

Direct synthesis of nanomaterials on carbon microfibre electrode material for superior electrocatalysis in lake sediment microbial fuel cells

Maheshi Somasiri^a, Tanusha Amandani^b, Charitha Basnayaka^a, Ahmed Ahsan^a,
Gayani P Dilangani^b, Ajith C. Herath^b, Sampath Bandara^c, Godfrey Kyazze^{c,d}, Eustace
Y. Fernando^{a,e,*}

^a Department of Biology, Faculty of Applied Sciences, Rajarata University, Mihintale 50300, Sri Lanka

^b Department of Chemistry, Faculty of Applied Sciences, Rajarata University, Mihintale 50300, Sri Lanka

^c Faculty of Technology, Rajarata University, Mihintale 50300, Sri Lanka

^d University of Westminster, School of Life Sciences, 115 New Cavendish Street, London GB. W1W 6UW, UK

^e Stevens Institute of Technology, Charles V. Schaefer, Jr. School of Engineering and Science, Department of Civil, Environmental and Ocean Engineering, Hoboken, New Jersey 07030, United States

ARTICLE INFO

Keywords:

Sediment MFC

Carbon-microfiber electrode

Nanomaterial-modification

Electrochemical performance

ABSTRACT

The use of novel and inexpensive catalysts as replacements for platinum is desirable. In this study, we demonstrate for the first time that cost-effective metal oxide nanomaterials and the conductive polymer polyaniline (PANI) can be directly chemically synthesized on carbon microfiber electrodes to improve the performance of lake sediment inoculated MFCs. Nanomaterial of MnO₂, MnO₂/polyaniline (PANI), ZnO/NiO and ZnO/NiO/PANI attachments were directly chemically synthesized on the carbon material and used as cathode electrodes. The maximum power densities recorded for the different treatments were; MnO₂ 78.5 mW/m², MnO₂/PANI (Polyaniline) 141.6 mW/m², ZnO/NiO 67.6 mW/m², and ZnO/NiO/PANI 129.4 mW/m². Current and power densities were more than six-fold higher in ZnO/NiO/PANI and MnO₂/PANI nanoparticle modified cathodes compared to the control MFCs with no catalyst and more than 2.5 fold higher compared to Pt loaded conventional cathodes. In-excess of 50-fold reductions in catalyst application costs to obtain a unit amount of power was demonstrated with the novel nanomaterials direct deposition method when compared to traditional catalysts such as Pt. This study demonstrates that nanomaterials-incorporated carbon microfiber cathodes bring about significant enhancements to power densities and may potentially have applications in cost-effective MFCs.

1. Introduction

The energy needs cannot be sustained solely by fossil fuels at the end of the 21st century as they are not substantial enough and pose environmental problems such as contributing to global warming and climate change. Microbial fuel cells (MFCs) have emerged in recent years as a promising technology for renewable alternative energy and wastewater treatment [1,2]. Simply, MFCs employ microorganisms as biocatalysts to oxidize organic materials and transmit electrons to the anodic surface via substrate oxidation for bioelectricity production [3]. Genera such as *Pseudomonas*, *Rhodopseudomonas*, and *Clostridium* are involved in extracellular electron transfer (EET) pathways and some do not directly transfer electrons to the anode [4]. Identifying the limiting parameters in an MFC system is crucial for improving MFC performance. An MFC's

power output is limited by internal resistance, which includes anode resistance, cathode resistance, electrolyte resistance, and (if present) membrane resistance [5]. Internal resistance can be lowered by increasing the anode surface area, cathode surface area, proton exchange membrane surface area, electrolyte ionic strength, or pH [6].

The cathodic overpotential of oxygen reduction reaction (ORR) at MFC cathode-based graphite is a limiting factor for the technology's widespread development. The cathode performance can be improved in two ways, either by using a catalyst to reduce the activation energy or by increasing the specific surface area of the graphite material [7,8]. Currently, available ORR catalyst materials such as platinum or palladium powder are expensive and decrease the practical applicability of MFC systems [9,10].

Many studies have indicated a boost in ORR rates using novel and

* Corresponding author.

E-mail address: efernand3@stevens.edu (E.Y. Fernando).

<https://doi.org/10.1016/j.nexus.2024.100280>

Received 19 October 2023; Received in revised form 4 January 2024; Accepted 23 February 2024

Available online 24 February 2024

2772-4271/© 2024 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

inexpensive catalysts. Iron-based platinum group metal-free catalysts synthesized from novel and low-cost organic precursors demonstrate remarkable performance yielding a power density significantly higher than that of platinum (Pt) for the oxygen reduction reaction (ORR) [11]. Apart from catalysts, some other researchers have also employed non-catalyzed three-dimensional graphite in cathode fabrication, such as cloth, felt, sponge, or granules [12,13].

Carbon fiber fabrics enable 3D integration of electrode material in reactors, enhancing fuel mass transfer and mediator diffusion due to their porous features. Additionally, larger pores or channel diameters of 3D carbon materials allow bacterial cell penetration, generating interest among MFC anode researchers.

Over the past few years, there has been considerable research focused on metal oxide semiconductors, including MnO_2 , V_2O_5 , NiO , and CuO , as promising electrode materials [14]. This interest stems from their ability to exhibit multiple oxidation states, which proves highly beneficial in facilitating rapid redox reactions at the interfaces between the electrodes and the electrolyte [15].

MnO_2 is the most popular and extensively researched metal oxide semiconductor electrode material for electrochemical systems. Its widespread popularity can be attributed to its low cost, high activity, and non-toxicity. However, MnO_2 has some limitations that prevent it from being used optimally as an electrode material in a variety of applications. Specifically, its low electrical conductivity and susceptibility to instability in high proton-conducting environments are the primary drawbacks that need to be addressed to fully leverage its potential [16, 17]. These drawbacks can be enhanced by the fabrication of various MnO_2 /conductive matrix hybrid like C/ MnO_2 nanomaterials.

To enhance the performance of MnO_2 , numerous endeavors have been undertaken to combine it with various carbonaceous materials, including graphene [18], graphene oxide [19], carbon nanotubes [20], activated carbon [21], and conducting polymers [22,23]. Among these, conducting polymers like polyaniline (PANI) and polypyrrole have emerged as promising candidates for modifying MnO_2 nanocomposites due to their ability to significantly improve conductivity [24]. These recent developments mark significant strides in achieving higher efficiency and better overall performance for MnO_2 -based systems.

Among the plethora of conducting polymers, polyaniline (PANI) emerges as a highly promising choice for enhancing the overall electrode conductivity. Its merits include exceptional electrical conductivity, an impressive theoretical capacitance of 2000 Fg^{-1} [25], remarkable environmental stability, facile synthesis, controllable doping/dedoping chemistry, and reversible electrical properties facilitated by controlled charge transfer processes. These advantageous attributes make PANI an attractive candidate for optimizing the performance of electrodes in various applications.

The diverse range of morphologies and nanoscale structural features observed in PANI- MnO_2 composites has become particularly appealing due to their ability to enhance the effective surface area, improve charge accessibility on the electrode surface, and offer shorter diffusion paths for ions [26]. These combined effects contribute to a remarkable enhancement in charge/discharge rates, making these composite electrodes highly promising for a wide range of applications.

The use of nanomaterials and nanotechnology has revolutionized the fabrication of components in microbial fuel cells (MFCs), leading to improved performance in electron conductivity, power density, cost, thermal stability, and catalysis of ORR rate. Notably, modification of MFC electrodes (anode and cathode) with nanomaterials has a critical impact on overall MFC performance, enhancing bioenergy production. Examples of nanomaterials used for electrode modification in MFCs include metal nanoparticles and metal oxides (such as CeO_2 , TiO_2 , ZnO , SiO_2 , Al_2O_3 , and MnO_2) [27].

This study was designed to test how the nanomaterial-modified carbon microfiber electrode material can enhance the performance of lake sediment inoculated microbial fuel cells by enhancing the ORR at the cathodic component of the cells. The primary objective of the study

was to fabricate various nanoparticle-embedded carbon microfiber electrodes by using the techniques of direct electro-synthesis and electro-deposition and to conduct a comparative study into the electrochemical performance of these novel nanoparticle-embedded electrode constructs when used in two-chamber MFCs. Of particular interest was the performance of these novel materials was their capability and efficiency of catalyzing ORR reactions in MFCs.

2. Materials and methods

2.1. Construction of a chambered microbial fuel cell

The MFC system was constructed as shown in Fig. 1 using a cast acrylic sheet. Three cells were constructed, one as the control and the other two as the replicates.

2.1.1. Anode and cathode chambers

Both the anode and cathode chambers were roughly 300 cm^3 in capacity and were separated by a Nafion 212 Proton Exchange membrane. To maintain the anode chamber anaerobically, it was sealed with an airtight sealer, clay, or Silicon. To maintain the cathode chamber aerated, oxygen was supplied by an air pump at a constant flow rate of 0.5 L/min .

To maintain the cells aerated, oxygen was delivered to the cathode chambers of all cells using an air pump with a constant flow rate of 0.5 L/min .

2.1.2. Pretreatment of Nafion 212 proton exchange membrane

The Nafion 212 proton exchange membrane was first immersed in 3 % H_2O_2 , then in deionized or distilled water for two hours (2 h), and then in 0.5 M sulfuric acid for another hour. All the solutions were approximately 80°C , and the membrane was rinsed in deionized water before and after each step. To keep it from shriveling, it was kept in deionized water until it was put into the cell.

2.1.3. Electrodes

Electrodes were connected externally by insulated copper wire, with resistors (10Ω to $10,000 \Omega$) in-between. A programmable data logging Voltmeter (PicoLog™ 1012, Pico Technology, UK) was attached parallelly to the respective resistor.

2.1.4. Media of each MFC chamber

In the anode chamber, 250 cm^3 of Semi defined minimal media (Glucose/ acetate as carbon source) was added. Semi-defined media contain Glucose or acetate 2 g/L , NH_4Cl 0.46 g/L , yeast extract 0.1 g/L , peptone 0.5 g/L , K_2HPO_4 5.05 g/L , KH_2PO_4 2.84 g/L .

In the cathode chamber, 50 mmol/dm^3 phosphate buffer with pH 7 (K_2HPO_4 5.05 g/L and KH_2PO_4 2.84 g/L) was used.

2.1.5. Sample collection

Pankulama Lake (8.6264915, 81.0407939), Morawawa, North Central Province, Sri Lanka, was used to gather lake sediment samples. Water-logged locations with dark/black color sediments due to the presence of pyrite deposition and a strong sulfide smell were carefully chosen for sampling because they are a good source of exoelectrogens (especially those that can reduce manganese and iron oxides) [28]. Sediment samples were collected into 50 ml Sample collecting tubes and immediately sealed and kept at room temperature until they were used in MFC experiments.

2.1.6. Microbial inoculum

Approximately 250 cm^3 of semi-defined minimal media with a glucose solution of 2 g/L was added to the anode chamber. Glucose 2 g/L , NH_4Cl 0.46 g/L , Yeast extract 0.1 g/L , Peptone 0.5 g/L , K_2HPO_4 5.05 g/L , KH_2PO_4 2.84 g/L make up the anode solution. The salt solution and glucose solution were autoclaved separately for 20 min at 121°C and 15

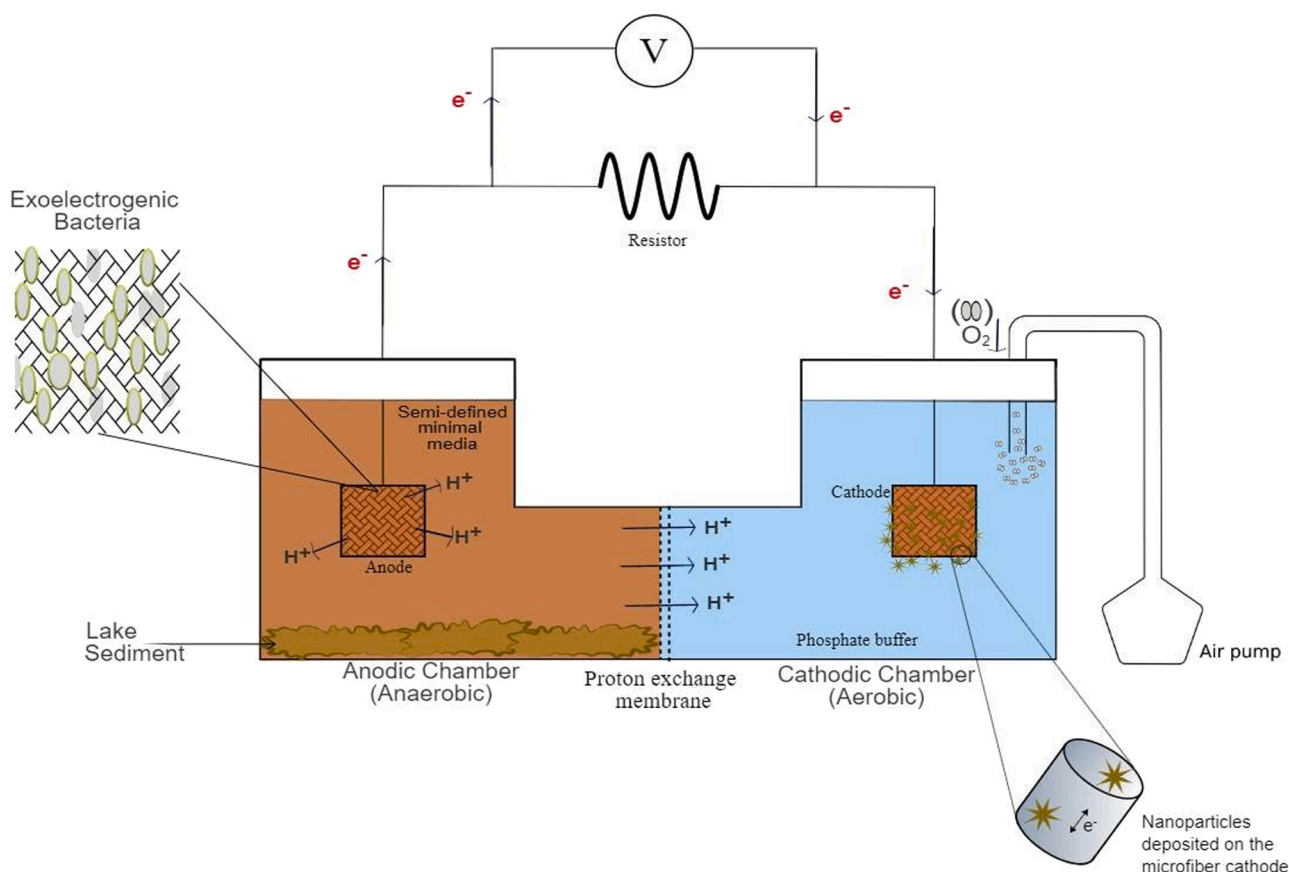


Fig. 1. Schematic diagram of the two chamber MFC system with nanomaterials deposited woven microfiber cathode.

psi and added later in the anode compartment. The anode compartment was sealed airtight with silicon glue after the addition of approximately 5 g of sediment sample and 200 cm³ of semi-defined media to maintain an anaerobic environment for exoelectrogens.

A Non-treated CMM was used as the electrode of the anode in all the experiments.

2.1.7. Batch operation of the MFC

After filling the anode chamber with sediment and the semi-defined minimal medium, it was operated in batch mode with intermittent substrate feeding. After 2–3 days, when the output voltages had stabilized, approximately 30 % of the anode volume was replenished with fresh semi-defined media containing glucose as the exogenous feeding substrate. The final glucose concentration at the beginning of each batch cycle was 2 g/L.

2.2. Preparation and modification of electrodes

The carbon microfiber material (CMM) was obtained from Carbon Energy WT (Taiwan) as a custom-fabricated woven carbon material for electrode construction. The carbon microfiber material had an average fiber diameter of $8 \pm 0.5 \mu\text{m}$ as per the manufacturer's data. Each woven carbon microfiber electrode was approximately 4 mm thick and had 5 cm X 5 cm in width and length dimensions [29].

2.2.1. Base treatment of electrodes

Base-treated CMM electrodes were prepared by submerging a 5×5 cm CMM electrode into KOH (3 M) solutions and heating at 85 °C for six hours (6 h). After the solutions cooled down to room temperature, the CMM electrode was soaked in an alkaline solution for twenty-four hours (24 h) and was rinsed in deionized water three times. Finally, the CMM electrode was air-dried for twelve hours (12 h) [30].

2.2.2. Acid treatment of electrodes

Acid-treated CMM electrodes were prepared by submerging a piece of CMM electrode into HNO₃ (5.6 M) solutions and heating at 85 °C for six hours (6 h). After the solutions cooled down to room temperature, CMM was soaked in an acidic solution for twenty-four hours (24 h) and rinsed in deionized water three times. Finally, the CMM electrode was dried in a vacuum drier for twelve hours (12 h) [30].

2.2.3. Nanomaterial modification of electrodes

2.2.3.1. Pre-treatment of the electrode material. The untreated carbon microfiber electrode material was cut into 5 cmx5 cm dimensions and was dipped in a 1 M sulfuric acid solution and sonicated for 15 min. It was then sonicated again after dipping it in an acetone solution for 15 min. And finally, it was sonicated again in distilled water for 15 min. It was then air-dried for twenty-four hours (24 h).

2.2.3.2. Electrodeposition of polyaniline (PANI) on the electrodes. To prepare PANI, 0.1 M double distilled aniline was added dropwise to 100 ml of 1 M HCl until it reached a pH of 1.5. The deep green color of polyaniline was formed by a chemical oxidation process.

An electrochemical study was conducted using Scanning Electrochemical Microscope (CH instruments (Austin, TX, USA). Cyclic voltammetry Programme with a standard three electrode configurations. A modified CMM electrode (m-CMM) (2.2.3.1) (working area 5 cm × 5 cm) was used as the working electrode, platinum (Pt) was used as a counter electrode, with an Ag|AgCl (KCl 0.1 molar) reference electrode completing the cell assembly. Above mentioned electrodes were placed horizontally in 10 mL glass container with formed PANI and connected them with Scanning Electrochemical Microscope instrument by connecting appropriate connecting wires. Then cyclic voltammetry

Programme was chosen from the software for the run. After the m-CMM electrode became coated with PANI it was washed with distilled water and air-dried for 24 h at ambient temperature.

2.2.3.3. Direct synthesis of manganese oxide (MnO_2) nanoparticles on the CMM electrodes. A 100 ml solution of equal volumes of 0.1 M Sodium Sulphate (Na_2SO_4) and 0.1 M Potassium permanganate (KMnO_4) was prepared. m-CMM electrode was dipped in this solution for 6 h. Then it was kept at room temperature until it was completely dry. After deposition, this electrode was washed with distilled water to eliminate any loosely attached chemical substances.

2.2.3.4. Direct deposition of MnO_2 nanoparticles on a PANI-deposited CMM electrode. An m-CMM electrode (2.2.3.1) which was treated with PANI as mentioned in Section 2.2.3.2 was treated with direct deposition of MnO_2 nanoparticles as mentioned in Section 2.2.3.3.

2.2.3.5. Direct deposition of zinc oxide (ZnO) nanoparticles on m-CMM electrodes. m-CMM electrode was dipped in a 100 ml of equal volumes of 3 mM Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), 7 mM Urea ($\text{CO}(\text{NH}_2)_2$) and Nickel sulfate ($\text{NiSO}_4(\text{H}_2\text{O})_6$) solution in a crucible. It was kept under 180°C for 2 h and then under 360°C for 1 hour. It was then washed with distilled water to eliminate any loosely attached chemical substances.

2.2.3.6. Direct deposition of zinc oxide (ZnO) and nickel oxide (NiO) nanoparticles on m-CMM/PANI electrodes. m-CMM/PANI electrode was dipped in a 100 ml of equal volumes of 3 mM Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), 7 mM Urea ($\text{CO}(\text{NH}_2)_2$) and Nickel sulfate ($\text{NiSO}_4(\text{H}_2\text{O})_6$) solution in a crucible. It was kept under 180°C for 2 h and then under 360°C for 1 hour. It was then washed with distilled water to eliminate any loosely attached chemical substances.

2.3. MFC performance characterization

The voltage across the resistance was measured using a PicoLog 1020 (Pico Technology, UK) data logging system. Different resistances were connected ranging from 22Ω to $10,000,000\Omega$ and the current flowing through each resistance was calculated using the equation $I = E/R$ (where, I – current, E – voltage and R – resistance). The power dissipated across each resistance was calculated using $P = IE$ (where, P – Power, E – voltage and I – current). The power dissipated across the resistance was normalized to the area of the electrode (25 cm^2). The electrochemical performance of each MFC experiment was analyzed using polarization curves and power-current plots. In the control MFC system, a non-treated CMM electrode with a $5\text{ cm} \times 5\text{ cm}$ surface area was used as an electrode in both the cathode and anode. Additional control MFC with a cathode containing a Pt loading of 0.5 mg cm^2 was also used for comparison.

2.4. Cyclic voltammetry (CV) to investigate the performance of electrodes

Before initiating the Cyclic Voltammetry apparatus (CH Instruments, Inc., USA), the counter and reference electrodes were gently washed with deionized water. The electrochemical cell was prepared by assembling the working electrode, reference electrode, and counter electrode according to the experimental setup. The working electrode is the Nanomaterial modified electrode, and the reference electrode and the counter electrode are $\text{Ag}|\text{AgCl}$ and platinum (Pt) respectively.

The phosphate buffer was used as the electrolyte, and a sweep rate of 50 mV/s was used in all CV experiments. The potential range was determined by running a few cycles. Then the CV experiment was performed, and the CV curves were obtained.

2.5. Scanning electron microscopy (SEM) analysis of functionalized microfiber electrode surfaces

Woven carbon Microfiber material samples after chemical treatments and after introducing them to the MFC were imaged for SEM on a Carl Zeiss EVO 18 (Germany) scanning electron microscope with an optical magnification range of $20\text{--}135\times$, electron magnification range of $5\times\text{--}1,000,000\times$, maximal digital zoom of $12\times$, acceleration voltage of 10 kV , equipped with secondary electron (SE) and energy dispersive X-ray spectrometer (EDS) detectors, with a nominal resolution of 10 nm or less. The microscope had a temperature-controlled sample holder (temperature range -25°C to 50°C).

2.6. Fourier transform infrared spectroscopy (FTIR) analysis of functionalized cathodes

FTIR was used to examine chemical functionalization on pretreated electrodes [31]. Dried cathode fragments were extracted from acid and base pretreated electrode MFC experiments and examined with an FTIR spectrometer (Shamadz, UK, National Institute for Fundamental Studies, Sri Lanka). Fully dried samples were put on the instrument analysis pedestal, and transmittance spectra in the mid-IR region (400 cm^{-1} – 4000 cm^{-1}) were acquired [28].

3. Results and discussion

3.1. MFC performance characterization

Polarization curves were obtained by recording the voltage via varying the external resistance from 22Ω to $1\text{ M}\Omega$ when MFC voltages across the set external resistance stabilized at the maximum steady value after substrate feeding cycles. Fig. 3(B) indicates the power density of each experiment incorporating different nanomaterials in the cathode, acid/alkali pretreated cathodes and the controls (non-treated electrode and Pt loaded). Polarization curves of all the treatments indicated notable enhancements to the electrochemical performances of the MFC systems in terms of maximum power density (P_{max}) and current density (J_{max}) values, when compared to the non-treated control MFC systems. The maximum current, power production, and open circuit voltage obtained in each MFC with respective treatments are given in Table 1.

The polarization curves and power-current plots of the MFC experiments clearly demonstrate that the nanoparticle loading on carbon electrodes makes a significant improvement on the electrochemical performance of all MFCs tested. In particular, PANI+ MnO_2 and PANI+ ZnO/NiO nanoparticle-loaded carbon microfiber electrodes demonstrated a significant enhancement of their electrochemical performances over the non-treated carbon control electrodes, Pt-loaded control electrodes and KOH/acid-treated electrodes containing MFC systems (Fig. 3A and 3B).

A direct comparison of the power and current densities of the control (untreated) electrode materials suggests that treatment of the electrode materials aids in increasing ORR catalysis. All other treatments tested showed significant increases in both power and current densities when compared to the control (Fig. 4). As a result, MFC with MnO_2/PANI treated electrode achieved the highest power density of $141.6 \pm 22.06\text{ mW/m}^2$, which is 7-fold higher than the control ($20.96 \pm 6.54\text{ mW/m}^2$) with no treatment. PANI+ MnO_2 and PANI+ ZnO/NiO nanoparticle incorporated electrodes also demonstrated more than 2-fold increases in power and current densities when compared to Pt loaded control MFC experiments.

The findings of this study demonstrated that notably high-power densities can be obtained using metal oxides/polyaniline nanoparticles incorporated woven carbon microfiber cathodes devoid of noble metal catalysts such as platinum powder. PANI+ MnO_2 and PANI+ ZnO/NiO nanoparticle incorporated electrodes also demonstrated that they can produce sufficient current and voltage to power small low-voltage

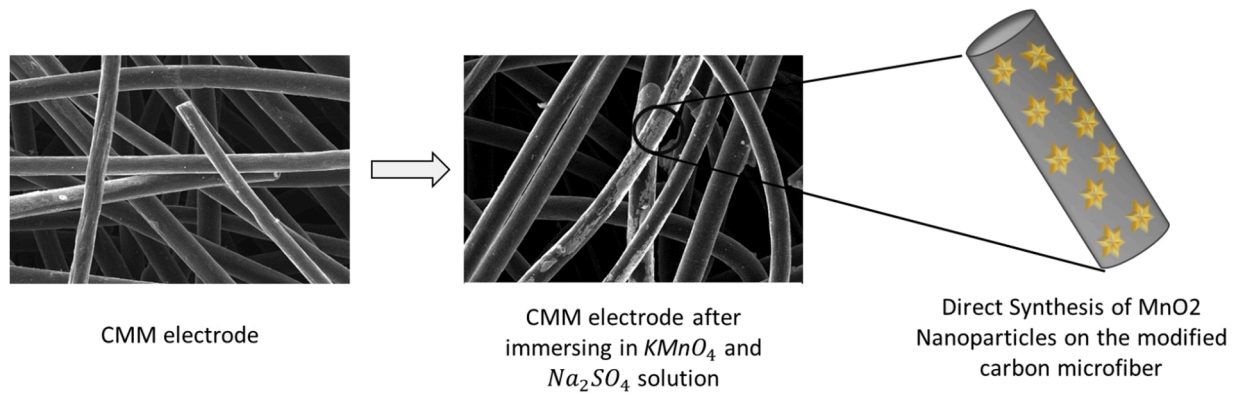


Fig. 2. Graphical representation of direct synthesis of Manganese oxide nanoparticles on the carbon microfiber material electrode.

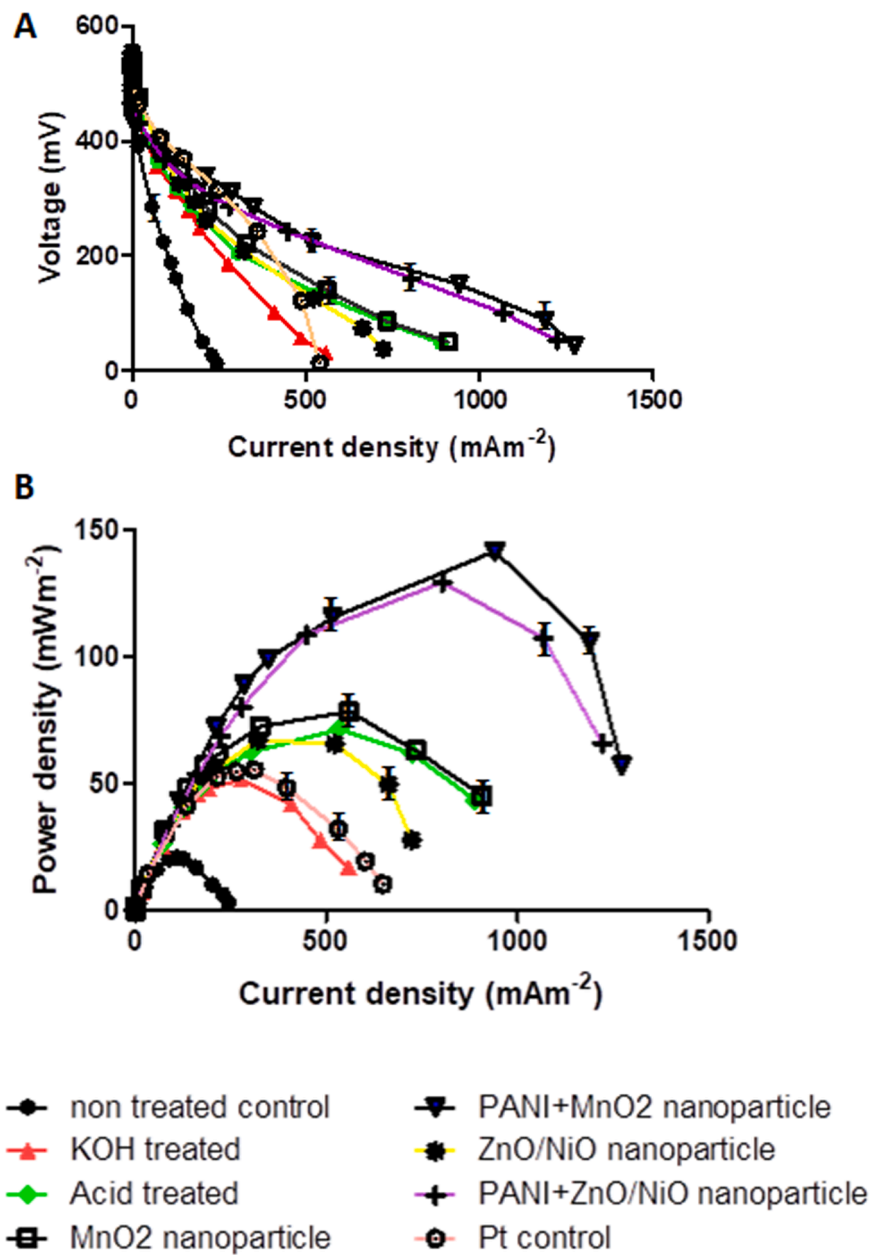


Fig. 3. (A) Polarization plots of MFCs with different treated Carbon microfiber material electrodes as cathode and (B) Power-Current plots of MFCs with different, treated Carbon microfiber material electrodes as cathode.

Table 1

Maximum current density ($J_{\max}$), maximum power density ($P_{\max}$), and open circuit voltages recorded in MFCs with each treated carbon microfiber material electrode used as the cathode.

Treatment	Maximum current density (mA/m ²)	Maximum Power density (mW/m ²)	Maximum open circuit voltage (mV)
Non treated Cathode	244.30 ± 72.78	20.96 ± 6.54	509.3 ± 90.07
KOH treated Cathode	557.58 ± 106.58	31.7 ± 8.34	513.4 ± 37.28
Acid treated Cathode	889.7 ± 158.5	41.4 ± 6.4	503.1 ± 21.5
Zinc nanoparticle treated Cathode	724.1 ± 45.47	67.6 ± 1.50	573.8 ± 24.72
Zinc oxide+ Nickel oxide nanoparticle + Polyaniline treated Cathode	1222.7 ± 196.56	129.4 ± 7.34	502.3 ± 12.57
Manganese nanoparticle treated Cathode	908.6 ± 172.16	78.5 ± 5.08	538.7 ± 27.78
Manganese oxide nanoparticle+ Polyaniline treated Cathode	1272.7 ± 156.93	141.6 ± 22.06	456.9 ± 80.54
Pt loaded control	642.1 ± 39.3	54.3 ± 12.2	497.2 ± 44

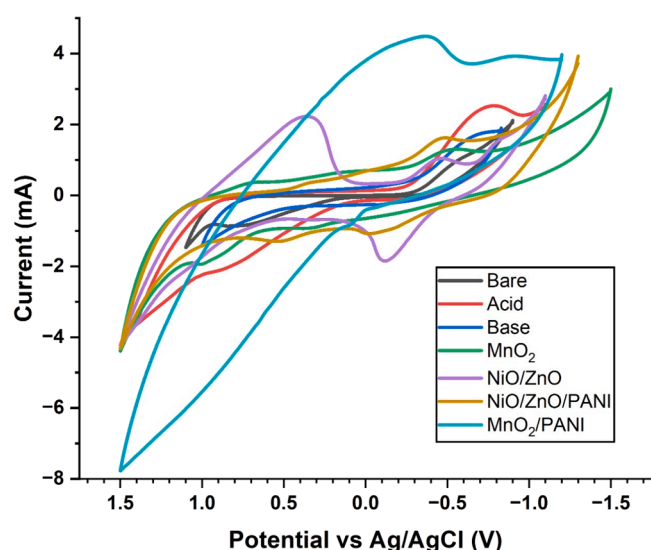


Fig. 4. Cyclic voltammograms acquired at a scan rate of 50 mV/s on bare CMM and all other chemically functionalized and nanoparticles deposited CMM electrodes.

electronic devices such as light emitting diodes (LEDs) for prolonged periods of time (Supplementary fig. S6).

3.2. Cyclic voltammetry analysis of the performance of electrodes

Cyclic voltammetry is an electrochemical technique that has been widely used to describe the electron transfer interactions in the interface electrode-biomass/biofilm-liquor in the anode chamber or in the cathode/catholyte interface of MFCs.

CV involves scanning the voltage of a working electrode forward and backward at a predetermined pace (often 5 to 100 mV s⁻¹). The reversible nature of the forward and reverse sweep plots of cyclic voltammograms represent a reversible oxidation and reduction reaction within the electrochemical system tested and therefore, indicative of the presence of reversible electrochemical reactions taking place within it. The presence of any mediators is detected by the production of a current during the mediator's cyclic oxidation and reduction if the mediator can take (accept) reducing equivalents from the working electrode [32]. The

current-voltage map may then be used to calculate the mediator's midpoint potential [33].

A comparison of cyclic voltammograms acquired at a scan rate of 50 mV/s on bare CMM and all other treated electrodes used in this study is indicative of the presence of large oxidation and reduction CV peaks in the nanoparticle embedded MFC cathodes (Fig. 4). Particularly, MnO₂/PANI and NiO/ZnO/PANI nanoparticles incorporated cathodes demonstrated large reversible oxidation/reduction signatures compared to other types of nanoparticle incorporations in cyclic voltammograms. This demonstrated that better ORR electrochemical catalysis is attributable to MnO₂/PANI and NiO/ZnO/PANI nanoparticles incorporated cathodes is responsible for notable oxidation/reduction peaks in cyclic voltammetry analysis. This observation is further backed by the fact that these two types of nanomaterial modification of MFC cathodes (MnO₂/PANI and NiO/ZnO/PANI) produced the biggest power and current densities recorded in this study.

Generally, in cyclic voltammetry (CV), higher current values on the Y-axis during both forward and reverse sweeps indicate that oxidation/reduction reactions occur more readily for the tested material. Based on the obtained CV plots, it was observed that MnO₂/PANI (manganese dioxide/polyaniline) exhibits more readily reversible electron transfer for oxygen reduction reaction (ORR), making it the most effective catalyst material among the modifications tested in the MFC system. The CV plots of other treatments also showed reversible oxidation/reduction peaks, indicating that none of the materials were irreversibly oxidized.

3.3. Scanning electron microscopy (SEM) analysis of functionalized microfiber electrode surfaces

Substrate selection is critical in the growth of nanomaterials such as stainless steel [34], nickel foam [35], and carbon cloth [36], which are commonly used as substrates for electrode material deposition in the case of nanomaterial electrode treatments. We chose woven carbon microfiber material (CMM) as the substrate in this experiment to increase the efficiency of the electron transfer due to high surface area, cost effectiveness. It was deemed a good substrate for nanomaterial deposition because of its large surface area and meshwork structure. This may allow the deposited nanomaterials to participate in electrochemical reactions and catalysis.

A morphological investigation is one of the available means to understand the prepared electrode samples. Supplementary fig. S5 shows SEM images of each treatment before and after they have been introduced to the MFC at the magnification of 1000x. It is evident from these images that the directly synthesized nanoparticle layer in each case of the electrode modification is robust enough to withstand the shear forces of air sparging into the MFC catholyte. This is indicative of sustained maintenance of good ORR catalysis levels through the application of the nanoparticle direct synthesis onto the CMM materials in MFC cathodes.

From the SEM images it is evident that the incorporated nanoparticles have remained on the novel microfiber electrodes and have been essential in catalyzing the ORR in the cathode compartments of the tested MFC systems.

Fig. 5 provides a surface morphological comparison between the nanoparticles deposited CMM electrodes versus the bare CMM electrodes (Fig. 5a, b and c compared to d, e and f). It indicates that almost the entire available surface area of the CMM fibrils are fully occupied by nanomaterial types directly synthesized onto the CMM surface. This suggests a good surface area occupied by the directly synthesized nanoparticles to conduct the ORR more efficiently. This could account for the superior electrochemical performance these directly synthesized nanoparticles produce compared to the traditional Pt powder catalyst loading onto CMM electrode surfaces using a conductive binder solution such as Nafion resin, where the distribution and the attachment of the catalyst material on the CMM surfaces is expected to be sparse and uneven.

The CMM as the substrate has provided a well-connected porous

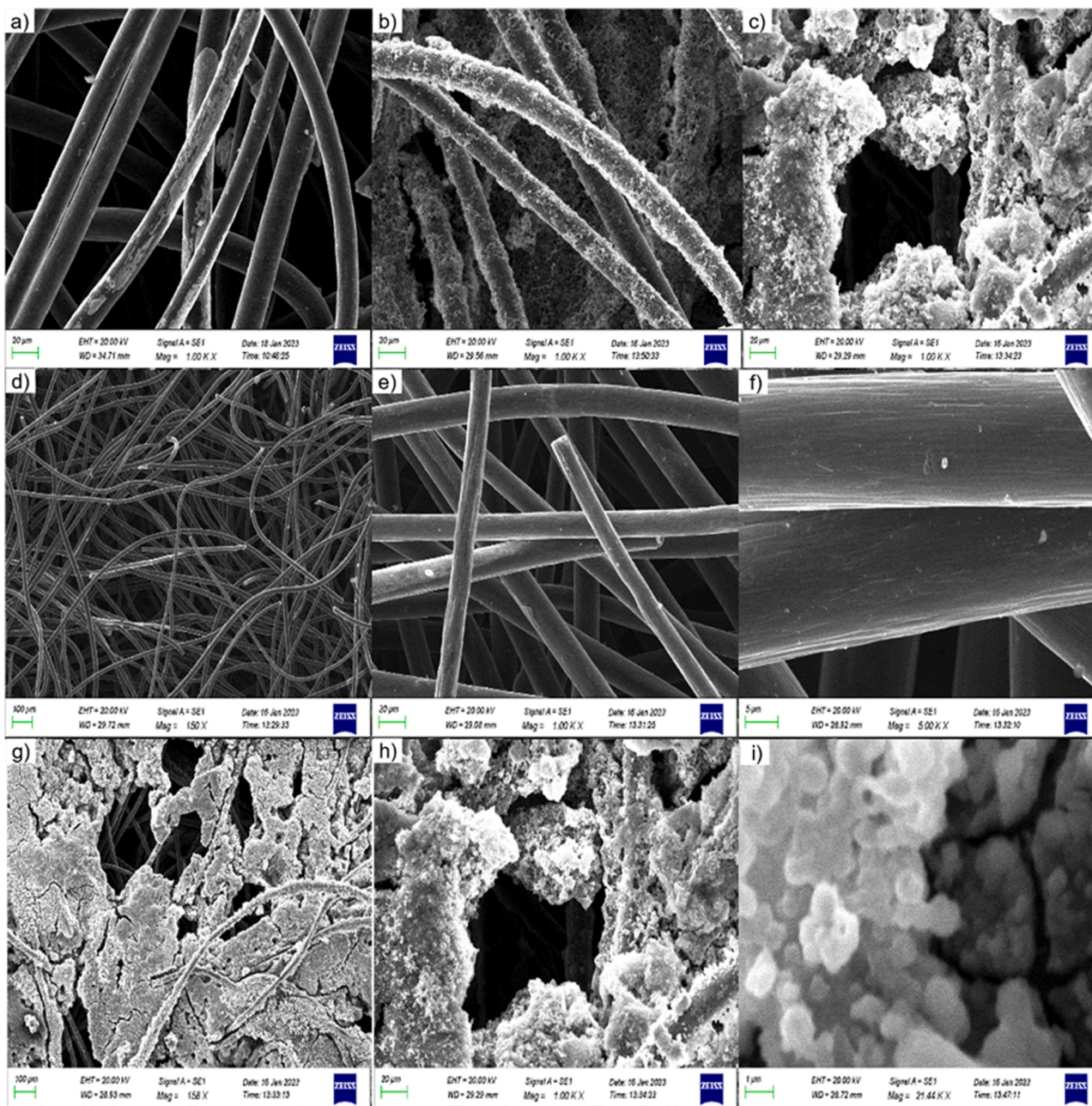


Fig. 5. (a) MnO_2 is directly deposited on the electrode material. (b) PANI synthesized by the electrodeposition method on the electrode (c) MnO_2 /PANI nanomaterials are deposited on the electrode material. (d) Bare Carbon microfiber material under 150x magnification (e) 1000x magnification (f) 5000x magnification. (g) MnO_2 and PANI treated Carbon microfiber material under 150x magnification (h) 1000x magnification (i) 22.44k x magnification.

platform for uniform and wide distribution of PANI on it [37]. This design aided in the reduction of fabrication time for electrodes. The PANI on the carbon electrode fiber network seemed to be well distributed and adhered to the CMM that could exhibit good conductivity and stability. Furthermore, the rough surface morphology and texture introduced by nanoparticle incorporations such as MnO_2 /PANI (Fig. 5C), suggests that large increases in available surface area for catalysis can be brought about by direct nanomaterial synthesis methods described in this study. Consequently, this would also mean that significant increases to ORR catalytic rates and ultimately better electrochemical performances in the electrochemical devices can be brought about by using this type of nanomaterial deposition. Additionally, the electrodes can be designed binder-free as PANI is directly deposited on the CMM. The neatly deposited PANI with CMM can be an efficient electrode for MFC applications.

Elemental analysis and mappings of the electrodes were obtained by Energy Dispersive X-Ray Analysis (EDAX) spectra. Fig. 6 indicates EDAX spectra of Non-treated CMM, MnO_2 /CMM, and MnO_2 /PANI/CMM electrodes before and after introducing them to MFCs under 150x magnification. Figs. 6(a) and 6 (b) shows the EDAX spectra of bare CMM before and after being introduced into the MFC cathode. EDAX spectrum from bare CMM before MFC operation (Fig. 6(a)) demonstrates no elemental signatures apart from carbon, whereas, additional elemental signatures were detected for potassium, nitrogen oxygen, sodium and phosphorus from the EDAX spectrum of bare CMM after being used as the MFC cathode. Elemental signatures such as sodium, potassium, oxygen and phosphorus comes from the residual phosphate buffer in the catholyte left over on the CMM and the nitrogen may result from unwanted biofilm formation on the MFC cathodes during its prolonged operation. Fig. 6(c) shows the EDAX spectrum of MnO_2 /CMM before

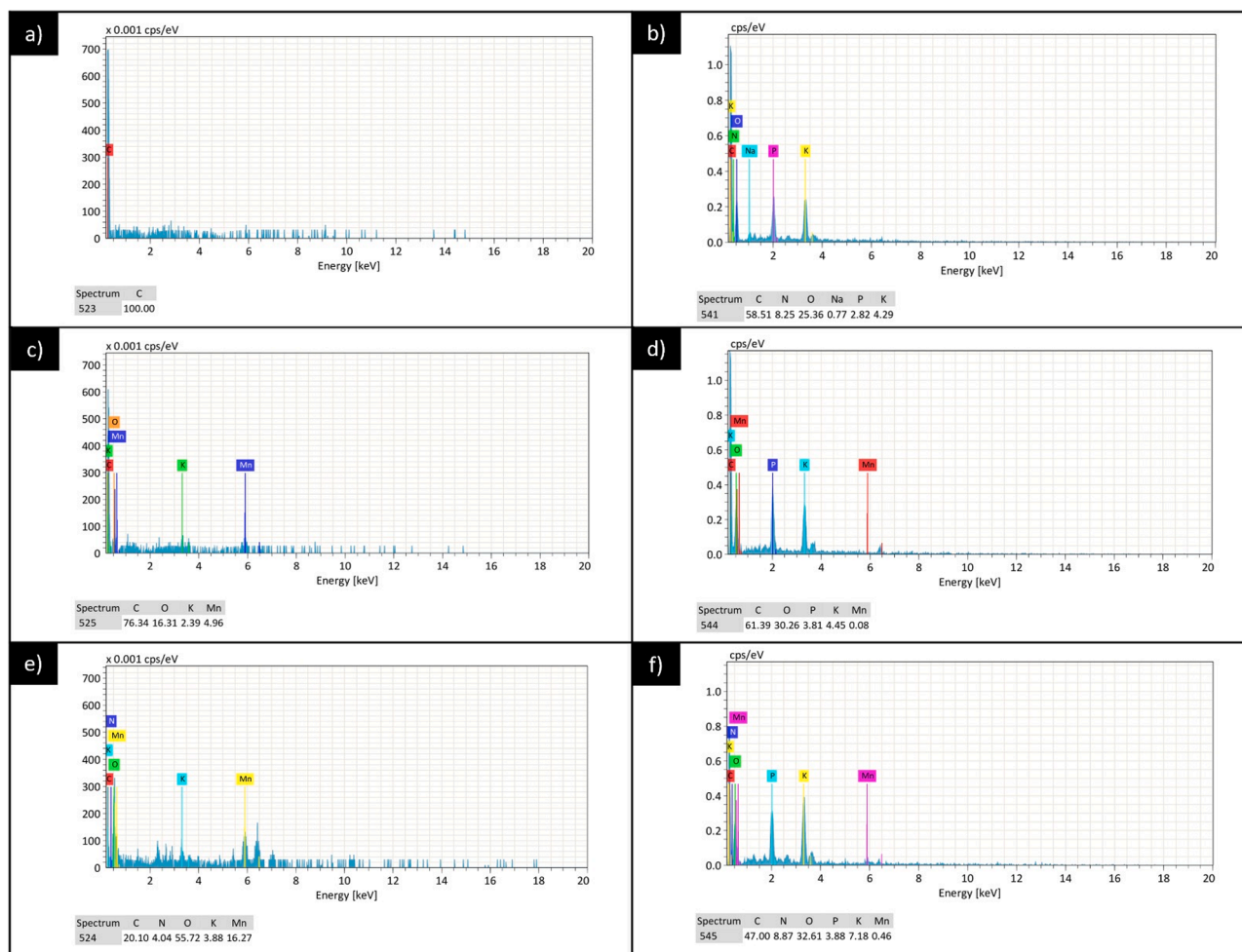


Fig. 6. Elemental analysis and mapping of bare CMM electrodes and nanoparticle modified CMM electrodes obtained using Energy Dispersive X-Ray analysis under magnification of 150x. (a) EDAX spectra of bare CMM before and (b) after being introduced into the MFC cathode. (c) EDAX spectrum of MnO_2/CMM before and (d) after being introduced to the MFC cathode and (e) EDAX spectra of $\text{MnO}_2/\text{PANI}/\text{CMM}$ before and (f) after being introduced into the MFC cathode.

introducing it to the MFC, where the respective peaks corresponding to the elements carbon, nitrogen, Oxygen, and Manganese are detected in the treated electrode surface with a 150X magnification. Fig. 6(d) shows the MnO_2/CMM electrode after being introduced to the cell, where the respective peaks corresponding to the elements carbon, nitrogen, Oxygen, Phosphorus, and Potassium and a lesser amount of Manganese are detected in the treated electrode surface with a 150X magnification, suggesting that some of the manganese from the cathode could be lost during prolonged (in excess of 10 consecutive days) MFC operation. Sodium, phosphorus and potassium peaks, appearing in the EDAX spectrum of the MnO_2/CMM surface after being introduced to the MFC, are due to the Phosphate buffer used as the media of the cathode chamber.

The elemental mapping images, shown in Figs. 6(e) and (f), reveal the uniform spatial distribution of the elements present in the $\text{MnO}_2/\text{PANI}/\text{CMM}$ before introducing the electrode to the cell and after introducing the electrode to the microbial fuel cell. EDAX spectrum of $\text{MnO}_2/\text{PANI}/\text{CMM}$ electrodes recovered after being used as MFC cathodes show signatures for Sodium, phosphorus and potassium, indicating residue leftover from phosphate buffer catholyte. Lessened intensity of manganese EDAX signature (Fig. 6f) in the $\text{MnO}_2/\text{PANI}/\text{CMM}$ recovered after MFC operation indicated that some loss of MnO_2 catalyst occurs when used as the ORR catalyst in the MFC cathodes, during prolonged operation (more than 10 consecutive days) of MFCs.

3.4. Fourier transform infrared spectroscopy (FTIR) analysis of functionalized cathodes

FTIR can provide information about the presence of functional groups on the surface of nanomaterials. By analyzing the infrared absorption spectra, it is possible to identify the types of chemical bonds and functional groups present in the nanomaterials, which can help in understanding the surface chemistry and composition of the modified electrodes that may ultimately improve the ORR performance of the novel electrodes. FTIR can be used to study the changes in the surface chemistry of the electrodes after nanomaterial modification. By comparing the FTIR spectra of the unmodified and modified electrodes, it is possible to determine the specific chemical changes that occur on the electrode surface as a result of nanomaterial deposition or surface functionalization.

It was confirmed by FTIR analysis that the woven CMM electrodes were modified with nanomaterials following treatment with metals and metal oxides.

Figure S1 compares the FTIR spectra of bare and treated electrodes.

The nanomaterial-treated CMM electrodes indicate the emergence of many additional major peaks compared to the Non treated electrodes.

The FTIR spectra (Supplementary fig. S1) of treated electrodes indicate key spectral differences between the nanoparticle treated electrodes and non-treated control electrodes in MFC cathodes

Obtained FTIR spectra of MnO_2 and MnO_2/PANI show the broad wave number bands at 3347.7cm^{-1} correspond to N—H stretching. The

wave number band at 1739.38 cm^{-1} shows a C = O which may represent the carbon and oxygen bond system of the carbon microfiber electrodes. Among the various peaks assigned to PANI, the characteristic peaks around 1654.12 cm^{-1} correspond to benzenoid $(-\text{C}_6\text{H}_4)-$ ring, C—H bond. Another main band at 1394.75 cm^{-1} can be assigned to the stretching of C—N in $-\text{NH}-(\text{C}_6\text{H}_4)-\text{NH}-$. The bands appeared at 876.87 cm^{-1} which corresponds to the stretching of C—H bonds.

ORR catalysis in MFCs is currently done using costly noble metal catalyst powders such as platinum. The prohibitive cost and difficulty of incorporation of such catalyst materials onto carbon electrodes greatly reduce the applicability of such electrodes in real-world applications of MFC systems. Cheap metal oxide nanoparticles such as ZnO, MnO_2 and NiO along with the conductive polymeric material polyaniline (PANI) can be directly synthesized onto carbon microfiber electrode materials using our novel nanoparticle synthesis method.

In this study, we have demonstrated for the first time that novel nanoparticle loaded electrodes such as $\text{MnO}_2 + \text{PANI}$ incorporated cathodes and $\text{ZnO/NiO} + \text{PANI}$ nanoparticle incorporated cathodes employed in two-chamber lake sediment MFC systems could be used to obtain a superior ORR electrochemical performance compared to control experiments with Pt catalyst loaded MFC systems.

3.5. Cost-benefit analysis of platinum loaded MFCs vs novel directly synthesized nanomaterial electrode MFCs

Cost analysis conducted on all catalyst materials used in this study using current market prices of each material (in USD), revealed that all of the alternative ORR materials are significantly cheaper than the platinum powder-vulcanized carbon (10:90 W/W) catalyst. For example the two best-performing nanoparticle catalysts $\text{MnO}_2 + \text{PANI}$ incorporated cathodes and $\text{ZnO/NiO} + \text{PANI}$ nanoparticle incorporated cathodes were significantly cheaper to apply per square meter of cathode electrode (\$340 and \$472 respectively per square meter) when compared to platinum coated electrode (\$ 10,300) for the same electrode surface area (Table 2). This demonstrated that the cost of direct-synthesis application of the novel nanoparticle electrode ORR catalyst material is significantly cheaper compared to the conventional Pt catalyst. Furthermore, it confers direct cost savings in power generation where the cost of catalyst application to generate a Watt of power using these MFC systems is significantly reduced when direct synthesis of nanomaterial is employed as opposed to Pt deposition on electrodes for the same purpose of ORR catalysis in MFCs. For example, the two best-performing nanomaterials catalysts in this study $\text{MnO}_2 + \text{PANI}$ incorporated cathodes and $\text{ZnO/NiO} + \text{PANI}$ nanoparticle incorporated cathodes cost \$2422 and \$3658 to generate the first Watt of power, whereas, the same system would cost more than 50 times to generate the first Watt of power when Pt is used as the ORR catalyst (Table 2). These findings imply that employing novel nanomaterial direct synthesis on MFC cathodes can bring about significant cost reductions as opposed to using a traditional precious metal ORR catalysts such as platinum to generate a unit amount of power. The high-cost of ORR catalyst materials have hindered the meaningful applicability of MFC systems for many decades. As such, the novel nanomaterial synthesis methods described herein, would serve to improve the applicability and scalability of MFC systems for purposes such as renewable energy recovery during wastewater treatment and using MFCs to power devices with a larger current drain (Fig. 2).

4. Conclusion

The findings of this study demonstrated that using direct deposition of cost-effective nanomaterials such as $\text{ZnO/NiO} + \text{PANI}$ and MnO_2 on carbon microfiber electrode material can significantly improve the electrochemical performance of lake sediment inoculated microbial fuel cells. This can be used as an alternative to expensive cathode catalysts like platinum in MFCs to catalyze ORR. The electrochemical

Table 2

Comparison of cost of application of each catalyst material per m^2 area of electrode and catalyst application cost for generating a Watt of power from the MFC systems used in this study.

Treatment	*Cost of catalyst application per m^2 of electrode (USD/ m^2)	**Catalyst application cost for generating a Watt of power (USD)
Non treated Cathode	N/A	N/A
KOH treated Cathode	196	6272
Acid treated Cathode	277	6371
Zinc nanoparticle treated Cathode	346	5655
Zinc oxide+ Nickel oxide nanoparticle + Polyaniline treated Cathode	472	3658
Manganese nanoparticle treated Cathode	622	8086
Manganese oxide nanoparticle+ Polyaniline treated Cathode	340	2422
***Pt loaded control	10,300	190,653

* Considers the current market value of respective catalyst material.

** Assumes that 1 m^2 of cathode electrode area is used.

*** Assumes that Pt is loaded using the standard protocol as described earlier [38] and the Pt loading is 0.5 mg/cm^2 of electrode area.

performances obtained in this study by using these nanomaterial-modified electrodes in two-chamber MFCs were comparable to or better than the P_{max} and J_{max} values obtained in previous studies by operating similar two-chamber MFC systems employing noble metals as the ORR catalysts. In particular, the $\text{MnO}_2 + \text{PANI}$ incorporated cathodes and $\text{ZnO/NiO} + \text{PANI}$ nanoparticle incorporated cathodes demonstrated approximately 6 fold increase in P_{max} and J_{max} values over non-treated cathode controls. The application of direct synthesis of nanomaterials described in this study can bring about over 50-fold cost reductions to generate a unit amount of power compared to the usage of conventional ORR catalysts such as a platinum.

CRedit authorship contribution statement

Maheshi Somasiri: Investigation, Methodology, Writing – original draft. **Tanusha Amandani:** Formal analysis, Investigation, Methodology. **Charitha Basnayaka:** Formal analysis, Investigation, Methodology, Writing – review & editing. **Ahmed Ahsan:** Data curation, Formal analysis, Writing – review & editing. **Gayani P Dilangani:** Investigation, Methodology, Writing – review & editing. **Ajith C. Herath:** Methodology, Writing – review & editing. **Sampath Bandara:** Formal analysis, Methodology, Writing – review & editing. **Godfrey Kyazze:** Formal analysis, Validation, Writing – review & editing. **Eustace Y. Fernando:** Conceptualization, Data curation, Funding acquisition, Investigation, Project administration, Supervision, Writing – original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

Technical staff who assisted in carrying out the experimental work in

numerous ways at all collaborating institutions and laboratories are thankfully acknowledged. Authors wish to acknowledge the Rajarata University of Sri Lanka (RUSL) for providing funding, materials and instrumentation support under the microbiology special degree program for conducting and completing this research. They also wish to thank the Faculty of Technology, RUSL for providing access to SEM and EDX analysis of specimens.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.nexus.2024.100280](https://doi.org/10.1016/j.nexus.2024.100280).

References

- [1] Liu, H., Ramnarayanan, R., & Logan, B.E. (2004). Production of Electricity during Wastewater Treatment Using a Single Chamber Microbial Fuel Cell. *Environmental Science and Technology*, 38(7), 2281–2285. <https://doi.org/10.1021/es034923g>.
- [2] B.E. Logan, Exoelectrogenic bacteria that power microbial fuel cells, *Nature Reviews Microbiology* 7 (5) (2009) 375–381.
- [3] Logan B. (2009). Exoelectrogenic bacteria that power microbial fuel cells.
- [4] E.Y. Kononova, D.I. Stom, G.O. Zhdanova, D.A. Yuriev, Y. Li, L. Barbora, P. Goswami, The microorganisms used for working in microbial fuel cells, in: AIP Conference Proceedings, 2018, <https://doi.org/10.1063/1.5031979>, 1952.
- [5] Logan, B.E., Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., & Rabaey, K. (2006). Microbial fuel cells: Methodology and technology. In *Environmental Science and Technology* (Vol. 40, Issue 17, pp. 5181–5192). <https://doi.org/10.1021/es0605016>.
- [6] S.E. Oh, B.E. Logan, Proton exchange membrane and electrode surface areas as factors that affect power generation in microbial fuel cells, *Appl. Microbiol. Biotechnol.* 70 (2) (2006) 162–169. <https://doi.org/10.1007/s00253-005-0066-y>.
- [7] K. Ben Liew, W.R.W. Daud, M. Ghasemi, J.X. Leong, S. Su Lim, M. Ismail, Non-Pt catalyst as oxygen reduction reaction in microbial fuel cells: A review, *Int. J. Hydrogen Energy* 39 (10) (2014) 4870–4883, <https://doi.org/10.1016/j.ijhydene.2014.01.062>.
- [8] B. Erable, N. Duteanu, S.M.S. Kumar, Y. Feng, M.M. Ghangrekar, K. Scott, Nitric acid activation of graphite granules to increase the performance of the non-catalyzed oxygen reduction reaction (ORR) for MFC applications, *Electrochem. Commun.* 11 (7) (2009) 1547–1549, <https://doi.org/10.1016/j.elecom.2009.05.057>.
- [9] W. Kai, L. Liwei, X. Wen, Z. Shengzhe, L. Yong, Z. Hongwei, S. Zongqiang, Electrodeposition Synthesis of PANI/MnO₂/Graphene Composite Materials and its Electrochemical Performance, *Int. J. Electrochem. Sci.* 12 (9) (2017) 8306–8314, <https://doi.org/10.20964/2017.09.06>.
- [10] M. Li, M. Zhou, X. Tian, C.T. McDaniel, D.J. Hassett, T. Gu, Microbial fuel cell (MFC) power performance improvement through enhanced microbial electrogenicity, in: *Biotechnology Advances*, 36, Elsevier Inc, 2018, pp. 1316–1327, <https://doi.org/10.1016/j.biotechadv.2018.04.010>.
- [11] C. Santoro, A. Serov, L. Stariha, M. Kodali, J. Gordon, S. Babanova, O. Bretschger, K. Artyushkova, P. Atanassov, Iron based catalysts from novel low-cost organic precursors for enhanced oxygen reduction reaction in neutral media microbial fuel cells, *Energy Environ. Sci.* 9 (7) (2016) 2346–2353, <https://doi.org/10.1039/C6EE01145D>.
- [12] N.K. Abd-Elrahman, N. Al-Harbi, N.M. Basfer, Y. Al-Hadeethi, A. Umar, S. Akbar, Applications of nanomaterials in microbial fuel cells: a review, *Molecules* 27 (21) (2022) 7483, <https://doi.org/10.3390/molecules27217483>.
- [13] M. Sharma, S. Bajracharya, S. Gildemyn, S.A. Patil, Y. Alvarez-Gallego, D. Pant, K. Rabaey, X. Dominguez-Benetton, A critical revisit of the key parameters used to describe microbial electrochemical systems, *Electrochim. Acta* 140 (2014) 191–208, <https://doi.org/10.1016/j.electacta.2014.02.111>.
- [14] W. Ni, D. Wang, Z. Huang, J. Zhao, G. Cui, Fabrication of nanocomposite electrode with MnO₂ nanoparticles distributed in polyaniline for electrochemical capacitors, *Mater. Chem. Phys.* 124 (2–3) (2010) 1151–1154, <https://doi.org/10.1016/j.matchemphys.2010.08.050>.
- [15] M. Mustaqeem, G.A. Naikoo, M. Yarmohammadi, M.Z. Pedram, H. Pourfarzad, R. A. Dar, S.A. Taha, I.U. Hassan, M.Y. Bhat, Y. Chen, Rational design of metal oxide based electrode materials for high performance supercapacitors – A review, *J. Energy Storage* 55 (2022) 105419, <https://doi.org/10.1016/j.est.2022.105419>.
- [16] C.M. Julien, A. Mauger, Nanostructured MnO₂ as Electrode Materials for Energy Storage, *Nanomaterials* 7 (11) (2017) 396, <https://doi.org/10.3390/nano7110396>.
- [17] Z. Zhang, D. Zhang, C. Miao, L. Zhang, L. Chou, Research Progress in MnO₂-Carbon Based Supercapacitor Electrode Materials, *Small* 14 (24) (2018) 1702883, <https://doi.org/10.1002/sml.201702883>.
- [18] J. Zhu, J. He, Facile Synthesis of Graphene-Wrapped Honeycomb MnO₂ Nanospheres and Their Application in Supercapacitors, *ACS Appl. Mater. Interfaces* 4 (3) (2012) 1770–1776, <https://doi.org/10.1021/am3000165>.
- [19] C. Xiong, Q. Yang, W. Dang, M. Li, B. Li, J. Su, Y. Liu, W. Zhao, C. Duan, L. Dai, Y. Xu, Y. Ni, Fabrication of eco-friendly carbon microtubes @ nitrogen-doped reduced graphene oxide hybrid as an excellent carbonaceous scaffold to load MnO₂ nanowall (PANI nanorod) as bifunctional material for high-performance supercapacitor and oxygen reduction reaction catalyst, *J. Power Sources* 447 (2020) 227387, <https://doi.org/10.1016/j.jpowsour.2019.227387>.
- [20] H. Jia, Y. Cai, X. Zheng, J. Lin, H. Liang, J. Qi, J. Cao, J. Feng, W. Fei, Mesoporous Carbon Nanotube-on-MnO₂ Nanosheet Composite for High-Performance Supercapacitors, *ACS Appl. Mater. Interfaces* 10 (45) (2018) 38963–38969, <https://doi.org/10.1021/acsami.8b14109>.
- [21] M.E. Doloksaribu, K. Harsojo Triyana, B. Prihandoko, The effect of concentration nanoparticles MnO₂ doped in activated carbon as supercapacitor electrodes, *Int. J. Appl. Eng. Res. (IJAER)*, [online] 12 (19) (2017) 8625–8631. Available at, <http://digilib.unimed.ac.id/eprint/51518> [Accessed 2 Aug. 2023].
- [22] S.I.A. Razak, A.L. Ahmad, S.H.S. Zein, A.R. Boccacini, MnO₂-filled multiwalled carbon nanotube/polyaniline nanocomposites with enhanced interfacial interaction and electronic properties, *Scr. Mater.* 61 (6) (2009) 592–595, <https://doi.org/10.1016/j.scriptamat.2009.05.030>.
- [23] Y. Li, Z. Sun, D. Liu, Y. Gao, Y. Wang, H. Bu, M. Li, Y. Zhang, G. Gao, A composite solid polymer electrolyte incorporating MnO₂ nanosheets with reinforced mechanical properties and electrochemical stability for lithium metal batteries 8 (4) (2020) 2021–2032, <https://doi.org/10.1039/c9ta11542k>.
- [24] Z. Huang, L. Li, Y. Wang, C. Zhang, T. Liu, Polyaniline/graphene nanocomposites towards high-performance supercapacitors: A review, *Composites Communications* 8 (2018) 83–91, <https://doi.org/10.1016/j.coco.2017.11.005>.
- [25] Sajid Ali Ansari, N. Parveen, Thi Hiep Han, Mohammad Omaish Ansari, Moo Hwan Cho, Fibrous polyaniline@manganese oxide nanocomposites as supercapacitor electrode materials and cathode catalysts for improved power production in microbial fuel cells 18 (13) (2016) 9053–9060, <https://doi.org/10.1039/c6cp00159a>.
- [26] Y. Wei, W. Luo, X. Li, Z. Lin, C. Hou, M. Ma, J. Ding, T. Li, Y. Ma, PANI-MnO₂ and Ti3C₂Tx (MXene) as electrodes for high-performance flexible asymmetric supercapacitors, *Electrochim. Acta* 406 (2022) 139874, <https://doi.org/10.1016/j.electacta.2022.139874>.
- [27] K.S. Khoo, W.Y. Chia, D.Y.Y. Tang, P.L. Show, K.W. Chew, W.H. Chen, Nanomaterials utilization in biomass for biofuel and bioenergy production, in: *Energies*, 13, MDPI AG, 2020, <https://doi.org/10.3390/en13040892>.
- [28] Z. Nazeer, E.Y. Fernando, A novel growth and isolation medium for exoelectrogenic bacteria, *Enzyme Microb. Technol.* 155 (2022) 109995.
- [29] Jayathilake, C., Dilangan, G.P., Bandara, S., Nazeer, Z., Thilini, N., Bandara, W., Herath, A.C., Kyazze, G., & Fernando, E.Y. (n.d.). The use of Statin-class compounds to suppress methanogenesis in lake sediment inoculated microbial fuel cells. <https://doi.org/10.1101/2022.08.24.505145>.
- [30] X. Wang, N. Gao, Q. Zhou, H. Dong, H. Yu, Y. Feng, Acidic and alkaline pretreatments of activated carbon and their effects on the performance of air-cathodes in microbial fuel cells, *Bioresour. Technol.* 144 (2013) 632–636, <https://doi.org/10.1016/j.biortech.2013.07.022>.
- [31] M. Dissanayake, N. Liyanage, C. Herath, S. Rathnayake, E.Y. Fernando, Mineralization of persistent azo dye pollutants by a microaerophilic tropical lake sediment mixed bacterial consortium, *Environ. Adv.* 3 (2021) 100038.
- [32] D. Ucar, Y. Zhang, I. Angelidaki, An overview of electron acceptors in microbial fuel cells, in: *Frontiers in Microbiology*, 8, Frontiers Research Foundation, 2017, <https://doi.org/10.3389/fmicb.2017.00643>.
- [33] Z. He, J. Kan, F. Mansfeld, L.T. Angenent, K.H. Nealson, Self-sustained phototrophic microbial fuel cells based on the synergistic cooperation between photosynthetic microorganisms and heterotrophic bacteria, *Environmental Science and Technology* 43 (5) (2009) 1648–1654, <https://doi.org/10.1021/es803084a>.
- [34] Fátima Borja-Maldonado, Miguel Ángel López Zavala, Contribution of configurations, electrode and membrane materials, electron transfer mechanisms, and cost of components on the current and future development of microbial fuel cells, *Heliyon* 8 (7) (2022) e09849, <https://doi.org/10.1016/j.heliyon.2022.e09849>. ISSN 2405-8440.
- [35] Rengasamy Karthikeyan, Navanietha Krishnaraj, Ammaiappan Selvam, Jonathan Woon-Chung Wong, Patrick K.H. Lee, Michael K.H. Leung, Sheela Berchmans, Effect of composites based nickel foam anode in microbial fuel cell using *Acetobacter aceti* and *Gluconobacter roseus* as biocatalysts, *Bioresour. Technol.* 217 (2016) 113–120, <https://doi.org/10.1016/j.biortech.2016.02.114>. ISSN 0960-8524.
- [36] Mustakeem, Electrode materials for microbial fuel cells: nanomaterial approach, *Mater. Renew. Sustain. Energy* 4 (2015) 22, <https://doi.org/10.1007/s40243-015-0063-8>.
- [37] M. Kim, C. Lee, J. Jang, Fabrication of Highly Flexible, Scalable, and High-Performance Supercapacitors Using Polyaniline/Reduced Graphene Oxide Film with Enhanced Electrical Conductivity and Crystallinity, *Adv. Funct. Mater.* 24 (17) (2014) 2489–2499, <https://doi.org/10.1002/adfm.201303282>.
- [38] E. Fernando, Treatment of Azo Dyes in Industrial Wastewater Using Microbial Fuel Cells (Doctoral Dissertation, University of Westminster, 2014).