Improvement of the oxygen reduction cathodes of microbial fuel cells designed to treat municipal wastewater

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Richard John Burkitt

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Thesis committee

Thesis supervisor
Dr Eileen Hao Yu
Lecturer
Newcastle University

Thesis co-supervisor
Prof. Keith Scott
Professor of electrochemical engineering
Newcastle University

Viva panel chair
Prof. Justo Lobato Bajo
Chemical Engineering Department Campus Universitario, Ciudad Real, Spain.

Viva panel internal examiner
Prof. Sudipta Roy
Professor of electrochemistry and nano-materials
Newcastle University

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Richard John Burkitt
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Abstract

The Microbial Fuel Cell is a technology for self-powered pollution remediation, receiving widespread academic interest only since the turn of the 21st century. The device centres on immobilised anaerobic microbes that oxidise organic pollutants in industrial or domestic wastewater and generate an electrical charge. To generate useful energy from this charge, oxygen is commonly used as an electron acceptor at a cathode to complete the cell. This oxygen reduction reaction (ORR) requires catalysis and is thought to produce H$_2$O at pH7. High cost materials such as Platinum and energy inefficient materials such as activated carbon are typically used to catalyse this reaction in MFC’s. The majority of ORR catalysis research is based in acid or alkali media. To facilitate MFC commercialisation the project aim was to enhance cathode performance by developing an active, selective, stable and low cost oxygen reduction catalyst. Presented within this thesis is a fundamental study of the enzyme mimic catalyst Iron Phthalocyanine (FePc). With the addition of a novel anion selective binder and membranes, the low cost cathodes are applied to laboratory scale single chamber MFC’s fed with primary clarifier influent wastewater.

With use of a rotating ring disc electrode, the O$_2$ reduction mechanism was found to produce OH$^-$ and the O$_2$ adsorption step was not rate limiting. The mechanism with the lowest overpotential proceeds through an intermediary of strongly adsorbed peroxide. Unfortunately, partial release of this H$_2$O$_2$, ranging from 0.5 to 7%, caused catalyst destabilisation. The traditional approach of catalyst pyrolysis was found to be ineffective remedy, reducing the number of viable sites (by 96%) and overall activity.

It was hypothesised that pH splitting from OH$^-$ production could be reduced with anion selective materials. A Quaternary-1,4-diazabicyclo-[2.2.2]-octane Polysulfone (QDPSU) anion exchange ionomer utilising a Dabco anion exchange group was implemented in thin films and MFC cathodes as a substitute for Nafion. A facile tafel slope of 25.4 mV per decade of current implied a decrease in the overall activation energy for ORR. Oxygen diffusivity was comparable with Nafion and in real wastewater the air cathodes producing an average of 34% more power in MFC’s. An impedance spectroscopy study identified a numerical way of quantifying the poisoning of anion exchange groups. The addition of ion selective membranes increased the
resistance showing this process to be related to ion diffusion, thin membranes with quaternary ammonium produced the best results.
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For my parents John and Dorothy,
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Nomenclature

**Electrochemical and physical parameters**

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<th>Meaning</th>
<th>Usual Unit</th>
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<td>Electrochemical Double Layer resistance</td>
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</tr>
<tr>
<td>$R_{dbl}$</td>
<td>Diffusion layer Mass transfer resistance</td>
<td></td>
</tr>
<tr>
<td>$s$</td>
<td>Laplace plane variable</td>
<td></td>
</tr>
<tr>
<td>$t_{\text{step}}$</td>
<td>Time period of potential step in staircase cyclic voltammetry</td>
<td></td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature $\text{°K}$</td>
<td></td>
</tr>
<tr>
<td>$VOL_{\text{an}}$</td>
<td>Anode chamber volume $\text{cm}^3$</td>
<td></td>
</tr>
<tr>
<td>$VOL_{\text{cat}}$</td>
<td>Cathode chamber volume</td>
<td></td>
</tr>
<tr>
<td>$V_{\text{cell}}$</td>
<td>Cell Voltage $\text{V, mV}$</td>
<td></td>
</tr>
<tr>
<td>$W_{1/2}$</td>
<td>Peak Width at Half Maximum height $\text{X-axis scale}$</td>
<td></td>
</tr>
<tr>
<td>$x$</td>
<td>Distance from electrode surface $\text{cm}$</td>
<td></td>
</tr>
<tr>
<td>$Z$</td>
<td>Charge of a particle or intermediary</td>
<td></td>
</tr>
</tbody>
</table>
These symbols are used throughout the thesis to refer to the axis of the graph and the numerical treatment, e.g. $\sigma$ vs. $E$ plot.

**Material and chemical abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEM</td>
<td>Anion Exchange Membrane</td>
</tr>
<tr>
<td>ASR</td>
<td>Area specific resistance</td>
</tr>
<tr>
<td>BDE</td>
<td>Bond Dissociation Energy</td>
</tr>
<tr>
<td>BES</td>
<td>Bio-electrochemical Systems</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>CE</td>
<td>Counter Electrode</td>
</tr>
<tr>
<td>CEM</td>
<td>Cation Exchange Membrane</td>
</tr>
<tr>
<td>DABCO</td>
<td>Di-azobicyclo-[2.2.2]-octane</td>
</tr>
<tr>
<td>DMAC</td>
<td>Di-methyl Acetamide</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------------------------------------------------</td>
</tr>
<tr>
<td>DMSO</td>
<td>Di-Methyl Sulfoxide</td>
</tr>
<tr>
<td>DIW</td>
<td>De-ionised Water</td>
</tr>
<tr>
<td>DFT</td>
<td>Density Functional Theory</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>EPPG</td>
<td>Edge Plane Pyrolitic Graphite</td>
</tr>
<tr>
<td>emf</td>
<td>Electromotive Force</td>
</tr>
<tr>
<td>FePc</td>
<td>Iron Phthalocyanine</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width Half Maximum</td>
</tr>
<tr>
<td>GC</td>
<td>Glassy Carbon</td>
</tr>
<tr>
<td>GDE/GDC</td>
<td>Gas Diffusion Electrode/Cathode</td>
</tr>
<tr>
<td>HF</td>
<td>High Frequency</td>
</tr>
<tr>
<td>LF</td>
<td>Low Frequency</td>
</tr>
<tr>
<td>NPc</td>
<td>Napthalocyanine</td>
</tr>
<tr>
<td>PBS</td>
<td>Phosphate Buffer Solution</td>
</tr>
<tr>
<td>PP</td>
<td>Porphyrin</td>
</tr>
<tr>
<td>GC</td>
<td>Glassy Carbon</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly Orientated Pyrolitic Graphite</td>
</tr>
<tr>
<td>IHP</td>
<td>Inner Helmholtz Plane</td>
</tr>
<tr>
<td>KJB</td>
<td>Ketjen Black ECJ300 (Carbon Black)</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear Sweep Voltammetry</td>
</tr>
<tr>
<td>MON</td>
<td>Monarch 1000 (Carbon Black)</td>
</tr>
<tr>
<td>MEC</td>
<td>Microbial Electrolysis Cell</td>
</tr>
<tr>
<td>MFC</td>
<td>Microbial Fuel Cell</td>
</tr>
<tr>
<td>MeO₅ₓ</td>
<td>Transition Metal Oxides of varying oxidation state</td>
</tr>
<tr>
<td>NADH</td>
<td>Nicotinamide Adenine Dinucleotide</td>
</tr>
<tr>
<td>OCP</td>
<td>Open Circuit Potential</td>
</tr>
<tr>
<td>OHP</td>
<td>Outer Helmholtz Plane</td>
</tr>
<tr>
<td>ORR</td>
<td>Oxygen Reduction Reaction</td>
</tr>
<tr>
<td>PEM(FC)</td>
<td>Proton Exchange Membrane (Fuel Cell)</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>QDPSU</td>
<td>Quaternary-1,4-diazabicyclo-[2.2.2]-octane Polysulfone</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating Disc Electrode</td>
</tr>
<tr>
<td>RE</td>
<td>Reference Electrode</td>
</tr>
<tr>
<td>RHE</td>
<td>Reversible Hydrogen Electrode</td>
</tr>
<tr>
<td>RRDE</td>
<td>Rotating Ring Disc Electrode</td>
</tr>
<tr>
<td>RDS</td>
<td>Rate Determining Step</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated Calomel Electrode</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoemission Spectroscopy</td>
</tr>
<tr>
<td>WE</td>
<td>Working Electrode</td>
</tr>
<tr>
<td>WW</td>
<td>Wastewater</td>
</tr>
</tbody>
</table>
Chapter 1. Background on principles of bioelectrochemical systems
1.1 Sustainable treatment of wastewater

The demand placed upon water and power resources continually escalates as land use and population growth intensifies. Wastewater treatment allows sustainability of water resources but at the cost of high electricity consumption. Centralised collection of wastewater generated from the domestic wastewater of cities offers a unique opportunity for turning a source of pollution into a resource. Domestic wastewater contains approximately 9.5 kJ litre⁻¹ of unutilised energy in the form of oxidizable organic pollutants. The current treatment method of oxygenation and microbial remediation does not attempt any recovery of this energy. The processes involved in wastewater collection and treatment can incur 4% of the electricity output of a first world nation [1].

In terms of global warming, this electricity consumption relates to significant environmental damage. In addition, the anaerobic methods used to treat domestic wastewater release large quantities of N₂O and methane, a greenhouse gas 19 times as potent as CO₂ (20 year scale). An analysis of traditional wastewater treatment showed that 1 megalitre of wastewater produced 340g of CH₄ and 335kg of CO₂ [2]. The introduction of a technology that transforms all organic pollution to CO₂ and most importantly, avoids consuming 4% of the national grids consumption would significantly improve the green credentials of the wastewater treatment industry. Wastewater companies in a first world country such as the US would not consume ~$18,000 million of electricity per year¹. Electricity current produced via means incurring CO₂ discharge.

In third world nations the electricity and construction cost can lead local government to discharge untreated effluent, resulting in a significant environmental cost. Eutrophication in freshwater streams and a reduction in freely available potable water are problems that are rife in landlocked third world countries, impacting human health and the ability to grow food. Attempts to cultivate food by using human sewage and industry wastewater result in cytotoxicity of the most basic and essential foodstuffs [3], toxins that show bio-accumulation effects.

¹ US consumes 28,714 TWh year⁻¹. Treatment stage needs 1.6% of US consumption. Industry price $0.06 kWh⁻¹
In first world nations the environmental impact of sewage is largely abated due to treatment. Some pollutants such as Estrogens [4], endocrine disruptors [5] and antibiotics [6] can survive traditional sewage treatment processes and require energy intensive tertiary treatment or are discharged into river courses. These can result in problems for animal reproduction and microbial imbalances favouring antibiotic tolerant pathogens. An approach that does not simply rely on anaerobic and aerobic bacteria may be more effective at removing these pollutants. Approaches such as contact adsorption, oxidising agents or electrochemical decomposition are areas of intense academic interest. These approaches are promising but can incur the problems of adsorption saturation and energy consumption when producing the oxidising agents, while the electrochemical approach lacks a direct power source of its own.

New sewage treatment technologies that can be applied on locally and at a small scale can potentially abate many of these environmental effects. Anaerobic digestion plants have been successfully applied to make nutrient rich earth in such settings as used mine pits and farming communities. They produce 40% CO₂ and up to 60% methane, a concentration high enough to burn for electricity generation. The cost of large reactor units is still high and mechanised equipment is required to handle the larger units. A scalable design with no moving parts or the need for mechanised equipment beyond the construction stage would improve quality of life around the world.

1.2 Established technologies and the monetary case for MFCs

The typical energy content of domestic wastewater is 1,750 kWh per mega-litre [2]. In England and Wales this means ~730,000 kW of unused energy finds its way to sewage treatment facilities in the UK. Remediation of this energy could also occur without centralised collection, such sources may include intensive agriculture, and select industries associated with organic products. This would have the combined benefit of remediating pollution and avoiding the construction of expensive centralised collection infrastructure to rural or remote locations.

The impact of the MFC has not yet been felt in the realm of popular science. The first full Life Cycle Analysis of MFCs, MECs and Gasification was carried out by Foley et al [7] in 2010, a Microbial Electrolysis Cell approach was recommended due to the transportable nature of the H₂. Established technologies for wastewater treatment
include Upstream anaerobic baffled tank reactor, Aeration tank, Gasification, Activated Sludge, Trickling filters, Membrane ultrafiltration (bacteria and micro-agglomerates), Electrochemical treatment and consumable oxidising agents.

1.3 The microbial fuel cell

A fuel cell can be defined as, “An electrochemical device that oxidises a substrate, creating a diffusive chemical species and electrons which are captured by the electrode (anode) which is connected in an external circuit to an electrode (cathode), an electrode that is in the presence of an oxidising agent. This allows the diffusive chemical element created at the anode to recombine with electrons in the presence of the electron acceptor, thus creating a continual current.” [8]

A microbial fuel cell (MFC) fits this description by offering a unique way of harvesting the metabolic efforts of microbial life, utilising the potential difference across the periplasmic membrane.

In the simplest description, microbial metabolism relies on the diffusion of substrate through cellular membrane and the removal of metabolic product through the same avenue. The process requires a thermodynamically favourable net energy gain between the reaction of an electron donor and an electron acceptor. The oxidation of organic substrate produces electrons, initiating a chain of chemical conversions that result in a potential difference inside and outside the cell membrane. In an exocellular setting, the electron acceptor does not readily perform the reaction without catalysis, in the cell the reaction is broken into many steps.

The cell voltage \( V_{cell} \) ideal for an MFC is equated to the free energy liberated by full cell reaction with a thermodynamic energy change of \( \Delta G \) (J mole\(^{-1}\)), illustrated in Eq.1-1. Where \( n \) = no. of electrons liberated/consumed, \( F \) = Faraday’s constant, \( T \) is temperature (°K), \( E^0' \) is the formal potential (V) and \( K \) is the concentration equilibrium value between reactants and products when net reaction rate is zero (variable units). For a full fuel cell reaction at two electrodes \( E^0' \) approximates \( V_{cell} \) when the electrodes are electrically isolated. A full cell reaction is divisible into two half-cell reactions (a) anode, (b) cathode, where eq.1-1 applies to the \( \Delta G_f \) change between reactants and products for either half-cell reaction, generating \( E^0' \), a formal electrode potential.
\[ \Delta G = -nFE^o = -RT \ln K \quad \text{(Eq.1-1)} \]

The first paper on a bioelectrochemical system was released in 1911 by Potter [9]. The study utilised a yeast anolyte and received little follow up interest due to the modest \( V_{cell} \), of 0.32 Volts.

Some bacteria regulate metabolism by dumping electrons via transfer to redox proteins in the periplasmic membrane. From this point transfer to an extra-cellular acceptor is achieved with nano-wires, mediators or direct electron transfer from membrane bound redox enzymes to solid surface. These organisms are known as exo-electrogens and oxidise organic pollutants in an MFC [10]. The anode replaces oxygen as the electron acceptor under certain anerobic conditions. Exo-electrogens may be present in a consortia or a pure strain, thriving in anaerobic (no oxygen) and occasionally anoxic (low oxygen) environments.

Exoelectrogenic biocatalysis of acetate (a volatile fatty acid) at the anode produces protons, electrons, biomass and \( \text{CO}_2/\text{HCO}_3^- \) by product. At the cathode, the protons and electrons from the anode reduce a suitable electron acceptor. This process is depicted in Figure 1-1. Protons typically diffuse along a concentration gradient against the direction of the electric field. Anaerobic conditions are maintained at the via (a) a sufficient microaerobic body of biotic electrolyte or (b) an electrolyte permeable barrier to \( \text{O}_2 \) diffusion [11]. The cathode reaction is biocatalysed (aerobic bacteria) or chemically catalysed (electro-catalyst).
An MFC can be equipped with a biotic cathode, allowing reduction of solvated pollutants (i.e. NO$_3^-$, SO$_4^{2-}$, ClO$_4^-$, CH$_2$Cl$_2$) at cathode potentials ($E_{\text{cat}}$) lower than obtainable with an electrocatalyst [12, 13]. The cathode may become the electron donor to the bacteria as it mimics a metal or mineral surface found in nature.

1.3.1 Anode

In a PEM fuel cell H$_2$ gas is pumped through a porous catalyst layer at overpressure (30-80°C), producing pure H$^+$ and e$^-$ product at the anode. In an MFC this process does not require an acid and thermally resistant support material, but one that is biocompatible, presenting a large conductive surface area for biofilm growth. Biofilms can form on substrates that include silica, minerals, some plastics, biopolymers, metals, carbons and alloys [14] but only conductive materials are able to support large electrogenic biofilms if a solvated electron acceptor is not present. Labscale MFCs primarily use graphite and activated carbons as passivity is not an issue.

Electrostatic repulsion between bacteria and support can result in slow biofilm formation. It originates from charge in bacterial outermembrane/lipopolysaccharide and
the columbic shielding from a charged double layer arrayed around the anode surface (see Figure 2-5). Therefore control of the electrical potential of the anode surface during the growth phase is commonplace [15]. The anode potential \( E_{an} \) has a profound effect on metabolic kinetics of acetate consumption [16]. The acetate oxidation reaction (Eq.1-2) produces 8 electrons, many of which are not utilised at the anode. Electrons are primarily lost to metabolic processes or cross-over. This effect is quantified by the anolyte coulombic efficiency \( \varepsilon_c \) for an MFC fed with acetate and using O\(_2\) at the cathode (Eq.1-3) [17].

\[
\text{CH}_3\text{COO}^- \rightarrow CO_3^{2-} + 8e^- + 9H^+ \ (E^{0'}=-0.504V \text{ vs. Ag|AgCl, pH7[17]}) \quad \text{(Eq.1-2)}
\]

\[
\varepsilon_c = 8.29 \times 10^{-5} \times \int_{t=0}^{i_{\text{applied}}} \left[ \frac{i \Delta t}{\text{VOL}_{\text{an}} \cdot \Delta \text{COD}} \right] \quad \text{(Eq.1-3)}
\]

Where “\( i \)” is external electric cell current (amp), “\( \text{VOL}_{\text{an}} \)” is the anode chamber volume (cm\(^3\)), \( \Delta \text{COD} \) is the change in chemical oxygen demand (COD) content from the start of the batch cycle to the end (g of O\(_2\) / cm\(^3\)).

1.3.2 Polarisation of electrogenic biofilms

The \( E^{0'} \) in Eq.1-2 is set by the formal redox potential of the membrane protein or mediator delivering electrical charge [17, 18]. Imposing a more positive potential than this (anodic polarisation) causes the flow of electrical current and allows cell metabolism to increase. Acetate fed MFCs typically select for the nano-wire producing \textit{Geobacter Sulfurreducens} [19-22] with optimum polarisation potentials differing between co-species in consortia, electrode porosity, reactor geometry, electrolyte conditions and study. An applied upper potential limit on the terminal reductase is thought to be feasible [19]. Variance between studies in consortia is further compounded by synergistic effects from other bacteria, including removal of auto-inhibiting respiration products in the electrolyte (localised acidity and VFA).

1.3.3 Electrolyte

Wastewater plant influent (Table 1-1) contains a significant amount of dissolved organics, a large portion of which (40%) are soluble volatile fatty acids whose oxidation incurs little overpotential. 30 mg/L of acetic acid can be found in wastewater influent
from pre-treatment fermentation [23]. High COD removal values (60%) show that fermentation processes occur in wastewater fed MFC reactors as the VFA are consumed.

### Table 1-1. Typical make-up of wastewater adapted from [24]

<table>
<thead>
<tr>
<th></th>
<th>Conc. mg/L</th>
<th>Conc. mM/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Dissolved Solids</td>
<td>780</td>
<td>n/a</td>
</tr>
<tr>
<td>Bicarbonate Alkalinity, as CaCO₃</td>
<td>240</td>
<td>n/a</td>
</tr>
<tr>
<td>Na⁺</td>
<td>160</td>
<td>6.96</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.7</td>
<td>0.043</td>
</tr>
<tr>
<td>Calcium</td>
<td>76</td>
<td>1.9</td>
</tr>
<tr>
<td>Magnesium</td>
<td>33</td>
<td>3.1</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>220</td>
<td>6.2</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>88</td>
<td>0.916</td>
</tr>
<tr>
<td>F⁻</td>
<td>0.48</td>
<td>0.025</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>24</td>
<td>0.387</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>~2.5</td>
<td>0.054</td>
</tr>
<tr>
<td>Phosphorus, as PO₄</td>
<td>0.081</td>
<td>0.0026</td>
</tr>
<tr>
<td>pH</td>
<td>7.2-7.4</td>
<td></td>
</tr>
<tr>
<td>Specific Conductance</td>
<td>2700 μS cm⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

If a large body of electrolyte separates the anode and cathode, an increase in MFC internal resistance, referred to as i-R drop or $R_u$ (uncompensated resistance) occurs along the direction of current flow. The relationship between electrode separation and conductivity of the electrolyte is given in Eq.1-4.

$$R_u = \frac{L}{A\kappa}$$  \hspace{1cm} (Eq.1-4)

Where $L$ is the distance, cm; $A$ is the cross-sectional area (cm²), over which the ionic conduction occurs; $\kappa$ is the ionic conductivity of the electrolyte, S cm⁻¹.

### 1.3.4 Membrane

Ideally membranes for air cathodes would be both hydrophilic and an oxygen separator. Producing such membranes may rely on small diffusion channels capable of differentiating between polar and non-polar molecules. Such a membrane would be susceptible to pore clogging and high internal resistance.

Utilisation of cheap separator materials in mass production such as J-cloth have been attempted, but are susceptible biofilm fouling [25]. Materials such as visking tubing may not allow sufficient ionic current and remain susceptible to bio-corrosion, short circuiting the MFC. Detailed literature discussions are continued in chapter 3.
1.3.5 Cathode Assembly

A common configuration for the oxygen electrode is the air cathode. This design performs the oxygen reduction reaction (ORR) with minimal oxygen mass transfer limitation. Detailed discussion continues in further chapters. Briefly, a conductive catalyst layer (typically carbon) is bound to the solid surface an ionomer (charged) or binder (dispersing agent). The porous conductive layer may support an electrocatalyst. The design is optimised for electrochemical oxygen reduction. The substrates and products of ORR are pH dependent, as shown in Eq.1-5 and Eq.1-6, the opposing half-cell reactions to the anodic half-cell reaction (Eq.1-2). Cathode materials and design studies are reviewed in chapter 3.

\[
4H^+ + 4e^- + O_2 \xrightarrow{\text{catalyst}} 2H_2O \quad \text{(Eq.1-5)}
\]

\[
4e^- + 2H_2O + O_2 \xrightarrow{\text{catalyst}} 4OH^- \quad \text{(Eq.1-6)}
\]

1.4 Electrochemistry in electrocatalysis

Application of electrochemical engineering allows reactions which normally require large pressurised or high temperature vessels to overcome the activation energy, \( E_a \) (kJ mol\(^{-1}\)), when compared to heterogeneous catalysts without polarisation. Potentially explosive processes such Hydrazine oxidation can be controlled by polarisation and partially separating reactants into half-cells. The oxidation of a graphite electrode in contact with a water interface can be powered by a household battery (<1V vs Ag|AgCl) using H\(_2\)O as a substrate. The process of surface oxygen insertion would typically require 500°C in Solid-Gas reaction to dissociate the O=O bond. Anodic de-hydrogenation reactions of alkane [26], CO oxidation [27] allow specific products to form. Researching reaction specificity and reducing \( E_a \) of individual steps will become increasingly important, in particular, those linked to the chemistry of the important oxidants such as O\(_2\).

1.4.1 Heterogeneous catalysts and electrochemical catalysts

In heterogeneous catalysis the net balance of electrons in reactants and products is identical. In electrochemical catalysis electrons and protons can be used as substrate or are liberated as a reaction product in each half-cell reaction. As the half-cell reaction
occurs on the solid surface and not in the electrolyte a potential gradient is created between the two. Manipulation of the potential difference (polarisation) allows the reaction to occur in a net direction. When the electrode is unpolarised it is said to be in open circuit when no net rate of reaction or electron exchange occurs. Polarisation is effected by connection to the opposing electrode (counter electrode). The counter electrode is in the same process electrolyte as the working electrode. The unpolarised rate of reaction is defined as the exchange current density, $J_0$ (A cm$^{-2}$). It is akin to exchange rate of reaction at reactant-product equilibrium seen in heterogeneous catalysis, eg. $k_f$ or $k_b$ (variable units) with the same catalyst, substrate and electrolyte.

1.4.2 $E^0$, $E^{0'}$ and Open Circuit Potential

Potentials are reported relative to a reference electrode (RE). The RE is situated in the electrolyte at close proximity to the electrode. On the metal wire surface of the RE a facile (non-polarisable) and reversible reaction involving an electron occurs with a high degree of reaction specificity. The metal surface and an ion (product or reactant) are in equilibrium with no net current flowing through the RE solution electrolyte (Appendix section 10.8).

For the reaction occurring on the surface of the working electrode most literature values for a given reaction are reported as the standard redox potential ($E^0$). The $E^0$ is defined as the midpoint in a reversible/quasi-reversible reaction on a Platinum surface where the concentration of each aqueous phase substrate and product are present in the pure aqueous solution at a concentration of 1M/litre under standard conditions (298°C). Substrates and products are seldom present at the ideal 1M concentration, in which case the formal redox potential ($E^{0'}$) is often applied. In this instance the concentration of reactants and products in the process electrolyte are factored into the equilibrium, as is ionic strength. In equations where $\text{H}^+$ or $\text{OH}^-$ are involved in the reaction as substrate or product the $E^{0'}$ value shifts significantly from $E^0$.

$$E^{0'} = E^0 + \ln \Pi * 2.303RT/nF$$  \hspace{1cm} (Eq.1-7)

$$\Pi = [S1]^a[S2]^b/[P1]^y[P2]^z$$  \hspace{1cm} (Eq.1-8)

$$aS1 + bS2 \rightarrow yP1 + zP2$$  \hspace{1cm} (Eq.1-9)
In real world implementation of electrochemical cells it is usually the case that mixed reactions occur on the surface of an electrode, resulting in a mixture of formal potentials of each reaction [28]. In this case the **open circuit potential** (OCP) describes the observed equilibrium potential between each reaction. In an ideal electrochemical cell (pure electrolyte, single-anion, single reaction, chemically homogenous electrocatalyst surface, 100% selective electrocatalyst) the formal potential should equal the open circuit potential. The largest discrepancy between \( E^0' \) and OCP in pure electrolyte is:

1) Non-selective catalyst producing different products. An example would be the mixture of 2e\(^-\) ORR \((E^0' = +0.074V \text{ vs. } \text{Ag|AgCl})\) and 4e\(^-\) ORR \((E^0' = +0.605V \text{ vs. } \text{Ag|AgCl})\) that occurs at pH7 on a catalyst supported on carbon electrode.

2) Exorgenic losses in non-electrochemical reactions acquiring electrical energy [29].

3) Differing ratios and concentrations of oxidised and reduced couple in the vicinity of the active site than in the process electrolyte.

4) Different local chemical environment for the electrocatalyst, such as ligands and substrate resulting in differing activation energy of rate limiting steps.

5) Difference in electrostatic repulsion between substrate or product [30].

6) Impurities solvated in the electrolyte (eg. Carbonate from air, trace metals).

The relationship between \( E^0' \) and pH in any process involving \( m \text{ H}^+/\text{OH}^- \) and \( n \) electrons is represented in Eq.1-10. A -59mV shift per pH unit is applicable for \( \text{O}_2 \) reduction to \( \text{H}_2\text{O}/\text{OH}^- \) or \( \text{H}_2\text{O}_2 \). This affects any reactions involving an \( \text{H}^+ \) or \( \text{OH}^- \).

\[
\frac{\partial E^0'}{\partial p\text{H}} = -2.3RTm/nF \quad [31] \\
\text{(Eq.1-10)}
\]

### 1.4.3 The cathode and the electron acceptor

Strong cathodic electron acceptors facilitate continual organic degradation at the anode biofilm by increasing the proton concentration gradient. Figure 1-2 lists the biocatalysed electron donor and receptor reactions relevant to an MFC. Quick growing organisms efficiently biocatalyse terminal donor and acceptor reactions with the largest potential gap.

---

\[2 \text{ Eg. If the product of ORR is OH}^- \text{ it will bind strongly to a positively charged electrode, shifting } E^0'. \text{ Additionally, } [\text{O}_2] \text{ at the site may differ from that in the electrolyte due to de/adsorption.}\]
Thermodynamic performance of an electron acceptor ($E^0$) is closely linked to the bond dissociation energy (BDE). The BDE of O-O in O$_2$ is 494 kJ mole$^{-1}$ [32]. The kinetic performance of an electro-catalyst is determined by the activation energy of the rate-determining step. In aqueous electrolytes the reaction proceeds via the rate constant $k_{app}$ (cm s$^{-1}$) which when under electron transfer control obeys the Arrhenius form (eq.1-11), meaning $\ln(k_{app}) \propto 1/T$, and yielding plots with slope $\Delta G^\ddagger / R$ and intercept $\ln(A)$.

$$k_{app} = Ae^{-\Delta G^\ddagger / RT} \quad \text{(Eq.1-11)}$$

Where $\Delta G^\ddagger$ is the standard free energy of activation (kJ mole$^{-1}$), reduced with polarisation, A is an Arrhenius prefactor constant (s$^{-1}$, 1$^{st}$ order). The rate constant of electron exchange ($k^b$) at OCP is related polarisation by Eq.1-12. Polarisation reduces the ‘hump’ of RDS activation energy increasing $k_{app}$. In the case of a single electron transfer at reasonably large overpotential (making $k_b$ negligible) [33]...
1.5 Motivation of study

1.5.1 Justification and aims of research in chapter 5

Primary aim

- To uncover the neutral pH electrochemical behaviour of a non-precious metal fuel cell cathode material of intense academic interest (Iron Phthalocyanine).
- To isolate and quantify the means of catalyst destruction in operating conditions.
- To improve the reaction kinetics of ORR.

Secondary benefits

- Phosphate is the main pH buffering anion in blood. Transplantable medical devices can utilise non-toxic haemoglobin like compounds for selective cathodes in bioelectrochemical sensor devices, oxidising target substrate at the anode. A parallel could be drawn between haemoglobin breakdown to bilirubin and the stability of Iron Phthalocyanine (FePc). The information may be useful to artificial blood design or anaemia treatment.
- Oxy-FePc is a moderately powerful oxidising agent that is inert to the majority of volatile fatty acids [28]. More powerful oxidising agents (such as H₂O₂) oxidise everything. While its anti-bacterial properties are not know, a fundamental study may be useful in designing devices with FePc adsorbed on a flat surface, scavenging selected solvated substances in biotic aerated streams [28].

1.5.2 Justification and aims of research in chapter 6

Primary aim

- To assess the effect of a novel anion exchange material on the ORR kinetics of FePc and other electrocatalytic surfaces at neutral pH.
- To assess O₂ interaction with and diffusion through the anion exchanger.

Secondary benefits

- Dabco is used in a variety of organic synthesis reactions, catalytic side reaction of use to chemical synthesis could be identified.
• New materials for selective dialysis membranes are required for medical and purification processes. Information of their selectivity and interaction with different electrolytes may find applications.

1.5.3 Justification and aims of research in chapter 7

Primary aim
• Evaluate the first application of an anion exchange material not to be based on quaternary ammonium or tri-methyl amine in MFC cathodes.
• Assessment of Dabco based anion exchange binder in real wastewater.
• The use of impedance spectroscopy to identify performance bottlenecks in catalyst layer design.

1.5.4 Justification and aims of research in chapter 8

Primary aim
• Assess membrane phase conductivity and interfacial resistances of ion exchange membranes in MEA form in neutral pH media.
• Compare manufacturer reported conductivity in NaCl to that obtained using impedance spectroscopy.
• Evaluate impedance spectroscopy method by comparing predicted performance of membranes to multiple batch tests of MFCs with the MEA.
• Recommend materials of interest and produce a finalised MEA representing the optimal balance of cost and performance.
Chapter 2. Theory of electron transfer analysis and laws governing experimental systems
2.1 Potential ramping techniques for studying electron transfer

2.1.1 Staircase voltammetry for assessing electron transfer

Staircase voltammetry relies on steps in applied potential $E_{\text{step}}$ (Volts) over a time period of $t_{\text{step}}$ (seconds) to generate a profile of $i$ vs $E$. Figure 2-1 indicates changes in $E$ vs $t$ over a portion of a staircase Cyclic Voltammogram (CV) or Linear Sweep Voltammogram (LSV).

![Staircase voltammogram](image)

Figure 2-1. $E$ vs $t$ plot for staircase voltammetry. Used to obtain all $i$-$E$ data in this thesis

The effective scan rate $\nu$ (V s$^{-1}$) is computer controlled and is used to calculate $t_{\text{step}}$ via Eq.2-1.

$$E_{\text{step}}/\nu = t_{\text{step}}$$  \hspace{1cm} (Eq.2-1)

2.2 Theory of electron transfer

2.2.1 Energy barriers of single electron transfer to an adsorbed reactant

For the general case of 1e$^-$ electron transfer...

$$\text{Ox} + e^- \xleftrightarrow[k_f]{k_b} \text{Red}$$  \hspace{1cm} (Eq.2-2)

In some cases it is useful to separate the heterogeneous rate constant into forward and backward components ($k_f$) and ($k_b$), varying as a function of overpotential ($\eta$), obtained from $E$-$E^{0'}$. In multi-step reactions, the change in Gibbs free energy of the adsorbed intermediary complexes before and after each step produces a series of $E^{0'}$ values, the median of which is akin to OCP. The same electro-catalyst is unlikely to be able to efficiently catalyse each stage and so the RDS must be found to identify process
bottlenecks. Julius Tafel identified a linear relationship between log_{10}|i| vs η. This has been used as the mark of kinetic current (i_k) of a polarised surface ever since.

![Figure 2-2. Effect of cathodic polarisation on free energy barriers of 1e⁻ electron transfer. Subscript 'b' 'f' represent forward and backward reaction. Cathodic polarisation (Blue) and E=OCP (brown)](image)

In Figure 2-2 the reduction of activation energy with overpotential can be visualised by viewing the transfer as a transition over an energy barrier. The x-plane represents a solvent co-ordinate. The term α is a measure of symmetry in the energy barrier. If the activation energy barrier of electron transition is located closer to the adsorbed oxidised couple then the electrocatalyst, α is increased. For a cathodic reaction ΔG^\text{f}_{\text{c}} \text{(kJ mol}^{-1}\text{)} is the activation energy is reduced with polarisation from that at \( E^0' \) (ΔG^\text{f}_{\text{0c}})...

\[
\Delta G^\text{f}_{\text{c}} = \Delta G^\text{f}_{\text{0c}} + \alpha F (E - E^0)
\]

(Eq.2-3)

The effect of cathodic polarisation on an adsorbed oxidised couple causes the energy barrier to shift closer to the electrocatalyst, meaning α is a function of potential [34], though if the potential range is small α is relatively consistent. A change in the orientation of reactant can also affect energy barrier geometry, affecting α. The influence this reaction co-ordinate plays on the faradic current is depicted in Figure 2-3.
An electrode at equilibrium is known to take on an OCP relative to bulk concentration of Ox and Red (Eq.2-4). Large values of $i_0$ mean that the system attains equilibrium quickly. Under certain conditions $OCP \neq E^0$, primarily when the reverse couple is not present in solution the reverse reaction becomes negligible...

$$\log_{10}(i_0) = \log_{10}(FAk^0) + (1-\alpha)\log_{10}(C_{0,\alpha}) + \alpha \log_{10}(C_{0,Red})$$  \hspace{1cm} (Eq.2-4)

$$i_0 = FAk^0C_{0,\alpha} \exp\left[-\left(OCP - E^0\right)\alpha F / RT\right]$$  \hspace{1cm} (Eq.2-5)

Eq.2-5 can be used to determine $\alpha$ by varying Red when Ox is kept consistent. In the case of ORR this may be problematic, as Red can correspond to H$_2$O or OH$^-$. For a reaction with a single step reversible reaction the kinetic current is obtained by the Butler-Volmer equation [35]...

$$i_k = i_0\left[e^{-\alpha n\eta / k_{app}T} - e^{-(1-\alpha)n\eta / k_{app}T}\right]$$  \hspace{1cm} (Eq.2-6)

A multi-step reaction may be thought of as a series of the steps governed by Eq.2-6. In multi-step reactions the OCP is a mixture of each step, whereby $k_{app}=0$ and $i_k=0$ but for each individual step $i_k \neq 0$ may occur if multiple pathways are present. The concentration of each reactant applies to intermediates. In this case, it could be assumed that an adsorbed intermediary controls the OCP, as described by Eq.2-7. The subscript ‘a’ describes this situation and the superscript ‘RDS’ denotes the oxidised or reduced couple of the RDS.

---

Figure 2-3. Model tafel plot of reversible 1e$^-$ transfer at $\eta=0V=E^{0'}$ as $f(\alpha)+C_{0,Red}=C_{0,Ox}$.

$\alpha=0.5, A=1cm^2, i_0=1x10^{-8}$ Amps, $T=298.15^0K$. 
2.2.2 Multiple electron transfer to an adsorbed reactant

For multiple electron transfers a series of energy barriers must be overcome. Plotting the change in Gibbs energy of formation between the reduced and oxidised couple of each step allows the rate determining step to be obtained. Figure 2-4 depicts a half-cell four electron reduction reaction. The Y-axis of Gibbs free energy includes all substrates.

\[ i = n F A k_{RDS} (\alpha) \left[ e^{-(E^v - E^R) F/RT} - (\alpha) e^{-(E^v - E^R) (1-\alpha) F/RT} \right] \]  \hspace{1cm} (Eq.2-7)

Figure 2-4. Standard free energy change in a cathodically polarised reduction reaction.

Four step reduction reaction. Key; R–Reactants, P–Products, V–State of complex prior to RDS, W–state of complex after RDS

In this relationship the change in Gibbs free electrical energy incurred by the RDS (\( \Delta G^0 \)) if the reverse reaction is negligible is shown in Eq.2-8 [36]. This is related to the current under electron transfer control via Eq.2-9.

\[ \Delta G^0 = \sum_i Z_{RV} F \Delta \phi_{RV} + Z_{VW} F \Delta \phi_{VT} \]  \hspace{1cm} (Eq.2-8)

\[ \Delta G^0 = -RT \ln(\bar{i}) + C \]  \hspace{1cm} (Eq.2-9)

Where \( Z_{RV} \) is the charge of an intermediary particle transferred from state R to V, \( \Delta \phi_{VT} \) is the local potential difference (V) through which the particle moves travelling from state W to transition transition complex T. T is a transition complex, other subscripts correspond to points on Figure 2-4. This yields a generalised tafel equation, considering
the case where intermediaries remain adsorbed causes the values to deviate. Eq.2-10 is the corrected equation which involves the terms “f” to describe the fraction of the \( \phi_S - \phi_{bulk} \) electrical field involved in the charge transfer process.

\[
-b_c = \frac{2.303}{\sum Z_{ZV} f_{ip} + Z_{ZV} \beta_c f_{WV}} \frac{RT}{F}
\]  
(Eq.2-10)

Figure 2-5. Potential profile across the double-layer and diffuse layer region without the case of adsorbing ions. Key; S-Surface, IHP- Inner Helmholtz Plane, OHP- Outer Helmholtz Plane

The double layer forms at the boundary between an electronic and ionic conductor. Anions tend to form the IHP, owing to their ability to strip elements of their solvation shelf and form van der Waals interactions with the surface. Counter charges orientate around these charges, additional counter charges form the diffuse layer (section 2.2.3), producing a series of capacitors which charge and discharge over different time periods. The inner potential drop across the \( \phi_s \) to \( \phi_{OHP} \) region has previously been modelled as linear, or in more concise models the drop is most significant at the IHP.

The drop \( \phi_{OHP} - \phi_{bulk} \) is referred to as the zeta potential \( (\zeta) \). This form of columbic shielding controls agglomeration of particulates in colloidal suspension (eg. catalyst
inks) or flocculation of material onto electrodes (eg. early biofilm formation). For higher ionic strengths the diffuse layer compresses and $\zeta$ becomes nearly irrelevant and $E=\phi_{\text{IHP}}-\phi_{\text{OHP}}$.

### 2.2.3 Capacitance

Capacitance arises from the arrayed orientation of countercharges separated by a dielectric or relative permittivity with breakdown constant ($\varepsilon_r$) with plate-plate thickness (d). This is formalised in Eq.2-11, which is valid for perfect capacitor of two facing parallel plates with opposing charge.

$$\varepsilon_r \varepsilon_0 / d$$

(Eq.2-11)

Typically $\varepsilon_r$ is 80 for H$_2$O solvent (no units), $\varepsilon_0$ the permittivity of free space 8.854x10$^{-12}$ F m$^{-1}$), and the separation of the plates is approximately half the diameter of a typical hydrate cation (c.a. 0.2nm). The orientation of counter charges around the IHP gives rise to the Helmholtz double layer capacitance ($C_H$) in which Eq.2-12 holds true.

$$Q_{\text{IHP-OHP}} = C_{\text{IHP-OHP}} (\phi_{\text{IHP}} - \phi_{\text{OHP}})$$

(Eq.2-12)

With the addition of the diffuse layer and the capacitance of dipole rotation (typically the majority of $C_H$) each capacitance can be measured in series (Eq.2-13). Considering the capacitance of the diffuse layer $C_{\text{dl}}$ is produced from Eq.2-14. The influence of $C_{\text{diffuse}}$ on $C_{\text{dl}}$ is greater in dilute solutions. In general $C_{\text{dl}}$ is within the range 5-50μF cm$^{-2}$ for flat metal surfaces [35].

$$\frac{1}{C_H} = \frac{1}{C_{\text{dipole}}} + \frac{1}{C_{\text{IHP-OHP}}} = \frac{a_{\text{H}_2\text{O}}}{\varepsilon_0 \varepsilon_{\text{dipole}}} + \frac{a_{\text{ion}}}{2\varepsilon_0 \varepsilon_{\text{IHP-OHP}}}$$

(Eq.2-13)

$$\frac{1}{C_{\text{dl}}} = \frac{1}{C_H} + \frac{1}{C_{\text{diffuse}}}$$

(Eq.2-14)

$$C_{\text{diffuse}} = \kappa \varepsilon_0 \varepsilon_r$$

(Eq.2-15)

$a_{\text{H}_2\text{O}}$ and $a_{\text{ion}}$ is the diameter of a water molecule and hydrated ion diameter respectively. The term $\varepsilon_{\text{dipole}}$ and $\varepsilon_{\text{IHP-OHP}}$ refer to the relative dielectric constant ($\varepsilon_r$) of
electrolyte between surface-IHP and between IHP-OHP respectively, typically c.a. 6 and 30 respectively. $\kappa$ is the bulk solution conductivity (S m$^{-1}$), for the diffuse layer $\nu_r \rightarrow 80$ for H$_2$O solutions. Adsorption may be weakened or strengthened by changes in potential. For anions van der Waals interact with the electrode. A precursor step to this process would be the stripping of co-ordinating solvent molecules in-between anion and solid surface. As anions are capable of direct electrode contact this gives rise to the inner Helmholtz plane. The potential where the surface charge on the electrode and adsorbed ion charge reaches a minimum ($z_{IHP}$) is termed the potential of zero charge ($E_{pzC}$). The corresponding counter charge orientates around the solid and IHP charge in the form of the OHP and diffuse layer and electroneutrality is maintained. At this point $E_{pzC}=\phi_{IHP}-\phi_{bulk}$ reflects the point where the net surface charge on the solid phase and IHP is zero.

For porous electrodes performing no reaction additional capacitance ($C_z>5$-$50 \mu$F cm$^{-2}$) can appear in parallel rather than series with $C_{dl}$ and can possess a separate time constant if both placed in parallel with a resistance. For this reason $C_z \neq 0$ at $E_{pzC}$ in Figure 2-6. $C_{dl}$ may be determined from electrochemical impedance spectroscopy, whilst $C_z$ is simply obtained from linearly ramping $dE/dt$ as in Figure 2-6. In Figure 2-6 the blue line at $E>E_{pzC}$ represent the relative affinity of anions to the anodic porous electrode surface. At $E<E_{pzC}$ the opposite relation is seen.

![Figure 2-6](image)

Figure 2-6. Capacitance of a porous electrode in mono-anionic dilute electrolyte in the absence of a faradic reaction. (A) Cyclic Voltammogram and (B) Derivate total capacitance ($C_z$) vs $E$. $\nu = 20$ mV/s.
The total capacitance (DC) of a porous electrode is calculated via Eq.2-16 from cyclic voltammetry.

\[ C_\Sigma = 0.5(J_{an} - J_{cat})/\nu \]  

(Eq.2-16)

If an irreversible faradic reaction is present Eq.2-16 does not necessarily hold. If no faradic reaction or redox surface state change occurs then the surface may possess the ability to store charge with perturbation in applied potential, known as differential capacitance \( C_{diff} \). In mono-anionic solutions adsorbed charge may vary linearly with applied potential (Figure 2-6). The accumulation of surface charge \( Q_{ads} \) is obtained with the deviation from \( E_{pzc} \). At \( E_{pzc} \) the capacitance form this charge should be 0.

\[ Q_{ads} = C_{diff}(E - E_{pzc}) \]  

(Eq.2-17)

The total electrode capacitance \( C_\Sigma \) is typically dominated by differential capacitance \( C_{diff} \) in the absence of substrate. In the presence of a faradic reaction the large \( C_\Sigma \) values attached to porous electrodes can result in large potential dependent capacitances. This means in the presence of the reaction total steady state is not acquired at relatively low imposed potential scan rates (\( \nu \)).

2.2.4 Relevance of tafel slopes

A tafel slope is the inherent polarisation arising from the process of electrical charge transfer across the double layer via a solvated diffusible reactant/product couple. Two factors must be compensated for accurate \( \log_{10}(I) \) vs \( E \) values; 1) uncompensated ohmic resistance \( (R_o) \) due to potential from RE-WE separation in the field of ionic flow [35], 2) Concentration polarisation.

Tafel slopes can be expressed as the number of reaction steps involving an \( e^- \), \( H^+ \) or \( OH^- \) that occur before the rate determining step (RDS) [37], as defined in Eq.2-18. Selective single step reactions incur uniform tafel slopes (-120, -60, -40 or -30mV dec\(^{-1}\)). However, contributions from steps before RDS [38], multiple pathways, and reaction reversibility can cause a variety of reported tafel slopes for similar reactions.
\[-b_c = 2.303 \nu_j RT / [F(n_c + \beta_c n_j)]\]  
\hspace{1cm} (Eq.2-18)

Where \(-b_c\) is the tafel slope (V dec\(^{-1}\)), \(\nu_j\) is the no. of occurrences of the RDS that is required for one complete reaction (typically 1), \(n_c\) is the number of electrons transferred before the RDS. \(\beta_c\) is the symmetry factor of the RDS (c.a. 0.5 in precious metal catalysis) [39]. \(n_j\) is the number of electrons transferred in the RDS (usually 1 for an charge transfer RDS or 0 for a chemical step RDS) [36]. 2.303 is used as the integer to convert \(\ln(I)\) vs \(E\) to \(\log_{10}(I)\) vs \(E\).

By this token, it is suggested that the improved tafel slopes occur when; the RDS occurs later in the reaction mechanism, the RDS preferably transfers two electrons as opposed to one (unlikely [39]), the RDS is not repeated in the same catalytic turnover (rarely the case). At 20°C this simplifies Eq.2-18 to Eq.2-19.

\[-b_c = 0.058148 \nu_j / (n_c + \beta_c n_j)\]  
\hspace{1cm} (Eq.2-19)

The symmetry factor (0<\(\beta\)<1.0) is defined as ‘the fraction of the electrical free energy \((G=nFE)\) applied to the system which activates the complex,’ or ‘the fraction of overpotential that activates the forward reaction [40].’ Symmetry factor and electron activity co-efficient \((\alpha_c)\) of the RDS are related by Eq.2-20.

\[\alpha_c = n_c + (1 - \beta_c)\]  
\hspace{1cm} (Eq.2-20)

2.3 Mixed Potential theory
2.3.1 Application to MFC electrodes as cross-over

Cross-over is the diffusion of a reducing agent to the cathode (ie. Formate or \(S^2^-\)), or diffusion of an oxidising agent to the anode (ie. \(NO_3^-\) or \(O_2\)), thus reducing cell voltage. This is seldom a problem for MFC cathodes. Harnisch et al studies the effect of fermented organics on the \(OCP\) of Pt and pyrolised Iron Phthalocyanine cathodes [28]. Platinum displayed poor selectivity for oxygen reduction as seen by a small decrease in OCP in the presence of ethanol, lactate and methanol and a large decrease with addition of Sulphide and Formate, indicating significant oxidation. At 1mM \(S^{2-}\) and \(CH_3COO^-\) decreased \(OCP\) of 52mV and 72mV respectively. Crucially to this thesis, they
demonstrated that carbon, iron macrocycle and platinum materials are not severely affected by acetate in phosphate buffer (see chapter 3 and 6).

Figure 2-7. Mixed Potential theory for an unpolarised electrode with one cathodic and one anodic reaction occurring on the surface. (A) Relative potentials of either reaction, (B) simplified model of steady state polarisation of electrode in the presence of either O$_2$ (orange) or SO$_3^{2-}$ (red). OCP in mixed solution when (i) [O$_2$]=0, (ii) [SO$_3^{2-}$]=0, (iii) CO$_2$ and [SO$_3^{2-}$] are large, (iv) [O$_2$] is small. Dotted line implies O$_2$ diffusion limitation.

An example is shown for a two mixed redox couples sulphite/sulphate ($E^0$=0.172V) and H$_2$O/O$_2$ reaction ($E^0$=1.223V) on a metal electrode. A similar situation could arise from organic oxidation on the cathode, such as formate/CO$_2$ ($E^0'= -0.42$V) and H$_2$O/O$_2$.

MFC anodes may suffer from cross-over of O$_2$ unless membranes or large electrode separation is used. Cross-over of strong electron acceptors other than O$_2$ is less of a problem due to their low molarity presence in wastewaters. However, dissolved O$_2$ may partially impede growth of anaerobic exoelectrogens. Cheng et al [41] found this to be a problem under batch configuration but not continuous flow. Dissolved oxygen concentrations$^3$ of 0.005–0.01 mg/L were detected 2cm away from an air cathode operating a peak power density ($P_{max}$). This is relevant to the reactor design used in

$^3$ The author calculates that such concentrations at the biofilm surface would reduce oxidation current by only 3.2mA m$^{-2}$ in stagnant electrolyte. Based on 9.2mg/L equating to 3A m$^{-2}$ limit at the cathode.
2.4 Oxygen and H₂O₂ and H₂O/OH⁻

2.4.1 Oxygen adsorption and reduction pathways

The basis of oxygen reduction catalysis is reduction in the strength of the O=O bond after adsorption onto a surface. Oxygen adsorption primarily occurs via Langmuir (isolated homogenous adsorption site), freundlich (inhomogeneous surface with distributed adsorption energies) or Temkin (adjacent inter-site interaction) isotherms describing surface coverage. The Langmuir model is described by Eq.2-21. The Langmuir isotherm accounts for a consistent adsorption site. The Temkin isotherm describes a situation where adsorption sites are located closely to one another (e.g. Pt surface) and adsorption energies are affected by the occupancy of the adjacent site. The free energy change of adsorption ΔGₘₐₓ applies as Eq.2-22.

\[
\Gamma = \frac{\Gamma_{\text{max}} K_{\text{ads}}[O]}{1 + K_{\text{ads}}[O]} \quad \text{(Eq.2-21)}
\]

\[
\Delta G_{\text{ads}} = -RT \ln[K_{\text{ads}}] \quad \text{(Eq.2-22)}
\]

\[
\theta = \frac{[O]_{\text{surf}}}{[A]} \quad \text{(Eq.2-23)}
\]

Where \( \Gamma \) is the actual surface coverage (in this instance Mole g⁻¹ site) and \( \Gamma_{\text{max}} \) is the maximum surface coverage (Mole g⁻¹ site) where species O is present in excess. The partial surface coverage then becomes Eq.2-23 in the case of Langmuir adsorption, where in a film or layer capable of adsorption of O the terms \([O]_{\text{surf}}\) and \([A]\) are the surface concentrations of adsorbed substrate and bare adsorption site (mole cm⁻³) respectively. In reality O₂ will not be the only molecule capable of adsorption. Many electrocatalysts are ionophores and the site may be partially occupied by ions or intermediaries from a reaction involving O₂.

Figure 2-8 describes the various pathways of electro-reduction of oxygen to water, from the reaction starting point (O₂(bulk)) to the desired end-point (OH⁻(cl)). The mechanism is not specific to a single catalyst and intermediate oxygen forms vary according to pH. 4e⁻ reduction is preferable to 2e⁻ reduction path, releasing almost twice the free energy \([32]\). \( k_1 \) selective catalysts that either avoid \( k_{2j} \) or avoid \( H_2O_2 \) desorption \( k_{6j} \) are preferable for
cathode energy efficiency. $k_2$ is less problematic, but in neutral media the bond between H$_2$O$_2$ and surface is weaker than that in alkali (HO$_2^-$) and has a tendency to desorb. The scheme considers a single electro-catalyst, though $k_5$, $k_7$ and $k_8$ all describe H$_2$O$_2$ decomposition away from the original site of generation. In the light, the latter two may be indistinguishable from $k_5$. Via a single electrocatalyst ($k_{D,O2}$$\rightarrow$$k_{SC}$$\rightarrow$$k_1$ or $k_2$$\rightarrow$$k_3$ or $k_2$$\rightarrow$$k_6$). Cleavage of the first O$_2$ double bond results in a peroxo intermediary with both the $k_1$ and $k_2$ pathways, the difference being that the peroxo species in $k_1$ is incapable of desorption. All heterogeneous rate constants refer to Figure 2-8.

According to Appleby et al [42], all of the rate constants are a function of potential with the exception of chemical disproportionation steps ($k_{4ii}$ and perhaps $k_{4i}$). The overall apparent rate constant ($k_{app}$) should be similar to the rate-constant of the Rate Determining Step (RDS). The dominant pathway of ORR is heavily influenced by the initial orientation of O$_2$ adsorption [32, 36].

‘Side on’ adsorption results in H$_2$O product whilst an ‘End on’ produces H$_2$O$_2$ unless present as a bridge adsorption between two sites and resulting in H$_2$O [32]. Deposition of organic catalyst multilayers between graphite sheets may allow bridge adsorption, see Figure 2-9 with co-facial and monolayer configurations of the organic catalyst FePc.
In bridge mechanism catalysis the Me-Me separation is of critical importance. In noble metal catalysis, ORR occurs via a bridge like mechanism, each oxygen bonds to adjacent metal atoms. Me-Me distance strongly influences activity so nano-particle geometry and crystal phase become important. The same is true of macrocycle catalysis (section 3.3) where Me-Me atomic distance is controlled by separation between layers in a polymeric film. Following deposition from a solvent the Me-Me separation is a fixed distance, dictated by π-bond overlap on FePc benzene atoms.

2.4.2 Methods of peroxide destruction

Peroxide is capable of self-oxidation in the solution phase (Eq.2-24) also known as disproportionation, \( k_{d\text{ii}} \). This reaction is catalysed by trace metal contaminants (including ions) and is only inert in Pyrex, Quartz, some Plastics and Aluminium [43]. Decomposition occurs on graphite and is very quick on a noble metal surface [43], regenerating to chemisorbed \( \text{O}_2 \), for this reason \( k_{d\text{i}} \) is included where absent in most schemes [44]. Where it is difficult to separate \( k_{d\text{i}} \) and \( k_{d\text{ii}} \) they are amalgamated, \( k_{d\text{i}}+k_{d\text{ii}}=k_d \). The rate of \( k_{d\text{ii}} \) increases with \( T \) and solvated \( \text{O}_2 \) concentration. This is generally not a potential dependent process as no exogenous electrons are involved (Figure 2-8, rate \( k_{d\text{ii}} \)), though some materials perform improved disproportionation in either an oxidised or reduced form.

\[
H_2\text{O}_2 + H_2\text{O}_2 \xrightarrow{\text{catalyzed/noncatalyzed}} \text{O}_2 + 2H_2\text{O} \tag{Eq.2-24}
\]

Critically to the scope of this thesis, \( \text{H}_2\text{O}_2 \) decomposition is not catalysed by \( \text{Na}^+ \) or Phosphate [45], indeed Phosphate ions partially stabilise \( \text{H}_2\text{O}_2 \).
Another mechanism of removal of produced \( \text{H}_2\text{O}_2 \) is \textbf{electro-reduction} in an aqueous media (Eq.2-25) in the presence of a solid surface \((k_3)\).

\[
\text{H}_2\text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O} \quad E^0 = 1.142\text{V} \text{ (Ag|AgCl at pH7)} \quad (\text{Eq.2-25})
\]

Eq.2-25 shows irreversible behaviour \([35]\) and shifts by \(|b_i| = 59\text{mV pH}^{-1}\). \(\text{H}_2\text{O}_2\) is a strong electron acceptor with a short half-life in a catalyst layer. The ramifications for RRDE study are that a portion of \(4e^-\) reduction is consecutive \(2e^-\) to \(\text{H}_2\text{O}_2\) followed by \(2e^-\) to \(\text{H}_2\text{O}\). Reducing \(\text{H}_2\text{O}_2\) residence time in catalyst films by using thin films reduces the amount of subsequent peroxide reduction, making pathway determination less problematic.

\textbf{Photo-homolysis} \((k_7)\) is typically the least significant pathway and is important in photocatalysis. Produced \(\cdot\text{OH}\) would damage MFC components due to the strong oxidising capabilities of \(\cdot\text{OH}\); \(E^0 = 2.19\text{V Ag|AgCl at pH7}\). \(\cdot\text{OH}\) has a typical half-life of only 0.1-0.5\text{μs} \([46]\).

\[
\text{H}_2\text{O}_2 \xrightarrow{h_\text{f}} 2\cdot\text{OH} \quad \text{wavelength}<370\text{nm} \quad (\text{Eq.2-26})
\]

\textbf{Chemical oxidation} of organics may decrease \(\text{H}_2\text{O}_2\) detection and affect the concentration of organics in wastewater and artificial wastewater electrolyte, particularly when a carbon cathode is employed.

\subsection*{2.4.3 Transients and the Cottrell equation in unstirred solution}

In an unstirred solution, a model for the diffusion layer is seen in Figure 2-10. The flux of material to the surface, \(J_{\text{flux}}\) (\text{Mol cm}^{-2} \text{ s}^{-1}) is described by Fickian diffusion (Eq.2-27). As the scan proceeds from \(E_{\text{ORR}}\) in a cathodic direction, a concentration gradient increases as the surface concentration \((C_s)\) tends to zero at \(E_p\). At this point the Nernst diffusion layer thickness \((\delta)\) is still increasing by Eq.2-28 as reactant is depleted at the disc surface via concentration gradient in Eq.2-27. Transient decay is predicted in the absence of convection, natural or forced, this is never the case in real systems where natural convection produces only finite transient decay, producing \(J_L\) \([48-51]\). This results in the current decreases at potentials more negative than \(E_p\) (reduction).
\[ J_{\text{flux}} = D \left( C_0 - C_x \right) / \delta \]  
(Eq.2-27)

\[ \delta = (\pi Dt)^{1/2} \]  
(Eq.2-28)

**Figure 2-10.** Example concentration profile for reactant depletion at the electrode surface \((x=0)\), creating Nernst Diffusion Layer. Two different electrode potentials, case of diffusion limited current (black) and mixed kinetic, diffusion control.

For a porous electrode \(C_x\) could be considered the inner portion of the film/solution interface. With small cathodic polarisation \(C_x\) does not decrease to 0 provided transport is sufficiently quick. The presence of natural convection assures that \(i_L\) and a steady \(\delta\) are obtained. In a cathodic LSV sweep with and without dissolved oxygen (Figure 2-11) a peak is observed \((J_p)\).
Figure 2-11. i-E response of a strongly adsorbed metal based electrocatalyst in the presence (red) or absence (black) of dissolved reactant. Example is for chelated Fe$^{2+}$/Fe$^{3+}$ redox flat film with competitive electrocatalyst adsorption between reactant and anion. Features used in analysis are annotated in (A) the raw data, and (B) enlargement of Y-axis. $u=5$mV/s.

For a totally irreversible 1e$^-$ reduction reaction the wave possesses the following attributes [35]…

Cathodic

$$|E_p - E_{p/2}| = 1.857RT/\alpha F$$  \hspace{1cm} \text{(Eq.2-29)}

$$\frac{\partial E_p}{\partial V} = \frac{1.15RT}{\alpha F} = 0.03/\alpha (298^\circ K)$$  \hspace{1cm} \text{(Eq.2-30)}

In the more useful case of multi-electron transfer, provided the RDS is a single 1e$^-$ heterogeneous transfer as the 1$^{st}$ step, the above equations can be used. Equations describing peak current must be multiplied by ‘$n$’ in this case. Hence the result of Eq.2-34 changes for this case.

In Figure 2-11(A), $J_L$ describes the ORR limiting current at $E=-0.4$V in the case where an anion adsorption blocks the reaction site for ORR, but surface coverage of anion X ($\theta_{FePc-X^-}$) decreases as the scan moves in a cathodic direction. The ORR diffusion limiting current ($J_L$) is strongly potential dependent. Without this effect, $J_L=J_p$ in stirred
solution approaching steady state (low \( \nu \)) and a \( J_L \) plateau is seen provided \( n \) is constant. It cannot be ascertained from extrapolation of a linear \( i-E \) response in the diffusion limiting region [52].

For unstirred solutions the Cottrell equation (Eq.2-34) is obtained from Laplace transform of the relationship between flux to surface and current (Eq.2-35). A derivation is found in section 10.1.2. A maximum occurs in \( k_D \) when \( C_s=0 \) and \( C_0-C_s\approx ca. C_0 \). Though this is a function of applied potential if substrate is being converted upon contact with the disc at the maximum rate, Eq.2-31 holds if the reverse reaction is negligible, as is usually the case at \( i_L \).

\[
i_L = nF A k_D C_0 \quad \text{(Eq.2-31)}
\]
\[
\frac{i}{nFA} = k_D \left[ C_0 - C_s(x=0) \right] \quad \text{(Eq.2-32)}
\]
\[
C_s(x=0) = \frac{i_L - i}{nFA k_D} \quad \text{(Eq.2-33)}
\]

Where \( k_D \) is the planar mass transfer co-efficient (cm s\(^{-1}\)). Eq.2-32 describes the volume flow of reactant per unit area per second. Using Eq.2-31 and substituting into Eq.2-31 produces Eq.2-33. It is shown that the concentration of the electroactive species is linearly related to the current, with \( C_s\rightarrow 0 \) Mole cm\(^{-3}\) when \( i\rightarrow i_L \).

In substrate-less redox electrocatalyst electrodes the diffusion of electrons can be obtained from the gradient of \( i \) vs \( t^{0.5} \) which is linear for Fickian diffusion [53]. The charging current \( (i_{dl}) \) decays according to:

\[
J(t) = \frac{nFD^{0.5}C_0}{\pi^{0.5}t^{0.5}} \quad \text{(Eq.2-34)}
\]
\[
-J_{flux}(0,t)=-\frac{i(t)}{nFA} = D \left[ \frac{\partial C_0(x,t)}{\partial x} \right]_{x=0} \quad \text{(Eq.2-35)}
\]

In which \( \pi \) is the number pi, \( t \) is the time after the potential step (secs)
2.4.4 Randles-Ševčík analysis of unstirred solutions

As a result of the transient behaviour described at substrate depletion at the surface the Randles-Ševčík equation can be used to predict the peak current density in the presence of an increasing diffusion layer thickness in stationary electrolytes over time.

\[ J_p = -0.496\sqrt{(n_e + \alpha_a)nFC_0}\sqrt{\frac{FuD}{RT}} \]  
(Eq.2-36)

\[ \sqrt{(n_e + \alpha_a)} = J_p\left(-0.496nFC_0\sqrt{\frac{FuD}{RT}}\right) \]  
(Eq.2-37)

\[ D = RT\left[J_p/\sqrt{0.496nFC_0\sqrt{(n_e + \alpha_a)}}\right]/F\nu \]  
(Eq.2-38)

\[ \frac{\partial \ln(i)}{\partial E} = \frac{(n_e + \alpha_a)F}{RT} \]  
(Eq.2-39)

The transposability factor between \(\frac{\partial \ln(i)}{\partial E}\) and \(\frac{\partial \log_{10}(i)}{\partial E}\) is a factor of \(e=2.303\).

2.5 Methods of substrate diffusion control and peroxide detection

2.5.1 Methods of peroxide detection – RDE and RRDE

The Rotating Ring Disk Electrode (RRDE), Figure 2-12, is used to study ORR in aqueous or aprotic media. The RRDE allows quantification of substrate mass transport by disc rotation to force laminar convective flow. The axially rotating electrode assembly consists of a disc embedded into an insulating material. Around the disc is a concentric ring, allowing electrochemical detection of disc products. Electrical contact is made with between rotor and RRDE stator assembly through a conductive brush.
Figure 2-12. (B) Schematic of a Rotating Ring Disc Electrode (RRDE) tip for the evaluation of quantitative 2/4e⁻ electro-reduction of dissolved O₂

Hydrodynamic forces under a steady state produce a consistent velocity profile. At this stage the mass transfer can be explained in terms of cylindrical co-ordinates, velocity profiles in each dimension (x, y and ϕ) and the limiting conditions applied. Laminar flow velocities are divided into three dimensions (υₓ, υᵧ and υϕ), which are expanded by hydrodynamic theory in section 10.1.3.

Figure 2-13. Model of (B) laminar flow regime and (A) co-ordinates approaching disc reaction site in axially rotated electrode.

With axial rotation a linear flow profile is produced (section 10.1.3). The fluid is dragged across the surface of the disc. Other substrates/products leave or enter the reaction site at rates influenced by rotation speed (Figure 2-12). The following conditions should exist:
(a) laminar flow, bearing solvated substrate towards a rotating reaction surface at fixed concentration
(b) flow perpendicular to axis of rotation and
(c) a first order reaction.

A similar equation to Eq.2-31 is valid even if only natural convection is present towards a stationary horizontal plate [51]. \( k_D \) is consistent with \( A \) provided \( A \) is large enough that only planar diffusion occurs, i.e. via \( v_y > 0 \) and \( v_r = \text{c.a.} 0 \), or \( v_y \gg v_r \).

2.4.2. Levich Equation

Diffusion limiting current density \((J_L)\) is a function of \( \delta \). As such in porous electrodes \( J_L \) lacks comparability between studies. Under steady state, the diffusion layer model is described by equation the Levich equation, which only applies to totally mass-transfer limited condition \((|\eta| > 0V)\). The Levich equation derivation in the appendix (section 10.1.3.) is placed under the limiting condition of current \( i = i_L \) and using Eq.A-30 and Eq.A-31 we obtain the Levich equation, Eq.2-40.

\[
|J_L| = 0.62nFD^{2/3}\omega^{0.5}v^{-1/6}C_0 \tag{Eq.2-40}
\]

Where \( D \) is the diffusion co-efficient of electroactive species \((\text{cm}^2 \text{ s}^{-1})\), \( v \) is the kinematic viscosity of the electrolyte \((\text{cm}^2 \text{ s}^{-1})\), \( \omega \) is the radial velocity of the electrode \((\text{rad s}^{-1})\) and \( C_0=\text{Bulk Concentration of electroactive species (moles cm}^{-3})\). For diffusion to a planar electrode at steady state Eq.2-41 applies with substitution for \( k_D = D/\delta \).

\[
i_L = nFAk_DC_0 = nFA\left(\frac{D}{\delta}\right)C_0 \tag{Eq.2-41}
\]

Substituting Eq.2-41 into the Levich equation, the terms \( D/\delta \) becomes equivalent to \( \dot{m} \) producing Eq.2-42.

\[
k_D = \frac{D}{\delta} = 0.62D^{2/3}\omega^{0.5}v^{-1/6} \tag{Eq.2-42}
\]

Re-arranging in terms of diffusion layer thickness \((\delta)\) produces Eq.2-43.

\[
\delta = 1.61D^{1/3}v^{1/6}\omega^{-0.5} \tag{Eq.2-43}
\]
This equation has since been improved upon by correction for situations of large Schmidt numbers \([54]\), where the fluid is viscous or migrating ions/substrate are physically large molecules. This impacts the original derivation of Levich \([55]\), by a small amount, around 3% change in \(i_{DL}\) for \(Sc=1000\).

Physical constants for \(O_2\) saturated PBS at 20\(^\circ\)C, are located see appendix Table A-2. Eq.2-43 shows that \(\delta\) is proportional to \(\omega^{-1/2}\). In addition to transition of the diffusion layer an additional concentration impedance can be resent from a non-electrocatalytic active coating of the film \((J_{film})\). This ionomer coating prevents obtaining \(\delta\) from multiplying \(J_L\) by \(N_{ORR}\), which can be isolated with a Koutecký-Levich (K-L) plot.

An example Levich plot \((i\ vs\ \omega^{0.5})\) are displayed in Figure 2-14. This case shows a transition between diffusion control and kinetic control in a solution containing one half of a redox couple.

![Figure 2-14. Example Levich plot of transition between kinetic and diffusion control at constant potential for dissolved substrate](image)

The Levich gradient observes Eq.2-40 when the reaction is purely mass transfer limited.
2.4.3. Koutecký-Levich (K-L) Equation and kinetic current

Considering a totally irreversible reaction the Eq.2-44 and Eq.2-45 are valid from a change in integration limits of Eq.A-29, producing Eq.2-46.

\[ i = FAk_f (E)C(y = 0) \]  \hspace{1cm} (Eq.2-44)

\[ k_f (E) = k^0 \exp \left( -\frac{(E - E^0)\alpha F}{RT} \right) \]  \hspace{1cm} (Eq.2-45)

\[ C_0 - C(y = 0) = \left( \frac{\partial C}{\partial y} \right)_{y=0} \int_0^\infty \exp \left( -\frac{y^3}{3B} \right) dy \]  \hspace{1cm} (Eq.2-46)

Where \( i \) is the measured current (Amps), \( k_f \) is the heterogeneous rate constant of the forward reaction (cm s\(^{-1}\)). Writing Eq.2-46 is written in terms of \( \delta \) as defined by Eq.2-43 to yield Eq.2-47.

\[ i = \frac{nFAD[C_0 - C(y = 0)]}{\delta} = nFAd_p[C_0 - C(y = 0)] \]  \hspace{1cm} (Eq.2-47)

Whilst from Eq.2-40..

\[ i = i_{L,c} \left[ \frac{C_0 - C(y = 0)}{C_0} \right] \]  \hspace{1cm} (Eq.2-48)

Where \( i_{L,c} \) is the limiting current in one direction (cathodic). Combining Eq.2-48, Eq.2-47 and Eq.2-44 produces Eq.2-49.

\[ i = FAk_f (E)C_0 \left( 1 - \frac{i}{i_{L,c}} \right) \]  \hspace{1cm} (Eq.2-49)

As a portion of equation represents the forward component of the reaction based on the heterogeneous rate constant, it can be expressed as a kinetic current.

\[ i_k = FAk_f (E)C_0 \]  \hspace{1cm} (Eq.2-50)

Applying for multi-electron transfer, inclusion of “\( n \)” produces the Koutecký-Levich plot, with the terms from Eq.2-40 incorporated for the full equation. At diffusion
limitation the reverse reaction is negligible and $k_{\text{app}} = k_f$. Eq.2-51 is expressed as a linear function at axial rotations speeds where...

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{L,c}} = \left( \frac{1}{0.62nFAD^{2/3}v^{-1/6}C_{0,\alpha}} \right) \frac{1}{\sqrt{\omega}} \left( \frac{1}{nFAC_{\text{app}} C_{0,\alpha}} \right)$$

(Eq.2-51)

$$y = [\ m\ ]^* \ x + [\ C\ ]$$

The most accurate extrapolation of a linear equation least squares fit is applied to the low rotation speed data as a linear equation $y=mx+c$ [33] as in Eq.2-51. For this equation to be universally applicable the reaction must occur at the solution/film interface. In terms of kinetic current density Eq.2-52 is in the form.

$$J_k = \frac{J}{[1 - (J/J_L)]}$$

(Eq.2-52)

Figure 2-15 depicts a K-L plot in the case of electrocatalysis at a poised potential where high rotation speeds cause kinetic limitation (zero order) and low rotation cause mass transfer limitation (1st order).

![Figure 2-15. Example K-L plot of transition between kinetic and diffusion control at constant potential. Slope is typical of ORR in aqueous media, $n=4$, $A=0.24718\text{cm}^2$, $C_0=5.67\times10^{-7}\text{M cm}^{-3}$](image)

The $i^1$ vs $\omega^{-0.5}$ plot is predicted to have a zero gradient at infinitely high rotation speeds in the case of a transition to total kinetic control. The true kinetic current ($i_k$) describes a
situation where mass transfer effects are absent. In other words, if reactant concentration in the vicinity of the reaction site is identical to that in bulk solution ($C=C_0$).

Extrapolation from the K-L plot is typically used to obtain $i_K$ as in Figure 2-15. In certain limiting cases experimental data may deviate from the slope if a non electrochemical reaction limits electron transfer at high current [56]. In the case where the electrode surface is covered with a redox active electrocatalyst of loading $\Gamma$ (moles cm$^{-2}$) the relationship between $i_k$ and the heterogeneous rate constant is described in Eq.2-53 [57].

$$i_k = nFkC_{O_2}\Gamma_{\text{Electrocatalyst}} \quad \text{(Eq.2-53)}$$

To obtain $n$ from K-L slopes, accurate estimations of viscosity and substrate diffusivity are required. Use of the RRDE with ultra-thin films allows intermediate detection prior to further decomposition in a thick film. In the case of ORR, the transfer co-efficient, $K_{app}$ (cm$^3$ M$^{-1}$ s$^{-1}$), relative to the no. of redox electrocatalyst active sites, is shown by Eq.2-54.

$$K_{app} = J_K/4FT_{\text{Electrocatalyst}}[O_2]_{\text{bulk}} \quad \text{(Eq.2-54)}$$

The electro-active redox catalyst loading $\Gamma$ should be used as opposed to calculated loading $\Gamma$, as only the catalyst involved in the reaction should be considered.

In situations where electrode is modified with an inert non redox active film (no reaction) through which reactant must diffuse an additional term can be substituted into Eq.2-51[58]…

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{L,c}} + \frac{\delta_{\text{coating}}}{nFC_{\text{coating,O}_2}D_{\text{coating,O}_2}} \quad \text{(Eq.2-55)}$$

Where $\delta_{\text{coating}}$ is the thickness of the inert coating, $C_{\text{coating,O}_2}$ is the concentration of reactant (ie. $O_2$) in the inert coating (Moles cm$^{-3}$), and $D_{\text{coating,O}_2}$ is the diffusion co-efficient of reactant in the inert coating (cm$^2$ s$^{-1}$). Should a reaction occur throughout the film and the position of reaction shift from the disc surface with potential a set of
criteria are present to determine $i_k$ [59, 60]. For applicability of this criteria the film must be uniform and has not been applied to redox polymers coating carbon in porous electrodes. This criteria has not been applied in this thesis.

**2.4.4. 2/4 e\(^{-}\) ratio calculation**

Disc currents and disc mass transfer limited ring currents are separated into data sets grouped by the same applied disc potential ($E$). The sets are plotted as a function of rotation frequency ($\omega$) to yield a mass balance on the RRDE tip. For the %H\(_2\)O\(_2\) vs. $E$ data, the proportional H\(_2\)O\(_2\) production was assessed by Eq.2-56. $i_{\text{ORR}}(i_{\text{O2}}-i_{\text{N2}})$ has been used instead of $i_D$ to remove non-faradic process currents.

$$X_{H2O2} = \left(\frac{(i_R - i_{R-BG})}{CE}\right)\left(\frac{i_{D,[O2]} - i_{D,[N2]}}{i_{D,[N2]}}\right)$$

(Eq.2-56)

$$N_{\text{ORR}} = 4 - [X_{H2O2} \times 2]$$

(Eq.2-57)

Where $X_{H2O2}$ is no. of moles of H\(_2\)O\(_2\) released from the catalyst layer per mole of O\(_2\) electrochemically reduced, $i_{D,[O2]}$ is the disc current obtained in O\(_2\) at a specified potential, $i_{D,[N2]}$ is the disc current obtained in N\(_2\) at a specified potential, $i_R$ is recorded ring current, $i_{R-BG}$ is the ring background current recorded at the point during LSV immediately before detecting increased H\(_2\)O\(_2\) oxidation. $i_{R-BG}$ was habitually specified as 10nA lower than the lowest ring current recorded for each LSV (see appendix Figure A-9). Briefly, ring current was processed by removing mainly currents from H\(_2\)O oxidation and PtO formation (Eq.2-58). The remaining current arises from H\(_2\)O\(_2\) oxidation.

$$i_R - i_{R-BG} = i_R - i_{dl} - i_{O2,\text{ev}} - i_{Pt\rightarrow PtO}$$

(Eq.2-58)

Where $i_{O2,\text{ev}}$ is H\(_2\)O/OH\(^{-}\) oxidation current (A), $i_{dl}$ is the double layer current (A), $i_{Pt\rightarrow PtO}$ is the PtO formation current after anodic polarisation is stopped.

**2.4.5. Wroblowa analysis for distinction of $k_1$ from $k_2\rightarrow k_3$**

In oxygen reduction, $k_1$ passes the same current as $k_2\rightarrow k_3$ (4e\(^{-}\)). This poses an interesting experimental problem of how to differentiate between the two. If the $k_2$ intermediary is
capable of desorption then residence time becomes a function of electrode rotation. Therefore analysis of the \( \% \text{H}_2\text{O}_2 \) vs \( E \) type plot at single rotation speed is insufficient to determine whether \( k_1 \) or \( k_2 \rightarrow k_3 \) is the dominants mechanism. Should an equilibrium adsorption of \( \text{H}_2\text{O}_2 \) on the surface of the electrocatalyst occur, then a lack of electrode rotation would cause a situation where it accumulates in the catalyst layer, potentially damaging the membrane.

A common analysis for mechanistic determination in Oxygen Reduction is the treatment originally derived by Wroblowa et al [61]. The guidelines are set out by Wroblowa et al [61] have been applied in neutral medium [62], tabulated as a simple summary by Hsueh et al [44] and then modified to include disproportionation effect on \( i_{D,L} \) in porous electrodes in Appleby et al [42] with the addition of \( \tau \) for \( \text{O}_2 \) recycled from disproportionation \( (1<\tau<2) \). Appleby’s derivation makes consideration of \( \text{H}_2\text{O}_2 \) that is reduced elsewhere from the main electrocatalyst site (ie. carbon or trace metal or non-adsorbed reduction). This analysis is frequently applied to porous films [63-66], due to the consideration of the term \( k_d \), an attribute with strong dependence on film thickness and residence time from rotation.

The data is able to offer mechanistic information even when the disc current is not limited by rotation \( (|i|<|i_{L,c}|) \) [63, 67], occasionally being able to determine \( k_1, k_2 \) and \( k_3 \) over the entire potential range [44]. In most instances \( k_1/k_2 \) ratios are obtained for the most active ORR mechanism for redox polymer electrocatalyst films [67].

**Wroblowa derivation**

In Wroblowa’s paper \( k_6, k_5 \) and diff are referred to as \( k_{6b}, k_{6f} \) and \( k_{D,H2O2} \) respectively for comparability with Appleby’s study. Considering the electrocatalyst to contain an adsorbed portion of \( \text{H}_2\text{O}_2 \) \( C_{a,H_2O_2} \) in equilibrium with the concentration at the IHP or catalyst layer \( (C_{c.l,H_2O_2}) \) whereby a portion is lost to the bulk \( C_{0,H_2O_2} \) and another portion oxidised by the ring. The situation where \( i_D \) is controlled by desorption or reduction of \( \text{H}_2\text{O}_2 \) can be examined. Applied in its entirety, this criteria can identify situations where the overall reaction rate \( (k_{app}) \) is controlled by \( k_1, k_2, k_3 \) or \( k_6 \). At steady state..
A mass balance on \( C_{a,H_2O_2} \) under \( i_{D,L} \)...

\[
k_2 C_{cl,O_2} = \left( -k_{2b} + k_3 + k_4 + k_6f \right) C_{a,H_2O_2} - k_{6b} C_{cl,H_2O_2}
\]  
(Eq.2-59)

A mass balance on \( C_{a,H_2O_2} \) under \( i_K \)...

\[
k_2 C_{a,O_2} = \left( -k_{2b} + k_3 + k_4 + k_6f \right) C_{a,H_2O_2} - k_{6b} C_{cl,H_2O_2}
\]  
(Eq.2-60)

A mass balance on \( C_{cl,H_2O_2} \) under any condition...

\[
k_6f C_{a,H_2O_2} - k_{6b} C_{cl,H_2O_2} = Z \alpha^{0.5} C_{cl,H_2O_2}
\]  
(Eq.2-61)

Where \( Z \) is the value obtained from the Levich Eq.2-40, though the \( H_2O_2 \) flow is now tangential to the disc surface...

\[
Z = 0.62D^{2/3}V^{-1/6}
\]  
(Eq.2-62)

Note that the 0.62 value assumes laminar flow from disc to ring and is an approximation which does not account for the change in Schwartz number for dealing with solvated \( H_2O_2 \). Very accurate determination of \( O_2 \) and \( H_2O_2 \) transport are required, otherwise, the diagnostic graph can shift left or right and yield inaccurate \( S \) or \( C \) values, which cause a misdiagnosis of the mechanism. Disc and ring currents are..

The current \( i_D \) under \( i_{D,L} \)...

\[
i_D = 2AF \left[ (2k_1+k_2) C_{cl,O_2} + (k_3 - k_{2b}) C_{a,H_2O_2} \right]
\]  
(Eq.2-63)

The current \( i_D \) under \( i_K \)...

\[
i_D = 2AF \left[ (2k_1+k_2) C_{a,O_2} + (k_3 - k_{2b}) C_{a,H_2O_2} \right]
\]  
(Eq.2-64)

\( i_R \) under any condition..

\[
i_R = 2AF(CE)Z \alpha^{0.5} C_{a,H_2O_2}
\]  
(Eq.2-65)

It is clear that the disc current does not need to be under \( O_2 \) diffusion limitation for this analysis to be valid, though \( i_R \) must be under diffusion limitation of \( H_2O_2 \) from the disc. The ring potential must be selected accordingly to oxidise the amount of \( H_2O_2 \) passing over the surface (see appendix section 10.5.3.).
Making concentrations the subject, the following equations resolve to describe the condition at \( i_{D,L} \): Eq.2-59, Eq.2-63, Eq.2-65 and Eq.2-61. Under the disc condition \( i_{k} \) Eq.2-60, Eq.2-64, Eq.2-65 and Eq.2-61. Irrespective of whether the situation is totally kinetically controlled or totally controlled both sets of equations combine to produce…

\[
i_{D}/i_{k} = \left( 1/N \right) \left[ 1 + 2k_{1}/k_{2} + A + \left( k_{6b}/Z\omega^{0.5} \right) A \right] \quad \text{(Eq.2-66)}
\]

Where \( A = \left( 2k_{1}/k_{2}k_{6f} \right) \left( k_{2b} + k_{3} + k_{4} \right) + \left( 2k_{3} + k_{4} \right)/k_{6f} \quad \text{(Eq.2-67)} \)

Making…

\[
\frac{S}{J} = \frac{k_{6b}A}{Z\left( 1 + A + 2k_{1}/k_{2} \right)} \quad \text{(Eq.2-68)}
\]

Substituting \( k_{1}=0 \) into Eq.2-66 reduces the equation to…

\[
i_{D}/i_{k} = \left( 1/N \right) \left[ 1 + \left( 2k_{3}/k_{4} \right)/k_{6f} + \left( k_{6}/Z\omega^{0.5} \right) \left( 2k_{3} + k_{4} \right)/k_{6f} \right] \quad \text{(Eq.2-69)}
\]

In this case the slope (\( S \)) and intercept (\( J \)) of this linear function show…

\[
J = 1 + \left( Z/k_{6f} \right) S \quad \text{(Eq.2-70)}
\]

For a linear portion of the \( S \ J^{1} \) plot of \( k_{1}\neq0 \) but \( S \ J^{1} \) is linear \( k_{1} \) and \( k_{2} \) must have the same potential dependence. The intercept of the \( S \ J^{1} \) graph extrapolates to \( J' \). If the \( S \ J^{1} \) graph is not linear then no easy conclusion can be drawn. If the graph is linear a trendline can be applied, reducing the situation to …

\[
J' = 1 + 2k_{1}/k_{2} \quad \text{(Eq.2-71)}
\]

This criterion predicts a good fit of the data at high and low potential. At intermediate potential neither Eq.2-64 or Eq.2-63 applies as both as \( i_{D} = f(C_{d,0z}, C_{o,0z}) \). The terms do not cancel out in this instance. Data may take the form of a minimum in \( R^{2} \) of the \( i_{D}/i_{k} \) vs \( \omega^{-0.5} \) plot at intermediate potentials, for example Figure 2-16. From an engineering
perspective, the low overpotential reaction is of most interest, for cell components susceptible to the prospect of $\text{H}_2\text{O}_2$ release.

![Figure 2-16. Validity of slope and intercept data $CE^*i_D/i_R$ vs $\bar{\omega}^{0.5}$ as a function of potential. Expressed an example trend in $R^2$ as $f(E)$](image)

**Appleby derivation**

An alternate method may find importance when considering $\text{O}_2$ diffusion limited current ($i_{D,L}$). The method derived by Appleby [42] examines $\text{H}_2\text{O}_2$ disproportionation to regenerate $\text{O}_2$ in the catalyst layer via $k_4$. The additional current under $i_{D,L}$ is now considered. In addition Appleby considers $\text{H}_2\text{O}_2$ reduction at a site outside the initial reaction zone, $k_5$. In this thesis the initial reaction zone is FePc. Carbon modification [66] or trace metals [68] remaining from pyrolisation or doping may perform $k_5$. The mathematical treatment followed five similar steps to Wroblowa’s criteria.

1) Perform mass balance on unadsorbed $\text{H}_2\text{O}_2$ in the catalyst layer, $C_{c,H_2O_2}$, make it the subject of the equation.

2) Obtain balance relating the rate of $\text{H}_2\text{O}_2$ departure from the catalyst layer to the ring current via heterogeneous rate constant, ie. $i_R = f(C_{c,H_2O_2})^*k_{D,H2O2}$ and integrate this equation into step (1).

3) Re-arrange the equation resulting from step (2) to make the precursor chemical step to electroreduction the subject, being $C_{a,O_2}$, $C_{c,O_2}$ depending on whether the disc current is under kinetic or diffusion control respectively.

4) Obtain relationship between disc current ($i_D$) to $C_{a,O_2}$, $C_{c,O_2}$ depending on whether disc current is under kinetic or diffusion control respectively. Re-arrange to make this term the subject.

5) Substitute step (4) into step (3) and re-arrange the resultant equation to obtain one in the form $i_D/i_R=f(k_{d,H2O2})^{-1}$. 

---

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Eq.2-72 links electrode rotation to the heterogeneous transport of H$_2$O$_2$ to the ring ($k_{D,H2O2}$), in a similar formulae Eq.2-62. According to Eq.2-72 the intercept value of $CE^*i_D/i_R$ vs. $ω^{-1/2}$ and $CE^*i_D/i_R$ vs. $1/k_{D,H2O2}$ should be identical with a different value for the slope.

$$k_{D,H2O2} = 0.62D^{2/13}ν^{-1/6}ω^{-1/2}$$

[42, 69] (Eq.2-72)

A mass balance on $C_{d,H2O2}$ under $i_{D,L}$...

$$C_{d,H2O2} = k_{2f}C_{d,0} \left( k_3 + k_4 + k_{D,H2O2} \right)$$

(Eq.2-73)

Substituting this into Eq.2-75 produces Eq.2-76. In this case $k_2$ is approximately equal to $k_{2f}$ and can be substituted for simplicity. Eq.2-76 is valid for kinetic limitation or O$_2$ diffusion limitation into the disc layer, provided cathodic overpotential is high enough and $k_{2b}$ negligible.

The Ring current expression is valid for all cases under study, “A” represents the disc area.

Under diffusion controlled oxidation of H$_2$O$_2$...

$$i_R = CE^*2AFk_{D,H2O2}C_{d,H2O2}$$

(Eq.2-74)

If $(k_3 + k_4) < 5k_5$ and $k_{D,H2O2} >> k_{5b}$ then the ring current is described by...

$$i_R = CE^*2Fk_{D,H2O2}C_{d,H2O2} = CE^*2F \left( \frac{k_{5f}k_{D,H2O2}}{k_{3b} + k_{D,H2O2}} \right) C_{a,H2O2}$$

(Eq.2-75)

This equation differs from that of Wroblowa’s. In Appleby’s instance, the case where the breakdown of adsorbed H$_2$O$_2$ becomes rate limiting can be evaluated using $CE^*i_D/i_R$ and a mass balance around adsorbed H$_2$O$_2$. Characters are referred to in Figure 2-8. At pH7 O$_2$\textsuperscript{-} (aq) is unstable [32], it is assumed all O$_2$\textsuperscript{-} in the catalyst layer is bound to the electrocatalyst, awaiting reduction. It is also assumed that $K_{ads}$ is large at all potentials considered and $k_{3Cf}/k_{3cb}$ is large as seen for FePc [70]. In Appleby’s model $k_{2b}$ is 1\textsuperscript{st} order with respect to H$_2$O$_2$ and OH\textsuperscript{-}. To make this term negligible only cases where the
potential is too cathodic for oxidation of H$_2$O$_2$ on the electrocatalyst will be considered 
($E <$0.18V). The mass balance around H$_2$O$_2$ becomes...

$$i_R = CE * 2 AFC_{cl,0_2} \frac{k_2 k_{D,H2O2}}{k_3 + k_4 + k_{D,H2O2}} \tag{Eq.2-76}$$

When considering $i_D$, the rate of O$_2$ entering the film at steady state equilibrium is given
by Eq.2-77 for a single potential. The consequential steps of $K_{ads}$ and $k_{3C}$ are irrelevant
to the balance as they overwhelmingly favour the forward reaction. As long as $k_{2b}$ is
negligible....

$$I = I_{D,L} \quad I = I_k$$

$$k_{D,O2} C_{a,O2} = (k_1 + k_2) C_{d,O2} = (k_1 + k_2) C_{a,O2} \tag{Eq.2-77}$$

The disc current is provided from Eq.2-78. To modify for the unknown concentration of
O$_2$ adsorbed on the electrocatalyst surface Eq.2-77 is used.

$$i_D = 4 AF (k_1 + k_2) C_{a,O2} \tag{Eq.2-78}$$

If a descriptor ($\tau$) is added with a value between 1 and 2 depending on ratio of H$_2$O$_2$ is
recycled back to O$_2$ and OH$^-$ from that reduced the mass balance on $i_{D,L}$ becomes Eq.2-79 under .

$$i_{D,L} = 2 AF (2k_1 + \tau k_3) C_{cl,O2} \tag{Eq.2-79}$$

If $\tau$=2 then $k_3$ or $k_4$ predominate, whilst in $\tau$=1 the ring current $k_{D,H2O2}$ dominates. $k_4$ is
expected to be a function of $\omega$ but not $E$ [71]. To perform the analysis recommended by
Wroblowa and Appleby a $CE * i_D/i_R$ vs $\omega^{-0.5}$ plot is produced by re-arranging Eq.2-78 to make $C_{a,O2}$ the subject and inserting into Eq.2-76. This term can then be combined with
that for $i_R$ in Eq.2-76 to yield Eq.2-80. In the case of kinetic disc limitation $\tau$=1.

<table>
<thead>
<tr>
<th>Y-axis</th>
<th>X-axis</th>
<th>Gradient</th>
<th>+</th>
<th>Y-axis intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CE * i_D$</td>
<td>$i_R$</td>
<td>$1/k_{DH2O2}$</td>
<td>$\left(\frac{2k_1}{k_2 + \tau} + \frac{(k_3 + k_4) k_{5b}}{k_{5f}}\right)$</td>
<td>$\left(\frac{2k_1}{k_2 + \tau} + \frac{(k_3 + k_4) k_{5f}}{k_{5f}}\right)$</td>
</tr>
</tbody>
</table>
In the expanded version the intercept value is still equal to \(2k_1/k_2+\tau\) provided \(k_3\) and \(k_4\) are insignificant compared to \(k_{5f}\). Under \(O_2\) diffusion limitation the \(k_1/k_2\) the value of \(\tau\) must be identified.

For further mechanism analysis the \(S/J\) values are plotted as a function of \(E\) to determine the kinetics of intermediary reduction/oxidation only, one term dominates with the \(\log_{10}\) plot being linear.

\[
S = \frac{(k_3 + k_4)k_{5b}}{k_3 + k_4 + k_{5f}} \quad \text{(Eq.2-81)}
\]

If \(2k_1/k_2+\tau=1\), as must be the case with \(J'=1\) then Eq.2-80 reduces to..

\[
S = (k_3 + k_4)k_{5b}/k_{5f} \quad \text{(Eq.2-82)}
\]

Electron transfer rate constants \(k_1\), \(k_2\) and \(k_3\) are expected to show tafel behaviour whilst \(k_5\) and \(K_{ads}\) are only weakly dependent on potential whilst, \(k_{4ii}\) is potential independent [42].

Plots of \(CE^*i_D/i_R\) vs \(\omega^{-0.5}\) are recommended by each model for diagnostic criterion [42, 44, 61, 62, 72] with additional data being provided by \(CE^*(i_D-i_R)/i_R\) vs \(\omega^{-0.5}\) [61] or the similar plots of \(CE^*(i_{D,L}-i_D)/i_R\) vs \(\omega^{-0.5}\) [73] or \(CE^*i_{D,L}/(i_{D,L}-i_D)\) vs \(\omega^{-0.5}\) with some authors claiming the latter method to be a simplification [74], though relies on fewer theoretical assumptions on the mechanism. To evaluate which model best applied the Iron Phthalocyanine case, the plot of \(CE^*i_D/i_R\) vs \(\omega^{-0.5}\) was made.

The plot of \(CE^*i_{D,L}/(i_{D,L}-i_D)\) vs \(\omega^{-0.5}\) produces \(k_{app}\), through Eq.2-84. Where \(Z_{O2}\) refers to the use of \(O_2\) limiting diffusion in Eq.2-83.

\[
i_{D,L} = NFAZ_{O2}\tilde{\omega}^{0.5} \quad \text{(Eq.2-83)}
\]

\[
i_{D,L}/(i_{D,L}-i_D)=1+k_{app}/(Z_{O2}\omega^{0.5}) \quad \text{(Eq.2-84)}
\]

Under kinetic disc limitation \(\tau\) is neglected...

\[
k_{app}=(2k_1 + k_2) \quad \text{(Eq.2-85)}
\]
Hsueh trialled a variety of models on the entire potential range [44] on a Pt electrode in H₂SO₄, finding only a model omitting disproportionation to fit the entire range. They report S/C data up to 100mV of cathodic overpotential. All methods of analysis [44, 61, 75] report the intercept of $CE \frac{i_D}{i_R} \text{ vs. } \phi^{0.5}$ to be equivalent to $k_1/k_2$ in some form. The general method applied to cases in neutral media [61, 75] contains a term for the intercept that could equate to 0 making the intercept $1+2k_1/k_2$.

2.6 Capacitance, charge motion and the redox polymer electrode

2.6.1 Rate limiting conditions in porous redox polymer thin films analysis

Ion diffusion through ionomer coated pores may become a limiting case in certain conditions in thin film. The criterion of several limiting cases of the K-L plot are outlined by Andrieux et al [59, 60, 76], Anson et al [77] and Lyons [78]. All models pertain to analysis of systems under steady state [78], which may not be present in cyclic voltammetry. Electron movement in semi-conductive electrodes can be modelled as a diffusive process, loosely obeying Fick’s law [60]. A model has yet to be produced for counter-ion diffusion dependent electro catalysis in a porous electrode with a non-homogenous coating of redox polymer electro-catalyst (ie. FePc) at potentials higher than limiting current. The effect of counter-ion on electron hopping has been conveyed [79] but not adapted to K-L plots. A graphical representation of the major processes is shown in Figure 2-17. In this figure two scenarios of electrocatalysis occurring a) at film-electrolyte interface or b) at the electrode-film interface.
2.6.2 **Assessment of electrode constrained redox active species**

When a faradic reaction is catalysed by a redox electrocatalyst a study of the CV response in the absence of substrate can yield useful information on loading, dispersion and layer conductivity. The equations used to analyse an electrode modified with a redox material where both the oxidised and reduced state are strongly adsorbed is outlined by Laviron [80]. The dependence of factors such as $E_{pa}$, $E_{pc}$, $J_p$ and $W_{1/2}$ on scan rate and pH yields kinetic data. These factors are obtained by treatment of the experimental data as in Figure 2-18(A) with baseline subtraction of contributions from charging current in Eq.2-16 to produce Figure 2-18(B). Generally, a widening and flattening of the peak points to a distribution of ionization energies for the adsorbed redox active material. A shift in the value $E_{pa} - E_{pc}$ with increasing scan rate allows the value of rate of surface electron exchange reaction $k_E$ ($s^{-1}$) to be determined.
Figure 2-18. \(i-E\) response of a strongly adsorbed metal based electrocatalyst in the absence of dissolved reactant. Example is for chelated Fe\(^{2+}/\)Fe\(^{3+}\) redox. Features used in analysis are presented for (A) the raw data, and (B) after subtraction of capacitive current. \(v=20\text{mV/s}\).

In the case of FePc, the amount which is electroactive, \(\Gamma_{\text{FePc}}\) (moles cm\(^{-2}\)) is calculated from the Fe(II)Pc\(\rightarrow\)Fe(III)Pc redox peak area during CV in quiescent de-aerated solution \(v=20\text{mV/s}\). The actual redox area was obtained by fitting a 6 order polynomial baseline to purely capacitive currents (0.45\(<E<0.5\) and \(-0.4\;<E<0\)) using the NOVA software package (autolab) as in the example in appendix, Figure A-3. The resulting current for each reading was multiplied by the time period, obtained by the change in \(E\) for each reading divided by \(v\), thus producing the total charge passed. Eq.2-87 is produced by integrating the recorded current for each \(t_{\text{step}}\) time period. Each time period is then multiplied for each current then integrating the time between each recorded current. Integration of the charge passed in oxidising the redox polymer \((i_{\text{Red\rightarrow Ox}})\) via applying Eq.2-87 to Figure 2-18(B) was deemed more accurate than peak height as peaks become non-Gaussian at high scan rate [80].

Laviron’s equation for electrodes bearing films of surface confined species [80] allows modelling of electroactive coverage using Eq.2-86. For this equation to be valid the oxidised and reduced state are irreversibly adsorbed. This equation is valid when no diffusive element is present in the cell and electron removal/insertion occurs reversibly.
\[ J_p = n^2 F^2 \frac{\nu \Gamma}{4RT} = nFQ \nu/4RT \]  
(Eq.2-86)

\[ A\Gamma F = I_{\text{step}} \int_{t=0\% \text{Ox}}^{t=100\% \text{Ox}} i_{\text{Red}+s \text{Ox}} \]  
(Eq.2-87)

Where \( J_p \) is the current density at the redox peak (A cm\(^2\)), \( n \)=no. of electrons involved in the exchange, \( F \)=Faradays Constant, \( \nu \)=Scan Rate (V s\(^{-1}\)), \( \Gamma \)=Surface loading of redox active material (mole cm\(^{-2}\)), \( Q \)=total charge passed during redox (C cm\(^2\)).

The electron insertion mechanism of a strongly adsorbed species is calculated using the width of the peak at half the maximum peak height (\( W_{1/2} \)). In an ideal situation with Gaussian peaks with no steric hindrance, peak splitting from a subsequent slow step or a lag caused by large \( \nu \), the \( W_{1/2} \) can be calculated using Eq.2-88 [81].

\[ W_{1/2} = \left( \frac{2RT}{nF} \right) \ln \left( 3 + 2\sqrt{2} \right) \]  
(Eq.2-88)

Assuming \( T=293^\circ \text{K} \) the ideal \( W_{1/2} \) value would be 0.0445V for \( n=2 \) and 0.089V for \( n=1 \). This method was used to the ease of electron transfer from co-ordinated Iron moieties and peak splitting. Additionally it has been utilised in chapter 6 to assess \( \text{O}_2 \) chelation by QDPSU binder.

### 2.6.3 Trumpet plot of redox active film

In the absence of substrate plotting \( E_p \) vs \( f(\log_{10} \nu) \) produces a trumpet shaped plot with linear section at high \( \nu \) with gradient \(-2.3RT/\alpha nF\) for the anodic branch and \( 2.3RT/(1-\alpha)nF\) for the cathodic branch [82]. When these branches are extended to \( E^{0'} \) they produce scan rates \( \nu_{an} \) and \( \nu_{ca} \) respectively...

\[ k_E = \alpha nF \nu_{ca}/RT = (1-\alpha)nF \nu_{an}/RT \]  
(Eq.2-89)

\( k_E \) (s\(^{-1}\)) is the rate constant for the reaction of a single redox moiety in the film where \( \Gamma_{an} = \Gamma_{\text{Red}} \) and \( E=E^{0'} \) for \( n=1 \) [83]. This electron exchange rate describes how quickly the film can be oxidised/reduced. To convert \( k_E \) to a heterogeneous rate constant \( k_{E,h} \) Eq.2-90 is used…
\[ k_{E,b} = \delta \text{film}_E k_E \]  

(Eq.2-90)

### 2.6.4 Anson plot for surface coverage and charge carrier concentration

The Anson plot of bolometric data (\(\Sigma Q\) vs \(t^{0.5}\)) of current decay following a potential step is governed by Eq.2-91.

\[
\Sigma Q = \frac{2nFAC(Dl)^{0.5}}{\kappa^{0.5}} + Q_{ads} + Q_{dl}
\]  

(Eq.2-91)

\[
Q_{ads} = nF\Gamma
\]  

(Eq.2-92)

In this case \(Q_{ads}\) is the charge injected into the electrode to compensate for specific adsorption onto the electrocatalyst surface of substrate or counter-ion. Repeating this experiment with and without solvated substrate produces information on partial surface coverage. The approximation of \(Q_{dl}\) can be obtained from impedance spectroscopy using \(C_{dl} = Q_{dl}/(\phi_{IHP}-\phi_{OHP})\). In situations where \(Q_{ads} >> Q_{dl}\) the intercept of the Anson plot (\(>>50 \mu\text{F cm}^{-2}\)) in de-aerated and aerated electrolyte provides relative surface coverage of anion adsorption and \(O_2\) adsorption via Eq.2-93 [84].

\[
Q_{ads} = (nF\Gamma_{FePc})(\theta_{FePc-X} + \theta_{FePc-O2})
\]  

(Eq.2-93)

Due to the issues highlighted in section 5.2.5 two distinct terms are used in this thesis where a faradic reaction occurs on an electrode possessing large \(C_\Sigma\).

1) \(E_{onset}\) (Onset Potential). “A potential during voltammetry where net current changes direction.”

2) \(E_{ORR}\) (Potential of ORR). “The potential where faradic current recorded in aerated electrolyte increases relative to non-faradic current in de-aerated electrolyte, indicating ORR.”
2.7 Electrochemical impedance spectroscopy

2.7.1 Impedance

Impedance is a composed of a real part \(Z'\), and an imaginary part \(Z''\), associated with capacitance. The resulting complex plane impedance is defined by Eq.2-94.

\[ Z = Z' + jZ'' = \sqrt{\left(Z'\right)^2 + \left(Z''\right)^2} \]  

(Eq.2-94)

Where \(j = \sqrt{-1}\), a complex term in the imaginary plane, typically solved by Laplace transform and nyquist or complex plane plots (\(Z'\) vs. \(-Z''\)) can be generated. Following an AC perturbation over a DC signal the resulting phase lag (capacitance) and reduction in amplitude (resistance) generate a complex plane plot. Typical input and output signals for a system are shown in Figure 2-19.

![Figure 2-19. Potentiostatic input (A) and corresponding current output (B) of an AC perturbation in applied potential (EIS).](image)

The decrease in anticipated current (ohm’s law) provides the real component, whilst the lag in phase angle (\(\phi\)) quantifies the degree of capacitance. In the absence of solvated substrate or surface reaction a purely capacitive response (\(\phi=-90^\circ\)) is obtained where the electrode is charged but e⁻ are not conveyed to the solution via reaction or consumed in a surface confined reaction (etc. corrosion). The thermodynamic lag associated with bond-reorganisation and energy barriers means that over certain time scales (AC frequencies) capacitance is observed in the response. The time scale for bonds to break and form produces an arc, where the HF limit (\(Z'_0\)) and LF limit (\(Z'_\infty\)) describe the timescales at which the reaction is complete and unable to be affected by changing surface conditions. The difference \(Z'_0-Z'_\infty\) is akin to the amount of electrical energy lost in the process of bond reorganisation.
Several elementary components are used to generate equivalent circuits of electrochemical processes. The total impedance as a function of frequency \( f \), phase angle and the obtainable kinetic information from the individual unit in series are shown in Table 2-1. The equations are frequently expressed as radial frequency \( \tilde{\omega} \) (rad s\(^{-1}\)) as opposed to Hz frequency \( f \), the relation between them as in Eq.2-95. The relationship between \( f^{-0.5} \) vs. \( \tilde{\omega}^{-0.5} \) and \( f^{-1} \) vs. \( \tilde{\omega}^{-1} \) are also linear. The conversion factor is written in Eq.2-96 and 4-4 respectively.

\[
0.159155 \tilde{\omega} = f \quad \text{(Eq.2-95)} \\
0.398942 \tilde{\omega}^{-0.5} = f^{-0.5} \quad \text{(Eq.2-96)} \\
6.28318306 \tilde{\omega}^{-1} = f^{-1} \quad \text{(Eq.2-97)}
\]

### 2.7.2 Equivalent circuit components modelling physical processes

Table 2-1 describes the phase discrepancy between bias voltage and corresponding current, the overall impedance of the unit as a function of DC perturbation frequency and the obtainable kinetic parameters of circuit elements connected in series. When connected in parallel other kinetic information is obtained.

**Table 2-1. Individual elements of equivalent circuits models of electrodes.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Overall Impedance</th>
<th>Phase Discrepancy (( \phi ))</th>
<th>Obtainable Kinetic Info</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td>( Z = R )</td>
<td>0°</td>
<td>N/A</td>
</tr>
<tr>
<td>Capacitor</td>
<td>( Z = \frac{1}{(j \tilde{\omega} C)} )</td>
<td>-90°</td>
<td>N/A</td>
</tr>
<tr>
<td>Constant Phase Element</td>
<td>( Z_{\text{CPE}} = \frac{1}{C(j \tilde{\omega})^N} )</td>
<td>f(( N )), when; ( N = 0, \quad 0° ) ( N = 0.5, \quad -45° ) ( N = 1, \quad -90° )</td>
<td>Low frequency limit on capacitive response. Slope indicates pseudocapacitance.</td>
</tr>
<tr>
<td>Inductance</td>
<td>( Z = \frac{1}{(j \tilde{\omega} L)} )</td>
<td>+90°</td>
<td>N/A</td>
</tr>
</tbody>
</table>
| Warburg Impedance | Infinite; $Z_w = \sigma(\omega)^{1/2} - j\sigma(\omega)^{-1/2}$ | Infinite; -45° Reflective finite; Low f lim. $Z' = \left(\frac{\delta}{Y^0 \sqrt{D}}\right)/3$
Finite reflective (general); $Z_w = \sigma(\omega)^{1/2} \coth \left( \frac{j\omega D^{0.5}}{\delta} \right)$
Open ended diffusion [85]; $Z_w = \sigma(\omega)^{1/2} \tanh \left( \frac{\delta}{D^{0.5} j\omega} \right)$
Reflective finite; A -45° region changing to a -90° region
Open ended diffusion; -45° region and gradual approach to 0°
Low f lim. $Z' = \delta / Y^0 \sqrt{D}$ |
|------------------|-------------------------------------------------|-----------------------------------------------|
| Gerischer Impedance | $Z = 1/Y^0 (k_a + j\omega)^{0.5}$ | -45° region and gradual approach to 0°
Low f lim. $Z' = 1/Y^0 k_a^{0.5}$ |

$N$ is the exponent of the constant phase element, $d$ is the distance of diffusion and can be used interchangeably as the Nernst diffusion layer $\delta$ (cm) or film thickness $\delta_f$ (cm) in cases of reactions at the electrode/film interface. $D$ is a general diffusion co-efficient of the diffusing species (cm² s⁻¹), $Y^0$ (Ω⁻¹ cm²) is the equivalent admittance at $\omega = 1$ rad s⁻¹, $k_a$ is the rate of a preceding chemical reaction in the bulk (s⁻¹), $C$ is capacitance associated with that unit (F cm⁻²) and $Z$, $Z_w$ or $Z_{CPE}$ are total impedances associated with the various units (Ohm cm²). The Warburg diffusion co-efficient $\sigma$ (Ohm cm² s⁻⁰.⁵) is described in Eq.2-98.

$$\sigma = \sigma_o + \sigma_R = \left(\frac{RT}{n^2 F^2 \sqrt{2}}\right)\left[1 / \left(C_{0,\text{red}} \sqrt{D_0}\right) + 1 / \left(C_{0,\text{red}} \sqrt{D_R}\right)\right]$$  \hspace{1cm} (Eq.2-98)

The diffusion factor $\sigma$, has mainly been amalgamated from the reduced ($\sigma_R$) and oxidised ($\sigma_o$) form (Ω cm² s⁻⁰.⁵). Symbols $D_O$ and $D_R$ relate to the individual diffusion co-efficient (cm² s⁻¹) and $A$ is electrode area (cm²). The oxidised and reduced parts of the couple can be amalgamated into a single diffusion co-efficient $D$ present at concentration $[X]$. This equation can be used to model reversible and quasi-irreversible reactions such as ion diffusion and adsorption. Most equivalent circuit fit programmes return $Y^0$ of a diffusion unit as opposed to $\sigma$, the two are related by Eq.2-99.

$$\sigma = 1/Y^0 \sqrt{2}$$  \hspace{1cm} (Eq.2-99)
When plotting $\sigma$ vs. $E$, the plot can show no peaks (as with ion diffusion) or can show a minima at a redox couple if electron diffusion control is present. The minima can be skewed from the $E^0'$ of a couple if a disparity exists between the chemical activities coefficients of the reduced ($a_{\text{red}}$) and oxidised couple ($a_{\text{ox}}$). This relationship follows the Eq.2-100.

$$E_{\text{red}} - E_{\text{ox}}^0 = \left(\frac{RT}{2nF}\right)\ln\left(\frac{a_{\text{ox}}}{a_{\text{red}}}\right)$$

(Eq.2-100)

Warburg impedance arises when diffusion of a substrate to, or diffusion of a product from an electrode becomes rate limiting. When no significant faradic reaction happens, charge transfer takes the form of ion desorption and diffusion to maintain electro-neutrality. Warburg diffusion can take several forms;

1) Semi-infinite Warburg diffusion, where the bulk concentration is unchanged and a linear concentration gradient exists between flat electrode surface and the reaction site impedance.

2) Reflective finite transmissive diffusion, where $e^-$ transfer from a redox active polymer into the solution occurs, via buffer or mediator, resulting in a highly charged double layer. Layers that respond this way are characterised by a finite amount of electro-active material, producing near infinite impedance when consumed.

3) Open ended or transmissive finite diffusion, where the diffusion boundaries are not set and no ions in solution can accept charge. In this situation charge transfer from the electrode to the polymer has become rate limiting.

Gerischer impedance manifests itself in the complex plane plot as a reflective transmissive Warburg impedance with a depressed semi-circle. It is frequently applied to porous electrodes but also situations where reactions occur in the bulk electrolyte [86].

In responses with well distributed time constants the response of a single parallel capacitor-resistor time constant ($r$) can be given by Eq.2-101. As pure capacitance has infinite impedance at 0Hz and zero impedance at $\infty$Hz the standard admittance is used for a constant phase element, $Y_0$. Only in the case of a CPE and resistor in parallel can the true capacitance be found from the frequency at the peak of the arc in Eq.2-103. The relation between capacitance and resistance follows Eq.2-102.
\[ \tau = R_0 C \quad \text{(Eq.2-101)} \]
\[ \tilde{\omega}_p = 1 / R_0 C \quad \text{(Eq.2-102)} \]
\[ C = Y^0 (\tilde{\omega}_p)^{N-1} \quad \text{(Eq.2-103)} \]

Where \( R_0 \) is the \( Z' \) value of the arc when extrapolated to 0Hz (-\( Z' = 0 \)). \( \tilde{\omega}_p \) is the frequency at the peak of the arc, also known as the ‘hopping frequency’ (rad s\(^{-1}\)).

If a multi-component equivalent circuit is limited (the vast majority of current loss and phase discrepancy) by a single one of these components under given conditions, the entire equivalent circuit may be approximated by the equations that describe that single component. The frequency range where a single component dominates can also be examined and linear regression used on the modified frequency term to obtain (\( \sigma \)) in diffusion control (\( Z \) vs. \( \omega^{-0.5} \) plot [87, 88]).

The rather complex term for finite Warburg impedance simplifies towards the higher frequency end of the region of mass diffusion control, approximated by \( Z_\| = 2\sigma \times \tilde{\omega}^{-1/2} \) in a narrow frequency region, analogous to infinite diffusion. If plotting the real component only to avoid noise from adsorption capacitance, the plot \( Z' \) vs. \( \omega^{-0.5} \) produces a gradient where Eq.2-98 can be applied, providing the \( \sqrt{2} \) term is removed.

### 2.7.3 Faradic reactions in EIS

In the instances where the resistance to charge transfer (\( R_{ct} \)) of a faradaic reaction has been successfully separated from other impedance effects, the \( R_{ct} \) at \( E = \text{OCP} \) is related to exchange current by Eq.2-104 and charge transfer kinetics by Eq.2-105. In a narrow potential range around \( \text{OCP} \) the \( dI/dE \) response is nearly linear, provided \(|b_c| = b_a\). Charge transfer resistance is measured as the width of the semi-circle or arc in the nyquist plot. The arc is easily identified by its significant potential dependence, with \( R_{ct} \) reaching a parabola maxima at \( \text{OCP} \).

\[ R_{ct} = \frac{RT}{nF i_0} \quad \text{(Eq.2-104)} \]
\[ i_0 = nFAk^0 C_0^{1-\alpha} C_0^{\alpha} \quad \text{(Eq.2-105)} \]
\[ k^0 = \frac{RT}{n^2 F^2 AC_{0,\text{Ox}}^{1-\alpha} C_{0,\text{Red}}^\alpha R_{\alpha}} \]  \hspace{1cm} \text{[90]} \hspace{1cm} \text{(Eq.2-106)}

At open circuit potential these equations combine to produce is transformed in using Eq.2-106 to yield \( k^0 \) from \( R_{\alpha} \) [91]. This analysis is valid for Randles plots, where \( R_{\alpha} \text{W}[C] \) circuits occur. The relative diffusion co-efficients of the oxidised and reduced couple cannot be applied to irreversible reactions such as ORR.

![Figure 2-20. Model of R_{\alpha}[C] circuit as a function of potential No substrate diffusion limitation. \( C=10^{-4} \text{ F, } C_{0,\text{Red}}=10^{-10} \text{ Moles cm}^{-3}, \text{ C}_{0,\text{Ox}}=10^{-6} \text{ Moles cm}^{-3}, \alpha=0.5, A=1\text{cm}^2, i_0=1\times10^{-8} \text{ Amps, } T=298.15^\circ\text{K.} \)](image)

In Figure 2-20(B) it can be seen that when the contribution from the resistor is relatively high the gradient of the \( -Z'' \) vs \( \omega^{-1} \) plot is linear, it’s inverse yielding the low frequency capacitance. In this example \( k^0=2.6\times10^{-6} \text{ cm s}^{-1} \) is obtained from a semi-circle fit as seen in Figure 2-20(A) using the previous formulae.

If the faradic reaction contains a substrate adsorption step that may become the RDS of the reaction, then a time constant may need to be included [92]. \( R_{\text{ads}} \) and \( C_{\text{ads}} \) of this process are expressed as…

\[ R_{\text{ads}} = \frac{RT}{n^2 F^2 C_{d,\text{Ox}} kA} \]  \hspace{1cm} \text{(Eq.2-107)}

\[ C_{\text{ads}} = \frac{n^2 F^2 AC_{d,\text{Ox}}}{RT} \]  \hspace{1cm} \text{(Eq.2-108)}
Where \( C_{cl,Ox} \) is the surface concentration of the oxidised couple (in the case of a reduction reaction). The rate constant (s\(^{-1}\)) of this process is given by…

\[
k_{ads} = \frac{1}{R_{ads}C_{ads}} \quad \text{(Eq.2-109)}
\]

This can be transformed into a heterogeneous rate constant by multiplication by the film thickness (\( \delta_{film} \)). In many processes reactant adsorption is strong and this feature may not be visible on the nyquist plot.

### 2.7.4 Analysis of intersecting time constants in EIS

The difference in \( Z''=0 \) intercept values of the HF arc and \( Z''=0 \) intercept from linear regression of Warburg response in the low frequency diffusive arc in the Nyquist plot (\( Z'' \) vs. \( Z' \)). This process is only accurate with poorly defined diffusive and faradic process, time constants of 1-2 orders of magnitude. If time constants are well separated error increases.  (e.g. Figure A-18). The formula depends on the other components present in the time constant and the nature of the diffusive species, for a \( C_{dl}[R_{ct}W] \) time constant where a neutrally charged substrate (i.e. \( O_2 \)) is diffusing, \( \sigma \) (\( \Omega \) cm\(^2\) s\(^{-0.5}\)) is given by Eq.2-110. In the instance where ion charge diffusion through a medium is limiting Eq.2-111 is applied [93]. This relationship can be analysed for a relation to binder.

\[
R_w - R_0 = 2\sigma * C_{dl} \quad \text{(Eq.2-110)}
\]

\[
R_w - R_0 = 2\sigma^2 * C_{dl} \quad \text{(Eq.2-111)}
\]

\( R_w \) (Ohm cm\(^2\)) is the resistance obtained from extrapolating the Warburg gradient (\( m=1 \)) back to the \( Z' \) axis to \( \omega=\infty \) Rad s\(^{-1}\).

### 2.7 Analysis of ion exchange materials and redox polymers with EIS

There are many instances where e\(^-\) ion diffusion though polymeric film determines catalytic turnover [91, 94-100] and overall electrode impedance. This diffusion can occur via three main ways [100]; 1) electron hopping, 2) Physical migration of the redox centre in the film (not applicable to irreversibly adsorbed FePc, or 3) anion or
cation migration to maintain electro-neutrality. Broadly speaking, a Warburg response transforms to that of capacitive response, as seen in the model for finite reflective diffusion in Figure 2-21. The physical explanation being that \((2D/\omega)^{0.5}\) becomes comparable to the penetration depth \(\delta_{film}\) of the AC signal at a certain low frequency. The descriptor \(B\) terms the limit of diffusion in Eq.2-112.

\[
B = \delta_{film} / \sqrt{D} \quad \text{(Eq.2-112)}
\]

![Figure 2-21. Model of finite reflective diffusion as (A)(B) Nyquist plot, or (C) Randles plot showing \(Z'\) vs \(\omega^{-0.5}\) for \(1.0>B>0.4\) and \(-Z''\) vs \(\omega^{-0.5}\) plot for \(B=1\). \(Y^2=1\)Mho, red line on (A) reflects \(\omega_2\) at \(-dZ'/d\omega=2\). \(\omega_2\) labelled for \(B=1\)](image)

![Figure 2-22. Model of finite open-ended diffusion (A) Nyquist plot, (B)(C) Randles plot showing \(Z'\) vs \(\omega^{-0.5}\) for \(1.0>B>0.4\) and \(-Z''\) vs \(\omega^{-0.5}\) plot for \(B=1\). \(Y^2=1\)Mho. \(\omega_2\) labelled for \(B=1\)](image)
Figure 2-21 depicts the response for a perfect conducting polymer. The HF intercept is at value $R_{W,\infty}$. When no reaction occurs the LF response is capacitive, extrapolating this LF nyquist response to the real axis produces $R_{\text{low}}$ (Figure A-19). Eq.2-113 is valid for both types of diffusion, the response being identical up to $\tilde{\omega}=B^2$.

$$\tilde{\omega}_2 = \frac{2}{B^2}$$  \hspace{1cm} (Eq.2-113)

A series of equations governing the situation of mixed ion resistance and electron diffusion resistance is provided by Armstrong et al [94], Mathias et al [101] and Cameron [102]. Provided the entire film is oxidised/reduced, the diffusion of electrons, $D_E$ (cm s$^{-1}$) can be related to film thickness, $\delta_{\text{film}}$ (cm) by Eq.2-114. The other variable can be obtained from slope extrapolation (see appendix).

$$D_E = \frac{\delta_{\text{film}}^2}{R_E} / 5.12$$ \hspace{1cm} (Electron diffusion) \hspace{1cm} [103] \hspace{1cm} (Eq.2-114)

$$D_E = \frac{\delta_{\text{film}}^2}{R_E C_{\text{diff}}}$$ \hspace{1cm} (Electron diffusion) \hspace{1cm} [102] \hspace{1cm} (Eq.2-115)

$$R_E = 3(R_{\text{low}} - R_{W,\infty})$$ \hspace{1cm} (Electron diffusion) \hspace{1cm} [102] \hspace{1cm} (Eq.2-116)

$$R_w = R_s + \left[ \frac{1}{1/R_{\text{ion}} + 1/R_E} \right]$$ \hspace{1cm} (Mixed e$^-$/ion diffusion control) \hspace{1cm} [102] \hspace{1cm} (Eq.2-117)

$$R_{\text{low}} = R_s + \left( \frac{R_{\text{ion}} + R_E}{3} \right)$$ \hspace{1cm} (Mixed e$^-$/ion diffusion control) \hspace{1cm} [102] \hspace{1cm} (Eq.2-118)

$$R_{\text{low}} = \frac{\delta_{\text{film}}^2}{3D_{\text{ion}} C_{\text{low}}}$$ \hspace{1cm} (Ion diffusion) \hspace{1cm} [87] \hspace{1cm} (Eq.2-119)

Where $R_E$ is the resistance (Ω) from electron diffusion or Fe(II)Pc towards the active site, $R_{\text{ion}}$ is the resistance to ionic movement in the film (Ω) stern layer to GC, $C_{\text{diff}}$ is the capacitance of the immediate boundary response (F) after Warburg control, $\tilde{\omega}_1$ is the radial frequency prior during a switch from Warburg to capacitive behaviour, where the gradient $d|Z'|/dZ'=2$ [94]. $R_{\text{low}}$ is the resistance (Ω), obtained from extrapolating the semi-bounded response back to the $Z'$ axis. In the some instances of bounded diffusion within the film a term $d$ (cm) can be used. This may also describe the mean diffusion distance in the high frequency portion.

The overall capacitance of an electrode without a significant faradic reaction can be obtained at the lowest frequency gradient in Eq.2-120 [104].
Two low frequency capacitances were termed due to the non-ideal response of the system, in some instances the linear capacitance after warburg control (see appendix Figure A-19) produced a different response to the lowest frequency \( -Z'' \) vs. \( \bar{\omega}^{-1} \) behaviour. In electro-catalytic systems a differential capacitance \( (C_{\text{diff}}) \) arises in redox polymers in oxidising/reducing the film and should form a perfect distribution around \( E^0' \) of the diffusion couple, this should provide mechanism confirmation [100]. This quantity is calculable for reflective finite diffusion from the \( -Z'' \) vs. \( \bar{\omega}^{-1} \) plot with the gradient equalling \( 1/C_\Sigma \) comprising almost exclusively of the pseudo capacitance \( (C_{\text{diff}}) \) [102]. If the double layer capacitance can be removed (typically negligible) then Eq.2-122 can be used to confirm \( (n) \), or film thickness \( (\delta_f) \) or diffusion length \( (d) \).

\[
C_\Sigma = C_{\text{diff}} + C_{db} + C_{\text{ads}} \quad \text{(Eq.2-121)}
\]

\[
C_{\text{low}} = \left( \delta_f n^2 F^2 / RT \right) \left( [O]^* [R] / [X] \right) \quad \text{(Eq.2-122)}
\]

\[
C_{\text{low}} \sigma = 0.5 \left( \delta_f / \sqrt{D_{\text{app}}} \right) \quad \text{(Eq.2-123)}
\]

\[
\sigma = \delta_f / \sqrt{2D^0} C_{\text{diff}} \quad \text{(Eq.2-124)}
\]

Various cases can be tested by inputting likely values of \( \delta_f \) and \( n \) the value for \([O]^*[R]/[X]\) can be obtained. This can then be compared to Eq.2-98, the Warburg coefficient in an amalgamated condition \( (1/[X]^{*} \sqrt{D_{\text{app}}} \), and as individual rate constants \( (1/[O]^{*} \sqrt{D_{o}}) + (1/[R]^{*} \sqrt{D_{o}}) \) to find a case that fits all values and confirms the mechanism of charge transfer.
Chapter 3. Literature Review of Electrocatalysis of $O_2$, Ion exchange polymers, Bioelectrochemical systems and their materials
3.1 Summary of Electron Acceptor Performances in MFCs

Table 3-1 summarises the performance of electron acceptors and their associated catalysts in MFC systems. The Power density ($P$) of each system (W m$^{-2}$) is quoted based on a geometric cathode area. In some instances reactor geometry is not been provided and volumetric power density (W m$^{-3}$) is used. $P$ is reported for the electron acceptor relative to a control setup, such as ORR on a Platinum catalyst benchmark. The ratio of $P$ in experiment: control is reported by an improvement factor, $'F'$ (unit less). Improvements ($F>1.0$) and some studies with $F<1.0$ are included if representing a major cost saving.

Table 3-1. Electron acceptor and associated catalysts previously studied in MFCs. All potentials quoted vs Ag|AgCl (3M NaCl)

<table>
<thead>
<tr>
<th>Electron Acceptor / Catalyst</th>
<th>Cell Design (#Chambers/Anode / Membrane)</th>
<th>Catholyte</th>
<th>Control Setup</th>
<th>Increase $P_{\text{max}}$ mW m$^{-2}$</th>
<th>$F$</th>
<th>OCP or $E^\circ$ / mV Ag/AgCl</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Biocathode</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_2$ / Consortia Fe$^{3+}$ and Mn$^{4+}$ oxidisers</td>
<td>2Ch/G-Granules/Nafion/C-Granules-MnOx-FeO cat.</td>
<td>Acetate PBS AWW=anolyte</td>
<td>MnOx-FeO C-Granule anode</td>
<td>28 Wm$^{-3}$</td>
<td>168</td>
<td>242 [106]</td>
</tr>
<tr>
<td>$O_2$ / Consortia-Xanthomonas Sp.</td>
<td>2Ch/Carbon/Nafion/Pt Cathode</td>
<td>PBS and minerals</td>
<td>Biofilm removed</td>
<td>570</td>
<td>2.85</td>
<td>- [107]</td>
</tr>
<tr>
<td><strong>NO$_2$</strong> / <strong>NO$_3$</strong> / Consortia</td>
<td>2 Ch /Carbon/CM7000</td>
<td>Spent Anolyte – PBS, NO$_3^{-}$</td>
<td>Cat. biofilm fed O$_2$ instead of NO$_3^{-}$</td>
<td>6.1 W m$^{-3}$</td>
<td>0.37</td>
<td>21 (NO$_3$) 8 (NO$_2$) [108]</td>
</tr>
<tr>
<td><strong>NO$_2$</strong> / Consortia-grown in O$_2$</td>
<td>2Ch/Carbon/Carbon separator</td>
<td>N$_2$ sat. Glucose PBS AWW-trace NO$_3$</td>
<td>Re-aerated catholyte</td>
<td>42</td>
<td>0.5</td>
<td>- [109]</td>
</tr>
<tr>
<td><strong>MnO$^x$</strong> / generated by Leptothrix Dischomera#</td>
<td>2Ch/G-Rod /2x J-Cloth + CEM</td>
<td>ATTC Medium, pH 7.2</td>
<td>O$_2$(aq) red. on abiotic carbon</td>
<td>126.7</td>
<td>32.5</td>
<td>418.5 [110]</td>
</tr>
<tr>
<td><strong>ClO$_2$</strong> / Dechloromonas Sp.</td>
<td>2 Ch /Carbon/CEM</td>
<td>PBS+ Growth Media, ClO$_2$ and NO$_3$ - no O$_2$</td>
<td>No ClO$_2$, only NO$_3$</td>
<td>0.0746 Wm$^{-3}$</td>
<td>n/a</td>
<td>c.a. -350 [111]</td>
</tr>
<tr>
<td><strong>Fe(III)</strong> / Acidithiobacillus Ferroxidans #</td>
<td>2Ch/C-Felt/Bi-polar membrane</td>
<td>Biocathodal, FeSO$_4$, Nutrients, pH2 Air sat.</td>
<td>No control</td>
<td>1200</td>
<td>n/a</td>
<td>c.a. 580 [112]</td>
</tr>
<tr>
<td><strong>Macrocyycles</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_2$ / FePc-C pry. (0.5 wt. Fe) AC</td>
<td>1Ch/G-Sheet</td>
<td>Acetate PBS AWW</td>
<td>0.5mg$_{\text{Fe}}$ cm$^{-2}$</td>
<td>720</td>
<td>0.88</td>
<td>c.a. 187 [113]</td>
</tr>
<tr>
<td>$O_2$ / FeAc - NH$_3$ pry. AC</td>
<td>1Ch/C-Felt/J-Cloth</td>
<td>Acetate PBS AWW</td>
<td>0.5mg$_{\text{Fe}}$ cm$^{-2}$</td>
<td>300</td>
<td>0.37</td>
<td>c.a. 207</td>
</tr>
<tr>
<td>$O_2$ / FeTMPP-Cl-C pry. AC</td>
<td>1Ch/G-Felt/Cloth</td>
<td>Acetate PBS AWW</td>
<td>0.5mg$_{\text{Fe}}$ cm$^{-2}$</td>
<td>660</td>
<td>0.8</td>
<td>c.a. 240</td>
</tr>
<tr>
<td>$O_2$ / CoTMPP-Carbon pry. – AC</td>
<td>2Ch/C-Cloth / Naion117</td>
<td>High Saline (250 mM)</td>
<td>Acetate PBS AWW</td>
<td>1062</td>
<td>1.3</td>
<td>c.a. 200 [114]</td>
</tr>
<tr>
<td>$O_2$ / FeEDTA – Carbon pry. AC</td>
<td>1Ch/G-Brush – Carbon layer</td>
<td>Acetate PBS AWW</td>
<td>0.5mg$_{\text{Fe}}$ cm$^{-2}$</td>
<td>11.22</td>
<td>0.96</td>
<td>814 # [115]</td>
</tr>
<tr>
<td><strong>Transition Metal Oxides</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_2$ / Octahedral Sieve Co-MnO$_2$ - AC</td>
<td>1Ch/GG/ Membrane-less</td>
<td>High [Acetate] AWW Continuous</td>
<td>0.5mg$_{\text{Fe}}$ cm$^{-2}$</td>
<td>897</td>
<td>3</td>
<td>124 # [116]</td>
</tr>
<tr>
<td>$O_2$ / Octahedral Sieve Co-MnO$_2$ - AC</td>
<td>1Ch/GG/ Membrane-less</td>
<td>Acetate+ Wastewater Batch</td>
<td>0.5mg$_{\text{Fe}}$ cm$^{-2}$</td>
<td>180</td>
<td>0.91</td>
<td>147 # [117]</td>
</tr>
<tr>
<td>$O_2$ / Sputtered CoO, on carbon - AC</td>
<td>1Ch/Carbon/ Naion layer</td>
<td>Acetate PBS AWW</td>
<td>0.5mg$_{\text{Fe}}$ cm$^{-2}$</td>
<td>28</td>
<td>0.34</td>
<td>- [118]</td>
</tr>
<tr>
<td>$O_2$ / MnO$_2$ – AC</td>
<td>2Ch/Carbon/Nafion</td>
<td>250mM PBS, pH7 - open to air</td>
<td>Glucose-trace PBS</td>
<td>0.82mg$_{\text{Fe}}$ cm$^{-2}$</td>
<td>161</td>
<td>0.83</td>
</tr>
<tr>
<td>$O_2$ / 8 phase-MnO$_2$ – AC</td>
<td>1Ch/G-Granules/Nafion</td>
<td></td>
<td></td>
<td>0.5mg$_{\text{Fe}}$ cm$^{-2}$</td>
<td>172</td>
<td>0.64</td>
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</table>
Carbon modification

<table>
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<tr>
<th>Oxygen Source</th>
<th>Electrode Material</th>
<th>Medium</th>
<th>Potential (V)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(_2)/HNO(_3) treat. Vulcan-AC</td>
<td>1Ch/C-felt/CEM</td>
<td>Acetate PBS AWW</td>
<td>170</td>
<td>[121]</td>
</tr>
<tr>
<td>O(_2)/Carbon Nanotube-AC</td>
<td>1Ch/G-Brush/PTFE</td>
<td>Acetate PBS AWW</td>
<td>329</td>
<td>[122]</td>
</tr>
<tr>
<td>O(_2)/(PPy-AQDS)-Carbon</td>
<td>2Ch/ADQS-Carbon/CEM</td>
<td>PBS</td>
<td>823</td>
<td>[123]</td>
</tr>
<tr>
<td>O(_2)/1000m3/g Activated Carbon Felt</td>
<td>1Ch/C-Felt/100μm pore separator</td>
<td>Aerated Glucose PBS AWW</td>
<td>52.5</td>
<td>[124]</td>
</tr>
<tr>
<td>O(_2)/Polypropylene-Carbon-AC</td>
<td>1Ch/C-Felt/Membrane-less</td>
<td>Glucose PBS AWW</td>
<td>40.18</td>
<td>[125]</td>
</tr>
<tr>
<td>O(_2)/Crumpled Graphene on Carbon Cloth</td>
<td>2Ch/Crumpled Graphene/CEM</td>
<td>100mM PBS, pH7</td>
<td>440</td>
<td>[126]</td>
</tr>
</tbody>
</table>

Chemical Acceptor (finite)

<table>
<thead>
<tr>
<th>Acceptor</th>
<th>Cathode Material</th>
<th>Medium</th>
<th>Potential (V)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO(_4) / Carbon</td>
<td>2Ch/Carbon/Naion</td>
<td>PBS-10mM KMnO(_4)</td>
<td>4.35</td>
<td>[127]</td>
</tr>
<tr>
<td>ClO(_4) / Graphite Rod</td>
<td>2Ch/G-Rod/NaCl Bridge</td>
<td>20g/L (Cu(OCl)(_2))</td>
<td>12.2</td>
<td>[128]</td>
</tr>
<tr>
<td>SO(_4^{2-}) / Carbon Paper</td>
<td>2Ch/C-paper/Naion</td>
<td>10mM K(_2)SO(_4)</td>
<td>211.9</td>
<td>[129]</td>
</tr>
<tr>
<td>[Fe(CN)(_6)](^{3-}) / C-Felt</td>
<td>2Ch/C-Felt/Naion-115</td>
<td>PBS+100mM [Fe(CN)(_6)](^{3-})</td>
<td>6130</td>
<td>[130]</td>
</tr>
<tr>
<td>V(_{[V]}) (VO(_2))(^{2+}) and Cr(V) (CrO(_2))(^{2+}) / Carbon</td>
<td>2Ch/C-Felt/Naion-117</td>
<td>Simulated mine WW, pH2 continuous -no O(_2)</td>
<td>970</td>
<td>[131]</td>
</tr>
<tr>
<td>PbO(_2)/C</td>
<td>2Ch/Carbon Cloth/KCl-Agar Bridge</td>
<td>PBS, pH7</td>
<td>77</td>
<td>[132]</td>
</tr>
<tr>
<td>Cu(_{[Cu]})/Carbon-Copper</td>
<td>2Ch/Graphite plate/Bipolar membrane</td>
<td>CuCl(_2), pH3</td>
<td>800</td>
<td>[133]</td>
</tr>
<tr>
<td>Fe[Fe(CN)(_6)](^{3+}) / PANI</td>
<td>2Ch/Granular graphite/Naion-117</td>
<td>KCl/H(_2)SO(_4)</td>
<td>1.4 x 10(^{-6})</td>
<td>[134]</td>
</tr>
<tr>
<td>Cr[Fe(CN)(_6)](^{3+}) / Carbon</td>
<td>2Ch/C-felt, Hanselau Nafion</td>
<td>KCl(pH6), KCl(pH2) or PBS (pH7)</td>
<td>0.45</td>
<td>[135]</td>
</tr>
</tbody>
</table>

**Key:** Ch(Chambers), G-Rod(Graphite rod), C-Felt(Carbon Felt), G-Granules (Graphite Granules), G-Brush (Graphite brush), Cat.(Cathode), AC(air cathode), PPy-AQDS(Polypropylene-anthraquinone-2,6-disulphonate), PANI(Polyaniline), *Suspected reference electrode drift, °OCV = 1.56V, xNo cathode control study

Electron acceptors with lower or similar formal potential (\(E^0\)) to anode biofilms such as H\(^+\) (Microbial Electrolysis Cell), CO\(_2\) and SO\(_4^{2-}\) require external electrical energy input and are omitted from Table 3-1. To the best of the author’s knowledge, environmentally relevant electron acceptors such as SrO\(_2\), S\(_2\)O\(_3^{2-}\), BO\(_3^-\) and CrO\(_4^{2-}\) have not been assessed in MFCs. If reference electrodes are not used cathode \(E^0\) is formulated from OCV and \(E^0\) of Geobacter type outer membrane cytochromes when fed with acetate (Eq.1-2).
From the formal potentials of Table 3-1 it is apparent that the electron acceptor with the highest $E^{0'}$ which requires no electrochemical regeneration is O$_2$. Other electron acceptors are rare in nature (ie. V(V)$_{aq}$, S$_2$O$_8^{4-}_{aq}$). Whether electron acceptor Ox is confined to the electrode to loading, $\Gamma_{Ox}$ (mole) or solvated in the catholyte, $C_{Ox}$ (mol cm$^{-3}$) the maximum theoretical charge that could be passed $Q$, associated with its reduction obeys Eq.3-1. The symbol ‘e’ is the elementary charge 1.6022x10$^{-19}$ C mole$^{-1}$ and $n$ the number of electrons used to reduce one molecule of Ox.

$$Q = n(\Gamma_{Ox} + VOL_{cat}C_{Ox})e$$ \hspace{1cm} (Eq.3-1)

Notable exceptions are Fe(III) and MnO$_2$, (c.a. $\Delta G$=76kJ mol$^{-1}$ and $\Delta G$=242kJ mol$^{-1}$ for 1e$^-$ and 4e$^-$ reduction with Eq.1-1) which can be produced via certain strains of microbes at the cathode and electrochemically reduced extracellularly on the biocathode surface. Maintaining an isolate at the cathode complicates cell design. The catalysis of oxygen reduction at pH7 is the focus herein.

### 3.2 Oxygen reduction catalysts

Literature on ORR catalysis is extensive with at least 45 papers being released per annum [138]. Discussion is limited to those applied to pH7 Bioelectrochemical Systems (BES) and Half-Cell studies with catalysts such as metal chalcogenides receiving no attention.

#### 3.2.1 Pure metals

Un-alloyed transition metals are rarely implemented in electrochemical devices unless as an electron donor (ie. Zn) or as a noble metal (ie. Au, Pt, Pd). For an electro-catalyst the surface oxide phase of pure metals (other than Au) is required to be ORR active.

Tang et al have implemented carbon supported Ag nanoparticles as a cathode for acetate fed membrane-less single chambered microbial fuel cell (SCMFC) [139]. They demonstrate some inhibition of oxygen respiring heterotrophic bacteria that would otherwise form a parasitic biofilm on the cathode. Prietto et al applied a highly active Au(100) bead that catalysed an ORR wave at $E$=0.21V (Ag|AgCl) in Na$_2$SO$_4$ (pH6)
[140], producing H₂O₂ when phosphate buffer was added highlighting the importance of the anion.

An evaluation of the formal potentials of ORR and competitive adsorption on Platinum in Phosphate can be found in section 10.5.3. In an MFC system Platinum remains the benchmark cathode catalyst [113, 141].

### 3.2.2 Alloys

The catalytic activity of a metal surface is a function of the binding energy of O₂ and the subsequent intermediates (O, OH, O₂H and H₂O₂) [142]. This forms the basis of an approach to understanding catalytic activity called Density Functional Theory (DFT).

Microbial Fuel Cell anodes and cathodes and current collectors [143, 144] frequently use passive Stainless Steel. On the atomic level, the surface possesses a distribution of O₂ binding energies and ORR activity. As such it is widely used as a current collector for cathodes of a large area. It is also used as a hydrogen evolution electrode in the microbial electrolysis cell [145]. The wide variety in activity comes from surface forms owing from differing interactions between the Mn, Cr, Mo, Ni and Fe. The specific activity (A cm⁻²) of active surface area is low but can be compensated for by high surface areas. Alloys with non-metal components cover a wide variety of materials such as chalcogenides. Isolated metal nitrides and metal carbides have not previously been implemented in MFC cathodes.

### 3.2.3 MeOₓ with and without graphite support

The surface oxide phase possesses low conductivity, oxide layer thickness determines whether the metal is a suitable current collector. Metals that are reactive in their elemental state possess thick oxide layers such as Titanium are seldom used as electro-catalyst supports unless they possess desirable photocatalytic properties [146]. In MFC Titanium is widely used as current collector [147], being electrochemically inert electro catalytically inactive and un-corrodible [148] in pH7 PBS [149].

The catalytic activity of MeOₓ is documented primarily for its reactivity with H₂O₂ [146] a quality that has seen it used as a co-catalyst with another 2e⁻ ORR catalyst [150-
The crystal phase may also determine activity [120, 157].

### 3.2.4 Graphite with and without chemical or thermal treatments

Carbon forms available as commercial electrodes are shown in Figure 3-1;

- Highly Ordered Pyrolytic Graphite (HOPG)-inter-sheet $\pi$-bonds overlap at regular intervals presenting a basal plane to the electrolyte. This aligned carbon has few pores or defects. [158]
- Edge Plane Pyrolytic Graphite (EPPG). Graphite sheets are perpendicular to the electrolyte. Electrons flow unimpeded along planes and do not traverse non-conductive ordered sheets. EPPG catalytic activity for ORR is altered by electrochemical or chemical modification.
- Carbon Nanotubes (CNT). Deposited in end-on configuration are highly conductive with smallest peak potential ($E_p$) Ferricyanide redox probe voltammetry [158]. CNT basal planes are low temp chemically modifiable unlike HOPG.
- Glassy Carbon (GC). A highly compressed and temperature annealed ribbon like matrix of non-graphitic carbon (produced from heated resins of phenolic aldehyde, furfuraldehyde and hexamethylene tetramine). No nitrogen or pores are contained in the $\text{Sp}^2$ bonding matrix which is resistant to chemical attack [159].

![Figure 3-1. Forms of commercial carbon electrode. EPPG – graphite edge plane is oxidised. Ribbon like structure of Glassy Carbon liquid and gas impermeable](image)

Graphitic carbons are also used in a porous matrix for increasing the relative area in contact with an electrolyte. As such they can greatly increase the relative rate of
reaction in circumstances where linear substrate diffusion is not a limiting factor. Interaction between graphite sheets due <0.335nm from strong π-π influence the electron density and may influence ORR activity. While graphite electrodes are widely used, Graphene electrodes have not been widely studied at pH 7.0 [160] but would omit plane-plane interaction effects.

No commercial activated carbon is devoid of small concentrations of metal, the only way to completely remove metal being aqua regia [161]. ORR activity of carbon materials can be attributed to edge plane impurities (non C or H elements). Zheng et al examined three methods of metal impurity removal from carbon [162]. Carbon nanofibres were; 1) Chemically cleaned–4M NaOH wash at 80°C, 4hrs then 2M HCl 60°C, 2hrs, or 2) Thermally cleaned–de-aerated to vacuum then thermally treated in Argon to 1700°C for 12hrs, or 3) Electrochemically cleaned–in de-aerated 0.5M HClO₄ (0V to 0.6V vs. SCE) by repeated CV. Electrochemical cleaning in de-aerated media (no H₂O₂) was performed until CV responses were purely capacitive (dI/dE=constant). The cleaned catalyst displayed mild ORR activity, $E<0.28$V vs SCE (0.32V Ag|AgCl). Thermally and chemically cleaned carbons produced an ORR wave at low potentials, $E<0.1$V for chemical cleaning and $E<0$V after heat-treatment.

The ratio between two carbon signals in raman spectroscopy (1345 cm⁻¹ and 1585 cm⁻¹) was used to show relative prevalence of edge plane atoms, halving after the thermal treatment. This demonstrates that pyrolysis causes edge planes to coalesce into larger graphite sheets. The value was unaltered by electrochemical cleaning, showing it to be a non-destructive process to the graphite.

### 3.2.5 Chemical treatment/pyrolisation of graphite

Quinones are among the most ORR active edge plane groups produced from non-metal based oxidative chemical treatments. This activity is attributed to the quinone/•quinone⁻ redox potential, the anionic quinone radical then binds O₂ via the scheme [163].

$$Quin + e^- \rightarrow •Quin^-$$

(Eq.3-2)

$$•Quin^- + O_2 \rightarrow Quin + O_2$$

(Eq.3-3)

Chemical or thermal treatment may produce materials that are inactive to ORR at $E=-0.45$V in pH7 PBS making them an ideal inactive support for testing dispersed catalysts.
Valarselvan et al. deposited quinones on a Polypyrrole support to ascertain the ORR activity of each type. It is feasible the author’s choice resulted in unique active sites from strong π-π bonds producing active sites between Pyrrolic Nitrogen and quinone which is not raised by the author. The general structure of quinone comprises aldehyde groups on benzene, shown in the 1,4 position (anthraquinone) as seen in Figure 3-2. It is feasible the authors choice to deposit quinones All quinones produced H₂O₂ from ORR. An oxygen reduction wave was catalysed by 2,6-dihydroxyanthra-9,10-quinone (c.a. $E=+0.38\text{V Ag|AgCl in pH6}$) [164].

Larsen et al showed that selective OH or COOH functionalization of nanotubes causes H₂O₂ production to increase ≈72% H₂O₂ and ≈38% H₂O₂ respectively [165] in comparison to unmodified CNT. In addition this group linked higher pyrolysis temperatures to lower the ORR activity.

Wet chemistry approaches for modification include conc. HNO₃ or ClO₃⁻(aq), O₃(aq) or H₂O₂. Edge plane groups that are quinolic, carboxylic or phenolic structures (Figure 3-2) can be produced. Erable et al, improved ORR activity of graphite granules as an MFC catholyte filler using concentrated HNO₃ [166]. Duteanu et al compared HNO₃ treatment of activated carbon (Vulcan XC-72R) to treatment with strong KOH, H₂O₂,
H₃PO₄ solutions [121]. ORR current increased with HNO₃ treatment from 1 to 2 Am⁻² at $E=-0.3V$ (vs. Ag|AgCl). The $E_{ORR}$ was largely un-affected by the oxidative treatment of HNO₃.

In pyrolysis the carrier gas, maximum temperature ($T_{max}$) and duration affect edge plane chemistry and morphology of re-graphitisation. Pirjamali et al outline a matrix of treatment methods of Ketjen Black carbon [167] that involve (a) HF/HCOOH acid treatment, (b) heat-treatment; $T_{max}=600/900°C$ in H₂/N₂/CO₂. All treatments produced uniform ORR performance ($E=294-206mV$ at $50mA cm^{-2}$), with highest temperatures in non-reducing carrier gases creating greatest ORR current. Significant increases in surface area are obtained with $T_{max}>900°C$ in all carrier gases (753 to 913 m² g⁻¹ in N₂). Symański et al compiled information on degradation temperatures of carbon structures. They report on Pyrones and some quinol (Figure 3-2) groups are the only original C-Oₓ species to survive $T_{max}=900°C$ pyrolysis.

Metal can be incorporated into the graphite sheet itself using 1) pyrolysis in a carrier gas (such as NH₃) that will produce chelating sites 2) adsorption of readily chelated metals (N₄, N₂S₂ or S₄) on basal planes and pyrolysing [168, 169] or plasma-treating [170, 171] the resulting carbon. This is discussed in more detail in 2.2.8.

3.2.6 Enzymes

Enzymes are the most active ORR catalysts available, typically harvested purified from fast growing gram negative aerobic organisms such as the fungi *Myrothecium Verrucaria*. The active site is a multi-copper oxidase consisting of three copper atoms each co-ordinated by 2-3 imidazole’s [172]. Gupta et al incorporate this enzyme into an air cathode [173], the response to polarisation is impressive, from $OCP=0.65V$ (Ag|AgCl) and $J₀=2x10^{-5}$ A cm⁻² an ORR wave of $bᵦ=-26.6mV$ dec⁻¹ is seen, offering a significant improvement over Platinum. The authors offer a kinetic explanation of 2e⁻ transfer with $α=0.5$ or 4e⁻ transfer with $α$ being far from 0.5. In the view of the author of this thesis, migration of the adsorbed oxo-species between multiple sites complicates this issue. Establishing the RDS and $E^0$ of each sequential activated complex will provide an answer.
Some organisms prioritise enzyme stability over activity, the Fe-heme/Cu oxidase possesses an active site potential of $E=0.142\text{V vs } \text{Ag|AgCl at pH7}$, (roughly analogous to $OCP$) [18]. The opposing copper site scavenges toxic peroxo species, even so enzyme lifetimes are only days [18] for mammalian mitochondria. Such a stability limitation makes utilisation of enzymes in cathodes for wastewater treatment impossible even with ion selective membranes.

### 3.2.7 Biocathodes

Biocathodes may operate over a wide pH range, many organisms acidify ($Leptothrix$ $Discophera$ [110]) or alkalify (catalase +ve organisms) as a result of their metabolism. They are typically employed in MFC for removal of electron acceptors that are viewed as a pollutants, such as $\text{NO}_3^-$, $\text{ClO}_4^-$, Cr(IV) azo dyes or even $\text{O}_2$ [174]. Examples can be found in Table 3-1. You et al [175] attained ORR at $E<0.525\text{V (Ag|AgCl)}$ from an biofilm grown from activated sludge. The conditions required to cultivate such a biofilm from wastewater may not apply to an air cathode with chemical electrocatalyst, fouling is not anticipated to be beneficial.

### 3.3 Transition metal macrocycles for ORR

Transition metal macrocycles are inspired by enzymes found in cell membranes, blood and cytoplasm [18]. All chlorophyll and bacteriochlorophyll comprise of a porphyrin type macrocycle ligand with a magnesium nucleus. Cobalt nucleus macrocycles can perform isomerisation’s, demethylation or dehalogenation in the body (Vitamin B$_{12}$). Iron nucleus macrocycles react with oxygen species such as $\text{O}_2$ (catalase, haemoglobin) or $\text{H}_2\text{O}_2$ (cytochrome-C). All consist of a transition metal co-ordinated by four pyrrole nitrogen atoms [18]. They are capable of adsorption of oxygen providing $\text{O}_2$ can substitute the existing ligand (such as $\text{H}_2\text{O}$ or $X^-$). In nature, planar Iron N$_4$-macrocycles may possesses aliphatic tails or electronegative groups, altering the $E^0'$ of the heme. These “periphery groups” are attached to the outer pyrrole. Synthetic Phthalocyanine ligands contain periphery benzene making them insoluble (MePc). The similarity between the $\text{O}_2$ binding site in haemoglobin (Haem B) and Iron Phthalocyanine (FePc) can be seen in Figure 3-3.
Figure 3-3. Similarities between Haemoglobin and Iron Phthalocyanine

After co-ordination by a tetra dentate N₄-macrocyclic ligand such as porphyrin or phthalocyanine, the iron possesses two remaining vacant ligand spaces for mono dentate ligands [176, 177]. Typically in aqueous solution each one of these spaces can be occupied by “axial ligands” that can be; 1) H₂O 2) a reactive oxygen species; O₂, •OH, H₂O₂, OOH₂ or elementary •O 3) a solvated anion; Cl⁻, HPO₄²⁻, NO₃⁻, SO₄²⁻, CN⁻ etc. 4) a nucleophilic compound; imidazole, pyridine, ammonia etc [177]. The response to polarisation from an Iron-N₄ macrocycle varies with the axial ligand. Stronger ligands substitute weaker ones as seen in the spectrochemical series [178]. Previous studies attribute the total electro negativity of all ligands to the redox potential of the metal ion [179-181].

Metal phthalocyanine’s have been studied for ORR in neutral media. Firstly by Savy et al [182] (Me=Co, Cu, Fe and Ni), who assessed monomer and polymer phthalocyanine’s for oxygen reduction in pH 6.7 PBS. This study demonstrated an important aspect for the most active Phthalocyanine forms; ordered polymeric deposition improved (−bₑ) tafel slopes.

Heat treated versions of various metal macrocycles on carbon support supports were assessed in a gas diffusion half-cell (GDC) by HaoYu, et al [169]. Pyrolysis alters the active site. This study performed the first neutral pH comparison of different chelated metals when embedded into graphite by pyrolysis [183]. A Platinum air cathode was used as a performance bench-mark. Macrocycles of Manganese, Cobalt, Iron and mixtures of Iron-Copper and Iron-Cobalt were precipitated on carbon supports from concentrated H₂SO₄ solutions then washed then pyrolised at 800°C. Composite
macrocycle mixtures of copper and cobalt did not improve intrinsic activity, Cobalt and Iron Phthalocyanine’s (Ketjen Black support) produced the best result. In an MFC the FePc on Ketjen Black produced the highest power output (634mW m\(^{-2}\)) with a biofilm on a NH\(_3\) activated carbon cloth in 50mM PBS and Glucose.

Following this result the pyrolysed FePc catalyst was studied with electrochemical impedance spectroscopy (EIS) and Galvanostatic polarisation [184]. Air cathodes were subjected to potentiostatic EIS, the resistance associated with electron insertion into O\(_2\), the resistance to charge transfer (\(R_{\text{ct}}\)) was 131.8Ω at OCP and reduced to 40Ω at an applied potential of 0V (Ag|AgCl). A separate term associated with resistance from O\(_2\) adsorption rate onto the iron site produced a less significant resistance (0.1Ω) at -0.2V but increased between 0V and -0.2V, reaching 3.16Ω at OCP. At OCP this is value is 1/40 the \(R_{\text{ct}}\) value, demonstrating that O\(_2\) adsorption is not a limiting step below OCP. ORR proceeded by a -62mV dec\(^{-1}\) tafel slope in PBS.

The nature of the active site after pyrolysis was explored by Lalande et al using time of flight secondary ion mass spectrometry [183]. Pyrolysis at 500-600°C (of FePc on carbon black) yielded the most active catalyst in acid media but reasonable stability was only observed at 700-800°C. This active form was correlated to surface evolution of Iron and Nitrogen indicating the nature of chelation has drastically changed. The FePc molecule suffered complete deterioration between 500-600°C, though partial deterioration initiated at lower temperature.

The catalytic activity is linked to the Fe(II)/Fe(III) redox potential [32, 169]. Due to large variation in produced sites resulting from pyrolysis it is easier to draw conclusions about ORR mechanisms catalysed by FePc without pyrolysis. Li et al use the density functional theory approach, asserting that the sequence of oxygen reduction starts with the Fe(II) state, in FePc. The basis being the low binding energy of Fe(II)-H\(_2\)O=0.10eV [185] making H\(_2\)O substitution by O\(_2\) favour the forward reaction, compared to the generated intermediary state; Fe(II)-O\(_2\)=0.12eV.

The rate constant of the next step (\(k_{\text{H}_2\text{O}}\)) is thought to vary drastically according to pH [186]. The rate constant is very high and instantaneous in all but low pH, favouring the forward reaction.
Baker et al show irreversible FePc attachment to basal plane graphite when immersed upside-down in a FePc solution of Isopropanol, a solvent that forms a weak ligand [179]. The known geometry of molecular Iron Phthalocyanine on a basal plane (1.5x10^14 cm^2). They establish that this method produced an average deposition equating to 2.1 monolayers, suggesting primarily flat adsorption (see Figure 3-4). ‘Edge on’ adsorption of FePc Benzene groups perpendicular the graphite plane was the explanation for the value being larger than anticipated. Coulometric analysis on the thin FePc layers show linear correlation between Fe(II)→Fe(III) peak height (J_p) and the scan rate (υ). As such, they demonstrate that the removal/insertion of electrons from the monolayer requires no diffusive element.

\[ \text{Fe(II)Pc} - O_2 \xrightarrow{k_c} \text{Fe(III)Pc} - O_2 \]  \hspace{1cm} (Eq.3-5)

In neutral media, Kozawa et al provide a series of i-E responses for FePc and elementary metals in Phosphate Buffered Saline [187, 188]. Cl^− and H_2PO_4^− adsorption are accounted for in FePc activity. They investigate potential catalysts supports for intended blood medium applications. FePc layers catalysed ORR waves more efficiently than metallic Au, Ag, Ni, Mo, Ti, Nb, Ta, Zr and TiB_2 alloy, only Pt and Pd outperformed FePc-Graphite electrodes.

CH_3COO^- (acetate) Me^{2+} adsorption onto FePc are evaluated by RRDE [176]. The information can be adapted to FePc use in an artificial and real wastewater medium (Table 1-1). Adsorption of Mg^{2+} and Pb^{2+} cations to Pyrrolic nitrogen in FePc increased the potential of the oxygen reduction wave while Ca^{2+} had no effect. FePc catalysed ORR waves at E=c.a. 0.18V in PBS and E=c.a. 0V in CH_3COONa, though H_2O_2 reduction was identical in either anion at equivalent pH. Acetate and PBS adsorption to the FePc was used to account for the difference, though pH change in the un-buffered...
CH₃COO⁻ may also have occurred in the view of this thesis author. CN⁻ caused FePc de-activation. This was reversible with washing in neutral sodium acetate solution and the i-E response of ORR was restored. This suggests that if strong X-type axial ligand adsorption is reversible other substances could reversibly adsorb.

Chen and co-workers also observed reversible •OH adsorption [70]. DFT calculations on (H₂O, OH, HOOH, O₂H and H₂O₂) intermediary oxygen species adsorbed on FePc [70]. They demonstrate that the binding energy of FePc-OH (-3.41eV) is significantly stronger than Pt(111)-OH (-2.39eV) as such desorption without further reduction is unlikely. The orientation of all adsorbed peroxide forms (-0.99eV, -1.01eV) is slightly less stable than adsorbed water (-1.05eV), suggesting H₂O substitution of H₂O₂ and peroxide release is possible if H₂O₂ is formed, enhancing rate k₆f. FePc passivation as the FePc(OH)₂ moiety with a DFT value of -1.05eV may result from H₂O₂ homolysis. This was suggested as the de-activating ROS species for FePc. The implications being that inert FePc will regain activity by washing with aerated or de-aerated alkali. OH-FePc-OH would be gradually substituted by two H₂O ligands or O₂.

Scherson et al draw attention to the HO₂ and OH intermediary/product, with O₂ adsorption being blocked and FePc de-activated. Another de-activation mechanism arising from H₂O₂ was highlighted by Nilekar et al who detected cleavage of the nitrogen atoms connecting the pyrrole ring as the likeliest point of chemical/thermal disintegration [189]. The product of reaction between FePc and strong H₂O₂ would be phthalic anhydrides, detectable by Mößbauer spectroscopy.

Van der Brink, et al present an important study where they isolate the individual reaction rate constants k₁, k₂f and k₃f (Figure 2-8) in alkali media [67]. In the unsupported thick FePc film direct 4e⁻ route dominated by two orders of magnitude at low overpotential (k₁=10⁻⁴ m s⁻¹ at +0.7V vs RHE). As such, peroxide release by FePc films should be below 1% at low η in alkali. Secondary H₂O₂ reduction (k₃) increases in unison with peroxide production (k₂f) in this region. At high η the rate constant of peroxide production (k₂f) increases to be larger than direct 4e⁻ reduction (k₁) at E=+0.18V vs RHE. It has been demonstrated that in porous carbon supported FePc electrodes the actual rate of H₂O₂ reduction ([FePc-H₂O₂]⁺k₃) and disproportionation ([H₂O₂(aq)]⁺k₄ii) cannot keep pace with H₂O₂ production [190].
Savy et al studied α and β FePc forms deposited on Au [191] or carbon [182, 192]. These films are crystalline and stacked along the molecular plane with 0.373nm Fe-Fe separation (α-FePc). The most pertinent aspect is the use of Phosphate of various pH, allowing direct comparison to this thesis. A linear relationship was uncovered between ΔG of the RDS and solution pH of approximately 19kcal mole⁻¹ in pH6.7 PBS, increasing by 2.7kcal mole⁻¹ per pH unit [192]. A Langmuir adsorption isotherm was established [192]. In their last study they show that the reduction of Fe(III)Pc-O₂⁻ form sets the electrode OCP [191] and polymeric (multilayer) FePc deposited on carbon black reduces activation energy, with |b|e|=37mV dec⁻¹, in comparison to monomeric (monolayer) FePc on Au, |b|e|=82mV dec⁻¹ [182]. Substrate plays a large effect at monolayer coverage [191], GC supported monolayers may yield a different result. The effect of multilayer or monolayer FePc coverage on J₀ was not reported, but extrapolating the graph to the OCP produced ~1.1x10⁻⁸ A cm⁻² for FePc on Acetylene Black carbon. The importance of co-facial ‘polymer’ for FePc is noted in some of the literature [191] and could feasibly be destroyed by pyrolysis.

3.3.1 Approaches to enhancing ORR through macrocycle modification

Functional groups on the periphery of the macrocycle ring can be used to change the electron withdrawing/donating characteristics of the macrocycle ligand [191, 193]. This in turn affects the redox potential of the metal [32]. As described by Coowar et al.,

“the effect of ligand substitution introducing electron donation to the central ion would be to shift the associated redox potential to more positive values.” [194]

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5 Based on this value, the author of this thesis calculates η=0 of the RDS adsorbed reactant and product to occur at 0.619V (Ag|AgCl).
Figure 3-5. Approaches to modifying Me Phthalocyanine activity for ORR; (A) A co-facial oligomer [195] and [196]. (B) Axial ligand X, or periphery groups R, for Fe metal.

In unmodified FePc position R contains Hydrogen (Figure 3-5). Substitution with Cl, F, NO₂, SO₃, OCH₃, NH₂ or COOH and replacing benzene molecules with pyridines and methyl pyridines have been studied [32]. A near perfect correlation was found between the electron withdrawing strength of the new macrocycle ligand (Hammet Parameter) and the redox potential $E^{0'}$ of the metal ion it co-ordinates [197]. In FePc, the Hammet parameter value, $\Sigma\sigma=-0$ for the Pc ligand [198], negative $\Sigma\sigma$ values increase the $E^{0'}$ of Fe(II)/Fe(III) and the overall rate constant, $k_{app}$. The maxima for the Fe(II)/Fe(III) has not been found for planar ring modified FePc [199]. The drawback of this approach is increased solubility and that $E^{0'}$ can only be ‘tuned’ within a certain range.

Zagal et al show a plot of $E$ at $J_k=30\mu A \text{ cm}^{-2}$ vs Me(II)/Me(III) $E^{0'}$ of O₂ reduction creates a linear relationship with Fe, Mn or Cr for periphery modified Phthalocyanine’s. The gradient was 0.8 (dimensionless) and the $E^{0'}$ ranged across 0.25V for each metal [199]. Multilayer deposition on carbon blacks may be affected by periphery ligands, disrupting the $\pi$-bond lattice (Figure 3-4).

**Co-facial oligomers with molecular spacers** can be formed with periphery group modification Figure 3-5(A) to alter Me-Me separation. For FePc this results in two faces being available for ligand addition from the electrolyte. The co-facial oligomer is better suited for 5-valent metals such as CoPc (one ligand vacant). Frémond et al [195] demonstrated this turning a 2e⁻ ORR CoPc catalyst into a 4e⁻ catalyst.

**Axial ligands** may be added by treatment of FePc treatment or adsorb from the electrolyte. This produces an adduct (AB) or bis adduct (AB₂), which can be defined as a combination of two distinct molecules (A and B) with no loss of electrons or protons and the formation of two bonds with a net reduction in bond multiplicity present in at
least one of the reactants (Eq.3-6). The resultant species may have unique electrochemical properties not present in A or B.

\[
A + B \rightarrow AB \\
A + 2B \rightarrow AB_2
\]  
(Eq.3-6)  
(Eq.3-7)

In FePc, the adsorption of the 5\textsuperscript{th} and 6\textsuperscript{th} mono dentate or a single bi dentate ligand form adducts with a significant shift in \(E^0\)\textsuperscript{[67]}. Ponce and Zagal improved FePc monomers (low activity) by tethering them to the Au support by a thiol presenting a phenyl amine or pyridine axial ligand to FePc. This produced an increase in the potential of the ORR wave of 0.1V and 0.2V respectively (pH4). In pH4 de-metallation will have a strong impact, the author of this thesis expects this approach to stabilise the FePc from demetallation (Eq.3-8) but the effect on stability was not reported.

Contamin et al state that Phosphate adsorption from the electrolyte (position X on Figure 3-5\textsuperscript{[181]}) displaces H\(_2\)O adsorption on FePc \textsuperscript{[84]}. As with O\(_2\), Phosphate may adsorb as a mono dentate or bi dentate ligand \textsuperscript{[200, 201]}. Simultaneous ligands of mono dentate O\(_2\) (end on) and mono dentate Phosphate are feasible, as such the activity in PBS may be unique amongst anionic salts. They state that electrocatalytic activity to O\(_2\) binding and reduction on the remaining ligand position will be affected.

Table 3-2 lists kinetic parameters of electrochemical studies on Iron Phthalocyanine with different deposition methods and electrolytes. In alkali media slopes of 30<\(|b_c|<40\text{mV dec}^{-1}\) are generally reported. However, there is generally discord as to the reason why. Appleby et al, suggest that the low tafel gradient (30mV dec\(^{-1}\)) is due to a chemical reaction RDS between H\(_2\)O and adsorbed HO\(_2^\cdot\) \textsuperscript{[202]} to produce two \(\cdot\text{OH}\) radicals. The \(\cdot\text{OH}\) radical could be reduced in the inner Helmholtz plane meaning a \(N_{ORR}\) of almost 4. In two studies by Zagal et al, large tafel slopes dominate (\(|b_c|=150\text{mV dec}^{-1}\) \textsuperscript{[186, 199]}, the author observed higher surface loading decreases \(|b_c|\). The ‘dipping’ in FePc solution method of surface attachment may have resulted in monolayer or sub-monolayer coverage. Table 3-2 aims to link the RDS to deposition method and media.
### Table 3-2: Summary of ORR kinetic studies on Iron Phthalocyanine.

Influence of deposition method and electrolyte. Plotted from earliest to latest to assess evolution of theory.

<table>
<thead>
<tr>
<th>Deposition Method</th>
<th>Electrode / Electrosynthesis</th>
<th>Electrolyte</th>
<th>Tafel Gradient (β/10)</th>
<th>4e-/2e- or N_{ave}</th>
<th>Rate Determining Step (RDS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer FePc film vacuum deposition on Au (1000Å) / (1300Å FePc film)</td>
<td>Au / no binder</td>
<td>pH6.7 PO_{4}</td>
<td>55mV dec^{-1}</td>
<td>2e or 2e+2e</td>
<td>-</td>
</tr>
<tr>
<td>10% wt. FePc on Acetylene Black – Polymer film 30Å</td>
<td>Au / no binder</td>
<td>pH1.3 PO_{4}</td>
<td>82mV dec^{-1}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>10% wt. FePc on Acetylene Black (30Å film)</td>
<td>Au / no binder</td>
<td>pH1.3 PO_{4}</td>
<td>38mV dec^{-1}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Monomer FePc films vacuum deposition on Au (4100Å)</td>
<td>Au / no binder</td>
<td>pH12 PO_{4}</td>
<td>29mV dec^{-1}</td>
<td>-</td>
<td>O_{2}(ads)+2H_{2}O+4e^{-}</td>
</tr>
<tr>
<td>Vacuum deposited film</td>
<td>Au / no binder</td>
<td>pH6.7 PO_{4}</td>
<td>37mV dec^{-1}</td>
<td>-</td>
<td>4OH^{-}</td>
</tr>
<tr>
<td></td>
<td>Au / no binder</td>
<td>pH1.3 PO_{4}</td>
<td>45mV dec^{-1}</td>
<td>-</td>
<td>H_{2}O_{2}(ads)+3H^{+}+3e^{-}</td>
</tr>
<tr>
<td></td>
<td>Au / no binder</td>
<td>pHH_{2}PO_{4}</td>
<td>62mV dec^{-1}</td>
<td>2e or 2e+2e</td>
<td>-</td>
</tr>
<tr>
<td>Monomer FePc films vacuum deposition on Au (1000Å)</td>
<td>Au / no binder</td>
<td>pHH_{2}PO_{4}</td>
<td>60mV dec^{-1}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Au / no binder</td>
<td>pHH_{2}PO_{4}</td>
<td>55mV dec^{-1}</td>
<td>-</td>
<td>H_{2}O_{2}(ads)+H^{+}+e^{-}</td>
</tr>
<tr>
<td>Gas phase dep. FePc; on Cl_{2} treat Carbon at 2000°C</td>
<td>Thin PTFE on Al mesh/PTFE</td>
<td>6N KOH</td>
<td>40 mV dec^{-1}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>on Ar treat Carbon at 2700°C</td>
<td>Thin PTFE on Al mesh/PTFE</td>
<td>6N KOH</td>
<td>55-65 mV dec^{-1}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FePc-Pyridine equilibrium ads. on carbon</td>
<td>Au screen / PTFE</td>
<td>8N H_{2}SO_{4}</td>
<td>85mV dec^{-1}</td>
<td>-</td>
<td>1^{e} e^{-} transfer</td>
</tr>
<tr>
<td>FePc-H_{2}SO_{4} prec. (20% wt. FePc on carbon)</td>
<td>Au screen / PTFE</td>
<td>6N KOH</td>
<td>35 mV dec^{-1}</td>
<td>-</td>
<td>2^{e} e^{-} transfer</td>
</tr>
<tr>
<td>Non-suppl. – Deposited from H_{2}SO_{4} (polymer FePc)</td>
<td>PG/</td>
<td>8N H_{2}SO_{4}</td>
<td>85mV dec^{-1}</td>
<td>-</td>
<td>1^{e} e^{-} transfer</td>
</tr>
<tr>
<td>Non-suppl. – Deposited from Pyridine (monomer FePc)</td>
<td>PG/</td>
<td>6N KOH</td>
<td>35 mV dec^{-1}</td>
<td>-</td>
<td>2^{e} e^{-} transfer</td>
</tr>
<tr>
<td>H_{2}SO_{4} prec. Or Pyridine equilibrium ads. on BRX</td>
<td>Au/</td>
<td>1M KOH</td>
<td>60mV dec^{-1}</td>
<td>4e to \eta=100mV</td>
<td>1^{e} e^{-} transfer RDS; OH desorption not limiting at pH13</td>
</tr>
<tr>
<td>Vacuum deposit (450°C) on Gold</td>
<td>Au/</td>
<td>1M KOH</td>
<td>120 mV dec^{-1}</td>
<td>at low \eta \leq 0.7V</td>
<td>Fe(III)Pc-O_{2}+e^{-}</td>
</tr>
<tr>
<td>Non-supported – Equilibrium ads. from Pyridine solution</td>
<td>PG/</td>
<td>1M KOH</td>
<td>120 mV dec^{-1}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>BRX Carbon – FePc from DMSO equilibrium ads. or H_{2}SO_{4} prec.</td>
<td>Au / PTFE</td>
<td>8N H_{2}SO_{4}</td>
<td>-72mV dec^{-1}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Non-supported – Equilibrium ads. from FePc-DMSO on PG</td>
<td>PG/</td>
<td>0.5M NaOH</td>
<td>-72mV dec^{-1}</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Non-supported – Equilibrium ads. from FePc-DMSO on PG</td>
<td>PG/</td>
<td>0.1M NaOH</td>
<td>40mV dec^{-1} \left(\eta=0.50mV\right)</td>
<td>Fe(III)Pc-O_{2}; \rightarrow intermediates</td>
<td>[186]</td>
</tr>
<tr>
<td>Equilibrium ads. FePc-Ethanol to Vulcan (α-phase)</td>
<td>GC/</td>
<td>0.5M H_{2}SO_{4}</td>
<td>40mV dec^{-1} \left(\eta=0.50mV\right)</td>
<td>-</td>
<td>Fe(III)Pc-O_{2}; \rightarrow products</td>
</tr>
<tr>
<td>(\alpha)-phase Heat treatment 450°C produces (β-phase)</td>
<td>GC/</td>
<td>0.1M H_{2}SO_{4}</td>
<td>-65mV dec^{-1}</td>
<td>Fe(III)Pc-O_{2}; \rightarrow products</td>
<td>[211]</td>
</tr>
<tr>
<td>Non-supported – Equilibrium ads. IPA/H_{2}O sol. Monolayer Vulcan XC-72R carbon</td>
<td>GC/</td>
<td>0.1M NaOH</td>
<td>92 mV dec^{-1}</td>
<td>-</td>
<td>O_{2}(ads)+3H^{+}+3e^{-}</td>
</tr>
<tr>
<td></td>
<td>GC/</td>
<td>0.1M H_{2}SO_{4}</td>
<td>-65mV dec^{-1}</td>
<td>-</td>
<td>RDS of H_{2}O_{2} adsorption</td>
</tr>
</tbody>
</table>

**Key**

Poly=Polymer, Mono=Monomer, CNT=Carbon Nanotubes, THF=Tetrahydrofuran, ads.=adsorption, GC=Graphite, PG=Pyrolitic Graphite, BRX=Norit BRX carbon black brand, TCB=Tetracyanobenzene, prec.=precipitation, pyr.=pyrolysed, ““=as

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80 | Page
above, ¶=remaining Pyridine adduct, no thermal removal (T>245°C). Results for highest BET area carbon. Low BET carbon resulted high |b_i|. Additional studies on FePc kinetic information; [176, 183, 187, 188, 214-221]. Studies were plotted earliest to most recent to assess theory evolution.

Some key observations on kinetic studies;

- Van de Brink suggests that the back-binding step with oxygen is not the RDS [67].
- Van de Brink [67] and Zagal [222] show discord on the nature of the RDS in alkali. Van der Brink et al argues that the Fe(III)Pc-O_2^- oxidation state would not be stable and that a single e^- accepting RDS would result in |b_i|=120mV dec^-1.
- Zagal et al [32] state the onset of ORR should be strongly controlled by electro-reduction of Fe(III)Pc-O_2^- or Fe(III)N_x-O_2^- adduct.

An unusual characteristic of FePc is H_2O_2 production at high potential, as seen from N_ORR values in Table 3-2. Metals and alloys release H_2O_2 at higher overpotential. The E^0' of H_2O_2 release from Pt in pH7 depends on the C_{0,O_2} and anion activity co-efficient. The E^0 of H_2O_2 is between 0.075V (p[O_2]=1, 1M H_2O_2, 1M SO_4^{2-}) [223] or 0.12V for a more realistic conditions (C_{0,O_2}=0.2, 5mM H_2O_2, 1M SO_4^{2-} [17]). It is likely that C_{0,H_2O_2} is not a consistent concentration and significantly smaller than 5mM , causing a larger E^0'.

3.3.2 Approaches to enhancing stability through macrocycle modification

Baranton et al showed deactivation from de-metallation (Eq.3-8) is significant in FePc [211]. A 65% reduction in ORR current occurred from polarisation of unpyrolysed FePc for 3hrs (E=0.5V vs RHE).

$$FePc - O_2 + 2H^+ \rightarrow H_2Pc + FeO_x$$  \hspace{1cm} (Eq.3-8)

The reaction occurs from certain formation of non-redox active adducts. Stefan et al showed that •OH and H_2O adducts cause Fe^{2+} heme to ‘pop’ out of the macrocycles plane changing the Fe-N distance from 1.95 to 1.98Å [224]. With O_2 adsorption this distance increases even further, and iron is then susceptible to demetallation.
Demetallation of FePc has been studied in K$_3$PO$_4$ electrolyte [176]. Tang et al found that stability occurred ~pH9 but rapid deterioration at pH5-7.

**Heat-treatment** increases performance in acidic media with pyrolysis [183, 209, 225]. Pyrolysis of FePc in inert atmospheres (argon, N$_2$) completely disintegrates the macrocycle at $T>$400°C. This has been confirmed by ToF-SIMS data and XRD [183], and thermo-gravimetric analysis [226]. FePc catalysts may retain a small peak after pyrolysis at high temperatures [227, 228], but surface concentration of viable catalyst is higher at $T\leq$500°C [183], though less stable.

In PBS-artificial wastewater medium pyrolised FePc on Ketjen Black ($T$=700°C) retained a redox peak [113]. After pyrolysis at 1000 or 800°C no increase in $E^{0'}$ of Fe(II)/Fe(III) is seen [183, 229]. In alkali media, the stability improvement of FeN$_4$ chelate pyrolysis is relatively unstudied. Savy et al report that air cathodes of FePc perform better at 300mA cm$^{-2}$ without pyrolysis ($E$=-0.49V vs Hg|HgO) than with ($E$=-0.6V vs Hg|HgO). They reported galvanostatic potentials to be higher for FePc than pyrolised FeTPP [230], requiring 500hrs of operation at 150mA cm$^{-2}$ before significant de-activation.

The model of Fe-N$_x$ intercalation into the graphite sheet with pyrolysis is proposed by Lalande et al [183]. If accurate, the prevalence of co-facial mechanism sites could be greatly reduced and the O$_2$ binding in Figure 2-10(D) would be less prevalent. The Fe-Fe separation in θ-FePc is 3.73Å [191], graphite sheets are separated by 3.35Å. The former distance allows for Fe-Fe sites to form staggered di-oxygen fixation across the Van der Waals planes between graphite sheets. It is plausible that the number of sites with an Fe-Fe distance of 3.6Å<3.9Å is negligible in number.

In conclusion the methods employed to enhance FePc activity can be broadly split in to two groups 1) axial ligand modification (Me-N distance), and 2) controlling Me-Me distance, and 3) periphery ligand modification. As noted by leading authors [32], the effect of the Phosphate ligand is largely unstudied for FePc, though a PO$_4^{3-}$ ligand should impede charge donation to O$_2$ [231].
3.4 Anion Exchange Materials

3.4.1 Anion exchange material implemented in MFC

Saito et al. put forward [232] a study on Polyphenylsulfone of various degrees of sulfonation, which affect the cation exchange capacity in MFC cathodes. The most hydrophobic binder with 0% sulfonation produced the highest current in half-cell LSV and single chamber MFCs. The decrease in performance with increased sulfonation was attributed to charge transfer resistance ($R_{ct}$) rather than O$_2$ mass transfer resistance. $R_{ct}$ ranged from 8Ω (no sulfonation) to 23Ω with an ion exchange capacity of 2.34 meq/g. They propose an uneven dispersion of non-ionic binder is beneficial, exposing some Pt surface[232], making uncovered Pt highly active which was evident from the decreased $J_0$ but increased $\alpha$ value suggesting that sulfonate ionomer covered Pt to be a different active site. Though $\alpha$ values (<0.1) are low when compared to literature values in the presence of Phosphate [233]. In the view of the author of this thesis the high ionomer loading (400µl of 5%wt. ionomer per cathode) will cover a large portion of the Pt surface, $\frac{1}{4}$ this binder loading being a typical amount.

3.4.2 Anion exchange groups

A small number of cationic groups have been assessed in alkali media and one in neutral media (quaternary ammonium). The list of eligible anion exchange groups is extensive and can be based on Phosphorous or Nitrogen cations [234].

3.4.3 Dabco chemistry

Dabco is an organic chemical that functions as a quencher of singlet oxygen in both air and liquid media [235]. It is also capable of metal chelation, iodide fixation and catalyses a variety of organic synthesis reactions [236]. Several patents have implemented supported Dabco as an anion exchange material [237-239]. A polyepchlorohydrine supported Dabco [237] focused on chloride exchange and found to be suitable for exchange of large anions (eg. boric acid sugar esters) which would otherwise block the pores.

The study by Ogryzlo and Tang [240] suggests that Dabco quenches O$_2$ by a partial transfer of charge to upon contact, the O$_2$ then being adsorbed. This occurs at a potential
closely linked to the ionisation potential \((IP)\) of such \(O_2\) quenching compounds [235]. The \(IP\) of methyl-Dabco and \(O_2\) fixated methyl-Dabco are not known.

Titration of Dabco reveals two buffering regions; Dabco\((H^+)\)/Dabco\((H^+)\) \(pK_a=2.97\) and Dabco\(H^+\)/Dabco \(pK_a=8.82\) [241]. Dabco is also a weak base exchanger \(pK_b=5.18\) [242]. Methyl-Dabco is usually represented in the ionic state [243]. The \(pK_a\) of ethyl-Dabco or QDPSU is anticipated to shift relative to Dabco. In addition, chelation of oxygen, metal or a counter-ion may alter the base equilibrium. Protonated Dabco on an Ag|AgCl electrode in de-oxygenated Chloride [241] has previously shown adsorption on AgCl as a function of potential, indicating amine-Cl bond formation. A similar effect has been observed with Phosphate [244]. In acid media Phosphate binding to Dabco produces doubly protonated Dabco and one bound phosphate Dabco:HPO$_4^{2-}$ of 1:1.2 [244].

The Dabco ring opening nucleophilic substitution reaction was outlined by Maras [245], usually requiring high temperature and catalyst. Methyl-dabco is thought to be impervious to this kind of degradation [245] it could plausibly be facilitated by localised environments in the catalyst layer, graphite edge planes or \(H_2O_2\). This would result in soluble Dabco or polymerised two-trimethylated nitrogen sites, possibly redox active.

As in Dabco-Polyepichlorohydrin, the substitution of \(\beta\)-Hydrogen on the Polysulfone backbone (Hoffman degradation) may cause Dabco ejection [246]. This would result in a soluble Dabco moiety. The Dabco moiety itself is not susceptible to beta-hydrogen substitution [246], but an accumulation of \(H_2O_2\) in the catalyst layer could plausibly facilitate other moiety decomposition reactions.
3.5 Anion exchange membranes in bioelectrochemical systems

An improved performance in single chamber Microbial Electrolysis Cells (MEC) with anion exchange materials is also documented by Rozendal et al [247]. The pH gradient was reduced from 6.4 pH units (cation) to 4.4 pH units (anion), thus demonstrating the improved pH balancing (Phosphate) performance of AEM’s. An MFC configuration was also used by Rozendal et al [248]. The total amount of charge transferred externally was largest for AEM indicating columbic efficiency benefits. The AEM (Fumasep-FAB) showed a preference for exchange of OH\(^-\) over H\(_2\)PO\(_4\)\(^-\) despite the molarity presence of the former being significantly smaller than the later. When viewed as H\(^+\)/OH\(^-\) exchange as a portion of the total charge exchanged, in other words the selectivity to avoid pH splitting, the highest performance was Bi-polar>Aion>Cation Exchange Membrane.

Van Sleutels et al [249] demonstrate the relative amount of exchanged anions and cations over a batch performance MEC. The clearly demonstrate that H\(^+\)/OH\(^-\) exchange is increased with an AEM. The CEM shows a proclivity for exchange of K\(^+\) with an initial concentration change of -0.6 M in the anode compared to a practically unchanged K\(^+\) concentration in the MEC using AEM. Critically, they report that charge transfer resistance in PBS (80\(\Omega\) cm\(^2\)) is significantly larger than membrane resistance (2\(\Omega\) cm\(^2\)) [249]. They also compared cationic charge transport facilitated by HPO\(_4\)\(^{2-}\) to that performed by H\(^+\) and OH\(^-\) (membrane dependent). Compared to the sum of electrical charge transferred approximately 37% of this value was H\(^+\)/OH\(^-\) ionic charge transport for the CEM compared to 77% by the AEM. In comparison implementation of the AEM increased transfer by HPO\(_4\)\(^{2-}\) to only 4% from 1.5% in the MEC utilising a CEM. This would seem to conflict the model put forward by Fan et al [250], who study non-ion selective separators (J-cloth) and identify a carbonate or phosphate cycle as the main mechanism for proton delivery and pH stabilisation in the catalyst layer, ie. HCO\(_3\)\(^-\)\(\leftrightarrow\)CO\(_3\)\(^{2-}\)+H\(^+\) or H\(_2\)PO\(_4\)\(\leftrightarrow\)HPO\(_4\)\(^{2-}\)+H\(^+\). Instead, the study by Van Sleutels et al of ion selective membranes demonstrates the selectivity of the OH\(^-\) transit through the membrane followed by neutralisation from a higher pH on the anode side. For PEM membranes, Harnisch et al note that with Nafion 117 trans-membrane diffusion constants are relatively similar for most anions [251].
Ji et al clearly define the interface region of a dual chamber MFC for microbial fuel cell scientists, based on the work on dialysis membranes by Długołęcki et al [252]. They break charge transport resistances down into (i) electrical double layer ($R_{dl}$) at the membrane-electrolyte interface, (ii) diffusion boundary ($R_{dbl}$), and (iii) membrane polymer phase ionic resistance ($R_m$) [253]. The double layer (100-300Ω) and diffusion layer resistances (>700Ω) become more dominant at the low solute concentrations (10mM PBS) seen in typical microbial fuel cell applications. The resistance of the membrane and electrolyte ($R_u$) cannot be separated in Nyquist plots. This study also offers typical maximum $O_2$ flux rates for anion exchange membranes 140-180µm thick in contact with a gas diffusion electrode open to the air, the values range from 1.6-3x10$^{-8}$ mmol s$^{-1}$ cm$^{-2}$. This provides a guideline for balancing $O_2$ utilisation against target $O_2$ diffusion into the cell from a dissolved $O_2$ source in order to avoid aerobic conditions.

The typical method of ascertaining membrane ionic resistance is the four electrode setup [252, 254, 255]. Fixating a membrane in a two electrolyte chambers between two Platinum foil plates and sensing the potential drop with two Pt wires [256] or two reference electrodes [252, 254]. Gu et al, state that AC impedance analysis with EIS at a frequency range of 1Hz to 100kHz produces a semi-circle on the $Z''$ vs. $Z'$ plot, the right side of which ($R_0$) corresponds to the membrane resistance. The frequency range employed in this thesis has produced a dielectric relaxation response in some studies of membranes in aqueous electrolyte [257], though the authors seldom state the nature of the desorbing species.

Nguyen et al provided an equivalent circuit model for a porous electrode with a membrane and current collector [258]. Dielectric relaxation spectroscopy of membranes typically utilises a higher frequency range and is not anticipated to be a problem with this investigation [259]. In Długołęcki et al the equivalent circuit for a DC flow of ions is an $R_s + R_m(C_{dl})(R_{dl}[Q_{dbl}])$ in standard notation. In contrast Nikonenko et al [255] observe open ended Warburg diffusion behaviour in place for $R_{dbl}[Q_{dbl}]$ (see Figure 2-22) to explain a linear region in the nyquist plot.
3.6 Analysis of ion exchange materials and redox polymers with EIS

The nature of ion exchange polymer is expected to play a critical role. As stated by Cameron ‘it is important to establish whether electron or ion diffusion limits the performance [102].’

Contamin et al demonstrate that High Frequency (HF) capacitance is associated with Phosphate adsorption on FePc [84], but a linear HF response in the domain of impedance versus square inverse of frequency (Z vs. $f^{-0.5}$) signifies limitation from diffusion of minority carriers that control performance, namely Fe(II) centres in the case of a binder-less vacuum deposited crystalline film. This process could be applied to air cathodes for assessment of binders which facilitate or hinder this process. The intercept of the $Z$ vs. $f^{-0.5}$ linear region extrapolates to the total resistance value of all resistors in series with the Warburg element.

A H$_2$Pc film [95] was vacuum deposited on a gold electrode and immersed in strong KOH solutions. Charge diffusion accounted for the majority of the resistance. H$_2$Pc is a p-type semi-conductor as is FePc but O$_2$ adsorption is reversible (Eq.3-5). Contamin and co-workers evaluate the movement of electrons through this film utilising Eq.2-114, and establish diffusion through the entire film thickness and reaction at the electrolyte/film interface. In their study on FePc films [84], $\sigma$ vs. $E$ plots and effect of O$_2$ were not reported, but the idea of competitive adsorption between Phosphate, Oxygen and Glutathione was investigated, using FePc as an analogue of cellular cytochromes.

To the author’s knowledge the approach has not been used to evaluate ionomers in catalyst layer for neutral media, the Koutecký-Levich approach being favoured instead. A study on a Nafion ionomer film in NaCl [99] by Komura et al, focused on the $\sigma$ vs. $E$ and $\sigma$ vs. pH behaviour of the film with and without immobilised redox mediator. It was found that electron hopping accompanied by H$^+$ migration in the opposite direction controlled the overall diffusion constant, present at $D=1.1\times10^{-11}$ cm$^2$ s$^{-1}$ in 0.4M HCl, with an abrupt decrease at higher pH.
3.7 MFC systems – Architecture and Substrate Treatment

3.7.1 Anode biofilm dispersion and models

Picireanu et al performed computer modelling of anodic biofilms on flat and porous electrodes [260]. They input physical constants and initial estimates for parameters, considering charge balance, electromigration, convection (cross-flow) in a porous layer. The models generated concentration gradient maps of localised pH and soluble electron shuttles generated by the bacteria and current production and biomass as a function of time. They mixed fermentive, methanogenic and exoelectrogenic biofilm was fed with mixed organics in wastewater under carbonate buffering. Overall maximum current was expected to decrease in the case of a consortia $J=0.3 \text{ A/m}^2$ vs $J=0.9 \text{ A/m}^2$ for single species as exoelectrogens are reliant on the rate of hydrolysis and fermentation and must compete with fermentive bacteria for acetate. Surprisingly the planar electrode (0 roughness factor) produced more current $J=0.9 \text{ A/m}^2 (5 \text{ g biomass/m}^2)$ than the porous electrode for a single species utilising a mediator. Forced convection, artificial buffering or electogenesis via nanowires could improve this further. Carbon felt is therefore anticipated to produce a similar power output to that of roughened carbon cloth, with the majority of biofilm being distributed on the felt surface.

Logan et al circumvented this problem by a graphite brush, possessing distinct bristles. Organic diffusion limitation is overcome and extra current collector is required [261]. In this seminal study for lab scale reactor design, maximum biomass and power density was increase with a brush (2.4 Wm$^{-3}$) designed to fit a cube reactor with a geometrically flat carbon felt (1.07 Wm$^{-3}$). Such a design would not increase the volumetric power density (W m$^{-3}$) if the felt were placed closer to the membrane in a compact design.

3.7.2 Wastewater and coulombic efficiencies

Velasquez-Orta has obtained high coulombic efficiencies ($\varepsilon_c$) from real wastewater. Paper, dairy, bakery or brewery industry wastewater produced $\varepsilon_c = \text{c.a. 80%}$ in single chamber MFC [262]. Autoclaving the wastewater did not drastically alter the result and de-aeration was used prior to insertion. A seven fold increase in conductivity to 7.1mS cm$^{-1}$ resulted double power output. Fornero et al compile tabulated lists of maximum power densities from various substrates and coulombic efficiencies in batch operation [263]. They cite studies with acetate fed reactors producing $\varepsilon_c=99\%$. 
Although high COD removal rates for single chamber cubed cell systems up to $167\text{kg}_{\text{COD}} \text{m}^{-3} \text{day}^{-1}$ are obtained [23], the $\varepsilon_C$ should be quoted with COD removal rates to avoid consideration of non-electrogenic degradation of organic matter. In this study fermentive and non-electrogenic metabolism caused only $\varepsilon_C=0.7\%$ making exogenous COD removal $1.169 \text{ kg}_{\text{COD}} \text{ m}^{-3} \text{ day}^{-1}$. Increasing residence time to 4hrs (loading $1.75\text{kg}_{\text{COD}} \text{ m}^{-3} \text{ day}^{-1}$) increased COD removal to $33\%$ and $\varepsilon_C=26\%$ making exogenous removal $0.150\text{kg}_{\text{COD}} \text{ m}^{-3} \text{ day}^{-1}$.

### 3.7.3 Cathodic limitation

In an important study on the limitation of charge transfer observed for the cathode, Fan et al. mathematically correlated cathode limitation to electrode area by reducing the size of the anode. They reported $R_{ct}$ and $P_{\text{max}}$ (anode based) in single chambered membrane-less MFCs when anode area was altered relative to a fixed Pt air cathode. An infinitely large cathode could be extrapolated from the experimental results. With this approach the theoretical $P_{\text{max}}$ obtainable with no solution resistance or cathode polarisation was calculated to be $19,369 \text{ mW cm}^{-2}$ (based on anode area planar diffusion).

By contrast, Table 3-3 highlights cathode design improvements to MFCs using $\text{O}_2$ as an electron acceptor. Not all are mutually implementable (ie. Flow through cathode and PTFE diffusion layers), some could be combined.
Table 3-3. Studies on cathode design improvements effect on $P_{\text{max}}$ and OCP.

<table>
<thead>
<tr>
<th>Design Improvement / Purpose or effect</th>
<th>Cell Design (#Chambers/Anode / Membrane)</th>
<th>Catholyte</th>
<th>Control Setup</th>
<th>Increase $P_{\text{max}}$ mW m$^{-2}$</th>
<th>OCP or $E^\circ$ vs Ag/AgCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sandwich Design (Pt-C, AC) / + Volumetric Power Density</td>
<td>1Ch/C-Paper / Naion 115</td>
<td>PBS, Acetate, pH7-Agitated</td>
<td>Anode spaced from cathode MEA-4cm</td>
<td>1180</td>
<td>3.33 =+400</td>
</tr>
<tr>
<td>Nafion binder (35% wt) for Pt-C, AC / Improved proton conductivity</td>
<td>1Ch/C-paper / membrane-less</td>
<td>PBS, Glucose, pH7</td>
<td>35% wt. PTFE binder for Pt-C, AC</td>
<td>480</td>
<td>1.33 =+304</td>
</tr>
<tr>
<td>Low pH (2) Catholyte – FePt-C, pyr. - AC / Higher $E^\circ$</td>
<td>2Ch/G-Granules, C-Felt/Gore-Tex</td>
<td>1% NaCl/HCl, pH2. Circulated</td>
<td>pH7 NaCl catholyte</td>
<td>256</td>
<td>1.13 =+568</td>
</tr>
<tr>
<td>4xPTFE layers air side of Pt-C, AC / reduce $O_2$ crossover</td>
<td>1Ch/C-Cloth, an-cat=4cm / membrane-less</td>
<td>PBS, Glucose, pH7</td>
<td>No PTFE diffusion layers</td>
<td>766</td>
<td>1.4 302</td>
</tr>
<tr>
<td>Growth of N-doped nanofibres on SS mesh / reduce cat. resistance</td>
<td>2Ch/Graphite Paper / PEM</td>
<td>50mM PBS, pH7</td>
<td>Platiniised SS Mesh</td>
<td>1900</td>
<td>1 -</td>
</tr>
<tr>
<td>Flow through cathode / Improve oxygenation and pH balance</td>
<td>Catholyte flow through cathode to anolyte/G-plate/Membrane-less</td>
<td>Glucose AWW</td>
<td>Up flow without De-oxygenation</td>
<td>30</td>
<td>2.1 -</td>
</tr>
<tr>
<td>30 Mesh size SS Current Collector and PDMS for Pt-C, AC / balance conductivity and $O_2$ diff.</td>
<td>1Ch/G-Brush / Membrane-less</td>
<td>Acetate 50mM PBS AWW</td>
<td>SS-90 Mesh</td>
<td>1616</td>
<td>3.1 177</td>
</tr>
<tr>
<td>Increase specific area of Pt-C, AC (24cm$^2$) / reduce $R_\alpha$</td>
<td>1Ch/G-Brush / Membrane</td>
<td>Acetate PBS AWW</td>
<td>7cm$^2$ cathode area</td>
<td>2031</td>
<td>1.3 -</td>
</tr>
<tr>
<td>PDMS + SS current collector diffusion layer / Improve $O_2$ diff.</td>
<td>1Ch/G-Brush / Membrane-less</td>
<td>Acetate PBS AWW</td>
<td>C-Cloth Current Collector</td>
<td>1610</td>
<td>1.03 585</td>
</tr>
<tr>
<td>Mix CO$_2$/Air sparged catholyte for Pt-C / use flue gas sparge, replace PBS</td>
<td>2Ch/C-Cloth / PEM-AMI 7001</td>
<td>CO$_2$ contact H$_2$O HCO$_3^-$ / CO$_3^{2-}$</td>
<td>CO$_2$ sparge + 0.1M PBS Catholyte</td>
<td>83</td>
<td>0.74 =+310</td>
</tr>
<tr>
<td>AC fed moist gas: 21% CO$_2$, 79% Air mix for Pt-C / Catholyte pH balance</td>
<td>2Ch/C-Cloth / PEM-AMI 7001</td>
<td>Moist AC –some HCO$_3^-$</td>
<td>Moist air, no CO$_2$ (few solvated ions)</td>
<td>50</td>
<td>2.5 -</td>
</tr>
<tr>
<td>Nickel based paint for MnO$_2$-C, AC. on cloth / Conductive diffusion layer</td>
<td>1Ch/C-felt / CEM</td>
<td>Brewery WW- NaG, pH8</td>
<td>Graphite based Paint MnO$_2$-C, AC</td>
<td>86</td>
<td>3.5 =+130</td>
</tr>
<tr>
<td>Glass Fibre 1 Separator for MEA (Pt-C, AC) / non-biodegradable separator and higher CE, 2 biofilms</td>
<td>1Ch/C-Cloth, 2cm from cathode/GF-Separator</td>
<td>Acetate PBS AWW</td>
<td>CEM membrane (CMI-7000)</td>
<td>791</td>
<td>4.47 -</td>
</tr>
<tr>
<td>AC cleaned of bio fouling (Aged Pt-C) / OBR selectivity by facile Pt</td>
<td>1Ch/C-Cloth, 2cm from cathode/Membrane-less</td>
<td>Acetate PBS AWW</td>
<td>Before biofilm removal</td>
<td>425</td>
<td>1.05 -</td>
</tr>
<tr>
<td>Glass Fibre 1 Separator for sandwich MFC / stop short-circuit - reduce $\Omega$ and $O_2$ crossover</td>
<td>1Ch/Carbon Cloth /GF-Separator</td>
<td>Acetate PBS AWW</td>
<td>2x J-Cloths, Sandwich configuration</td>
<td>1195</td>
<td>1.09 -</td>
</tr>
</tbody>
</table>

Additional Symbols and abbreviations: AC-Air Cathode, Ch-Chambers, PDMS-Polydimethylsiloxane, MEA-Membrane Electrode Assembly, AWW-Artificial Wastewater, SS-Stainless Steel, diff.-Diffusion, GF-Glass Fibre, CEM-Cation Exchange Membrane, CMI-7000-Type of CEM, pyr-Pyrolyised, cat.-Cathode, C-Felt-Carbon Felt, G-Carbon (Graphite carbon type=Rod, Granules, Brush, Plate).

### 3.7.4 MFC lab scale designs

In Figure 3-7 the main MFC lab scale designs are depicted. The single chambered model (A) is the simplest to assemble.
Zhang et al [272] demonstrate that the highest volumetric current density (and therefore COD removal rate) is obtained with a sandwich type MFC, Figure 3-7(C). This improvement is attributed to a decrease in ionic resistance (Table 3-3). Design choice for anode-anode electrode spacing are constrained by clogging of the anolyte channels. This design has been used to produce the largest volumetric power density and COD removal rate by Fan et al [25] and Shimoyama et al [273] respectively, 1.01kW m$^{-3}$ (0.4cm anode spacing) and 5.8kg$_{\text{COD}}$ m$^{-3}$ day$^{-1}$. Methanogenesis is suppressed due to trace oxygen cross-over through the membrane. The COD removal rate is equivalent to state of the art up flow anaerobic sludge blanket (UASB) technology ($\approx$1.5-5.3 kg$_{\text{COD}}$ m$^{-3}$ day$^{-1}$) [274].
Chapter 4. Experimental methodologies
4.1 Chapter 5 and 6 Experimental

4.1.1 Catalyst Preparation

Iron Phthalocyanine +95% wt. purity (Alfa Aesar) was deposited using concentrated H$_2$SO$_4$ (98% wt. Alfa) or Di-Methyl Formamide (99.7% wt. Alfa). Carbon supports; Carbon Monarch 1000 (Cabot) and Ketjen Black EC300J (Akzo Nobel) are referred to as MON and KJB here-after. Synthetic Graphite, <20µm particle size (sigma), was used to assess the effect of treatments during carbon black production on the activity in PBS. A 20% wt. Pt/C benchmark (Alfa Aesar) and the Iron Phthalocyanine were used as received. Stepwise preparation method and abbreviated names are shown in appendix Table A-1. Millipore water with 18 MΩ cm$^{-1}$ resistivity was used to prepare solutions. All chemicals were analytical grade unless otherwise stated. Pyrolysis was performed by placing the catalyst in a ceramic boat (Alfa Aesar) inside an air tight tube (snoop tested). The pyrolysis was preceded by N$_2$ flushing of the chamber for 2hrs (0.5L min$^{-1}$) followed by heating at the target temperature of 800°C for 2 hours, at a heating and cooling ramp rate of 300°C hr$^{-1}$ in a dark room [210]. A preparation chart of all catalysts used in this study is contained within the appendix (Table A-1).

4.1.2 Unsupported iron phthalocyanine films

A fully solvated 1.76 mM solution of FePc in DMF was ultrasonicated in an ice bath and a 10µl aliquot ($\Gamma_{FePc}=6.77\times10^{-8}$ Moles cm$^{-2}$) was applied to a clean RRDE disc. It was allowed to evaporate slowly (40°C) over 1hr. As FePc deposition from a DMF solution onto graphite is instantaneous [70, 275] and yields similar results to deposition from H$_2$SO$_4$ [70] in an anticipated $\alpha$-FePc crystalline form [220]. The resulting electrode was immersed in air saturated PBS, the N$_2$ sparging under electrode rotation, followed by several polarisations to remove adsorbed O$_2$ then the data presented in Figure 5-2 was collected.

For potentiostatic scan analysis (Figure 5-10) an RRDE tip with $\Gamma=4\times10^{-9}$ Moles cm$^{-2}$ of FePc was prepared as above, from a 0.105mM FePc DMF solution. In this instance, no prior polarisation was applied before the presented results.
4.1.3 Binder materials

Binding agents used; PTFE, pH7 Na\(^+\)-Nafion, protonated H\(^+\)-Nafion and a Dabco-Polysulfone based ionomer (QDPSU) were prepared in-house [276]. PTFE (60% wt. emulsion) was purchased from Sigma Aldrich and was diluted (x10) in de-ionised water before use. Neutralised Nafion was prepared from (5% wt.) ionomer (Sigma) received with a H\(^+\) exchange cation; 15mg of NaOH crystals (Merck) was incrementally added to 10ml of the resin under temperature control (<40°C), the resulting Ionomer had a pH of 6.5 and was fully solvated (Na\(^+\) exchange cation). This was done to remove problems of catalyst damage or micro-acidic environments which have previously been reported as a problem [113]. A novel in-house anion exchange material consisting of a Dabco based anion exchange material (Cl\(^-\) exchange anion) side chain grafted onto a Polysulfone backbone was prepared [277], referred to hereafter as QDPSU unless referring to the functional group. Preparation procedure in this study [276] resulted in a loading of 12-15% wt. of ionomer in Di-methyl acetamide. Polymerisation and extrusion of this material successfully produced a membrane in this study.

4.1.4 Ink preparation for thin films

Catalyst inks with high binder contents were prepared. Unless otherwise mentioned, catalyst inks consisted of 10mg of catalyst powder, two drops of DIW, then 340µL of protonated Nafion (Sigma) and 3mL of absolute ethanol. This resulted in binder:catalyst powder wt. of 1.565:1. Inks were ultrasonicated with ZrO\(_2\) balls in a sealed vial in an ice bath until a colloid was formed. An aliquot of 6µl was pipetted onto the clean RRDE GC disk (A=0.2475 cm\(^2\)), completely covering it. The loading was 71µg cm\(^{-2}\) for all catalyst powders. Inks were used within 30 minutes of preparation (exception in section 10.4) to prevent catalyst dissolution, side reactions and irreversible O\(_2\) adducts forming.

For chapter 6 different binder materials were used. A volume (X)µl of unmodified binding agent was added to the 10mg of catalyst powder followed by 3ml of absolute Ethanol (VWR). Volumes of unmodified binding agents (2.1.) were 340µl of H\(^+\)-Nafion (Sigma) or 85µl of QDPSU solvated by DMAC. This resulted in binder to catalyst powder weight ratios of binder:powder=124.5% for QDPSU and 156.5% for Nafion. Inks were ultrasonicated with ZrO\(_2\) balls in a sealed vial placed in an ice bath until a colloid was formed. Resulting inks of pH2 (Nafion) and pH7 (QDPSU).
4.1.5 Deposition of thin films on glassy carbon disc electrode

Surface cleaning of RRDE electrode tip (Pine research instrumentation, model E7R9) was performed prior to each modification of the GC disc. This consisted of abrading the GC and Pt ring surface with 1µm and 15µm diamond micro-crystal emulsion (BASi). After ethanol rinsing the disc was polarised in 1M H₂SO₄ electrolyte (-0.2<E<+1.0V vs Ag|AgCl) and the ring (-0.2<E<+1.2V vs Ag|AgCl), using a separate reference electrode for H₂SO₄. CV was performed until stable i-E response then rinsed with DIW. This electrode is hereafter referred to as the ‘clean RRDE GC disc.’

For the RRDE analysis in chapter 6, $\Gamma_{QDPSU}=88.4 \mu g \ cm^{-2}$ should be present on the disc (assuming even distribution on carbon black), the molecular weight of the repeating unit is 703µg µmol⁻¹, each repeating unit contains 2 Dabco molecules. The resulting density was calculated at 1.12g cm⁻³. [Dabco]=0.251 µmol cm⁻² is expected to be present on the disc.

4.1.6 Air cathode preparation for Gas Diffusion Cell

The Gas Diffusion Cell (GDC) is designed to model an air cathode in the intended electrolyte without overall performance being subject to biofilm variation at the anode. Performance constraints relevant to thicker catalyst layers that cannot be modelled effectively in thin films, such as three-phase contact region and ion/electron diffusion can be quantified in GDC. The air cathode (working electrode–WE) in Figure 4-1 is prepared as follows;

Some of the air cathodes prepared in section 4.3.1 were cut with a circular hole punch (diameter 1cm) for the Gas Diffusion Half Cell. Working electrodes were fixed into the Gas Diffusion cell with silicon gaskets reducing the area in contact with the electrolyte to $A_{WE}=0.2826 \ cm^2$ which was the basis for all calculations. Upon removal of the air cathode only this area is wetted. The approximate catalyst thickness was calculated at 0.01cm (see appendix), irrespective of binder.
Figure 4-1. Gas Diffusion Cell (GDC) used in assessment of air cathodes in isolation of biofilm variance. Pyrex glass body, acrylic ends.

The distance between the luggin tip and the catalyst layer is 2mm. The counter electrode is titanium foil boiled in oxalic acid and platinised with chloroplatinic acid to produce a Pt foil which is then further galvanostatically platinised at higher current density to produce a Pt black surface.

4.1.7 Electrochemical experiments

The RRDE apparatus can be seen in the appendix (Figure A-6) and the basic principle illustrated in figure 2-3. Electrocatalytic activity was evaluated by CV, potentiostatic polarisation and LSV. All electrochemical measurements were taken using an Autolab PGSTAT303 bipotentiostat controlled with GPES software produced by EcoChemie.

RRDE experiments used a custom made single compartment 3-electrode cell with a reference electrode in a luggin capillary with a tip 0.8cm from the disc. The Pt ring potential was maintained at $E=+0.6\,\text{V}$ (see appendix discussion). The counter electrode was a Pt wire spiral, 0.5mm diameter by 200mm (Pine). An electrolyte of 50mM PBS pH7 ($5.5<\kappa<6.2\,\text{mS cm}^{-1}$) was used for all experiments unless otherwise stated. A BASi (RE-5B) Ag|AgCl 3M NaCl reference electrode (+0.208V vs. NHE) was used. All potentials are reported relative to this electrode unless otherwise stated. The reference electrode potential was checked regularly against new electrodes for drift (section 10.8).
Most experiments used potential operating range of \(-0.4<E<0.5\text{V}\), exceptions are noted (eg. Figure 5-3). This potential window includes typical MFC cathode potentials but avoids the onset of \(\text{O}_2\) and \(\text{H}_2\) evolution by \(\text{Pt}\) in PBS and aryl-aryl formation in FePc catalysts and Fe(I)Pc formation.

**For CV and LSV** experiments, electrodes were \(\text{H}_2\text{O}\) wetted to prevent gas bubbles then inserted in air saturated electrolyte and \(\text{OCP}\) recorded. \(\text{N}_2\) sparging (BOC Gases) for 20 minutes was accompanied by electrode rotation to de-aerate the electrolyte and catalyst layer, then a low flow rate blanket \(\text{N}_2\) gas stream over the electrolyte to maintain anoxic conditions. The first polarisation detected redox soluble species \((\omega=800\text{rpm} \ \nu=5\text{mV/s LSV})\). The following de-oxygenated experiments LSV and CV experiments were performed in quiescent electrolyte at varying scan rate.

\(\text{O}_2\) sparging (BOC gases) for 20 minutes and electrode rotation fully saturated the solution and catalyst layer with \(\text{O}_2\). ORR activity was assessed with electrode rotation or in quiescent solution (blanket \(\text{O}_2\)) at \(\nu=5\text{mV/s}\) then \(\nu=1\text{mV/s}\) (tafel analyses). Higher scan rates assessed redox peak characteristics in \(\text{N}_2\) or \(\text{O}_2\). RRDE experiments were then carried out at \(\nu=5\text{mV/s}\) at \(100<\omega<3200\text{rpm}\). The electrolyte was then resparged with \(\text{O}_2\) with electrode rotation for 15 minutes before recording stabilised \(\text{OCP}\) of the aged film.

In all cases mentioned above, 30s of potentiostatic polarisation \((E=0.35\text{V})\) was applied to provide a consistent starting transient response from the step from \(E=0.35\text{V}\) to \(E=0.5\text{V}\). Scans then proceeded in a cathodic direction to \(E=-0.4\text{V}\) unless otherwise stated. Ring polarisation was only used with electrode rotation.

**For the potentiostatic scan** experiments, no polarisation was used prior to data recording. The disc was subject to single potentiostatic potential for 3 minutes and \(J\) recorded. The last five \(J\) values were averaged for the stable current at that potential. This was performed at 10mV intervals from high to low applied potential.

**In the electrochemical stability assessment**, the RRDE tip was immersed and \(\text{N}_2\) sparged as in method 1). Then the disc was subjected to 100 consecutive CV at \(\nu=50\text{mV/s}\) in quiescent solution. The electrolyte then \(\text{O}_2\) sparged (as in method 1) and the procedure repeated in quiescent oxygen saturated electrolyte.
Trumpet plots and Randles-Ševčík analysis, were performed in quiescent solution. The modified electrodes were electrochemically cleaned for 20CV at 100mV/s, data was gathered on the cleaned electrode at $\nu=0.001,0.005,0.01,0.02,0.03,0.05,0.08,0.1,0.2,0.3,0.5,0.8,1,1.5,2,3$ and $5\text{Vs}^{-1}$. In the case of Randles-Ševčík, after the experiment in air saturated solution the solution was de-aerated and the charging current obtained for each of the scan-rates above to produce $i_p$.

4.1.8 Air cathode half-cell

Phosphate diffusion and wetted surface area were analysed by potentiostatic EIS at $E=0.28\text{V}$. Gas diffusion electrodes were inserted and the EIS polarisation started after 2hrs of catalyst layer wetting at $OCP$. A frequency range $100,000\text{Hz} \rightarrow 0.01\text{Hz}$ was used at $10\text{mV}$ sinusoidal potential. A potentiostatic scan (section 4.1.7) was then performed. A Titanium wire current collector was abraded and immersed in acetone between use. The resistance of the oxide layer of Ti was sporadically recorded to check for over-oxidation. The Ti wire was pressed against the catalyst layer.

4.1.9 Determination of kinetic current

Kinetic current was determined at high overpotential by the intercept $j^l$ over $\omega^{-1/2}$ Koutecký-Levich (K-L) plot. At low overpotential $O_2$ concentration polarisation was removed from $\nu=1\text{mV/s}$ LSV data using Eq.2-52 [278]. $O_2$ reduction wave kinetics are reported using Eq.2-52 (see appendix, Figure A-2 for description).

4.1.10 QDPSU redox peak analysis

Dabco redox peaks were treated with the baseline subtraction e.g. Figure 2-18 with Eq.2-86, Eq.2-88 and charge integration being used to evaluate surface coverage. Linear least squares fits were applied in excel.

4.1.11 Koutecký-Levich analysis of film with different binder

Reliance on binder is assessed by K-L examination at high over-potential [279]. The linear fit is applied to the four lowest rotation speeds, 100rpm, 200rpm, 400rpm, and 800rpm to minimise the effect of small kinetic currents as $\omega \rightarrow 3600\text{rpm}$. The slope,
intercept and ‘goodness of fit’ of linear K-L regions are reported by the $R^2$ value obtained using Microsoft Excel 2010 default settings of the functions “slope” “intercept” and “RSQ.”

4.1.12 RRDE methodology

Broadly outlined in section 10.5.3, continual polarisation of the disc was not used to attain steady state [61] as this situation is affected by $\text{H}_2\text{O}_2$ accumulation in the bulk electrolyte, yielding non-linear $I_{D,L}/(I_{D,L}-I_D) \text{ vs } \omega^{-0.5}$ plots. The RRDE tip was centred in the glass cell prior to experimentation.

4.3 Chapter 7 Experimental

4.3.1 Air cathode preparation for MFC

Binding agents were prepared as in section 4.1.3. Catalyst inks of different binding agents were prepared from mixing 40mg of FePc/C, a volume (X)$\mu$l of prepared binding agent (volume adjusted for loading) and 6ml of Iso-propanol. Volumes (X) of prepared binding agents (2.1.) were 38.2$\mu$l of $x10$ diluted PTFE, 86.9$\mu$l of neutralised Na$^+$ Nafion, 86.9$\mu$l of untreated protonated H$^+$ Nafion, and 27.3$\mu$l of QDPSU. Inks were manually stirred to reduce FePc/C agglomeration then ultrasonicated with ZrO$_2$ balls in a sealed vial placed in an ice bath until a colloid was formed. The entire contents of each vial were pipetted onto a circular (19.6cm$^2$) air cathode (Hesen). The commercial carbon paper contains a Gas Diffusion Layer, catalyst was deposited and evaporated in layers (in 1ml portions) on the anterior side to the GDL to produce the best results [266]. The binder to catalyst weight ratios of all cathodes were binder:FePc=20% and binder:FePc+Carbon=10%. Platinum air cathodes were prepared for the MFC using this methodology but Iso-propanol was substituted for Ethanol and omitting the Nafion neutralisation step (used as received). Pt metal loading was 0.5mg cm$^{-2}$ (Alfa Aesar 20%wt. Pt). Nafion neutralisation was used in air cathode preparation for GDC as the process electrolyte was smaller and recording OCP was an experimental factor.
### 4.3.2 MFC polarisations and batch cycle

Anode and cathode potentials were determined using Eq.4-1, as used by Cheng and Logan [41]. This method is highly accurate at open circuit but includes iR-loss. Therefore reference electrode position can be accounted for to produce the actual driving force over the double layer for individual electrode potentials. The iR-loss subtracted electrode potentials are referred to in the text.

\[
E_{an} = E_{cat} - V_{cell} \quad \text{(Eq.4-1)}
\]

The relationship between solution resistance (\(R_s\)) and the separation of the anode to the RE-frit (true \(E_a\)) and cathode to the RE-frit (true \(E_{cat}\)) is outlined in Eq.4-2. \(L_{An-Cat}\) represents the distance of anode and cathode electrode spacing, for illustration of distances \(L_{An-RE}\) and \(L_{Cat-RE}\) see Figure 4-2.

\[
E_{An} = E_a - R_s \left( \frac{L_{An-RE}}{L_{An-Cat}} \right) I_{cell} \quad \text{(Eq.4-2)}
\]

\[
E_{Cat} = E_c - R_s \left( \frac{L_{Cat-RE}}{L_{An-Cat}} \right) I_{cell} \quad \text{(Eq.4-3)}
\]
The distance from the RE-tip to the surface of the Ag wire can be ignored in these equations as negligible current flows in this direction. This modification of electrode potentials has only been done for comparison of air cathodes during MFC polarisation and the Half-cell tests.

Silicone rubber, 1.5mm thick (Cole Palmer) was used to place the air cathodes and Ti wires under compression. The Ti wire was compressed along the diameter of the air cathode. The resulting separation between biofilm and WE surface is 31.75mm. The RE (diameter 5.7mm) was fixed perpendicular to the cell wall using washers. The resulting separations in the direction of current are described in the caption of Figure 4-2.

Electrode potentials were corrected by measuring the RE after every cycle vs. a new electrode in 3M NaCl. The result was a consistent anode potential, $OCP = -0.482V \pm 0.007V$ for all polarisation curves in PBS and PBS amended wastewater.

The electrolyte for all MFC tests was one of 1) artificial wastewater, consisting of 500-5000mg/L CH$_3$COONa + 50mM PBS + trace nutrient (see appendix Table A-7), 2) 50mM Phosphate buffered primary clarifier influent wastewater, or 3) un-supplemented primary clarifier influent wastewater. COD tests were carried out using the Hg and Chromate oxidant method previously described [280, 281].

Steady state polarisation curves are carried out by;

1) Injection of fresh electrolyte (N$_2$ sparged) into the cell.
2) Setting the cell at open circuit and covering the air cathode with parafilm to prevent electrolyte oxygenation, leaving the MFC for a period of 16hrs.
3) Removing parafilm until a maximum plateau in $V_{cell}$ is obtained (typically 5-10 minutes) then fixing a 1MΩ external resistor.
4) Allow cell to stabilise for 20 minutes and record $V_{cell}$ and $E_{cat}$, decrease external resistance with resistor box and allow 20 minutes stabilisation again before recording.
5) Repeat step 4 with external resistance 600kΩ, 300kΩ, 100kΩ, 60kΩ, 30kΩ, 10kΩ, 6kΩ, 3kΩ, 1kΩ, 600Ω, 300Ω, 100Ω.
4.3.3 EIS analysis on thin films

The Frequency Response Analyser programme from Autolab® was utilised. Electrode preparation and solution de-aeration (as in method 1) was used before EIS analysis in quiescent solution. A potentiostatic signal with a 10mV square wave sinusoidal amplitude was applied with perturbation frequencies from 100kHz to 0.1Hz at 90 readings over a logarithmic frequency distribution. The impedance response was measured for several applied potentials, starting at high potential to low potential. This procedure was then repeated in fully O₂ saturated electrolyte.

4.3.4 EIS analysis of Air cathodes

Electrode preparation for GDC half cells were carried out according to the methodology outlined in 4.3.1 and 3.3.3. Experiments on MFC air cathodes were conducted in the cube cells (see appendix) with the biofilm being substituted by a high surface area platinised mesh [282]. The reference electrode (RE-5B, BASi) was placed with the tip c.a. 1mm from the catalyst layer surface. No temperature control was used to avoid convection arising from temperature gradients; convection may impact low frequency measurement. Cells were left un-polarised for 2hrs (GDC) or 40minutes (MFC air cathode) following electrolyte insertion. This approach ensured layer wetting. Both MFC air cathodes and GDC air cathodes were polarised and a 10mV square wave perturbation was applied to obtain an impedance spectra. GDC air cathodes were polarised at \( E=0.28V \) (0.01Hz<\( f <100,000\)Hz), and MFC air cathodes were polarised at a range of potentials in the order \( OCP, 0.4V, 0.2V, 0.15, 0.1, 0.05, 0, -0.05, -0.1, -0.15, -0.2 \) and -0.3V.

4.3.5 Data analysis

Where a linear trend in \(-Z'' \) vs. \( \omega^{-1} \) plots was found capacitance was extracted. Where a linear trend in \( Z \) vs. \( \omega^{-0.5} \) plots was found Eq.2-98 was applied. Wherever possible, the oxidised and reduced couple were amalgamated into a single diffusion co-efficient and molarity presence. This approach was selected to determine this parameter, as opposed the iteration of values in an entire equivalent circuit. The reason being that a minimum number of frequency dependent components should be selected for the equivalent
circuit is advised [283], this leads to large inaccuracies at high frequency as fitting at low frequency produces a larger improvement in $\chi^2$ values.

The diffusion factor ($\sigma$) was obtained from least squares fit of the linear regions of a) the $Z$ vs. $\omega^{-0.5}$ plot, b) the $Z'$ vs. $\omega^{-0.5}$ plot [284] or c) Eq.2-110 or Eq.2-111. Double layer capacity was calculated according to $Y^0$ and $N$ [285] with Nova software, but can be calculated by Eq.2-102 and Eq.2-103. For air cathodes and MEA the manual arc fitting, $R_\infty$ and $R_0$ values are obtained by fitting three points from at $f_p$ and at the LF and HF limits of the arc response using Nova software (ie. Figure A-18).

4.4 Experimental – Chapter 8

4.4.1 Physical parameters of membranes

To extrapolate the resistance from the conductivity of the membranes tested, some literature had to be consulted. AMI-7001 in de-ionised H$_2$O after treating with OH$^-$ and rinsing with DIW was 1.72x10$^{-2}$ S cm$^{-1}$. QPSU (Quaternized Polysulfone) was 0.72x10$^{-2}$ S cm$^{-1}$ [286]. The QDPSU membrane produced an OH$^-$ conductivity of 26mS cm$^{-1}$ at room temperature [276]. A similar calculation was performed on FAA reported by Gu et al [256], a value of 0.017S cm$^{-1}$ in 1M KOH equates to 2.38x10$^{-4}$ $\Omega$ for a membrane of unknown area. In the review by Xu et al [287], the ADP membrane is described as having a high demineralisation activity, while the FAA and FAD membranes are described as base stable and acid dialysis membranes respectively.
Table 4-1. Physical and chemical properties of commercial membranes used.

<table>
<thead>
<tr>
<th>Membrane / Manufacturer</th>
<th>Functional X-change group / Solvated ion</th>
<th>Backbone</th>
<th>Thickness (wet) / (μm)</th>
<th>Reported κ (Ω cm²) / in electrolyte</th>
<th>Working pH</th>
<th>Price / (m²)</th>
<th>Pore Size / (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM F-930 / Fumatech</td>
<td>PerFlu-SO₃⁻ / H⁺</td>
<td>PTFE-Co-polymer</td>
<td>30</td>
<td>&lt;0.2 / 0.5M NaCl</td>
<td>N/A</td>
<td>€833</td>
<td>-</td>
</tr>
<tr>
<td>CMI-7000 / Membranes International</td>
<td>SO₃²⁻ / Na⁺</td>
<td>Gel Polystyrene/ divinyl benzene</td>
<td>450</td>
<td>&lt;30 / 0.5M NaCl</td>
<td>(1-10)</td>
<td>$97</td>
<td>-</td>
</tr>
<tr>
<td>AEM FTAM-A (PA) / Fumatech</td>
<td>Q-Ammonium / Cl⁻</td>
<td>Polyamide (Nylon)</td>
<td>500-600</td>
<td>&lt;8 / 0.5M NaCl</td>
<td>(5-13)</td>
<td>€333</td>
<td>-</td>
</tr>
<tr>
<td>FAA (PEEK) / Fumatech</td>
<td>Q-Ammonium / Cl⁻</td>
<td>PEEK</td>
<td>130-150</td>
<td>&lt;2 / 0.5M NaCl</td>
<td>(1-14)</td>
<td>€583</td>
<td>-</td>
</tr>
<tr>
<td>AMI-7001 / Membranes International</td>
<td>Q-Ammonium / Cl⁻</td>
<td>Gel Polystyrene/ divinyl benzene</td>
<td>450</td>
<td>&lt;40 / 0.5M NaCl</td>
<td>(1-10)</td>
<td>$97</td>
<td>-</td>
</tr>
<tr>
<td>Morgane ADP® / Solvay</td>
<td>Q-Ammonium / Cl⁻</td>
<td>PTFE - Xlink</td>
<td>150</td>
<td>1.5-4.5 / 0.6M NaCl</td>
<td>0.5 / 1M NaOH</td>
<td>(0-10)</td>
<td>-</td>
</tr>
<tr>
<td>QDPSU-PTFE x-link / made in house</td>
<td>Methyl-DABCO⁺ / Cl⁻</td>
<td>Polysulfone + PTFE - Xlink</td>
<td>30</td>
<td>N/A</td>
<td>N/A</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Separator</td>
<td>None / Oil content</td>
<td>High Mol.W. Polyethylene</td>
<td>250°</td>
<td>N/A</td>
<td>0.06 / 1M H₂SO₄</td>
<td>N/A</td>
<td>26°</td>
</tr>
</tbody>
</table>

4.4.2 Method for membrane fixation

Membranes were assessed in three electrolytes (a) 50mM PBS, pH 7.0 (b) 50mM NaHCO₃ (Sigma Aldrich #401676), pH 7.91 (c) 50mM NaCl (VWR #27788.297), pH 7.0. Membranes were rinsed in de-ionised water then soaked in target solutions for at least 12hours with electrolyte replacement until the pH of the spent electrolyte and new electrolyte matched (3-8 washes). Catalyst layers were wetted with target solution prior to fixation of wet membranes to maintain osmolarity. A rigid stainless steel mesh was introduced to prevent bulging and air pockets forming. The SS-mesh produced an non-uniform surface for EIS but aided catalyst layer contact and abated pockets of electrolyte. The MEA half-cell setup is show in Figure 4-2(B). The air cathode was 5.5cm in diameter and the membrane 5.7cm. The preparation procedure is as follows.

1) Cut and rinse membrane with de-ionised water then place in 50mM PBS solution for 1hr.
2) Pipette 50mM PBS solution onto catalyst layer to allow pore ion saturation.
3) Assemble cell with a fresh FePc air cathode. A slightly wider membrane is placed on top of gas diffusion layer and then bound with 304 stainless steel mesh. Holes at top remain unplugged.

---

6 There is no foreseeable reason thermosetting biofoul resistant plastics cannot be used for this application, provided embrittlement was no problem.
4) Fill cell with air Saturated 50mM PBS 2 hours before start of experiment to allow for Phosphate Diffusion through membrane into wetted pores.
5) Rinse and insert RE-5B reference electrode (BASi) into cell at an angle until contact is made with the steel mesh (separation of Ag wire and mesh will mean no short circuit).

4.4.3 Batch performance and polarisation of MFCs with MEA.

Batch performance tests with MEA utilise the same methodology described in section 4.3.4. The cell configuration was Figure 4-2(C) but utilising the cathode MEA assembly of Figure 4-2(B). All batch tests and polarisation curves used artificial wastewater.

4.4.4 EIS evaluation of membrane electrode assembly

1) Record open circuit potential (should range from 0.25 to 0.32V).
2) Start EIS run programme of various applied potentials (OCP, 0.4, 0.2, 0.15, 0.1, 0.05, 0, -0.05, -0.1, -0.15, -0.2, -0.3V). This should use a range of frequencies from 100,000 Hz to 0.01Hz on a logarithmic distribution scale of 103 readings. Sinusoidal amplitude 10mV in either direction [288].

![Diagram of Half Cell assembly used to assess membrane performance with EIS](image)

*Figure 4-3. Diagram of Half Cell assembly used to assess membrane performance with EIS. RE – Reference Electrode. SS-304 Stainless Steel. CL – Catalyst layer. Ti – Titanium.*
Chapter 5. Results - oxygen reduction catalysed by carbon supported iron phthalocyanine at neutral pH
5.1 Introduction

Research with the aim to augment the kinetics of the oxygen reduction reaction in neutral media is quite limited. The majority of MFC cathode work focuses on architecture, and periphery equipment as opposed to catalyst design. In this chapter a first principles electrochemistry study has been applied to a heme-like catalyst. The large reaction overpotential incurred by base-metal or Carbon materials at pH7 [188] and the possibility of medical applications may justify the fundamental research. Precious metal catalysts are believed to constitute 40-50% of complete MFC unit cost [289] and cannot be used.

Iron phthalocyanine (FePc) has been employed in MFCs as a low cost ORR catalyst and showed promising performance [125, 216]. At pH 7 the ORR mechanism is not well studied, particularly for non-Pt catalyst. This chapter attempts to draw parallels from acid and alkali media studies where kinetic analysis in neutral is not present. Two terms have been defined to allow clarity in expression of catalyst activity.

5.2 Catalyst activity

5.2.1 Carbon supports in phosphate buffer

In Figure 5-1, thin films of carbon materials are deposited onto a GC tip to a consistent loading. Relative charging currents are evaluated with CV (C) and (D) whilst steady state conditions (A) and (B) evaluate parameters of ORR.
Modifying GC with synthetic graphite and Nafion produces a similar $i$-$E$ profile to the unmodified electrode, Figure 5-1(D). A reduction in total capacitance ($C_\Sigma$) of 16-25% (Eq.2-16) from unmodified GC shows Nafion to be inert to accumulation of Phosphate anion charge. When modified with carbon black, the GC electrode acts as a electrochemical double-layer capacitor in de-aerated media, with $C_\Sigma$ increasing in the trend Monarch>KJB>HT Monarch. Electrocatalysis of water splitting is not observed and overpotentials of di-oxygen reduction are $\eta>0.4V$ ($E^{0'}=0.605V$).

All carbon materials in Figure 5-1(A) and (B) perform ORR at low potential ($E<-0.05V$) attaining $O_2$ diffusion limitation at c.a. $E=-0.4V$. Divergence in $i$-$E$ response in $O_2$ and $N_2$ electrolytes at high potential ($0.3>E>0V$) is not of a diffusion limitation or kinetic type as a log$_{10}$($i$)$vs E$ relationship is not present and could be attributed to chemisorbed $O_2$ enhancing charging current. At $v=1mV/s$ current in $N_2$ and $O_2$ diverge at; Monarch ($E=0.05V$), HT Monarch ($E=0.28V$), KJB ($E=0.28V$) and Synthetic Graphite ($E=0.28V$).
Monarch 1000 was pyrolised ($T=800^\circ C$) to assess thermal stability of groups that may possess electrocatalytic properties in carbons. This effect must be separated from pyrolysis of carbon supported catalyst in section 5.4.1-5.4.3. Redox activity occurring in Monarch ($E<0.1V$) is attributed to edge plane oxygen [163, 290] and is removed by pyrolysis resulting in $C_\Sigma$ decreases of 70-90%. Szymanski et al report inert atmosphere thermal decomposition of quinone structures at $T=600-980^\circ C$ [291], which would account for a loss of redox activity. Oxidative decomposition of electrocatalysts adsorbed onto these sites may occur with pyrolysis.

5.2.2 Unsupported FePc films in phosphate buffer – electron transfer activity

Unsupported FePc was studied to avoid the influence of binder or reactions such as $k_5$ or $H_2O_2$ production from a carbon substrate. FePc typically forms co-facial polymer ($\pi-\pi$ stacking) when deposited from DMF [70] (section 10.5.1), Figure 5-2 shows the $i-E$ response in de-aerated PBS.

![Figure 5-2](image-url)

Figure 5-2. (A) Scan rate effect on Fe(II)$\rightarrow$Fe(III) peak of FePc adsorbed onto Glassy carbon from FePc-DMF solution to c.a. $\Gamma_{FePc}=6.77x10^{-8}$ Moles cm$^{-2}$. (B) Subtracted charging current ($\nu=20$mV s$^{-1}$). Electrolyte; $N_2$ sat. 50mM PBS, pH 7.0; $\nu=20-500$mV s$^{-1}$
A thin but visible dark purple layer was produced from DMF-FePc solution. In Figure 5-2(B) a non-Gaussian distribution of the Fe(II)→Fe(III) peak is seen in contrast to that predicted from the Gaussian response from the theory of unhindered redox polymers in conductive films [82]. The baseline was applied with the same $i$-$E$ profile as from Glassy Carbon in Figure 5-1(D), equating the magnitude of anodic and cathodic for each peak; $Q_{an} = |Q_{cat}| = 4.08 \times 10^{-5}$ C cm$^{-2}$. Without solvated O$_2$ significant ‘tailing’ in the Fe(III)→Fe(II) reaction are apparent [292, 293] and no clear peak is seen from slow electron transfer through multi-layers. At higher scan rates, the Fe(III) was not fully reduced at $E=-0.4$V. From $Q_{an}$ the redox active FePc is $4.23 \times 10^{-10}$ mol cm$^{-2}$, similar to that from Eq.2-86 $(3.3 \times 10^{-10}$ mol cm$^{-2}$), the slight irregularity caused from the lag in peak symmetry. The value from $Q_{an}$ is a fraction (0.6%) of the overall loading calculated from solution aliquot, showing electronically insulated regions are formed. For Fe(II)↔Fe(III) charge conservation the cathodic redox charge must equal that of the anodic redox charge.

It was shown that reversibility of Fe(II)/Fe(III) redox is low in thick FePc films. The behaviour is analogous to a ‘gated’ periplasmic enzyme [294] in the absence of substrate, where the reduced product insulates electron transfer in one direction, only oxidation is facile.

### 5.2.3 Unsupported FePc films in phosphate buffer – activity in O$_2$

Figure 5-3 displays the $i$-$E$ response from the FePc film in Figure 5-2 when aerated and subjected to CV until a stable response is obtained (3 scans).
Figure 5-3. CV of unsupported FePc film in N\textsubscript{2} or O\textsubscript{2} saturated electrolyte (see Figure 5-2). (B) enlarged 0<E<0.5V region of (A). Electrolyte; 50mM PBS, pH 7.0. \(\omega=0\)rpm. \(\nu=20\text{mV/s}.

In Figure 5-3(B) the aerated FePc film no longer displays an Fe(II)\(\rightarrow\)Fe(III) peak indicating partial O\textsubscript{2} coverage of the electrocatalyst in contact with the solution tends towards 1.0. The process is reversible with de-aeration and cathodic polarisation indicating a strong bond between FePc and O\textsubscript{2} displacing a ligand of H\textsubscript{2}O or Phosphate. Zagal states that the \(E_{\text{ORR}}\) potential is set from the reduction of the Fe(III)Pc-O\textsubscript{2} adduct [32]. As the reaction between FePc and O\textsubscript{2} has occurred at \(E>0.19\text{V}\), this step is not the RDS. Fe(II)Pc must be regenerated prior to O\textsubscript{2} adduct formation, a reaction such as Eq.5-1 (anaerobic), or Eq.5-2 (aerobic)[186] occurs with cathodic polarisation.

\[
\text{Fe(III)Pc} - H_2O + e^{-} \rightarrow \text{Fe(II)Pc} - H_2O \quad \text{(Eq.5-1)}
\]
\[
\text{Fe(III)Pc} - OH^- + e^{-} \rightarrow \text{Fe(II)Pc} + OH^- \quad \text{(Eq.5-2)}
\]

5.2.4 Confocal microscopy of carbon supported FePc films

In Figure 5-4 an Olympus BX-41 confocal microscope was used to view FePc/KJB catalyst (A) and a thin film of FePc/KJB catalyst with binder on a GC tip, prepared as per section 4.1.3-4.1.5.
Figure 5-4. Confocal microscope image of (A) FePcKJB powder and (B)(C)(D) FePcKJB film on GC disc. Binder of (B)(C) Nafion or (D) QDPSU at magnifications of (A) 20x (B) 5x or (C)(D)50x.

The 320μm insulating gap between disc and ring can be seen in Figure 5-4(C). Typically no bare GC was left when applying the film, for the purposes of confocal microscopy the film was not applied all the way to the edge in this instance only. When depositing from colloids (no sedimentation) the film appeared evenly dispersed with a reflective surface from the ionomer applied to excess. Though the GC surface was scarred from repeated polishing the thickness could be seen from confocal microscopy between the edge of the film and the GC support, eg. Figure 5-4(B). The difference between the focal length was 1.5μm. An example is found in Figure A-23 in the appendix.

5.2.5 \textit{O}_2 \textit{diffusion limitation in carbon supported FePc films}

The influence of forced convection on the FePc/KJB Nafion thin film is seen in Figure 5-5. An attempt to determine $C_x$ in the presence of ORR is made through the treatment
described in Figure 2-6. iR-drop and concentration over-potential correction (Eq.2-52) are applied.

![Graph](image)

Figure 5-5. Influence of electrode rotation on CV for FePc/KJB film with Nafion binder. (A) J vs. E response and (B) \((0.5(J_{an}-J_{cat})/u)\) vs. E. iR correction=125Ω (Figure 7-1).

Electrolyte; 50mM PBS, pH7. \(u=20\text{mV/s}\)

Observing Figure 5-5(A) a definite change in \(i-E\) response could be seen c.a. \(E=-0.05\text{V}\) with the current increasing. It is clear that the lack of reversibility in the ORR produces negative \((0.5(J_{an}-J_{cat})/u)\) values which mean that Eq.2-16 does not hold at potentials which ORR is occurring \((E<0.22\text{V})\). At higher potentials \(C_{s}=1.18\times10^{-3}\text{C cm}^{-2}\) can be concluded and is not a function of potential, indicating surface state capacitance only.

At high electrode rotation the limiting current does not form a definitive plateau. If “\(n\)” is consistent (e.g. 3.95) the continual rise in \(J_L\) indicates increased prevalence of surface sites at the electrolyte interface, i.e. at \(E=-0.4\text{V}, \theta_{\text{FePc-X}}>0\), where X hinders \(O_2\) adsorption. The \(\log|J_k|\) vs. \(E\) plot (not shown) of the data in Figure 5-5(A) produced two tafel regions; \(0.17>E>0.09\text{V}\) and \(-0.08>E>-0.18\text{V}\) with the high overpotential tafel region possessing a \(-b_c\) value \(\times1.46\) larger than the \(0.17>E>0.09\text{V}\) region. The high scan-rate \((u=20\text{mV/s})\) means Eq.2-18 or Eq.2-10 cannot be applied. After i-R correction two linear \(J_k\) vs. \(E\) regions \((0.12>E>-0.02\text{V}\) and \(-0.08>E>-0.22\text{V}\) are still present showing resistance in the catalyst layer.
At $\omega=100\text{rpm}$ Figure 5-5(B) is similar to the result obtained by Van der Brink in KOH medium [208] for FePc, with $C_\Sigma$ maxima at 0.82V and 0.38V vs RHE (0.2V and -0.24V Ag|AgCl). In Figure 5-5 maxima in $(0.5(J_{\text{act}}-J_{\text{cat}})/\nu)$ at obtained at $E=0.02\text{V}$ and $E=-0.22\text{V})$. Their explanation was a p-type semiconductor covering the electrode surface. If this is the case it is striking that coverage of an ORR intermediary rather than process anion causes an accumulation of surface capacitance.

5.2.6 **PBS effect of pH buffering and adsorption for FePc activity**

Thin films of FePcKJB Nafion are immersed in mono anionic solutions with solvated O$_2$. Figure 5-6(A) depicts the first cathodic polarisation from $E=0.5\text{V}$, the second CV is shown in Figure 5-6(B).

FePc is a strong ionophore [295], yet O$_2$ adsorption is feasible in the presence of Cl$^-$, H$_2$PO$_4^-$/$\text{HPO}_4^{2-}$, and CH$_3$COO$^-$ ions in Figure 5-6(A). Without prior cathodic polarisation, $E_{\text{ORR}}=0.25$-0.32V for all three electrolytes. The catalyst layer alkalifies and log$_{10}(J)$ vs $E$ plots of the data in Figure 5-6(A) are non-linear until pH stabilisation
occurs. The $i$-$E$ response of scan#2, Figure 5-6(B), is similar to scan# 100 (not shown) indicating local pH stability within the catalyst layer. A cathodic shift in $E_{ORR}$ of 0.22V has occurred in the non-buffering electrolytes. No change in $E_{ORR}$ is seen in Phosphate. This concurs with findings of Kozawa et al [187], who also noted increased reversibility of CV with Phosphate but did not offer an explanation.

5.2.7 Peroxide generation of FePc

Facile H$_2$O$_2$ oxidation can occur at potentials higher than the Fe(II)/Fe(III) redox ($E>E^0$) [67]. The production of H$_2$O$_2$ was evaluated with RRDE, disc modifications of carbon supported and unsupported FePc in Figure 5-7.

Figure 5-7. RRDE study of disc modifications of FePc/MON or FePc film from DMF. (A)(C) $i_R$ vs. $E$ and (B)(D) $i_D$ vs. $E$. (C)(D) show 0.1<$E$<0.25V enlarged x-axis. O$_2$ saturated 50mM PBS, pH 7.0. $\omega$=200rpm. $\nu$=5mV s$^{-1}$

Figure 5-7 shows the $i_R$ vs. $E$ and $i_D$ vs. $E$ plot for 1) FePc/MON (Nafion) 2) FePc film (from DMF). The ring is poised at $E$=0.6V and oxidises H$_2$O$_2$ released from the disc;

- $i_D$ vs. $E$ produces a similar profile for both films yet H$_2$O$_2$ release is significantly decreased with Nafion and carbon support.

- H$_2$O$_2$ is detected at potentials as high as $E$=0.22V in this study (see Figure 5-7).

In the unsupported film, only a few layers of FePc are active (Figure 5-2), yet H$_2$O$_2$ lifetime in the unsupported film is larger than in FePc/MON. Either disproportionation/reduction ($k_d$) accounts for the difference or the reaction on the unsupported film occurs at the electrolyte/film interface. The data was modified with Eq.2-56 to with the treatment described in the text accompanying Figure A-9. In Figure
5-8 the ratio of H$_2$O$_2$ leaving the layer to the ratio of O$_2$ reduced as a function of potential.

Figure 5-8. %H$_2$O$_2$ vs. $E$ profile from RRDE study on FePc films and Pt benchmark. Data manipulated with (Eq.2-56) from LSV. Electrolyte; 50mM PBS, pH 7.0. $\nu$=5mV s$^{-1}$. $\omega$=200rpm.

With FePc/MON and FePc/KJB films the %H$_2$O$_2$ increased at $E$$<$-0.25 V, a feature not present in unsupported FePc films. The result indicates that ORR occurs on the carbon surface at high overpotential, a process that releases H$_2$O$_2$ [296]. All FePc film produce less than 10% H$_2$O$_2$, with and without carbon support. Accuracy decreases with overpotential, as amounts of H$_2$O$_2$ become small. A linear decrease in %H$_2$O$_2$ is seen in unsupported FePc films $E$$<$0V, a process invariant of film thickness. A process that confers linear dependence between H$_2$O$_2$ creation/decomposition kinetics and applied potential is sought. It is plausible the influence of Phosphate surface coverage $\theta_{\text{FePc-X}}$ [84] or mode of O$_2$ adsorption may inhibit 4e$^-$ active sites at high potential. Further studies in mono anionic electrolyte evaluate the former possibility.

The parabolic decrease in %H$_2$O$_2$ attains a minima at $E$=0.125V and is present in the $[i_{\text{R-BG}}]/[i_{\text{D}*CE}]$ vs $E$ plot (not shown) as with the $[i_{\text{R-BG}}]/[i_{\text{ORR}*CE}]$ vs $E$ plot (Figure 5-8), indicating a change in the product of electrocatalysis as opposed to the influence of a redox of the type in Figure 5-2. The influence of film thickness is negligible at $E$$<$0V and significant at $E$$>$0V. As $k_3$$>$0 with FePc catalysed ORR [67], movement of
the reaction site from electrode/film interface ($E>0$V) to film/electrolyte interface ($E<0$V) is present, in agreement with the observation of van der Brink et al [208] of a decrease in $i_k$ with increasing film thickness. An analysis capable of discriminating the successive $k_2 \rightarrow k_3$ from the direct $k_1$ mechanism is required following the detection of significant $\text{H}_2\text{O}_2$.

5.3 Catalyst kinetics

5.3.1 Kinetic rate of ORR quinone activity in the support

Thin films of HT Monarch and Monarch (as received) were subjected to potentiostatic steps applied at 10mV intervals (3min) in a cathodic direction, Figure 5-9. At the end of the 3 min transient decay a stable current is produced. The aim is to create steady state condition for measuring small ORR current at low $\eta$.

![Figure 5-9. Potentiostatic sweep of Monarch 1000, used as received or with pyrolysis prior to thin film modification of GC tip. Catalyst loading 71µg cm$^{-2}$, Nafion loading 111µg cm$^{-2}$. Electrolyte; O$_2$ sat. 50mM PBS, pH 7.0](image)

The oxygen reduction current obeys the tafel equation when measured at steady state in Figure 5-9. Large values, $b_c=-360$ mV dec$^{-1}$ for Monarch and $b_c=-250$ mV dec$^{-1}$ for HT-Monarch indicate a complex reaction mechanism and sluggish kinetics. The high values are consistent with low overall values for ‘n’ and an early limiting step in the reaction.
The $b_c$ values for oxygen reduction on carbon at low potential ($E$<0.05V) are common to all graphitic materials [297] and are not depicted in Figure 5-9. This study highlights the need to separate multi-component exchange currents [298] from carbon supported catalysts to that of pristine carbon. For the thesis duration, $J_0$ is reported by extrapolating the ORR wave catalysed by the supported catalyst.

### 5.3.2 Unsupported FePc

Thin films of unsupported FePc or Pt/C Nafion are subjected to the same potentiostatic step experiment applied as in Figure 5-9. The result is shown in Figure 5-10.

![Figure 5-10. Potentiostatic scan of a) 20% wt. Pt/C (Nafion) or b) unsupported FePc. Loading of a) 14.2μg Pt cm$^{-2}$ or b) $\Gamma=4\times10^{-9}$ Moles cm$^{-2}$ FePc. iR-correction. Acid or alkali mechanism tafel slope ($b_c$) and OCP are marked. Electrolyte; O$_2$ saturated 50mM PBS, pH 7.0.](image)

The Pt/C benchmark was used to verify the validity of this method. Log$_{10}[I_i]$ vs. $E$ plots produced consistent Pt/C tafel slopes ($b_c$=-62.5mV dec$^{-1}$) to that recorded at $\nu=1$mV/s ($b_c$=-63.2mV dec$^{-1}$) in Table 5-1, verifying steady state in both experiments and consistent with literature [169] (PBS, pH7).

The result from FePc was obtained prior to previous polarisation to observe film reordering if present [208]. Protons as a substrate may be used low $\eta$; the $|b_c|=73$mV dec$^{-1}$ at 0.26$E$>0.22V is more typical of FePc O$_2$ catalysis in acid media [205, 210] and was
not observed after the first cathodic polarisation, indicating re-ordering may occur. The remaining tafel region at $E<0.2\text{V}$ ($|b_c|=37.4\text{mV dec}^{-1}$) produces the majority of current. Extrapolation to $OCP=0.25\text{V}$ yields $J_0=1.5\times10^{-8} \text{A cm}^{-2}$. The comparability with carbon deposited or vacuum deposited films in pH 6.7 PBS [182, 191, 192]; $|b_c|=37-38\text{mV dec}^{-1}$, is in good accord with Figure 5-10. The results differ from the result for monomeric FePc [191] ($|b_c|=60\text{mV dec}^{-1}$).

Savy et al noted OH$^-$ product from ORR in Phosphate media [192], predicting local pH swings, this relevance of this aspect to engineering is addressed in further sections of this thesis. Reviewing Table 3-2, the alkali mechanism pathway is prevalent in highly buffered neutral media, and is studied in detail herein, predicting rapid catholyte alkalination.

Eq.2-19 predicts $|b_c|=38.8\text{mV dec}^{-1}$ if $\beta_c=0.5$ [299] with the RDS occurring on the 2$^{\text{nd}}$ electron transfer ($n_c=1$). In Figure 5-10, $(n_c+\beta_c n_j)=1.55$ shows a close fit and requires $\alpha$ to be determined independently. This scenario was postulated by Zagal et al [193].

A film identical to that in Figure 5-3 was applied examined by CV in air saturated electrolyte to apply the Randles-Ševčík criteria in Eq.2-36. The raw data is plotted in Figure 5-11(A) whilst (B) contains the $I_p$ vs $\nu^{0.5}$ data.
Figure 5-11. (A) i-E data of ORR on unsupported FePc films as a function of scan rate. (B) Randles-Ševčík plot of peak current ($i_p$) vs $\nu^{0.5}$ with two identical films from FePc-DMF solution. Electrolyte; Air saturated 50mM PBS, pH 7.0.

Cathodic limit extension would permit a scan rate range to be evaluated but generates Fe(I)Pc [186] with unknown effect on reversibility and unfeasible in MFC operation. The slope of $-7.99 \times 10^{-5}$ A s$^{0.5}$ V$^{-0.5}$ is relatively low for ORR in this media [300]. Treating with physical data in Table A-2 and $C_{O_2}$ measurements from Table A-3 in Eq.2-36, yields $n_c + \alpha_n$ is 0.048, an unfeasibly low response (0.2<$\alpha$<0.8). Reviewing the terms of Eq.2-36 it would appear that an additional film resistance from $O_2$ diffusion to the active site is present, as the use of Eq.2-39 produces $n_c + \alpha_n$=1.51. If the reaction site is located at the disc/film interface this discrepancy could be accounted for provided $O_2$ percolation through the film is slow. Without the presence of $O_2$, electron percolation was slow (Figure 5-2) and no cathodic peak is seen rendering trumpet plot analysis on the TFE unfeasible. A plot of $E_{pc}$ vs $\log_{10}(\nu)$ of a similar film in air (Figure A-5) produced a gradient of $-0.03629 V/log_{10}(Vs^{-1})$ generating a more plausible $\alpha$=0.413, more consistent with the $n_c$=1, $\alpha_n$=0.51 of the tafel plot. Evaluation in thinner or carbon supported films is required.
5.3.3 Kinetic performance of carbon supported FePc/Nafion films

A plot of $E_{pc}$ vs $\log_{10}(\nu)$ of the Fe(II)/(III) reaction in an FePc/KJB Nafion film is shown in Figure 5-12.

In de-aerated PBS the peak potentials produced a linear $E_p$ vs $\log_{10}(\nu)$ response in the 0.1-1V s$^{-1}$ range. Using Eq.2-89 the anodic slope and cathodic responses produce $2.3RT/(1-\alpha)nF$ and $2.3RT/\alpha nF$ respectively, resolving to $\alpha=0.44\pm0.03$ for the de-aerated electron transfer. A low error margin is attached as the value $\alpha$ and $(1-\alpha)$ summate to 1.053. Where the extrapolated line meets $E_p-E^0=0V$, Eq.2-89 can be resolved at the corresponding scan rates, $\nu_{an}=0.013857$ V s$^{-1}$ and $\nu_{ca}=0.0811$ V s$^{-1}$ to produce an electron exchange value $k_E$ at $E^0$, the average of the oxidation and reduction scan is $k_E=0.9$s$^{-1}$ with and error margin $\pm0.55$. Using Eq.2-90 and $\delta_{film}=1.5\mu m$ the heterogeneous rate of electron exchange is $k_{E,h}=0.000135cm$ s$^{-1}$, a non-limiting process compared to typical $k_{app}$ [67]. This illustrates the importance of the carbon support. With the introduction of $O_2$, two cathodic peaks are present (Figure 5-13), one associated with ORR visible at low $\nu$. In porous films the surface coverage of $O_2$ does not appear to be complete (eg. Figure 5-6), the Fe(II)/Fe(III) process is still present at high $\nu$ (ie. Eq.5-1 or with phosphate ligand). Comparison of Eq.2-36 and Eq.2-86 predict $I_p \propto \sqrt{\nu}$ and $I_p \propto \nu$ for aerated faradic and de-aerated surface reactions respectively. Hence the ORR reaction is obscured by the Fe(II)/Fe(III) surface reaction at high scan-rate.

Figure 5-12. Trumpet plot of Fe(II)$\leftrightarrow$Fe(III) redox of FePcKJB Na-Nafion thin film

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7 Valid for $E_{pc}-E_{pa}>0.2V$.
8 $E^0$ estimated from $E_{pa}-E_{pc}$ at 0.001V s$^{-1}$, near as possible to steady state.
Figure 5-13. Trumpet plot same FePcKJB Nafion electrode in the presence of O₂. Two $E_{pc}$ are present; ORR (orange) and Fe(III)$\rightarrow$Fe(II) (red).

Figure 5-13 shows that the gradient of the anodic peak (no bound O₂) has possibly decreased, though $\alpha=0.366\pm0.1$ (from $\alpha=0.44$ in N₂). This value is obtained from $(1-\alpha)$ in the anodic slope. In air, the $R^2$ co-efficients are lower for all peaks compared to N₂, a larger error margin is attached. $E_p$ is discernable from nearly amalgamated peaks from points of inflexion in the $i-E$ response at $\nu=0.15$ V s⁻¹, the linear trend in the $E_p$ vs log₁₀($\nu$) is maintained with this method. The cathodic ORR peak in Figure 5-13 produces a gradient of -0.02016 V/log₁₀($\nu$), Eq.2-30 is non-applicable unless the 1ˢᵗ ET is rate determining [35]. With the addition of O₂, a complex situation occurs on the Fe(III)$\rightarrow$Fe(II) peak. The gradient decreases relative to the N₂ data (Figure 5-12), though for conservation of the anodic charge the reaction is predicted to be the same. Applying the predicted $n=1$ variable produces an unfeasibly high transfer co-efficient. Analysis on the anodic slope with Eq.2-89 produces $k_E=1.7$ s⁻¹ (0.000425 cm s⁻¹), a minor source of rate constriction.

Using the LSV method outlined for method 1, a tabulated summary of all catalysts applied to a GC as thin films with nafion binder thin film electrode catalysts was compiled in Table 5-1. Catalyst preparation and names, Table A-1.
Table 5-1. Various catalyst ORR activity in thin films-Nafion binder. Total powder loading; 71μg cm$^{-2}$, Nafion ionomer; 111μg cm$^{-2}$ on GC discs. Tafel and $J_0$ reported from $\nu=1$ mV/s LSV data, $\omega=0$ rpm. Electrolyte; 50mM PBS, pH7.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tafel Slope (αν2 corrected)</th>
<th>$J_0$</th>
<th>$E_{onset}$</th>
<th>$E_{RAS}$</th>
<th>$J_{IR}$ at -0.1V</th>
<th>$<a href="mailto:E@0.4A">E@0.4A</a>$ m$^{-2}$</th>
<th>Initial OCP</th>
<th>OCP</th>
<th>$O_2$</th>
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<td></td>
<td>Process</td>
<td>mV dec$^{-1}$</td>
<td>A cm$^{-2}$</td>
<td>mV</td>
<td>$10^{-13}$ site cm$^{-2}$</td>
<td>mV</td>
<td>A cm$^{-2}$</td>
<td>mV</td>
<td>mV</td>
</tr>
<tr>
<td>Composites</td>
<td>MnO$_x$, red.(N$_2$)</td>
<td>-163</td>
<td>-</td>
<td>419</td>
<td>27.0</td>
<td>-7.89E-05</td>
<td>165</td>
<td>430</td>
<td>270</td>
</tr>
<tr>
<td>FePcMnO$_x$/MON</td>
<td>ORR(Mn-FePc)</td>
<td>-35.9</td>
<td>1.1E-07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FePcMnO$_x$/KJB</td>
<td>MnO$_x$, red.(N$_2$)</td>
<td>-58.2</td>
<td>2.0E-07</td>
<td>414</td>
<td>38.8</td>
<td>-1.41E-04</td>
<td>106</td>
<td>460</td>
<td>260</td>
</tr>
<tr>
<td>(Mn$^{2+}$+KMnO$_4$)</td>
<td>ORR(Mn-FePc)</td>
<td>-39.0</td>
<td>2.7E-07</td>
<td>386</td>
<td>4.4</td>
<td>-1.56E-04</td>
<td>156</td>
<td>460</td>
<td>260</td>
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<tr>
<td>TiO$_x$FePc/MON</td>
<td>OR(Ti-FePc)</td>
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<td>21.0</td>
<td>-1.64E-04</td>
<td>150</td>
<td>310</td>
<td>290</td>
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<tr>
<td>Supported FePc</td>
<td>FePc/MON</td>
<td>ORR(FePc)</td>
<td>-33.4</td>
<td>5.1E-08</td>
<td>407</td>
<td>38.8</td>
<td>-1.60E-04</td>
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<td>320</td>
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<tr>
<td>FePc/KJB</td>
<td>ORR(FePc)</td>
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<td>2.0E-07</td>
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<td>223.0</td>
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<td>Pyrolysed FePc</td>
<td>FePc/MON pyr</td>
<td>ORR(FeNx)</td>
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<td>2.4E-07</td>
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<td>-</td>
<td>-1.51E-04</td>
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<td>FePc/KJB pyr</td>
<td>ORR(FeNx)</td>
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<td>3.7</td>
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<td>Supported MeOx</td>
<td>MnOx/MON</td>
<td>MnO$_x$, red.(N$_2$)</td>
<td>-125</td>
<td>-</td>
<td>400</td>
<td>-</td>
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<td>(Mn-C)</td>
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<tr>
<td>TiO$_2$/MON</td>
<td>ORR(C-TiO$_2$)</td>
<td>-89.8</td>
<td>-</td>
<td>379</td>
<td>-</td>
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<td>-186</td>
<td>190</td>
<td>-</td>
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<tr>
<td>TiO$_2$/MON pyr</td>
<td>ORR(C-TiO$_2$)</td>
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<td>-</td>
<td>-7.86E-06</td>
<td>-199</td>
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<td>120</td>
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<td>Carbon Supports</td>
<td>Synthetic Graphite</td>
<td>2e$^-$ ORR</td>
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<td>3.8E-08</td>
<td>323</td>
<td>-</td>
<td>-7.33E-07</td>
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<td>160</td>
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<td>KJB</td>
<td>2e$^-$ ORR</td>
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<td>n/a</td>
<td>329</td>
<td>-</td>
<td>-4.26E-06</td>
<td>-230</td>
<td>160</td>
<td>-</td>
</tr>
<tr>
<td>Monarch</td>
<td>2e$^-$ ORR</td>
<td>-79.4</td>
<td>2.3E-07</td>
<td>400</td>
<td>-</td>
<td>-1.25E-05</td>
<td>-145</td>
<td>260</td>
<td>50</td>
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<tr>
<td>Monarch HT</td>
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<td>-141.7</td>
<td>1.3E-07</td>
<td>326</td>
<td>-</td>
<td>-1.00E-05</td>
<td>-197</td>
<td>300</td>
<td>190</td>
</tr>
<tr>
<td>Pt/C</td>
<td>First Tafel</td>
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<td>2.2E-06</td>
<td>414</td>
<td>-</td>
<td>-2.31E-04</td>
<td>307</td>
<td>390</td>
<td>400</td>
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<td>Second Tafel</td>
<td>-110.4</td>
<td>8.7E-06</td>
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</tbody>
</table>

An example of tafel slopes determination is seen in Figure 5-14. Tafel slopes for carbon materials occurred in the potential range (-0.1<E<0.05V). Redox active site (RAS) for Fe(II)Pc/Fe(III)Pc is obtained as Figure 2-18 ($\nu=20$ mV/s). “$J_{ORR}@E=-0.1V$” represents current obtained in $\nu=1$ mV/s LSV in N$_2$ subtracted from the $\nu=1$ mV/s LSV in O$_2$ at a potential of $E=-0.1V$. “$E@0.4A$ m$^{-2}$” represents the potential at $J=0.4A$ m$^{-2}$. $J_0$ is obtained by extrapolating the tafel slope to OCP as in Figure 5-14.

Data obtained under N$_2$ is shown in green, ORR tafel response in blue for carbon and black for FePc/KJB. The dash black line is OCP for the FePc/KJB electrode.
The OCP of iron porphyrin based catalysts is controlled by the FePc-O₂/4OH⁻ couple [192]. If this premise holds for carbon supported FePc films, extrapolating the tafel slope of ORR to OCP produces $J_0$ of the RDS. Comparing Figure 5-10 to Figure 5-14 shows a 13 fold increase in geometric exchange current related to this mechanism, the average electroactive FePc, $\Gamma_{FePc}=3.9\times10^{-9}$ Moles cm⁻² (Table A-8) resulting in the increase in $J_0$ over the unsupported film. The tafel slope is present at $E<0.22$V and shows improved kinetics, $|b_c|=33.4$ to $35.7$ mV dec⁻¹, over the unsupported film with a small influence of type of carbon support.

The KJB film produced tafel behaviour at $E>-0.05$V. A comparison between $E_{onset}$ (KJB; 0.329V. Monarch; 0.4V) and OCP (0.05 to 0.019V of all carbon materials) indicates $E_{onset}$ is a poor method of validating ORR activity in porous films. Small discrepancies between N₂ and O₂ for KJB may be due to additional surface charges nucleating around chemisorbed O₂ increasing $C_\Sigma$.

Key observations on other carbon and FePc/C catalysts in Table 5-1;

- Tafel slopes of FePc materials in Table 5-1 are among the best recorded when compared to literature values (Table 3-2).⁹

- For carbon black, tafel behaviour $120>|b_c|>90$ mV dec⁻¹ is within value range reported in literature [214], the increase consistent with HNO₃ treatment [301].

⁹ It should be stated that use of O₂ concentration and iR correction in cited studies is unknown.
Combining exchange current from the high and low potential mechanism [298] on Pt produced $J_0 = 1.1 \times 10^{-5}$ A cm$^{-2}$.

5.3.4 FePc – influence of rotation on kinetic current

Electrode rotation was used to examine the influence of substrate diffusion limitation on catalytic turnover. The result for thin films of FePc deposited from DMF (a) and FePc/KJB films with Nafion binder (b) are depicted in Figure 5-15.

Electrode rotation inhibited current at potentials of kinetic control ($E > 0.05$V) in FePc films in Figure 5-15(A) and (B). The simultaneous occurrence of catalyst de-activation made application of limiting current scenarios [33, 59, 60, 77] unfeasible. In 1e$^-$ ET kinetic control situations a $J \neq f(\omega)$ could be expected [35]. The Koutecký-Levich (K-L) plot for Carbon and Pt/C layers indicated a 1$^{st}$ order reaction with O$_2$ over the majority of the potential range. The plot could not be made for FePc indicating a significant chemical step in PBS media. Homolysis of adsorbed peroxide could feasibly be cleaved.

Figure 5-15. Influence of $\omega$ on kinetic control region of $J$ vs $E$ plot in thin films; (a) unsupported FePc ($Γ = 4 \times 10^{-9}$ Moles cm$^{-2}$) or (b) FePc/KJB Nafion, inset (c) enlarging the 0$<E<0.25$V region of (b). $v =$5mV/s. Electrolyte; 50mM PBS, pH7.
by OH$_{(aq)}$ as opposed to further electroreduction. Rapid agitation may neutralise alkalination and explain the rotation dependent chemical step in Figure 5-15(A), further evidence is required. This response is briefly observed by Mamuru et al for FePc-Multiwalled Carbon Nanotubes [89] and immobilised Iron Porphyrins and cytochrome C in PBS [302].

The data in Figure 5-15(A) and (B) produced linear tafel slopes at all rotation (not shown). Inhibition of $|b_c|$ was greater for FePc than FePc/Nafion. Reduction in $|b_c|$ would exclude the possibility of active site blocking [70], this blocking phenomenon causes tafel plots to shift down the current axis, maintaining a constant gradient. A more detailed mass balance is required to test the hypothesis of an important chemical step.

5.3.5 Wroblowa analysis of intermediates and heterogeneous rate constants

This analysis aims to differentiate between direct 4e$^-$ reduction to H$_2$O ($k_1$) and sequential 2e$^-$ reduction to H$_2$O$_2$ ($k_2$) followed by 2e$^-$ reduction to H$_2$O ($k_3$). Mechanism evaluation at $E$=c.a. 0.2V is the primary aim. Unsupported FePc film was used as $k_5$ is negligible; no other species than FePc are present in the film. In a carbon supported film $k_5$ and $k_3$ occurring simultaneously.

In Figure A-11 the slope of the $I_{D,1}/(I_{D,1}-I_D)$ data can be converted to $m^2 s^{-1}$ ($k_{app}$) using Eq.2-84, multiplying the slope (Figure 5-16) by $Z$=8.68x10$^{-6}$. The linearity of this graph indicates H$_2$O$_2$ flux back from the solution ($k_{D,H2O2,b}$) is negligibly small over the experiment timescale [74] and $k_4$ is small [44]. Unfortunately the intercept≠1 in all cases, so no simple assumptions about $k_1+k_2$ can be made [61, 72, 303].
The $CE^*i_D/i_R$ vs. $\omega^{-1/2}$ plot for unsupported FePc is presented in Figure 5-17 ($\Gamma_{FePc}=4\times10^{-9}$ Moles cm$^{-2}$). The goodness of fit of the 200<$\omega<$1000rpm data is plotted in Figure 5-17 as a function of potential in Figure 5-18. The data was modified to $CE^*i_D/i_R$ vs. $k_{D,H_2O_2}^{-1}$ plot using Eq.2-72 and the corresponding slope vs. intercept ($S$ vs $J$) is represented in Figure 5-17. Each approach or correction for $CE$ and the effect on the general shape of the $S$ vs. $J$ plot is located in the appendix.

Figure 5-17. $CE^*i_D/i_R$ vs $\omega^{-0.5}$ plot for unsupported FePc film ($\Gamma=4\times10^{-9}$ Moles cm$^{-2}$). Split into several graphs of similar Y-axis range, least squares best fit lines applied, $CE=0.37\%$ for all $\omega$. $\nu=5$mV/s. Electrolyte; 50mM PBS, pH7.

The plots of $CE^*i_D/i_R$ vs $\omega^{-0.5}$ are linear in all instances. This indicates a) all disc reactions are first order [74], and b) the only reaction occurring on the ring is H$_2$O$_2$ oxidation [74].
Figure 5-18. Intercept and $R^2$ fit of data from the $CE^*i_D/i_R$ over $\omega^{1/2}$ plot of the film in Figure 5-17.

The $R^2$ value of the fit displayed two regions of high correlation; 0.05<$E<$0.18V and -0.4<$E<$-0.18V. According to the derivation these regions correspond to kinetic control and diffusion control respectively. The highest $R^2$ values were obtained using $CE$ vs $\omega$ correction from Glassy Carbon for the unsupported Iron Phthalocyanine. For catalysts films such as FePc/MON the $CE$ vs $\omega$ correction from a film of synthetic graphite (Figure A-8) produced linear trends. The reason could be interpreted as physical unevenness of carbon film surfaces and Nafion coatings affecting distribution of H$_2$O$_2$ to the ring.

Figure 5-18, the FePc film;

- The intercept value is potential dependent, increasing above unity with increasing potential, passing through unity at $E$=0.19V.
- The intercept $J$ is relatively constant from 0.2>$E$>0.14V, implying a constant $k_1/k_2$ ratio.

In Figure 5-19 the $CE^*i_D/i_R$ vs $\hat{\omega}^{-0.5}$ slope values are modified from rad$^{0.5}$ s$^{-0.5}$ to m s$^{-1}$ using Eq.2-62 or the analogous Eq.2-72 and data presented as an $S$ vs $C$ plot for the unsupported film.
Linear regions in this plot are seldom acquired [44], when they are \( k_1, k_2, k_6 \) and \( k_3/k_5 \) are usually acquirable [44]. A minimum \( C \) value of unity should be observed [42], the intercept approaches \(<1\) for regions of high correlation \((R^2>0.99)\) at \( 0.18>E>0.12 \). Regardless of whether the Appleby or Wroblowa criteria is applied, Eq.2-71 is applicable for linear \( S \) vs \( J \) regions. Though negative rate constants can sometimes be obtained [44], the scenario where \( k_1=\text{c.a.}-0.3k_2 \) at low overpotential is an unlikely scenario considering \( \text{H}_2\text{O}_2 \) oxidation is not possible \( E<E^{0'}_{\text{Fe(II)/Fe(III)}} \) for Iron Phthalocyanine. With ring current background subtraction (Figure A-9) an intercept value \( J'=1 \) was obtained, hence this result is treated as \( k_1 \ll k_2 \). This interpretation is consistent with Figure 5-8 where \( \text{H}_2\text{O}_2 \) release is highest in this potential region.

Two linear regions at high potential were observed and one at low potential. The high potential regions are 1) \( 0.21>E>0.18\text{V} \) and 2) \( 0.09>E>0.04\text{V} \). Interestingly, the gradient of \( S \) vs. \( J \) (m s\(^{-1}\)) for these regions are -1.54x10\(^{-4}\) m s\(^{-1}\) (0.18>E>0.15V) and -1.542x10\(^{-5}\) m s\(^{-1}\) (0.1>E>0.06V), one order of magnitude lower. The negative gradient cannot be explained. It did not occur in any other carbon catalysts, only Pt.

Potentials where gradient \( S \rightarrow 0 \) such as \( E=0\text{V} \) show that \( k_3+k_4 \) is insignificant in relation to \( k_{5f} \). If it can be shown that \( k_{5f} \) is negligible (ie. \( k_1 \gg k_2 \)) then it can also be proved disproportionation is negligible. As \((S \neq 0)\) it must be concluded \( \text{H}_2\text{O}_2 \) is capable of adsorption onto FePc as anticipated and an adsorption equilibrium described by

---

Figure 5-19. \( S \) vs \( J \) plot of unsupported FePc film. Film \( \Gamma=4\times10^{-9} \text{ Moles cm}^{-2} \). Dash black line extrapolates to \( J \) axis at \( J=J' \). (A) low \( \eta \) region (B) \( 0.24>E>-0.03\text{V} \) region.
Wroblowa must be considered. This conclusion supports the body of work in H$_2$O$_2$ electrolyte described by many authors [187, 208].

The high overpotential $J'$ intercept is 9.8 (0.09>E>0.04V), producing $k_1$=+4.4$k_2$. The second linear region (0.04<E<0.9V) is associated with the direct 3e$^-$ electrochemical reduction of FePc-O$_2^-$ to OH$^-$ as postulated by Savy [192]. Behret et al [206] studied Iron Napthalocyanine films in 1M KOH, producing $k_1/k_2$=75 for polymeric Fe(III) and $k_1/k_2$=8 for polymeric Fe(II) at similar $\eta$ to this study. Suggesting the thin fully reduced underlayers catalyse an electron “conveyor belt” that would be blocked with Fe(III)Pc and facilitates $k_2$.

Figure 5-20 displays log$_{10}(S \ J^1)$ vs $E$ plot to obtain H$_2$O$_2$ oxidation/reduction data. Depending on whether the Appleby or Wroblowa criteria reflect the system, Eq.2-81 or 2-68 reflects the linear (tafel) regions of the residual plot. Numerous solutions are applied depending on which method of $CE$ vs $\omega$ correction is used (see appendix 10.5.3.), the method producing the highest $R^2$ fit (Figure 5-18) is shown with orange dots.

![Figure 5-20. S/J vs. E plot of the data from Figure 5-19. CE* i_D/i_R vs. k_D,H2O2$^{-1}$ data treated with different means (see key). Kinetic rate of intermediary reactions separated from ORR tafel plot. Tafel regions indicate dominance of one term in the Eq.2-81.](image)

The $S/J$ vs. $E$ plot in Figure 5-20 reaches a minima at $E$=-0.05V. The complex behaviour could not be described by Eq.2-70, as $k_I\neq0$. The tafel like behaviour describes...
the fate of H₂O₂ on the FePc surface, becoming apparent when one of the rate constants in Eq.2-81 dominates. Conversely this process reaches a rate maxima at $E=0.16\text{V}$. Reconciling the fact that $k_d \neq f(E)$ this would suggest that $k_d$ is negligible at all potentials, otherwise the tafel behaviour in Figure 5-19 would not be seen.

The $S/J$ vs $E$ plot is potential dependent at all potentials, inputting the reasoning $k_d$ is negligible. In which case, the $S/J$ value is equal to $k_3+k_5/k_1k_5b$ in Appleby’s method. Clearly, $k_3$ increases with cathodic $|\eta|$, resulting in a plot inverse to Figure 5-20. Another tafel dependent rate constant is missing from the balance. $k_{E,h}$ from Figure 5-13 could not be determined for unsupported films but neither Wroblowa or Appleby’s theorem account for the effect of polarisation on electron propagation in the film. $k_3$ shows that this term dominates the equation and $k_{5b}$ and $k_{5f}$ relatively consistent in the $E>0\text{V}$ region. The assumption $2k_1/k_2=0$ cannot be used to reduce Eq.2-68 or Eq.2-81.

Other Materials..
- The $S/J$ maxima at $E=0.16\text{V}$ is also seen in FePc/MON (not shown), though the lower minima is convoluted from disproportionation.
- For FePc/MON two linear $S$ vs $C$ regions 1) $(0.2>E>0.17\text{V})$ at $J'=1.2$ ($k_1=0.1k_2$) and 2) $(0.1>E>0.04\text{V})$ producing $J'=15.7(k_1=7.35k_2)$.
- For Pt/C, the $S$ vs. $J$ intercept ($J'$) produced a large linear range of $-0.15>E>-0.4\text{V}$ with $J'=69.8$ ($k_1=34.4k_2$). This suggests ~3% of ORR on Pt/C proceeds through $k_2$, cross-referencing with Figure 5-8 shows 0.9% H₂O₂ is detected at the ring, suggesting the majority is further reduced to H₂O.

In terms of $k_1$ and $k_2$ the reaction regime is essentially the same on supported and unsupported carbon. For the low overpotential ORR wave the release of H₂O₂ is controlled by adsorption strength and duration. As H₂O₂ is degenerative to the catalyst, potentials greater than $E=+0.1\text{V}$ should be avoided for MFC operation of FePc and FeN₅ cathodes.

### 5.3.6 The rate limiting step

Each scheme is dependent on FePc preparation method. Anticipated tafel slopes are reported for cases of $4e^-$ reduction for a value of $-\beta_c=0.5$ using Eq.2-19. The scheme
proposed by Zagal and Savy both depend on electroreduction of Fe(III)Pc-\(O_2^-\). The scheme by Savy represents the direct 4e\(^-\) route \(k_1\).

\[
\begin{align*}
O_2^-_{(ads)} + 2H_2O + 3e^- &\rightarrow 4OH^- & \text{Savy et al [192]} \quad \text{(Expected } |b_c| = 23.3 \text{mV dec}^{-1}\text{)} \quad \text{(Eq.5-3)} \\
HO_2^-_{(ads)} + H_2O &\rightarrow 2•OH + OH^- & \text{Appleby [202]} \quad \text{(Expected } |b_c| = 29 \text{mV dec}^{-1}\text{)} \quad \text{(Eq.5-4)} \\
\text{Fe(III)Pc-}O_2^- &\rightarrow \text{intermediates} & \text{Zagal [186]} \quad \text{(Expected } |b_c| = 38.8 \text{mV dec}^{-1}\text{)} \quad \text{(Eq.5-5)}
\end{align*}
\]

A small range in FePc tafel slope values (-37.4 to -25.4mV dec\(^{-1}\)) shows dependence on support and binder (chapter 6). Improved tafel slopes with the hydrophilic anion exchange binder is accompanied by a larger \%H\textsubscript{2}O\textsubscript{2} in supported catalyst. It is known that the symmetry factor is indirectly affected by binder [304]. Appleby et al propose a chemical step where electron insertion is not the RDS so symmetry factor is irrelevant, meaning a fixed tafel gradient.

In the scheme proposed by Appleby, •OH is produced, an extremely strong oxidising agent \(E^0 = 2.19V\), catalyst damage would be extensive as the ring may be susceptible to oxidation, and free Fe detected. Deactivation would increase with \(k_3\). Electroreduction of •OH would not require adsorption (outer sphere).

From the K-L study, the non-linearity two potential explanations remained; 1) An chemical step consisting, accompanying or following the RDS, or, 2) severe electron propagation limitation with a reaction located at the electrode-film interface and not occurring at the film-electrolyte interface [305]. If this model is applicable non-linearity may disappear in thinner films with monolayers and low loading of FePc. In the authors opinion this is an implausible reason; electron conductance and propagation through the film would not be impeded by high rotation and it appears that the K-L non-linearity ‘doubled back’ on itself as opposed to reaching a plateau. In other words, the film should not be less e\(^-\) conductive at high \(\omega\). Electron propagation limit appears unlikely.

This suggests a chemical step following electron transfer [306]. No chemical step would follow electron transfer in the scheme proposed by Appleby. The non-linearity occurs over a wide range and is present in the region dominated by the \(27.7 < |b_c| < 37.4 \text{mV dec}^{-1}\) and the \(|b_c| < 60 \text{mV dec}^{-1}\) regions suggesting both perform a significant chemical step.
For supported FePc;
Low \(\eta\): \((0.2>E>0.17V)\) \(k_2\) (RDS) \(\rightarrow k_3\) electro-reduction and chemical step (Eq.5-5)
Medium \(\eta\): \((0.1>E>0.04V)\) \(k_4\) (RDS) electro-reduction and chemical step \(\) \(\) (Eq.5-6)

5.4 Iron Phthalocyanine stability

5.4.1 De-activation of FePc - Consecutive cyclic voltammetry in \(O_2\)

A mechanism of de-metallation was identified in the catalyst ink in appendix section 10.4. This study demonstrates FePc de-metallation does not require polarisation. The timescale is relatively long and included the presence of ethanol. To establish what cofactors and conditions are required for Eq.3-8 to occur, the stability of the main Fe(II)/Fe(III) peak was evaluated with consecutive cyclic voltammetry (Potentiostatic scan in section 4.1.7) and depicted in Figure 5-21.

![Figure 5-21. FePc stability in de-aerated PBS. (A) Consecutive CV of FePc/KJB (Nafion) films. (b) Enlarged -0.2<E<0.05 region showing no H\(_2\)Pc redox. Electrolyte; N\(_2\) saturated 50mM PBS, pH 7.0. \(\omega\)=0rpm. \(v\)=50mV/s/]

In de-aerated PBS the surface active FePc increases with electrochemical surface cleaning. No H\(_2\)Pc redox was detected. The adsorption of Phosphate does not cause the Fe to dislocate from the macrocycles plane [211], a process making Fe susceptible to proton cleavage from the macrocycle plane when \(O_2\) is the ligand.
Consecutive CV (100 scans) over (A) -0.4<E<0V or (B) -0.4<E<0.5V with (c) showing H$_2$Pc redox (-0.2<E<0.05) in (B). Electrolyte; O$_2$ saturated 50 mM PBS, pH 7.0. ω=0rpm.  

$\nu=50$mV/s

Following polarisation in N$_2$-PBS (Figure 5-21) the solvent was sparged with O$_2$ the procedure repeated for the same potential range, Figure 5-22(B). A fresh FePc/KJB Nafion film was subjected to CV in the range of (-0.4<E<0V) in Figure 5-22(A).

The H$_2$Pc peak observed after creation in the catalyst ink is also generated electrochemically from O$_2$ turnover. From the ink the anodic peak occurs at a similar potential $E_{p_a}$=-0.076V as from electrochemical degradation $E_{p_a}$=-0.032V in Figure 5-22(B), but the corresponding cathodic peak shows an anodic shift, pointing to interaction between ethanol and oxidised Phthalocyanine in the ink. The produced moiety increases with repeated CV to 13.2% the charge of the de-aerated Fe(II)/Fe(III) redox by scan# 100. When the anodic range is cropped to $E$=0V the H$_2$Pc is not created in significant quantity, as the peak ($E_{p_a}$=0.134) did not grow with consecutive scans. The explanation being avoidance of the O$_2$ free Fe(III) state. The explanation of H$_2$O$_2$ production chemically oxidising the aza-nitrogen [142] of the macrocycle causing ring opening has been offered by some authors. However, the produced Pyrrole-2-amine type moiety is not anticipated to yield the redox activity in Figure 5-22(C).
To omit the possibility of residual protons in acidified Nafion binder exacerbating demetalation, the test was repeated with Na⁺Nafion, using a higher rotation speed to remove produced soluble material and increase O₂ turnover. In Figure 5-23 the i-E plot was obtained in N₂ (A) prior to extensive ORR (B) in air saturated PBS, then the solution de-aerated again and the effect of ORR on the redox properties of residual FePc was shown (B).

Figure 5-23. Redox properties of moieties generated from ORR induced FePc de-activationCV of FePc/KJB films with Na⁺Nafion binder in 50mM PBS pH 7.0 Electrolyte; (A) Air saturated, ω=100rpm followed by (B) N₂ saturated, ω=0rpm. υ=20mV/s

The result indicates that the single Fe(II)/Fe(III) redox was split into 3 redox couples with peaks, P1, P2 and P3. Forward and reverse peak potentials of Fe(II)Pc/Fe(III)Pc...
(P2) was consistent after electrochemical aging. Only the moiety P1 produces an oxygen reduction wave in plot (A). Moreover, the redox feature P2 is approximately the same size ($Q$) and peak potential $E_p$ in aerated media and de-aerated media, indicating minimal interaction between an O$_2$ ligand to the P2 moiety. This is in keeping with studies on H$_2$Pc, which describe no ORR activity of this molecule, and the conclusions in Figure 5-22. The creation of this moiety under rapid turnover conditions (high rotation) meant that quiescent solutions frequently had to be used.

5.4.2 Pyroliisation effect on active site

The reduction in Fe(II)/Fe(III) redox charge in the $-0.4V<E<0.5V$ range after pyroliisation of FePc/KJB is seen in Figure 5-24 and the peak characteristics described in Table 5-2.

![Figure 5-24. Redox potential of Fe chelate. The effect of pyroliisation on the Fe(II)/Fe(III) redox potential of FePc/KJB, Capacitive current subtracted. Inset shows FePc/KJB pyr. Electrolyte; N$_2$ saturated 50mM PBS, pH 7.0. $\nu=20mV/s$](image)

<table>
<thead>
<tr>
<th>$\nu=20mV/s$</th>
<th>FePc/KJB</th>
<th>FePc/KJB (pyr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(II) =&gt; Fe(III)</td>
<td>3.57E-04</td>
<td>1.24E-05</td>
</tr>
<tr>
<td>Fe(III) =&gt; Fe(II)</td>
<td>-3.58E-04</td>
<td>-1.25E-05</td>
</tr>
<tr>
<td>Charge / C cm$^2$</td>
<td>0.149</td>
<td>0.143</td>
</tr>
<tr>
<td>$W_{1/2}$ / V</td>
<td>0.145</td>
<td>0.127</td>
</tr>
<tr>
<td>Distribution</td>
<td>Gaussian</td>
<td>Gaussian</td>
</tr>
<tr>
<td>$J_p$ / A cm$^2$</td>
<td>4.47E-05</td>
<td>1.80E-06</td>
</tr>
<tr>
<td>$E_p$ / V (Ag</td>
<td>AgCl)</td>
<td>0.2229</td>
</tr>
</tbody>
</table>
At this pyrolysis temperature no intact Phthalocyanine chelate remains [183]. The peak is reduced from 357 to $12.4\mu$C cm$^{-2}$ after pyrolysis, while the peak remains Gaussian, indicating sites are still accessible to electrolyte and are not electrically insulated. The remaining Iron was detected as a ring current in the original polarisation of the film in de-aerated media. Re-organisational energy is lost during Fe(II)/Fe(III) redox as the ideal $W_{1/2}$=0.089V (Eq.2-88) is not seen, with $W_{1/2}$ being 0.149 and 0.143 prior and after pyrolisation. A slight anodic shift in $E^{0'}$ is attained from 0.2V to 0.231V which results in a shift in $E_{ORR}$ provided the produced moiety can bind O$_2$.

### 5.4.3 Pyrolisation effect on potential of the ORR wave

In Figure 5-25 the value of $E_{ORR}$ is obtained from subtracting current in N$_2$ from that in O$_2$ during $\nu$=1mV/s LSV. No peak was observable for pyrolised FePc/KJB at $\nu$=1mv/s, becoming visible at $\nu$=5mV/s.

![Figure 5-25. Components of current ($J_{ORR}$ and Fe(II)/Fe(III)) in thin FePc/KJB films with Nafion binder, data from $\nu$=1mV/s LSV of a) FePc/KJB in N$_2$, b) $J_{ORR}$ of FePc/KJB in O$_2$, or c) Pyrolised FePc/KJB in O$_2$. $\omega$=0rpm. Electrolyte; 50mM PBS, pH7.](image)

$E_{ORR}$ remained constant (0.3-0.31V) before and after pyrolisation despite $E^{0'}$ FeII/III shifting anodically. This result indicates the Fe(III)N$_x$-O$_2^-$ adduct reduction potential [32] is influenced by the electron donating strength of the new iron chelate site. The
decrease in tafel slope is marginal (Table 5-1) indicating reaction mechanism remains unchanged.

5.4.4 Peroxide generation of pyrolised FePc

With use of Eq.2-56 the ratio of ring H\textsubscript{2}O\textsubscript{2} oxidation ORR current at the disc is presented for FePc/C materials before and after pyrolisation (T=800ºC) in Figure 5-26.

![Figure 5-26. Effect of pyrolysis on %H\textsubscript{2}O\textsubscript{2} vs. E profile of thin films applied to 71µg cm\textsuperscript{-2}. (A) supported FePc materials (B) carbon supports with and without pyrolysis.]

Electrolyte; 50mM PBS, pH 7.0. \(\omega=200\text{rpm.}\ u=5\text{mV s}^{-1}\)

For pyrolised Iron chelates Figure 5-26(A) the proportion of H\textsubscript{2}O\textsubscript{2} released drops with potential until \(E<0.1\text{V}\) where %H\textsubscript{2}O\textsubscript{2} becomes relatively constant. The %H\textsubscript{2}O\textsubscript{2} vs. \(E\) profile generally shows comparability with alkali media \([208, 215]\). The environment of FePc deposition appears to be differ between the two carbons, with pyrolisation decreasing %H\textsubscript{2}O\textsubscript{2} in Monarch and increasing %H\textsubscript{2}O\textsubscript{2} with KJB. The basic, high surface area carbon (KJB) supports the catalyst in a surface environment that efficiently decomposes H\textsubscript{2}O\textsubscript{2}.

Up to 23% H\textsubscript{2}O\textsubscript{2} could be detected from FeNx/KJB warranting significant investigation as to whether \(k_3\) is inhibited by pyrolysis. Peroxide ring current was detected at disc potential 0.03V before and 0.06V after HT treatment of Monarch. Despite a significant quantity of edge plane oxygen susceptible to thermal decomposition the %H\textsubscript{2}O\textsubscript{2} vs \(E\) for
Monarch following appears similar before and after pyrolysis, indicating minimal influence of re-graphitization on $k_4$.

5.5 Conclusions

Activity;
Unpyrolysed FePc produces superior tafel slopes to carbon and platinum, the MFC cathode materials of choice. They release less than 10% peroxide showing good energy efficiency, and supporting FePc on carbon black reduces this amount to a minimum 0.6%, recorded for FePc/KJB thin films at a realistic MFC cathode operating potential. The primary product of the ORR reaction was OH$^-$ when catalysed by FePc, this has design ramifications for air cathodes, explaining why alkali crystals occur in catalyst layers after extended operation in chapter 6.

The Phosphate anion affects the activity of FePc, future work on anion effect on FePc catalysis is recommended as it should influence membrane and ionomer selectivity. This may be accomplished with buffered mediums with weak complexing ligands, such as NaCl–PIVES buffered electrolyte.

The nature of ORR on carbon materials was advanced by pH7 study, allowing potential carbon treatments to be assessed and capacitive effects omitted from reporting. A recommendation for carbon supports for FePc would be for high surface area inactive materials with a purely capacitive response to voltammetry.

Mechanism;
ORR is strongly linked to surface concentration of Fe(II)Pc (Figure 5-25). No rate limitation is associated with the O$_2$ adsorption step, unlike in acid media [307]. Large tafel gradients associated with H$^+$ utilisation were insignificant in comparison to the $|b_t|<60$mV dec$^{-1}$ associated with alkali media ORR. An electron transfer limiting step must be at-least the 2$^{nd}$ $e^-$ transfer. The RDS is not thought to be exclusively of a chemical nature due a small variation in tafel slopes for FePc, as if influenced by symmetry factor in inner sphere electron transfer. A scheme was presented with an RDS that varied with potential. Increased H$_2$O$_2$ release at high potential suggests a peroxo intermediary in a strong adsorption at equilibrium. It is almost certain the last step in the reaction is electron insertion into an Fe(III)Pc-PO$_4$$^{2-}$ or Fe(III)Pc-H$_2$O moiety devoid of
oxygen. The decrease or absence of the Fe(III)↔Fe(II) peak in O₂ suggests that O₂ cannot bind to Fe(III)Pc by replacing a H₂O ligand. Unlike Haemoglobin, O₂ desorption from FePc appears slow and low in reversibility, unless substituted by a stronger ligand.

Stability;

New techniques for quantifying iron macrocycle de-activation are outlined and should be valid for measurements in solutions of Phosphate/Phosphoric acid. The reduction in Fe(II)Pc→Fe(III)Pc peak and rise of H₂Pc redox can be used to quantify demetallation rate and separate from reactive oxygen species deactivation. De-activation requires the presence of oxygen and cannot occur with Phosphate alone. The de-activation rate is greatly increased by polarisation, though de-metallation is higher than ROS deactivation when an acidified binder is used. De-metallation increases significantly with polarisation at high potentials and was not negligible at pH7.

Pyrolysis may not be required for neutral media application unless significant stability improvements can be demonstrated.

Pyrolysis;

For neutral media, pyrolysis may result in a small number of sites with an increase in thermodynamic performance (lower $E_a$), as with CoN₄ moieties in acid media [301]. However, the kinetic performance ($k_{app}$) is greatly impeded, resulting in inferior tafel slopes, unlike acid media studies [225, 301]. Pyrolysis of two carbon supported FePc catalysts was repeatedly inferior to the unpyrolysed version.

Post pyrolysis performance and chemical treatment of the carbon support may be strongly related. The carbon support with fewer quinolic structures (FePc/KJB) resulted in a higher pyrolised FePc performance, due to large amounts of wasted chelated precursor. Some solid Fe(III)Oₓ/Fe(IV)Oₓ was produced. The best tafel slope of pyrolised FePc was $|b|=39.9$ mV dec⁻¹. Though pyrolysis caused a decrease in %H₂O₂ release at low potential, the overall life of the catalyst was short. On balance, the author would not recommend pyrolisation of FePc for MFC cathodes.
Chapter 6. Results - Improved kinetic performance of Iron Phthalocyanine from a novel anion exchange ionomer
6.1 Background - inspiration from alkali membrane fuel cells

It has been demonstrated that the low selectivity of protons in Cation Exchange Membranes (CEM) creates a large performance barrier to MFC performance [308]. In CEM’s the low molarity presence of protons ($10^{-7}$ M) is dwarfed by the abundant presence of cations such as Na$^+$, K$^+$, NH$_4^+$, Ca$^{2+}$, Mg$^{2+}$, representing a portion of the overall ion transport 4-5 orders of magnitude higher than H$^+$ transport [308]. The conductivity of sulfone based ion exchange materials decreases rapidly with increasing pH [254]. H$^+$ transport can be partially balanced in Anion Exchange Membranes (AEM) by the HCO$_3^-/CO_3^{2-}$ and H$_2$PO$_4^-$/HPO$_4^{2-}$ couples [250] in systems where the concentration of these anions greatly exceeds that of OH$^-$. In chapter 5 it was demonstrated that the alkaline pathway is responsible for the majority of ORR in FePc cathodes. The lessons on AEM could be applied to pH balancing and ion transport in a catalyst layer containing anion exchange ionomer (AEI). The ionomer comprises of exchange group and polymer backbone.

Several qualities are sought for the AEI, resistance to irreversible adsorption or nucleophilic attack from anionic pollutants in wastewater capable of membrane permeation. Ion selectivity to the OH$^-$ or pH balancing anions present in the process wastewater are desirable according to the influence Eq.1-10 possesses over pH dependent faradic reactions. Novel AEM and AEI synthesised in academia are applied to alkali fuel cells or water treatment, this study [309] being the first exception. Exchange group stability is rarely reported other than OH$^-$ [310] or carbonate [311] nucleophilic substitution. The chemical stability of exchange groups in real wastewater has not been reported from an electrochemical perspective to the best of the author’s knowledge.

In this study a new AEI, Quaternary-1,4-Diazabicyclo-[2.2.2]-octane Polysulfone (QDPSU) has been trialled with catalyst layers of FePc/KJB, KJB or Pt/C in neutral pH conditions. This material was originally produced for alkali media and is based on Polysulfone and Diazabicyclo-[2.2.2]-octane (Dabco) [276, 277], an oxygen scavenging molecule widely used in organic catalysis [236]. Methylated side chains have been added to Polysulfone and serve as a site for grafting Dabco producing the polymer displayed in Figure 6-1. The polysulfone backbone possesses broad spectrum chemical
resistance (organic solvents, mineral acids, \( \text{OH}^- \) and \( \text{H}_2\text{O}_2 \) produced by the cathode) and a broad window of electrochemical stability [246]. This makes it a viable candidate for an MFC binder.

![Figure 6-1. Structure of QDPSU repeating unit [276, 277].](image)

### 6.2 QDPSU binder in thin carbon black films

#### 6.2.1 An \( \text{O}_2 \) related redox peak in QDPSU electrodes

Thin films of KJB with Nafion or QDPSU binder were prepared and the \( i-E \) response assessed in Figure 6-2. Evidence was sought for the redox activity or ion interaction of the Dabco moiety.

![Figure 6-2. Redox active Dabco/\( \text{O}_2 \) moiety. CV of KJB carbon with (A) Nafion or (B) QDPSU binder on GC disc in Electrolyte; 50mM PBS, pH 7.0. \( \omega=0\)rpm, \( \upsilon=20\text{mV s}^{-1} \)](image)
The most notable observation in Figure 6-2 is the redox peak present in oxygenated electrolyte which occurs only when QDPSU is used. To the authors knowledge this has not been isolated in electrochemical studies based on Dabco oxygen scavenger at the date of publication [234, 240, 243, 312-318]. The Polysulfone is redox inactive [319], when coated on carbon. Several possible explanations are examined:

1) Redox active Dabco fixated \( \text{O}_2 \) in all Dabco ionomer in electrolytic contact.
2) Redox active Dabco interacting with graphitic edge planes that contain chemisorbed \( \text{O}_2 \). A portion of all Dabco in electrolytic contact.
3) Redox active Dabco inert to \( \text{O}_2 \) chelation by phosphate in equilibrium adsorption to the triethyl Nitrogen.
4) Hoffman degradation or nucleophilic substitution (see Figure 3-6). This might plausibly be mediated by phosphate.
5) Trace metal chelation by Dabco resulting in a redox active moiety with dispersion of formal potentials.

The high ionisation potential of Dabco [320] may explain why no redox is seen without \( \text{O}_2 \). The redox seen in Figure 6-2 is approximate to the second photo-excitation \( IP \) [313, 316]. Partial charge transfer to \( \text{O}_2 \) may produce a cationic hole on the nitrogen [321] and reverse this process during oxidation. In RRDE experiments, no increase in \( i_R \) accompanied the redox on the disc suggesting no released intermediary from partial ORR. The possibility of nucleophilic degradation must be eliminated for QDPSU to be a viable candidate for air cathode implementation; accordingly effort was made to determine the nature of this feature.

6.2.2 Redox peak geometry

The KJB QDPSU thin film was subjected to CV of various scan rate. The corresponding effect on peak potential \( (E_p) \) and shown in Figure 6-3.
Figure 6-3. Redox active Dabco/O₂ moiety – influence of scan rate. 

(A) CV data and (B) $E_p$ vs. $\nu$ plot using least squares fit. A thin film of KJB carbon with QDPSU ionomer on a GC disc Electrolyte; 50mM PBS, pH 7.0. $\omega$=0rpm. $\nu$=20-400 mV s⁻¹

When $\nu\rightarrow 0$ mV/s a surface constrained redox should show symmetrical peaks [82]. $W_{1/2}$ is predicted to obtain a $W_{1/2}$=89/n mV minimum when reversibility is high and thermodynamic lag (bond re-organisation) is negligible [82, 293, 322]. The QDPSU ionomer the scan rate affects $W_{1/2}$: 0.094V ($\nu$=20mV/s), 0.101V ($\nu$=100mV/s), 0.11V ($\nu$=200mV/s), 0.118V ($\nu$=300mV/s) and 0.129V ($\nu$=400mV/s), a linear relationship between $W_{1/2}$ vs $\nu$ ($R^2<0.9974$) with slope $d(W_{1/2})/d\nu=0.0907$s. Eq.2-88 anticipates $W_{1/2}$=89/n mV at low scan rate (20°C). Peak broadening can be due to interactions between redox active sites [323] or steric hindrance of adsorption [324].
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$E_p$ vs. $\nu$ produces a linear plot in Figure 6-3(B), though scan rate was not increased high enough for $E_p$ vs $\log_{10}(\nu)$ region to be observed. The gradient for $E_p/\nu=0.1567s$ and $E_{pc}/\nu=-0.1623s$ are nearly identical indicating $\alpha=c.a. 0.5$ [82].

In cases where no diffuse element or thermodynamic lag is present, as $\nu \rightarrow 0V$ s$^{-1}$ the term $E_{pa} - E_{pc} \rightarrow 0V$ [293]. In cases with a diffuse element an extrapolation to 59/n for 25°C should be seen (100% reversible). Therefore the redox is quasi-reversible. In addition, a comparison of $E^0$ from peak extrapolation (0.14V) and the OCP = 0.16V demonstrates that the oxidised state is thermodynamically favourable. Figure 6-4 shows that a linear relationship between $J_p$ and $\nu^{1/2}$ occurs.

![Figure 6-4. $J_p$ vs. $\nu^{1/2}$ plot for redox peak of O$_2$ insertion in Dabco (A). Thin-film of KJB and QDPSU binder. Inset (B) shows peak profile after baseline subtraction. Electrolyte; 50mM PBS, pH 7.0. $\omega=0$ rpm. $\nu=20-400$ mV s$^{-1}$](image)

This is usually indicative of a diffusion controlled process [325]. The physical dispersion of ion exchange sites along the binder backbone means the Laviron’s multilayer model [293] cannot apply to Methyl-Dabco sites. The QDPSU ionomer acts more like a conducting polymer film. This can mean either 1) slow ion (H$^+$/Na$^+$/OH$^-$ or PO$_4^{3-}$) transfer from solution to redox active site [98], 2) slow transfer from site to graphite. A least squares linear fit produces a relationship of $J_p=0.0002\nu^{1/2}-0.00001$. The $\nu=5$mV/s scan produces $J_p=4.8\times10^{-7}$ A cm$^{-2}$ confirming that the axis does not bisect.
the origin but at $J_p=1 \times 10^{-5} \text{ A cm}^{-2}$, as previously seen for the Fe(II)$\rightarrow$Fe(III) oxidation of FeNPc with a variety of anions [194]. This can be due to:

1) The redox species possesses no uniform $E^{0'}$ but is distributed according to local environment on the graphite surface, causing peak splitting at low $\nu$ and peak amalgamation into one peak at high $\nu$.

2) The ad/desorption of counter-ions which show increased adsorption the potential of $J_p$ ($E_p=0.1607 \text{ V}$, Figure 6-3).

### 6.2.3 Electrolyte effect on QDPSU

The presence of a diffusive element (Figure 6-4) may suggest desorption and diffusive movement of Phosphate or OH$^-$ to maintain electro-neutrality as electrons move throughout the film [77], if this process were slow. To discount this possibility fresh KJB QDPSU films were applied and subjected to consecutive polarisation (method 3-chapter 4). The peak size was recorded with consecutive scan number in order to ascertain whether the process is irreversible and electrode constrained.

![Figure 6-5](image)

**Figure 6-5.** Redox activity of Dabco/O$_2$ moiety – role of Cl$^-$ and PO$_4^{3-}$ anion. Thin film of KJB carbon with QDPSU binder. Consecutive CV in N$_2$ sat. followed by O$_2$ sat. electrolyte (scan# shown in key). Electrolyte; (A) 50mM PBS, pH7.0 or (B) 50mM NaCl, pH 7.0 (right). $\omega$=0rpm. $\nu$=50mV s$^{-1}$

In Figure 6-5, scan #1 and #100 are shown for PBS and NaCl electrolyte. During scan# 1 the Dabco/O$_2$ redox peak did not exist in PBS, the Dabco is initially ORR active but
the site de-activated within one CV. The peak was reported in a previous communication [309], increasing in size ($Q_{an}$), becoming visible by scan #10, reaching the maximum size by scan #40, gradually decreasing thereafter. The relative charge passed by ORR wave in scan#1 and the redox in scan#100 shows that de-activation required more than a single turnover. The behaviour indicates de-activation by ORR intermediary, though the Dabco moiety is rendered ORR active initially by interaction with Phosphate. In NaCl, Figure 6-5(B), the largest forward peak is seen at scan #5 and the reverse peak has cathodically shifted (pH dependent) to be obscured by the carbon catalysed ORR wave, indicating a possible OH$^-$ ligand to amine. Peak characteristics were examined to determine which explanation applies;

- 100th anodic scan; $E_p$=0.163V (NaCl), $E_p$=0.144V (PBS)
- Peak area ($Q_{an}$) on scan #100; 9.5x10$^{-5}$ C cm$^{-2}$ (NaCl) and 6.3x10$^{-5}$ cm$^{-2}$ (PBS).
- In O$_2$ sat. PBS in the anodic scan, the peak remained Gaussian throughout as in Figure 6-3 and $W_{1/2}$=c.a. 94mV at all scan#>10.
- In O$_2$ sat. NaCl, at scan #5 $E_p$=0.163V, $W_{1/2}$=0.135V (Lorentzian) but shifted cathodically to a more Gaussian distribution by scan #100 to $E_p$=0.134V, $W_{1/2}$=0.153V.

The rapid alkalination of the film in NaCl appears not to have influenced $E_{pa}$ while $E_{pc}$ is cathodically shifted in unbuffered NaCl. The anodic peak is not influenced by catalyst layer pH or adsorbed solution anion. The reverse peak is a function of one of these aspects. The comparable size in the peak (Cl$^-$ is x1.5 than PO$_4^{3-}$ after 100 CV scans) demonstrates the counter anion is not crucial to formation. The result suggests that in PBS Phosphate binds to an amine, while in NaCl OH$^-$ is bound to the amine.

In PBS the symmetrical nature of the peak proves charge is not transferred to a soluble phase. The peak size between Cl$^-$ and PO$_4$ is identical, whereas OH$^-$ concentration is expected to be larger in un-buffered NaCl catalyst layers. These factors make nucleophilic substitution by the solution anion or OH$^-$ an unfeasible explanation. This shows consensus with the study of Iojou et al [246] who demonstrate this process to not be feasible.
6.2.4 Redox mechanism of QDPSU $O_2$ fixation

The QDPSU content predicts a Dabco loading $I=2.51 \times 10^{-7} \text{mol cm}^{-2}$ (Eq.2-87). Using Eq.2-86 this would correspond to $2.4 \times 10^{-2} \text{A cm}^{-2} (v=100 \text{mV/s})$ if all QDPSU is redox active. Instead only $0.208\% \ (J_p=4.98 \times 10^{-5} \text{ A cm}^{-2})$ of the predicted loading is active. Therefore the redox may be particular to interaction with a certain graphitic edge plane group and $O_2$. Peak splitting at low $v$ would support this assertion. $O_2$ is clearly required, meaning an interaction between Dabco-$O_2$ and Phosphate/OH$^-$ or a carbon group.

![Diagram of redox mechanism](image)

**Figure 6-6.** Quasi-reversible $O_2$ insertion into Dabco group in QDPSU. Oxidised methyl-Dabco groups at higher potentials (B) and (C) are postulated. Two charge distribution scenarios $\text{NC}_4^{+/-}\text{NC}_3^{+}$ or $\text{NC}_4^{2+/-}\text{NC}_3$ are shown in (C).

Considering that $O_2$ is required for this redox to occur the first step of the reaction is not the electro-reduction of the oxygen-less dabco. Several factors should be considered;

- $e^-$ transfer from the Dabco amine to fixated $O_2$ isn’t detected by the potentiostat unless immediately followed by insertion of an externally sourced electron.
- The electrode is initially inserted into air saturated PBS giving ample time for $O_2$ fixation. Following $N_2$ sparging no redox peak is detected during scan #1. Therefore the $O_2$ fixation reaction must be reversible.

6.2.5 QDPSU interaction with ORR active carbon sites

The possibility of QDPSU interaction with carbon edge planes of know ORR activity was evaluated with LSV experiments performed at steady state in Figure 6-7.
Figure 6-7. (A) $i-E$ response showing interaction between Dabco in QDPSU with KJB. (B) Corresponding tafel plot. Electrolyte; $O_2$ saturated (solid) or $N_2$ saturated (dash) 50mM PBS, pH 7.0. $\omega=0$rpm. $\nu=1$ mV s$^{-1}$

Figure 6-7(A) shows that an oxygen reduction wave is enhanced with the use of QDPSU binder. Figure 6-7(B) shows a new faradic reaction occurring at $E=0.2$V, for which region the log$_{10}(J)$ vs $E$ response is curved when Nafion is used. This indicates creation of a new site rather than increased exchange current of an existing site. K-L analysis of KJB films with binders of Nafion and QDPSU at $E=-0.4$V is presented in Figure 6-8.

Figure 6-8. K-L plots of current obtained with thin films of KJB with binders of (A) Nafion or (A)(B) QDPSU at (A) $E=-0.4$ or (B) various $E$. Least squares fit applied to $100<\omega<800$rpm. Electrolyte; 50mM PBS, pH 7.0. $\nu=5$ mV/s.
In Figure 6-8(A) the transition from O\textsubscript{2} limiting current to kinetic limitation is seen with Nafion binder, and absent with QDPSU. A linear fit applied to lower electrode rotation rates (100<\(\omega<\)800rpm) to the QDPSU electrode produced an \(R^2=0.9998\), corresponding to \(k_{\text{app}}=0.034\text{cm s}^{-1}\) using Eq.2-51. In this instance, the difference in the number of electrons exchanged is significant, any error due to collection efficiency loss is causes a significant effect on calculated \(D_{O2}\) from Eq.2-51, nevertheless \(D_{O2}=\text{6.05 x10}^{-5} \text{ cm}^2 \text{ s}^{-1}\) is calculated when the corresponding value of \(n\) is determined from RRDE work in section 6.3.1. With QDPSU the ORR was 1\textsuperscript{st} order w.r.t [O2] at all potentials cathodic enough for mass transport limitation.

6.3 QDPSU binder in thin films of FePc/KJB and Pt/C

Using the same electrochemical methods described for Table 5-1, Table 6-1 is produced for catalysts using PTFE or QDPSU binder.

Table 6-1. Various catalyst ORR activity in thin films–QDPSU or PTFE binder. Total catalyst powder; 71µg cm\(^{-2}\), Binder content; QDPSU; 88.4µg cm\(^{-2}\), PTFE; 28.4µg cm\(^{-2}\).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Tafel Slope ((\eta_{O2}) corrected)</th>
<th>(J_0) A cm(^{-2})</th>
<th>(E_{\text{cross}}) mV</th>
<th>RAS (J_{\text{ave}}) (10^9\text{ site cm}^{-2}) mA cm(^{-2})</th>
<th>(E@) 0.4Am(^{-2}) mV</th>
<th>OCP Air→N(_2) mV</th>
<th>OCP O(_2) mV</th>
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</thead>
<tbody>
<tr>
<td><strong>QDPSU</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FePc/KJB</td>
<td>ORR (FePc)</td>
<td>-27.7</td>
<td>5.1E-08</td>
<td>396</td>
<td>205</td>
<td>-1.92E-04</td>
<td>216</td>
</tr>
<tr>
<td>FePc/KJB pyr</td>
<td>ORR (FeNx)</td>
<td>-35.2</td>
<td>1.0E-07</td>
<td>353</td>
<td>-</td>
<td>-1.88E-04</td>
<td>201</td>
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<tr>
<td>KJB</td>
<td>((i_{dl})+) trace ORR</td>
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<td></td>
<td>388</td>
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<td>-1.71E-05</td>
<td>-145</td>
</tr>
<tr>
<td>Pt/C</td>
<td>2e\textsuperscript{-} ORR Wave</td>
<td>-97.8</td>
<td>4.5E-08</td>
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<td>-</td>
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<td>First Tafel</td>
<td>-63.6</td>
<td>1.8E-06</td>
<td>407</td>
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<td>-1.50E-04</td>
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<td></td>
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<td>N/R</td>
<td></td>
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<tr>
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<td></td>
<td></td>
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</tr>
<tr>
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<td>ORR (FePc)</td>
<td>-32.9</td>
<td>-</td>
<td>385</td>
<td>422</td>
<td>-1.29E-04</td>
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The films are predicted to be identical in carbon/catalyst compared to the Nafion films when applied from a colloid. Table A-8 shows that electro-active availability may differ within less than a fifth of an order of magnitude.
6.3.1 Binder influence on kinetics in thin films

Slow scan rate ($\nu=1\text{mV/s}$) LSV in aerated quiescent PBS highlights the effect of binder on $E_{1/2}$ and kinetics in Figure 6-9.

![Figure 6-9. (A) LSV of FePc/KJB with QDPSU, PTFE or Nafion binders - quiescent solution. (B) Tafel plot of (A). Electrolyte; 50mM PBS, pH 7.0. $\nu = 1\text{mV/s}$](image)

In Figure 6-9 a cathodic shift in $E_{1/2}$ is present when PTFE or QDPSU binder is used. Although agitation is not used, cathodic of the minima in current (at $0<E<0.5\text{V}$) the current increases after $\delta$ obtains a stable size. Phosphate desorption is observed with all binders indicating it to be an FePc, and is a reversible process on the FePc heme [176]. The data obtained under forced convection also shows this feature. The $i$-$E$ response for a cathodic LSV scan at low rotation speed is shown in Figure 6-10.
In Figure 6-10, the $\text{d}I/\text{d}E$ gradient at $E<-0.2\text{V}$ is larger for FePc than Pt, though figure 5-26 predicts an increase in the portion of $\text{H}_2\text{O}_2/\text{OH}^-$ product with $E\rightarrow-0.4\text{V}$, thus showing proportional increases in $i_D$, with the same reaction product.

Electrocatalysis on Pt was examined to discern the influence of binder on $\text{O}_2$ diffusion and counter ion charge compensation, at low $\eta$ gradients of $\log_{10}(J_k)$ vs $E$ are consistent with Nafion and QDPSU (Table 6-1 vs Table 5-1). Two tafel slopes are observed for both catalysts, a c.a. $|b_1|=\text{c.a. 60mV dec}^{-1}$ and $|b_2|=\text{c.a. 120mV dec}^{-1}$, as usual [278]. The cathodic limit of the facile tafel slope is extended from $E=0.3\text{V}$ $|J_k|=6\times10^{-5}$ $\text{A cm}^{-2}$ to $E=0.28\text{V}$ $|J_k|=2.5\times10^{-4}$ $\text{A cm}^{-2}$. No considerable difference was found in the CV of deaerated Pt/C samples (Figure A-16) indicating the Pt/PtO couple was not affected by QDPSU surface coverage, though more reliable result are obtained with monocrystalline Pt. For Nafion ($J_L=1.32\text{mA cm}^{-2}$) is similar to QDPSU ($J_L=1.35\text{mA cm}^{-2}$) indicating a consistent reaction product and surface mechanism with QDPSU covering the Pt surface. At this cathodic potential $\text{O}_2$ diffusion through the film is not required. As Dabco is a known $\text{O}_2$ chelator, the QDPSU electrodes are assessed with K-L analysis.
In FePc as $J_0$ and $\dot{\Gamma}_{FePc}$ are only marginally lower with QDPSU, ionomer dispersion is reasonable.

![Figure 6-11. K-L plots of limiting current obtained with FePc/KJB (left) or Pt/C (right) thin films with binders of a) Nafion b) QDPSU and c) PTFE at $E=-0.4V$. Least squares fit of $100<\omega<800$ rpm. Electrolyte; 50mM pH 7.0. $\upsilon=5$mV/s.](image)

The K-L plot is linear at low potential indicating the film is fully reduced. In Figure 6-11 the least squares fit for electrode rotation speeds $100<\omega<800$ rpm was highly linear; $R^2$ was above 0.9994 for both Pt and FePc electrodes with all binder.

When applying Eq.2-51 to the K-L gradient one assumes several criteria are either identical or have a negligible effect, such as $\upsilon$ and $[O_2]$ in the hydrated ionomer phase. Using $N_e$ obtained from Figure 6-13 and adjusting these values for %H$_2$O$_2$ of 0.6% (QDPSU) and 0.8% (Nafion) and 1% (PTFE). Though the reaction occurs at the sol/film interface the catalyst particles are covered in an ionomer film of Nafion/QDPSU (Figure 5-4) through which O$_2$ must diffuse. From Eq.2-51 $D_{film}=6.76\times10^{-5}$ cm$^2$ s$^{-1}$ (Nafion), $D_{film}=6.17\times10^{-5}$ cm$^2$ s$^{-1}$ (QDPSU) and $D_{film}=3.32\times10^{-5}$ cm$^2$ s$^{-1}$ (PTFE). Adjusting for $\dot{\Gamma}_{FePc}$ from Table A-8 with Eq.2-54, produces $K_{app}$ values; $5.17\times10^9$ cm$^3$ M$^{-1}$ s$^{-1}$ (QDPSU), $3.13\times10^9$ cm$^3$ M$^{-1}$ s$^{-1}$ (Nafion), $0.686\times10^9$ cm$^3$ M$^{-1}$ s$^{-1}$ (PTFE). The K-L gradients that can be reliably obtained ($R^2>0.999$) are displayed in Figure 6-12 for a number of films.
In Figure 6-12, K-L gradients of QDPSU and Nafion films show relative consistency with potential at that at high overpotential. In the case of Pt, the Levich currents ($E=-0.375V$) obtained matched $D_{film}=5.994\times10^{-5}$ cm$^2$ s$^{-1}$ with Nafion and $D_{film}=5.68\times10^{-5}$ cm$^2$ s$^{-1}$ with QDPSU. With QDPSU ionomer, the $D_{film}$ value for KJB (Figure 6-8) was marginally lower than FePc/KJB. With both films poised at $E=-0.4V$, the diffusion path length to the site of reaction is larger in the KJB film. The approach of mixing KJB with FePc/KJB to enhance conductivity may not enhance $O_2$ diffusion.

$D_{film}$ for PTFE binder is x1.946 higher than $D_{O2}$ in PBS electrolyte (Table A-2). This is frequently observed, as oxygen diffuses through gaseous phases arising from hydrophobic domains, in-between graphite sheets or small pores. This Knudsen diffusion constant can be as high as 0.12939 cm$^2$ s$^{-1}$ [326], approximately x43,130 faster than through pure hydrated Nafion ionomer (0.3x10$^{-5}$ cm$^2$ s$^{-1}$) [327].

The $J'$ intercept values for FePc correspond to $J_k=38.5$mA cm$^2$ (QDPSU), $J_k=10.5$mA cm$^2$ (PTFE), $J_k=25.3$mA cm$^2$ (Nafion), orders of magnitude higher than air cathodes. Using Eq.2-51 at $E=-0.4V$, $k_{app}=0.0435$cm s$^{-1}$ (QDPSU), $k_{app}=0.0286$cm s$^{-1}$ (Nafion), $k_{app}=0.01187$cm s$^{-1}$ (PTFE), the value for OH$^-$ exchanging QDPSU being similar to that obtained by Van den brink [67] in KOH.

The implication of this study being that K-L plots cannot be used to determine $\%H_2O_2$. As anticipated by models [60, 77], other factors influence $J_L$ in neutral pH redox catalyst. The RRDE investigation is shown in Figure 6-13.
Figure 6-13. Effect of binder on %H₂O₂ released from ORR thin films of (A) Pt or FePc or (B) KJB.Relative binder:powder weight of a) QDPSU (124.5% wt.), b) PTFE (40% wt.) or c) H⁺-Nafion binder (156.5% wt.). Electrolyte; 50mM PBS, pH7.0. ω=200rpm. u=5mV s⁻¹

The method aims to assess relative contributions FePc de-activation from H₂O₂, and H₂O₂ decomposition by QDPSU. With QDPSU a dip in %H₂O₂ exiting a KJB film was seen with a minima at $E=-0.05V$ and not present with Nafion. No corresponding decrease in %H₂O₂ vs. $E$ occurred in Pt/C or FePc/KJB films, signifying QDPSU scavenging of H₂O₂(aq) is not present and QDPSU had a negligible impact on $k₄$, ie. $k₄≠f(E)$. The result indicates QDPSU and graphitic edge plane interaction, yield small loadings of 4e⁻ ORR active sites.

For FePc/KJB, proportionally more H₂O₂ is released at $-0.04V<E<0.15V$ with Nafion. Relatively nafion impedes $k₃$. As also seen in Pt/C, where QDPSU caused a 50% decrease in %H₂O₂ compared to Nafion at $E<0.05V$.

With FePc/KJB the profile of %H₂O₂ vs. $E$ was similar for PTFE and QDPSU, significantly more H₂O₂ is detected with Nafion. A working theory can be generated; H₂O₂ is in equilibria with FePc catalysts and it’s release is a function of adsorption residence time prior to reduction ($k₃$), which requires an initial chemical step. With QDPSU, residence time is shorter than with Nafion or PTFE, indicating $k₃$ may require an anion in a chemical step, following a C₃EE mechanism, by classic nomenclature, an irreversible chemical reaction followed by two electron transfer steps. If this theory is valid, rate determining $k₁/k₂$ should remain un-affected with binder change, whilst $k₃$
increases. A K-L plot of FePc/KJB QDPSU is depicted in Figure 6-14 to evaluate changes in \( k_{app} \).

![K-L plot of FePc/KJB QDPSU thin film.](image)

Electrolyte; 50mM pH 7.0. \( \nu = 5 \text{mV/s} \).

In Figure 6-11, the K-L plot is linear at low potential with no significant shift up the axis, indicating \( k_{app} \) is consistent at low potential. The slope is in the range 2180-2209 cm\(^2\) rad\(^{0.5}\) s\(^{-0.5}\) A\(^{-1}\) for all potentials -0.4<\(E\)<-0.25 with \( R^2 > 0.9997 \). From 3-26, \( n \) is consistent in this range. At high potential the results are difficult to interpret, and \( J_k \) cannot be extrapolated. At fixed potential, oxidation of the film would be more rapid if the local pH were alkali, as is the case at low \( \omega \). In order to establish whether the reaction at low overpotential occurs at constant \( k_1/k_2 \) ratio the situation lends itself to the criteria specified in section 2.4.5. The raw data and goodness of fit are located in Figure A-12 and Figure A-13 respectively. The \( S \) vs \( C \) plot is from \( CE*I_D/I_R \) vs \( k_{D,H_2O_2}^{-1} \) plot using conversion from \( CE*I_D/I_R \) vs \( \omega^{-0.5} \) data of the utilised conversion using Eq.2-72 for FePc/KJB QDPSU is presented in Figure 6-15.
In comparison to the unsupported film Figure 5-19 the region $E \geq 0.2$V is more visible than in FePc/KJB. Two linear regions were observed, corresponding to two ORR mechanisms.

0.25V > $E$ > 0.16V;
- A least squares fit ($R^2 = 0.981$) produced a gradient 17.34 rpm$^{0.5}$ with a $C$ axis intercept of $C' = 0.992$.

0.15V > $E$ > -0.01V;
- A least squares fit ($R^2 = 0.991$) produced a gradient -34.24 rpm$^{0.5}$ with a $C$ axis intercept of $C' = 37.38$.

The 0.25V > $E$ > 0.16V region is c.a. $C = 1$ and corresponds to a region where $k_1/k_2$ is a consistent value, showing $k_2 >> k_1$ (see Figure 5-19). The high potential mechanism is the same as on unsupported FePc, namely a strongly adsorbed peroxo intermediary. As the intercept $C = 1$, the $k_{D,H_2O_2}$ is significantly larger than $k_3 + k_4$. In other words, in this potential region all the peroxide that is released from FePc ends up at the ring. In Figure 6-13 the $i_R/i_D$ value for the film is 1.7% at $E = 0.16$V. Therefore 96.6% of H$_2$O$_2$ is undergoes disproportionation. The $k_2$ domination region occurs over a wider potential range with QDPSU (0.25V > $E$ > 0.16V) than Nafion (0.18 > $E$ > 0.15V).
The 0.15V > E > -0.01V region is also observed for carbon supported FePc with Nafion binder (0.12V > E > 0.04V). In chapter 5 it was established as direct 4e⁻ reduction. The value \( k_1 = 18.9k_2 \) (Eq.2-71) was consistent in this large potential bracket, both pathways appear to have a similar dependence on potential, growing in unison. The corresponding S/C vs E values (not shown) produce a maxima at \( E = -0.05V \) as opposed to the minima observed with unsupported films and the Nafion FePc/KJB electrode. All S/C values possess a flat baseline \( 10^{-3} \) to \( 10^{-5} \) m s\(^{-1} \), generally faster than \( k_{app} \) recorded as \( 4.35 \times 10^{-4} \) m s\(^{-1} \) at \( E = -0.4V \) from Figure 6-14 and Eq.2-51.

### 6.3.2 Binder influence on kinetics in air cathodes

In Figure 6-16 air cathodes with different binders were subjected to potentiostatic sweep (LSV method, section 4.1.7). This method removes charging current of the large FePc surface.

![Figure 6-16. Potentiostatic scan of FePc/KJB air cathodes using Na⁺-Nafion, PTFE or QDPSU binder. Plotted as (A) LSV with (B) low overpotential region or (C) log\(_{10}(J)\) vs E. Electrolyte; air-saturated 50mM PBS, pH 7.0.](image-url)
OCP was recorded (2hrs) prior to recording the data in Figure 6-16. Comparison to the data in Figure 6-16:

- After 2hrs OCP=0.271V (QDPSU), OCP=0.232V (PTFE) and OCP=0.259V with Nafion, though Nafion had not produced a stable result indicating continual alkalination, This follows the same trend in $E_{onset}$ in Figure 6-16(C).
- At 0.14>E>0.08V an i-E plateau is seen with QDPSU. The cause for limitation warrants evaluation with EIS.
- $J_0=8\times10^{-7}A \text{ cm}^{-2}$ (QDPSU), $J_0=9\times10^{-8}A \text{ cm}^{-2}$ (PTFE) and $J_0=4.5\times10^{-8}A \text{ cm}^{-2}$ (Na-Nafion).
- Linear tafel behaviour occurs over a large potential range for QDPSU (0.29>E>0.22V) relative to PTFE (0.23>E>0.21V) or Nafion (0.25>E>0.23V).
- For QDPSU air cathodes $|b_c|=25.4\text{mV dec}^{-1}$ and Nafion air cathodes $|b_c|=29.9\text{mV dec}^{-1}$.

To the authors knowledge the tafel slope recorded for FePc/KJB QDPSU is the highest recorded for ORR in any electrolyte, comparable to air cathodes of Bilirubin Oxidase ($|b_c|=26.6\text{mV dec}^{-1}$) [173]. However, the intermediate complexes possess a higher $E^{0'}$ with BOX, as is the exchange current.

6.3.3 Anion influence on QDPSU and FePc in de-aerated medium

Consecutive CV was carried out on thin films of QDPSU or Nafion binder with FePc/KJB in several electrolytes. The aim was 1) establish unselectivity of QDPSU Dabco moiety towards oxidation/reduction of a variety of anions present in real wastewater, 2) establish stability of QDPSU in the presence nucleophilic anions, 3) establish a spectrochemical series for FePc.

Prior to polarisation in O$_2$, localised pH is similar to bulk electrolyte pH. Thus, changes in $E^{0'}$ of reversible Fe(II)/Fe(III) peaks in N$_2$ are due to ligand influence on the electrocatalyst as opposed to pH. The mean amount of electro-active FePc in both layers is discussed in Table A-8 and is found to be slightly lower QDPSU ($\Gamma=3.4\times10^{-9} \text{ mole cm}^{-2}$) than Nafion ($\Gamma=3.9\times10^{-9} \text{ mole cm}^{-2}$), though this is within a standard deviation. This may be due uneven ionomer dispersions from QDPSU following precipitation from DMF solution upon dilution with ethanol. $Q_{an}$ is anticipated to be similar for each
anion. Common anions of CH$_3$COO$^-$ and Cl$^-$ are supporting electrolytes for CV experiments depicted in Figure 6-17.

In CH$_3$COONa electrolyte peak splitting was observed. Dissociated CH$_3$COOH binds weakly in comparison to CH$_3$COO$^-$ [176, 328] producing competitive forms of heme/ligand adsorption [176], meaning electrode blocking occurs over time. No detectable redox reaction or wave was associated with QDPSU, neither oxidative chemisorption nor electrooxidation of acetate. Two redox couple peaks were seen with Nafion and QDPSU binder, suggesting reorientation of adsorbed acetate with polarisation. With QDPSU binder Fe(II)/Fe(III) $E^0$ potential shifted positive.

A peak in Cl$^-$ ($E_{pc}=-0.06V$) is observably larger with QDPSU than Nafion. The redox activity is not attributed to QDPSU due to absence in KJB-QDPSU films (Figure 6-5). This peak increased with consecutive scan# and is present in other non-buffering electrolytes with a consistent reduction potential (Figure 6-18). It is established [329] that AEM fouling with anionic pollutants increases electrode capacitance ($C_\Sigma$). With acetate, the 11% increase in $C_\Sigma$ with QDPSU vs Nafion is negligible (Eq.2-16, $E_0=-0.3V$). The interpretation being that exchange capacity is not lost from the action of the Cl$^-$ or CH$_3$COO$^-$ ion with polarisation.
Figure 6-18. (A) Anion adsorption in the CV response of FePc/KJB (QDPSU) thin films. (B) Subtraction of charging current. N₂ saturated electrolytes; 50mM PBS pH 7.0 (black), 50mM NaCl pH 7.0 (cyan), 50mM NaNO₃ pH 5.5 (purple), 50mM NaHCO₃ pH 8.5 (red), 50mM Na₂SO₄ pH 6.5 (green). ω=0rpm, u=50mV/s

In Figure 6-18(A), a similar stabilised response from Cl⁻, NO₃⁻ and SO₄²⁻ was seen (Figure 6-18), despite being anions predicted to be strong ligands [181, 295, 330] of FePc and Iron in general. In NaHCO₃ the \( Q_{aw} \) for Fe(II)→Fe(III) increased, a larger portion of the FePc surface had become electrochemically active, a phenomenon hitherto only observed in KOH [67]. The NaHCO₃ produced a broader single peak (\( W_{1/2} \) = 0.256V) than with other electrolytes, ie. PBS (\( W_{1/2} \) = 0.150V). Peak broadening indicates H⁺ release from adsorbed HCO₃⁻ upon Fe(III)Pc reduction. In air cathodes, limitation from electron diffusion is expected to be more severe in NaHCO₃ media than PBS. Partial splitting of the forward Fe(II)/Fe(III) peak with FePc/KJB QDPSU air cathodes has been observed in NaHCO₃ [331], in tandem with x1.5-2.5 fold \( C_2 \) increase (\( E=-0.3V \)) with NaHCO₃ vs any other electrolyte, this indicates strong interaction between QDPSU and HCO₃⁻. No significant redox active interactions with QDPSU can be isolated from fast scan voltammetry, nor did QDPSU catalyse any anion electrooxidation/reduction in de-aerated environments. The results are summarised in Table 6-2.
Table 6-2. Influence of anion and binder on features of Fe(II)/Fe(III) redox. Electrolyte; as Figure 6-17. †Charge integration for all oxidation peaks, ‡for a single corresponding redox couple, ⃰largest reduction peak, °reduction peak where ORR occurs, ND – non-distinguishable. ω=0rpm, υ=50mV/s

<table>
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<tr>
<th>Electrolyte</th>
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<th>E_{p1} (Ox) / V</th>
<th>E_{p2} (Red) / V</th>
<th>Ox-Red</th>
<th>E’0 ‡ / V</th>
<th>W_{1/2} (Red) / V</th>
<th>ΔQ vs. Scan#</th>
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<tr>
<td>Na₂SO₄</td>
<td>QDPSU</td>
<td>0.17</td>
<td>0.407</td>
<td>0.368</td>
<td>0.039</td>
<td>0.388</td>
<td>0.168 *</td>
<td>Grow</td>
<td>3.10E-09</td>
<td></td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>QDPSU</td>
<td>0.18</td>
<td>0.090</td>
<td>-0.027</td>
<td>0.117</td>
<td>0.031</td>
<td>0.2 °</td>
<td>Shrink</td>
<td>3.76E-09</td>
<td></td>
</tr>
<tr>
<td>NaNO₂</td>
<td>QDPSU</td>
<td>0.18</td>
<td>0.398</td>
<td>0.354</td>
<td>0.044</td>
<td>0.376</td>
<td>0.295 *</td>
<td>Grow</td>
<td>5.41E-09</td>
<td></td>
</tr>
<tr>
<td>NaNO₃</td>
<td>QDPSU</td>
<td>0.24</td>
<td>0.456</td>
<td>0.407</td>
<td>0.049</td>
<td>0.432</td>
<td>0.191 *</td>
<td>Grow</td>
<td>2.87E-09</td>
<td></td>
</tr>
</tbody>
</table>

The range 1.6-5.4x10^-9 Moles cm^-2 the values of Q_an for FePc in all anions are in the same range as Table A-8 where all binders are tested in Phosphate. This indicates no anion totally blocks electron transfer in FePc. The general trend in non-buffering electrolytes was a redox couple at high potential, increasing in Q_an with consecutive scan#, whilst a peak that produced ORR active catalyst at low potential decreased with consecutive scan#.

Redox activity of FePc in PBS appears to be unique. This is supported by the observation of Contamin et al [84], that Phosphate will replace a water ligand, making E’0 of the Fe(II)/Fe(III) redox unique to PBS. From the split peak response of HCO₃^- and CH₃COO^- these ligands preferentially bind to FePc ahead of H₂O.

All anions examined (bar Cl^-) are capable of forming a monodentate (ORR active) or bidentate (inactive) ligands of metals. As such the spectroscopic series can only be...
accurately determined by repetition of this experiment with a non-complexing, non-ionic buffer. With QDPSU FePc/KJB electrodes the redox couple linked to ORR has the peak separation series:

\[ E_{pa} - E_{pc} \; : \; \text{PO}_4^{3-} < \text{Cl}^- < \text{SO}_4^{2-} < \text{NO}_2^- < \text{CH}_3\text{COO}^- < \text{NO}_3^- \]

### 6.3.4 Anion influence on QDPSU and FePc in oxygenated medium

As established in chapter 5, the 2\(^{nd}\) consecutive CV produces near stabilised response in terms of \(E_{ORR}\) and the low overpotential region is similar in the 2\(^{nd}\) and 100\(^{th}\) CV in \(O_2\).

![Figure 6-19. Effect of binder on pH swing from ORR in non-buffered electrolytes. FePc/KJB with a) Nafion or b) QDPSU binder on GC disk. 1\(^{st}\) and 2\(^{nd}\) CV. \(O_2\) saturated electrolytes; (A) 50mM CH\(_3\)COONa pH 8.9 or (B) 50mM NaCl pH 7.0. \(\omega=0\)rpm, \(u=50\)mV/s](image)

On scan#1 the reduction peak c.a. \(E=0.4\)V was absent in all electrolytes, consecutive CV created this feature in \(\text{SO}_4^{2-}, \text{NO}_3^-, \text{Cl}^-\) and \(\text{CH}_3\text{COO}^-\) but remained largely absent in \(\text{HCO}_3^-\) and \(\text{NaNO}_2\). This is also present in de-aerated media, Figure 6-18(B). This result
can be interpreted as the rate of anion ligand substitution of O$_2$, a competitive adsorption.

Peak 1 ($E_{pa}=0.285±0.01$V) occurs after O$_2$ sparge with both binders in SO$_4^{2-}$, NO$_3^-$, Cl$^-$ and CH$_3$COO$^-$, disappearing after several scans, completely absent from scan#1 for HCO$_3^-$ and NO$_2^-$

Two interpretations are possible; (1) incomplete anion surface coverage of FePc (Eq.5-1), or (2) FePc with a weakly adsorbed orientation of O$_2$, lower than NO$_3^-$ and HCO$_3^-$ in the spectrochemical series. Comparison with Figure 6-18 suggest the series occurs in the order HCO$_3^-$/CO$_3^{2-}$, H$_2$PO$_4^-$/HPO$_4^{2-}$, NO$_2^-$ > SO$_4^{2-}$, NO$_3^-$, Cl$^-$, CH$_3$COO$^-$.

Peak 2 varies $E_{pa}$ with binder but not solution anion, CH$_3$COONa; QDPSU ($E_{pa}=0.06±0.005$V), Nafion ($E_{pa}=0.022±0.005$V). NaCl; QDPSU ($E_{pa}=0.051±0.005$V), Nafion ($E_{pa}=0.022±0.015$V). For peak 2 the $E_{pa}$ difference between Nafion and QDPSU shows agreement with the relative improvement of OH$^-$ diffusion with QDPSU [309], of significant importance in unbuffered electrolytes.

The slope and potential range of a linear log$_{10}(J_k)$ vs $E$ response is a function of solution anion, the results are summarised in Table 6-3.

**Table 6-3. ORR influence by anion for FePc/KJB QDPSU thin films. Non-steady state response over high and low potential ORR limit, lowest linear $|b_c|$ value. $u=50$ mV/s, $\omega=0$ rpm.**

| Electrolyte | Binder | $|J_k|$ vs. $E$ linear region - Non-steady state $|b_c|$ $E$ (high) / $V$ | $E$ (low) / $V$ | $|b_c|$ / V dec$^{-1}$ |
|-------------|--------|-------------------------------------------------|----------------|-----------------|
| PBS         | Nafion | 0.144                                           | 0.105          | 119             |
| PBS         | QDPSU  | 0.173                                           | 0.129          | 51              |
| KCl         | Nafion | 0.012                                           | -0.018         | 81              |
| NaCl        | QDPSU  | 0.017                                           | -0.018         | 66              |
| CH$_3$COONa | Nafion | 0.017                                           | -0.008         | 80              |
| CH$_3$COONa | QDPSU  | 0.022                                           | -0.042         | 71              |
| Na$_2$SO$_4$ | QDPSU | 0.041                                           | -0.042         | 59              |
| NaHCO$_3$   | QDPSU  | 0.041                                           | -0.042         | 100             |
| NaNO$_2$    | QDPSU  | 0.002                                           | -0.047         | 62              |
| NaNO$_3$    | QDPSU  | 0.007                                           | -0.032         | 56              |

Variance in $|b_c|$ proves anion adsorption influences ORR in some cases. This may take the form of adjacent sites or mono dentate ligands, allowing mono dentate O$_2$
adsorption. At \( \nu = 50 \text{mV/s} \) the amount of viable Fe(II)Pc is limited in a partially reduced film, \( |b_c| = f(k_E) \), thus mechanism conclusions and comparison with \( \nu = 1 \text{mV/s} \) data cannot be made. The lag in FePc activity with Nafion (\( |b_c| = 119 \text{mV dec}^{-1} \)) compared to QDPSU (\( |b_c| = 51 \text{mV dec}^{-1} \)) establishes limitation from \( k_E \). The series for \( |b_c| \) is \( \text{PO}_4^{3-} < \text{NO}_3^- < \text{SO}_4^{2-} < \text{NO}_2^- < \text{Cl}^- < \text{CH}_3\text{COO}^- << \text{HCO}_3^- \). The linearity of the tafel gradient suggests that electrostatic repulsion of \( \text{CH}_3\text{COO}^- \) explanation [176] is not applicable.

QDPSU cannot produce \( \text{H}_2\text{O}_2 \) (Figure 6-13). Evidence of \( \text{H}_2\text{O}_2 \) scavenging by QDPSU was sought with thin film RRDE technique in several electrolytes. The data in Figure 6-20 was obtained following electrochemical aging in the \(-0.4 < \text{E} < 0.5 \text{V} \) range. The initial current IR current at \( \text{E} = 0.5 \text{V} \) follows a transient decay until \( \text{H}_2\text{O}_2 \) oxidation is detected at \( \text{E} = 0.2 \text{V} \).

In Figure 6-20(B) the results of \( i_D \) vs \( E \) at high over-potential are comparable, making quantitative analysis of \( i_R \) vs \( E \) simple. At low overpotential \((-0.15 < \text{E} < 0.15 \text{V})\), FePc produces \( \text{H}_2\text{O}_2 \) in \( \text{Cl}^- \) and \( \text{SO}_4^{2-} \), as in PBS, but \( \text{H}_2\text{O}_2 \) is less significant at \( E_{\text{ORR}} \) in \( \text{CH}_3\text{COO}^- \). Literature on \( \text{H}_2\text{O}_2 \) release in alkali at low overpotential [176, 208] suggests...
a different working pH in CH$_3$COO$^-$ is not the explanation. Release of H$_2$O$_2$ from FePc shows a similar dependence on potential between CH$_3$COO$^-$ and PBS with the results of Kozawa et al [176].

Viewed in conjunction with Figure 6-19 it appears either $k_3$ or $k_4$ may enhanced by acetate adsorption. No Wroblowa analysis is performed on this data, so $k_j/k_2$ is not known, thus meaning $k_j$ domination (at low $E$) and inhibition of $k_2$ with acetate cannot be determined. Potential H$_2$O$_2$ scavenging to form peroxyacetic acid can be excluded due to a) low conversion rate [332] and b) a similar proportion being released at low potential as in NaCl.

Electrode blocking from CH$_3$COO$^-$ coverage accounts for $J_L$ reduction in quiescent acetate solutions [176]. MFC tests on Iron macrocycles with acetate based artificial wastewater are anticipated to produce lower power outputs than predicted by phosphate electrolyte due to acetate adsorption identified here. This work has ramifications for proposed design of dissolved oxygen probes [333] and sensors that detect neurologically and pharmaceutically important molecules in PBS medium [334, 335] and use of cyclic voltammetry for assessment of selectivity and stability.

6.4 Stability

6.4.1 *FePc/KJB QDPSU stability in PBS*

The large $\Gamma_{FePc}$ in air cathodes increases the timescale of deactivation. The effect of QDPSU on FePc de-activation is assessed by thin films, in identical method to Figure 5-22.
Figure 6-21. FePc stability in FePc/QDPSU thin film from (A) polarisation in N\textsubscript{2} or (B) ROS production. Consecutive CV (100scans). (c) Inset is magnification of -0.2\textless E\textless 0.05V region in O\textsubscript{2}. Electrolyte; 50mM PBS, pH 7.0. \(\omega=0\)rpm, \(\nu=50\)mV/s.

In de-aerated media no FePc deactivation occurs as is the case with Nafion. The \(\Gamma_{FePc}\) increased with consecutive CV, consistent with electrochemical surface cleaning. With O\textsubscript{2} the H\textsubscript{2}Pc formation in Figure 6-21(C) was negligible, unlike with H\textsuperscript{+}-Nafion binder. \(E_{pc}\) is consistent up to scan#40 as with Nafion, as would be seen for a decrease in viable \(\Gamma_{FePc}\) on the surface. This is confirmed in Figure 6-22, where the tafel slope is plotted for scan#2 and scan#100, as predicted by Eq.2-53.
In Figure 6-22 the lines of the tafel plot are linear and parallel (decreased geometric $J_0$, consistent $|b|$). The line shifted down the axis with consecutive polarisation. This is indicative of increasing partial coverage of a blocking ligand or permanent de-activation to the active site [84], rather than a shift in reaction mechanism. From scan#2 to scan#100 $|J|$ decreased 49.2% with Nafion and 32.5% with QDPSU at $E=0.16$V. The work by Chen et al [70] suggests FePc passivation with •OH from H$_2$O. The fact that blocking appeared more extreme with Nafion than QDPSU pointed to a mobile species.

### 6.4.2 FePc/KJB QDPSU stability in other electrolytes

To establish whether deactivation occurred by anion site blocking, ROS or demetallation, current density at a potential c.a. $i_p/2$ was selected ($J=0.3$mA cm$^{-2}$) and plotted vs consecutive scan# in Figure 6-23.
QDPSU produced higher catalytic activity in PBS, NaCl and CH$_3$COONa than Nafion. After stable responses were obtained from catalyst layer consumption of O$_2$, the QDPSU electrode produced a plateau in activity c.a. $E=0.16-0.15$V from scan#10 to scan#100 in PBS, with no deterioration in this potential in NaCl, CH$_3$COONa, NaNO$_3$, NaNO$_2$, Na$_2$SO$_4$ or NaHCO$_3$. With Nafion binder sustained deterioration is seen, from scan#10 to scan #100 the decrease is 15.2mV (NaCl) and 29.3mV (PBS) with no sustained deterioration in CH$_3$COONa.

In conclusion, the de-activation of FePc showed no correlation with aqueous phase H$_2$O$_2$ (Figure 6-13). Reconciling the results in Figure 6-22 with Figure 6-23 was possible by demonstrating de-activation with QDPSU appeared finite. A situation which occurs if de-activation is from an equilibrium adsorbed ROS species, FePc-OH or FePc-(OH)$_2$, as postulate by Chen [70]. With Nafion de-metallation was not separated from this reaction but de-activation was irreversible.

6.5 Conclusions

QDPSU was shown to have a similar O$_2$ permittivity to Nafion. In PBS, the QDPSU enhanced the catalytic activity of unmodified carbon, originally a 4e$^-$ ORR active site is produced which becomes redox active and non-catalytic on initial polarisation. The
chelation ability of Dabco may be instrumental in lowering O_2 binding energy by weakening the dioxygen pi-bond, indicating the use of F-tiR investigation to establish splitting of the O_2 bond strength is warranted for electrodes at various potentials.

The FePc catalyst layers demonstrated greater stability when using QDPSU in place of Nafion, though this improvement was not linked to decreased H_2O_2 release. The change in tafel plot with consecutive scan showed the number of viable sites remained higher with QDPSU, as if the process described by Chen et al [70] were partially mitigated with a covering of the anion exchange material. De-metallation of the FePc was also reduced with implementation of QDPSU relative to Nafion.
Chapter 7. Results - Performance and stability of cation and anion exchange binder in wastewater half cells and Microbial Fuel Cells
7.1 Introduction

7.1.1 EIS analysis of cathodes

Impedance spectroscopy was used to quantify sources of impedance by resolving them in the time domain. Once established, the influence of catalyst binder in the air cathode was used to separate the changes in the types of impedance in PBS, NaCl and Phosphate Buffered Wastewater. Some of these techniques and equations are used in chapter 8 for membranes. Relating these observations to performances in MFC’s, conclusions on the role of binder in cell operation were made.

7.2 Results and Discussion

7.2.1 Impedance response of thin film electrodes in $N_2$ and $O_2$

EIS has not been applied to unpyrolysed FePc/C material in phosphate buffer [84, 184], background impedance spectra were obtained for thin films to build up the theory. The thin film technique accurately establishes features relating to $O_2$ electrocatalysis by providing a totally anoxic FePc film, requiring a glove box to obtain with air cathodes. Focus was temporarily reverted to Nafion, in order to discount the QDPSU/$O_2$ redox activity observed in chapter 6. This permitted charge and ion percolation through the FePc/KJB film to be resolved in the time domain, in the absence of faradic reaction. The thin film technique (chapter 4) was applied to FePc/KJB Nafion film.
Figure 7-1. LF Impedance spectra of thin FePc/KJB Nafion film in (A) de-aerated (B) or aerated PBS media. Applied frequency, $f=10,000\text{Hz} \rightarrow 0.1\text{Hz}$.

The LF portion of the impedance spectra for FePc/KJB films is shown in Figure 7-1 in O$_2$ and N$_2$ saturated PBS. The main aspects of the complex plane plot are:

- A single arc is observed relating to ORR charge transfer ($R_{ct}$). It starts to become prevalent at $E \leq 0.22\text{V}$, starting at $f=316\text{Hz}$.
- At $E=0.28\text{V}$ the complex plane plot is identical in O$_2$ and N$_2$ at all frequencies, bar a +ve shift in $Z'$ of $1\Omega$ in N$_2$.
- Deviation from the $R_{ct}$ semi-circle at $E=0.17\text{V}$ is seen clearly at $f<0.4\text{Hz}$. The gradient of the deviation from an $RC$ time constant is dependent on potential. At
\[ 0.28 \leq E \leq 0 \text{V} \] the arc is skewed with \( -dZ''/dZ' < 1.0 \). At \( E < 0 \text{V} \) the gradient increases higher than warburg behaviour \((m > 1)\) indicating an approach to reflective finite transmissive behaviour [336] with a CPE as opposed to a purely capacitive boundary.

- At \( 0.08 > E > 0 \text{V} \), \( R_{ct} \) starts to increase (Table 7-1).
- Resistance of adsorption \((R_{ads})\) [184] could not be isolated in thin films within the \(10 \text{kHz} > f > 0.1 \text{Hz} \) range.
- Eq.2-110 or 4-26 could not be applied in the case of thin films with this frequency range, as no overlap between time constants of Warburg diffusion and \( R_{ct} \) is seen.

### Table 7-1. Influence of applied potential on \( C_z \) and \( R_{ct} \) for FePc/KJB Nafion thin film in \( \text{O}_2 \) and \( \text{N}_2 \). Determined from least squares fit and manual arc fit respectively.

<table>
<thead>
<tr>
<th>( E ) / ( \text{V} )</th>
<th>0.35</th>
<th>0.28</th>
<th>0.22</th>
<th>0.17</th>
<th>0.12</th>
<th>0.07</th>
<th>0</th>
<th>-0.15</th>
<th>-0.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>In ( \text{O}<em>2 ) ( R</em>{ct} / \text{Ohm} \text{cm}^2 )</td>
<td>--</td>
<td>1782</td>
<td>374</td>
<td>230</td>
<td>213</td>
<td>400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In ( \text{N}_2 ) ( C_z / \text{F cm}^2 )</td>
<td>6.89E-04</td>
<td>1.09E-03</td>
<td>2.42E-03</td>
<td>7.84E-03</td>
<td>7.16E-04</td>
<td>1.09E-03</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Eq.2-120 was applied to the thin film at the LF limit to generate the capacitance reported in Table 7-1. The plateau of \( C_z = 1.2 \text{mF cm}^2 \) seen at \( E > 0.2 \text{V} \) in CV (0rpm) is different to that observed in Table 7-1 with capacitance increasing with decreasing potential. With EIS in \( \text{O}_2 \), the total capacitance was not accurately determined due to convolution from ORR. This is due in part to the fast scan rate \((\nu = 20 \text{mV/s})\). As there is little difference in \( C_z \) between \( \text{O}_2 \) and \( \text{N}_2 \) saturated electrolyte it can be deduced that adsorbed \( \text{O}_2 \) at high potential, Fe(III)Pc-\( \text{O}_2^- \), does not drastically alter surface state capacitance \((C_{ads})\).

Table 7-1 shows the \( R_{ct} \) value in \( \text{O}_2 \), the value in \( \text{N}_2 \) being immeasurably high. \( R_{ct} \) becomes significantly higher near to \( \text{OCP} \) and drops to a measured minimum of 213 \( \Omega \text{cm}^2 \) at \( E = 0.07 \text{V} \). The \( R_{ct} \) increases again between \( E > 0.08 \text{V} \), showing consistency with the transition range between two mechanisms described in Figure 5-5.
An equivalent circuit fit had to be used to generate an $R_{ct}$ value at $OCP (E=0.28V)$ for the FePc/KJB Nafion film as manual fitting of a large arc is arbitrary with a large degree of error. In thin films Warburg limitation of oxygen diffusion was present at $E \leq 0.22V$, above this potential and in $N_2$ another diffusion component had to be placed in the circuit ($O_2$ diffusion could be removed). This Warburg diffusion was placed in series with a constant phase element (see Figure 7-10). The resulting value of $R_{ct}=8.94 \text{k}\Omega \text{ cm}^2$ equated to $J_c=8.3 \times 10^{-7} \text{ A cm}^2$, a value x4.2 higher than that observed in Table 7-1 from extrapolating the tafel slope of the alkali mechanism.

7.2.2 High frequency ion diffusion through thin films

Figure 7-2 depicts the response of 2-3μm thick FePc/KJB films with aged in bottle (1.5 year) QDPSU binder in de-aerated media. Two distinct features occur, an ultra-high frequency arc (discussed section 7.2.6) and a high frequency electrode resistance was shown to be diffusive by linear regions in the $(Z)$ vs. $\tilde{\omega}^{-0.5}$ plot at high frequency only, in Figure 7-2 [96, 337, 338]. An example with Nafion binder is shown in with FePc/KJB thin films (Figure 7-4), present in aerated and de-aerated media. The markers $f_1$ and $f_2$ represent the high and low frequency limits of the linear $Z'$ vs. $\tilde{\omega}^{-0.5}$ plot. In all cases the marker $f_2$ increased when plotting the real component only; $Z'$ vs $\tilde{\omega}^{-0.5}$ as opposed to $Z$ vs $\tilde{\omega}^{-0.5}$ [87]. The gradient of the $Z'$ vs $\tilde{\omega}^{-0.5}$ plot decreased slightly compared to $Z$ vs $\tilde{\omega}^{-0.5}$ (though not by a factor of $\sqrt{2}$ as mathematically predicted [87]). To extract kinetic information, Eq.2-96 has been used to convert the slopes in $Z$ vs. $\tilde{\omega}^{-0.5}$ plots to $Z'$ vs. $\tilde{\omega}^{-0.5}$ in order to report $\sigma$ values using radial frequency [96]. $\tilde{\omega}_1$ and $\tilde{\omega}_2$ correspond to $f_1$ and $f_2$ when the plot is expressed in radians s$^{-1}$. As there is no solvated $O_2$ for a faradic reaction into which electrons can be sunk, the thin film saturates with charge and the warburg regime displays reflective finite diffusion at the high frequency limit as the plot tends towards charge accumulation $(dZ''/dZ>>1)$. 
Figure 7-2. (A) High and (B) Mid frequency complex plane response, invariant of applied potential in FePc/KJB-QDPSU thin film in de-aerated media. Frequency range $1\text{MHz}>f>0.1\text{Hz}$. $E=0.35\text{V}$. Electrolyte; 50mM PBS, pH 7.0.

Figure 7-3. Corresponding warburg plot to data in Figure 7-2. Data of (A)(B) imaginary and (C) real impedance as a function of the root inverse of radial frequency.

With both Nafion and QDPSU, two linear $Z'$ vs. $\tilde{\omega}^{-0.5}$ regions were identified at mid-high frequency. In FePc/KJB thin films with Nafion binder regions occurred at; 1) $8260>\tilde{f}>2500\text{Hz}$, $R^2>0.9991$ and 2) $204>\tilde{f}>40\text{Hz}$, $R^2>0.9993$. Though these ohmic contributions are relatively small in the thin film (2-3 Ohm cm$^2$ each), their importance
becomes apparent in thick air cathodes and wastewater electrolyte. In the $-Z''$ vs $\tilde{\omega}^{-0.5}$ plot, Figure 7-4(A), this region is not linear as with QDPSU, Figure 7-3(A). The presence in both electrodes allows both singlet oxygen diffusion and $O_2$ chelation to be discounted as an explanation and suggests a capacitive element occurs in series with the Warburg element within the same time constant.

Figure 7-4. (A) $Z'$ vs. $\tilde{\omega}^{0.5}$ and (B) $-Z''$ vs. $\tilde{\omega}^{-0.5}$ plot to illustrate diffusive control in thin FePc/KJB Nafion film. $E=0.35V$. Electrolyte: 50mM PBS, pH 7.0.

Figure 7-5. HF linear regions of $Z$ vs. $\tilde{\omega}^{-0.5}$ plot in thin FePc/KJB Nafion film. Expressed as $\sigma$ vs $E$ for diffusion controlled behaviour in frequency ranges i) 8kHz>$f>$2kHz, or ii) 200Hz>$f>$60Hz. Quiescent electrolyte of $N_2$ sat. or $O_2$ sat. 50mM PBS, pH 7.0.
In Figure 7-4 the Warburg diffusion parameter for the Nafion electrode is plotted as a function of potential. Similar gradients were observed at all potentials (Figure 4-4 bottom) in O\textsubscript{2} and N\textsubscript{2}. The main features of this plot are:

For the highest frequency range (8kHz>f>2kHz):
- The $Z'$ value and Z value form a plateau at $f>f_2$, this indicates that in this high frequency no capacitance is in series with this diffusive element.
- The dip in $\sigma$ at c.a. $E=OCP$ in O\textsubscript{2} indicates a charge migration process [98, 99] with FePc, the speed of which is marginally increased with adsorbed O\textsubscript{2}.
- Diffusion appears faster in the presence of O\textsubscript{2} suggesting the minority charge carrier utilises O\textsubscript{2}. I.e. the ion interacts with FePc-O\textsubscript{2} as anticipated by [339].

For the 2\textsuperscript{nd} frequency range (200Hz>f>60Hz):
- The $Z'$ value and Z value increases at $f>f_2$, this indicates a capacitance is in series with this diffusive element or $f_2$ occurs at a higher frequency still.
- The dip in $\sigma$ presents an anticipated minima c.a. 0.2V in O\textsubscript{2} and 0.16V in N\textsubscript{2}, this potential is somewhat more negative than $OCP$ (0.28V) and is discussed below.
- The difference in $\sigma$ between O\textsubscript{2} and N\textsubscript{2} is negligible at potentials above 0.22V and below 0V, indicating O\textsubscript{2} does not affect transport of this limiting species.

It was established by Albery and co-workers that a characteristic of the Warburg coefficient for limiting ion diffusion is a limited dependence of potential [340]. The Warburg coefficient shows a minima c.a. $E^{\prime\prime}$ of a redox, this can be associated with limiting electron diffusion [103] or limiting ion diffusion [98, 99] when the ion interacts with a redox centre. The minima is due to the fact that the product of [O]*[R] is smallest when [O]=[R], referring to the entire complex [98].

It is possible that the low frequency response could be the same redox Fe(II)/Fe(III) couple; it is predicted that the minima is skewed from the formal potential when the log ratio of the chemical activity coefficients $\ln([a_{ox}/a_{red}])$ is large or very negative [98]. Using Eq.2-100 a negative shift in Warburg minima of 0.08V in O\textsubscript{2} and 0.12V in N\textsubscript{2} would equate to an $a_{ox}/a_{red}$ ratio of 565 in O\textsubscript{2} and 13446 in N\textsubscript{2}. Alternatively it corresponds to another redox couple other than that which controls $OCP$. Two potential explanations; 1) a mixed case of resistance from both ion diffusion and accompanying electron diffusion, or 2) a secondary effect of ion diffusion, being enhanced when able to utilise free FePc sites.
Eq.2-98, Eq.2-112, Eq.2-113 are utilised with several assumed concentrations, ie. [OH⁻] = 10⁻¹⁰ Mole cm⁻³, [O₂] = 5.67x10⁻¹⁰ Mole cm⁻³ and [Na⁺] = 7.88x10⁻⁵ Mole cm⁻³ and maximum δfilm measurements of 2.5x10⁻⁴ cm ±20% (see section 10.7.2). The obtained diffusion constants (1.24x10⁻¹¹, 9x10⁻⁴ and 7.8 cm² s⁻¹ respectively) are not in the same order of magnitude as the anticipated 10⁻⁶-10⁻⁸ cm² s⁻¹ for ions in solution. Thus OH⁻, O₂ and Na⁺ may be discounted as either rate limiting diffusive species or limiting charge carriers in Figure 4-4.

An attempt to model the scenario of exclusive electron diffusion control was made with Eq.2-115 and Eq.2-116 by the treatment shown in appendix Figure A-19 using Cdiff, the capacitance extrapolated from the steepest portion of the -Z'/Z' plot in Figure 7-1. This method avoids the requirement for known concentrations of the exact diffusing species. By assuming the thin film thickness (0.00038cm) the electron diffusivity of D_E=2.3-2.5x10⁻⁴ cm² s⁻¹ is obtained, clearly D_E from electron hopping is not the limiting factor in thin Nafion films. The possibility of electron hopping along diffusion distances less than the entire length of the film is excluded, as the diffusion boundary frequency was related to film thickness. To see which Warburg co-efficient the Cdiff capacitance is related to, Eq.2-123 is applied to the σ values in Figure 4-4 and δ_f = 0.00038cm assumed. For the E=0.35V data the c.a 45 Ω cm² s⁻⁰·⁵ produces D=5.4x10⁻⁶ cm² s⁻¹, an entirely plausible link, whilst the c.a 305 Ω cm² s⁻⁰·⁵ produces 1.18x10⁻⁷ cm² s⁻¹, a value rather low for limiting ion diffusion and a high value for electron hopping.

In cases where an ion does not interact with a site but merely diffuses through a medium the Warburg co-efficient is not a function of potential [101]. The minima with E°' seen in Figure 4-4 asserts a scenario of coupled ion/electron diffusion limitation, with precedence in the literature, whereby Coowar et al claim that adsorbed anionic oxygen is a charge carrier [194] and the process is influenced by solution anion. A scenario that can occur when diffusivity of the electron is in the region of 1-1000 times greater than that of the ion [101].

7.2.3 AC field phase lag in Nafion/QDPSU air cathodes

At potential proxy to OCP, a 10mV AC amplitude produces a double layer current that dwarfs ORR at high and mid frequency. Oxygen concentration is expected to remain
constant throughout the catalyst layer, a feat difficult to achieve with N₂ or O₂ sparging of an air cathode. The aim of EIS investigation on air cathodes is to assess to what degree anion and cation exchange binders limit electrode performance.

In Figure 7-6 the phase angle (φ) is plotted as function of frequency for each air cathode. QDPSU produces a smaller phase angle over the frequency range 10,000Hz>f>0.03Hz. A response of φ=45º is anticipated for limiting ion diffusion, the electric field permeation requires the movement of charge carriers to maintain electroneutrality this indicates the movement of H₂PO₄⁻, HPO₄²⁻, OH⁻, H⁺ and Na⁺ ions does not control the phase lag in PBS buffer.

### 7.2.4 High frequency ion diffusion in pores of Nafion and QDPSU

To resolve whether the phase lag is purely capacitive or mixed diffusive-capacitive a linear relationship was sought between; 1) total impedance (Z) vs. ω⁻¹, or 2) (Z) vs. ω⁻⁰.⁵. A linear -Z'' vs. ω⁻¹ correlation was found at very low frequency (84mHz>f>10mHz). The lack of linear Z vs. ω⁻⁰.⁵ behaviour at low frequency at E=−0.3V denotes no O₂ mass transport limitation in air cathodes, as anticipated. Table 7-2 contains the gradient of the highest frequency linear aspect in the Z vs ω⁻⁰.⁵ plot, the f² range was difficult to report due to obscuring from Rct. The result from applying each
candidate for limiting charge carrier is presented in Table 7-3, molarity in the film or solution is the input. The lower binder loading may be a factor in determination of diffusion co-efficients in air cathodes.

Figure 7-7. Total electrode impedance, $Z$ vs. $\tilde{\omega}^{0.5}$, for high frequency diffusion related impedance of air cathodes as a function of binder. Example of Nafion binder shown (inset=PTFE). Air cathodes and conditions outlined in Figure 7-6.

Table 7-2. Air cathode binder effect on high frequency Warburg co-efficient. Resulting slopes and linear regions. Calculated film thickness; 0.01cm. Electrolyte; 50mM PBS, pH7.

<table>
<thead>
<tr>
<th>Binder</th>
<th>$f_1$ /Hz</th>
<th>$f_2$ /Hz</th>
<th>$Z$ at $f^{0.5}$= 0</th>
<th>$\sigma$ / ( \Omega \ cm^2 s^{-0.5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>QDPSU</td>
<td>1791</td>
<td>73.31</td>
<td>51.9</td>
<td></td>
</tr>
<tr>
<td>PTFE</td>
<td>3605</td>
<td>83.42</td>
<td>429.1</td>
<td></td>
</tr>
<tr>
<td>Nafion</td>
<td>6093</td>
<td>69.44</td>
<td>284.4</td>
<td></td>
</tr>
</tbody>
</table>
Table 7-3. Utilising data obtained in Table 7-2 and testing various species that may cause a diffusion limiting scenario. The factor $d$ is produced with Eq.2-114 to search for evidence of electron limited diffusion.

<table>
<thead>
<tr>
<th>Limiting Charge Carrier</th>
<th>n</th>
<th>$[X]$ Mole cm$^{-3}$</th>
<th>$D$ cm$^2$ s$^{-1}$</th>
<th>$f_3$ / Hz</th>
<th>$d / \mu$m</th>
<th>Binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma$ PO$_4$</td>
<td>1</td>
<td>5.00E-05</td>
<td>5.09E-09</td>
<td>15.941</td>
<td>1.61E-05</td>
<td>QDPSU</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5.00E-05</td>
<td>7.44E-11</td>
<td>22.616</td>
<td>1.64E-06</td>
<td>PTFE</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>5.00E-05</td>
<td>1.69E-10</td>
<td>2.774</td>
<td>7.05E-06</td>
<td>Nafion</td>
</tr>
<tr>
<td>H$^+$ / OH$^-$</td>
<td>1</td>
<td>1.00E-07</td>
<td>1.27E-03</td>
<td>15.941</td>
<td>8.06E-03</td>
<td>QDPSU</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.00E-07</td>
<td>1.86E-05</td>
<td>22.616</td>
<td>8.19E-04</td>
<td>PTFE</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.00E-07</td>
<td>4.23E-05</td>
<td>2.774</td>
<td>3.53E-03</td>
<td>Nafion</td>
</tr>
<tr>
<td>H$_2$PO$_4$</td>
<td>1</td>
<td>2.11E-05</td>
<td>2.84E-08</td>
<td>15.941</td>
<td>3.81E-05</td>
<td>QDPSU</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2.11E-05</td>
<td>4.16E-10</td>
<td>22.616</td>
<td>3.87E-06</td>
<td>PTFE</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2.11E-05</td>
<td>9.46E-10</td>
<td>2.774</td>
<td>1.67E-05</td>
<td>Nafion</td>
</tr>
<tr>
<td>HPO$_4$$_2^{-}$</td>
<td>2</td>
<td>2.88E-05</td>
<td>9.55E-10</td>
<td>15.941</td>
<td>6.99E-06</td>
<td>QDPSU</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.88E-05</td>
<td>1.40E-11</td>
<td>22.616</td>
<td>7.09E-07</td>
<td>PTFE</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.88E-05</td>
<td>3.18E-11</td>
<td>2.774</td>
<td>3.06E-06</td>
<td>Nafion</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>1</td>
<td>7.88E-02</td>
<td>2.05E-15</td>
<td>15.941</td>
<td>1.02E-08</td>
<td>QDPSU</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>7.88E-02</td>
<td>2.99E-17</td>
<td>22.616</td>
<td>1.04E-09</td>
<td>PTFE</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>7.88E-02</td>
<td>6.81E-17</td>
<td>2.774</td>
<td>4.47E-09</td>
<td>Nafion</td>
</tr>
<tr>
<td>FePc loading ($\Gamma$$_{FePc}$)</td>
<td>1</td>
<td>6.25E-05</td>
<td>3.26E-09</td>
<td>15.941</td>
<td>1.29E-05</td>
<td>QDPSU</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>6.25E-05</td>
<td>4.76E-11</td>
<td>22.616</td>
<td>1.31E-06</td>
<td>PTFE</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>6.25E-05</td>
<td>1.08E-10</td>
<td>2.774</td>
<td>5.64E-06</td>
<td>Nafion</td>
</tr>
<tr>
<td>Electro-active FePc ($\Gamma$$_{FePc}$)</td>
<td>1</td>
<td>3.77E-07</td>
<td>8.96E-05</td>
<td>15.941</td>
<td>2.14E-03</td>
<td>QDPSU</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3.77E-07</td>
<td>1.31E-06</td>
<td>22.616</td>
<td>2.17E-04</td>
<td>PTFE</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3.77E-07</td>
<td>2.98E-06</td>
<td>2.774</td>
<td>9.36E-04</td>
<td>Nafion</td>
</tr>
<tr>
<td>O$_2$ (Not a charge carrier)</td>
<td>4</td>
<td>5.67E-07</td>
<td>1.55E-07</td>
<td>15.941</td>
<td>8.89E-05</td>
<td>QDPSU</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5.67E-07</td>
<td>2.26E-09</td>
<td>22.616</td>
<td>9.03E-06</td>
<td>PTFE</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>5.67E-07</td>
<td>5.15E-09</td>
<td>2.774</td>
<td>3.89E-05</td>
<td>Nafion</td>
</tr>
</tbody>
</table>

After establishing in section 7.2.2. couple ion/electron diffusion resulted in diffusive behaviour various charge carrier scenarios were tested, though contributions are frequently left unseparated in analysis [105] producing a joint diffusion co-efficient. This may appear to be the case in air cathodes aswell as the thin film. Since the transition from Warburg control to capacitance occurs via the relation $\tilde{\delta} \propto D/\delta t^2$, the transition region could be expected to occur at a frequency x700 higher in the TFE than the Nafion air cathode, considering the layer is x26 thinner [88]. The influence of binder concentration and pore volume will mean relationship between diffusion co-efficient is not exact. It is worth noting this type of analysis would not be possible in ultra-thin films (<0.5μm) [87].
Scrutinizing the scenarios generated in Table 7-3 with the $\delta f/\delta_3/5.12$ (Eq.2-114) it can be suggested that this equation does not accurately describe the phenomenon or else electrons do not diffuse the whole film thickness (0.01cm). It could be assume that this process is not electron diffusion.

Nb. The $[\text{HPO}_4]^{2-}$ could potentially be considerably lower than bulk concentration at the reaction site. With Nafion binder the linear region occurred over a large frequency range ($6.1\text{kHz}<f<155\text{Hz}$) with $R^2=0.9995$. In the study by Contamin et al [84], a lower frequency region of 4Hz to 0.24Hz produced a linear response in thin FePc binder-less films in PBS, attributed to electron hopping. The conductive nature of the pores in the carbon supported catalyst layer makes this possibility less likely. They attributed a scenario of $\tilde{\Gamma}_{\mu\nu}$ being the charge carrier, splitting the response of diffusion of holes and electrons by applying Eq.2-98 to the $\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Fe}^{2+})$ and $\text{Fe}^{2+}/(\text{Fe}^{3+}+\text{Fe}^{2+})$ ratio respectively. The ratio cannot be established at $E=0.28\text{V}$ in aerobic air cathodes, the diffusion co-efficient cannot be split in such a fashion. It is clear from Figure 6-21 that $\text{Fe}(\text{III})>\text{Fe}(\text{II})$ at $E=0.28\text{V}$. The amalgamated diffusion co-efficient being 4 and 6 orders of magnitude larger than that for electrons and holes respectively in [84], as would be anticipate for the addition of the carbon support.

In Table 7-2, the $\sigma$ value occurred in the order PTFE>Nafion>QDPSU. The upper frequency limit could only be reliable obtained with QDPSU ($1790>f>890\text{Hz}$). With Nafion ($6093>f>155\text{Hz}$) the detectable low frequency limit was increased, being linked to anion retardation as opposed to cation selectivity [258].

For QDPSU, “$\sigma$” is in the order of magnitude of an ion diffusing through a film of a redox active material of the opposing charge immobilised on graphite in an aqueous systems [98]. Using Eq.2-114 at $d|Z''/dZ'=2$ the diffusion distance $(d)$ is obtained. This equation is derived for a sharp transition for Warburg to reflective finite limit. In the case of porous electrodes where the low frequency limit $d|Z''/dZ'
eq\infty$, the maximum value was 2.12 (PTFE) and 2.16 (Nafion). This behaviour is well documented with porous electrodes [87, 88]. The transition frequency ($f_3$ or $\tilde{\sigma}_3$) occurs at different points, close to $f_2$ or at significantly lower frequency. This uncertainty introduces a potential
source of error in reporting \( d \) or \( \delta_f \) using this equation. The number of electrical charge transferred \( "n" \) was set at 1 [94, 96], the charge on most carriers in the electrolyte.

To summarise the effect of binder, thickness and anion, the findings are presented in Table 7-4 and evaluated in following sections.

Table 7-4. Summary of linear regions in \( Z \) vs. \( f^{-0.5} \) plots at high frequency, EIS of half-cells at potentials approximate to \( OCP \).

| Experiment   | Binder / % wt. | Electrolyte / Dissolved Gas | Poised \( E \) (V) / Amplitude (V) | Linear range in \( Z \) vs. \( f^{-0.5} \) high \( f_1 \) / low \( f_2 \) \( \Omega \) cm\(^2\) s\(^{-0.5}\) | \( \sigma \) / \( \Omega \) cm\(^{-2}\) s\(^{-0.5}\) | \( \sigma = f(E)? \) | Change in \( \frac{dZ}{df} \) (\( \mu \)m) at \( f < f_2 \) of linear region | Z increase / Z plateau |
|--------------|----------------|-----------------------------|----------------------------------|-------------------------------------------------|-----------------|-----------------|-----------------|----------------|----------------|
| Thin film    | Nafion/156%    | PBS / \( O_2 \)            | 0.22 / 0.01                      | 8260 / 2060 / 268 NO                  | Plateau m      | Increase m      | Increase m      | Increase m      |                |
| Thin film    | Nafion/156%    | PBS / \( N_2 \)            | 0.22 / 0.01                      | 8260 / 2060 / 300 NO                  | Plateau m      | Increase m      | Increase m      | Increase m      |                |
| Thin film    | Nafion/156%    | PBS / \( O_2 \)            | 0.22 / 0.01                      | 204 / 40 / 39.1 YES                  | Increase m     | Increase m      | Increase m      | Increase m      |                |
| Thin film    | Nafion/156%    | PBS / \( N_2 \)            | 0.22 / 0.01                      | 204 / 40 / 39.1 NO                   | Plateau m      | Decrease m      | Decrease m      | Decrease m      |                |
| GDC          | Nafion/15%     | PBS / Air                  | 0.28 / 0.01                      | 6100 / 155 / 284 N/A                | Increase m     | Increase m      | Increase m      | Increase m      |                |
| GDC          | QDPSU/10%      | PBS / Air                  | 0.28 / 0.01                      | 1800 / 900 / 51.9 N/A               | Plateau m      | Increase m      | Increase m      | Increase m      |                |
| GDC          | PTFE/10%       | PBS / Air                  | 0.28 / 0.01                      | 3600 / 1260 / 429 N/A               | Increase m     | Increase m      | Increase m      | Increase m      |                |
| Air cathode  | QDPSU/10%      | PBS / Air                  | 0.20 / 0.01                      | 12260 / 4300 / 290 YES              | Increase m     | Increase m      | Increase m      | Increase m      |                |
| Air cathode  | QDPSU/10%      | PBS / Air                  | 0.20 / 0.01                      | 10300 / 5115 / 128.6 YES            | Plateau m      | Increase m      | Increase m      | Increase m      |                |
| Air cathode  | NaCl/Air       | PBS / Air                  | 0.20 / 0.01                      | 24700 / 890 / 9810 YES              | Plateau m      | Increase m      | Increase m      | Increase m      |                |
| Air cathode  | WW+PBS/10%     | PBS / Air                  | 0.20 / 0.01                      | 110 / 23 / 187 YES                  | Plateau m      | Plateau m       | Plateau m       | Plateau m       |                |
| Air cathode  | QDPSU/10%      | WW+PBS / Air               | 0.20 / 0.01                      | 110 / 23 / 187 YES                  | Plateau m      | Plateau m       | Plateau m       | Plateau m       |                |

In Figure 7-6 the final column, “change in gradient at frequencies lower than linearity”, indicates whether capacitance is present at low frequency (increase \( m \)), meaning that \( f_2 \) may be inaccurate, or whether a finite diffusion barrier has been reached at low \( f \) (decrease \( m \)), indicating an accurate \( f_2 \). Thickness and binder content of the thin film differs from the air cathode, thus frequency (\( f_1 \)) is not as comparable as \( \sigma \).

### 7.2.5 Phosphate and Chloride effect on diffusive resistance

The role of counter-anion was examined in FePcKJB QDPSU air cathodes and the properties of the Warburg parameter presented in Figure 7-8.
At OCP, the $\sigma$ is x3.3 larger with Chloride than Phosphate. At $E<0.05V$ polarisation in NaCl, $\sigma$ decreased from $\sigma=423\Omega$ cm$^2$ s$^{0.5}$ at OCP and $E=0.2V$ respectively. This could be interpreted as generation of a more motile charge carrier (such as OH$^-$$^-$$^-$. $Z'$ vs $\omega^{0.5}$ slope inversion was seen in NaCl at $0V$ to $E>-0.2V$, this phenomenon cannot be explained in terms of rapid alkalination. With PBS buffering a $\sigma$ minima occurred at OCP, contrary to NaCl. This would indicate the divalent anion (HPO$_4^{2-}$) did improve charge compensation over H$_2$PO$_4^-$ resulting from alkalinity.

In Figure 7-8(A) the similarity in $\sigma$ for PBS and NaCl shows initial molarity of the charge carrier is within an order of magnitude. In Table 7-4, the $Z'$ vs $\omega^{0.5}$ frequency range is largest for Nafion>PTEF>QDPSU. Therefore limitation from cationic diffusion (ie. Na$^+$) is not the case.

The $\sigma$ vs $E$ plot in PBS is similar for Nafion thin film, Figure 4-4 as for air cathode, Figure 7-8(A), indicating chemistry relating FePc with Phosphate. In Table 7-4, $\sigma$ values are within 40-430 Ohm cm$^2$ s$^{0.5}$ across all electrodes with different binders. A notable exception is the addition of wastewater to the QDPSU air cathode, data from

---

**Figure 7-8.** HF warburg parameter (A) $\sigma$ vs $E$, and (B) $f_1$ vs. $E$ and $f_2$ vs. $E$, in FePc/KJB QDPSU air cathodes in electrolytes of a) 50mM PBS, pH7.0 b) 50mM NaCl, pH 7.0 or c) Primary clarifier influent with 50mM PBS, pH 7.0.
Figure A-21 is converted from Hz and displayed in Figure 7-8(A). A minima at 0.1V overlaps the Dabco redox from \( \sigma=10,000-7,000 \) Ohm cm\(^2\) s\(^{0.5}\), equating to a rise of electrode resistance of 100-120\(\Omega\) cm\(^2\) which is not present in PBS alone. This shows another pollutant from wastewater is interacting with Dabco, which is likely redox active, according to the presence of a minima [101]. A drastic loss of ion diffusivity appears to be indicated for QDPSU in wastewater when relating Figure 7-8(A) to Eq.2-98.

### 7.2.6 Impedance spectra of QDPSU and Nafion air cathodes in PBS

In Figure 7-9, FePc/KJB air cathodes are mounted in a GDC. Binder loading is 10% wt. is applied for QDPSU, PTFE and Na-Nafion. The important aspects of nyquist impedance spectra are displayed. The entire frequency spectrum is examined.

![Impedance spectra](image)

**Figure 7-9.** -Z” vs. Z’ plots of air cathodes in Figure 7-6. HF region (A), LF region (B) and Mid freq. region (C), (D) and (E) of Nafion, QDPSU and PTFE binder respectively. Red line=Warburg gradient \((m=1)\), orange=linear Z vs. \( \omega^{0.5} \) range.
Table 7-5. Characteristics of high and mid frequency region displayed in Figure 7-9

<table>
<thead>
<tr>
<th>Binder</th>
<th>( R_n / \Omega \text{ cm}^2 )</th>
<th>( R_0 / \Omega \text{ cm}^2 )</th>
<th>( f_p / \text{Hz} )</th>
<th>( Y'' / \Omega \text{ cm}^{-1} )</th>
<th>( C_{\text{HF}} / \text{ F cm}^{-2} )</th>
<th>( R_{w,\infty} / \Omega \text{ cm}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td>-56.24</td>
<td>70.59</td>
<td>70484</td>
<td>1.45E-08</td>
<td>1.78E-08</td>
<td>68.6</td>
</tr>
<tr>
<td>PTFE</td>
<td>-57.52</td>
<td>85.49</td>
<td>70484</td>
<td>1.32E-08</td>
<td>1.58E-08</td>
<td>80.7</td>
</tr>
<tr>
<td>QDPSU</td>
<td>-62.10</td>
<td>73.53</td>
<td>70484</td>
<td>1.34E-08</td>
<td>1.66E-08</td>
<td>74.4</td>
</tr>
</tbody>
</table>

The HF response of the air cathodes produced an arc that extrapolated to negative \( Z' \) value at \( f>1 \text{MHz} \), a capacitance which appeared to be in parallel with solution resistance. As this feature is not a source of internal resistance it is not evaluated but discussed in the appendix section 10.6.2.

From Figure 7-9, \( R_0 \) of the HF time constant was linked to the Warburg co-efficient by \((R_{w,\infty}-R_0)\) as in (see Figure A-18). Application of Eq.2-110 and Eq.2-111, using the HF capacitance rather \( C_{\text{H}} \) found that values for \( \sigma \) were dissimilar when compared to the \( Z \) vs \( \omega^{-0.5} \) plot in Table 7-2. Using this method the \( \sigma \) values for PTFE were larger than Nafion. For a \( R_{w,\infty}-R_0 \propto \sigma^2 \) relationship \([35] \sigma=3-5x10^4 \text{ Ohm cm}^2 \text{ s}^{-0.5} \) is followed as opposed to a \( R_{w,\infty}-R_0 \propto \sigma \) relationship \((\sigma=8-24x10^8 \text{ Ohm cm}^2 \text{ s}^{-0.5})\), so was deemed an unreliable method for \( \sigma \) determination. This indicated the HF arc was not linked to the diffusion process and could be neglected as a source of electrode impedance.

As a result of convolution from this capacitance in parallel with \( R_t \) the HF and LF regions were treated separately; an equivalent circuit was applied to the LF only, Figure 7-10(C). This approach produced the lowest \( \chi^2 \) of any equivalent circuit fit, and has been used before with FePc films [84]. A fixed value of \( R_{w,\infty} \) from Table 7-5 was placed in equivalent circuit 4-9 (C) as \( R_t \). This approach allowed accurate determination of \( R_c \) as a priority. This was evaluated from the \%error report for \( R_c \) in the Nova programme.
Figure 7-10. Equivalent circuit (C) fit to mid frequency (A) or low frequency (B) data in NOVA software for FePc/KJB (Nafion) air cathodes poised at E=0.28V.
Electrolyte; 50mM PBS, pH 7.0.

Table 7-6. Characteristics of LF region displayed in Figure 7-10. A=0.2826cm²

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<th>Binder</th>
<th>$C_x$ ($\times 10^5$)</th>
<th>CPE</th>
<th>CPE</th>
<th>$Z_w$</th>
<th>$R_w+R_{ion}$</th>
<th>$R_{ct}$ / Ohms</th>
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<td>0.804</td>
<td>4.61E-01</td>
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<td>5.41E+06</td>
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<tr>
<td>QDPSU</td>
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For the data in Figure 7-10 various equivalent circuit fits were attempted. These included; $R_{ct}$ leading to a parallel split between $R_{dl}+Z_w$ (series) and CPE, in standard notation [R(Q[RW])] [184], also [R([RW][RQ])] [84], and [R(CCR)(RC)R] [208]. A point of inflexion in the LF response indicated a very slow charge transfer reaction at $E=0.28V$. Accordingly the [R(R[QW])] circuit in Figure 7-10(C) produced the smallest $\chi^2$. The decision to include a HF Warburg element shows consistency with the $N=\text{c.a.} 0.5$ seen at $OCP$ in Yu et al [184] and by Alcaide et al [341].

Several factors of the LF response are noted;

- Using Eq.2-103 the CPE capacitance and correcting for area produces $C_{dl}$, and $C_{dl}<C_x$ from CV.
- The CPE exponent (N) was equivalent for Nafion and QDPSU, with near perfect capacitance (0.923 and 0.927 respectively), producing transitory behaviour in

---

10 Obtained at $E=0.28V$ with Eq.2-16 during CV ($\nu=20\text{mV/s}$)
PTFE (0.804) with the most uneven surface. This explanation fits the trend in total non-faradic current observed during CV ($C_\Sigma$ in Table 7-5).

- Using Eq.2-104 the geometric $J_0$ of the QDPSU air cathode is, $J_0$=8.15x10$^{-7}$ A cm$^{-2}$, similar to that of the thin films (Table 6-1).

The Warburg co-efficients from the EC fit were a relatively minor source of impedance in the QDPSU electrode, therefore generating $Z_w$ from the Nova iteration, $A/\omega^0$ (Eq.2-99), produced a less accurate fit that the $Z \text{ vs } \omega^{-0.5}$ plot. Nafion produced the most accurate fit, iteration produced 259 $\Omega$ cm$^2$ s$^{0.5}$ (Eq.2-99) vs. 284.4 $\Omega$ cm$^2$ s$^{0.5}$ from $Z \text{ vs. } \omega^{-0.5}$. QDPSU produced 32.2 $\Omega$ cm$^2$ s$^{0.5}$ with circuit iteration and 51.9 $\Omega$ cm$^2$ s$^{0.5}$ in Table 7-3. With PTFE, the iteration result was exactly three orders of magnitude lower than that in Table 7-3. It can be concluded that equivalent circuit fitting was found to be a poor method for estimating $R_{ct}$ in FePc/KJB binder air cathodes in PBS and $Z'$ vs. $\omega^{-0.5}$ regression should be used instead.

7.3 Nafion and QDPSU binders for MFC air cathodes

7.3.1 Impedance of QDPSU air cathodes in buffered wastewater

The impedance study herein aims to show how binder influences components of resistance in the FePc/KJB air cathode in the presence of wastewater. Figure 7-11 depicts the Nyquist response of half-cell air cathodes in 50mM PBS wastewater.

![Figure 7-11](https://example.com/figure7_11.png)

Figure 7-11. Nyquist plot of air cathodes described in legend, in a WW-PBS filled cube half-cell. Auxiliary Electrode; Pt mesh. (A) $E=OCP$, (B) $E=0$ V. Red line=Warburg impedance ($m=1$), blue semi-circle; parallel $R_{ct}/C_{diff}$ related to ORR, orange semi-circle $R_{dl}/C_{dl}$ parallel. Electrolyte; air saturated Wastewater+PBS(50mM), pH 7.0.
In Figure 7-11 the constant phase element is clearly applicable from depression of the semi-circle. This is due to inhomogeneity on the surface presented to the electrolyte. With QDPSU the $R_{dl}$ produced 150Ω cm$^2$ with wastewater addition (Figure 7-11), analogous to the relaxation of accumulated countercharges at the IHP. This indicates strong bonds between QDPSU and numerous countercharges. $C_{dl}$ was largely invariant with potential and occurred in parallel with this component. The response of Pt-Nafion was convoluted due to the non-specificity of Pt for oxidation/reduction reactions of wastewater contaminants. The time constants were amalgamated for these processes and total AC impedance ($R_{AC}$) or equivalent circuit fits could not be obtained.

As anticipated, $O_2$ permeation to the reaction site was not impeded by accumulation of wastewater pollutants; the QDPSU LF response at $E=0V$ in Figure 7-11 did not represent transmissive diffusion boundary resistance. The LF semi-circle could be manually measured for $R_{ct}$ [342].

7.3.2 Wastewater pollutant and $R_{ct}$ of QDPSU and Nafion air cathodes

Figure 7-12 shows manual arc fits at low frequency ($R_0-R_{ct}=R_{ct}$) in wastewater PBS. $\log_{10}(R_{ct}^{-1})$ vs $E$ is akin to a tafel plot ($R_{ct}^{-1}x i_k$) [343], provided all other resistances are successfully removed.

![Figure 7-12](image-url)
The circle diameter represents $R_{ct}$ of oxygen reduction in a PBS wastewater environment. Maximum $R_{ct}$ only corresponds to the $E^0'$ of the RDS couple when $\alpha=0.5$ and the reaction is nernstian and it is the only reaction occurring on the electrode. Electroanalysis of this type cannot be applied to chemically diverse electrolytes. Several observations can be made;

- At $E$>$-0.2$V, $R_{ct}$ is lower with QDPSU than Nafion.
- With QDPSU electrodes in PBS a linear fit occurred at $0.197V \log_{10}(R_{ct})^{-1}$ (-0.05$<E<0.1$V) with an extremely accurate fit ($R^2=0.99993$). In NaCl this linear region is $-0.15<E<0$V at $3.98V \log_{10}(R_{ct})^{-1}$ ($R^2=0.973$).
- A ‘noisy’ $R_{ct}$ response from -$0.1<E<0.1$V was not observed in PBS or NaCl and may indicate complex adsorption processes. The QDPSU redox with O$_2$ (section 6.2.1.) is unlikely to account for the result at 0.1V as it was not observed in PBS.
- Using Eq.2-104 (and assuming $n=4$), the corresponding geometric $J_0$ values for $R_{ct}$ recorded at OCP is $1.45\times10^{-6}$A cm$^{-2}$ with Nafion and $5.3\times10^{-6}$A cm$^{-2}$ with QDPSU in PBS-Wastewater.

It is perhaps unusual that the magnitude in difference in $J_0$ with Nafion and QDPSU air cathodes in wastewater, x3.5 larger with QDPSU, is similar to that of thin films in PBS, ca. x2.5 larger with QDPSU (Table 6-1 and Table 5-1). Especially considering the Nafion electrode displayed a lower $OCP=0.23$V while QDPSU produced an $OCP$ similar to that in PBS; $OCP=0.27$V.

### 7.3.3 Equivalent circuit in PBS WW for QDPSU and Nafion

It was established that it would be impossible for the resistance element at high frequency (Figure 7-11) to relate to $R_{ct}$ due to 1) the unfeasible $J_0$ values (c.a. $3.5\times10^{-5}$ A cm$^{-2}$) that would correspond to this at $OCP$ and, 2) the $Z'$ value is consistent at all potentials above and below $\eta=0$V ($\pm20\%$). This was the case in every system tested using the FePc/KJB catalyst, both thin film and air cathode, Nafion and QDPSU.

Due to the result in Figure A-21 a semi-infinite Warburg element was place in series with a capacitance. This capacitance was established to be the double layer capacity ($C_{dl}$) [84] from the consistent values 1-1.5$\mu$F cm$^{-2}$ for all potentials and binders (Table 7-7). The two components were connected in parallel to the resistance offered by the double-layer ($R_{dl}$). The fit at low frequency was very accurate, yet the presence of a
UHF arc (>50,000Hz) meant iteration produced an electron diffusion impedance dissimilar to that obtained by Z vs. $f^{-0.5}$ analysis, the latter being the more accurate representation. None of the values were constrained, and the $C_{\text{diff}}$ consistently produced an exponent ($N>0.86$) suggesting capacitance in an in-homogenous surface.

The $R_{dl}[C_{\text{dl}}W]$ components could also be substituted (Table 7-3) with an open ended diffusion element ($\chi^2=0.227$) or Gerischer impedance [344] ($\chi^2=1.02$), both producing 1.65-1.25mMho. However, the need to identify $C_{\text{dl}}$ required these components to be separated. It was theorised that resistance to O2 adsorption may increase in the presence of wastewater, but no such feature could be identified on the nyquist plots (Figure 7-11 which would call for a parallel $R_{\text{ads}}[C_{\text{ads}}]$ component. A slight depression in the arc did not fit the bounded adsorbing Warburg unit modelled in Figure 2-22, and no physical explanation can be found for a Gerischer unit (electrolyte reaction). The equivalent circuit presented in Figure 7-13 was valid for FePc/KJB air cathodes with QDPSU binder in PBS amended wastewater at all potentials in the range 0.4$E>-0.3V$.

![Figure 7-13. Equivalent circuit used to model FePc/KJB QDPSU air cathodes with contamination and blocking from adsorption of species in PBS buffered wastewater.](image)

Table 7-7 contains the results of manual arc fitting of the components in equivalent circuit 4-14 to the iteration stabilised values of this equivalent circuit.
Table 7-7. FePc QDPSU electrodes in WW-PBS, parameters of fitted circuit Figure 7-13, comparison of fitting high and low frequency arc manually with both FePc Nafion and FePc QDPSU electrodes.

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Manual arc fit - QDPSU FePc/KJB

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Manual arc fit - Nafion FePc/KJB

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The admittance (Y) of the C_diff component was x10 lower with Nafion than QDPSU. In QDPSU electrodes, the resistance due to surface states is extremely large (c.a 220-150Ω
cm²). By comparison, in 50mM PBS the typical performance of an anion exchange membrane is 12.4Ω cm² [254] and that of all aspects of the anode biofilm in a sandwich MFC can be 340Ω cm² [264]. Applying Eq.2-107 to $R_{ss}$ produced unfeasibly high rate constants ($3 \times 10^3$ cm s⁻¹) for O₂ adsorption, indicating convolution with $R_{dl}$ and inseparable time constants.

An LF impedance was observed for Nafion at all potentials $0.4 > E > -0.1$V and absent in QDPSU (Figure 7-14). This appeared to be the reason behind the superior performance of QDPSU in wastewater.

![Figure 7-14. Nafion FePc/KJB air cathode, low frequency impedance in wastewater. Data with manual $R_{ct}[C_{diff}]$ circuit arc applied.](image)

The absence at low potential excluded O₂ diffusion limitation, $Z'$ vs $\tilde{\omega}^{-0.5}$ and $Z'$ vs $\tilde{\omega}^{-1}$ plots were non-linear and convective effects were not present in QDPSU. A cationic pollutant such as Mg$^{2+}$ has previously impeded ORR on FePc [176], via adsorption onto the pyrrole ring. Mg$^{2+}$ is present at 3mM in Wastewater (Table 1-1) and is capable of transport in a Nafion film, a process blocked by exclusion with QDPSU, indicating a benefit of anion exchange.

**7.3.4 MFCs polarisation with QDPSU air cathodes in artificial wastewater**

Two MFCs with established biofilms were run continuously for over a year. Initial inoculation was from acetate supplemented primary clarifier influent with PBS buffer. The MFCs were used to analyse the anticipated improvements with QDPSU binder by swapping electrodes across both MFCs. All phosphate buffered wastewater inoculum was consistent in conductivity, 6.6±0.2 mS cm⁻¹ and pH, 7.0-7.1. Steady state
polarisation minimises power “overshoot” over potentiostat [345]. Example polarisations from 20 minute interval changes in $\Omega_{ext}$ can be seen in Figure 7-15 and the average of all tests summarised in Table 7-8.

![Graph](image)

Figure 7-15. Steady state polarisation curves of MFCs with FePc/KJB air cathodes containing QDPSU or Nafion binders. (A) $E_{cat}$ and $E_{an}$ vs $J$ and (B) $V_{cell}$-$J$ and $P$-$J$ power curved. Electrolyte; wastewater amended with 50 mM PBS, $\kappa$=6.6mS cm$^{-1}$, pH 7.0

Table 7-8. Summary of repeated MFC performance at fixed external load (left column) or steady-state polarisation (right column). Electrolyte; wastewater amended with 50mM PBS, $\kappa$=6.6mS cm$^{-1}$, pH 7.0

<table>
<thead>
<tr>
<th>Cathode</th>
<th>$P$ ($\Omega_{ext}$=1k$\Omega$) / W m$^{-2}$</th>
<th>$P_{max}$ / W m$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Old/New</td>
<td>FePc QDPSU FePc Nafion Pt Nafion</td>
<td>FePc QDPSU FePc Nafion Pt Nafion</td>
</tr>
<tr>
<td>New</td>
<td>0.210 0.131</td>
<td>0.340 0.124</td>
</tr>
<tr>
<td>New</td>
<td>0.173 0.201</td>
<td>0.201 0.297</td>
</tr>
<tr>
<td>New</td>
<td>0.155 0.210</td>
<td>0.174 0.215</td>
</tr>
<tr>
<td>Old</td>
<td>0.189 0.140</td>
<td>0.235 0.158</td>
</tr>
<tr>
<td>Average</td>
<td>0.191 0.142 0.205</td>
<td>0.259 0.152 0.256</td>
</tr>
</tbody>
</table>
In every polarisation QDPSU FePc consistently outperformed Nafion FePc, obtaining an average over three experiments of $P_{\text{max}}$ of 0.259 W m$^{-2}$ vs. 0.152 W m$^{-2}$ respectively (A=12.56cm$^2$). The performance was comparable to Pt, average $P_{\text{max}}$=0.256 W m$^{-2}$.

In Figure 7-15 the anode potential is consistent until metabolic limitation from the viable exoelectrogen population size of the biofilm is reached. Higher surface area materials, such as carbon brush used in several studies [169, 261], could be used to resolve this issue. As such, the difference in cathode potential prior to this point is used to highlight the improvement with QDPSU binder. The biofilm variance was mitigated by rotating cathodes across cells.

Figure 7-16. $E_{\text{cat}}$ of QDPSU or Nafion binder. Obtained during polarisation curves of MFC’s FePc/KJB catalyst. Red dashed lines; $R_{\text{dl}}$ and $R_{\text{ct}}$ at $E$=0.1V and OCP respectively. Electrolyte; wastewater amended, 50mM PBS, 6.6mS cm$^{-1}$, pH 7.0

The data represented in Figure 7-16 was overlaid with parameters recorded in Table 7-7. Before the anode potential reaches limiting current $E_{\text{av}}$=-0.410 ±0.015V, the average cathode potential for this $E_{\text{an}}$ is highest for FePc QDPSU (0.096V) followed by Pt Nafion (0.078V) then FePc Nafion (-0.012V). In all instances the cathode potential was higher with QDPSU.

$OCP$ was consistently higher for QDPSU (0.229-0.254V) than Nafion (0.189-0.216V), showing agreement with the EIS experiments; QDPSU (0.27V), Nafion (0.24V). Variance in ohmic drop is due to absence of a current collector and connection with Ti wire via a thick TiO$_2$ layer. This approach was taken to allow improved sealing and remove surface of active metal (ie. stainless steel) from electrolyte contact.
The uncompensated solution resistance ($R_u$) was calculated using Eq.1-4 for $\kappa=6.6\ \text{mS cm}^{-1}$ solution and a WE-RE i-R drop of $R_u=20.26\Omega$ was and represented on Figure 7-16. With QDPSU electrodes a large portion of non-potential dependent resistance remained unaccounted for. Voltage loss at low current is not exclusively $R_u$ (Figure 7-16), accounting for a comparison of the $R_{dl}$ value obtained from section 7.3.3 and the actual drop shows this resistance to be minor ($11.7\Omega$ at $E=0.1\text{V}$). The linearity of this region reflects the fact that admittance for the $C_{\text{diff}}$ unit is x10 larger for QDPSU than Nafion. In contrast the unidentified low frequency impedance of the Nafion electrode drops after $OCP$ and so the line curves upwards. As such the non-linear result of the Nafion is due to the capacitive effect, which decreases below $OCP$.

7.3.5 MFCs polarisation using QDPSU FePc air cathodes in wastewater

In Figure 7-17 polarisation curves of MFC using new or old air cathodes of Pt/Nafion or FePcKJB/QDPSU are presented. The peak power densities of the same electrodes over the following batch cycle are presented in Table 7-9.

![Figure 7-17](image)

Figure 7-17. (A) $V_{\text{cell}}$ and Power density vs $J$ and (B) $E_{\text{an}}$ and $E_{\text{cat}}$ vs $J$ in polarisation of SCMFC’s with air cathodes of Pt/C (Nafion), or FePc/KJB (QDPSU). Electrolyte; primary clarifier influent, pH 7.2. $\kappa=1.82\text{mS cm}^{-1}$. 

- $R_u$ resistance
- $OCP$ open-circuit potential
- $C_{\text{diff}}$ diffusion capacitance
- $R_{dl}$ double-layer resistance
- $J$ current density
- $E_{\text{an}}$, $E_{\text{cat}}$ anodic and cathodic overpotentials
- $V_{\text{cell}}$ cell voltage
Table 7-9. MFC performance in batch mode ($\Omega_{ext}=300\Omega$) or steady-state polarisation. 

Electrolyte; Unbuffered Wastewater, $\kappa=1.82\text{mS cm}^{-1}$, pH; 7.2.

<table>
<thead>
<tr>
<th>Old/New</th>
<th>$P\ (\Omega_{ext}=300\Omega)$</th>
<th>$P_{\text{max}}/ \text{W m}^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FePc QDPSU</td>
<td>Pt Nafion</td>
</tr>
<tr>
<td>New</td>
<td>0.158</td>
<td>0.113</td>
</tr>
<tr>
<td>Old</td>
<td>0.180</td>
<td></td>
</tr>
<tr>
<td>Old</td>
<td>0.211</td>
<td>0.103</td>
</tr>
<tr>
<td>Average</td>
<td>0.183</td>
<td>0.108</td>
</tr>
</tbody>
</table>

The average $P_{\text{max}}$ for FePc/KJB QDPSU air cathodes was larger in wastewater without phosphate supplementation, 0.297W m$^{-2}$ vs. 0.259W m$^{-2}$. A superior biofilm was cultivated without phosphate presence. However, the FePc/KJB QDPSU cathodes outperformed Pt Nafion in unbuffered wastewater (0.297 vs. 0.21W m$^{-2}$) with a similar limiting solution resistance and biofilm conditions.

Using Eq.1-4 the internal solution resistance is 140$\Omega$, ($R_u=0.263\text{V in 1.5A m}^{-2}$). From Figure 7-17 the linear $E$ vs. $J$ response of both electrodes show the cell is limited by ohmic loss, which can be countered by reducing electrode separation [264]. The cathode response is less consistent than with PBS owing to electrode fixation.

Applying $iR$-correction with Eq.1-4 on the lateral distances shown in Figure 4-1 for RE-frit produces $R_u=73.5\Omega$ and for RE-biofilm $R_u=56.87\Omega$. After $iR$ loss subtraction linear $E$ vs. $J$ response is observed for Pt, the best Pt polarisation producing 1k$\Omega$cm$^{-2}$ in wastewater. In this current range the best FePc/KJB QDPSU polarisation produced the maximum resistance at 0.84k$\Omega$cm$^{-2}$ ($J=0.1$-0.5 A m$^{-2}$). With FePc/KJB QDPSU the resistance was not consistent with potential, in-line with the findings in Table 7-7. The same observation is made in un-buffered wastewater.

### 7.3.6 Batch performance of MFCs with QDPSU air cathodes

Batch performance of MFCs with cathodic biofilm contaminated air cathodes were air dried until totally dry in-between batches, then re-inserted with fresh media to evaluate the effect of biofilm sterilisation (Figure 7-18). At the end of a batch cycle the acetate is
depleted and the reaction on the anode ceases, power output drops rapidly as $E_{\text{an}} \rightarrow 0.2V$ ($OCP$ of $E_{\text{cut}}$).

![Figure 7-18. Batch performance of FePc/KJB in single chamber MFCs using air cathodes with a) QDPSU or b) Nafion ionomer. Air cathodes with dried cathode biofilm reinserted at $t=3$ days. Electrolyte; Wastewater-PBS, (6.6mS cm$^{-1}$) pH 7.0.]

The batch performance of new, aged and biofilm contaminated QDPSU electrodes was consistently higher than Nafion, with and without Phosphate supplementation. Cathode biofilm sterilisation by evaporation ($30^\circ$C) regenerated the performance of both Nafion and QDPSU electrodes (Figure 7-18), suggesting any damage chemical decomposition of QDPSU in wastewater was minor and did not irreversibly affect electrodes.

![Figure 7-19. Batch performance of single chamber MFCs using Pt/C-Nafion or FePc/KJB-QDPSU air cathodes. Electrolyte; Unbuffered Wastewater, (1.82mS cm$^{-1}$) pH; 7.2.]

MFCs were dismantled, components and biofilm gently rinsed with de-ionised water, new air cathodes inserted to remove entrained phosphate then loaded with un-supplemented primary clarifier influent. Figure 7-19 shows the results immediately thereafter. For new electrodes, FePc/KJB QDPSU ($P_{max}=0.178\text{W m}^{-2}$) outperformed Pt/C ($P_{max}=0.136\text{W m}^{-2}$).

Comparison of maximum power densities obtained over all FePc/KJB (QDPSU) batch tests were $P_{max}=0.224\text{W m}^{-2}$ (un-supplemented) and $P_{max}=0.243\text{W m}^{-2}$ (+PBS). By comparison, Pt/C Nafion produced $P_{max}=0.166\text{W m}^{-2}$ (un-supplemented) and $P_{max}=0.199\text{mW m}^{-2}$ (+PBS, not shown).

The result is perhaps surprising, considered FePc/KJB QDPSU performance was established to be higher in PBS than other mediums. Therefore unbuffered wastewater may be expected to perform significantly worse in FePc.

### 7.3.7 QDPSU/FePc interaction with organics in wastewater

The columbic efficiency ($\varepsilon_c$) reported in Figure 7-20 for Pt/C or FePc/KJB air cathodes.

![Figure 7-20. Batch performance of MFCs fed with acetate (1 or 2g/L). $\Omega_{ext}=300\Omega$. Electrolyte; 50mM PBS + Acetate, pH 7.0.](image)

The $\varepsilon_c$ values of 20-40% for CH$_3$COONa electrolyte is largely a function of biofilm population vs. reactor volume as opposed to a cathode effect. Similar $\varepsilon_c$ values were obtained for wastewater. The FePc/KJB QDPSU electrodes still produced a superior performance over Pt Nafion even with the presence of large quantities of CH$_3$COO-.
anion. Pt performance is affected by CH$_3$COO$^-$ [113, 346], though FePc QDPSU electrodes continually outperform Pt. This suggests oxygen reduction adopts the kinetics observed for PBS electrolytes when occurring in mixed PBS/CH$_3$COO$^-$. It would not be possible for FePc/KJB QDPSU to outperform Pt if the reaction kinetics seen in pure CH$_3$COO$^-$ electrolyte (Table 6-3) were apparent in PBS/CH$_3$COO$^-$. This result shows good agreement with that seen for pyrolised FePc/C [113].

In light of the oxygen fixing properties of QDPSU, evidence was sought for organic oxidation on the cathode surface in phosphate amended wastewater. Chemical oxygen demand (COD) content was measured for two consecutive batch cycles with a fixed external resistor (1kΩ). A degree of error is anticipated on the concentration axis, due to organic solute diversity and interfering Hg complexes during titration, this error is estimated at 2.3% (g m$^{-3}$) at highest concentration [281], error bars have not been added so data can be easily read. As COD removal is primarily an anodic issue, biofilms were numbered and electrodes rotated across both cells. Cathode effect on COD removal has only been investigated with biocathodes, though oxidation of fermented organics can occur on Pt [28].
At a point c.a. 50% COD removal $V_{cell}$ decreases rapidly, this is consistent with the idea that volatile fatty acids must be replenished by hydrolysis organisms [2], and consumption by the biofilm outstrips production causing the concentration to be negligible at this point. Difference in batch time from the first cycle to second cycle can be explained by an increased degree of hydrolysis and fermentation occurring in the sealed wastewater sample container.

Initial COD removal rates were largest, reflective of initial fermented organic concentration being the highest. In the first 70 minutes removal rates ranged from 2.125 kgCOD m$^{-3}$ day$^{-1}$ to 0.46 kgCOD m$^{-3}$ day$^{-1}$, the highest being with Pt. The removal rate is being higher than the potential margin of error, suggesting Pt cathodes have a significant organic oxidation effect in MFCs [347]. With FePc/KJB no relation between QDPSU and COD removal could be established.
The average OCP of air cathodes in PBS buffered wastewater was; FePc QDPSU (0.27V), FePc Nafion (0.24V) and Pt-Nafion (0.34V). The OCP recorded in PBS; FePc QDPSU (0.28V), FePc Nafion (0.235V) and Pt-Nafion (0.43-0.4V). The disparity between these electrolytes with Pt/C is consistent proclivity to organic oxidation demonstrated herein.

7.4 Conclusions

This study provides the first analysis of coupled electron/counter-ion diffusion rates in MFC air cathodes. Many of the conclusion are specific to semi-conductive polymer electro-catalysts and some are specific to only to FePc. However, the methodology allows a comparable means for MFC researchers to quantitatively assess process bottle-necks in real wastewater.

It was demonstrated that anion’s were able to move through the catalyst layer more freely with QDPSU than Nafion or PTFE binders. This resulted in a faster diffusion of electrons from GC surface to the active sites, where reduced Fe(II)Pc is required for oxygen reduction to occur.

This approach is highly focused on kinetics and modelling for an engineering project, but the importance of electron and ion diffusion for FePc was tantamount to electrode performance producing additional resistances of 100-230Ωcm², a resistance larger than $R_{ct}$ at potentials below 0.15V, being approximately 20% of internal resistance of the SCMFC under external load. With removal of the 3cm electrode separation this feature may comprise the majority of cell resistance. Poisoning of anion exchange groups is likely to be a severe issue even with membrane introduction. Functional anion exchange groups designed for alkali fuel cells may not compatible in MFC’s. This electron propagation resistance was not observed with Nafion, showing sulfonate groups to be less susceptible to ion exchange blocking than methyl dabco. However, with Nafion $R_{ct}$ was x6 larger at low over-potential and accounted for the poor performance in PBS half-cell tests. Thus the QDPSU anion exchange material is highly recommended for non-precious redox polymer ORR catalysts in pH7.
Conventional wisdom on air cathode design may need to be dispelled when considering the case of non-precious redox polymer catalyst air cathode design for neutral media; ultra-thin catalyst layers may be required (ie. 0.1 mg cm$^{-2}$), with relatively high loadings of selective anion exchange ionomers. The layer thickness and catalyst loading should be explored to balance reduced electron diffusion distance with $R_{ct}$ and stability, with a reasonably high initial loading of catalyst required to counter catalyst de-activation. Particular attention should be paid to the interface of current collector and catalytic film. More work is recommended using this approach on thin films and air cathodes to demonstrate the stability of QDPSU relative to quaternary ammonium for MFC’s.
Chapter 8. Results - Cation and anion exchange membranes for Microbial Fuel Cells
8.1 Background – Factors affecting membranes in MFCs

The purpose and benefits of MFC membranes is briefly discussed in chapter 3. In this section experimental techniques for their analysis are addressed. Typically membranes are assessed with EIS by using a two chamber electrolyte system and either Pt wire’s placed either side of the membrane or two reference electrodes measuring potential drop across a fixed current [254]. An important aspect of this approach is the removal of solution resistance or $R_u$. The membrane is usually modelled in an equivalent circuit as an impedance in series with $R_u$. Where specific adsorption occurs a capacitive term $C_{ads}$ can becomes significant [92]. In some instances RC time constants associated with double layer ion resistance and the diffusion boundary layer are added in series to the basic membrane resistance [348]. Ohmic resistances are typically of the order $1\text{--}10\Omega \text{ cm}^2$ [248].

Two chambered systems are also used to analyse ion diffusion from one reservoir to another. In this chapter, the membrane has been pressed against air cathodes developed in chapter 4 and analysed with EIS. This approach aims to assess the finished MEA configuration and suitability for MFC air cathodes.

Despite the extra cost to an MFC unit, a membrane ensures the degree of biofouling present in appendix Figure A-25 can be largely avoided. Therefore in extended operation the air cathode displays the rest potential of the catalyst and not the periplasmic redox enzymes present in an aerobic biofilm.

8.2 Results - Analysis of MEA impedance spectra

8.2.1 General Nyquist plot response of MEA in pure electrolyte

In Figure 8-1 the AC impedance response of all MEA half cells is shown under cathodic polarisation.
The main features of the complex plane response are two arcs in all cases. A potential dependent LF arc was attributed to Oxygen reduction, the $R_{ct}$ only becoming measurable with manual arc fit at potential low enough for ORR to be observed in $i-E$ plots. The HF arc was largely invariant of potential. In Figure 8-1 the Morgane ADP membrane produced the best result in PBS as the total electrode AC resistance ($R_{AC}$) was smallest. An annotated example of the interfacial and boundary resistances is shown in Figure 8-2 with manual arcs applied.
Figure 8-2. Nyquist plot of typical MEA impedance data. FePc/KJB (QDPSU) air cathodes. Red line; Warburg gradient. Orange semi-circle; high frequency arc. Blue semi-circle; low frequency ORR arc. Electrolyte; 50mM PBS, pH 7.0.

Usually $R_m$ was determined under OCP to avoid changes in the relative presence of di-basic and mono-basic anions in the membrane. In Figure 8-2 an example of how ionic resistance ($R_m$) is calculated relative to the membraneless stainless steel mesh electrode. This is done as the mesh presents a similar face to the reference electrode. All other parameters ($R_{dl}, R_{dlb}, R_{ct}$) are compared to the meshless FePcKJB-QDPSU electrode as a $f(E)$, as an electrified mesh surface would be capable of performing faradic reactions. In the case of the meshless FePcKJB-QDPSU electrode and all MEA the mesh is unelectrified.

8.2.2 **Membrane ionic resistance ($R_m$)**

The ionic resistance in the membrane phase could be determined with Arrhenius plot. Yet the temperature sensitivity of some of the AEM (>60°C) reduce the range from which a linear range can be obtained. Instead the half-cell MEA method (Figure 4-3) was used to obtain the values according to the data treatment illustrated in Figure 8-2. The results are compared to manufacturer reported area specific resistance ($\Omega \text{ cm}^2$) in 0.5M NaCl in Figure 8-3(A). It was established in section 8.2.1 and previous works [252, 255] that the ionic resistance is devoid of interfacial resistances, moreover that the
concentration profile is similar throughout the bulk membrane phase [255]. Therefore the area specific resistance was normalised by hydrated membrane thickness (μm) in Figure 8-3(B). The thickness was measured in dry (delivered) and hydrated states for each ion with a digital Vernier (Table A-9). The resulting term (Ω cm² μm⁻¹) exacerbated the relative difference between conductivity of each anion across the trend in membranes.

Figure 8-3. Area specific resistances and thickness normalised ASR of several membranes. Obtained from HF impedance data. Electrolyte; air sat. 50mM Na-Phosphate (pH 7.0), NaCl (pH 7.0) or NaHCO₃ (pH 7.81).

The relative trend in ionic phase conductivity (A) is the same across most membranes, in line with anticipated behaviour. A notable exception can be seen in Figure 8-3(B) in which FAA shows low chloride and bicarbonate normalised ASR but an abnormally high resistance to Phosphate (10Ωcm² μm⁻¹) compared to the trend. As the anion exchange group (Q-Ammonium) is also used in the other membranes, the only feature unique to FAA is the PEEK backbone. The degree of through plane swelling was compared to the dry state. For FAA this was c.a. 0%, as reported by the manufacturer. The PEEK reinforcement produces a rigid polymer lattice though the 24.1% weight increase in NaCl suggests constrained diffusion channels did not produce the disproportionately high $R_m/d=10Ωcm^2 μm^{-1}$. An alternative explanation could be the
backbone ether linkage, this is the only chemical moiety present in PEEK and absent in the other membranes. It could be hypothesised that Hydrogen bonding between H$_2$PO$_4$ and the ether group may retard ion diffusion in the membrane.

8.2.3 *High Frequency response of MEA in pure electrolyte*

The HF arc possessed the following aspects;

- The arc width was found to be a function of ion exchange type and membrane thickness. The smallest arc was observed for FePc with and SS-mesh. And without the mesh disappeared.
- The first arc covered at larger frequency range when the membrane was added.

Plotting the intercept of the $Z''=0$ axis at different potentials conclusively proved that the $Z''=0$ intercept did not represent $R_s+R_m$ as 1) Using the Membranes International as a comparison with a similar backbone showed the $R_s+R_m$ value to be larger for Q-Ammonium functional groups than for Sulfonate, counter to previous works in PBS [288]. The results of the first arc were analysed as a function of bias potential to explain the response, the term infinity denotes the HF intercept and the 0 subscript the LF intercept of the arc (orange on Figure 8-1);
Figure 8-4. Characteristics of HF arc of MEA as a function of applied potential (x-axis in all graphs). (A) depression of the arc below $Z'=0$ axis, (B) capacitance, (C) semi-circle width at $Z''=0$ Ω (inset is high Y-axis values). FePc/KJB (QDPSU) air cathodes in air saturated PBS. Electrolyte; 50mM PBS, pH 7.0.

The results of the first arc as a function of $E$ showed the following characteristics;

- The ‘smoothest’ membrane produced the lowest capacitance, Morgane ADP.
- The diameter of the HF arc remained largely unchanged w.r.t potential. The only membrane that was an exception was Morgane ADP. Some change was noted low potential with QDPSU-PTFE membrane.
- In the case of the F-930 membrane the MEA high frequency arc behaved as a near perfect capacitor ($N=0.999$).
- In the case of the Stainless steel mesh only the arc was heavily depressed, possibly owing to non-uniformity in the double-layer.
The Morgane ADP membrane behaved unusually, with resistance increasing x5 between 0.1 to 0.3V and capacitance remaining relatively unchanged.

It appears as if the double layer capacitance comprises the majority of the capacitance in Figure 8-4(B). The smoother membranes produce the lowest capacitances and the lowest arc depression angle. This is borne out by the fact that the stainless steel mesh becomes electrically connected to the cathode when the membrane is removed and the depression angle is higher than many membranes.

The unusual behaviour of the Morgane ADP membrane appeared as if the $R_{ct}$ element where somehow incorporated in the high frequency arc, the only membrane for which this was the case. The capacitive element of the high frequency arc did not significantly change with potential.

Amongst anion exchange membrane materials the $R_{\infty}-R_0$ resistance followed the general trend of the resistance for Cl$^-$ by manufacturers. In terms of $\Omega$, the trend was; FAA ≈ Morgane < FTAM-A < AMI-7001. The resistance in Table 4-1 also following this trend. However, the cation exchange membranes appear to possess significantly less selectivity to Phosphate than Cl$^-$. For instance the $R_{\infty}-R_0$ value is marginally lower for F-930 in Phosphate than for FTAM-A, whereas in Cl$^-$ it is reported as x40 smaller in F-930 due to the F-930 membrane being thin.

Direct comparison of CMI-7000 and AMI-7001 allows the effect of the anion exchange group on the HF arc to be assessed as the backbone and thickness are identical. The Q-ammonium increases capacitance by 40-60%, reduces resistance x7-8, decreases CPE depression angle by x2-2.7 closer to Warburg and further from an ideal capacitor.

This was not the case, for instance the FTAM-A membrane was the thickest membrane (500-600µm) but performed well in comparison to the thinner anion exchange membrane AMI-7001 despite having a larger conductivity in NaCl. As information on pore volume is not provided in the products this cannot be discounted as a potential explanation. However, it did appear that Poly-styrene/divinyl benzene was not conductive to HPO$_4^{2-}$/H$_2$PO$_4^-$ diffusion.
It was found that a portion of the high frequency arc response was related to the stainless steel mesh. Adding the mesh to a bare FePc/KJB QDPSU air cathode caused an arc of 24.54 Ohm cm\(^2\) (OCP), invariant at potentials above 0V (not shown). The associated parallel CPE produced \(Y^0=8.197 \ \mu\text{F cm}^{-2}\). Though this capacitive arc large it is significantly increased with the introduction of a membrane (Figure 8-2). Addition of the SS-mesh reduces the \(R_{ct}\) of the oxygen reduction reaction from c.a. 430 Ohm cm\(^2\) to only 194 Ohm cm\(^2\) at a potential of 0V. No significant linear \(Z\) vs. \(\omega^{-0.5}\) region existed with or without the mesh.

### 8.2.4 Resistance from diffusive elements in MEA

As van Sleutels et al report ion transport may limit membrane MFC systems [249], diffusive elements were sought by plotting \(Z^'\) vs. \(\omega^{-0.5}\) as in chapter 6. This Warburg plot of the transition region between the high and low frequency arc is shown in Figure 8-5.

![Figure 8-5. Example Warburg plot for MEA of FAA (crosses) or capacitance response without a membrane (dot). \(E=0.2\text{V}\). Conditions as in Figure 8-1.](image)

Figure 8-5 depicts an example of bounded finite diffusion occurring in the linear process as a capacitive element. The open ended diffusion element applied ubiquitously to two chamber models [251, 252, 255] is not apparent in the air cathode setup; The model depicted in Figure 2-22 shows an upward inflexion in the \(Z^'\) vs. \(\omega^{-0.5}\) plot which is clearly not present in Figure 8-5 or any other membranes tested in this configuration.
This is to be expected considering a sustained DC flow of ions into the catalyst layer is clearly not possible. The physical interpretation of diffusion in redox films followed by adsorption holds for the membrane system. This feature was present with NaCl, Na$_2$PO$_4$ and NaHCO$_3$ across the majority of the 0.4$<E<0.4$V potential range. The factor $f_2$ increases in the trend of $(D_i/f_2)^{0.5}$ being proportional to diffusion length in the thin film system. Increasing the thickness of the FePc/KJB film from 1.5μm (TFE) to c.a. 100μm (Air Cathode) results in $f_2$ decreasing from c.a. 500-2000 rad s$^{-1}$ to 14.63 rad s$^{-1}$ depending on ionomer. The knee frequency $f_2$ is in the same range for all MEA 0.63$<\omega<14.63$ rad s$^{-1}$ (in PBS), differences in diffusion co-efficient can be interpreted as counter-ion diffusion through the membrane. This resistance is comparatively low ($Z'=9Ω$ cm$^2$) in this FAA example (PBS) but could significantly increase in MFC wastewater system where membrane or ionomer ion selectivity is lost from poisoning of the fixed charge.

8.2.5 General Equivalent Circuit

The generalised equivalent circuit (B) for FePcKJB-QDPSU AEM membrane electrode assemblies is shown in Figure 8-6. This circuit was applicable for all mono-anionic experiments Cl$^-$, H$_2$PO$_4$/HPO$_4^{2-}$ and HCO$_3^-$ at all potentials at which ORR is observed. An example fit using the iteration programme in Nova software is displayed (A).

![Figure 8-6. Equivalent circuit (B) and fit of data (A) of FePcKJB-QDPSU air cathodes. Example is for FAA membrane. Electrolyte; air saturated 50mM NaHCO$_3$, pH7.91.](image)
It is clear from Figure 8-6 that the two time constants in (A) are separated and an additional unit must be applied. The linearity of this region \(-dZ/dZ=1\) in the nyquist plot again lends itself to a diffusive process as in the previous chapter. Open ended diffusion element behaviour could occur as the test is not performed under de-aerated conditions. If so this unit is obscured by the charge transfer element \((R_{ct})\) which is the only component that is strongly potential dependent. The low value of the \(C_{dl}\) ‘N’ exponent (<0.95) did not occur when mesh was not used or thicker membranes. Compression from the stainless steel mesh must then disrupt this boundary resistance on the electrolyte interface.

8.3 MEA performance in artificial wastewater

8.3.1 Polarisation curves

![Image of polarisation curves](image_url)

**Figure 8-7.** \(E_{cat}\) vs \(J\) polarisation curves of MFC utilising MEA listed in Table 4-1 and FePc/KJB QDPSU air cathodes. Polarisations over two MFCs, activation region in red box enlarged (top). Electrolyte; 50mM PBS + 1g/L CH3COONa, pH7.
In Figure 8-7 it is apparent that the initial cathode potential drop from activation (<2x10^{-3} \text{ A m}^{-2} on Figure 8-7) appeared not to be significantly affected by the membrane. As current marginally increased the CEM membranes incurred a large degree of overpotential. This drop was not linear in CEM and weakly linear in AEM, suggesting an effect other than ion diffusion resistance was present, such as a space charge capacitance. It was noted that the cathode potential of the cation exchange membranes was still marginally decreasing after 20 minutes of stabilisation. This was not previously observed with membraneless electrodes (ie. Figure 7-16) and was not observed with anion exchange membranes. As this is a low frequency capacitance it is not described in Figure 8-4. The linear \( E-J \) responses at \( J > 0.1 \text{ A m}^{-2} \) seen with membraneless air cathodes in Figure 7-16 were not observed with membranes.

### 8.3.2 EIS spectra of batch fed MFC

Single Chamber MFC were constructed operated with a permanent reference electrode and fed with artificial wastewater as per Figure 4-1(B) with the addition of a membrane and steel mesh. This cathode configuration produced an identical MEA to those used to obtained Half-Cell EIS data Figure 4-3. Cells were injected with fresh AWW and left at OCP for 30min to attain a stable \( E_{an} \) prior to EIS characterization (Figure 8-8). At the end of the same batch cycle (\( V_{cell} < 0.05 \text{V} \)) the cells were left at 30 min to attain OCP and the spectra in (C) and (D) recorded.
Figure 8-8. Nyquist plot of full MFC utilising MEA.

$E=OCP$. EIS spectra taken at (A) and (B) start of batch cycle, or (C) and (D) end of same batch cycle. (A) and (C) HF response, (B) and (D) LF response. Electrolyte; 50mM PBS+1g/L CH$_3$COONa, pH7.

In comparison to $R_{dl}$ values obtained in the half cell experiment (Figure 8-4) it is clear that the interfacial impedance in Figure 8-8 has increased for each cell. The effect of [CH$_3$OOO$^-$]=1g/L on the HF response (A) was a 0-20% increase in $R_{dl}$ using MEA of Quaternary Ammonium or Dabco relative to acetate depleted conditions (C). This indicates acetate co-ordination to the positive charges at the membrane interface may pose small cell resistance, as ionic conductivity was consistent over the batch. In pure PBS, at open circuit $E_{oc}>0.2V$ was recorded for each MEA. After 30 minutes of stabilization, $OCP$ prior to (A) and (C) was; QDPSU (0.1V), Rhinohide (0.09V), AMI-7001 (0.19V), FTAM-A (0.13V), F-930 (0.13V), FAA (0.19V), indicating varying degrees of acetate cross-over and local alkalinity. The LF response in (B) and (D) is less useful to analyse as a result.
8.3.3 Membrane SCMFC batch performance

During periods of 24 illumination a red microbe appeared to thrive under acetate-nutrient inoculum [349], as seen in previous single chamber MFC studies [350]. As these microbes are capable of photoheterotrophic and photoautotrophic growth [349] then they may use acetate or photosynthesis depending on conditions. The bacteria were found to have an extremely detrimental effect on COD. The usual 80-90% COD observed in single chamber MFCs loaded with acetate decreased with long batch cycles.

Table 8-1. Peak $E_{\text{cat}}$ and $V_{\text{cell}}$ obtained under fixed external resistance with FePc/KJB (QDPSU) air cathodes and a membrane strapped down with SS304 mesh. Information obtained following polarisation curves. Electrodes connected by fixed resistors of a) 308Ω and b) 330Ω. Electrolyte; 50mM PBS+1g/L CH$_3$COONa, pH 7.0.

<table>
<thead>
<tr>
<th>Membrane / Manufacturer</th>
<th>MFC1 - 308Ω</th>
<th>MFC2 - 330Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{\text{cat}}$ / mV</td>
<td>$V_{\text{cell}}$ / mV</td>
</tr>
<tr>
<td>Cation Exchange Membranes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-930 / Fumatech</td>
<td>-28</td>
<td>344</td>
</tr>
<tr>
<td>CMI-7000 / Membranes International</td>
<td>-27</td>
<td>301</td>
</tr>
<tr>
<td>Anion Exchange Membranes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AMI-7001 / Membranes International</td>
<td>16</td>
<td>350</td>
</tr>
<tr>
<td>FTAM-A (PA) / Fumatech</td>
<td>54</td>
<td>389</td>
</tr>
<tr>
<td>FAA (PEEK) / Fumatech</td>
<td>27</td>
<td>379</td>
</tr>
<tr>
<td>Morgane ADP® / Solvay</td>
<td>127</td>
<td>440</td>
</tr>
<tr>
<td>QDPSU / made in house</td>
<td>48</td>
<td>402</td>
</tr>
<tr>
<td>Separator</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhinohide / Entek</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 8-2. Averaged peak $E_{\text{cat}}$ and $V_{\text{cell}}$ obtained over batch cycles over two MFC. MFC with FePc/KJB (QDPSU) air cathodes and membrane. Fixed external resistor of 308Ω or 330Ω. Electrolyte: 50mM PBS+1g/L CH3COONa, pH 7.0.

<table>
<thead>
<tr>
<th>Membrane / Manufacturer</th>
<th>$E_{\text{cat}}$ / mV</th>
<th>$V_{\text{cell}}$ / mV</th>
<th>#batch cycles</th>
<th>Standard Deviation (σ) $E_{\text{cat}}$/ mV</th>
<th>$V_{\text{cell}}$/ mV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cation Exchange Material</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-930 / Fumatech</td>
<td>-49</td>
<td>302</td>
<td>14</td>
<td>30</td>
<td>47</td>
</tr>
<tr>
<td>CMI-7000 / National Membranes</td>
<td>N/A</td>
<td>N/A</td>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Anion Exchange Material</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FTAM-A (PA) / Fumatech</td>
<td>-23</td>
<td>289</td>
<td>13</td>
<td>31</td>
<td>20</td>
</tr>
<tr>
<td>FAA (PEEK) / Fumatech</td>
<td>0</td>
<td>324</td>
<td>12</td>
<td>50</td>
<td>49</td>
</tr>
<tr>
<td>AMI-7001 / National Membranes</td>
<td>-54</td>
<td>309</td>
<td>6</td>
<td>33</td>
<td>31</td>
</tr>
<tr>
<td>Morgane ADP® / Solvay</td>
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<td>N/A</td>
<td>0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>QDPSU / made in house</td>
<td>-63</td>
<td>307</td>
<td>13</td>
<td>33</td>
<td>40</td>
</tr>
<tr>
<td><strong>Separator</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhinohide / Entek</td>
<td>-121</td>
<td>257</td>
<td>13</td>
<td>74</td>
<td>89</td>
</tr>
</tbody>
</table>

In Table 8-2 the peak stabilised $V_{\text{cell}}$ over a batch cycle and the corresponding cathode potential reported [265]. Average and standard deviation of the sample size over all batch cycles make the results less subjective than peak $E_{\text{p}}$ and $V_{\text{cell}}$ in the single cycle recorded in Figure 8-5. In most results the standard deviation for $E_{\text{cat}}$ is approximate to that for $V_{\text{cell}}$, indicating biofilm variance is negated over repeated batch cycles.

From this data it can be seen that the rank of performance is FAA>FTAM-A>F-930 ≈QDPSU≈AMI-7000>Rhinohide. With the exception of the QDPSU membrane which performed marginally worse than anticipated an improved performance with thin anion exchange membranes can be seen.

It was observed that the Rhinohide membranes were relatively slow to reach equilibrium. In other words, after inserting fresh electrolyte maximum $V_{\text{cell}}$ was attained before $E_{\text{cat}}$ had finished decreasing. This can be explained by the low distribution of pores on the surface of the Rhinohide (25nm diameter) causing a long time for the electroneutrality to be established. Interestingly this was not observed for F-930, where the $V_{\text{cell}}$ max corresponded to a relatively stable cathode potential. As such, the $V_{\text{cell}}$ values for Rhinohide membranes may be over approximated by 50-60mV in Table 8-2, this effect was less than 30mV in all other membranes. For instance in AMI-7000 the
average value of the minimum cathode potential corresponded to an average cell voltage only 17mV lower.

The presence of CH\textsubscript{3}COO\textsuperscript{-} providing an alternate charge carrier, thought diffusion of this species is anticipated to be sluggish in comparison to OH\textsuperscript{-} and monobasic Phosphate. This may be the reason why the result shows good comparability with the EIS and Polarisation curve results.

8.3.4 **EIS half-cell as a predictor of MFC batch performance**

The data taken from Table 8-2 for repeat batch cycles in acetate phosphate buffered artificial wastewater was expressed as peak current density and plotted against total impedance recorded during AC Impedance spectroscopy (\(R_{AC}\)) in PBS. The graphical representation is seen in Figure 8-9 is obtained. \(R_{AC}\) was obtained from extrapolation of the LF arc to \(-Z''=0\) Ohms at an applied potential approximate to \(P_{\text{max}}\) in 8.2.1 (\(E=-0.05\)V).

![Graphical representation](image)

**Figure 8-9.** Comparison of half-cell \(R_{AC}\) obtained from EIS and the batch MFC performance using identical MEA. \(R_{AC}\) at \(E=-0.05\)V.

No comparison to full MFC can be made as EIS data was collected at \(OCP\). The comparison with half-cell EIS allows biofilm variance to be discounted.
8.4 Conclusion

With the thin cation exchange membranes a significant space charge capacitance produced polarisation curves without an ohmic drop region. The EIS data showed that the high frequency response of the thin F-930 membrane was relatively in-exorbitant in terms of resistance. By contrast the thick Polystyrene-Divinyl benzene membranes produced a significant low frequency response suggesting significant inhibitory adsorption and blocking with this back-bone material. As such it’s use is not recommended.

More work should be done to assess whether the cation exchange membrane is simply incompatible with an anion exchange ionomer catalyst layer. It must be conceded that the interface between QDPSU ionomer catalyst layer and a cation exchange membrane may cause a charge interface and ‘trapped’ deposits in a real wastewater MFC system.
Chapter 9. Conclusions and recommendations for further work
9.1 Recommendations for further work

While the ligand itself was not improved in this thesis, it has been demonstrated that the nature of polymeric redox catalysts can be increased without altering the chemistry, but improving the ion and charge transfer throughout the catalyst layer. The work on optimal ionomer loadings and catalyst layer thickness established for nano-particles in PEMFC and AFC is possibly not applicable to polymeric electrocatalysts and most certainly not applicable to their implementation in MFC’s with low ionic concentration electrolytes. It has been demonstrated that superior anion exchange materials will be susceptible to decrease of trans-membrane ion diffusion rates with wastewater. Other more established anion exchange ionomers (eg. Quaternary Ammonium) can feasibly be equally susceptible to wastewater pollutants. Therefore the author recommends EIS study on cathodes exposed to continuous flow of wastewater to ascertain whether this process is irreversible and these superior anion selective materials could be used in a finalised design.

In general, materials that scavenge oxygen by O\textsubscript{2} co-ordination may become a promising avenue of ORR research. If the dioxygen bond strength is decreased by coating a metal surface with a planar O\textsubscript{2} chelating molecule (such as Dabco), reaction kinetics can be improved. This could provide an alternative to bi-metallic catalysts for obtaining the optimum binding energy point in a volcano plot, as suggested from the promising result on Platinum in this thesis (Table 5-1 vs Table 6-1). Combination of oxygen scavengers with activated carbon may produce cheap and simple air cathodes. The influence of planar O\textsubscript{2} chelator covering pure metal surfaces could be analysed from the perspective of volcano plots as a new avenue of ORR research, as suggested by the promising results for Pt.

The interest in reaction pathways expressed in this thesis was evolved from the discovery of H\textsubscript{2}O\textsubscript{2} release at high potential in neutral media. With specific ligand design and systematic testing of film preparation a polymer configuration may be produced that exclusively yields H\textsubscript{2}O\textsubscript{2} at potentials higher still than Cobalt Phthalocyanine. The effect of solution anion will be important to such a process. In certain settings (eg. Medical), H\textsubscript{2}O\textsubscript{2} is required to be generated in-situ due to its short shelf-life. An electrocatalyst that would generate oxidative sterilant’s with microelectrodes could prove useful.
9.2 Capital cost of materials

Rozendal et al state that 85% of the MFC capital cost is currently (2008) incurred by the membrane and cathode [351], stating a predicted cost of optimised membrane and electrodes of €10 m⁻² and €5 m⁻² respectively. While the FePc/KJB QDPSU catalyst layer of the non-precious metal cathode is within this target range (£1.24 m⁻²), the membrane is still outside.

Table 9-1. Cost analysis of materials discussed in this thesis. Price estimates (£ m⁻²) for catalysts, ionomers and ancillary equipment. Key (s) solid, (l) liquid form.

<table>
<thead>
<tr>
<th>Material / Supplier</th>
<th>Lab-scale material price / £ kg⁻¹ (s) or £ L⁻¹ (l)</th>
<th>Bulk-scale material price / £ kg⁻¹ (s) or £ L⁻¹ (l)</th>
<th>Required Use / g m⁻²</th>
<th>Price / £ m⁻²</th>
<th>F_{expen.} / Control</th>
<th>Factor</th>
<th>Figure / Table</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst Pt/C (20% wt.) / Alfa Aesar</td>
<td>618000</td>
<td>20000</td>
<td>25</td>
<td>200</td>
<td>8.8 / KJB v</td>
<td>J at E = -0.1V</td>
<td>Table 5-1.</td>
</tr>
<tr>
<td>KJB Carbon / Cabot</td>
<td>N/A</td>
<td>47</td>
<td>10</td>
<td>0.47</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FePc / Alfa Aesar</td>
<td>6140</td>
<td>6</td>
<td>10</td>
<td>0.06</td>
<td>1.28 / Pt/C v</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane/Ionomer</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion ionomer / Sigma</td>
<td>3852w</td>
<td>N/A</td>
<td>2</td>
<td>3.95</td>
<td>1.86 / PTFE v</td>
<td>J at E = 0.15V</td>
<td>Figure 6-16.</td>
</tr>
<tr>
<td>PTFE resin / Sigma</td>
<td>4.97w</td>
<td>2</td>
<td>2</td>
<td>0.11</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>QDPSU / Made in house</td>
<td>8w</td>
<td>2</td>
<td>2</td>
<td>0.016</td>
<td>7.37 / Nafion v</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ancillary equipment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Paper (20% PTFE) / Toray</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>481</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon Paper (P75T Hydrophobic) / Avcarb</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>323</td>
<td>N/A</td>
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<td></td>
</tr>
<tr>
<td>Generic Activated Carbon paper + PTFE</td>
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<td>N/A</td>
<td>N/A</td>
<td>4</td>
<td>N/A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Membrane Electrode Assembly</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Membraneless) FePc QDPSU / In house</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>482</td>
<td>2.4 / FePc Nafion</td>
<td>R_{dl} + R_{ct} at E = 0.1V</td>
<td>Figure A-21</td>
</tr>
<tr>
<td>(AMI-7001) FePc QDPSU / In house</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>543</td>
<td>0.777 / PEM</td>
<td>R_{dl} + R_{ct} at E = 0.1V</td>
<td>Figure 8-9</td>
</tr>
<tr>
<td>(Rhinohide) FePc QDPSU / In house</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>495</td>
<td>1.4 / PEM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(FTAM-A) FePc QDPSU / In house</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>759</td>
<td>1.28 / PEM</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Alibaba.com was used to source a bulk price of a generic lead/acid battery separator, H_{2}Pc pigment (Fe^{2+} chelation), PTFE and generic activated carbon paper. Industrial pigments being the cheapest source of Phthalocyanine, FePc is not as widely used as H_{2}Pc is widely available. Dissolving in DMSO with FeSO\textsubscript{4} until saturated will cause FePc crystals to deposit.
9.3 Closing comments on cathode development

The development of non-precious cathode catalysts attracts a large amount of research funding. The development is the charge primarily of chemical engineers as opposed to chemists. The common approach is in bimetallic synthesis and non-precious pyrolysis precursors and conditions. With a few exceptions [32, 195, 196, 352], very little effort is expended in the direction of controlled ligand design. This is in part due to the limited stability reported for these moieties, and in part due to the limited stability of chelating complexes in nucleophilic (OH-) or oxidising (H+) environments. The primary aim of chelation is to increase the oxidation potential and stabilise the metal.

9.4 Closing comments on balance of the MFC

In consideration of a finalised design for MFCs an eye must always be kept on the cost. The appeal of sophisticated control systems for maximal power output may not be justifiable if the MFCs are stacked in series. In this instance a control system requiring a reference electrode would be required for every anode-cathode array, controlling anode potential or O2 diffusion into the cell. MFCs are primarily a COD treatment technology with the potential to remove pollutants more effectively than even the anaerobic upstream baffled reactor (UASB). It may be deemed that the electricity generated from MFC stacks is not of a ‘harvestable’ quantity and the cells may be run at a fixed external resistance with no energy recovery. In this instance the anode and cathode may simply be short circuited and oxygen diffusion into the cell controlled until a suitable anode biofilm has developed. If this be the case then MFC designers should be wary of an upper potential limit for the anode [19], beyond which exoelectrogens will not grow during the start-up period when no net reaction occurs on the anode, thus adopting the potential of the cathode in air. As such, a cathode catalyst with an extremely low activation energy (eg. Bilirubin Oxidase, \( OCP=0.65V \) vs. Ag|AgCl [173]) may cause the biofilm never to develop if the anode and cathode are simply short-circuited. Aelterman et al established that 0V (Ag|AgCl) was not too high to stop formation of an anode biofilm [20]. An extension of this study with increments of up to +0.6V (Ag|AgCl) will allow MFC scale-up engineers to assess what the maximum potential an anode biofilm could withstand in the initial growth stages, should a superior cathode catalyst be implemented and the cell started at short circuit. Thus they will know
whether design consideration such as oxygen constraint should be factored into the start-up phase.

For a suitable power density the ‘sandwich’ type MFC stack is likely to be applied. In this case, a suitably inexpensive membrane will separate the anode-cathode pairs. For this design a carbon cathode could not be used. The amount of H₂O₂ generated by 2e⁻ ORR would degrade almost all known polymer materials, causing the need for regular maintenance and replacement. As such an inexpensive and robust 4e⁻ catalyst is sought. The reaction should be facile with electron transfer incurring the smallest of resistances. As such a superior tafel slope (25<|b_e|<35 mV dec⁻¹) should be associated with the 4e⁻ ORR reaction. This gives macrocycles the edge over carbon or alloy catalysts where the rate determining step involves a H⁺ or complex cleavage of a bond (50<|b_e|<120mV dec⁻¹). Combining this edge with a stabilising chemistry or MFC architecture will ensure its implementation into a commercial scale MFC plant.
Chapter 10. Appendices
10.1 Derivations

10.1.1 Derivation of tafel slope equation

Relating to Eq.2-8 it is clear that the symmetry factor of the rate determining reaction is produced by Eq.A-1.

\[
\beta_c = \frac{\Delta \phi_{TV}}{\Delta \phi_{VW}} \quad \text{(Eq.A-1)}
\]

Using this equation in Eq.2-8 the single rate determining step portion of the Eq.2-8 becomes Eq.A-2

\[
\Delta G^0 = \sum_i Z_{RV} F \Delta \phi_{RV} + Z_{VW} F \beta_c \phi_{VT} \quad \text{(Eq.A-2)}
\]

Which is re-organised to relate the inner potentials to the metal surface \(\phi_m\), using the term \(n_c\) to describe the no. of electrons transferred prior to the RDS and considering only electrons yields Eq.A-3. In this equation the terms \(n_{RV}/n_c\) and \(n_{VW}/n_c\) describe the number of electrons transferred before and during the RDS respectively from surface to bulk solution. Then substituting with Eq.2-9 generates Eq.A-4. It is this equation which simplifies to Eq.2-18, provided all electrons and charges traverse the total double layer [36].

\[
\Delta G^0 = \frac{n_{RV}}{n_c} F (\phi_s - \phi_{bulk}) + \frac{n_{VW}}{n_c} F \beta_c (\phi_s - \phi_{bulk}) \quad \text{(Eq.A-3)}
\]

\[
\frac{n_{RV}}{n_c} F (\phi_s - \phi_{bulk}) + \frac{n_{VW}}{n_c} F \beta_c (\phi_s - \phi_{bulk}) = -RT \ln(i) + C \quad \text{(Eq.A-4)}
\]

The term \((\phi_s - \phi_{bulk})/\ln i\) is not akin to \(|b_c|\) which uses \(\log_{10}\) as opposed to the natural logarithm (ln). Hence the multiplication factor of 2.303 is applied to convert \((\phi_s - \phi_{bulk})/\ln(i)\) to \((\phi_s - \phi_{bulk})/\log_{10}(I)\).

10.1.2 Derivation of Cottrell equation

After a step in applied potential sufficient to initiate a reaction, the concentration of electroactive species \(C\) at a given distance \((x)\) from the electrode surface is a function
of time \((t)\) produces the linear diffusion equation \(\partial C_0(x,t)/\partial t = D \partial^2 C(x,t)/\partial x^2\). The three boundary conditions of \(t, x\) and \(C\) are…

\[
\begin{align*}
C(0,t) &= 0 \text{ (for } t > 0) & \text{semi-infinite diffusion} \quad (\text{Eq.A-5}) \\
C_0 &= C(x,0) & \text{initial condition} \quad (\text{Eq.A-6}) \\
\lim_{x \to \infty} C(x,t) &= C_0 & \text{after E step} \quad (\text{Eq.A-7})
\end{align*}
\]

Performing Laplace transform on \((t)\) we obtain

\[
\begin{align*}
s\overline{C}(x,s) - C_0 &= D \frac{d^2 \overline{C}(x,s)}{dx^2} \quad (\text{Eq.A-8}) \\
\frac{d^2 \overline{C}(x,s)}{dx^2} - \frac{s}{D} \overline{C}(x,s) &= \frac{C_0}{D} \quad (\text{Eq.A-9})
\end{align*}
\]

The ordinary differential equations above can be solved using a boundary condition derived in [35] from a similar circuit where “\(s\)” is set to zero. In this derivation \(A’\) and \(B’\) are obtained from expanded Laplace transform treatment of constant \(A\) and \(B\).

\[
C(x) = \frac{b}{a^2} + A'e^{-ax} + B'e^{ax} \quad (\text{Eq.A-10})
\]

Inputting this equation into Eq.A-9 produces Eq.A-11

\[
\overline{C}(x,s) = \frac{C_0}{s} + A'(s)\exp\left[-(s/D)^{0.5}x\right] + B'(s)\exp\left[(s/D)^{0.5}x\right] \quad (\text{Eq.A-11})
\]

The limit of semi-infinite diffusion becomes

\[
\lim_{x \to \infty} \overline{C}(x,s) = C_0/s \quad (\text{Eq.A-12})
\]

Inputting \(B'(s)=0\) for the conditions at hand.
\[ \bar{C}(x,s) = \frac{C_0}{s} + A'(s) \exp \left[ -\left( \frac{s}{D} \right)^{0.5} x \right] \]  

(Eq.A-13)

The conditions \( \bar{C}(x,s) \) and \( C(x,t) \) depend on the third boundary condition. The application of conditions \( \lim_{x \to \infty} C(x,t) = C_0 \) produces Eq.A-14.

\[ \bar{C}(x,s) = \frac{C_0}{s} - \frac{C_0}{s} \exp \left[ -\frac{x(s/D)}{s} \right] \]  

(Eq.A-14)

A Laplace transform of the term relating proportionality of flux of material to the electrode to current (Eq.2-35) produces Eq.A-15.

\[ \frac{i(s)}{nFA} = D \left[ \frac{\partial \bar{C}(x,s)}{\partial x} \right]_{x=0} \]  

(Eq.A-15)

The derivative term in Eq.A-15 can be evaluated with Eq.A-14 with substitution yielding Eq.A-16.

\[ i(s) = \frac{nFAD^{0.5}C_0}{s^{0.5}} \]  

(Eq.A-16)

The Inverse produces the current-time response of the Cottrell equation (Eq.2-34) applicable for a potential sweep on a planar electrode under diffusion control.

**10.1.3 Derivation of the Levich equation**

The velocity of fluid approaching the disc is given by the sum of laminar velocity in each direction according to Eq.A-17.

\[ V = \mu_1 \nu_r + \mu_2 \nu_y + \mu_3 \nu_\phi \]  

(Eq.A-17)

In this instance \( \mu_1, \mu_2, \mu_3 \) are unit vectors in the positive direction of \( r, y \) and \( \phi \) respectively at a certain co-ordinate relative to the centre of the disc surface. “\( y \)” is the distance from the RDE/RRDE surface (cm), \( \nu_x, \nu_y \) and \( \nu_z \) are fluid velocities (cm s\(^{-1}\)) in
the 3D plane of x, y and z. “r” is the radial distance from the centre of the electrode (cm), and \( \phi \) is the electrical potential. \( C \) does not vary with \( \phi \) provided the flow is symmetrical and perpendicular to the electrode. After a potential step at steady state (\( \omega = 0 \) rpm) in the mass transfer control region, the transient decays to a steady value, contrary to unstirred solution, \( \partial C / \partial t = 0 \). The steady state laplacian operator is derived at length elsewhere, but the result is Eq.A-18 in the case of a reduction.

\[
\frac{\partial C_{ox}}{\partial t} = D_{ox} \nabla^2 C_{ox} - v \cdot \nabla C_{ox}
\]  

(Eq.A-18)

Where \( \nabla^2 \) is the laplacian operator \( \partial^2 / \partial x^2 \), where \( x \) is the distance in the plane of the diffusion band. Writing Eq.A-18 in terms of reaction cylindrical co-ordinates for steady state Eq.A-19 is obtained.

\[
v_r \left( \frac{\partial C}{\partial r} \right) + \frac{v_\theta}{r} \left( \frac{\partial C}{\partial \phi} \right) + v_y \left( \frac{\partial C}{\partial y} \right) = D \left[ \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} + \frac{1}{r^2} \frac{\partial^2 C}{\partial \phi^2} \right]
\]  

(Eq.A-19)

The limiting current condition at \( y = 0 \), \( C = 0 \) and \( \lim_{y \to \infty} C = C_0 \). Assuming that \( C \neq f(\phi) \) and \( v_y \neq f(r) \), so the portion \( \partial C / \partial \phi = \partial^2 C / \partial \phi^2 = 0 \) the situation across the face of the disc is \( \partial C / \partial r = 0 \), in other words reactant concentration does not change across the face of the disc or at any point the same distance from the disc centre, allowing significant simplification in Eq(A-20).

\[
v_y = \left( \frac{\partial C}{\partial y} \right) = D \frac{\partial^2 C}{\partial y^2}
\]  

(Eq.A-20)

Kármán and Cochran’s [353] treatment was described by Levich [55], in which laminar velocities are reported for the y and r ordinate, Eq.A-22 and Eq.A-23. This approach is based on the Schmidt number \( (S_c) \) for a known substrate in a known solute (section 10.2.5.) and is an approximation of Eq.A-21 [54], where only the first term has been expanded.

\[
v_y = (\bar{\omega} \nu)^{0.5} \left[ -0.51023 \left( \frac{\bar{\omega}}{\nu} \right)^{0.5} y^2 + \frac{1}{3} \left( \frac{\bar{\omega}}{\nu} \right)^{3/2} y^3 - 0.10265 \left( \frac{\bar{\omega}}{\nu} \right)^2 y^4 \right] \]  

(Eq.A-21)
\[ \nu_y = \left( \frac{a}{\nu} \right)^{0.5} \left[ 0.51023 \left( \frac{a}{\nu} \right)^{0.5} \right] = -0.51a \nu^{3/2} y^{-1/2} \]  
(Eq.A-22)

\[ \nu_r = r a \left( -0.51023 \left( \frac{a}{\nu} \right)^{0.5} y \right) = 0.51a \nu^{3/2} y^{3/2} r y \]  
(Eq.A-23)

Substituting Eq.A-22 into Eq.A-20 produces Eq.A-24. Where \( B = D_0 \nu^{3/2} \nu^{1/2} / 0.51 \)

\[ \frac{\partial^2 C}{\partial y^2} = - \frac{y^2}{B} \frac{\partial C}{\partial y} \]  
(Eq.A-24)

Letting \( M = \partial C / \partial y \) to make \( \partial M / \partial y = \partial^2 C / \partial y^2 \) at \( y=0 \), \( M=M_y = \left( \partial C / \partial y \right)_{y=0} \), then Eq.A-24 becomes..

\[ \frac{\partial M}{\partial y} = \left( - \frac{y^2}{B} \right) M \]  
(Eq.A-25)

\[ \int_{M_0}^M \left( \frac{dM}{M} \right) = \left( - \frac{1}{B} \right) \int_0^y y^2 \, dy \]  
(Eq.A-26)

\[ \frac{M}{M_0} = \exp \left( - \frac{y^3}{3B} \right) \]  
(Eq.A-27)

\[ \frac{\partial C}{\partial y} = \left( \frac{\partial C}{\partial y} \right)_{y=0} \exp \left( - \frac{y^3}{3B} \right) \]  
(Eq.A-28)

\[ \int_0^y dC = \left( \frac{\partial C}{\partial y} \right)_{y=0} \int_0^y \exp \left( - \frac{y^3}{3B} \right) \, dy \]  
(Eq.A-29)

Setting the limits as limiting current conditions \( C(y=0) \). Substituting \( z=y^3/3B \) or \( 0.8934(3B)^{1/3} \) we obtain Eq.A-30.

\[ C_0 = \left( \frac{\partial C}{\partial y} \right)_{y=0} 0.8934 \left( \frac{3D_0 \nu^{3/2} \nu^{0.5}}{0.51} \right)^{1/3} \]  
(Eq.A-30)

Expressing in terms of the flux at the electrode surface (current);
\[ i = nFAD \left( \frac{\partial C}{\partial y} \right)_{y=0} \] 

(Eq.A-31)

10.2 Calculations and estimates

10.2.1 FePc/KJB Nafion film thickness for EIS calculation on TFE

Using an assumed density of 0.1325 g cm\(^{-3}\) for KJB (assume +50% wt. FePc=0.19875 g cm\(^{-3}\) FePc/KJB) and the density of dry Nafion ionomer=2.1 g cm\(^{-3}\) [354]. Loadings are; FePc/KJB; 71\(\mu\)g cm\(^{-2}\)+Nafion; 111\(\mu\)g cm\(^{-2}\). Producing loading of FePc/KJB; 17.55\(\mu\)g+Nafion; 27.4368\(\mu\)g. Dividing by density produces volumes of FePc/KJB; 8.83x10\(^{-5}\) cm\(^3\) + Nafion; 1.3x10\(^{-5}\) cm\(^3\). The void fraction is greatly reduced after FePc incorporation, assuming 50% of the Nafion fills the pores with the remainder forming a surface film. The combined thickness is 9.5x10\(^{-5}\) cm\(^3\)/0.24718=3.8x10\(^{-4}\) cm (±30%)

Predicted loading of FePc (\(\Gamma_{FePc}\)=23.66\(\mu\)g cm\(^{-2}\) of Fe=1.09618x10\(^{-4}\) Moles cm\(^{-3}\)
Electro-active FePc (\(\Gamma_{FePc}^{\ast}\)=2.26x10\(^{-10}\) Moles cm\(^{-2}\)
=Volumetric electro-active FePc=5.95x10\(^{-7}\) Moles cm\(^{-3}\)

10.2.2 FePc/KJB QDPSU air cathode thickness for EIS calculation

0.19875g cm\(^{-3}\) FePc/KJB and the density of dry Nafion ionomer=2.1g cm\(^{-3}\)
Applied weights: 2mg cm\(^{-2}\) FePc/KJB and 0.2 mg cm\(^{-2}\) QDPSU.
In air cathodes the ionomer loading is small enough to be completely entrained in the carbon pores, therefore the volume of the ionomer is neglected.
Volume=12.56cm\(^2\)*0.002g cm\(^{-2}\)/0.19875g cm\(^{-3}\)=0.126cm\(^3\)
Thickness=0.01cm (±30%) c.a. the maximum limit deemed efficient for a catalyst layer [355].

10.2.3 Cost calculation for QDPSU synthesis

The rough cost ratio between Nafion and DABCO was added. QDPSU was synthesised in our lab. Nafion resin is £127.30/10g\(^{11}\), and DABCO is £12.90/100g\(^{12}\), PSU around

---

\(^{11}\) Alfa Aesar
\(^{12}\) Alfa Aesar
£380/kg\textsuperscript{13} or £10/kg\textsuperscript{14} bulk. For the QDPSU, the cost could be around x10 the material cost, approximately £140-300/kg, significantly lower than Nafion. A QDPSU membrane 30μm thick ($\rho_{dry}=1240$kg m\textsuperscript{-3}) produces a price £110,000m\textsuperscript{-3} or £8 m\textsuperscript{-2}, though with PTFE cross-linker the price will rise.

10.2.4 Non-precious cathodes and MEA

The charge carrier concentration in the membrane phase is obtained from (Eq.A-32) where $C_{c}$ is the membrane phase charge carrier concentration (moles of ion per cm\textsuperscript{3} polymer), $IEC$ is the ion exchange capacity in mMoles of ion per gram of polymer, $\rho_{m,i}$ is the wet density of the membrane for ion “i” (g cm\textsuperscript{-3}), $V_{s-H2O}$ is the volume based water uptake (cm\textsuperscript{3} cm\textsuperscript{-3}).

$$C_{c} = 0.001*IEC*\rho_{m,i}/\left(1 + 0.01V_{s-H2O}\right) \quad \text{(Eq.A-32)}$$

For the diffusion of ions in dilute solution ($D_{0}$) in cm\textsuperscript{2} s\textsuperscript{-1}, $k_B$ is the Boltzmann constant (1.3806488×10\textsuperscript{-23} m\textsuperscript{2} kg s\textsuperscript{-2} K\textsuperscript{-1}), $T$ is temperature (K) and $z$ is the ion charge.

$$D_{0} = \mu*k_{B}*T/z \quad \text{(Eq.A-33)}$$

The rate of ion diffusion through the membrane at $E=\text{OCP}$ from the Warburg diffusion co-efficient can then be used to express the relative diffusion of an ion compared to dilute solution ($D/D_{0}$).

10.2.5 Schmidt number of O\textsubscript{2} in aqueous solution

$$Sc_{0} = 1800.6 - 120.1t + 3.7818t^{2} - 0.047608t^{3} \quad \text{(Eq.A-34)}$$

$$Sc = Sc_{0}\left(1 + 3.14 \times 10^{-3} PSU\right) \quad \text{(Eq.A-35)}$$

\textsuperscript{13}Sigma Aldrich
\textsuperscript{14}Alibaba.com
Where PSU=practical salinity units=5.3828 for 50mM PBS (6.6mS cm\(^{-1}\)), and \( t \) is temperature (in ºC). Produces a value of \( \text{Sc}^{0} = 725.123 \), and \( \text{Sc} = 737.4 \) for 50mM PBS. For \( \text{H}_2\text{O}_2 \) this number is 1561 from Table A-2.

10.3 Tables

Table A-1. Preparation procedure for all catalysts prepared in-house.

<table>
<thead>
<tr>
<th>Catalyst Description</th>
<th>Catalyst Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unpyrolysed FePc on Monarch</td>
<td>FePc/MON</td>
</tr>
<tr>
<td>Pyrolysed FePc on Monarch</td>
<td>FePc/MON pyr</td>
</tr>
<tr>
<td>Manganese Oxides on Monarch</td>
<td>MnOx/MON</td>
</tr>
<tr>
<td>Unpyrolysed FePc and MnOx on Monarch</td>
<td>FePcMnOx/MON</td>
</tr>
<tr>
<td>Titanium Oxides on Monarch</td>
<td>TiOx/MON</td>
</tr>
<tr>
<td>Pyrolysed TiOx on Monarch</td>
<td>TiOx/MON pyr</td>
</tr>
<tr>
<td>FePc on Ketjen Black</td>
<td>FePc/KJB</td>
</tr>
<tr>
<td>Pyrolysed FePc on KJB</td>
<td>FePc/KJB pyr</td>
</tr>
<tr>
<td>FePc and MnOx on KJB from KMnO₄ action</td>
<td>FePcMnOx/KJB (KMnO₄)</td>
</tr>
<tr>
<td>Unpyrolysed FePc and MnOx on KJB</td>
<td>FePcMnOx/KJB (+Mn²⁺)</td>
</tr>
<tr>
<td>Pyrolysed Monarch Carbon</td>
<td>HT Monarch</td>
</tr>
</tbody>
</table>
Table A-2. Physical constants of 50mM PBS used in this study.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Chemical Species</th>
<th>O$_2$</th>
<th>H$_2$O$_2$</th>
<th>OH$^-$</th>
<th>H$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (saturated) / Mole cm$^3$</td>
<td></td>
<td>5.67 x 10$^7$</td>
<td>-</td>
<td>10$^{-10}$</td>
<td>10$^{-10}$</td>
</tr>
<tr>
<td>Diffusivity / m$^2$ s$^{-1}$</td>
<td></td>
<td>1.67 x 10$^{-9}$</td>
<td>0.66 x 10$^{-9}$</td>
<td>8.06 x 10$^{-9}$</td>
<td></td>
</tr>
<tr>
<td>$K_a$ / Mole dm$^{-3}$</td>
<td></td>
<td>-</td>
<td>1.5 x 10$^{-12}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K_b$ / Mole dm$^{-3}$</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

50mM PBS, pH7

Kinematic Viscosity ($\nu$) / m$^2$ s$^{-1}$: 1.0304 x 10$^{-6}$

Density ($\rho$) / kg m$^{-3}$: 1.00479

The information in Table A-2 is taken from [43] for 20°C for 100mM PBS. Reported values vary from 1mM to 0.22mM.

Table A-3. Dissolved O$_2$ in air equilibrated 50mM Na$^+$PBS, pH 7.0.

<table>
<thead>
<tr>
<th>Air equilibrated T / °C</th>
<th>[O2] T / °K</th>
<th>mg / L</th>
<th>Moles dm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.8 287.95</td>
<td>9.80</td>
<td>3.06E-04</td>
<td></td>
</tr>
<tr>
<td>18  291.15</td>
<td>9.37</td>
<td>2.93E-04</td>
<td></td>
</tr>
<tr>
<td>19.5 292.65</td>
<td>9.07</td>
<td>2.83E-04</td>
<td></td>
</tr>
<tr>
<td>22.1 295.25</td>
<td>9.04</td>
<td>2.83E-04</td>
<td></td>
</tr>
<tr>
<td>25  298.15</td>
<td>8.70</td>
<td>2.72E-04</td>
<td></td>
</tr>
<tr>
<td>25.9 299.05</td>
<td>8.63</td>
<td>2.70E-04</td>
<td></td>
</tr>
</tbody>
</table>

This data was acquired using a Jenway consumptive dissolved O$_2$ probe in rapidly agitated air equilibrated solutions. No dissolved bubbles were visible.

$^{15}$ The concentration of O$_2$(aq) at 20°C varies significantly (1mM to 0.22mM) across literature, but consensus shows that the phosphate or sodium ions cause no significant difference from that in DIW.
Table A-4. Physical constants of ions in 50mM PBS at T = 20°C. Protons and Hydroxide ions reported at infinite dilution, sodium and phosphates reported at 50mM where possible.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>H₂NaPO₄ / HNa₂PO₄</th>
<th>Na⁺</th>
<th>HPO₄²⁻</th>
<th>H₂PO₄⁻</th>
<th>H⁺</th>
<th>OH⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration / Mole dm⁻³</td>
<td>0.021147 / 0.028847</td>
<td>0.078841</td>
<td>0.028847</td>
<td>0.021147</td>
<td>10⁻⁷</td>
<td>10⁻⁷</td>
</tr>
<tr>
<td>Diffusivity / m² s⁻¹</td>
<td>n/a</td>
<td>1.29x10⁻⁹ [356] (16)</td>
<td>0.86 x10⁻⁹</td>
<td>1.0 x10⁻⁹</td>
<td>8.6x10⁻⁹ [357]</td>
<td>4.78x10⁻⁹ [357]</td>
</tr>
<tr>
<td>Molar Conductivity / S m⁻² mole⁻¹</td>
<td>n/a</td>
<td>50.1</td>
<td>66</td>
<td>57</td>
<td>349.6</td>
<td>200</td>
</tr>
<tr>
<td>Electrophoretic mobility (μ) / m² V⁻¹ s⁻¹</td>
<td>n/a</td>
<td>4.98x10⁻⁸ (17)</td>
<td>5.9x10⁻⁸ [358]</td>
<td>36.2x10⁻⁸ [357]</td>
<td>20.5x10⁻⁸ [357]</td>
<td></td>
</tr>
<tr>
<td>Hydrated Ionic radii / Nm [359]</td>
<td></td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.9</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Table A-5. Reported qualities of carbons from manufacturer and academic sources.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ketjen Black EC300J [360]</th>
<th>Monarch 1000</th>
<th>Synthetic Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Density / g cm⁻³</td>
<td>0.1325</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore Volume / cm³ g⁻¹</td>
<td>3.1-3.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Void fraction (from above) / cm³ cm⁻³</td>
<td>0.4286</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relative Surface Area (N₂ adsorption) / m³ g⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle diameter / μm</td>
<td>&lt;20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apparent pH / pH</td>
<td>9-10.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iodine Adsorption / mg g⁻¹</td>
<td>740-840</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table A-6. Collection Efficiency for Pt ring used in Wroblowa analysis.

<table>
<thead>
<tr>
<th>Assume 100% H₂O₂</th>
<th>100rpm</th>
<th>200rpm</th>
<th>300rpm</th>
<th>400rpm</th>
<th>600rpm</th>
<th>800rpm</th>
<th>1000rpm</th>
<th>1600rpm</th>
<th>3200rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synth Graphite/Nafion</td>
<td>0.2549</td>
<td>0.2543</td>
<td>0.2455</td>
<td>0.2359</td>
<td>0.2165</td>
<td>0.2016</td>
<td>0.1910</td>
<td>0.1648</td>
<td>0.1155</td>
</tr>
<tr>
<td>Assume 100% H₂O₂</td>
<td>100rpm</td>
<td>200rpm</td>
<td>300rpm</td>
<td>400rpm</td>
<td>600rpm</td>
<td>800rpm</td>
<td>1000rpm</td>
<td>1600rpm</td>
<td>3200rpm</td>
</tr>
<tr>
<td>Glassy Carbon</td>
<td>0.2328</td>
<td>0.2491</td>
<td>0.2501</td>
<td>0.2228</td>
<td>0.2117</td>
<td>0.2047</td>
<td>0.1910</td>
<td>0.1779</td>
<td>0.1366</td>
</tr>
<tr>
<td>% drop from CE=37%</td>
<td>100rpm</td>
<td>200rpm</td>
<td>300rpm</td>
<td>400rpm</td>
<td>600rpm</td>
<td>800rpm</td>
<td>1000rpm</td>
<td>1600rpm</td>
<td>3200rpm</td>
</tr>
<tr>
<td>Synth Graphite/Nafion</td>
<td>0.37</td>
<td>0.3691</td>
<td>0.3563</td>
<td>0.3423</td>
<td>0.3142</td>
<td>0.2926</td>
<td>0.2772</td>
<td>0.2391</td>
<td>0.1676</td>
</tr>
<tr>
<td>% drop from CE=37%</td>
<td>100rpm</td>
<td>200rpm</td>
<td>300rpm</td>
<td>400rpm</td>
<td>600rpm</td>
<td>800rpm</td>
<td>1000rpm</td>
<td>1600rpm</td>
<td>3200rpm</td>
</tr>
<tr>
<td>Glassy Carbon</td>
<td>0.3443</td>
<td>0.3685</td>
<td>0.3700</td>
<td>0.3297</td>
<td>0.3132</td>
<td>0.3029</td>
<td>0.2826</td>
<td>0.2632</td>
<td>0.2021</td>
</tr>
</tbody>
</table>

16 Infinite dilution, 25°C
17 Infinite dilution, 25°C
Table A-7. Ingredients of biofilm growth nutrient supplement. x10 concentrated stock solution.

<table>
<thead>
<tr>
<th>Stock mg/ L</th>
<th>Final Molarity / M dm⁻³</th>
<th>Stock mg/ L</th>
<th>Final Molarity / M dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄Cl</td>
<td>400</td>
<td>7.47E-04</td>
<td>FeSO₄•7H₂O</td>
</tr>
<tr>
<td>MgSO₄</td>
<td>150</td>
<td>1.25E-04</td>
<td>HBO₃</td>
</tr>
<tr>
<td>CaCl₂•2H₂O</td>
<td>50</td>
<td>3.40E-05</td>
<td>NiSO₄•6H₂O</td>
</tr>
<tr>
<td>MnCl₂•4H₂O</td>
<td>1.5</td>
<td>7.58E-07</td>
<td>CoCl₂•2H₂O</td>
</tr>
<tr>
<td>CuSO₄•5H₂O</td>
<td>1</td>
<td>4.00E-07</td>
<td>(NH₄)₆Mo₇O₂₄•4H₂O</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>1</td>
<td>7.34E-07</td>
<td></td>
</tr>
</tbody>
</table>

Table A-8. Reproducibility of electro-active FePc loading from 6μl aliquots of new catalyst inks. Data from integration of Fe(II)→Fe(III) peak obtained in N₂ sat PBS for separate inks produced from 10mg of FePcKJB catalyst in the presence of different binders.

<table>
<thead>
<tr>
<th>Binder</th>
<th>H⁺Nafion</th>
<th>Na⁺ Nafion</th>
<th>QDPSU</th>
<th>PTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>g̃FePc /</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moles cm⁻²</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.9E-09</td>
<td>1.7E-09</td>
<td></td>
<td>7.5E-09</td>
</tr>
<tr>
<td></td>
<td>3.7E-09</td>
<td>6.0E-09</td>
<td>3.1E-09</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.7E-09</td>
<td>6.0E-09</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.1E-09</td>
<td>6.0E-09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>3.9E-09</td>
<td>3.9E-09</td>
<td>3.4E-09</td>
<td>7.5E-09</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>8.9E-10</td>
<td>3.9E-09</td>
<td>3.4E-09</td>
<td>7.5E-09</td>
</tr>
<tr>
<td>Co-eff. of variation</td>
<td>0.23</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The co-efficient of variation is obtained from dividing the standard deviation by the mean.
Table A-9. Membranes thickness in NaHCO₃ PBS or NaCl solution and % swelling vs dry state. Standard deviation over 4 repeat Vernier thickness measurements.

<table>
<thead>
<tr>
<th>Membrane / Manufacturer</th>
<th>Dry Thick / μm</th>
<th>50mM NaCl Thick / μm</th>
<th>St. Dev. /μm</th>
<th>% swell vs. dry</th>
<th>50mM PBS Thick. / μm</th>
<th>St. Dev. /μm</th>
<th>% swell vs. dry</th>
<th>50mM NaHCO₃ Thick. / μm</th>
<th>St. Dev. /μm</th>
<th>% swell vs. dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-930 / Fumasep</td>
<td>26</td>
<td>35</td>
<td>2.0</td>
<td>35%</td>
<td>35</td>
<td>1.5</td>
<td>45%</td>
<td>38</td>
<td>3.2</td>
<td>47%</td>
</tr>
<tr>
<td>CMI-7000 / Membranes Int.</td>
<td>465</td>
<td>511</td>
<td>6.0</td>
<td>10%</td>
<td>520</td>
<td>3.0</td>
<td>12%</td>
<td>561</td>
<td>4.7</td>
<td>21%</td>
</tr>
<tr>
<td>Surrey / Surrey</td>
<td>59</td>
<td>80</td>
<td>1.0</td>
<td>36%</td>
<td>77</td>
<td>1.7</td>
<td>31%</td>
<td>83</td>
<td>1.3</td>
<td>40%</td>
</tr>
<tr>
<td>ADP / Morgane</td>
<td>146</td>
<td>154</td>
<td>0.6</td>
<td>5%</td>
<td>154</td>
<td>1.3</td>
<td>5%</td>
<td>152</td>
<td>1.5</td>
<td>4%</td>
</tr>
<tr>
<td>FAA / Fumasep</td>
<td>119</td>
<td>115</td>
<td>0.6</td>
<td>-3%</td>
<td>116</td>
<td>0.6</td>
<td>-2%</td>
<td>115</td>
<td>1.2</td>
<td>-3%</td>
</tr>
<tr>
<td>FTAM-A / Fumasep</td>
<td>557</td>
<td>637</td>
<td>11.4</td>
<td>14%</td>
<td>663</td>
<td>3.3</td>
<td>19%</td>
<td>639</td>
<td>41.5</td>
<td>15%</td>
</tr>
<tr>
<td>AMI-7001 / Membranes Int.</td>
<td>503</td>
<td>555</td>
<td>1.7</td>
<td>10%</td>
<td>578</td>
<td>3.2</td>
<td>15%</td>
<td>522</td>
<td>1.3</td>
<td>4%</td>
</tr>
<tr>
<td>QDPSU / Made in house</td>
<td>38</td>
<td>54</td>
<td>17.6</td>
<td>43%</td>
<td>60</td>
<td>16.8</td>
<td>57%</td>
<td>43</td>
<td>6.8</td>
<td>13%</td>
</tr>
<tr>
<td>ETFE Cranfield / Made out house</td>
<td>37</td>
<td>43</td>
<td>2.5</td>
<td>16%</td>
<td>40</td>
<td>4.1</td>
<td>7%</td>
<td>43</td>
<td>2.5</td>
<td>14%</td>
</tr>
<tr>
<td>Rhinohide / Entek</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>FAB / Fumasep</td>
<td>83</td>
<td>91</td>
<td>1.3</td>
<td>9%</td>
<td>97</td>
<td>2.6</td>
<td>16%</td>
<td>92</td>
<td>1.5</td>
<td>11%</td>
</tr>
<tr>
<td>FAD-PET / Fumasep</td>
<td>87</td>
<td>95</td>
<td>0.6</td>
<td>10%</td>
<td>115</td>
<td>1.5</td>
<td>32%</td>
<td>111</td>
<td>4.8</td>
<td>27%</td>
</tr>
</tbody>
</table>

Table A-10. Quantification of random sources of error in thin film experiment. Example is for FePcKJB Nafion film.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Error margin (+/-)</th>
<th>Error margin (+/-) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst weight (mg)</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Pipette - Nafion (μl)</td>
<td>340</td>
<td>1.02</td>
</tr>
<tr>
<td>Pipette - Ethanol (μl)</td>
<td>3000</td>
<td>9</td>
</tr>
<tr>
<td>Pipette - disc aliquot (μl)</td>
<td>6</td>
<td>0.036</td>
</tr>
</tbody>
</table>

Cumulative error in \( \Gamma / \% \) 10.6

10.4 Chemical de-activation of FePc catalyst

The stability of FePc in the presence of H⁺Nafion/Ethanol inks is shown from stabilised CV of the thin films in N₂ saturated PBS (Figure A-1). The aim was to assess whether polarisation was required for de-metallation (Eq.3-8).
As the catalyst aged in the presence of O₂ at pH 2 several observations were made about the redox peak:

1. The main Fe(II)Pc/Fe(III)Pc redox peak reduced in size with age of the ink.
2. The redox peaks at $E_p$=-0.264V and $E_p$=-0.076V grew with sample age. The mid-point of this redox couple is $E^\circ$=-0.17V.

Several possibilities must be eliminated before the $E^\circ$=-0.17V couple can be identified;

1) FePc solubility in ethanol (ink) is low, recrystallization of FePc is unlikely.
2) Sulfonate (from solvated Nafion) or ethanol may ligate FePc, altering $E^\circ$. It is implausible that a single sulfonate ligand may cause a large shift in $E^\circ$ [181].
3) The formation of µ-oxo FePc occurs within catalyst ink with O₂. The $E^\circ$=-0.17V redox may be a FePc-O-FePc moiety [179, 361].
4) De-metallation of FePc occurs, producing electrochemically detectable H₂Pc.

µ-oxo FePc is generated instantaneously during polarisation [212] yet the Fe(II)/Fe(III) can still be visible in O₂ at approximately the same $E^\circ$ (Figure 5-22) making (3) an unlikely explanation. Zagal shows the Phthalocyanine ring redox of H₂Pc occurs 0.3V lower than the Co(II)Pc/Co(III)Pc redox in alkali medium [193]. The $W_{1/2}$ and $E_{pcr}-E_{pe}$ of this couple suggests pH dependency, as if causing proton dissociation (-59mV pH⁻¹). Using Eq.3-8 would generate a corresponding peak at $E$=-0.17V for H₂Pc in pH7 media.
[362], close to that observed thus suggesting H\textsubscript{2}Pc. the characteristics of the H\textsubscript{2}Pc peak are;

- Quasi-reversible with the characteristics of the forward and reverse being -0.049 (\(W_{1/2}=0.0862\)V) and \(E_p=-0.250\) (\(W_{1/2}=0.0786\)V) respectively. A catalyst layer applied from 80 day old ink had a H\textsubscript{2}Pc peak 28.5% the size of the initial Fe(II)Pc/Fe(III)Pc peak, while the Fe(II)/Fe(III)Pc peak was 6-7% the original size after 80days.
- At \(t=80\) days deterioration in Fe(II)Pc \(\rightarrow\) Fe(III)Pc is >90% but the increase in H\textsubscript{2}Pc only 28.5% suggesting H\textsubscript{2}Pc decomposition or solvation has occurred.
- The oxidation peak of H\textsubscript{2}Pc is Gaussian and the reduction peak slightly Lorentzian as if charge insertion were impeded during Fe(III)Pc reduction.

The Fe(III)Pc \(\leftrightarrow\) Fe(II)Pc peak shape is initially Gaussian from new ink while it becomes Lorentzian in 80 day ink suggesting resistance to electron propagation.

10.5 Method Justification
10.5.1 Iron Phthalocyanine films, deposition solvent and support

FePc is readily solvated in concentrated H\textsubscript{2}SO\textsubscript{4} or several organic solvents that reversibly complex with iron, namely Pyridine, CHCl\textsubscript{3}, CH\textsubscript{2}Cl\textsubscript{2}, DMSO and DMF (insoluble in THF [363]). Thermal treatment or ligand substitution is required to remove some of these ligands. DMSO could not be used due to low volatility, requiring potentially harmful heating for removal. Deposition on GC disc from H\textsubscript{2}SO\textsubscript{4} may result in thermal decomposition from enthalpy of solution. Low FePc solubility in non-polar aliphatic and aromatic solvents, with additional problems of graphite pore entrainment (eg. Benzene) prevent consideration of this deposition method.

Therefore FePc was deposited from DMF, a relatively strong ligand solvent (though FePc complexing is reversible). Establishing DMF removal is an important aspect of the validity of this mechanism study. The FePc-DMF adduct displays a different electrochemistry than FePc-H\textsubscript{2}O. Chen et al show FePc to form self-assembled \(\pi\)-bond lattices from a DMF solution [70], displacing axial ligands with H\textsubscript{2}O. Axial DMF ligands (Figure 3-5, position X) will remain after evaporation at ambient temperature, [275]. O\textsubscript{2} did not displace the DMF ligand in acid electrolyte (SO\textsubscript{4}\textsuperscript{2-} anion) [275]. If
FePc was co-ordinated by two mono dentate DMF ligands, O$_2$ binding and ORR would not be possible without ligand substitution, yet the O$_2$ reduction wave is observed (Section 5.2.3). This may be due to Phosphate binding strongly compared to SO$_4^{2-}$ allowing DMF substitution to occur.

As seen in Table 5-1, deposition on KJB (BET=795m$^2$ g$^{-1}$ [218]) provided a larger FePc than on Monarch (BET=292m$^2$ g$^{-1}$ [364]), as the Brunauer Emmett Teller surface area is larger. Though the data is not presented in Table 5-1, FePc (50%wt.) was deposited on Vulcan XC-72R carbon (BET=250m$^2$ g$^{-1}$ [364]) with equilibrium adsorption from FePc-DMF solution (C:FePc=50:50 wt.) to produce 43.6x10$^{13}$ sites cm$^{-2}$. The area of the two carbons is comparable but loading from DMF is slightly higher than that from concentrated H$_2$SO$_4$ (FePc/MON). This validates the assertion that FePc was not blocked by axial DMF ligands at the point of polarisation in N$_2$ (Figure 5-3). Deposition in hydrophobic areas (via non-aqueous solvent) may influence effective loading. Deposition on carbon support increased the geometric loading of FePc in electrolytic contact by x9.2 for FePc/KJB at 223x10$^{13}$ redox active sites cm$^{-2}$ compared to $\Gamma$ =6.77x10$^{-8}$ Moles cm$^{-2}$ unsupported FePc layer in Figure 5-2 at 25.4x10$^{13}$ redox active sites cm$^{-2}$. If uniformly ordered, this crystalline form produces an expected thickness equating to 647 layers of FePc, using the molecule dimensions outlined by Baker et al [213] for an $\alpha$-FePc film.

10.5.2 Electroanalysis of redox polymer catalyst

Two methods of concentration polarisation correction are reviewed in Figure A-2. From K-L plot intercepts of $\nu$=5mV/s data and from applying Eq.2-52 to unstirred solutions with $\nu$=1mV/s LSV data.
Figure A-2. Effect of concentration polarisation and scan rate on tafel behaviour of an FePc/KJB film and correction techniques. Key: $J = \text{Recorded Current density, } J_k = \text{Kinetic Current Density.}$

Figure A-3. Fitting a polynomial baseline (6-order) to obtain integratable charge of Fe(II)Pc/Fe(III)Pc redox
This method has been adapted from the one used by Baker et al [179] and a study on the redox of immobilised proteins of Hirst et al [365]. The difference being that this group used a baseline of the current response by an electrode with the support carbon with no FePc. The integration of the peak was constrained to a 50mV range either side of the peak potential. As observed in Figure A-3 the higher surface loading in carbon black supported FePc causes the peak to cover a 0.4V potential range when using \( \nu=20\text{mV/s} \). As such the high and low potential limit for charge integration was established as the point where deflection from linear \( i-E \) response (capacitive current). The passed charge was integrated on both forward and reverse scans and a match (±0.5 %) demonstrated accurate baseline fitting of this finite and surface controlled process.

![Figure A-4. Fe(II)↔Fe(III) redox peaks (A) with adjustment of cathodic scan baseline. (B) Enlarged Y-axis](image)

When the peaks are checked for charge conservation (\( Q_{\text{Fe(II)}} \rightarrow \text{Fe(III)} = Q_{\text{Fe(III)}} \rightarrow \text{Fe(II)} \)) it is seen that cathodic tailing is present in carbon supported FePc in Figure A-4. This is consistent with the finding in Figure 5-2(A) which shows resistance to Fe(III)→Fe(II) in thick adsorbed multilayers.

For irreversible electrocatalytic reactions a linear \( E_p \) vs \( \log_{10}(\nu) \) is also anticipated [366]. In comparison, As a control, Figure 2-4 (B) shows that continual CV at the same scan rate causes no shift in \( E_{pc} \) for 40 scans. The cathodic shift -0.03/\( n \) V \( \nu_{\text{decade}}^{-1} \) in Eq.2-30 may not be applicable unless \( n_c=0 \) but the fit was attempted. The recorded slope is -0.02016 V per \( \log_{10}(V \ \text{s}^{-1}) \), which equates to \( \alpha=0.744 \) for a \( k_2 \) mechanism (\( n=2 \) or
\( \alpha = 0.372 \) for a \( k_1 \) mechanism \((n=4)\). The \( n \)-value for ORR is taken for FePc/KJB at 0.15V (c.a. \( n=3.94 \)).

The \( n \)-value for ORR is taken for FePc/KJB at 0.15V (c.a. \( n=3.94 \)).

\[ \alpha = 0.413 \] for \( k_2 \) mechanism \((n=2)\) or \( \alpha = 0.207 \) for \( k_1 \) mechanism \((n=4)\) if Eq.2-39 is applied. However, this equation is only applicable in the case of 1\textsuperscript{st} heterogeneous ET, showing poor comparability with the carbon supported case.

**10.5.3 RRDE methodology**

The unsupported FePc film was evaluated within the range of \(-0.75<E<0.35\text{V}(\text{orange})\) and \(-0.4<E<0.35\text{V}(\text{red})\), selected to avoid \( \text{H}_2 \) evolution \((E<-0.75\text{V})\) and aryl-aryl bond formation catalysed by Fe(III). The slope corresponds to a value of to \( \alpha = 0.413 \) for \( k_2 \) mechanism \((n=2)\) or \( \alpha = 0.207 \) for \( k_1 \) mechanism \((n=4)\) if Eq.2-39 is applied. However, this equation is only applicable in the case of 1\textsuperscript{st} e\textsuperscript{-} heterogeneous ET, showing poor comparability with the carbon supported case.

**Figure A-5.** Trumpet plot unsupported FePc film. Cathodic peak relates to ORR \( \Gamma_{\text{FePc}} = 6.77 \times 10^{-8} \text{ Moles cm}^{-2} \). Electrolyte; air saturated PBS, pH 7.0

**Figure A-6.** RRDE experimental apparatus
RRDE work with ORR is typically performed in KOH or H₂SO₄, several fundamental assumptions on oxygen electrochemistry [367] needed to be confirmed in PBS. This could not be achieved with the K₃Fe(CN)₆ / K₄Fe(CN)₉ method of determining CE. The most suitable approach was selecting 2e⁻ active materials. Synthetic Graphite (particle size <20μm) has received no surface functionalization and so was used to assess the influence of rotation on %H₂O₂ when a film is present. This proved a good selection of material for calibration of the cell because \(i_D= f(\omega)\) for KJB and Monarch. For synthetic graphite at \(E=0.4V\) disc current was \(i_D \neq f(\omega)\) showing strict kinetic limitation. For \(\omega=100\text{rpm} \ i_D=2.88 \times 10^{-6} \ \text{A cm}^{-2}\) and \(\omega=3600\text{rpm} \ i_D=2.99 \times 10^{-6} \ \text{A cm}^{-2}\). The data is represented as collection efficiency in Figure A-8.
With synthetic graphite, $i_R$ decreased drastically, at $\omega=200$rpm $CE=25\%$ while at $\omega=3200$rpm $CE=11.5\%$. Two possibilities are present; 1) disproportionation ($k_4$) increases significantly with rotation or 2) the flow regime of $H_2O_2$ rich disc product veers away from the ring at high rotation. If $k_3=f(\omega)$ or $k_5=f(\omega)$ ($H_2O_2(aq)$ reduction) was true then $i_D$ is anticipated to increase with $\omega$ which is not seen in would change.

It is assumed that $E_D$ does not affect CE once solvated $H_2O_2$ has left the inner Helmholtz plane of the disc catalyst layer. This model assumes that the catalyst layer is aerated being under kinetic control, therefore the consistent $i_D$ does not prove $k_4=f(\omega)$, this would only be proved under diffusion limitation.

$k_7$ and $k_8$ are assumed negligible.

$CE=f(\omega)$

$k_3\neq f(\omega)$, cannot assume for macrocycles

$k_5\neq f(\omega)$, assume this holds for macrocycles, though it cannot be assumed QDPSU does not catalyse $k_5$.

$k_6\neq f(\omega)$, for Graphite only, adsorbing as an isotherm.

$H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \quad E^0=1.142 \text{ V (Ag|AgCl at pH7)}$ \hspace{1cm} (Eq.A-36)
$\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \quad E^\theta = 0.074 \text{ V (Ag|AgCl at pH7)} \quad (\text{Eq.A-37})$

Though collection efficiency of metallic Pt and PtO layer should be identical, the kinetics of H$_2$O$_2$ oxidation may differ at low overpotential. Pine Research Instrumentation calculate $CE=37\%$ based on ring-disc geometry. At $E=0.6\text{V}$ the potential is anodic enough for significant PtO coverage and does not influence H$_2$O$_2$ oxidation kinetics at comparatively low concentrations being studied. The mixed potential of the reactions in Eq.A-36 and Eq.A-37 mean $J_0$ is large, though the anodic reaction is more facile at $E=0.6\text{V}$ in pH 7.0 PBS [368]. In this work, the potential of zero current on a polycrystalline PtO surface was not affected by [H$_2$O$_2$]$_\text{bulk}$ and found to be 0.244V from linear regression of $i$-$E$ plots at various [H$_2$O$_2$]$_\text{bulk}$.$^{18}$

A potential window of 0.244<$E_{\text{ring}}$<0.6V is identified, encompassing the OCP of the O$_2$/H$_2$O couple 0.4V [H$_2$O$_2$]$_\text{bulk}=0\text{mM}$ and the OCP of the mixed O$_2$/H$_2$O$_2$ and H$_2$O$_2$/H$_2$O couple in [O$_2$]$_\text{bulk}= \text{c.a 0mM}$ in the Khudaish study (0.244V) and a desire to avoid any kinetic limitation of H$_2$O$_2$ oxidation. $E_{\text{ring}}=0.6\text{V}$ was picked as a trade-off between trace Oxygen Evolution current and totally mass transfer limited H$_2$O$_2$ oxidation.

Khudaish found that 2mM H$_2$O$_2$ oxidation on polycrystalline PtO/PtOH reaches diffusion limitation plateau at $E=0.6\text{V}$ vs. Ag|AgCl (1000rpm) of 7mA cm$^{-2}$. In O$_2$ saturated solution [O$_2$]$_\text{bulk}=5.67x10^{-4}$ Mole dm$^{-3}$, for the RRDE E7R9 the area ratio of ring/disc =0.1859/0.2472=0.752. The study of Khudaish confirms that H$_2$PO$_4^-$ reversibly binds to Pt [43]. The kinetic control of H$_2$O$_2$ oxidation on Pt in PBS occurs at $b_n=58.5$ mV dec$^{-1}$ [368]. Trace Pt dissolution (Pt$^{2+}$) was disregarded as a significant current at $E=0.6\text{V}$ [369] in pH 7.28 PBS.

Collection efficiency ($CE$) may vary for substrate and electrolyte. For porous electrodes it is expected the $CE$ may vary with electrode rotation ($\omega$) [370]. The profile and magnitude of change in $CE$ with rotation in Figure A-8 is similar to that observed by Bouwkamp-Wijnoltz [63]. Therefore the CE data is collected for GC and Porous carbon films. The data represented in Figure A-8 is shown in Table A-6. Converting the % drop from that seen at the rotation of highest H$_2$O$_2$ detection from the factory reported

$^{18}$ Due to the limitation of the RRDE unit ($\omega_{\text{max}}=3000\text{rpm}$) similar experiments were not performed
CE=37% was frequently applied. For example, with synthetic graphite if 100% of the O\textsubscript{2} is converted to H\textsubscript{2}O\textsubscript{2} and 25.49% of the H\textsubscript{2}O\textsubscript{2} was detected by the ring if this value drops to 20.16% at 800rpm the % drop is calculated and subtracted from a CE=37% value, producing anticipated collection efficiencies listed in the bottom two rows of Table A-6.

Although H\textsubscript{2}O\textsubscript{2} residence time in the catalyst layer is anticipated to be smaller at high rpm it can be seen from Figure A-8 that the %H\textsubscript{2}O\textsubscript{2} was highest and most comparable at 200rpm. Film thickness is less of an issue than electrode rotation speed as the results from glassy carbon are comparable to KJB and Graphite, the two carbons without HNO\textsubscript{3} treatment that generates a small proportion of 4e\textsuperscript{-} ORR active sites.

Therefore %H\textsubscript{2}O\textsubscript{2} vs. E plots a rotation speed of 200rpm was selected as %H\textsubscript{2}O\textsubscript{2} was relatively uniform at this rotation speed. While K-L plots are verified as accurate by this experiment, the Wroblowa plots (CE\textsuperscript{}*i\textsubscript{D}/i\textsubscript{R} vs. \omega\textsuperscript{-0.5}) can be expected to produce inaccurate results high rpm unless collection efficiency adjustment is very accurate. Omitting these points produced noise in the J vs. C plots, suggesting the data was valid if accurately compensated.

With GPES software continual ring polarisation is not possible (unlike Nova). Therefore components of the current other than H\textsubscript{2}O\textsubscript{2} oxidation require subtraction in order to plot accurate %H\textsubscript{2}O\textsubscript{2} vs. E plots at high potential. An approximated example of i\textsubscript{R} decay profile encountered over an LSV is depicted in Figure A-9. Transients and surface oxidation kinetics have not been used to model decay in charging current, the point of H\textsubscript{2}O\textsubscript{2} oxidation current is apparent after overlaying i\textsubscript{D}.
Figure A-9. $I_R$ vs $E_{disc}$ recorded during LSV scan. Components of current. Thin film of synthetic graphite/Nafion on GC disc. Electrolyte; $O_2$ saturated 50mM PBS. $\nu=5$mV/s, $\omega=200$rpm. $E$(ring)=$+0.6V$

Figure A-10. $S$ vs. $C$ plot of $CE$*$I_D/I_R$ vs. $k_{D,H_2O_2}$ of FePc film ($4\times10^{-9}$ Moles cm$^{-2}$) on GC disc. Data treated with different means (see key). Data from $E=0.25$ to $E=-0.4V$ displayed at 10mV intervals. Best fit applied to all rotation speeds. $\nu=5$mV/s.

Electrolyte; 50mM PBS, pH7.
Examples of the S vs. C plot produced by application of different CE vs ω data. The \( i_d/(i_R-i_{R,BG}) \) with CE=37% at all ω data appears most accurate at low \( \eta \) but highly inaccurate at moderate-high overpotential.

10.5.4 RRDE data

Figure A-11. Slope and \( R^2 \) fit of data from Figure 5-16.

Figure A-12. CE*\( i_d/i_R \) over \( \omega^{1/2} \) plot for FePc/KJB film with QDPSU binder, CE adjusted to CE of Synthetic Graphite response. \( \nu \)=5mV/s.

Figure A-13. Intercept and \( R^2 \) fit of data from Figure A-12.
Figure A-14. $CE^*i_D/i_R$ over $\vec{\omega}^{1/2}$ plot for pyrolised (750°C) FePc/KJB film with Nafion binder, $CE$ adjusted to $CE$ of Synthetic Graphite response. $v=5$mV/s.

Figure A-15. Intercept and $R^2$ fit of data from Figure A-14.

It is apparent from Figure A-14 and Figure A-15 that the large at higher potential shows that pyrolysis drastically changes the nature of the active site.
10.5.5 QDPSU interaction with Pt and carbon surface

Figure A-16. CV of Pt/C-surface chemistry with Nafion or QDPSU. \( \nu = 5 \text{mV/s.} \) Electrolyte; \( \text{N}_2 \) saturated 50mM PBS, pH 7.0.

QDPSU-Pt surface interactions that present a redox active moiety are not detected.

Figure A-17. CV of Pt/C-surface chemistry with Nafion or QDPSU. \( \nu = 5 \text{mV/s.} \) Electrolyte; \( \text{N}_2 \) saturated 50mM PBS, pH 7.0.

An analysis of the type in Figure 2-6 was performed on KJB Nafion and KJB QDPSU films. The result of \( C_{\Sigma} \) vs \( E \) plot is shown in Figure A-17. The \( C_{\Sigma}/E \) gradient is reported anodic and cathodic of \( E_{\text{pzc}} \) in the potential ranges \( 0.2 > E > 0 \text{V} \) and \( -0.13 > E > -0.28 \text{V} \) respectively.
10.6 EIS

10.6.1 Nova arc fitting software for EIS

Figure A-18. Arc fitting and linear regression of Warburg element in Nova software. MEA of FTAM-A membrane fixed to FePc/KJB QDPSU air cathode with SS-mesh. $E=\text{0.2V}$. Red line is extrusion of ion transfer resistance. Electrolyte; 50mM PBS, pH 7.0.

Figure A-19. Example of determination of Electron/Ion hopping/diffusion resistance in reflective finite diffusion. FePcKJB air cathodes with PTFE binder in GDC. $E=\text{0.28V}$. Electrolyte; 50mM PBS, pH 7.0.
Note: $f_3$ does not mark the start of the $C_{diff}$ region, only in this instance. $f_3$ corresponds to the point $\tilde{\omega}_3$ where $-\delta Z'/\delta Z'' = 2$.

### 10.6.2 High frequency arc with FePc films/air cathodes

The HF arc feature observed in Figure 7-9 and Figure 7-2 is a process linked to the presence of FePc with PBS or bicarbonate ion, with or without a current collector [331]. The $C_{HF}$ values are reported in Table 7-5 are associated $f_p$ with time constant $RC_{HF} = \text{c.a.} 2.2\mu\text{s}$. Figure 7-9 illustrates how the LF limit of this HF time constant is the start warburg control.

Two explanations for the HF arc response were explored;

- Di-electric relaxation arc with negative $Z'$ intercepts [371]. This geometric capacitance is typically placed in parallel with $R_s$ [102].
- Constricted water dipole rotation at the IHP on FePc surface.
- A change in charge gradient along the thickness of the electrode [372]. This can be discounted from the 2hrs wetting time and stabilised OCP recorded.

In Figure 7-2 the HF arc ($f>100\text{khz}$) is also visible in thin film, discounting capacitances arising from grain boundaries that may arise from the current collector/catalyst layer or compression gasket interface.

### 10.6.3 Warburg impedance of QDPSU FePc/KJB air cathode in wastewater

Figure A-20 depicts the bode plot when real wastewater is added to PBS.
Figure A-20. Effect of wastewater on Bode Plot (-\( \phi \) vs. \( f \)) of Nafion and QDPSU binders. Air cathodes of FePc/KJB or Pt/C with 10% wt. binder. Polarisation at \( E= \) OCP or \( E=-0.3\text{V}. \) Electrolyte; air saturated Wastewater + PBS (at 50mM), pH 7.0. In Figure A-20 the (-\( \phi \)) increase is seen HF in QDPSU is non-potential dependent, (1790-1500Hz), corresponding to \( Z \) vs. \( \omega^{-0.5} \) type resistance (Figure A-21). This is also the case for Nafion (3.6-4.3kHz). With Nafion a large phase angle (-\( \phi \)) is retained at low frequency, as in NaCl and PBS. The LF phase angle is largest c.a. OCP, negligible at low potential but crucially is partially mitigated with QDPSU binder.

Figure A-21. |\( Z \)| vs. \( \omega^{-0.5} \) plot illustrating the effect of solution electrolytes on diffusion control at mid frequency. Conditions outlined Figure 7-8.
10.7 Physical characterisation data

10.7.1 X-ray Photoemission Spectroscopy of FePc catalyst

When depositing from concentrated H$_2$SO$_4$ the N1s signal dominates the other nitrogen groups in carbon. The XPS spectra of the catalyst FePc/MON is seen in Figure A-22 for the N1s signal. No peak splitting is observed for the primary peak indicating no large binding energy shift from the influence of the carbon support, as if deposited primarily on graphite [373].

![Figure A-22. XPS N1s spectra of FePc/MON. Demonstration of effective loading or Nitrogen signal in support relative to FePc. Figure on the left colour coded to N1s type. Shirley baseline subtracted, Monochromatic Al Kα radiation, Pass energy; 50eV. Analysed with CASA XPS. Carbon support diagram modified from García et al [374].](image)

10.7.2 Confocal microscopy on thin film

The surface roughness is depicted in the imaging software AnalySIS in Figure A-23 with x=0μm set as the GC disc surface.
Figure A-23. Confocal microscope surface image of FePcKJB QDPSU film on GC disc. X and Y axis are microns, taken near film edge.

It is anticipated that the transparency of the Nafion would not provide a focal surface and the presented surface be smoother than that shown in Figure A-23 which possess a resolution large enough to detect graphitic edges.

10.8 Stability of Ag|AgCl reference electrodes

All reference electrodes were stored in 3M NaCl when not in use. For voltammetry in pure electrolyte the RE-5B (BASi) was used with Vycor tip. For operation in wastewater/biotic artificial wastewater the RE-6 was modified with a NaCl/Agar salt bridge as in Figure A-24.
The Agar/NaCl bridge was made from 2g Agarose, 0.5g NaCl in 50ml deionised water, heated to 95°C till Agar melted then injected into the Silicone tubing and the RE pushed through and left to cool. The $E^0'$ of Ag|AgCl is a function of Temperature and [Cl$^-$] via Eq.A-39. In wastewater [Cl$^-$]=c.a. 220 mg/L [24] (6.2mM). This would correspond to a drift of $E=$0.365V vs NHE from $E=$0.208V were equilibrium allowed to be established. Despite Cl$^-$ diffusion through H$_2$O and 3% polymerised agar being approximately the same [375], the electrodes in Figure A-24 were consistently +30mV vs a new Ag|AgCl, showing AgCl layer integrity was maintained. Additionally bacterial colonisation in the frit is not possible.

\[
\text{Ag}_{(s)} + \text{Cl}^-_{(aq)} \rightleftharpoons \text{AgCl}_{(s)} + e^- \quad E^0 = 0.222V \\
E_0' = E^0 - \log[\text{Cl}^-]2.303RT/F \quad \text{(Eq.A-38)}
\]

In this thesis, mono-anionic solutions possess a lower chemical potential and higher $E_0'$ of the Ag|AgX couple than Ag|AgCl. This predicts no significant drift in rest potential in solutions where X is: Phosphate (Eq.A-40), Sulphate ($E^0=0.449V$), Nitrate (no surface reaction, AgNO$_3$ soluble), Nitrite ($E^0=0.564V$), Carbonate ($E^0=0.47V$) or Acetate (no reaction, AgCH$_3$COO soluble). Silver sulphate is semi-soluble and Silver Nitrate are highly soluble.

\[
3\text{Ag}_{(s)} + \text{PO}_4^{3-}_{(aq)} \rightleftharpoons \text{Ag}_3\text{PO}_4_{(s)} + 3e^- \\
E_0'(\text{pH7, 50mM PBS})=0.328V \text{ vs Ag|AgCl}^{19} [376]
\]

\[
^{19}\text{MFC cell alkalination increases }[\text{PO}_4^{3-}] \text{ meaning electrode life is reduced only at high pH.}
\]
$Ag_{(s)} \leftrightarrow Ag^{+}_{(aq)} + e^{-}$ \hspace{1cm} $E^0 = 0.76V$ \hspace{1cm} (Eq.A-41)

The Ag|AgCl redox is poisoned by the reaction of AgCl and anions possessing lower $E^0$ (pH7) than the Ag|AgCl couple. Dissolution of solid AgCl surfaces begins in the presence of ammonia above pH6.8 [377]. Common poisoning reactions of Ag|AgCl reference electrodes:

$2Ag_{(s)} + S^{2-}_{(aq)} \leftrightarrow Ag_2S_{(s)} + 2e^{-}$ \hspace{1cm} $E^0 = -0.691V$ \hspace{1cm} (Eq.A-42)

$Ag_{(s)} + I^-_{(aq)} \leftrightarrow AgI_{(s)} + e^{-}$ \hspace{1cm} $E^0 = -0.152V$ \hspace{1cm} (Eq.A-43)

$Ag_{(s)} + CN^-_{(aq)} \leftrightarrow AgCN_{(s)} + e^{-}$ \hspace{1cm} $E^0 = -0.017V$ \hspace{1cm} (Eq.A-44)

$Ag_{(s)} + Br^-_{(aq)} \leftrightarrow AgBr_{(s)} + e^{-}$ \hspace{1cm} $E^0 = 0.0732V$ \hspace{1cm} (Eq.A-45)

$Ag_{(s)} + SCN^-_{(aq)} \leftrightarrow AgSCN_{(s)} + e^{-}$ \hspace{1cm} $E^0 = 0.0895V$ \hspace{1cm} (Eq.A-46)

$4Ag_{(s)} + [Fe(CN)_6]^3-_{(aq)} \leftrightarrow Ag_4Fe(CN)_6(s) + 4e^{-}$ \hspace{1cm} $E^0 = 0.148V$ \hspace{1cm} (Eq.A-47)

$AgCl_{(s)} \leftrightarrow Ag^+ + Cl^- \leftrightarrow ^{+2NH_3}Ag(NH_3)^+_{(aq)} + Cl^-_{(aq)}$ \hspace{1cm} (Eq.A-48)

The concentration of these pollutants is relatively low in wastewater making potential drift and anion substitution of AgCl relatively slow. NH$_3$/NH$_3$OH is one of the primary pollutants in aerated wastewater, while in anoxic wastewater S$^{2-}$ may not permeate the agar tip with the salt bridge in place. The drift was <30mV with the agar bridge in place over repeated cycles with wastewater.

**10.9 MFC components**

The air reservoir created by the non-stretched parafilm cover was 8ml in volume. The oxygen permeability of the parafilm is unknown but aims to avoid aerobic conditions during OCP or start-up. For mature biofilm at $P=P_{max}$, O$_2$ constriction from parafilm causes $V_{cell}<0.01V$ in 40mins, due to a drop in $E_{cat}$. 
Figure A-25. Parasitic biofilm growth on air cathode. 17 day exposure to wastewater.

Figure A-26. SCMFC with parafilm cover used to control oxygen flux at OCP and start-up.
The lag in response after \( E \) is stepped from \( OCP \) to \( E=-0.3V \) is initially a capacitive response. The increase in current after equilibrium is established \((t=1.5\text{min})\) is minimised by the 20minute stabilisation time of polarisation curves, a factor that cannot be discounted when using potentiostat analysis for power curves.

**Conferences and Publications**

Aspects of this work were reported in:


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Figure A-27. Carbon felt supported biofilm (A); CV, \( u=2\text{mV/s} \). (B); Potentiostatic \( E=-0.3V \). Electrolyte; anaerobic WW-PBS, pH 7.0.

Poster competition of ICheme Catalysis Subject Group, 2009 meeting, Bath university. 1st prize (£250).
References


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Xu, Y., BIOCHEMICAL SOCIETY, 1970: p. 13P.

Bray, R., C., solutions

Dalton Jr. I, A.A., PA), Bauer, Jeffery V. (Macungie, PA), experimental analysis of the rotating ring


Khudaish, E.A., Electrocatalysis and Catalyst Layers


of hydrogen peroxide: Application to porous and rotating ring


Advective Flow through the Porous Anode and Reduced Electrode Spacing.


102. Cameron, C.G., Enhanced Rates of Electron Transport in Conjugated-Redox Polymer Hybrids in Department of Chemistry 2010, Memorial University, Newfoundland: St. John's.


348. Długolecki, P.E., Mass transport in reverse electrodialysis for sustainable energy generation, 2009, University of Twente: Enschede.
370. Balbuena, P. and V. Subramanian, Theory and experiment in electrocatalysis, ed. R.E. White and c.g. vayenas2010.