRef]

23. Zhang, S.; Su, W.; Li, K.X.; Liu, D.; Wang, J.J.; Tian, P. Metal organic framework-derived CoO₄/NiO₄ double-shelled nanocage modified activated carbon air-cathode for improving power generation in microbial fuel cell. J. Power Sources 2018, 396, 355–362. [CrossRef]

24. Pu, L.T.; Liu, D.; Li, K.X.; Wang, J.J.; Yang, T.T.; Ge, B.C.; Liu, Z.Q. Carbon-supported binary transition metal chalcogenide used as cathode catalyst for oxygen reduction in microbial fuel cell. Int. J. Hydrog. Energy 2017, 42, 14253–14263. [CrossRef]

25. Cao, C.; Wei, L.; Wang, G.; Shen, J. In-situ growing NiCo₂O₄ nanoplatelets on carbon cloth as binder-free catalyst air-cathode for high-performance microbial fuel cells. Electrochim. Acta 2017, 231, 609–616. [CrossRef]

26. Li, M.; Zhang, H.G.; Xiao, T.F.; Zhang, B.P.; Yan, J.; Chen, D.Y.; Chen, Y.H. Rose flower-like nitrogen-doped NiCo₂O₄/carbon used as cathode electrocatalyst for oxygen reduction in air cathode microbial fuel cell. Electrochim. Acta 2017, 258, 1219–1227. [CrossRef]

27. Wang, L.-l.; Zang, G.-l.; Wang, X.; Zhou, L.-a.; Li, T.; Zhou, Q.-x. Tiny crystalline grain nanocrystal NiCo₂O₄/N-doped graphene composite for efficient oxygen reduction reaction. J. Power Sources 2017, 345, 41–49. [CrossRef]

28. Dong, H.; Yu, H.B.; Wang, X.; Zhou, Q.X.; Feng, J.L. A novel structure of scalable air-cathode without Nafion and Pt by rolling activated carbon and PTFE as catalyst layer in microbial fuel cells. Water Res. 2012, 46, 5777–5787. [CrossRef]

29. Liao, C.M.; Wu, J.L.; Zhou, L.; Li, T.; An, J.K.; Huang, Z.L.; Li, N.; Wang, X. Repeated transfer enriches highly active electrocatalytic microbial consortia on biocathodes in microbial fuel cells. Biosens. Bioelectron. 2018, 121, 118–124. [CrossRef]

30. Wang, X.; Cheng, S.A.; Feng, Y.J.; Merrill, M.D.; Saito, T.; Logan, B.E. Use of Carbon Mesh Anodes and the Effect of Different Pretreatment Methods on Power Production in Microbial Fuel Cells. Environ. Sci. Technol. 2009, 43, 6870–6874. [CrossRef]

31. Li, T.; Zhou, L.A.; Qian, Y.W.; Wang, L.L.; Du, Q.; Li, N.; Wang, X. Gravity settling of planktonic bacteria to anodes enhances current production of microbial fuel cells. Appl. Energy 2017, 198, 261–266. [CrossRef]

32. Wang, X.; Feng, C.J.; Ding, N.; Zhang, Q.R.; Li, N.; Li, X.J.; Zhang, Y.Y.; Zhou, Q.X. Accelerated OH- Transport in Activated Carbon Air Cathode by Modification of Quaternary Ammonium for Microbial Fuel Cells. Environ. Sci. Technol. 2014, 48, 4191–4198. [CrossRef] [PubMed]

33. Zhang, Y.Y.; Wang, X.; Li, X.J.; Gao, N.S.J.; Wan, L.L.; Feng, C.J.; Zhou, Q.X. A novel and high performance activated carbon air-cathode with decreased volume density and catalyst layer invasion for microbial fuel cells. RSC Adv. 2014, 4, 42577–42580. [CrossRef]
34. Huang, W.; Cao, Y.; Chen, Y.; Peng, J.; Lai, X.Y.; Tu, J.C. Fast synthesis of porous NiCo2O4 hollow nanospheres for a high-sensitivity non-enzymatic glucose sensor. *Appl. Surf. Sci.* **2017**, *396*, 804–811. [CrossRef]

35. Xia, W.-Y.; Tan, L.; Li, N.; Li, J.-C.; Lai, S.-H. Nickel cobaltite@nanocarbon hybrid materials as efficient cathode catalyst for oxygen reduction in microbial fuel cells. *J. Mater. Sci.* **2017**, *52*, 7539–7545. [CrossRef]

36. Watson, V.J.; Delgado, C.N.; Logan, B.E. Influence of Chemical and Physical Properties of Activated Carbon Powders on Oxygen Reduction and Microbial Fuel Cell Performance. *Environ. Sci. Technol.* **2013**, *47*, 6704–6710. [CrossRef]

37. Li, T.; Wang, X.; Zhou, Q.; Liao, C.; Zhou, L.; Wan, L.; An, J.; Du, Q.; Li, N.; Ren, Z.J. Swift Acid Rain Sensing by Synergistic Rhizospheric Bioelectrochemical Responses. *ACS Sens.* **2018**, *3*, 1424–1430. [CrossRef]

38. Huang, J.J.; Zhu, N.W.; Yang, T.T.; Zhang, T.P.; Wu, P.X.; Dang, Z. Nickel oxide and carbon nanotube composite (NiO/CNT) as a novel cathode non-precious metal catalyst in microbial fuel cells. *Biosens. Bioelectron.* **2015**, *72*, 332–339. [CrossRef]

39. Aikens, D.A. Electrochemical methods, fundamentals and applications. *J. Chem. Educ.* **2004**, *60*, 669–676.

40. Logan, B.; Cheng, S.; Watson, V.; Estadt, G. Graphite fiber brush anodes for increased power production in air-cathode microbial fuel cells. *Environ. Sci. Technol.* **2007**, *41*, 3341–3346. [CrossRef]

41. He, W.; Wallack, M.J.; Kim, K.-Y.; Zhang, X.; Yang, W.; Zhu, X.; Feng, Y.; Logan, B.E. The effect of flow modes and electrode combinations on the performance of a multiple module microbial fuel cell installed at wastewater treatment plant. *Water Res.* **2016**, *105*, 351–360. [CrossRef] [PubMed]

42. Luo, S.; He, Z. Ni-Coated Carbon Fiber as an Alternative Cathode Electrode Material to Improve Cost Efficiency of Microbial Fuel Cells. *Electrochim. Acta* **2016**, *222*, 338–346. [CrossRef]

43. Bhowmick, G.D.; Das, S.; Adhikary, K.; Ghungekar, M.M.; Mitra, A. Using rhodium as a cathode catalyst for enhancing performance of microbial fuel cell. *Int. J. Hydrog. Energy* **2019**, *44*, 22218–22222. [CrossRef]

44. Yuan, Y.; Zhou, S.G.; Zhuang, L. Polypyrrole/carbon black composite as a novel oxygen reduction catalyst for microbial fuel cells. *J. Power Sources* **2010**, *195*, 3490–3493. [CrossRef]

45. Yuan, Y.; Ahmed, J.; Kim, S. Polyaniline/carbon black composite-supported iron phthalocyanine as an oxygen reduction catalyst for microbial fuel cells. *J. Power Sources* **2011**, *196*, 1103–1106. [CrossRef]

46. Li, M.; Zhou, S.Q. alpha-Fe2O3/polyaniline nanocomposites as an effective catalyst for improving the electrochemical performance of microbial fuel cell. *Chem. Eng. J.* **2018**, *339*, 539–546. [CrossRef]

47. Yang, T.; Li, K.; Pu, L.; Liu, Z.; Ge, B.; Pan, Y.; Liu, Y. Hollow-spherical Co/N-C nanoparticle as an efficient electrocatalyst used in air cathode microbial fuel cell. *Biosens. Bioelectron.* **2016**, *86*, 129–134. [CrossRef]

48. Ma, M.; You, S.; Gong, X.; Dai, Y.; Zou, J.; Fu, H. Silver/iron oxide/graphitic carbon composites as bacteriostatic catalysts for enhancing oxygen reduction in microbial fuel cells. *J. Power Sources* **2015**, *283*, 74–83. [CrossRef]

49. Noori, M.T.; Mukherjee, C.K.; Ghungekar, M.M. Enhancing performance of microbial fuel cell by using graphene supported V2O5-nanorod catalytic cathode. *Electrochim. Acta* **2017**, *228*, 513–521. [CrossRef]

50. Cao, C.; Wei, L.; Su, M.; Wang, G.; Shen, J. Enhanced power generation using nano cobalt oxide anchored nitrogen-decorated reduced graphene oxide as a high-performance air-cathode electrocatalyst in biofuel cells. *RSC Adv.* **2016**, *6*, 52556–52563. [CrossRef]

51. Zhou, Q.; Ma, S.; Zhan, S. Superior photocatalytic disinfection of Ag-3D ordered mesoporous CeO2 under visible light condition. *Appl. Catal. B Environ.* **2018**, *224*, 27–37. [CrossRef]

52. Huang, Q.S.; Zhou, P.J.; Yang, H.; Zhu, L.L.; Wu, H.Y. In situ generation of inverse spinel CoFe2O4 nanoparticles onto nitrogen-doped activated carbon for an effective cathode electrocatalyst of microbial fuel cells. *Chem. Eng. J.* **2017**, *325*, 466–473. [CrossRef]