Preparation and Characterization of Nanostructured FeN Electrocatalyst for Air Cathode Microbial Fuel Cell (MFC)

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Abstract—The present work represents a preparation of nonprecious iron-based electrocatalyst (FeN) for ORR in air-cathode microbial fuel cell by pyrolysis treatment. Iron oxalate which recovered from the industrial wastewater and Phenanthroline (Phen) were used as the iron and nitrogen precursors, respectively in preparing FeN catalyst. The performance of as prepared catalyst (FeN) was investigated in a single chambered air cathode MFC in which anaerobic sludge was used as inoculum and palm oil mill effluent as substrate. The maximum open circuit potential (OCV) and the highest power density recorded were 0.543 V and 4.9 mW/m², respectively. Physical characterization of FeN was elucidated by using Brunauner Emmett Teller (BET), X-Ray Diffraction (XRD) analysis and Field Emission Scanning Electron Microscopy (FESEM) while the electrochemical properties were characterized by cyclic voltammetry (CV) analysis. The presence of biofilm on anode surface was examined using FESEM and confirmed using Infrared Spectroscopy and Thermogravimetric Analysis. The findings of this study demonstrated that FeN is electrochemically active and further modification is needed to increase the ORR catalytic activity.

Keywords—Iron based catalyst, Microbial fuel cells, oxygen reduction reaction, palm oil mill effluent.

I. INTRODUCTION

Extensive study on the fuel cell technologies have led to the emergence of various type and categories of fuel cell in recent decade. Intermediate and low temperature fuel cell such as proton exchange membrane (PEMFC), direct methanol fuel cell (DMFC), direct borohydride fuel cell (DBFC) and microbial fuel cell (MFC) use different substances as fuel [1].MFC appears to be a new and prospective bioelectricity

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source and wastewater treatment in the future[2].Various designs such as tubular MFC[3], double chamber MFC[4], [5], single chamber MFC[6-8]and up-flow MFC[9]have been developed in order to optimize the performance of the MFC in power generation. Among them air-cathode MFC (single chamber MFC) is one of the promising MFC set up due to its sustainability, cost effectiveness, higher efficiency as well as the simple structured design[2], [10].

In air cathode MFCs, oxygen is used as the electron acceptors which highlighting the advantage of air cathode MFC in term of sustainability as it could simply obtained from the atmosphere[11]. However, the rate of oxygen reduction reaction (ORR) in the air cathode is the main drawback in this cell as it may affect the performance of air-cathode MFC[12], [13]. Oxygen reduction reaction is an electrochemical reactionthat occurs in the MFC air-cathode and MFC aqueous-cathode. In this reaction, oxygen in the cathode is reduced by accepting electrons from the anode and then combines with hydrogen ion to form water. *Oxygen reduction reaction* in aqueous solutions occurs mainly by *two pathways*: the 2-electron transfer pathway and the 4-electron transfer pathway as shownin Eq. (1), Eq. (2)and Eq. (3).

4-electron reduction pathway:

| $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ | E^0 | -1.23 | V | vs. | SHE |
|---|-------|-------|---|-----|-----|
| (1) | | | | | |
| 2-electron reduction pathway: | | | | | |
| $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ | E^0 | -0.70 | V | vs. | SHE |
| (2) | | | | | |
| $H_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$ | E^0 | -1.78 | V | vs. | SHE |
| (3) | | | | | |
| | | | | | |

Precious metal such as platinum (Pt)is commonly used for ORR activity in fuel cells. Ptis less favorable to be used in a large scale due to the high cost of the material and low catalytic stability which causes catalyst poisoning[14-16]. Alternatively, non-precious metal such as metal oxides[7], [17], [18], metal complexes[19], [20] and metal doped carbon [1], [12]have gained the attention of many researchers. Among them, metal complex poses high catalytic ORR activity because it involves four-electron transfer pathway which will not lead to high over-potential.

Application of Metal/N/C electrocatalyst(metal phthalocyanines) in fuel cell was first inspired byJasinski [21].

In recent, Khilari, et al. [19] and Tsai, et al. [22] studied the metal based catalyst for ORR in direct-methanol fuel cell and single-chambered MFCs, respectively.Li, et al. [17]reported that heat treatments of metal based catalyst create active sites for ORR. Metal based catalysts are capable to catalyze the ORR to water via four-electron pathway[12]. An effective ORR catalyst is suggested to follow the 4-electron pathway as closely as possible since the 2-electron pathway involve hydrogen peroxide production, which can lead to high over potential[23]. In this study, Iron complex catalyst (FeN) was prepared by pyrolysis method. An industrial wastewater derived iron oxalate was used as iron precursor in this study. The as-prepared FeN was characterized by X-ray Powder Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Brunauer-Emmett-Teller (BET) analysis. The catalytic activity towards ORR of FeN was characterized with cyclic voltammetry (CV) in neutral buffered solution. COD removal efficiency with various catalyst loadings was elucidated. The performance and efficiency of the air-cathode MFC with this catalyst were also examined.

II. MATERIALS AND METHODS

A. Sampling

Raw POME and anaerobic sludge were collected from Felda palm oil industries located at Kuantan, Malaysia. The Raw POME was collected from the inlet of the mixing pond and the *temperature* of *raw POME* during collection was around 80 to 90°C. Anaerobic sludge was obtained from bottom sampling port of anaerobic treatment plant. The samples were transported to the laboratory in sterile 1000 mL Schott bottles placed in ice and stored at 4°C until use.

B. Preparation of iron oxalate

Wastewater (low pH) was collected from mining and ore processing industry. Iron oxalate was prepared via precipitation method, where 1 M oxalic acid (OA) solution was added into the wastewater in volume ratio of 1:1 at 25 °C. The mixture was stirred for 1 h and left at room temperature until 2-layer phases separation formed. The precipitate was obtained and washes with D.I. water. The washed precipitate was dried in vacuum oven at 90 °C for 12 h. The precipitate was characterized by FESEM and XRD.

C. FeN preparation and characterization

The FeN was fabricated as described byTsai, *et al.* [22] via pyrolysis method. In brief, 1 g of iron (II) oxalate was mixed with 1 g of Phen in a 10 mL of ethanol to form a deep red complex solution. The complex was stirred for 30 min and followed by 30 min of sonication. The complex was then dried at 70 °C for overnight in an oven. After drying, the dried complex was grinded into fine powder. The powdered complex waspyrolyzed at 800 °C under N₂ atmosphere for 2 hrs. The pyrolyzed complex was then allowed to cool to room temperature under the N₂ atmosphere condition. Finally, the

sample was grounded to a fine powder. The FeN was characterized through FESEM, XRD and BET analysis.

D. Cathode preparation

The cathode of the MFC was fabricated by mixing 20 mg of the FeN with 0.15 mL of Nafion solution and 0.15 mL of isopropanol to form an ink. The ink was brushed evenly onto a PACF (polyacrylonitrile carbon felt) with the area dispersion of 7.02 cm². Nafion membrane was drenched overnight in dilute HCl and subsequently washed with deionized water before use.Nafion 117 membrane with a dimension of 5 cm x 5 cm was pretreated in diluted HCl at 100 °C for 1hr and followed by boiling in DI water for 1hr.Finally, the membrane was washed three times with deionized water. The pretreated membrane was kept by soaking in the DI water for overnight. The electrocatalyst coated PACF was hot pressed with the pretreated Nafion membrane at 100 °C with pressure of 1 tonne for 2 minutes[24] to fabricate a membraneelectrode assembly (MEA). Titanium wire was inserted into the PACF and used as the current collector for cathode electrode.

E. Material characterization

The surface morphology and microstructures of samples were observed by FESEM using a JEOL 7600F with an accelerating voltage of 15 kV. For FESEM sample preparation, the samples were placed on carbon tape and sputter-coated with platinum for 40 s.XRD patterns of the samples were recorded on a RigakuMiniFlex II operated at accelerating voltage of 30 kV and emission current of 15 mA with graphitemonochromatized Cu K α radiation and scanning speed 1°/min. The scanning step size 0.02° was over a range of 2 θ = 15–65°.The specific surface area was determined by a Brunauer–Emmett–Teller(BET) test using a Micromeritics ASAP-2020 nitrogen adsorption-desorption apparatus.

F. MFC set up

The single-chamber air cathode MFC was constructed using plexiglass (Shanghai, Sunny Scientific, China) with the dimension of 5 cm x 5 cm and working volume of 20mL.Carbon brush and PACF were used as anode and cathode electrode respectively. The membrane electrode assembly (MEA) was placed at the front opening side of the cubic chamber by facing the membrane side towards the anode substrate and the cathode (PACF) towards the open part of the MFC. After that, the whole MFC setup was tighten up with screws.POME sample was then diluted 50 times and 2mL of anaerobic sludge was added into the diluted POME. After mixing, the sample was then purged with N₂ gas to remove the dissolved oxygen in the sample and poured into the anode chamber of the air cathode MFC. The anode and cathode electrodes were connected by using titanium wires with a rheostat (Crotech DRB-9, UK)to form a circuit. The single chamber fuel cells were operated for 5 days at ambient temperature from 25 to 28°C.

G. Measurement and analyses

The voltage (V) and current (I) across an external rheostat (1 $k\Omega$) in the MFC circuit was monitored (1 hour intervals) using a digital multimeter with data logger (Fluke 289 True RMS Multimeter, USA) connected to the computer through USB cable adapter. External resistance was varied from 0.05 to 400k Ω using the rheostat (Crotech DRB-9, UK) to obtain polarization curve. Power density normalized by surface area (P_A) was measured using the following equation:

$$P_A = V^2 / A_{An} R \tag{1}$$

where A_{An} = area of anode electrode (m²), P = power (W), V = potential (V), R = external resistance (Ω) and I = current flow (A). The COD removal efficiency of MFC was calculated as described byBaranitharan, *et al.* [4].

H. Biofilm examination by FESEM

The samples for SEM analysis were prepared by a method described by Chae, *et al.* [25]. Parts of the carbon brush were cut and removed from the anode chamber then rinsed with a sterile medium, and immediately fixed with an anaerobic solution of 2% glutaraldehyde and 1% formaldehyde. After immersion in 1% osmium tetroxide for 24 h, samples were carefully rinsed three times in a HEPES buffer (pH 6.8) and once in deionized water. Samples were then subjected to a serial dehydration protocol using increased concentrations of ethanol (10, 25, 50, 75, 90, 100, 100, and 100) for 30 min for each stage with gentle periodic agitation and then dried completely at room temperature. Desiccated samples were coated with platinum and observed using a JEOL JSM7800F Field emission SEM at 3 kV.

I. Infrared spectroscopy (IR) and thermogravimetric analysis (TGA)

Samples were prepared for IR test by drying at 120° C overnight to remove the water, and then 1 wt% sample was ground with dry KBr. Samples were pressed into thin discs and analyzed on a Nicolet Avatar 370 DTGS FT-IR spectrophotometer under N₂ atmosphere. TGA samples (5 mg) were analyzed on TA Instruments Q500, thermogravimetric analyzer, at a heating rate of 10° C min⁻¹ in N₂ ambient.

J. Electrochemical characterization

Cyclic voltammetry (CV) analysis was done using an electrochemical workstation (PARSTAT 2273) to determine the ORR activity of the FeN. Three-electrode configuration was used where FeN coated on carbon paper served as the working electrode, Ag/AgCl as the reference electrode whereas Pt wire serves as the counter electrode. 0.1 M sodium sulphate (Na₂SO₄) solution aerated with oxygen was used as the electrolyte in the analysis.

III. RESULTS AND DISCUSSION

A. Biofilm characterization

Field Emission Scanning Electron Microscopy (FESEM) analysis of the biofilm

Figure 1 represents the SEM of the anode surface, conducted before (Figure 1a) and after the operation (Figures 1b and 1c) in the MFC in order to confirm the presence of biofilm on the electrode surface. In Figures 1b and 1c, the SEM images showed at different magnification of biofilm growth on carbon brush. Electron micrographs revealed unique biofilm structures and cell shapes. In the case of the higher magnification of SEM images (Figures 1c), the biofilm was formed by an interconnected fibre like structure which covers the electrode surface. Marsili, et al. [26]reported that the biofilm on an electrode surface contributed the key current through direct electron transfer. Figures 1c shows that biofilms were sparingly distributed on the carbon brush along with highly complicated structures comprised of morphologically different cells. The important component of biofilms known as extracellular polymeric substances (EPS), are high-molecular weight compounds secreted by microorganisms and have a significant influence on the physico-chemical properties including electron transfer. Bacteria of various sizes and shapes were scattered around the electrode, associated with a biofilm formed on its surface. Besides that many rod-shaped cells can also be seen on the biofilm (Figure 1c) including loosely associated microbial clumps present on the electrode surface (carbon brush). Kim, et al. [27]have proposed that these microbial clumps consist of bacteria that ferment the complex fuel into simple fermentation products. These products can then be used as substrate for electrochemically active bacteria within the biofilm to generate electricity [28], [29]





Figure 1 SEM images of (a) new Carbon brush (b and c) bacteria growing on anode carbon brush in the MFC fed with POME as electron source for 5 days

TGA analysis on biofilm

Anodes were also examined by TGA before and after MFC operation at different intervals $(1^{st}, 3^{rd} \text{ and } 5^{th} \text{ day})$ as shown in Figure 2. Distinct changes in overall weight losses were

observed in the conditions the operation carried out. The adhesion of a bacterial biofilm to an MFC anode affects the weight of the anode. Water adhered to the anode surfaces were probably contributed to the weight losses from 25 to 100°C due to evaporation [30]. Therefore, temperatures >100°C up to 900°C was considered remarkable for gravimetric analysis of the anode. A 5% of the total weight loss from 100 to 700°C was observed before anode operation. A slight increase to 9% in anode was observed for the 1st day while further weight losses were observed to be 11% and 18% corresponding to the 3rd and 5th days of the MFC treatment. A 3% change in weight loss was observed between 100°C and 200°C after 5 days of operation but there is almost no loss in anode before operation. This is a temperature range where bacterial organic matter is likely to decompose and burn, and thus this difference is attributed to a bacterial biofilm [30]. It is known that bacterial biofilms commonly form fibrilar and mushroom like structures [31]. The types of structures composing the biofilm and their densities are likely to affect the temperature that weight losses occur [30]. Two distinct weight loss events were observed during anode heating for 1^{st} , 3^{rd} and 5^{th} days of operation. On 1^{st} day, 2.04% from 100 to 290°C, 3.84% from 300 to 650°C were observed whereas on 3rd day, 2.8% from 100 to 290°C and 2.6% from 300 to 650°C were observed and on 5th day, 5% loss from 100 to 290°C and 10% loss from 300 to 550°C were observed. Moreover, at higher temperatures the weight loss showed sharp downward trends may be due to the decomposition of biofilms at the anode surface. The changes in TGA profiles may be attributed to the increased amount of biofilm formation on the electrode surface.



Figure 2 TGA spectrums of carbon brush anodes before and after MFC treatment

FTIR analysis of the biofilm

The anode examined by FT-IR before and after MFC operation at different intervals $(1^{\text{st}}, 3^{\text{rd}} \text{ and } 5^{\text{th}} \text{ days})$ is shown in Figure 3. The broad band observed in the 3500– 3300 cm⁻¹ range attributed to the free and bound O-H and N-H groups[32-36], which could form hydrogen bonding with the carbonyl group of the peptide linkage in the protein. The main bands of peptide linkage were related to C=O stretching at

1643 cm⁻¹ (amide I) and N-H banding at 1505 cm⁻¹ (amide II) [37]. The bands at 2917 cm⁻¹ and 2852 cm⁻¹ can be attributed to the functional groups of membrane fatty acids and also by some amino acid side-chain vibrations since here the characteristic C-H stretching vibrations of -CH₃ and =CH₂ functional groups dominate [38]. The FT-IR spectrum of the anode after MFC operation also revealed that the band observed in the 1200 and 900 cm⁻¹ range is due to the symmetric stretching vibration of PO₂⁻ groups found in nucleic acids and to C-O-C and C-O-P stretching, which exposes the occurrence of carbohydrates and polysaccharides in the cell wall but also the influence of nucleic acids [39]. These results confirm the presence of biofilm on the surface of the electrode.



Figure 3 IR spectra of carbon brush anodes before and after MFC treatment

B. XRD analysis



Fig. 4: XRD pattern of FeN catalyst and wastewater derived FeC₂O₄

The phase and crystallinity of the as-prepared FeN and recovered iron oxalate (FeC₂O₄) from industrial wastewater were examined by powder X-ray diffraction and presented Fig. 4. The XRD patterns of the iron oxalate (FeC₂O₄) shows

nine main peaks of (2 0 2), (0 0 4), (4 0 0), (0 2 2), (2 0 6), (2 2 4), (602), (0 2 6) and (4 2 6)[40] meanwhile iron (II, III) oxides (Fe₃O₄) peaks was detected in the XRD analysis at the peak of $(1 \ 1 \ 1)$, $(4 \ 0 \ 0)$ and $(5 \ 1 \ 1)$ [41] which confirmed the presence of FeC_2O_4 and Fe_3O_4 in the recovered industrial wastewater sample. The prepared catalyst was then analyzed by XRDand shows three FeN main peaks of (1 1 1), (1 1 0) and (2 2 0) [42] while 2 main peaks of Fe₂N at (-1 -1 1) and (-1 -1 2) [43]in the as prepared catalyst. This confirmed that the major phases present are FeN and Fe2N while iron (III) oxide (Fe₂O₃) phase wasalso found on 30.49°(2 2 0)[44].The average crystallite sizes of the Fe-based structures were 11-31 nm and 4-20 nm for Fe₂O₃ and FeN, respectively by using Scherrer's equation. Oxygen might have been participated in the pyrolysis to form Fe₂O₃ during the pyrolysis. Phen was used as the nitrogen precursor caused the formation of FeN.

C. FESEM analysis on FeN and FeC_2O_4

The surface morphology of synthesized FeNand FeC₂O₄ were examined by using FESEM and presented in Fig. 5. It can be seen that, irregular shape of FeC₂O₄ was obtained in the range of 1-10 μ m. After the pyrolysis, the particle size of formed FeNwas varies from 120-220 nm. Individual crystallite sizes vary from 10-50 nm which correspond to the size calculated via Scherer's equation using XRD data.This observation suggests that the synthesized catalyst is in nano-scale[45]. Growth of catalyst particles takes place via agglomeration and sintering upon heat treatment which is affected by catalyst loading whereby loading would yield higher agglomeration[46].



Fig. 5: FESEM images of the (a) $\text{FeC}_2\text{O}_4\text{and}$ (b) synthesized FeN





Fig. 6: N₂ desorption/adsorption isotherms of FeN

Porosities and pore sizes of the synthesized FeN was determined by nitrogen adsorption/desorption analysis and showed in Fig. 6. The specific surface area was calculated via 3 parameters fit method and found to be $31.74 \text{ m}^2\text{g}^{-1}$. The nitrogen adsorption/desorption isotherms of the catalyst showed a type II BET curve hinting the co-occurrence of micro- and mesopores. The median pore diameter was 18 nm and 0.67 nm for mesopores and micropores, respectively.

E. Electrochemical characterization of catalyst

The electrochemical activity of FeN in the electrolytes was characterized by cyclic voltammogram (CV) approach under an oxygen saturated Na₂SO₄ with the scan rate of 30 mVs⁻¹. As seen in Fig. 7, an obvious ORR peak of electrode coated with FeN at -0.44 mV at a similar level to that Pt/C catalyst corresponds to -0.0244 μ A current ORR at the electrode[47]. The ORR peak of FeN falls exactly at the same potential with Pt/MnO₂ under the same conditions and scan rate[6]. This indicates that the synthesized FeN is electrochemically active which can be potentially to be applied as ORR catalyst in aircathode MFC.



Fig. 7: Cyclic voltammogram for ORR of synthesized FeN and blank in O_2 saturated 0.1 M of Na_2SO_4 with scan rate of 30 mVs⁻¹



Fig. 8: COD removal efficiency $[\blacksquare-14.28 \text{ mgcm}^{-2}, \bullet-21.43 \text{ mgcm}^{-2}, \blacktriangle-28.57 \text{ mgcm}^{-2} (FeN)]$

The COD removal efficiency was presented in Fig. 8. Different catalyst loading was applied on the air cathode in order to investigate the effect of catalyst loading on the COD removal efficiency. 10 mg, 15 mg and 20 mg of FeN was used and labelled as 14.28 mgcm⁻², 21.43 mgcm⁻² and 28.57 mgcm⁻², respectively. As seen in Fig. 8, the highest catalyst loading of 28.57 mgcm⁻² provides the highest COD removal efficiency. The high catalyst loading could enhance the performance of air cathode MFC by increasing the ORR activities in the air cathode[7].

G.Performance of Air Cathode Microbial Fuel Cell



Fig. 9: Polarization curve and power density curve for the closed circuit air-cathode MFC

The single chamber air cathode MFCs were fed with 20mL of diluted POME with an initial COD concentration of 964 mg L^{-1} and anaerobic sludge as inoculum for all the experiments. In order to evaluate the efficiency of FeN as

cathodic catalyst, different loadings of FeN were used in the cathode of the MFCs andtheirperformancesweremonitored.The obtained polarization and power density curves werepresented in Fig. 9. The effective volumetric power density showed of about 231 W/m³on 5th day with a maximum open circuit voltage (OCV) of 0.543 V. The MFC performance was increased from day 1 to day 5 which is in consistent with the COD removal efficiency where the COD removal efficiency increases, the concentration of POME substrate decreases leads to the downfall of MFC performance[7].

In term of MFC performance, FeN is found to be comparable with the synthesized manganese dioxide (α -MnO₂). Table 1 presented the performance of FeN and other catalysts from previous study in air cathode MFCs.

Table I Performance comparison to literature on single chamber air cathode MFC systems

| Catalyst | Inoculum | Substrate | OCV (mV) | Max. power density (mW/ m ³) | Reference |
|----------------------------|----------------------------|-----------|-------------|--|----------------------------|
| FeN | Anaerobic sludge | POME | 543 | 231 | This study |
| No catalyst | K. pneumonia biofilm | Glucose | 395 | 102 | (L. Zhang et al., 2009) |
| α -MnO ₂ | Anaerobic sludge | POME | 549 | 338 | (Khan et. al., 2015) |
| Pt/C | K. pneumonia biofilm | Glucose | 627 | 726 | (L. Zhang et al., 2009) |

The open circuit voltages (OCV) for FeN, α -MnO₂ and Pt/C were 543 mV, 549 mV and 627 mV, respectively. The FeN catalyzed air cathode MFC produced higher OCV than the non-catalyzed air cathode MFC and it is only slightly lower than the α -MnO₂ catalyzed air cathode MFC. The maximum power density of FeN, α -MnO₂ and Pt/C were 231 mWm⁻³, 338 mWm⁻³ and 726 mWm⁻³, respectively meanwhile the maximum power density of non-catalyzed air cathode MFC was only 102 mWm⁻³. It is clearly seen that the performance of air cathode MFC has significantly improved by using FeN. Besides, it is worthy to highlight that the current study were fed with POME whereas artificial wastewater (K. pneumonia biofilm with glucose substrate) was used in the previous study byZhang, et al. [48]. The usage of domestic wastewater as anode substrate would only produce merely 30% power of that produced by artificial wastewater with similar design[24], [49]. Hence, FeN is a potential ORR catalyst which could be used in MFC.

IV. CONCLUSIONS

In this study, FeN was successfully developed from Phen and iron oxalate (recovered from industrial wastewater) via pyrolysis treatment and found that FeN has the potential to be used as electrocatalyst for air cathode MFCs. From the experimental results, we can conclude that the synthesized nanostructured FeN catalyst is electrochemically active and capable to catalyze ORR activity in air cathode MFC. In addition, the newly synthesized FeN could potentially improve the feasibility of scaling up MFC designs for real applications by lowering the cost of production as the iron precursor of this catalyst was recovered from industrial wastewater. However, further research is needed in the work in order to further improve the performance and accuracy of this research.

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