Carbon nanotube/polypyrrole nanocomposite as a novel cathode catalyst and proper alternative for Pt in microbial fuel cell

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ABSTRACT

This study demonstrates the use of carbon nanotube polypyrrole (CNT/PPy) nanocomposite as a novel cathode catalyst in microbial fuel cells (MFC). The CNT/PPy nanocomposite has been prepared using a chemical oxidative method and its performance in MFC was evaluated and compared with platinum, the traditional cathode catalyst. The attachment of microorganisms on the anode was confirmed using field emission scanning electronic microscopy (FESEM) analysis. The size of ppy nanoparticles was also observed using SEM. Cyclic voltammetry (CV) studies were done to investigate the catalytic properties of CNT/PPy nanocomposite. The maximum power density and coulombic efficiency attained by the usage of CNT/PPy nanocomposite was found to be ~113 mW/m² and 21% respectively, which is a significant comparison with the Pt catalyst, where the measured values were 122.7 mW/m² and 24.6% respectively. The COD removal of both systems was found to be more than 80%. The results indicate that CNT/PPy nanocomposite could be used as a possible lower cost alternative than Pt catalyst in MFC.

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Introduction

The depletion of fossil fuels and subsequent environmental problems, such as pollution and global warming, has forced societies to move towards renewable energy. Achieving this, whilst providing adequate sanitation for the people is one of the most important challenges of this century [1]. Recovering energy from wastewater appears to be one of the only methods for combined energy production and improved sanitation without the consumption of high amounts of energy [2,3]. A microbial fuel cell (MFC) is a device which converts organic matter to electricity using microorganisms as a biocatalyst [4,5]. Therefore, MFC is a device for simultaneous wastewater treatment and energy production. However, its low power density and poor long term stability limit its practical application [6,7]. The performance of MFC depends on several factors including bacteria composition, PEM, types of electrode, electrode distance and media. One of the most important factors that influence the MFC power production is the cathode catalyst. The cathode catalyst directly affects the electrical power production by oxygen reduction reaction [8–10]. In this study, we have used CNT/PPy as our nanocomposite cathode catalyst in MFC. PPy is a type of conducting polymer which can be formed by the polymerisation of pyrrole. It is a very popular polymer due to the ease of preparation, high conductivity, and its economic and environmentally friendly nature [11,12]. CNT is also a precious material, with a unique combination of stiffness, strength, and tenacity. It has very high thermal and electrical conductivity compared to other materials and high potential for making composites due to its high surface area [13]. Also, conducting polymers are excellent materials for the preparation of nanocomposites. There is previous research in making and applying carbon nanocomposite materials as cathode catalyst in MFC. Ghasemi et al. (2011) [14] have fabricated and tested activated carbon nanofiber as a proper alternative for Pt in MFC. It could produce the power of about 89% of Pt and the power per cost was 2.65 times more than Pt. In a further study by the same authors in 2013 [15] copper phthalocyanine was tested, which produced the power and CE equal to Pt. They also found that CNT increased the performance of the cathode catalyst as CNT/Pt has better performance than Pt [16].

Therefore, in this study we have synthesised PPy and made nanocomposites using CNT. It has been used as the cathode catalyst in MFC and the results were compared to Pt, which is the most common cathode catalyst used in MFC.

Materials and methods

MFC configuration

Two cubic shaped chambers were constructed from Plexiglas, with a height of 10 cm, width of 6 cm, and length of 10 cm and a working volume of 420 ml. They were separated by a Nafion 117 Proton Exchange Membrane (PEM). Air was continuously fed into the cathode compartment using a pump at a rate of 80 ml/min. Both the cathode and the anode projected surface areas were 12 cm². The cathode was carbon paper, coated with 0.5 mg/cm² Pt, PPy and CNT/PPy for comparison, and the anode (as described above) was plain carbon paper [17]. The schematic figure of MFC is shown in Fig. 1.

Enrichment

Anaerobic digester sludge collected from Indah Water Konsortium treating Palm Oil Mill Effluent (POME) was used to inoculate anode chamber of MFCs. The media contained 5 g of glucose, 0.07 g of yeast extract, 0.2 g of KCl, 1 g of NaH₂PO₄·4H₂O, 2 g of NH₄Cl, 3.5 g of NaHCO₃ (all sourced from the Merck company), 10 ml of Wolfe’s mineral solution and 10 ml of Wolfe’s vitamin solution (added per litre). All experiments were conducted in an incubator at 30 °C. Furthermore, the cathode chamber contained a phosphate buffer solution, which consisted of 2.76 g/l of NaH₂PO₄, 4.26 g/l of Na₂HPO₄, 0.31 g/l of NH₄Cl, and 0.13 g/l of KCl (all sourced from the Merck company) [18].

Preparation of PPy and CNT/PPY

Polypyrrole was synthesised using pyrrole monomer in chemical oxidative polymerisation. Ammonium sulphate was the oxidising agent for this reaction. After 3 h of polymerisation, the precipitates gained were filtered and washed out with methanol. The product was then put inside an oven to dry [19].

The CNT/PPy preparation was synthesised in situ via chemical oxidation. CNT was first dissolved in 1.0 M of HCl solution and ultrasonicated for 3 h. Then, the pyrrole monomer was dropped into the solution. The reaction occurred within 1 h and the precipitate was collected by a paper filter and dried in an oven at 50 °C [20].

Analysis and calculation

Conventional three electrode systems were used to measure the oxygen reduction reaction (ORR) of CNT/Pt, Pt, and pristine carbon by using a potentiostat (HAK-MILIK FRIM 04699A-2007). For this purpose, cyclic voltammetry (CV) and linear
sweep voltammetry (LSV) were performed. An Ag/AgCl electrode was used as a reference electrode, Pt electrode as a counter electrode, and carbon paste electrode as a working electrode. All the experiments were conducted at least three times, and the average value reported [21].

CNT/PPy nanocomposite samples were analysed using X-ray diffraction (XRD). The XRD patterns were recorded in a 2θ range of 10°–80° with step width 0.02° and step time 1.25 s using CuKα radiation (λ = 1.5406 Å). The diffractograms were analysed with diffraction software (PC-APD) using the smoothing factor of 2. Field Emission Scanning Electron Microscopy (FESEM, Supra 55vp-Zeiss, Germany) was utilised to observe the morphology of PPy and CNT/PPy as well as to observe the shape of microorganisms on the surface of the anode electrode. Moisture was required to be removed from the biological samples (POME mix culture sludge) by critical drying. Biological specimen is coated with metal, with a thickness of approximately 20–50 nm, in order to make them conductive for the SEM analysis.

To measure the COD, samples were first diluted 10 times and mixed 2 ml of diluted samples with the digestion solution of a high-range COD reagent, then heated at 150°C for 2 h in a thermoreactor (DRB200) and report by a spectrophotometer (DR 2800).

The voltage was measured using a Multimeter (Fluke 8846A), and the power density curve was obtained by applying different loads to the system and calculating the power at different loads.

The current was measured using the following equation:

\[ I = \frac{V}{R} \] (1)

where \( I \) is the current (amps), \( V \) is the voltage (volt), and \( R \) is the applied external resistance (ohm).

The power density was calculated using the following equation:

\[ P = R \times I^2 \] (2)

where \( R \) is the applied external resistance (ohm) and \( I \) is the current (amps) (calculated using Equation (1)).

The Coulombic Efficiency (CE) was calculated as the current over time until the maximum theoretical current was achieved. The evaluated CE over time was calculated using the following equation:

\[ CE = \frac{M}{FbV_{an}\Delta COD} \int_0^t Idt \] (3)

where \( M \) is the molecular weight of oxygen (32), \( F \) is Faraday’s constant, \( b = 4 \) indicates the number of electrons exchanged per mole of oxygen, \( V_{an} \) is the volume of liquid in the anode compartment, and \( \Delta COD \) is the change in Chemical Oxygen Demand (COD) over time, ‘t’.

**Pre-treatment of PEM**

Nafion 117 used as PEM should be pre-treated before use in a MFC system. The pre-treatment procedure involves boiling in distilled water, 3% hydrogen peroxide, or 0.5 M sulphuric acid for one hour each and then stored in water until required for use in the system [22].

**Results and discussion**

**Enrichment of the anode and microbial community**

Fig. 2 shows the FESEM image of the biofilm on the CP anode electrode surface formed by the microorganisms when the MFC reached a stable condition. As shown in the figure, different types of bacteria (microorganisms) were attached to the anode surface and act as a biocatalyst for the electron transfer to the electrode surface. In order to observe the electrochemical activity of the biocatalyst, CV tests were done before and after the inoculation, as shown in Fig. 3. There are no peaks for the oxidation and reduction reactions before the inoculation of media, whereas after the inoculation, one oxidation peak and two reduction peaks can be observed, confirming that the POME sludge or microorganisms inside the system can work as biocatalysts with the electrode [23].

**Morphology of PPy and CNT/PPy**

FESEM images of the synthesised samples are shown in Fig. 4. Nanospheres, like morphology, were observed for the polypyrrole as shown in Fig. 4(a). The nanospheres were homogeneously aggregated and had a spherical bundle-like appearance. The size of the nanospheres was found to be ranging from 50 to 80 nm, as shown in the inset figure. FESEM image of the CNT/PPy nanocomposite are shown in Fig. 4(b). The image confirms the uniform distribution of PPy nanospheres on the CNT matrix (inset figure). The homogeneous dispersion of the PPy over CNT increased the surface area as well as the catalytic activity of the nanocomposite.

**X-ray diffraction**

The XRD patterns of the synthesised samples are shown in Fig. 5. The well-resolved wide diffraction peaks at the 2θ values 25.8° and 42.8° shown in the XRD plot reveal the
diffraction patterns of nanocarbon. The asymmetric peak observed at ~42.8° is attributed to the turbostratic nature of multi-walled carbon nanotubes with the calculated lattice spacing of 0.34 nm. This result is consistent with previous academic reporting [24,25]. A broad and weak peak was noted for the polypyrrole at the 2θ value of ~24°, which further confirms the amorphous character of polypyrrole. The weak diffraction peak noted for this sample was due to the scattering of X-rays from the polypyrrole chains at intermolecular spacing. XRD pattern of the CNT/PPy nanocomposite shows the characteristic peaks of CNTs (at 25.80° and 42.75°) and PPy (at 25.4°). The addition of polypyrrole to CNT slightly decreased the intensity of the diffraction peaks, which indicates the reduction of crystallinity of the carbon nanotubes. However, the peaks of the composite are found to be more intense than those of the polypyrrole, depicting the tendency of the synthesised CNT/PPy nanocomposite to CNT structure.

**Power density and polarization curve**

Fig. 6(a) shows the power density curves of MFCs working with Pt, the fabricated CNT/PPy nanocomposite and PPy. The power density of the MFCs working with Pt and CNT/PPy was similar, as shown in the graph. A maximum power density of 122.85 mW/m² was obtained by the MFC using the Pt catalyst at 217.5 mA/m² current density. With the CNT/PPy nanocomposite, the MFC generated a lower power density of 113.5 mW/m² at 226.25 mA/m² current density. This result is significant and comparable with the Pt catalyst. The power density was followed by PPy with production of 69.12 mW/m² at 240 mA/m². Fig. 6(b) shows the polarization curves of two MFCs. The internal resistance of the two systems has been calculated from the polarization plot. The slope of the voltage versus current density curve divided by the surface area of the electrode resulted in the internal resistance [26]. The calculated internal resistance of the CNT/PPy nanocomposite was around 1540 Ω, which was found to be higher than that of Pt (1330 Ω). This can be attributed to better catalytic activity of Pt compared to CNT/PPy nanocomposite, which causes a lower activation potential, as reported by Logan et al. [27]. The MFC operating with PPy had the highest internal resistance of around 1930 Ω. This may be due to the lower conductivity of PPy, which makes movement of ions more difficult [28].

**Cyclic voltammetry**

CV analysis has been carried out to measure the catalytic activity of the used nanocomposite cathode catalyst and
compare it with Pt. The size and position of the peak determines the catalytic properties of a material. Due to different oxidation numbers of Pt (+2, +3 etc.), two peaks were observed in the upper and lower side of the Pt in linear sweep voltammetry test (LSV) test, as shown in Fig. 7, which indicate that Pt has a high potential to be used as a cathode catalyst as well as for oxidation reactions. For the CNT/PPy, the peak observed in the negative voltage (lower side) region indicates the spontaneous nature of the reduction reaction as an obvious oxidation peak cannot be found. Therefore, it can be concluded that CNT/PPy is more appropriate for the cathode side as the reduction reaction would have occurred at the cathode chamber. Besides this, it can be seen that the catalytic activity of PPy is lower than the two other catalysts. This may be due to no active structure of carbon for accepting or rejecting of electrons, which make it difficult for the oxidation and reduction reaction to occur.

The LSV curves of PPy, CNT/PPy and Pt are shown in Fig. 7b. The figure clearly shows the ORR activity of the studied catalysts. However, it can be observed that the activity of CNT/PPy is less than Pt, but compared to other parameters such as price and viability, it shows that it can be acceptable as a catalyst and should be considered. The difference between Pt and CNT/PPy is the result of different ORR mechanisms, which have been shown in the CV test to cause different overall electron transfer numbers [15]. Also, in accordance with the CV curve, PPy has the lower number of electron transfers due to lower catalytic activity, and therefore smaller LSV domain.

Table 1 reports the summary of the data taken from the system. As shown, CNT/PPy can be a proper alternative for Pt in MFC.

**COD and CE**

Fig. 8 depicts the COD removal and the CE of Pt, CNT/PPy and PPy catalyst applied to the MFC. As the figure shows, CE of the system using Pt is 27% while 23.4% was noted for the CNT/PPy system. This is acceptable since the system working with Pt

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Power density (mW/m²)</th>
<th>Current density (mA/m²)</th>
<th>Internal resistance (Ω)</th>
<th>OCV at SS condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy</td>
<td>69.12</td>
<td>240.00</td>
<td>1910</td>
<td>447</td>
</tr>
<tr>
<td>CNT/PPy</td>
<td>113.5</td>
<td>226.25</td>
<td>1540</td>
<td>628</td>
</tr>
<tr>
<td>Pt</td>
<td>122.85</td>
<td>217.5</td>
<td>1330</td>
<td>745</td>
</tr>
</tbody>
</table>
has more power to convert the wastewater to electricity. The lowest CE was found to be CNT at just 13.7%. The COD removal of the system using CNT/PPy was 96%, which is more than that of the system using Pt (87%), which confirms the potential role of CNT/PPy nanocomposite as an alternative to the traditional platinum in MFCs. The COD removal for PPy was 87%. These results show that MFC has high potential to be used as a tool for wastewater treatment and COD removal [29,30].

Conclusion

CNT/PPy can be used as a cathode catalyst in MFC for ORR. After measuring the catalytic properties of CNT/PPy, it was found that the nanocomposite structure of this catalyst make it a suitable candidate for ORR. It can also be used for the oxidation reaction at the anode. However, a biocatalyst is often used for this purpose. The power density produced, high CE and lower capital cost of the system when using this catalyst make it a strong alternative for Pt as the common cathode catalyst, which creates huge potential for commercialisation of MFC.

REFERENCES


