SYNTHESIS OF IRON BASED ELECTROCATALYST FOR AIR-CATHODE MICROBIAL FUEL CELL (MFC)

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
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JANUARY 2015

ABSTRACT

The world relies on major fossil fuels including oil and gas, which are predicted to deplete by 2042. At this critical stage, there is a dire need to look for alternative energy sources to reduce the dependency on fossil fuels. Rapid Industrialisation on the other hand has made the implementation of wastewater managements to be crucial even though it is energy intensive and money consuming. It has been known for the past decades that bacteria could be used to generate electricity from many substrates as in Microbial Fuel Cell (MFC). Thus, MFC could be a solution for environmental wastewater managements and at the same time would be able to solve the energy crisis by producing power. Platinum (Pt) for the past years has been widely used as the cathode catalyst to accelerate ORR and electron acceptance. Nevertheless, there is always been a driving force to produce a low-cost non precious metal catalyst for the cathode of a MFC. This work presents a preparation of non-precious iron-based electro catalyst responsible for ORR for air-cathode microbial fuel cell. Catalyst is synthesised by mixing Iron oxalate (recovered from industrial waste) and Phenanthroline in ethanol solution before being calcined under N2 atmosphere at 800^0C for 2 hours. The cathode was fabricated by coating the catalyst. Performance of the iron-based catalyst was investigated in a single chamber air-cathode MFC where palm oil mill effluent (POME) was used as the anode substrate and anaerobic sludge as inoculums. The maximum Open Circuit Voltage recorded was 0.543 mV and the highest Power density drawn was 4.9 mW/m^2 after 5 days. The physical properties of the catalyst were characterized via Brunauer Emmett Teller(BET), X-Ray Diffraction (XRD), Field Emmision Scanning Electron Microsopy (FESEM) analysis and the electrochemical properties was characterized by Cyclic Voltammetry (CV) analysis. This study shows that the synthesised catalyst is electrochemically active, and further surface modification should be done to increase its stability.

ABSTRAK

Dunia ini bergantung pada bahan api fosil utama termasuk minyak dan gas, yang diramal akan lupus menjelang tahun 2042. Pada peringkat kritikal ini, terdapat keperluan mendesak untuk mencari sumber tenaga alternatif untuk mengurangkan pergantungan kepada bahan api fosil . Perkembangan perindustrian secara mendadak sebaliknya telah membuat pelaksanaan pengurusan sisa-sisa kumuhan penting walaupun ia adalah tenaga intensif dan memerlukan wang yang tinggi . Ia telah dikenali untuk beberapa dekad yang lalu bahawa bakteria boleh digunakan untuk menjana tenaga elektrik dari pelbagai substrat seperti dalam *Microbial Fuel Cell (MFC)* . Oleh itu , MFC boleh menjadi penyelesaian bagi pengurusan air sisa alam sekitar dan pada masa yang sama akan dapat menyelesaikan krisis tenaga dengan menghasilkan kuasa . Platinum (Pt) bagi tahun yang lalu telah digunakan secara meluas sebagai pemangkin katod untuk mempercepatkan *oxygen reduction reaction ORR*. Walau bagaimanapun , terdapat sentiasa menjadi kajian yang mendorong untuk menghasilkan pemangkim logam kos rendah untuk katod dalam MFC a . Hasil kerja ini membentangkan satu penyediaan pemangkin logam kos rendah yang bertanggungjawab untuk ORR. Pemangkin ini direka bentuk dengan mencampurkan *Iron oxalate* (dipulih daripada sisa industri) dan *Phenanthroline* dan dilarutkan didalam etanol sebelum dipanaskan dengan N2 pada 800^0C selama 2 jam. Voltan litar terubukak maksimum yang direkodkan ialah 0.543 mV dan Kuasa tertinggi yang direkod adalah 4.9 mW / m2 selepas 5 hari . Ciri-ciri fizikal pemangkin telah dicirikan melalui analisa *Brunauer Emmett Teller(BET), X-Ray Diffraction (XRD), Field Emmision Scanning Electron Microsopy (FESEM) analysis and the electrochemical properties was characterized by Cyclic Voltammetry (CV)*. Kajian ini menunjukkan bahawa pemangkin yang direka memiliki cirri-ciri elektrokimia dan mampu mengantikan Pt dalam MFC.

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1 INTRODUCTION

1.1 Background of Research

Renewable energy has become nation's significant focus to solve world's environmental problems including global warming and green house effects. Thus the recent efforts have been considering waste as potential resource with the development of proper environmental technologies (Kim J.R, 2006). Microbial Fuel Cells (MFC) has received high interest and often referred to as an alternative renewable energy source which facilitates numerous ongoing researches on overcoming electricity crisis (B. Zhang, Feng, Ni, Zhang, & Huang, 2012). It is capable of producing electricity from degradation of organic and inorganic substrates in wastewater and in sludge (Hong Liu & Logan, 2004). Biochemical energy trapped in the organic matter is converted into electricity which is referred to as microbiologically mediated 'incineration' reaction (Rabaey & Verstraete, 2005).

Inventing a MFC with effective materials which are reasonably low-cost, providing sufficient surface area for oxygen reduction at the cathode and bacterial growth at the anode are among the challenges that need attention. In a MFC, electrode, catalyst and membrane are the three major materials that work together in producing electricity. Choosing the electrode material for anode and cathode should consider factors including conductivity, corrosion resistivity, cost and specific surface made available (S. Cheng, Liu, & Logan, 2006)

Theoretically, the anode is where oxidation takes place. The enzymatic capability of bacteria and the correlations between microbial communities determines the anode potential of a MFC reactor. As micro-organisms can be considered as catalyst which facilitates the electron transfer from the substrate to the anode, choosing an effective microbial consortium is vital for a MFC. Electron transfer process between the bacteria and the anode can occur either in a direct way from the bacterial membrane to the anode surface or indirectly with the aid of a mediator (Rabaey & Verstraete, 2005).

The reduction process on the other hand takes place and the second cathode chamber. This paper focuses on synthesizing a suitable catalyst which is an important yet challenging task to do considering many factors. Cathode can be positioned as a ‘membrane electrode assembly’, where it is precipitated above the conductive support or the proton exchange membrane and is exposed to open air. This method of assembly is much of a cheaper approach because there is no necessary additional effort for aeration, which got reduce electricity cost. Nevertheless, there are certain areas that should be given attention while using open air cathodes. The most important factor for an air cathode configuration is the necessity to have a non-soluble redox mediator to transfer the electrons effectively from the cathode to the electron acceptors (Rabaey & Verstraete, 2005). In MFC, many oxidants are possible candidates to perform an electron acceptors job yet oxygen is still the most suitable electron acceptor for MFC cathode, proven to be easily available, non-toxic behaviour, cheap and sustainable compared to any other alternatives for time being (Logan BE et. al., 2006).

The oxygen reduction reaction (ORR) at the cathode represents a complex four-electron reaction. Most widely used common catalyst includes carbon supported platinum (Pt/C) for the ORR at cathode (R.Basyam et. al., 2006). Nonetheless, even on a pure Pt, the over potential for ORR is in excess of 300mV. In addition, Pt is categorized as a precious metal of low abundance. Therefore, there are many ongoing studies and vast interest on developing Pt-free cathode for MFC (G. Liu, Li, Ganesan, & Popov, 2009).

Non precious metal based catalyst’s performance for the oxygen reduction in fuel cells is comparatively weak compared to Pt catalyst due to low number of active sites per unit volume. Thus, further research should be conducted on improving the performances of non precious metal catalysts.

1.2 Motivation

For the past years, it is commonly known that bacteria could be used to generate electricity from many different substrates. Advanced research on MFC would lead to venturing renewable energy and to harvest electricity from wastes. Wastewaters and palm oil mill effluent (POME) are not just wastes but could be a source of energy because they are among the industrial wastes which are capable of being converted into useful electricity using MFC in an anaerobic approach (Huang, Yang, Guo, & Zhang, 2011). The strength of MFC is that practically, any source of biodegradable organic matter can be utilised as a fuel for power generation. The versatility of MFC in the usage of vast range of microorganisms as substrate makes MFC an ideal technology for renewable bioelectricity generation from wastes (Lin, Wu, Chiu, & Tsai, 2014). There have been major developments which may direct to advances at the practical level in microbial fuel cells. The oxygen cathode in MFC is undergoing an ever-increasing level of scrutiny these days. At present, the most widely focused catalyst for ORR has to be Pt-based systems. Nevertheless, ongoing researches suggest that high possibilities are there to make significant improvements by replacing the costly Pt with other non-precious metal catalysts

1.3 Problem Statement

Since a MFC is never complete without the fundamentals of oxidation and reduction, the cathode has become a crucial factor that restricts the mechanism of a MFC in means of cost and the power that it could deliver. Oxygen is the most suitable electron acceptor abundantly available for MFC. Several materials and catalyst have been investigated for facilitating oxygen reduction at the cathode surface. The cathode materials and its design are the most vital part in developing an essential MFC (Khilari, Pandit, Das, & Pradhan, 2014). Noble catalyst including Pt, Pd, Au and Ag helps to reduce the activation energy thus improving ORR kinetics but high costs restricts their commercialization (Zhou, Chi, Luo, He, & Jin, 2011). Therefore there has been always a driving force for the synthesis of metal catalyst for improved ORR at the cathode. Oxygen electroreduction is a complicated system which closely relates electrons and may form multiple routes. The reaction mechanism is being studied by various researches and efforts are being made to improve the efficiency of catalysts without ignoring the cost.

1.4 Objective of Study

This study is conducted to synthesize and characterize Iron-based catalyst for MFC air cathode. The newly developed catalyst will be tested for its performance in MFC.

1.5 Scope

The scope of this study includes:

- Synthesise an Iron-based catalyst using iron oxalate recovered from industrial waste as the iron precursor and phenanthroline.

- Pyrolyse the catalyst in inert nitrogen at temperature higher that 700°C
- Mix catalyst with Nafion solution, paint it on carbon felt and hot pressed with Nafion membrane. The emerging electrode will be used as air cathode MFC.
- Characterize and study the performance of the newly developed catalyst in the simple chamber air cathode.

1.6 Rationale and Significance

Currently, platinum (Pt)-based catalysts and their corresponding cathode catalyst layers are among the major causes of limited performance and high cost for MFC, although these are the most promising and practical fuel cell catalysts. Some approaches to cost reduction and performance improvement have been put forward and researched for many years. However, there has been no real breakthrough yet. Through several decades, effort in the development of non-noble catalysts such as heat-treated Fe– and Co–N/C catalysts, tremendous progress has been made in catalyst synthesis methodologies and the understanding of the mechanism. The enhanced performance of the catalysts is strongly dependent on the carbon support, the source of metal and nitrogen, and the thermal treatment conditions. The mechanisms by which activity and stability are enhanced after the heat treatment of these Fe– and Co–N/C catalysts are not fully understood yet. It is necessary to answer the question of whether or not the metal is part of the active catalytic site, as well as to identify the nature of the catalytic site (Bezerra et al., 2008).

2 LITERATURE REVIEW

2.1 *Introduction to Microbial Fuel Cell (MFC)*

The microbial fuel cell (MFC) is a device that has the ability to convert chemical energy stored in the chemical bonds in organic matter to electricity using microorganisms as a catalyst under anaerobic conditions. Traditional MFCs consist of an anaerobic anode and an aerobic cathode (Li, Hu, Suib, Lei, & Li, 2010).

The organic matters are oxidized by the microorganisms and thus generate protons and electrons. The resulting electrons were transferred to the electrode meanwhile the protons were transferred through the Nafion membrane to the cathode (J. Cheng, Zhu, Ni, & Borthwick, 2010). Therefore, MFC provide new opportunities for the simultaneous wastewater treatment and electricity generation (X.-W. Liu et al., 2010). The most commonly used MFCs are constructed as a single-chamber or an “H” shape two-chamber. For this case study, single-chamber will be used with air cathode system. As the anode and the cathode compartments are similar to anaerobic and aerobic reactors, the design of MFCs that integrate these aspects in a batch reactor lead to substantial benefits in both electricity generation and the removal of organic pollutants from wastewater (J. Cheng et al., 2010).

2.2 *Electrons and protons transfer mechanism in MFC*

A MFC converts chemical energy trapped within a bio-convertible substrate into electricity. As mentioned in earlier contexts, MFC consist of an anode, a cathode, a proton exchange membrane and an electrical circuit which connects both the anode and the cathode.

Bacteria are used as a catalyst to convert organic compounds into CO_2, water and energy. Bacteria that exist at the anode are allowed to convert bio substrates such as glucose, acetate or even waste water (electron donors) into $CO_{2,}$ proton and electrons. Energy is gained by transferring electrons from the electron donor to an electron acceptor (oxidant). The energy emitted is then utilised by the microorganism to regulate its metabolism. Electrons then flow via an external circuit and arrive at the cathode where the oxidant is reduced using the electron delivered by the anode.

A potential difference (Volt) would be established across the anode and cathode incorporated with the flow of electros (Ampere) which leads to the generation of electrical power. To close the loop, protons migrate through the proton exchange membrane to the cathode. Electrons, protons and oxygen at the cathode combine to produce water (Demirel Y, 2012; Rabaey et. al., 2005; Freguia at. al., 2007).

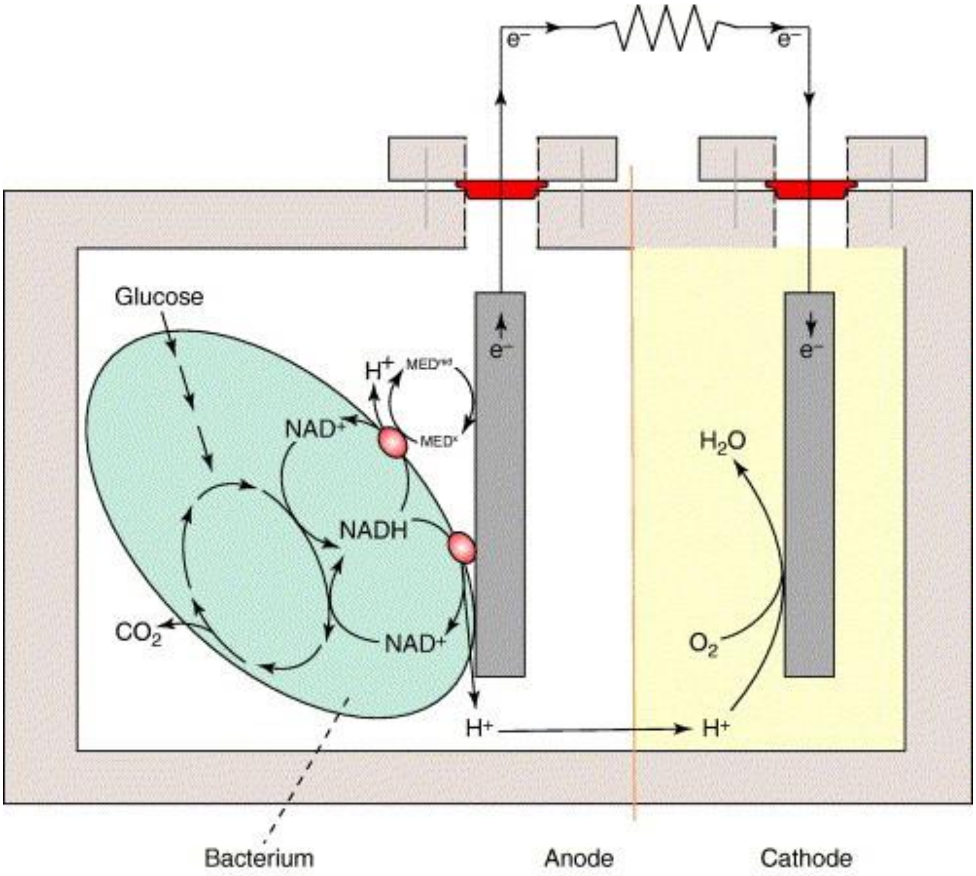

Figure 2-1: The working principle of a microbial fuel cell by Korneel Rabaey (2005).

From Figure 2-1, we can see that the substrate is metabolized by bacteria, which transfer the gained electrons to the anode. This can occur either directly through the membrane or via mobile redox shuttles, redox mediator, Red oval, terminal electron shuttle in or on the bacterium. (Korneel Rabaey et. al., 2005).

2.3 Kinetics and Mechanism of Oxygen reduction Reaction

The main reaction that occurs in the MFC cathode is an oxygen reduction reaction, in which oxygen molecules are reduced by accepting electrons from the electrode. Many oxidants are possible candidates for electron acceptors in MFC including cathodic mediators like permanganate, ferricyanide, persulfate and ferricyanide.

Nevertheless, Oxygen is most preferred electron acceptor being easily available, having a low cost, non-toxic behaviour and more sustainable than other oxidants down the line. Oxygen reduction reaction (ORR) consists of a series of electron transfer process that relies on the cathode's catalyst. General electroreduction of oxygen occurs via 2 pathways namely 2-electron and 4 electron pathways, whereby the latter is more favourable as 2-electron path would involve hydrogen peroxide formation leading to high over potential (Liew et al., 2014)

4-electron electroreduction of oxygen pathway: $O_2 + 4H^+ + 4e^-$ --> H_2O
2-electron electroreduction of oxygen pathway: $O_2 + 2H^+ + 2e^-$ --> H_2O_2

2.4 Catalyst

A catalyst is a substrate that initiates or facilitates a chemical reaction; a substance that boosts the kinetic of a given reaction

2.5 Pt-based Alloy Catalyst

Heterogeneous Pt catalysis was first commenced by Dobereiner for oxygen reduction in 1823 (G.B. Kauffman, 1999). Research and development (R&D) on enhancing the stability and activity of Pt-based electrocatalyst was dominant when United Technology Corporation (UTC) commercialized phosphoric acid fuel cell (PAFC) at a period where Pt was being referred to as the best catalyst. Kunz and Gruver introduced carbon black as support for polytetrafluoroethylene (PTFE)-bonded Pt which was a major upswing as carbon support provides: (i) uniform dispersion of highly loaded catalysts; (ii) better electrical conductivity; (iii) chemical stability of support material; (iv) Prevention of Pt agglomeration. Jalan in 1980 issued a patent for his binary Pt-V/C catalyst which showed good activity and durability towards ORR compared to pure Pt catalyst (V.M. Jalan, 1980). The group then found more stability improvements when they invented ternary catalyst of Pt-Cr-Co/C for PAFC system (F.J. Luczhak et. al., 1984). Ever since polymer electrolyte membrane fuel cell (PEMFC) was given priority, researches on electrocatalyst for ORR favored the development of carbon supported Pt-alloys.

Carbon supported Pt-alloys often come with four setbacks: (i) resource limitation and cost; (ii) Pt catalyses ORR via two-electron reaction, forming undesired Hydrogen Peroxide which gives negative impact to the cathode and membrane; (iii) Pt catalyst are sensitive towards contaminants including NO_x, or SO_x in the feed which will lead to irreversible catalyst active site poisoning at low temperature; (iv) Pt is capable of catalyzing oxidation of organic molecules over the anode which will result in mixed potential (Lei Zhang, Zhang, Wilkinson, & Wang, 2006).

2.6 Transition metal/N/C composites for ORR

Over the past years, some of the effort in producing a cathode electrocatalyst has been focused onto metal-N_4 macrocycles and such as Fe- and Co- macrocycles. This class of catalyst often show inertness to alcohol oxidation. Besides that, many of them are capable of catalyzing the ORR to water via a four-electron process without producing the undesired peroxide. Early studies regarding metal/N/C electrocatalyst was first inspired by Jasinki when he found that heat-treated macrocyclic structure containing nitrogen-metal coordination have potentials towards ORR (R.Jasinski. Nevertheless, this kind of catalyst possessed low stability in acidic media caused by loss of the active site due to the attack of hydrogen peroxide generated during the O_2 reduction. When this class of metal composite was exposed to high temperature heat treatment method aiming to create electrochemically active compounds for ORR, it was then found that the stability was improved. Researchers concluded that heat treatment is critical to produce better catalytic activity. (Bezerra et al., 2008). The nature of the bonding in macrocyclic compound is broken during heat treatment which forms new compounds with 1 metal coordinated by 2 N atoms, simply called metal-N_{2}/C as shown in the Figure 1 below, which is believed to host catalytic activity and selectivity towards four-electron reduction pathway and reducing the formation of hydrogen peroxide. (Wong et al., 2013).

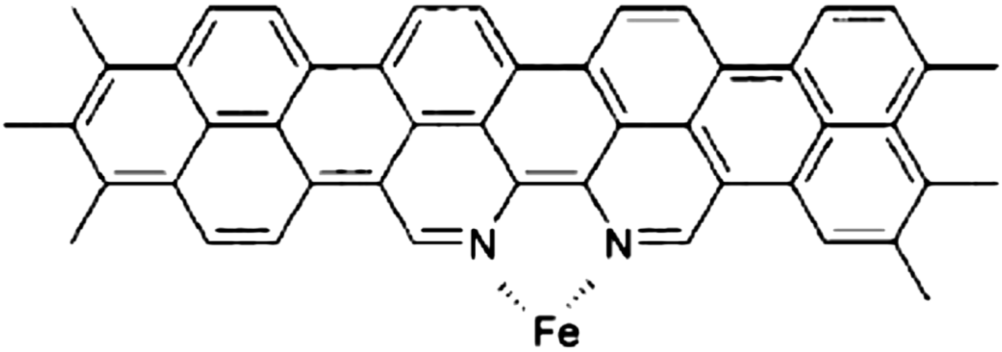

Figure 2-2: Proposed moiety of the FeN_2/C catalytic site by M. Lefevre.

Researches confirm that ORR activity of metal composites on nitrogen modified carbon is more superior that of the metal composite with only a carbon support or composites with metal-free nitrogen-modified carbon (Zhang et. al., 2010).

2.7 *Iron (Fe)-based electrocatalyst*

In early years, catalysts were obtained by adsorbing $Fe\text{-}N_4$ or $Co\text{-}N_4$ macrocycles on a carbon support and pyrolyzing the resulting material in an inert atmosphere (J.P. Dodelet et al., 2006). A great finding by Yeager revealed that these often-expensive macrocycles could be instead substituted by individual N and Co (or other metal) precursors (S. Gupta et al., 1989).

Michele Lefevre and his team started their effort by synthesizing non-precious metal catalysts (NPMC) by using NH_3 as a nitrogen precursor. They obtained their catalyst by wet impregnating FeAC onto carbon black and followed by heat treatment (pyrolysis) in NH_3. NH_3 partially gasifies the carbon support, leaving behind micropores on the carbon support. The mass loss at which maximum activity is reached corresponds to the largest microporous surface are etched carbon. These micropores are said to host the catalytic sites. The reaction of NH_3 with the disordered carbon domains creates a N-bearing functionalities which aids the binding of iron cations to the carbon support (Lefèvre, Proietti, Jaouen, & Dodelet, 2009). Fe/N/C catalytic sides have been proposed to have iron cation coordinated by four pyridinic functionalities attached to the edges of two graphitic sheets, each belonging to adjacent crystallites on either side of a slit pore in the carbon support (F.Charretuer et al., 2008).

Iron based catalysts have been poorly competitive with platinum catalyst due to the presence of comparatively low number of active sites per unit volume.

Lefevre’s team then came with another modified method. This time they found that high increment in site density was obtained when a mixture of carbon support, phenanthroline and ferrous acetate were ball-milled and then sent for first pyrolysis under argon followed by another consecutive pyrolysis in ammonia (Lefèvre et al., 2009). Phen acted as a pore filter which is small enough to enter and fill the micropores of the carbon support so that upon heat treatment it would produce a carbon poly-aromatic structure whose carbon originated from the Phen itself. Iron forms a deep red $[Fe(Phen)3]^{2+}$ complex upon mixing with phenanthroline as shown in Fig. 2(a). From their study, they presented Fe/N/C catalytic side, consisting iron cation coordinated by four pyridinic functionalities attached to the edges of two graphitic sheets, each belonging to adjacent crystallites on either side of a slit pore in the carbon support as proposed by F.Charretuer (F.Charretuer et al., 2008) as shown in Fig. 2(b). The current density of a cathode made with their best iron-based electrocatalyst reported to equal that of platinum in a polymer electrolyte membrane fuel cell (PEMFC).

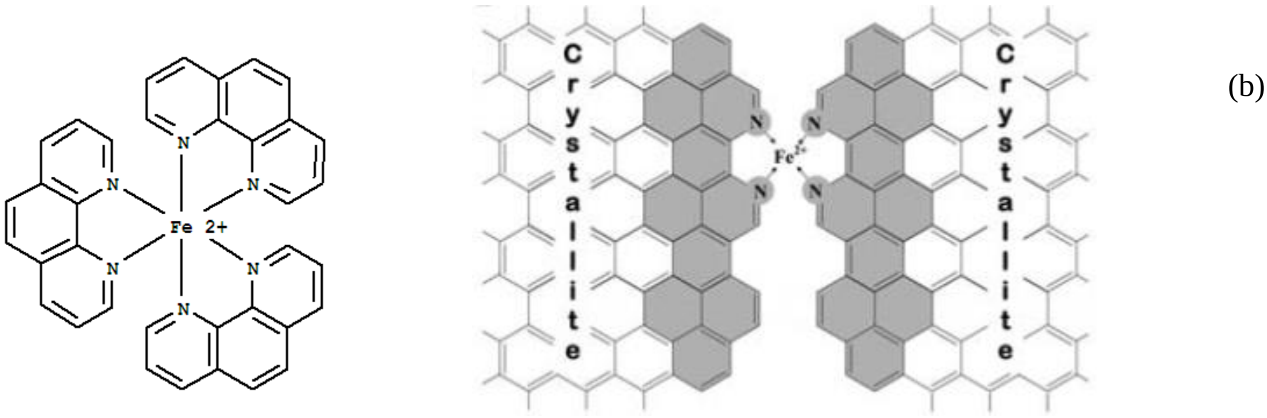

Figure 2-3: (a) The structure of Phens connected to 1 Fe atom to form a positively charged $[Fe(Phen)3]^{2+}$ (b) Plan view of the presumed catalytic site and graphitic sheet growth (shaded aromatic cycles) between two crystallites after pyrolysis. (M.Lefevre et. al., 2009)

2.8 Important factors for ORR

There are certain factors that need to considered and implemented in order to enhance the ORR activity of catalysts which iron-based. Metal precursors, nitrogen precursors, carbon supports, heat treatment and metal loading are among the factors that should be studied in order to produce high-performance iron-based electrocatalyst. These factors will further discussed in the following subtopics.

2.8.1 Metal Precursors

Metal precursors are often organometallic (ferrocene), N_x-metal chelates (FePc,CoPc, FePhen) or other simple metal salts including sulphates, nitrates and acetates. The structure of the metallic centre in the precursor is an important factor for improving activity after heat treatment. Reviews have shown that Fe and Co display numerically high activity among its other transition metal alternatives (Bezerra et al., 2008). A great experimental comparison was made by Ohm and his group by synthesizing and heat treating carbon-supported ORR catalyst using MSO_4 (M=Mn, Fe, Co, Ni, Cu) and $ZnCl_2$ as metal precursor and polyacrylocyanine (PAN) as nitrogen precursor. Co showed the greatest activity followed by Fe and Mn yet Fe-based catalyst showed more onset potential than Co catalyst. Fe-containing catalyst is capable of catalyzing the ORR via a quasi-four-electron reduction (Bezerra et al., 2008). Heat treated CoTPP/FeTPP prepared by Jiang and Chu was an example got the success of binary transition metal macrocycles which showed better catalytic activity than respective single metal-containing catalyst (R.Jiang et. al., 2000).

2.8.2 Nitrogen Precursors

Nitrogen has been identified as a major component of a catalytic active side. Wei et al. in his study noticed that surface concentration of Nitrogen directly influenced the catalytic activity. Therefore, it is important to choose an appropriate N-containing precursor from common precursors including NH_3, acetonitrile, pyrrole, N-containing polymers, and carbon carrier modified with N.

Cote and his group adsorbed $Fe(OH)_2$ on carbon black to produce $Fe(OH)_2/C$, which was then heat treated at 1000°C with various N-containing precursors such as PAN, TCNQ, H_2Pc, NH_3, and CH3CN. They found that the catalytic activity increased in the order of PAN<TCNQ<H_2Pc. NH_3 and CH_3CN were observed to have a similar effect on the catalyst activity, and did not qualify to be equivalent N-containing precursors. However, Faubert and his team indentified some differences in the behaviour of NH_3 and CH_3CN when they were used as N precursors. According to them, when NH_3 was used in the pyrolysis, not only were N atoms incorporated into the support, but also the carbon microstructure was modified (Faubert, Cgti, Dodelet, Lefi, & Bertrand, 1999). On the other hand, when CH3CN was used as the N precursor, the decomposition products were deposited on the support, forming thin graphitic structures(M. C. Martins Alves, J. P. Melet2 D. Guay, M. Ladouceur, 2006). NH_3 has been choice of nitrogen precursor for heat treatment for many researchers including Lefevre (Michel Lelevre, Proietti, J aouen, Dodelet, & Hay, 2013)

2.8.3 *Carbon Supports*

Carbon supports ensures good catalytic activity and stability of heat-treated metal macrocycles. Carbon support options include carbon black, carbon nanotube (CNT), and activated carbon. The degree of catalyst dispersion is heavily influenced by surface properties of the carbon support. Heterogeneous carbon surfaces with basal and the prismatic or edge crystalline planes have higher surface area compared to homogeneous ones. It is also a well-known fact that surface area, porosity, electrical conductivity, ordering (crystallinity), and ORR activity differ from one type of carbon support to another.

Since Nitrogen is a major component of an active site, the surface N content on the carbon is an important factor that needs to be considered. Studies done by varying carbon supports of iron-based catalysts showed that N concentration was proportional the catalytic activity. Carbon support which has the most N-binding groups performs better. Methods of introducing N groups on the carbon surface include reaction of carbon materials to N-containing gas at an elevated temperature and carbonizing N-containing compounds.(Bezerra et al., 2008).

Some researchers have tried have pre-treated the carbon support with HNO_3 before the heat treatment in the presence of an N- containing precursor which yielded higher ORR activity. It was described that the oxidized carbon surface has more oxygen-based functionalities such as quinone groups. These groups indulge the adsorption of amines and increase the polarity of the carbon support. This leads to a better dispersion of metal ion on the surface, resulting in higher ORR catalytic activity. (Bezerra et al., 2008)

Heat treatment of the carbon support in an inert atmosphere would lead to a loss of oxygen surface groups through their decomposition into CO and CO2, giving a better resistance of the support against corrosion (Hansan Liu, Song, Tang, Zhang, & Zhang, 2007). Gouerec and his team in their study encountered that catalyst synthesised using deoxygenated carbon surface showed better ORR activity than similar catalysts prepared without heat treatment(Goukec et al., 1999). They further hypothesised that oxygenated surface groups cover the chelate structure from breaking down during heat treatment.

2.8.4 Heat treatment/ Pyrolysis

Even though many researchers have put in a lot of effort in Fe- and Co- based ORR catalyst, the mechanism that ORR follows and the accurate structure of the active site are still unclear. Trouble is still there in disclosing the controlling parameter for the preparation of active catalyst though vast range of methodologies had been employed. Nevertheless, there is always a strong understanding in most literatures that heat-treatment improves both activity and stability of most electrocatalyst.

Van Veen and his group in 1988 proposed four models to explain the positive effects of heat- treatment: (i) improving the dispersion of the supported chelate; (ii) catalyzing the formation of a special type of carbon, which is actually the active phase; (iii) generating the M–N species; and (iv) promoting a reaction between chelate and subjacent carbon in such a way as to modify the electronic structure of the central metal ion with retention of its N_4 coordinated environment (J.A.R. van Veen et. al., 1988). Some papers supported model (iii) and (iv) by hypothesizing that the partial destruction of metal complexes throughout pyrolysis and the formation of secondary structures comprising of M-N/C are accountable for catalytic activity. Model (ii) was favoured by few more saying that metal atom is not part of the active site, yet it is vital for the generation of such active sites. Groups that supported model (i) reviewed that the adsorbed macrocycle forms several bonds with the support during the heat treatment, which can improve the catalyst stabil- ity (oxidative destruction and hydrolysis)(Bezerra et al., 2008).

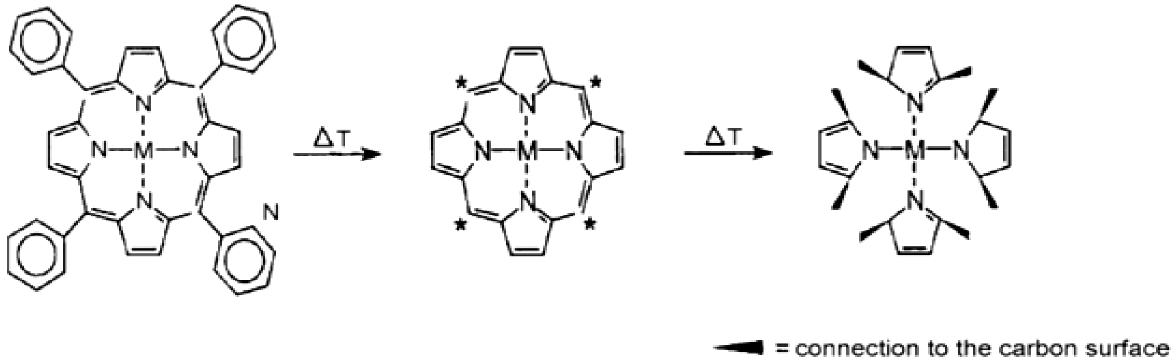

Figure 2-4 : The visualization of the reaction of porphyrin with carbon during the heat treatment by A.L. Bouwkamp-Wijnoltz et. al., (2002)

Polymerization of chelates is responsible for increased activity which facilitates the electron transfer from the carbon support to O_2. Should the emerging active site, be MN_{4-} or MN_2- units depend on the heat treatment. According to some studies, it was observed that the structure of the metal–N_4 moiety can be maintained at lower temperatures and gradually disappeared, partially or completely, at medium and high temperatures. The final catalyst seems to have two types of active sites: one is 1 metal coordinated by 4 N atoms, and the other is 1 metal coordinated by 2 N atoms, to form MN_4/C andMN_2/C, respectively (see Fig. 2.2 and Fig 2.3). The MN_4/C moiety is more abundant at low pyrolysis temperatures (below 700 ◦C) and it favours the reduction of the molecular oxygen to H_2O_2, while the MN_2/C moiety can be formed at temperatures around 700 ◦C and has both catalytic activity and selectivity towards the 4e− pathway mechanism to produce water.(Bezerra et al., 2008)

Lefevre observed that regardless of any metal precursor (simple salts or macrocycles) used, the same catalytic sites were formed. He concluded that MN_4/C and MN_2/C catalytic side should be independent of the way in which the catalyst is prepared and this conclusion was supported by XPS, thermogravimetric analysis, X-ray powder diffraction (Bezerra et al., 2008).

2.9 Characterization methods for Air-cathode MFC

The specific surface area of the synthesised electrocatalyst is to be calculated by a multipoint Brunauer-Emmett-Teller (BET) analysis of nitrogen adsorption/desorption isotherms on a surface area analyzer (Liu et al., 2009). The crystallographic structures for the electrocatalyst is to be analyzed using X-ray powder diffraction (XRD) under Cu Kα radiation (λ=1.5418 Å)(Tsai et al., 2011). By running the field emission scanning electron microscopy (FESEM), the morphological image of the synthesised electrocatalyst could be obtained (Harris et al., 2007). In order to study the electrochemical properties of the catalyst, Cyclic Voltammetry(CV) will be carried out where it will record the current drawn from the electrodes as it is cycled between the chosen high and low potentials. The resulting voltammogram will be used to analyze the electrochemical surface area, mass and area specific activities of the catalyst (Othman et al., 2012).

3 MATERIALS AND METHODS

3.1 Materials

All the materials (chemicals) that were used during the synthesis of Fe electrocatalyst will be listed and their physical properties will be detailed out as follows:

- **1,10-Phenanthroline (Phen)**

Table 3-1: Physical properties of 1,10-Phenanthroline

	Physical Properties
CAS Number	66-71-7
Molecular Formula	$C_{12}H_8N_2$
Physical State	Solid
Molecular Weight	180.21 g/mol
Appearance	Off-white
Odour	Weak Odour
Melting Point	97 - 102 °C
Purity	99.9 %

Source: Sigma-Aldrich MSDS for 1,10-phenanthroline