Aqueous Electrocatalysis in Concentrated Electrolyte Solutions

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A thesis submitted for the degree of Doctor of Philosophy

University of Bath
Department of Chemistry

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“No amount of experimentation can ever prove me right; a single experiment can prove me wrong.”
~ Albert Einstein (1879-1955)
# Abbreviations

## Roman symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Ionic size parameter</td>
<td>None</td>
</tr>
<tr>
<td>A</td>
<td>Area</td>
<td>m²</td>
</tr>
<tr>
<td>$a_i$</td>
<td>Activity of $i$ species</td>
<td>None</td>
</tr>
<tr>
<td>B</td>
<td>Constant for Extended Debye-Hückel Law</td>
<td>0.33 at 20 °C</td>
</tr>
<tr>
<td>$b_{int}$</td>
<td>Assumed Tafel slope</td>
<td>mV dec⁻¹</td>
</tr>
<tr>
<td>C</td>
<td>Capacitance</td>
<td>F m⁻²</td>
</tr>
<tr>
<td>$C_\infty$</td>
<td>Bulk concentration of $i$ species</td>
<td>mol dm⁻³</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Concentration of $i$ species</td>
<td>mol dm⁻³</td>
</tr>
<tr>
<td>$D_i$</td>
<td>Diffusion coefficient of $i$ species</td>
<td>m² s⁻¹</td>
</tr>
<tr>
<td>E</td>
<td>Electrode potential</td>
<td>V</td>
</tr>
<tr>
<td>$E^0$</td>
<td>Standard Electrode Potential</td>
<td>V</td>
</tr>
<tr>
<td>$E^0_{pH}$</td>
<td>Standard Electrode Potential at a given pH</td>
<td>V</td>
</tr>
<tr>
<td>$E_{1/2}$</td>
<td>Half-wave potential</td>
<td>V</td>
</tr>
<tr>
<td>$E_{onset}$</td>
<td>Onset potential</td>
<td>V</td>
</tr>
<tr>
<td>$dE/dx$</td>
<td>Potential gradient</td>
<td>V cm⁻¹</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant</td>
<td>96485 C mol⁻¹</td>
</tr>
<tr>
<td>$G^*$</td>
<td>Gibbs energy of transition state</td>
<td>kJ mol⁻¹</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Change in Gibbs Free Energy</td>
<td>kJ mol⁻¹</td>
</tr>
<tr>
<td>I</td>
<td>Ionic strength</td>
<td>mol kg⁻¹</td>
</tr>
<tr>
<td>$I_{cap}$</td>
<td>Capacitance current</td>
<td>A</td>
</tr>
<tr>
<td>$I_{cottrell}$</td>
<td>Cottrell current</td>
<td>A</td>
</tr>
<tr>
<td>Symbol</td>
<td>Meaning</td>
<td>Units</td>
</tr>
<tr>
<td>--------</td>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>$I_{kin}$</td>
<td>Kinetic Current</td>
<td>A</td>
</tr>
<tr>
<td>$I_o$</td>
<td>Exchange current</td>
<td>A</td>
</tr>
<tr>
<td>$J$</td>
<td>Flux</td>
<td>mol m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$J_i$</td>
<td>Diffusional flux</td>
<td>mol m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$J_{i,\text{conv}}$</td>
<td>Convective flux</td>
<td>mol m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$J_{i,\text{migr}}$</td>
<td>Migratory flux</td>
<td>mol m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$k_0$</td>
<td>Standard heterogeneous rate constant</td>
<td>m s$^{-1}$</td>
</tr>
<tr>
<td>$l$</td>
<td>Length of microwire electrode</td>
<td>m</td>
</tr>
<tr>
<td>$m_i$</td>
<td>molality of $i$ species</td>
<td>mol kg$^{-1}$</td>
</tr>
<tr>
<td>$P$</td>
<td>Pressure</td>
<td>Bar</td>
</tr>
<tr>
<td>$P_{O2}$</td>
<td>Partial pressure of oxygen</td>
<td>Bar</td>
</tr>
<tr>
<td>$pH$</td>
<td>Power of Hydrogen</td>
<td>None</td>
</tr>
<tr>
<td>$R$</td>
<td>Molar gas constant</td>
<td>8.314 J K$^{-1}$ mol$^{-1}$</td>
</tr>
<tr>
<td>$r$</td>
<td>Radius of electrode</td>
<td>m</td>
</tr>
<tr>
<td>$r_p$</td>
<td>Reference electrode potential</td>
<td>V</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature</td>
<td>K</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
<td>s</td>
</tr>
<tr>
<td>$v$</td>
<td>Scan rate</td>
<td>V s$^{-1}$</td>
</tr>
<tr>
<td>$v_x$</td>
<td>Fluid velocity</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$x$</td>
<td>Distance</td>
<td>m</td>
</tr>
<tr>
<td>$\gamma_i$</td>
<td>Activity coefficient of $i$ species</td>
<td>None</td>
</tr>
<tr>
<td>$\gamma_{\pm}$</td>
<td>Mean activity coefficient</td>
<td>None</td>
</tr>
<tr>
<td>$z_{\pm}$</td>
<td>Charge of ionic species</td>
<td>None</td>
</tr>
</tbody>
</table>

**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Transfer coefficient</td>
<td>None</td>
</tr>
</tbody>
</table>
\( \delta \) Nernst diffusion layer \( \text{m} \)
\( \eta \) Overpotential \( \text{V} \)
\( \Theta_{ox} \) Surface coverage of adsorbed oxygen None
\( \mu^0 \) Standard chemical potential of \( i \) species None
\( \mu_i \) Chemical potential of \( i \) species None
\( v \) Kinematic viscosity \( \text{m}^2 \text{s}^{-1} \)
\( \tau \) Transition time \( \text{s} \)
\( \Phi_m \) Electrode potential \( \text{V} \)
\( \Phi_s \) Solution potential \( \text{V} \)
\( \omega \) Rotation speed \( \text{rad s}^{-1} \)

**Chemical abbreviations**

CA Chronoamperometry
CE Counter electrode
CV Cyclic voltammetry
\( \text{H}_2\text{O}_2 \) Hydrogen peroxide
\( \text{H}_2\text{PtCl}_6 \) Hexachloroplatinic(IV) acid
\( \text{H}_2\text{SO}_4 \) Sulphuric acid
\( \text{HCl} \) Hydrochloric acid
\( \text{HClO}_4 \) Perchloric acid
HUPD Hydrogen underpotential deposition
IHP Inner Helmholtz Plane
\( \text{K}_4[\text{Fe(CN)}_6] \) Potassium ferrocyanide
LAM Laser Additive Manufacturing
LEED Low Energy Electron Diffraction
LSV Linear sweep voltammetry
MeOH Methanol
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OHP</td>
<td>Outer Helmholtz Plane</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton Exchange Membrane Fuel Cell</td>
</tr>
<tr>
<td>PIM</td>
<td>Polymer of Intrinsic Microporosity</td>
</tr>
<tr>
<td>RDE</td>
<td>Rotating disc electrode</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated Calomel Electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard Hydrogen Electrode</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
<tr>
<td>ZnCl$_2$$\cdot$2NH$_4$Cl</td>
<td>Zinc ammonium chloride</td>
</tr>
</tbody>
</table>
Abstract

The pH and ionic strength of a solution is important in the process of steel corrosion. The reduction of oxygen plays a role in steel corrosion and the influence of spectator ions in solution can affect the electrochemical reduction. Platinum alloys can enhance the reduction of oxygen in depending on the electrolyte solutions as well as altering the electrokinetics of the process. Understanding how the electrokinetics of the reduction of oxygen are affected in high ionic strength solutions is therefore of considerable importance, not only for steel corrosion but for also fuel cells that utilise the reduction of oxygen on platinum electrodes.

The concentration of dissolved oxygen decreases with increasing ionic strength. A method for determining the concentration and diffusivity of protons and oxygen in increasing saline media was developed using microwire electrodes. Data from double-step chronoamperometric measurements coupled with digital simulation, allowed simultaneous determination of the concentration, diffusion coefficients and salinity in a simple methodology.

The increase in ionic strength of a saline solution causes the viscosity to increase as well. Normal hydrodynamic methods such as the rotating disc electrode are subject to viscosity effects; however, the microwire electrode avoids this altogether by their ability to achieve quasi steady-state currents. Electrokinetic data such as, Tafel analysis, transfer coefficients and standard heterogeneous rate constants, in high chloride media was carried out for the reduction of oxygen on platinum. The rate constant for electron transfer is affected by the dissolved oxygen concentration and not by the activity of oxygen in solution or the chloride concentration. Initial experiments for the reduction of oxygen at elevated pressures were also carried out as preliminary experiments.

Modification of the microwire electrode surface with a Polymer of Intrinsic Microporosity (PIM-EA-TB) and its effect on the reduction of oxygen in high chloride media showed no effect on the electrochemical reduction using electrokinetic analysis. Due to the porosity of the PIM-EA-TB coating, local areas were free from
chloride blocking, allowing oxygen to diffuse through to be reduced and the electrode surface capacitance was explained with and without the PIM coating.

Specific spectator ions can poison the platinum surface preventing certain electrochemical processes to take place. A methodology for cleaning platinum microwire electrodes was developed using electrothermal annealing and the surface activation of platinum was investigated towards oxygen reduction and glucose oxidation in neutral phosphate buffer solutions. A simplistic micro membrane-free fuel cell was developed combined the oxygen reduction on commercial platinum and glucose oxidation on electrothermally annealed platinum, generating 2 nW cm$^{-2}$ at high glucose levels.

With the advent of 3D-printers, it is now possible to 3D-print electrodes. 3D-printed stainless steel electrodes from precursor powder allowed galvanic exchange with platinum to produce platinum modified steel electrodes due to the porosity of the steel surface, using a simple deposition methodology. The modified steel electrodes behaved as conventional platinum electrodes and the platinum films were found to be mechanically robust under continuous potential cycling in acidic solutions, with high catalytic activity towards methanol oxidation in acidic conditions observed. 3D-printed fuel cells can be mass produced and modified using this simple deposition methodology and potential possibilities of a new range of electrodes based upon different composite materials and alloys can be manufactured easily with any design.
Aims

The aims of this thesis are to;

- Investigate the use of mirowire electrodes over conventional hydrodynamic techniques in increasing chloride concentrations. Develop a multi-parameter double-step chronoamperometric method coupled with digital simulation to simultaneously determine both the concentration and diffusivity of protons and oxygen in increasing chloride electrolyte concentrations, using microwire electrodes.

- Analyse the electrokinetics of the reduction of oxygen in increasing chloride concentration. Calculate and compare the Tafel slopes to the expected $120 \text{ mV dec}^{-1}$ and calculate values for the standard heterogeneous rate constant and transfer coefficients. Explore the effects of increase oxygen pressure on the electrokinetics of the reduction of oxygen.

- Investigate the effects of polymer of intrinsic microporosity (PIM) coatings on the catalytic reduction of oxygen in increasing chloride concentrations. Develop a model to calculate the capacitance of the chloride solution at increasing scan rates with and without a PIM coating for the reduction of oxygen.

- Develop a simple methodology using electro thermal annealing to clean the surfaces of platinum microwires. Explore the ability to oxidise glucose in varying neutral phosphate buffer concentrations with the ability to fabricate a membrane-less microfuel and calculate the power output. Use Tafel analysis on the reduction of oxygen and oxidation of glucose to investigate the electrokinetics of glucose oxidation.

- Explore the electrochemical properties of 3D-LAM printed stainless steel electrodes in phosphate buffer solutions and develop a methodology to deposit stable platinum films for methanol oxidation fuel cell that utilises the porosity of the 3D-LAM printed electrodes.
Chapter 1

Introduction to Steel and Steel Reactivity Towards Oxygen

Chapter Abstract

Steel is a major material that is used globally. From construction material and food packaging to electrodes in Proton Exchange Membrane Fuel Cells (PEMFCs) for the next generation of power generating devices, the properties of steel make it extremely useful and versatile in many applications.

This chapter provides an overview about steel reactivity in aqueous solutions and how the properties are important industrially. The process of corrosion in steel is described as a fundamental electrochemical process and the methods of how it can be prevented or delayed are discussed.

The corrosion of steel is largely pH and ionic strength dependent. The issues surrounding the measurement of pH in ionic electrolytes are explained. How steel corrodes and the requirements for corrosion are also discussed.

The influence of the spectator ions in solution and crystal faceting on the electrokinetics of oxygen reduction are explained in relation to steel, platinum and platinum alloys, such as PtFe.
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1 – Introduction to Steel and Steel Reactivity Towards Oxygen

1.1 – Applications and Everyday Uses of Steel

Steel is a crucial material within the construction industry, with buildings, bridges, ships and infrastructures all using the material. As of 2015, the production of crude steel has steadily declined with approximately 10.9 million tonnes produced, down 37% since 1995 and the cost of production dropping year-on-year due to cheaper sources[1][2].

There are four areas that steel can be applied to:

Construction and Industry: Steel is mainly used as a skeleton to add strength to buildings in addition to concrete[3], but it can also be used on its own to create structures such as bridges or be used in household appliances[4], depending on the type of steel used[5].

Transport: The use of steel in transport is in the building of vehicles, cargo ships, trains etc. The type of steel required for transport vehicles must have certain properties; strength, safety, fuel efficient and more environmentally friendly to produce[6].

Packing: Packaging offers protection from the outside environment and help preserve perishable items such as food. The steel is designed specifically to be easily manipulated into various shapes, as well as being plated with tin and a polymer coating to not spoil the food inside, allowing quick packaging and transportation[7].

Energy: Pipelines on the seabed are the main method of transporting oil and gas for powering vehicles and heating homes. Over 40 million tonnes of oil and gas were produced and transported in 2014 alone from offshore platforms, however, this is slowly decreasing due to other sources of energy, namely renewable energy[1]. The main material of oil and gas pipelines used currently is the high-grade X70 steel, which is able to survive pressures up to 400 MPa[8]. Currently there is a vested interest in improving the steel used to reduce to frequency of parts corroding as well as reducing the cost of replacement[9]. X80 and X100 steel are being trailed as suitable replacements over X70 steel which can sustain pressures up to 700 MPa, allowing
larger quantities of oil and gas to be transported, but also have a higher resilience to cracks propagating under corroding conditions\textsuperscript{10,11} (Table 1.1).

Table 1.1. Atomic compositions and applications of 316, 316L, X70, X80 and X100 steels.

<table>
<thead>
<tr>
<th>Steel Grade</th>
<th>Applications</th>
<th>Atomic Composition (atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>High-temperature industrial machinery and medical implants\textsuperscript{[12]}</td>
<td>0.03 % C, 2.00 % Mn, 18.00 % Cr, 0.75 % Si\textsuperscript{[13]}</td>
</tr>
<tr>
<td>X70</td>
<td>Large diameter oil and gas pipelines\textsuperscript{[14]}</td>
<td>0.08 % C, 1.60 % Mn, 0.19 % Cr, 0.04% Nb\textsuperscript{[15]}</td>
</tr>
<tr>
<td>X80</td>
<td>High pressure oil and gas pipelines\textsuperscript{[16]}</td>
<td>0.02 % C, 1.95 % Mn, 0.26 % Si, 0.38 % Ni and 0.31 % Mo\textsuperscript{[15]}</td>
</tr>
<tr>
<td>X100</td>
<td>Large diameter oil and gas pipelines\textsuperscript{[16]}</td>
<td>0.07 % C, 1.90 % Mn, 0.10 % Si, 0.50 % Ni and 0.15 % Mo\textsuperscript{[17]}</td>
</tr>
</tbody>
</table>

1.2 – Composition of Steel

1.2.1 – Types of Steel

The general composition of steel is over 95 atom% Fe with some quantity of C present\textsuperscript{[18]}. With Fe as the base metal in steel, there are two lattice structures of Fe that can form depending on the temperature of heating, \( \alpha \)-iron (known as ferrite) or \( \gamma \)-iron (known as austenite). At high temperatures, the \( \gamma \)-iron is formed and will revert back to the \( \alpha \)-iron upon cooling (Fig. 1.1)\textsuperscript{[3]}. 
Figure 1.1. The two iron structures within steel. The $\alpha$-iron is formed at low temperatures, while the $\gamma$-iron is formed at high temperatures. [Ref. 3]

By adding varying atom% of elements such as C, Mn and Si, different types of steel, known as alloy steel, can be produced with different physical and mechanical properties. Upon rapid cooling, the additional elements added act as hardening agents during the process of making steel, which disperse throughout the steel. This prevents any slipping, sliding or dislocations to arise between the lattices, especially at the grain boundary where fracturing is likely to occur$^{[19]}$.

The added elements also prevent the growth of grains within steel and produce finer grains instead. The idea is that larger grains formed increase the brittleness of steel and as such, finer grains are desired in order to prevent fracturing$^{[20]}$. For example, the addition of Mn to steel increases the hardness of the Mn alloy steel, but it is not as effective as adding C and is used as a cheap alternative.

In the case of adding more C to steel, carbon steel is produced. Carbon steel has a higher tensile strength than adding any other elements such as Mn$^{[21]}$. The C forms an iron-carbide (Fe$_3$-C, known as cementite) where the C atoms lie in the holes between the Fe atoms, and as a result, there is a limit to how much C is added$^{[18]}$.

Another type of steel is stainless steel, which is commonly used for example in medical instruments and cutlery. The presence of high atom% of Cr is crucial in
order for steel to be classed as stainless. The addition of Cr forms Cr-rich carbides (typically Cr$_2$C$_6$)$^{[22]}$ as well forming a chromium-oxide layer (Cr$_2$O$_3$) on the surface of the steel that is resistant to oxidation. This is achieved by reducing the diffusion of oxygen through the protective Cr$_2$O$_3$ film to the steel surface underneath$^{[22]}$ and thus preventing rust (iron oxide) forming at the surface / film interface$^{[23]}$.

1.3 – Corrosion of Steel

1.3.1 – Mechanism of Steel Corrosion

Alloy steel requires protective coating to prevent it from corroding. This is due to the fact that alloy steel cannot create a passive layer, a dense layer of protective material such as a metal oxide on the surface that is impermeable to water and oxygen$^{[24]}$. Stainless steel, as mentioned above, does not need protection due to the high content of Cr present, which forms a Cr$_2$O$_3$ layer protecting it$^{[18][22][23][25]}$. Depending on the pH of the solutions which can be measured, various cathodic reactions take place on the steel. When steel is placed into a solution at neutral or high pH, an electrochemical reaction occurs (Fig. 1.2). Iron at the steel surface acts as an anode and is oxidised to iron(II), the electrons conduct through the steel to be used in reducing the dissolved oxygen, which acts as a cathode (equations 1.1 and 1.2)$^{[24]}$.

\[
\text{Anodic reaction: } \quad \text{Fe}(s) \rightarrow \text{Fe}^{2+}(aq) + 2 \, \text{e}^{-} \quad \quad [1.1]
\]

\[
\text{Cathodic reaction: } \quad \frac{1}{2} \text{O}_2(aq) + 2 \, \text{e}^{-} + \text{H}_2\text{O}(l) \rightarrow 2 \, \text{OH}^{-}(aq) \quad \quad [1.2]
\]
Figure. 1.2. Reaction pathways for the formation iron oxide (Fe₂O₃) on steel substrates when in contact with water and oxygen.

A pH gradient is established at the metal / electrolyte interface with the reduction of oxygen to hydroxide ions causing the pH to rise to alkaline levels and the continuous dissolution of iron causing the pH to decrease to acidic levels. With the aqueous iron(II) ions, several further reactions take place leading to the formation of the porous iron oxide layer, Fe₂O₃ (equations 1.3, 1.4 and 1.5)\[^{26}\]\[^{27}\]. Continuous dissolving of iron to iron(II) leads to structural weaknesses in the steel ending up with cracking and fractures.

Fe²⁺(aq) + 2 OH⁻(aq) → Fe²⁺(OH)₂(aq) \[1.3\]

4 Fe²⁺(OH)₂(aq) + O₂(aq) + 2 H₂O(l) → 4 Fe³⁺(OH)₃(aq) \[1.4\]

2 Fe³⁺(OH)₃ → Fe₂O₃·3H₂O(s) \[1.5\]

As iron(II) dissolves into solution (equation 1.1), electrons conduct through the steel to reduce protons to hydrogen gas at low pH values (equation 1.6).

Cathodic reaction: \[2 H⁺(aq) + 2 e⁻ → H₂(g) \][1.6]

Both the reduction of oxygen to water and the reduction of protons occur simultaneously. Iron(II) forms iron hydroxide with the water produced from the reduction of oxygen (equations 1.7 and 1.8)\[^{24}\].
\[ O_2(aq) + 4 H^+ + 4 e^- \rightarrow 2 H_2O(l) \] \[ Fe^{2+}(aq) + 2 H_2O(l) \rightarrow Fe^{II}(OH)_2(aq) \]

With the continuous dissolution of iron, more protons are reduced and so a continuous cycle is established, leading to the corrosion of steel.

In chloride containing media, such as seawater, the corrosion of steel is accelerated by the presence of chloride ions which enhance the electrical conductivity. As iron(II) dissolves, a build-up of Fe₂O₃ occurs at the site of corrosion generating a pit\[28\][29].

The oxygen present in the pit is slowly reduced until the pit becomes oxygen deficient at which point the pit becomes positively charged and draws in chloride ions to maintain electroneutrality and combine with the iron(II) ions (equation 1.9).

\[ Fe^{2+}(aq) + 2 Cl^-(aq) \rightarrow FeCl_2(s) \]

The FeCl₂ then reacts with water in the pit, producing iron(II) hydroxide which then undergoes further reactions to add to the growing Fe₂O₃ layer. Hydrochloric acid is produced as a by-product which continues to attack the steel and dissolving more iron(II) into the pit even through the pit is now oxygen deficient (equation 1.10)\[28\].

\[ FeCl_2(s) + H_2O(l) \rightarrow Fe^{II}(OH)_2(s) + 2 HCl(aq) \]

The amount of water produced as a cathodic reaction in neutral pH and in seawater is dependent on how much oxygen can diffuse through the solution, which can be measured.

The reduction of oxygen can be affected by the electrolyte (in the form of diffusion towards the metal surface) as well as being enhanced by certain metals or alloys. The reduction of oxygen to water is only one of two reactions, the other being the reduction to give hydrogen peroxide.

1.3.2 – Protecting Steel from Corrosion

While steel is used to strengthen structures as a skeleton, or used on its own for bridges, it will undergo processes that can weaken its structural integrity such as
mechanical, ageing, or come into contact with sulphate-reducing bacteria\cite{30}\cite{31}\cite{32}, and these can be overcome by selectively tuning the properties of steel.

The main issue with protecting steel is preventing direct contact with water and oxygen. Rust (iron oxide) forms which over time can lead to cracks and permanently damaging the steel\cite{33}. The formation of rust on steel is undesirable, particularly within the construction and oil and gas industry sectors due to the cost of replacing the corroded parts on a continuous cycle.

There are three main methods by which the corrosion of steel can be prevented:

*Galvanising*: The process of galvanising steel involves coating metal layer, usually Zn, on the top of steel which acts as a barrier to oxygen and water. The steel is first cleaned in alkaline solution to remove oil, pain, dust and dirt to leave behind a clean surface for the coating. After rinsing, the steel is placed into hydrochloric acid at around 60-80 °C to remove any inorganic compounds such as rust without attacking the underlying steel. Next, a zinc ammonium chloride (ZnCl₂·2NH₄Cl) bath is used to remove any oxides that may have formed on the clean steel surface after the acid cleaning. Finally, the steel is then placed into a bath containing molten Zn at 450 °C. The time taken to coat the steel with Zn is rapid with a thick coating forming in the early time period before slowing down after five minutes\cite{28}\cite{29}\cite{34}.

Immediately after removal and drying, the Zn layer is then attacked by the oxygen in the atmosphere and forms a layer of ZnO, but this layer is not fully impermeable to oxygen diffusion. The ZnO layer then continues to react with CO₂ forming ZnCO₃, which is impermeable to oxygen diffusion and is also insoluble in water thereby protecting the steel from corroding\cite{35}.

However, should the Zn coating be damaged by acid corrosion or corrosion by seawater, then the Zn coating acts as a sacrificial metal. A galvanic cell is established between the steel and the Zn, with the solution acting as an electrolyte. The Zn is the anode and the steel is the cathode within the cell. As the Zn coating has a lower galvanic potential to steel (referenced against a saturated calomel electrode), it is the Zn that is oxidised and is corroded in order to preserve the steel\cite{36}.

*Biofilms*: Biofilms are a layer consisting of various communities of bacteria that form a solid surface which adheres strongly to the substrate\cite{37}. Just as corrosion is an
electrochemical process, so is the inhibition of corrosion which can be achieved by using microorganisms to form biofilms that alter the conditions at the substrate / solution interface\[38\]. Attachment of the biofilm to the steel is attained when the bacteria culture is trapped within an exopolysaccharide matrix secreted by the bacteria, however, the bacteria must be metabolically active in order for attachment to occur\[39\].

Zuo et al. produced a live biofilm onto steel to investigate the prevention of corrosion using Bacillus subtilis. It was reported that the corrosion of steel was significantly reduced in the presence of a live B. subtilis biofilm, whereas corrosion was increased in the presence of a dead biofilm. The suggestion for the increased corrosion resistance was that a negative charge was produced by the live biofilm, unlike the dead biofilm, that repelled anions which would otherwise corrode the steel\[40\].

An alternative strain of bacteria, Pseudomonas fragi was investigated for corrosion inhibition. Jayaraman et al. concluded that in order for a biofilm to inhibit corrosion, cell metabolites near the steel surface were required. However, it was noted that initially corrosion occurred due to oxygen still being able to diffuse to the steel surface. It was only after a week that the corrosion was significantly reduced, implying there is a time delay for the cell metabolites to accumulate for the formation of the biofilm. Once the biofilm is fully established, it is able to prevent the diffusion of oxygen through to the steel\[39\][41][42].

**Polymers:** Conducting polymers can be applied to steel surfaces via paints, coatings, chemical or electrochemical deposition, using common polymers such as polypyrrole, polyaniline or polythiophene (Fig. 1.3).
Figure. 1.3. Chemical structures of (A) polyaniline, (B) polythiophene and (C) polypyrrole.

Polymers containing for example amines or thiophenes can form films on the steel which inhibit corrosion and are frequently used within the oil and gas sector\textsuperscript{[38]}. The primary way for polymers to prevent corrosion is similar to biofilms, which is creating a barrier at the substrate / solution interface\textsuperscript{[43]}, however, the barrier is only effective if there is no damage to the coating and is thicker than 1 µm, thicknesses less than 1 µm are permeable to oxygen diffusing through\textsuperscript{[44]}.

Using a thicker polymer coating, species that promote corrosion are adsorbed into the coating and are prevented from reaching the substrate. The coating also displaces any water that may be trapped between the substrate / solution interface, as reported by Santos \textit{et al.}\textsuperscript{[45]}. Polymers containing aniline were found to be the best at inhibiting corrosion, with strong adhesion onto the steel surface\textsuperscript{[46]} with analogues containing benzoquinone being reported to inhibit iron dissolution\textsuperscript{[47]}. Alternative polymers such as polyethylene glycols have been investigated which, depending on their molecular weight, are capable of reducing the corrosion rate of steel by reducing the rate of diffusion of oxygen to the steel substrate\textsuperscript{[48]}.

Currently, stainless steel is of interest within proton exchange membrane fuel cells (PEMFCs) as a cheap source for electrode material. However, corrosion of the stainless steel in acidic conditions is an obstacle\textsuperscript{[49],[50]}. Coating the stainless steel with
conducting polymers that inhibit corrosion, are conductive and do not impede the performance of the stainless steel electrode is of huge interest. Joseph et al. reported using a combination of polyaniline and polypyrrole where only 3 electrochemical deposition cycles were required to obtain adequate conductivity of the stainless steel electrode, as well as inhibiting the corrosion during performance\textsuperscript{51}.

Similarly, Wang et al.\textsuperscript{52} looked into how the deposition of polypyrrole affected the corrosion of the steel electrode in PEMFCs. It was noticed that different morphologies of the polypyrrole coating were obtained using either galvanostatic or potentiostatic methods and concluded that both methods produced thick films suitable for inhibiting the corrosion of the steel.

1.3.3 – The Rate of Corrosion and pH

Steel pipelines, comprised of high atom\% levels of Mn\textsuperscript{10} which allow pressures up to 700 MPa\textsuperscript{11}, are utilised to transport oil and gas along the seabed. However, with levels of CO$_2$ in the atmosphere increasing resulting from the increase in human activity\textsuperscript{53}, this has a direct effect on the pH of the sea and a direct effect of the local environment around the steel pipelines which encourage corrosion.

In 2010, approximately 31.2 billion metric tons of CO$_2$ were released into the atmosphere with predictions expecting this to rise to over 45 billion metric tons by 2040; a 46 \% increase in 30 years\textsuperscript{54}. In the 18\textsuperscript{th} century, the pH of the ocean was on average 8.2 (slightly alkaline), but due to human activity increasing the level of CO$_2$ being dissolved into the ocean since then, the pH has decreased by around 30 \% to 8.1, with predictions continuing the decline to 7.8 by the end of the century\textsuperscript{55}.

The decrease in the pH of seawater to acidic conditions has a large impact on the oil and gas industry and specifically the pipelines on the ocean floor. The low pH accelerates the corrosion of steel pipelines and thereby increasing the cost at which the pipes are replaced.

Measurement of pH in seawater is therefore a big importance in order to calculate the rate of corrosion of the steel pipes as well as fine tuning the composition of steel to have an increase resistance to corrosion in acidic solutions\textsuperscript{56}.
In 1907, Lewis\cite{57} introduced the concept of defining the activity of ionic species which is related to the concentration of the ionic species \((c_i)\) and an activity coefficient \((\gamma_i)\). The activity measures the behaviour at certain conditions of the ionic species in solution, whereby the activity coefficient is a factor that accounts for the solution deviating from ideal behaviour under those conditions\cite{58}(equation 1.11).

\[
a_{H^+} = c_{H^+}/\gamma_{H^+} \tag{1.11}
\]

Here, \(c_{H^+}\) is the concentration of protons (mol dm\(^{-3}\)) and \(a_{H^+}\) is the activity of protons.

Since the activity of protons is related to the concentration of protons in solution Sørensen\cite{59}, in 1924 with Linderstrøm-Lang, defined pH (equation 1.12).

\[
pH = -\log a_{H^+} \tag{1.12}
\]

With the activity of protons defined in equation 1.11, equation 1.12 can be rewritten in terms of the activity coefficient of protons (equation 1.3)\cite{59}.

\[
pH = -\log([H^+]\gamma^+) \tag{1.13}
\]

It should be noted that to experimentally measure the activity of a single ionic species directly is difficult using a suitable thermodynamic method, due to the principles of electroneutrality\cite{57}. An alternative way to define pH is to express the parameters in terms of the molality, \(m\) (mol kg\(^{-1}\)) of a solution, which is related in a similar way to equation 1.11 (equation 1.14)\cite{60}\cite{61}.

\[
a_{H^+} = m_{H^+}/\gamma_{H^+} \tag{1.14}
\]

Here, \(m_{H^+}\) is the molality of protons in solution.

And the pH is defined in terms of molality (equation 1.15)\cite{60}.

\[
pH = -\log(m_{H^+}/\gamma_{H^+}) \tag{1.15}
\]

The difference between \textit{molality} and \textit{molarity} is defined as follows; (i) molality is the amount of substance per weight (kg\(^{-1}\)) of solution and irrespective of temperature remains the same (ii) molarity is the amount of substance per volume (dm\(^{-3}\)) of solution and does change with respect to temperature. If the molar concentration is low and 1 L = 1 kg (i.e. water at 4 °C), it can be assumed that the molality of a
substance is equal to the molarity; and in the context of this study, this is assumed to be valid\textsuperscript{58}.

1.3.4 – Activity Coefficients and pH

However, due to the principles of electroneutrality, it is difficult to determine the activity coefficient for a single ion, such as protons for measuring pH. The reason for this is that if a single species is added to a solution, the interactions between the oppositely charged ions must be equal and so the solution must be uncharged overall\textsuperscript{62}, as explained by Taylor\textsuperscript{63} in 1927. Instead, it is therefore easier to measure the ‘mean activity coefficient’ ($\gamma_{\pm}$) for 1:1 electrolytes such as HCl and taking into consideration the charges on the anion and cation.

With this in mind, Debye and Hückel\textsuperscript{64} proposed that the behaviour of ions in solution can be calculated assuming that ions in solution act as point charges in water with long-range interactions between ions depending only on their charge and the attractions of ions of opposite charge. There are three assumptions\textsuperscript{65} to the Debye-Hückel law, which state that;

1) Salts completely dissociate into ions in solution.
2) Solutions are dilute.
3) Each ion is surrounded by ions of the opposite charge.

With these three assumptions, the mean ionic activity coefficient of a solution can be calculated using the Debye-Hückel limiting law which takes into account the individual charges on the cations and anions (equation 1.16)\textsuperscript{66}.

$$\log \gamma_{\pm} = -Az_{\pm}z_{-}\sqrt{I}$$  \hspace{1cm} [1.16]

Here, $\gamma_{\pm}$ is the mean ionic activity coefficient, $A$ is the constant (0.509 at 25 °C), $I$ is the ionic strength and $z_{+}$ and $z_{-}$ are the charge of cation and anion. Where the ionic strength, $I$, is given (equation 1.17)

$$I = \frac{1}{2}\sum_{i}m_{i}z_{i}^{2}$$  \hspace{1cm} [1.17]
Here, $m$ is the molality of species $i$ (mol kg$^{-1}$), $z$ is the ionic charge of species $i$. Thus, the ionic strength will be higher with higher charged ions, such as Mg$^{2+}$, than with ions of lower charge.

The ability to use and calculate the activity coefficient helps relate the behaviour of a solution (the activity) to the molality of the solution (the amount of ions in solution) and allows the pH of the solution to be calculated.

The Debye-Hückel limiting law is useful in calculating the activity coefficients at high dilutions, but deviates significantly for low diluted solutions due to the model being simplistic as it overcorrects for the ionic attractions and repulsions. Güntelberg adapted the Debye-Hückel equation which extended the range of ionic strength only slightly and can only be applied in solutions of simple compositions.

$$\log \gamma_z = -A z^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$$ \hspace{1cm} [1.18]

As the molality increases, there is a higher probability of increased interactions between the ions of opposite charge and so an extra parameter, $a$, the distance of closest approach of ions (also known as the ionic size parameter), is included. The ionic size parameter is essentially the size of the hydrated ion, forming the basis of the Bates-Guggenheim equation (also known as the Extended Debye-Huckel Law) (equation 1.19).

$$\log \gamma_z = -A z^2 \frac{\sqrt{I}}{1 + Ba\sqrt{I}}$$ \hspace{1cm} [1.19]

Here, $B$ is the constant (0.33 at 25 °C) and $a$ is the ionic size parameter. The term ‘$Ba$’ can be equated to approximately 1.5 (mol kg$^{-1}$)$^{1/2}$ to give a modified term which is commonly used in calculating the activity coefficient of chloride ions in solutions with ionic strengths not greater than 0.1 mol kg$^{-1}$. This approach is now conventional in determining the pH as defined by The International Union and Applied Chemistry (IUPAC).

IUPAC states that in order to use the Bates-Guggenheim for pH calculation, the ionic strength must not be greater than 0.1 mol kg$^{-1}$. If the ionic strength increases to...
higher molalities, then the observed activity coefficient will also increase and deviations arise between the observed values and those calculated using the Debye-Hückel law (equation 1.16)[69]. The deviation of the calculated results between these two equations is a result of volume effect where ions are forced into closer proximity of each other causing the solvent to become a mixture of water and salt thereby generating high activity coefficients with increasing ionic strengths[70].

1.4 – Oxygen Reduction Reactions

1.4.1 – Oxygen Reduction on Platinum

Platinum is a widely used metal for the reduction of oxygen and has been extensively investigated, especially for its use as a catalyst in fuel cells[71]. With any catalyst, there should be the ability to bind the reactants strong enough to the surface for the reaction to occur, but then must be able to release the products without any permanent adsorption to the surface that can inhibit further reactions from taking place[72].

Metals such as iron, nickel and rhodium bind oxygen too strongly to the surface and as such the metals are oxidised, the rate of oxygen reduction is limited by the desorption of the products[73]. On the other hand, metals such as gold and silver bind oxygen too weakly and so and the rate of oxygen reduction is limited by the dissociation of oxygen[74][75].

The reduction of oxygen in acid on platinum can undergo either a direct four electron reduction process to produce water, or two electron reduction process to produce hydrogen peroxide (Scheme 1.1)[66].
Scheme. 1.1. The reaction scheme for the reduction of oxygen on platinum to produce either water (via a four electron process) or hydrogen peroxide (via a two electron process. [Ref. 66].

The rate determining step for oxygen reduction (irrespective of a four electron or two electron route) is the first electron transfer to the adsorbed oxygen on oxide-free platinum, which corresponds to a value of 120 mV dec$^{-1}$ from Tafel analysis. However, in realistic cases, the surface of platinum is covered with adsorbed species, namely surface oxides and as such, the value of the Tafel slope decreases to 60 mV dec$^{-1}$ in the presence of platinum-oxide surfaces$^{[76][77]}$.

The reason for the change in the Tafel slope is due to formation of platinum oxides and the amount of water present. High water content in either HClO$_4$ or H$_2$SO$_4$ leads to platinum oxide forming and hence lowering the Tafel slope. Adsorbed hydroxide species, OH$_{ads}$, formed from the dissociative mechanism hinder the overall reduction of oxygen$^{[78]}$. On the other hand, a low water content has no effect on the standard 120 mV dec$^{-1}$ Tafel slope, implying that a certain amount of water is required to form the surface oxide in order to change the Tafel slope$^{[79]}$.

Taking into consideration the issue of surface coverage on platinum, the kinetics of the reduction of oxygen can be described in terms of the free sites available (equation 1.20)$^{[78][79]}$.

\[
I_{\text{ORR}} = I_0(1-\Theta_{\text{av}}) \exp \left( - \frac{E^0-E}{b_{\text{av}}} \right) \quad [1.20]
\]
The current for the reduction of oxygen, $I_{\text{ORR}}$, is given by $I_0$, the exchange current density, $\Theta_{\text{ox}}$, the surface coverage of adsorbed oxygen, $(E^0-E)$, the overpotential, and $b_{\text{int}}$, the assumed Tafel slope on a platinum surface without any sites blocked. Different spectator ions will preferentially adsorb on one plane over the other and block the reduction of oxygen and therefore it is crucial to ensure that certain sites on the surface are not blocked to allow oxygen to be reduced.

1.4.2 – Inhibiting the Reduction of Oxygen

A large amount of research has been carried out into the reduction of oxygen, in both HClO$_4$ and in H$_2$SO$_4$ on different platinum planes$^{[74]}$. Marković et al.$^{[80]}$ reported that using HClO$_4$, the order for the reduction of oxygen was higher on platinum (110) than platinum (100). It was concluded that there was a stronger interaction between the adsorbed oxygen and platinum (110) which had an associated lower activation energy for the four electron route to be favoured.

Similarly, Feliu et al. also observed the reduction of oxygen proceeding via a four electron route on platinum (110), but also noted that a two electron route could occur on platinum (111) and (100) if the sites were blocked by strongly adsorbed anions$^{[81]}$.

Meanwhile, reducing oxygen in the presence of H$_2$SO$_4$ changes the order of reactivity of the platinum planes. Instead of platinum (100) being active in HClO$_4$, it was found that platinum (110) was highly active instead$^{[82][83]}$. The difference in reactivity between the two acids is explained by anion adsorption, which also accounted for the decrease in the kinetics for reducing oxygen, as noted by Kadiri et al.$^{[84]}$. Feliu et al. also noted that sulphate anion adsorption on platinum (111) planes accounted for a low activity towards oxygen reduction, although this case was opposite when studied in HClO$_4$ media$^{[85]}$. Marković et al. reported that any oxygen containing anion, such as SO$_4^{2-}$ and ClO$_4^{-}$ significantly impede the reduction of oxygen regardless of the plane$^{[83]}$.

The composition of the electrolyte used to study the kinetics of oxygen reduction has a direct influence on the reduction of oxygen. Hsueh et al.$^{[86]}$ conducted experiments in both acidic and alkaline conditions and noted that in alkaline solutions, there was
minimal adsorption of hydroxide ions and so the reduction of oxygen was improved compared to using acidic solutions. Kadari et al.\cite{84} proposed that in acid solutions using HClO₄, it was weakly adsorbing onto platinum planes whilst bi(sulphate) ions could undergo strong adsorption and thereby hinder the reduction of oxygen.

Bismuth ions have been used to characterise the platinum planes by exploiting their preference to binding to certain platinum planes, specifically their selectivity to binding to platinum (100)\cite{87}. But recently, the use of cyanide to block the platinum (111) sites at which anions such as bi(sulphate) and ClO₄⁻ bind to have been reported by Strmcnik et al.\cite{88}. The use of cyanide to bind to platinum (111) was demonstrated to prevent the adsorption of anions, but did not interfere in the adsorption, or reduction, of oxygen which was significantly increased. However, in alkaline solutions, interactions between the cyanide groups and hydrated cations reduced the rate of reduction of oxygen due to size effects.

The platinum nanoparticles can be either be synthesised with a specific surface orientation or with a mixture (known as polycrystalline). Chloride ions can adsorb on to all three orientations\cite{89,90}, and it was reported by Stamenkovic et al.\cite{91} that due to the chloride ions having a stronger interaction on platinum (100), the reduction of oxygen is inhibited the most. The platinum (100) sites are blocked preferentially due to the strong adsorption interaction with the chloride ions, and with increasing chloride concentration the remaining platinum sites are also blocked, but not as strongly compared to platinum (100). It was noted by Arruda et al.\cite{89} that while surface adsorbed hydroxides on platinum (111) were able to displace the chloride ions, bi(sulphate) ions, however, were unable to do so. Similarly, Schmidt et al.\cite{90} observed on polycrystalline platinum, that while the chloride strongly adsorbed to the platinum (111), the production of hydrogen peroxide was found to increase significantly, via the two electron route on platinum (100).

Considering that platinum is currently the best catalyst for the reduction of oxygen, the cost of mining and production of platinum makes it undesirable for commercial use for example in fuel cells. The issue with oxygen reduction on platinum is that specific platinum planes are prone to adsorption of anions blocking the surface and so preventing the reduction of oxygen. Surface oxides hindering the rate of oxygen reduction makes it a further issue when reducing oxygen platinum and so the kinetics
of oxygen reduction is generally slow due to the high strength of the oxygen double bond, owing to the rate determining step of the first electron transfer[92]. As such, there is a need to look at other metals, or specifically alloys, that are cheaper to source but still have similar characteristics to platinum for reducing oxygen with improved kinetics.

1.5 – Crystal Surface Orientation Effects

1.5.1 – Platinum Facets

The surface of platinum can be arranged into certain (hkl) crystal orientations with the most widely studied being (111), (100) and (110) (Fig. 1.4)[93]. Polycrystalline platinum contains a mixture of these orientations instead of one orientation being the dominant surface feature. It is possible to produce platinum electrodes containing just one orientation of interest[85][94], which allows a more comprehensive investigation to be performed, specifically with the reduction of oxygen.

![Image](Fig. 1.4. The different arrangements of platinum atoms on the surface of bulk platinum, forming the three main planes, (111), (100) and (110). (Adapted with permission, ref. [75]. Copyright 2001, John Wiley & Sons.)

The characterisation of platinum orientation can be done using a combination of techniques such as cyclic voltammetry and Low Energy Electron Diffraction (LEED)[95][96]. In acidic conditions, the cyclic voltammograms display the typical “butterfly” signals which correspond to the potentials at which the hydrogen
underpotential deposition (HUDP) occurs on the platinum orientations. Platinum (111) is observed at more negative potentials, related to the strong adsorption of hydrogen over platinum (110)\cite{97}. Platinum (100)\cite{98} is observed at more positive potentials whereby the adsorption of hydrogen is weaker\cite{99}. Platinum is a complex metal due to the multifacets that exist on the surface. Depending on how the platinum is cut and the methodology at which certain platinum facets are defined, it is possible to enhance the reduction of oxygen. It is also possible to enhance the reduction further when alloying platinum with other metals such as Fe.

\section{1.5.2 – Oxygen Reduction on Platinum Alloys}

Synthesising platinum catalysts with defined surface crystal orientations gives the ability to tune the specific properties of the catalyst towards oxygen reduction. However, several platinum binary alloys have been reported where the platinum is alloyed with a non-precious metal, such as PtCo\cite{100} and PtNi\cite{101} with enhanced catalytic properties towards the reduction of oxygen. The overpotential at which oxygen reduction occurs is shifted towards the thermodynamic standard electrode potential for oxygen reduction, $E^\circ = +1.23$ V with a higher current output\cite{102}.

The process of alloying is thought to decrease the distance between neighbouring Pt atoms which favours the adsorption of oxygen onto the surface, particularly with the platinum (111) orientation, though this is dependent upon the solution used to investigate the reduction of oxygen in which the spectator ions can preferentially adsorb onto specific platinum orientations and inhibit the reduction of oxygen\cite{103,104,105,106}.

The enhancement of the reduction of oxygen is thought to be related to several factors, namely a rough surface morphology, a disordered crystalline structure, and dispersion of the platinum alloys on supported substrates\cite{107,104}. Glass \textit{et al.}\cite{108} reported that highly dispersed PtCr exhibited high catalytic activity towards the reduction of oxygen compared to low dispersed PtCr.

Similarly, Watanabe \textit{et al.}\cite{109} have also shown that dispersion through a nanocapsule method for various PtM alloys (M = Ni, Cr, Co and Fe) were found to have higher
catalytic activities towards oxygen reduction, which they attributed to selective PtM nanoparticle size during the synthesis.

With the low cost of production of iron, PtFe alloys are an attractive platinum alloy\(^\text{[110]}\). Watanabe et al.\(^\text{[111]}\) reported that PtFe alloys enhanced the reduction of oxygen due to a layer of Pt over the surface less than 1 nm thick, which was determined by XPS. The enhanced electrocatalysis of the reducing oxygen was thought to be linked to the 5d-valency orbitals of the platinum on the surface.

The technique of electrospinning platinum with iron to produce PtFe nanowires (between 10 and 20 nm diameter) was reported by Shui et al.\(^\text{[112]}\). The electrocatalytic activity of the PtFe nanowires were found to be higher than conventional platinum for the reduction of oxygen due to the nanowires forming a porous network for oxygen to diffuse through, thereby producing a higher catalytic surface area.

1.5.3 – Oxygen Reduction on Steel

While it has been shown that platinum alloys are able to enhance the reduction of oxygen, other non-platinum alloys such as steel can also reduce oxygen. The electrocatalytic ability at which steel can reduce oxygen is important within the oil and gas industry and how steel corrodes by reducing the oxygen in seawater.

Compère et al.\(^\text{[113]}\) reported that the rate at which oxygen was reduced in seawater depended on the composition of the surface oxide layer. Stainless steel samples that were mechanically polished were found to reduce oxygen quicker in comparison to samples which were chemically treated with a mixture of acids. The reason for the increased rate of oxygen reduction on polished samples was that the presence of iron(III) oxides helped reduce oxygen, which undergoes a two electron reduction (forming hydrogen peroxide) simultaneously with a four electron reduction. Cyclic voltammograms of stainless steel that were chemically treated, however, showed no redox peak for oxygen reduction due to surface oxides, consisting of \(\text{Cr}_2\text{O}_3\), which acted as a barrier preventing oxygen from diffusing through.

The specific role of iron oxide in reducing oxygen on steel surfaces has been proposed Stratmann et al.\(^\text{[114]}\), who reported that the ratios of Fe(II)/Fe(III) present on the
surface as oxides affected the reduction of oxygen. Stratmann et al.\textsuperscript{[115]} observed that surface oxides containing mainly Fe(III) inhibited the reduction of oxygen and concluded it is Fe(II) that is required for oxygen reduction.

Active Fe(II) sites are responsible for the electrocatalysis of oxygen reduction were noted by Calvo et al.\textsuperscript{[116]}. The process occurs via a two electron process, producing hydrogen peroxide which is then decomposed chemically by surrounding areas of Fe$_2$O$_3$ layer to give water.

Davydov et al.\textsuperscript{[117]} investigated the effects of high saline media on steel with increasing temperatures on the reduction of oxygen. It was observed that at temperatures above 90 °C, a decrease in the oxygen reduction limiting current arose. The reason given was that a competition between the solubility of oxygen at high temperatures and the mass-transport of oxygen to the steel surface. In solutions with a high pH it was noted that the reduction of oxygen proceeded through a two electron process forming hydrogen peroxide which was then further reduced to water.

The effect of chloride present on the reduction of oxygen was reported by Gojkovic et al.\textsuperscript{[118]}, who noted that without the presence of chloride, a two electron reduction occurred, but then rose to four electrons with the presence of chloride through Levich analysis. It was suggested that in the absence of chloride the oxide layer formed on the steel hindered the four electron pathway and so generated hydrogen peroxide instead via the two electron route.

The role of oxygen in the corrosion of steel is an important factor for the oil and gas industry, especially in saline solutions. Solutions of high ionic strength change the pH and affect the reduction of oxygen along with the diffusion and dissolved oxygen concentration. There are methods to prevent oxygen from reaching the steel using coatings and it has been shown that certain anions in solution can inhibit the reduction of oxygen. Certain platinum alloys have shown to either enhance or decrease the reactivity of oxygen reduction in different aqueous media and the reduction of oxygen on steel has been widely investigated. In this thesis, Chapter 3 demonstrates a methodology for simultaneously determining the concentration and diffusion coefficients of protons and oxygen in high saline media using platinum microwires. Chapters 4 and 5 continue the use of the platinum microwire to explore further the electrokinetics of the reduction of oxygen in high saline electrolyte media and how a
polymer of intrinsic microporosity (PIM) coating demonstrates no effect on the oxygen reduction process. A glucose micro-fuel cell was developed in Chapter 6 to show how an electro-thermal annealing cleaning method can produce highly catalytic platinum microwires that are able oxidise glucose and reduce oxygen in neutral phosphate buffer electrolyte solutions to generate a power output. Lastly, in Chapter 7, 3D-LAM-printing produced stainless steel electrodes whereby a simple galvanic exchange with platinum produced a robust, active platinum catalyst for methanol oxidation fuel cells in acidic electrolyte solutions.
1.6 – References


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Chapter 2

Introduction to Electrochemical Theory

Chapter Abstract

The fundamental concepts and theories of electrochemistry are discussed in this chapter. Starting off with the electrode / electrolyte interface and the models used to describe the Inner and Outer Helmholtz plane, Fick’s 1st and 2nd Laws of diffusion are introduced on how redox active species approach the electrode surface, along with the various modes of mass transport that can occur.

Once at the electrode surface, the flux of redox active species and the equilibrium established at the Open Circuit Potential are introduced using the Nernst equation. The kinetics of electrochemical reactions is explained using the Butler-Volmer model and how information about the electrokinetics of a redox reaction is obtained using Tafel plots are discussed. Within electrochemistry, the basic three-electrode electrochemical cell setup and the techniques used are explored.

In the last part of this chapter, the types of electrodes commonly used are explained and how digital simulations can match experimental data within a small error margin to allow quantitative determination of key parameters such as concentration and diffusion coefficients.
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2 – Introduction to Electrochemical Theory

2.1 – Overview of Electrochemistry

Electrochemistry, defined as “…the interrelation of electrical and chemical phenomena…”[1], is the study and understanding of chemical reactions that undergo oxidation or reduction at the electrode / electrolyte interface using various techniques such as cyclic voltammetry, chronoamperometry and digital simulations[2].

The origins of electrochemistry can be dated back to around 250 B.C where evidence discovered by archaeologists found some form of an electrochemical cell that was most likely used for electrochemical plating[3]. It was only until the 19th Century, however, that the very fundamentals and understanding of electrochemistry were fully explored. Theories, experiments and observations made by Volta, Faraday and Nernst[2] (to name a few) are now the very basis of electrochemistry today.

While electrochemistry, to some, is considered a part of chemistry, it has now grown into an interdisciplinary field with collaborations drawn in from engineering, physics, electrical engineering and biology. Over recent decades, the field of electrochemistry has grown considerably with the help of such collaborations, and advances have been made in fuel cells[4], lithium ion batteries[5], bio-medical sensors[6], wearable technology[7], solar cells[8] and water purification and desalination devices[9].

Not only has the field of electrochemistry grown with regards to research, but the impact of electrochemistry on society has allowed huge advances to be made in terms of industry and technology. For example, the development of batteries have allowed people to be able to connect and communicate around the world via portable devices, as well as providing crucial power to communities and hospitals after a natural disaster[10]. However, in the industry sector, the electrochemical study of the corrosion of metals in solution is vital for the oil and gas sector[11], where reducing the number of times corroded metal parts in pipelines are replaced can significantly reduce the cost, as well as reducing the chances of man-made environmental disasters such as oil leaks from happening[2].
2.2 – Interfaces, Transport and Equilibria

2.2.1 – Electrode / Electrolyte Interfaces

An interface between the electrode and electrolyte arises when a metal electrode is placed into an electrolyte solution\(^1\).

Helmholtz\(^12\), in 1853, first proposed this by explaining that when a metal is placed into solution, excess charge on the metal surface accumulates. In order for electroneutrality to be maintained, an equal amount, to form a monolayer, of counter ions must be attracted the metal surface\(^13\) (Fig. 2.1(A)). The resulting model by Helmholtz suggested that the electrode potential \((\phi_M)\) decreases linearly from the metal surface with increasing distance (known as the Helmholtz layer)\(^14\), until the potential was the same as the solution potential \((\phi_S)\).

Gouy\(^15\) and Chapman\(^16\) subsequently improved Helmholtz’s model by assuming that ions in solutions could be considered as point charges\(^13\) (similar to one of three Debye-Hückel’s assumptions) and as such, due to thermal energy \((kT)\), are allowed to move freely in solution (Fig. 2.1(B)). The resulting model retained Helmholtz’s idea electrostatic attraction of ions to the metal surface, but included the random motion of ions that would effectively be dispersed out into the bulk solution thereby producing a diffuse double layer\(^17\). The electrode potential would decay exponentially with increasing electrode distance.

In 1924, Stern\(^18\) combined the Gouy-Chapman and the Helmholtz models into one unified model taking into consideration the finite size of the ions in solution. Stern concluded that the ions could not approach the surface of the metal any closer than the size of their ionic radius, referred to as the plane of closest approach\(^19\). While some ions adsorbed onto the metal surface, Brownian motion also occurred, with the diffuse doubler layer maintaining electroneutrality\(^13\) (Fig. 2.1(C)). The significance of Stern’s model was that the potential dropped dramatically between the electrode and the Helmholtz layer, and then decayed gradually into the diffuse double layer\(^17\).

The diffuse double layer, also known as the electrical double layer\(^20\) is a narrow region in which a defined separation between positive and negative charges exist acting as a capacitor with a high capacitance.
The Inner Helmholtz plane (IHP) and Outer Helmholtz plane (OHP) were later added by Grahame to the previous models\textsuperscript{[21]}. Grahame suggested that the Inner Helmholtz plane mainly consists of solvation molecules, however, as solvated ions approached the surface; they can be specifically adsorbed to the surface upon losing their solvation shell. From this, the Outer Helmholtz plane consists of solvated ions, which can only approach the Inner Helmholtz plane depending on the size of their solvation shell and hence are non-specifically adsorbed\textsuperscript{[19]}. The diffuse double layer then extends from the Outer Helmholtz plane into the bulk solution where Brownian motion occurs, while the electrode potential with increasing electrode distance remained unchanged as originally proposed by Stern (Fig. 2.1(D)).

![Figure 2.1](image)

**Figure 2.1.** Comparisons of (A) the Helmholtz model, (B) the Guoy-Chapman model, (C) the Stern model and (D) the Grahame Model. Here, \( x \) is the distance from metal surface, \( \phi \) is the potential (V), \( \phi_M \) is the potential at the metal surface (V) and \( \phi_S \) is the potential in solution (V). (Ref. [20]).
2.2.2 – Mass Transport

In order for redox active species to undergo any electron transfer reactions, the species must first be transported to the electrode surface through solution, either towards or away from the electrode depending on the charge on the redox species. There are three modes\(^{[22]}\) of transport, (i) diffusion, (ii) convection and (iii) migration.

A gradient change in concentration leads to diffusion occurring. Species from an area of high concentration will diffuse through the solution to an area of low concentration, with the overall aim being to ensure the concentration is constant\(^{[23]}\). The diffusion of a chemical species can be described by Fick’s first law (equation 2.1), in which the movement of the species diffuse to low areas of concentration, thus causing the diffusion gradient to be negative\(^{[24]}\).

\[
J_i = -D_i \frac{\partial c_i}{\partial x} \quad [2.1]
\]

Here, \(J\) is the diffusional flux (mol m\(^2\) s\(^{-1}\)) of chemical species \(i\), \(c_i\) is the concentration (mol m\(^{-3}\)) of species \(i\), \(x\) is the direction (m) of diffusion and \(D_i\) is the diffusion coefficient (m\(^2\) s\(^{-1}\)) of species \(i\).

Fick’s second law\(^{[23]}\) (equation 2.2) of diffusion deals with how the concentration varies with respect to time, \(t\), at a specific point \(x\)\(^{[25]}\).

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad [2.2]
\]

If an external force acts upon the solution, movement of chemical species is produced known as convection\(^{[22]}\). The external force can be classified into two subcategories\(^{[13]}\), (i) natural convection, such as: thermal gradients or density differences or (ii) force convection, such as: gas bubbling, stirring or pumping. Of the two types of external forces, natural convection is irreproducible and unpredictable, however, natural convection can be eliminated by designing an experiment to operate at a time that is equivalent to 10 seconds\(^{[25]}\).
It is possible to describe the convective flux\textsuperscript{13,25} using the equivalent form of Fick’s first law (equation 2.3).

\[ J_{i,\ conv} = v_x c_i \]  

[2.3]

Here, \( J_{i,\ conv} \) is the convective flux (mol m\(^{-2}\) s\(^{-1}\)) of species \( i \) at a point \( x \) and \( v_x \) is the fluid velocity (m s\(^{-1}\)).

Likewise, it is possible using Fick’s second law, to describe the convective flux with respect to time at a point \( x \) (equation 2.4)\textsuperscript{25}.

\[ \frac{\partial c}{\partial t} = -v_x \frac{\partial c}{\partial x} \]  

[2.4]

The last type of mass transport, migration\textsuperscript{19}, arises due to the movement of a charged species under the influence of an applied electric field which generates an electrostatic force\textsuperscript{23} causing movement of the charged species, in contrast to convection and diffusion where both charged and neutral molecules are affected. The migratory flux can be described as (equation 2.5)\textsuperscript{22}.

\[ J_{i,\ migr} = -\frac{z_i F}{RT} D_i c_i \frac{\partial E}{\partial x} \]  

[2.5]

Here, \( J_{i,\ migr} \) is the migration flux (mol m\(^{-2}\) s\(^{-1}\)) of species \( i \), \( z_i \) is the charge on the ion, \( F \) is the Faraday’s constant (96485 C mol\(^{-1}\)), \( R \) is the molar gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), \( T \) is the absolute temperature (K), \( D_i \) is the diffusion coefficient of chemical species \( i \), \( c_i \) is the concentration of species \( i \) (mol dm\(^{-3}\)) and \( \frac{\partial E}{\partial x} \) is the potential gradient (V cm\(^{-1}\)).

Migration can be eliminated in experiments by the addition of an excess, inert, background electrolyte (usually KCl at 0.1 mol dm\(^{-3}\)) which do not undergo any electrolysis reactions and to shield ions from migratory effects\textsuperscript{13,19}. Use of background electrolytes helps the current pass through the solution, acting as a conductor as well as causing the double layer at the electrode to become compact. This is to aid diffusion of the redox species to approach close enough to the electrode surface for electron transfer to take place\textsuperscript{25}. 

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The Nernst-Planck\textsuperscript{19} equation (equation 2.6) combines all three types of mass transport into a single equation to describe the contributions of the types of mass transport towards the flux of a chemical species, $i$, along one direction.

$$J_i = -D_i \frac{\partial c_i}{\partial x} - \frac{z_i F}{RT} D_i c_i \frac{\partial E}{\partial x} + c_i v_i \tag{2.6}$$

2.2.3 – Electrode Dynamics and Equilibria

At the electrode / electrolyte interface, diffusion of the redox active species towards the metal surface arises generating a current\textsuperscript{25}. The current produced as a result of redox active species diffusing to the electrode surface is related to the flux (equation 2.7).

$$i = FAj \tag{2.7}$$

Here, $i$ is the current (A), $F$ is Faraday’s constant (96485 C mol\textsuperscript{-1}), $A$ is the electrode area (cm\textsuperscript{2}) and $j$ is the flux (mol cm\textsuperscript{-2} s\textsuperscript{-1}).

The current produced as a result from the flux of redox active species at the electrode surface is dependent upon several processes\textsuperscript{19};

1. Movement of the redox species from the bulk solution to the electrode by mass transport.
2. Adsorption of the redox species onto the surface of the electrode.
3. Electron transfer (causing either oxidation or reduction of the redox species)
4. Desorption of the redox species from the electrode surface.
5. Movement of the redox species back towards the bulk solution by mass transport.

At the electrode surface, equilibrium is attained where the loss of electrons oxidises the Fe\textsuperscript{2+} to generate a negative charge on the electrode shifting the equilibrium to the left hand side. Alternatively, if the equilibrium moves to the right hand side, a positive charge is left on the electrode surface and electrons transfer from the electrode to the Fe\textsuperscript{3+} to be reduced to Fe\textsuperscript{2+}\textsuperscript{19} (equation 2.8).

$$\text{Fe}^{3+} (aq) + e^- \rightleftharpoons \text{Fe}^{2+} (aq) \tag{2.8}$$
The concentration at the electrode surface is no longer the same as the bulk when there is a current passing through the electrode / electrolyte interface causing a depletion of the redox species at the electrode surface\textsuperscript{[23]}. For a reversible redox system in equilibrium (equation 2.9), there is both a forward ($k_c$) and backward ($k_a$) rate constant associated\textsuperscript{[24]}.

\[
Fe^{3+} (aq) + e^{-} \xrightleftharpoons{k_c}{k_a} Fe^{2+} (aq) \quad [2.9]
\]

Thus, the individual currents for Fe\textsuperscript{3+} and Fe\textsuperscript{2+} can be expressed (equations 2.10 and 2.11).

\[
i_c = -nFAk_c[\text{Ox}]_0 \quad [2.10]
\]

\[
i_a = nFAk_a[\text{Red}]_0 \quad [2.11]
\]

Here, $i_c$ is the cathode current, $i_a$ is the anodic current, $n$ is the number of electrons transferred and $k_c$ and $k_a$ are the heterogeneous transfer rate constants of the reduced species and oxidised species (m s\textsuperscript{-1}). Combining the two equations together gives an expression for the total current (equation 2.12).

\[
I_{\text{total}} = nFA(k_a[\text{Red}]_0 - k_c[\text{Ox}]_0) \quad [2.12]
\]

This can be rewritten in terms of the flux at the electrode surface from equation 2.7 (equation 2.13).

\[
j = k_c[\text{Ox}]_0 - k_a[\text{Red}]_0 \quad [2.13]
\]

With a reversible system at equilibrium, no current flows as both the forward and backward reactions have the same rate constants, known as the Open Circuit Potential (OCP), and is commonly known as the equilibrium potential when both the reduced and oxidised species are in equilibrium. The Open Circuit Potential is the potential at the working electrode (relative to the reference electrode) where no external voltage or current is applied\textsuperscript{[11]}.

Nernst\textsuperscript{[26]}, in 1897, proposed an equation (equation 2.14) which showed the overall cell potential, when no current is flowing, being equal to standard electrode potential and the activities of the both the reduced and oxidised\textsuperscript{[17]}.
\[ E_{eq} = E^0 + \frac{RT}{nF} \ln \left( \frac{a_{ox}}{a_{red}} \right) \]  

[2.14]

Here, \( E_{eq} \) is the overall cell potential at equilibrium (V), \( E^0 \) is the standard cell potential (V), \( n \) is the number of electrons transferred, \( F \) is the Faraday’s constant (96485 C mol\(^{-1}\)) and \( a_{ox} \) and \( a_{red} \) are the activities of oxidised and reduced species at the electrode surface. The activities of solids and pure liquids are equal to 1; however, often (for dilute solutions) it is more convenient to write the Nernst equation with the concentrations of both the oxidised and reduced species, instead of activities.

### 2.2.4 – Butler–Volmer Kinetics

Calculating, and describing, the rate of electron transfer between the electrode surface and the redox active species can be achieved using the Butler–Volmer model\(^{[11]}\). The kinetics of electron transfer for both the oxidised and reduced species can be expressed in the form of the Arrhenius equation (equations 2.15, 2.16 and 2.17) where a certain amount of energy is required to overcome the activation energy barrier, similar to chemical reactions\(^{[19][25]}\).

\[ \text{Ox} + e^- \rightleftharpoons \text{Red} \]  

[2.15]

\[ k_c = A_c \exp\left( -\frac{\Delta G^*_c}{RT} \right) \]  

[2.16]

\[ k_a = A_a \exp\left( -\frac{\Delta G^*_a}{RT} \right) \]  

[2.17]

Here, \( k_c \) and \( k_a \) are the rate constants for the anodic and cathodic redox reactions, \( A_c \) and \( A_a \) are the pre-exponential factors corresponding to the frequency of collisions\(^{[13]}\), \( \Delta G^*_c \) and \( \Delta G^*_a \) are the activation energies of the transition state at equilibrium for the anodic and cathodic processes, respectively (Fig. 2.2).
Figure 2.2. A plot showing the Standard free energies of the oxidant and reductant against the reaction coordinate when at equilibrium. The transition state, $G^*$ is the intersection of the two parabolas, which for both the oxidant and reductant have an associated standard Gibbs free energy, $\Delta G^*$. (Ref. [19]).

When a potential is applied to the equilibrated system, the Gibbs energy of the system will change relative to the applied potential (equation 2.18) (Fig. 2.3).

$$\Delta G = -nF\Delta E = -nF\eta$$ \hspace{1cm} [2.18]

Here, $n$ is the number of electrons transferred (1 in this example) and $\eta$, is defined as the overpotential (equation 2.19)

$$\eta = E - E^0$$ \hspace{1cm} [2.19]

Now that the system has changed with the applied potential, the Gibbs free energy of the reactants ($Ox + e^-$) at the new potential can be described (equation 2.20).

$$\Delta G_c^* = \Delta G_c^{0r} - F\eta$$ \hspace{1cm} [2.20]
Figure 2.3. The standard free energy profile of a system after applying a potential to cause the activation barrier of the cathodic reaction to become sufficiently small for the reaction to proceed. (Ref. [19]).

Along with this change upon applying the potential to the system, the anodic and cathodic energy barriers are altered and can be written as a fraction of the total energy change (equations 2.21 and 2.22).

\[
\Delta G_u^* = \Delta G_u^{0r} - (1 - \alpha)F\eta \quad [2.21]
\]

\[
\Delta G_c^* = \Delta G_c^{0r} + \alpha F\eta \quad [2.22]
\]

The transfer coefficient, \( \alpha \), has a value between 0 and 1 and is used to describe the transition state (Fig. 2.4).

If the value is near to 0, the transition state is said to resemble more of the reactant state and the applied potential has no effect on the Gibbs free energy barrier. While a value closer to 1 implies the transition state resembles more of the product state and the electrode potential can change the Gibbs free energy barrier leading to the products being formed. For a symmetrical transition state, \( \alpha = 0.5 \) and is independent upon the applied potential\(^1\|\text{[19]}\|\text{[25]}\).
Figure 2.4. A close-up section of the intersections of the standard free energy profiles before and after applying a potential. A negative potential causes the standard free energy profile of the oxidants to shift higher allowing reduction to occur. A positive potential causes the standard free energy profile of the oxidants to shift lower allowing oxidation to occur. (Ref. [19]).

With the Gibbs free energy of reactants and products defined, these can be substituted back into equations 2.16 and 2.17 (equations 2.23 and 2.24).

\[ k_a = A_a \exp \left( \frac{-\Delta G_a^\ddagger}{RT} \right) \exp \left[ \frac{(1-\alpha)F \eta}{RT} \right] \]  

\[ k_c = A_c \exp \left( \frac{-\Delta G_c^\ddagger}{RT} \right) \exp \left[ -\alpha F \eta \right] \]  

[2.23]  

[2.24]  

Here, \( R \) is the molar gas constant (8.31 J K\(^{-1}\) mol\(^{-1}\)) and \( T \) is the absolute temperature (K).

At the electrode / electrolyte interface, if the system is at equilibrium and the concentrations of the products and reactants are equal, as well as \( E = E_o \) then the rate of the anodic and cathodic processes are also equal (equation 2.25).

\[ k_0 = A_e \exp \left( \frac{-\Delta G_e^\ddagger}{RT} \right) = A_a \exp \left( \frac{-\Delta G_a^\ddagger}{RT} \right) \]  

[2.25]
Here, $k_o$ is the standard heterogeneous rate constant for electron transfer, and the anodic and cathodic rate constants to be expressed in relation to $k_o$ (equations 2.26 and 2.27).

$$k_c = k_o \exp\left(-\frac{\alpha F \eta}{RT}\right) \quad [2.26]$$

$$k_a = k_o \exp\left(\frac{(1-\alpha) F \eta}{RT}\right) \quad [2.27]$$

Now equations 2.26 and 2.27 can be substituted into equation 2.12 to give an expression for the total current at the electrode surface in relation to the contributions from the anodic and cathodic rate constants yielding the Butler-Volmer equation (equation 2.28).

$$I_t = F A k_o \left[\text{Red}_0 \exp\left(\frac{(1-\alpha) F \eta}{RT}\right) - \text{Ox}_0 \exp\left(-\frac{\alpha F \eta}{RT}\right)\right] \quad [2.28]$$

However, once the reaction taking place at the electrode surface reaches equilibrium, the cathodic and anodic rates of reaction are therefore equal. Despite the overall current being zero at equilibrium, there is still a current corresponding to the cathodic process and anodic process, giving the exchange current, $I_o$ [1] (equations 2.29 and 2.30).

$$I_o = F A k_o [\text{Red}_0] \left(\frac{(1-\alpha) F \eta}{RT}\right) \quad [2.29]$$

$$I_o = F A k_o [\text{Ox}_0] \left(-\frac{\alpha F \eta}{RT}\right) \quad [2.30]$$

The Butler-Volmer equation (equation 2.28) can then be simplified further if the solution is well stirred such that the concentrations of the reactants at the electrode surface are equal to their bulk concentrations (equation 2.31) [13].

$$I = I_o \left[\exp\left(\frac{(1-\alpha) F \eta}{RT}\right) - \exp\left(-\frac{\alpha F \eta}{RT}\right)\right] \quad [2.31]$$

But at equilibrium, the net current is zero which means that the electrode has a potential value based on the concentrations of the reactants and products in solution,
as given by the Nernst equation (equation 2.14). Therefore, equations 2.29 and 2.30 can be equated (equation 2.32) and simplified (equation 2.33).

\[
FAk_0[Ox]_0 \exp\left(\frac{-\alpha F \eta}{RT}\right) = FAk_0[Red]_0 \exp\left(\frac{(1-\alpha) F \eta}{RT}\right)
\]  

[2.32]

\[
\frac{\exp(- F \eta)}{RT} = \frac{[Ox]_0}{[Red]_0}
\]  

[2.33]

Equation 2.33 can then be substituted back into either equations 2.29 or 2.30 (equation 2.34).

\[
I_o = FAk_0[Ox]_0^{(1-\alpha)}[Red]_0^\alpha
\]  

[2.34]

If \([Ox]_0 = [Red]_0 = C\), then the exchange current is directly proportional to the rate constant (equation 2.35).

\[
I_o = FAk_0C
\]  

[2.35]

A system will achieve equilibrium in a short time period when \(k_o\) is large, but if \(k_o\) is small then it will take longer for the system to reach equilibrium\[^{19}\].

### 2.2.5 – Tafel Plots

Using the simplified version of the Butler-Volmer equation (equation 2.31), which uses the current density instead of the standard heterogeneous rate constant, \(k_o\), allows the current to be described in relation the overpotential, \(\eta\)\[^{19}\][\(^{23}\)].

If \(I_o\) is large and reversible, then a very small amount of overpotential is required to drive the reaction and current flows freely in both the anodic and cathodic directions and as such contribute towards the current. With a reversible system, \(I_o\) is large and as such the rate of electron transfer, \(k_o\), will also be large as the charge-transfer process at the electrode surface is in equilibrium (Fig. 2.5(A)). However, if \(I_o\) is small and irreversible, then a high overpotential is needed to drive the reaction as the rate of electron transfer is slow and the system takes a long time to achieve equilibrium\[^{13}\][\(^{19}\)] (Fig. 2.5(B)).
Figure 2.5. Plot of the current density against the overpotential. (A) For large $I_o$, a small overpotential is only required. (B) For small values of $I_o$, a large overpotential is needed to drive the reaction forward. (Ref. [19]).

When a high overpotential is applied, if the anodic process is favoured then the cathodic process becomes extremely small, causing the Butler-Volmer equation to be reduced (equation 2.36).

$$\ln I = \ln I_o + \frac{(1-\alpha)F}{RT} \eta$$

[2.36]

Likewise, the opposite holds true and if the cathodic process is favoured then the anodic process becomes extremely small (equation 2.37).

$$\ln(-I) = \ln I_o - \frac{\alpha F}{RT} \eta$$

[2.37]

Plotting the log values of the currents against the overpotential yields a plot known as the Tafel plot, which allows the exchange current, $I_o$, to be extrapolated. The gradients of the slopes for both anodic and cathodic processes can be used to calculated the transfer coefficient, $\alpha$ as well (Fig. 2.6)\textsuperscript{[13]}. 47
Figure 2.6. Tafel plots for the cathodic and anodic reactions. At the point of extrapolation, the exchange current, $I_o$ can be calculated. The gradients from the Tafel plots can be used to calculate the transfer coefficient, $\alpha$, for either or both processes. (Ref. [13]).

2.3 – Electrochemical Setup and Techniques

2.3.1 – Electrochemical Setup

The typical electrochemical cell setup for measurements is a three-electrode configuration\cite{27} (Fig. 2.7), which consists of a working electrode (WE), a counter electrode (CE) and a reference electrode (RE) (usually a saturated KCl or saturated calomel electrode, SCE). The working electrode is where the reaction being investigated takes place, and can be any type of electrode: a rotating disc, a microelectrode, or a microwire and can consist of any metal such as platinum, gold or glassy carbon (which are the common substrates used).

The reference electrode has a set potential with respect to the Standard Hydrogen Electrode (SHE) and it is between the working electrode and reference electrode that the voltage is applied; it also where the oxidation and reduction peaks are defined against the reference electrode. The current, however, passes through the counter electrode, which is typically platinum and is larger than the working electrode in order
to minimise any reactions taking place at the counter electrode so that all the electrochemistry occurring is centred on the working electrode.

![Schematic diagram of a standard three-electrode cell configuration.](image)

**Figure. 2.7** – Schematic diagram of a standard three-electrode cell configuration. (Ref. [15]).

At the working electrode, the electrochemical redox of interest takes place and there are two common electrochemical techniques used to investigate the mechanism, chronoamperometry (CA) and cyclic voltammetry (CV).

### 2.3.2 – Chronoamperometry

Measuring the current with respect to time after applying a potential step from a potential where no redox reaction occurs (i.e. where no current is observed), to a potential where the redox reaction does occur, is referred to as chronoamperometry\(^1\).

The flux at a planar electrode surface can be evaluated and differentiated with Fick’s second law of diffusion (equation 2.2), giving the Cottrell equation\(^{28}\) (equation 2.38).

\[
i = \frac{nFAD^2c}{\pi^{1/2}t^{3/2}}
\]  

[2.38]
Here, $i$ is the current (A), $n$ is the number of electrons transferred, $F$ is the Faraday’s constant (96485 C mol$^{-1}$), $D$ is the diffusion coefficient (m$^2$ s$^{-1}$), $c$ is the concentration (mol m$^{-3}$), $A$ is the electrode area (m$^2$) and $t$ is the time (s).

From equation 2.38, it can be seen that the magnitude of the current decreases with $t^{-1/2}$ (Fig. 2.8), implying that after a set period of time, rather than diffusion being the main mass transport property, convection becomes the dominating factor. Similarly, at small time periods, a capacitance current is also present within the chronoamperogram which needs to be removed for digital simulation purposes$^{[24]}$.

![Figure 2.8](image)

**Figure. 2.8** – Illustration of a typical chronoamperogram at a planar electrode. (Ref. [9]).

A plot of the current ($i$) versus $t^{-1/2}$ will produce a straight line in which the diffusion coefficient can be calculated from the gradient if all other parameters are known.

From Fig. 2.8, with increasing time, the magnitude of the current decreases where the concentration gradient$^{[24]}$ at the electrode surface also decreases, although the current remains at a steady-state value rather than converging towards zero$^{[25]}$.

In 1904, Nernst$^{[29]}$ proposed that at the electrode surface an immobile layer is formed in which only diffusion towards the electrode surface is the mode of mass transport; while outside of this the bulk concentration of the solution remains constant and convection then becomes the dominating transport$^{[30]}$. This immobile layer in which diffusion occurs is called the Nernst diffusion layer, $\delta^{[17]}$. (Fig. 2.9) and can be calculated from Fick’s first law of diffusion (equation 2.39).
\[ D \left( \frac{\partial c}{\partial x} \right) = D \left( \frac{c_x - c_0}{\delta} \right) \]  

[2.39]

Here, \( c_x \) is the concentration of the bulk solution and \( c_0 \) is the concentration at the electrode surface.

As such, from a chronoamperogram, assuming that a steady-state current is observed, then the diffusion layer at the electrode surface can be calculated\(^{[23]}\) (equation 2.40).

\[ i_{ss} = \frac{nFEcD}{\delta} \]  

[2.40]

Here, \( i_{ss} \) is the steady state current (A) and \( \delta \) is the diffusion layer thickness (m).

### 2.3.3 – Cyclic Voltammetry

Where chronoamperometry only applies a set potential step, cyclic voltammetry applies a continuous potential which measures the current with respect to time. The potential is stepped from \( E_0 \) to \( E_I \) where electron transfer takes place, forming the basis of linear sweep voltammetry\(^{[13]}\) (Fig. 2.10(A)). However, with cyclic voltammetry, once the \( E_I \) value is reached, the potential is the reversed and sweeps back to \( E_0 \) (Fig. 2.10(B))\(^{[23]}\).
Figure. 2.10 – Illustration of: (A) linear sweep voltammetry and (B) cyclic voltammetry for a reversible reaction. (Ref. [9]).

The shape of a cyclic voltammogram can be predicted\(^{25}\) by using Fick’s second law of diffusion in respect to the concentrations of A and B (equations 2.41 and 2.42), since the diffusion of the reactants is the main form of mass transport to the electrode surface.

\[
\frac{\partial [A]}{\partial t} = D_A \frac{\partial^2 A}{\partial x^2} \tag{2.41}
\]

\[
\frac{\partial [B]}{\partial t} = D_B \frac{\partial^2 B}{\partial x^2} \tag{2.42}
\]

In order for a reaction to be classed as electrochemically reversible\(^{19}\) (Fig. 2.11(A)), the concentration at the electrode surface should follow Nernst’s equation (equation 2.14) which implies fast electron transfer kinetics. However, measurement from the respective cyclic voltammogram will also satisfy the following specific tests (equations 2.43, 2.44, and 2.45\(^{23}\)).

1. Measuring the difference between the potentials of the anodic and cathodic peaks;

\[
\Delta E_p = E_p^a - E_p^c = 2.22 \frac{RT}{nF} \text{mV} \tag{2.43}
\]

2. Measuring the ratio of the peak heights of the anodic and cathodic peaks;

\[
\left( \frac{i_p^c}{i_p^a} \right) = 1 \tag{2.44}
\]
3. The peak height of either the anodic or cathodic peaks is proportional to the square of the scan rate;

\[ i_p \propto v^2 \]  \hspace{1cm} [2.45]

Equation 2.45 also takes the form of the Randles-Sevcik\textsuperscript{[19]} equation (equation 2.46), in which a plot of \( i_p \) versus \( \frac{1}{v^2} \) will produce a straight line, passing through the origin, allowing calculation of the diffusion coefficient from the gradient.

\[ i_p = 0.4463 \frac{n^3 F^2}{R^2 T} \frac{1}{2} AD^{\frac{1}{2}} \frac{1}{2} cv^{\frac{1}{2}} \]  \hspace{1cm} [2.46]

Here, \( i_p \) is the peak height current, \( R \) is the molar gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), \( T \) is the absolute temperature (K), \( A \) is the area of the electrode (m\(^2\)) and \( v \) is the scan rate (mV s\(^{-1}\)).

However, reactions which have slow electron transfer kinetics are classed as irreversible\textsuperscript{[23]} (Fig. 2.11(B)), due to the slow kinetics being unable to attain an equilibrium, and is dependent upon satisfying the following tests (equations 2.47 and 2.48).

4. The difference between the potentials of the anodic and cathodic peaks is greater than 59 mV;

\[ \Delta E_p = E_p^a - E_p^c > 2.22 \frac{RT}{nF} \text{mV} \]  \hspace{1cm} [2.47]

5. The peak height of either the anodic or cathodic peaks is proportional to the square of the scan rate;

\[ i_p \propto v^2 \]  \hspace{1cm} [2.48]
Figure. 2.11 – Comparison of: (A) an electrochemically reversible cyclic voltammogram, where $\Delta E_p = 2.22 \frac{RT}{nF} \text{mV}$ and (B) an electrochemically irreversible cyclic voltammogram, where $\Delta E_p > 2.22 \frac{RT}{nF} \text{mV}$ . (Ref. [9]).

2.4 – Electrodes

2.4.1 – Rotating Disc Electrodes

Hydrodynamic electrodes, such as rotating disc electrodes are able to draw redox active species towards the electrode surface in a very short time period by a mechanical action (i.e. stirring)\cite{17} forming a constant laminar flow of species to the electrode surface. Levich and coworkers\cite{31}\cite{32} first developed the theory for the analysis of data from a rotating disc electrode (Fig. 2.12).

This combination of diffusion and mechanical transport can be explained by using a modified form of Fick’s second law (equation 2.49).

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v_x \frac{\partial c}{\partial x} \tag{2.49}
\]

Here, $v_x$ is the fluid velocity (cm s$^{-1}$).
Figure 2.12 – Schematic diagrams of the flow patterns of electroactive species when using a rotating disc electrode. (Ref. [11]).

By assuming that at the electrode surface, the rate of change of the electroactive species with respect to time is zero (i.e. under steady-state conditions)\[23\] as the electrode rotates (equation 2.50).

\[ D \frac{\partial^2 c}{\partial x^2} = \nu \frac{\partial c}{\partial x} \]  

[2.50]

From this, Levich\[31\] derived an expression where at the electrode surface the velocity of the solution is uniform\[17\] and is reliant on the rotation speed of the electrode. An increase in the rotating speed increases the limiting current as more electroactive species is drawn up to the electrode surface (equation 2.51).

\[ i_{LM} = 0.62nFAcD^\frac{2}{3}v_{kin}^{-\frac{1}{2}}\omega^{-\frac{1}{2}} \]  

[2.51]

Here, \( i_{LM} \) is the limiting current (A), \( n \) is the number of electrons transferred, \( F \) is the Faraday’s constant (96485 C mol\(^{-1}\)), \( A \) is the electrode area (m\(^2\)), \( c \) is the concentration (mol m\(^{-3}\)), \( D \) is the diffusion coefficient (m\(^2\) s\(^{-1}\)), \( v_{kin} \) is the kinematic viscosity of the solution (m\(^2\) s\(^{-1}\)) and \( \omega \) is the rotation speed (rad s\(^{-1}\)).

A plot of the limiting current (\( i_{LM} \)) verses rotation (\( \frac{1}{\omega^2} \)) will yield a straight line in which the diffusion coefficient can be calculated from the gradient, providing the kinematic viscosity is known.
Two layers at the rotating disc electrode surface can be defined:\textsuperscript{[27]};

1. An immobile layer next to the electrode surface in which diffusion is the mode of transport (the diffusion layer), and;
2. A layer defined by convection which is uniform causing no gradient change in the concentration (Fig. 2.13).

\textbf{Figure. 2.13} – Illustration of the two layers (the diffusion layer and the convection layer) defined at a rotating disc electrode. (Ref. [9]).

As such, the diffusion layer at the electrode surface is reliant upon the rotation speed; as the rotating speed increases, the diffusion layer thickness decreases when the convection transport increases\textsuperscript{[24]} (equation 2.52).

\[
\delta = 1.61D^{1/4}v^{1/2}\omega^{-1/2} \tag{2.52}
\]

Here, \(\delta\) is the diffusion layer thickness (cm).

\textbf{2.4.2 – Microdisc Electrodes}

Instead of using forced convection as a means of mass transport of redox active species to the electrode surface, use of electrodes with diameters smaller than 50 \(\mu m\)\textsuperscript{[11]}, classed as microelectrodes, can achieve high current densities with a relatively small amount of redox active species diffusing to the electrode surface at a fast
rate\textsuperscript{[24]}. Here, diffusion is the only form of mass transport to the electrode surface. Microdisc electrodes were first pioneered by Fleischman and coworkers\textsuperscript{[33][34][35]}. At short time periods the diffusion layer is proportional to the electrode radius\textsuperscript{[17]} and as such the current is then proportional to the size of the radius ($r_0$).

In chronoamperometric measurements, both short- and long-time transients can affect the diffusion towards to the electrode surface (equation 2.53\textsuperscript{[23]}).

\[ j = \frac{nF D^2 c}{\pi^2 r^2} + \frac{4nF D c}{\pi a} \]  

[2.53]

Here, $j$ is the flux of electroactive species to the electrode surface (mol m\textsuperscript{-2} s\textsuperscript{-1}).

Linear diffusion towards the electrode surface is dominant at short time periods (the first term in equation 2.53, Fig. 2.14(A)) and is identical to the Cottrell equation (equation 2.38). At longer time periods, the linear diffusion changes to hemispherical diffusion (Fig. 2.14(B)) where a steady-state current\textsuperscript{[25]} is reached and allows fast electron transfer kinetics to be studied.

![Figure 2.14](image)

**Figure. 2.14** – Illustration of: (A) linear diffusion towards the electrode surface at short time periods and (B) hemispherical diffusion towards the electrode surface at long time periods. (Ref. [9]).

Shoup and Szabo\textsuperscript{[36]} developed an expression (equations 2.54 and 2.55) in which the current transient using a microdisc electrode could be predicted using digital simulation over both short- and long-time periods in chronoamperometric experiments, with an error between both experimental and simulated data of less than 0.5 %. 
\[ i = 4nFeDcD_{\tau}f(\tau) \]  

Where;

\[ f(\tau) = 0.7854 + 0.8863\tau^{\frac{1}{2}} + 0.2146e^{-0.7823\tau^{\frac{1}{2}}} \]  

Here, \( \tau \) is the time (s).

By simulating and fitting the experimental data, it is possible to simultaneously optimise both the \( c \) and \( D \) values for a given redox system. The expression also demonstrates[25] that the current varies with \( D^{\frac{1}{2}} \), while at longer time periods, this changes to \( D \).

### 2.4.3 – Microcylinder Electrodes

It is possible to achieve quasi-steady state currents without the use of hydrodynamic electrodes or waiting for long time periods with microdisc electrodes by using a different geometric design. Microwire (or microcylinder) electrodes have been used extensively by Gründler and coworkers[37][38] in various electrochemical measurements involving heat (termed “hot-wire electrochemistry”) using simple fabrication processes[39][40].

A cylindrical electrode is defined as an electrode where the size of the diffusion layer thickness is larger than the radius \( (r_0) \)[41]. With this in mind, diffusion is the same in any plane along the cylinder axis implying that no edge effects are observed unlike with a microdisc electrode where the diffusion can change from linear to hemispherical depending on the time period. As a result, use of a microcylinder allows a quasi-steady state current to be reached in a shorter time period.

The concentration gradient at a microwire can be described in terms of Fick’s second law[1] (equation 2.56).

\[ \frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right) \]  

Here, \( r \) is the distance from the central axis of the microwire (m).
It can be seen that with increasing distance from the microwire and with increasing time, the diffusion decreases. The current can be related to the time and the distance from the microwire by solving equation 2.56 (equation 2.57)\(^{[42]}\).

\[
I(t) = nFLDc \times \left( \frac{-e^{\frac{2}{3}} \sqrt{\frac{Dc}{16r^2}} + \frac{\pi}{4} \sqrt{\frac{Dc}{16r^2}} \ln \left[ \sqrt{64e^{-0.5772\frac{Dc}{16r^2}}} + e^{\frac{5}{3}} \right]}\right)
\]

\[\text{[2.57]}\]

Here, the current \(I\), is given by the \(n\), the number of electrons, \(F\), Faraday’s constant (96485 C mol\(^{-1}\)), \(l\), the length of the microwire (m), \(D\), the diffusion coefficient (m\(^2\) s\(^{-1}\)), \(c\), the bulk concentration (mol dm\(^{-3}\)), \(t\), time (s) and \(r\), the radius of the microwire (m).

At short time transients, the diffusion of the species is high over a short distance from the electrode surface. Whereas at longer time transients, the concentration gradient extends over a large range and diffusion now becomes dependant on time\(^{[1]}\). As such, no steady-state current is attained in comparison to using rotating discs and microdisc electrodes\(^{[41]}\), but a quasi-steady state current is reached where convection of the redox species dominates, and hence any external movement acting on the electrochemical cell will disturb the transport of species towards to the electrode surface.

The current at a microcylinder electrode in chronoamperometric measurements can be approximated such that theoretical results are within a 1.3 % error to the experimental data\(^{[41]}\) (which is adequate considering use of the Shoup and Szabo\(^{[36]}\) approximation is within a 0.5 % error for a microdisc electrode).

There is the ability to approximate the currents for a range of diffusion coefficient values and time scales. The diffusion coefficient obtained from electrochemical measurements and digital simulations can be used to calculate the activity coefficient of a chemical species in varying ionic strengths. In order to link the activity coefficient to the rate of diffusion and the current response in chronoamperometry, it is necessary to express the flux of the species \((f)\) in terms of the thermodynamic
driving force for diffusion and the chemical potential of the species (equation 2.58).}

\( f = -\frac{Dc}{RT} \frac{d\mu}{dx} \) \[2.58\]

Here, \( f \) is the flux of species (mol m\(^{-2}\) s\(^{-1}\)), \( D \) is the diffusion coefficient (m\(^2\) s\(^{-1}\)), \( c \) is the concentration (mol dm\(^{-3}\)), \( R \) is the molar gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), \( x \) is the distance from the electrode surface (m), and \( T \) is the absolute temperature (K).

The chemical potential, \( \mu \), is defined as (equation 2.59)

\[ \mu_i = \mu_i^0 + RT \ln a_i \] \[2.59\]

Here, \( \mu_i \), is the chemical potential of \( i \) species in solution, \( \mu_i^0 \) is the standard chemical potential of \( i \) species and \( a_i \) is the activity of \( i \) species in solution.

It therefore is possible to derive an expression for the change in chemical potential with respect to distance, \( x \) (equation 2.60).

\[ \frac{d\mu}{dx} = RT \frac{d \ln a}{dx} \] \[2.60\]

Since the activity can be expressed in terms of concentration and activity coefficient (see Chapter 1, equation 1.8), the following relationship can be derived (equation 2.61).

\[ \ln a = \ln c + \ln \gamma_z \] \[2.61\]

The rate of change of activity with respect to concentration can be expressed (equation 2.62).

\[ \frac{d \ln a}{d \ln c} = 1 + \frac{d \ln \gamma_z}{d \ln c} \] \[2.62\]

From this, the flux (combined with equations 2.62 and 2.64) can be expressed in terms of the concentration and the activity coefficient with the diffusion coefficient, \( D \) (equation 2.63).
\[ f = -Dc \frac{d \ln c}{dx} \left( 1 + \frac{d \ln \gamma_\pm}{d \ln c} \right) = -D \frac{dc}{dx} \left( 1 + \frac{d \ln \gamma_\pm}{d \ln c} \right) \] 

[2.63]

If we compared equation 2.63 with Fick’s first law (equation 2.1), it can be shown that the diffusion coefficient can be expressed in terms of the ideal diffusion coefficient, multiplied with a “thermodynamic factor” to take into account non-ideality, relating the diffusion coefficient to the concentration and activity coefficient (equation 2.64).

\[ D = D^0 \left( 1 + \frac{d \ln \gamma_\pm}{d \ln c} \right) \] 

[2.64]

Here, \( D^0 \) is the ideal diffusion coefficient. It should be noted that equation 2.64 is a generalised expression and as such does not take into account additional interactions within ionic electrolyte systems. However, it does provide a link between transient-current measurements (chronoamperometry), diffusion coefficients and the determination of activity coefficients, which can allow the pH to be estimated in a range of ionic strengths.
2.5 – References


Chapter 3

Microwire Chronoamperometric Determination of Concentration, Diffusivity, and Salinity for Simultaneous Oxygen and Proton Reduction

Chapter Abstract

The ease of fabricating a microwire electrode using commercial laminating foil makes it cost efficient with a variety of geometric designs available at hand. In this chapter, a simple microwire electrode design was used to develop a multi-parameter chronoamperometric method employing a 25 µm diameter and 3 cm long commercial platinum microwire.

Concentration and diffusion coefficients for the reduction of oxygen and for proton reduction in increasing saline electrolyte media ranging from 0.1 M NaCl to 4 M NaCl were obtained simultaneously. The chronoamperometric data was fitted to simulated data using the commercial simulation software package DigiElch, allowing optimisation of both the concentration and diffusion coefficients of oxygen and protons.

Optimised oxygen diffusion coefficients and concentration data allowed salinity levels to be determined without interference from viscosity effects at higher saline content, in contrast to using other conventional hydrodynamic methods.

Chapter Publications

This chapter has been published in;

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3 – Microwire Chronoamperometric Determination of Concentration, Diffusivity, and Salinity for Simultaneous Oxygen and Proton Reduction

3.1 – Digital Simulation and Diffusion Coefficients

The detection of foodborne pathogens[1] and the electroanalytical detection of drugs[2] have been achieved through the use of microcylindrical electrodes[3][4][5], commonly referred to as microwire electrodes. These electrodes have found uses in various applications from hydrogen peroxide and glucose determination[6], to trace metal ions or sulphide in seawater[7][8][9]. Fast temperature pulse (or “hot-wire”) voltammetry in analytical applications[10] have been used widely by Gründler and coworkers[11] using microwire electrodes. With the simplicity of fabricating such electrodes, modelling data from electrochemical measurements give microwire electrodes an advantage over more conventional electrode geometries[12].

Analysis of chronoamperometric data using microwire electrodes have been developed[13] extensively during recent years, allowing quantitative data from potential step transients to be obtained.

Planar diffusion in the early time period dominates, giving rise to a current which follows the Cottrell equation[14] (equation 3.1).

\[ I(t) = nF\sqrt{Dc} \times \frac{1}{\sqrt{\pi t}} \quad [3.1] \]

Here the current \( I \) is given by \( n \), the number of electrons transferred per molecule diffusing to the electrode surface, \( F \), the Faraday constant (96485 C mol\(^{-1}\)), \( A=2\pi rl \), the electrode area with \( r \) radius and \( l \) length, \( D \), the diffusion coefficient, \( c \), the bulk concentration and \( t \), the time.

However, at longer time periods, quasi-state cylindrical diffusion arises from additional current relating to the curvature of the diffusion field around the microwire, and so the current-time response for this regime at longer time periods can be calculated using the following analytical expression[15] (equation 3.2).
\[ I(t) = nFIDc \left( \frac{2 \pi \frac{Dc}{16r^2}}{\sqrt{4 \pi \frac{Dr}{16r^2}} \ln \left( \sqrt{64e^{-0.5772\frac{Dc}{16r^2} + e^{\frac{3}{2}}}} \right) \right) \] 

For short and long time periods, equations 3.1 and 3.2 provide relatively good approximations, although at intermediate timescales numerical methods, such as the commercial simulation package DigiElch\cite{16}\cite{17}, are more ideally suited for cases involving complex simultaneous redox processes through integrating the diffusion equation under a user-defined set of boundary conditions and allowing the current transients over a range of times to be computed numerically. A single variable is iterated by the program whilst simultaneously outputting the calculated standard deviation using the input data. From this, experimental parameters such as electrode length, concentration, diffusion coefficients etc., can be optimised manually without the need to use multi-parameter non-linear fitting.

The highlighted benefits of the microwire geometry can be shown using numerical simulation of chronoamperometric data and compared to conventional microdisc electrodes (Fig. 3.1) using transient data for microdisc (A) and microwire (B) electrodes generated by the DigiElch package. Each electrode is of identical diameter (25 \( \mu \)m) using a value of 10\(^{-9}\) m\(^2\)s\(^{-1}\) for \(D\). An initial rapid decay is shown in the simulated curves, immediately followed by a moderate decay that is consistent with the transition from planar diffusion (following the equation by Bard et al.\cite{18}) towards a (quasi) steady state regime, where the transient behaviour of both the microdisc\cite{19} and microwire\cite{18} is observed (see line (i)). When the diffusion layer thickness (\(\delta\)) equals approximately the radius of the electrode (12.5\(\mu\)m), a change in the diffusion regime occurs which is related to the transition time, \(\tau = \frac{\delta^2}{D} = 156\) ms.
Figure 3.1. Chronoamperometric current for (A) a 25 μm diameter disk and (B) a 25 μm diameter microwire simulated using DigiElch 4.F, with (i) the current trace, (ii) the Cottrell only current trace (assuming a planar electrode of the same area), and (iii) the percentage of “Cottrellness” (= 100 × \( I_{\text{Cottrell}} / I_{\text{Total}} \)) when going from planar transient towards steady state current with a transition point \( \tau \).

Due to the switch in the diffusion regime from planar diffusion to quasi-state cylindrical diffusion, it is possible to simultaneously determine both the concentration
and diffusion coefficient values mathematically. Given that the contribution of data regarding information within the transient from the planar diffusion in the early time period and from the quasi-steady state diffusion in the later time period is very little, determining $c$ and $D$ simultaneously can only be achieved through the analysis of the intermediate transient region\(^\text{[20][21]}\).

At a given time, the amount of useful information within the transient can be evaluated by seeing how the current compares to the hypothetical situation in which no transition to quasi-steady state diffusion occurs, which is defined as the “Cottrell only” response (Fig. 3.1, line (ii)). The Cottrell only current is also plotted (Fig. 3.1, line (iii)) as a fraction of the total current, referred to as the level of “Cottrellness” ($= 100 \times I_{\text{Cottrell}}/I_{\text{Total}}$), which in the case of the microwire electrode is considerably higher compared to the microdisc electrode during the transient period. From this, it is clear that more information is contained within the transient over a longer time period when using a microwire electrode, and is advantageous in simultaneously evaluating values of $c$ and $D$, as well as other electrochemical parameters.

When performing electrochemical measurements in concentrated salt media, obtaining reliable data is difficult since the heterogeneous kinetics\(^\text{[22]}\) and mobility of ions\(^\text{[23][24]}\) and electrode performance is affected by the salt. Solubility effects, such as the “salting out” of dissolved oxygen (i.e. a decrease in the dissolved oxygen concentration in saline solutions) become more apparent with increasing saline concentration\(^\text{[25]}\). Within the industry sector and in offshore applications, monitoring systems for multi-key parameters such as oxygen concentration, proton concentration are necessary for use in salt and brine solutions.

The challenge of simultaneously determining $c$ and $D$ values in high saline solutions using electrochemical measurements is reported in this chapter. The use of microwire electrodes and chronoamperometry measurements to determine both the concentration and diffusion coefficient data of protons and oxygen in increasing acidified saline (NaCl) media is demonstrated. Use of single-parameter fitting of simulations to experimental chronoamperometric data is achieved using the commercial software programme DigiElch to simultaneously determine the concentration and diffusion coefficient parameters. Information regarding the salinity of the solution can be
extracted and approximated from the obtained oxygen concentration and diffusivity data.

### 3.2 – Experimental

#### 3.2.1 – Chemical Reagents

Sodium chloride (NaCl, > 99.5 %), hydrochloric acid (HCl, stabilised at a concentration of 1 M) and potassium chloride (KCl, > 99 %) were purchased from Sigma Aldrich UK. Potassium ferrocyanide (K₄Fe(CN)₆, > 99 %) was purchased from Fisher Scientific and used as received. Solutions of NaCl/HCl ranging from 0.1 M to 4.0 M and containing different concentrations of HCl were prepared using purified water with a resistivity of not less than 18 MΩ at 22 °C (Millipore). Nitrogen gas (N₂) was purchased from BOC UK.

#### 3.2.2 – Instrumentation

Electrochemical experiments were carried out in a thermo-jacketed electrochemical cell connected to a water bath (Haake) maintained at 25 ± 0.5 °C. Electrochemical measurements were performed using a microAutolab III potentiostat system (Eco Chemie, Netherlands). A standard three-electrode set-up was used using a Pt wire counter electrode, a KCl-saturated calomel reference (SCE) electrode, and a 25 μm diameter Pt microwire as the working electrode (Fig 3.2). Digital simulation and data fitting was performed using the commercial software DigiElch 4.F selecting the semi-infinite one-dimensional model with cylindrical geometry on a PC running Windows 7 32-Bit with an Intel Core i3 2.53 GHz processor and 4 GB RAM.

#### 3.2.3 – Procedure for Microwire Electrode Fabrication

A 25 μm diameter Pt wire (Advent UK) was laminated using commercial laminating plastic foil following a literature procedure[26]. A rectangle of approximately 18 cm × 2 cm was cut out, with a window of approximately 3 cm × 1 cm, where after thermal
lamination (with a domestic iron) the platinum wire is exposed to the aqueous solution (Fig. 3.2). A piece of conducting copper tape (3M) was used to ensure electrical contact, with the use of silver conducting paint to enhance the electrical contact. The wire diameter needs to be confirmed by optical microscopy.

Figure. 3.2. (A) Schematic diagram of the fabrication process of the Pt microwire electrode of diameter of 25 µm. (B) Diagram of the cylindrical diffusion field around the microwire.

3.2.4 – Procedure for Calibrating the Microwire Length using Chronoamperometry

The length of the microwire electrode was calibrated using chronoamperometry for the one-electron oxidation of 2 mM potassium ferrocyanide in 0.1 M KCl. Cyclic voltammetry was initially performed in order to determine the suitable potential steps for chronoamperometry (Fig. 3.3A). Chronoamperograms were then recorded using potential steps from -0.1 V to +0.60 V vs. SCE and measuring the current for 1 s with a sampling time of 2.5 ms (Fig. 3.3(B)). The first 5 ms of the transient data were discarded to avoid double-layer charging effects for the numerical data fitting analysis.
Figure 3.3. (A) Cyclic voltammogram (at a scan rate of 20 mV s\(^{-1}\)) for the oxidation of 2 mM potassium ferrocyanide in aqueous 0.1 M KCl at a 25 \(\mu\)m diameter Pt microwire electrode. (B) Chronoamperometric response (black line) and simulation (red line) for the oxidation of 2 mM ferrocyanide. Insert: the standard deviation for data fitting of the simulation to experimental data as a function of the microwire length, which is calibrated to 3.08 cm.

Through using the commercial DigiElch 4.F\(^{[17][18]}\) digital simulation software (Gamry Instruments) and knowing the known diffusion coefficient, of \(0.65 \times 10^{-9} \text{ m}^2 \text{s}^{-1}\) at 25 \(^\circ\text{C}\)\(^{[27]}\) and the known concentration of 2 mM ferrocyanide used for calibration, the length of the microwire was calibrated by varying the electrode length parameter and plotting the standard deviation (Fig. 3.3B inset) within the data fitting. The point at
when a minimum was observed was the optimised length of the microwire, here 3.08 cm. The calibrated microwire length was then used in further measurements and triplicate measurements were conducted to calculate the standard error, based on the standard deviation.

3.2.5 – Procedure for Determining the Concentration and Diffusion Coefficient of Protons and Oxygen

From the cyclic voltammograms, appropriate potential steps were selected for chronoamperometric measurements. The data fitting of the experimental data to simulations was performed using DigiElch, where the concentration parameter was manually varied. The standard deviation of the fit was plotted, producing a parabolic curve giving the optimised concentration and diffusion coefficient.

3.3 – Results and Discussion

3.3.1 – Proton Reduction in High Ionic Strength Saline Media

Cyclic voltammetry for the reduction of 2 mM protons (Fig. 3.4(A)) (equation 3.3) in 2.0 M NaCl was carried out using a 25 μm diameter platinum microwire electrode. At -0.42 V vs. SCE, the reversible potential is observed, with water reduction occurring at -1.0 V vs. SCE.

$$2H^+ + 2e^- \rightarrow H_2$$  \[3.3\]

The proton concentration and diffusion coefficient was simultaneously obtained from chronoamperometric measurements where the potential was stepped from 0.0 V (where no electron transfer occurs) to -0.6 V vs. SCE (where electron transfer occurs) (Fig. 3.4B). The diffusion coefficient parameter was iterated and optimised by DigiElch as the proton concentration was manually varied between 1 mM and 3 mM. The standard deviation of the fit between the simulation and experimental data was plotted with each manual adjustment of the proton concentration, resulting in a parabolic standard deviation plot (Fig. 3.4(B) insert) where a minimum provided the “true” proton concentration and its corresponding optimised diffusion coefficient.
This methodology was used to obtain the proton concentrations and diffusion coefficients in increasing saline media with nominal proton concentrations of either 0.5 mM or 2 mM.

Using a nominal proton concentration of either 2.0 mM or 0.5 mM, the concentrations and diffusion coefficients of protons were determined in increasing saline media, with the optimised parameters being within ±5% of the nominal values (Fig. 3.4(C)). The diffusion coefficients measured in 0.1 M NaCl (8.1 ± 0.9 × 10⁻⁹ m²s⁻¹ for 2 mM HCl and 7.8 ± 0.9 × 10⁻⁹ m²s⁻¹ for 0.5 mM HCl) were found to be in excellent agreement with the previous literature value of $D_{H^+} = 7.8 \times 10^{-9}$ m²s⁻¹, measured for a solution of 0.1 M KNO₃^{[28]}.

With increasing saline concentration, the proton diffusion coefficients were observed to decrease significantly. At 4.0 M NaCl, the diffusion coefficient was found to be approximately half the value of the diffusion coefficient in 0.1 M NaCl, which is attributed to the parallel change in solution viscosity.
Figure 3.4. (A) Cyclic voltammogram (at a scan rate of 50 mV s\(^{-1}\)) for the reduction of 2 mM protons in deaerated aqueous 2.0 M NaCl at a 25 \(\mu\)m diameter Pt microwire electrode. (B) Chronoamperometric data (potential step from 0.0 to -0.6 V vs. SCE) shown as line and the corresponding digital simulation data shown as dots. Insert: The standard deviation plot for concentration optimisation. (C) Plot of the proton diffusion coefficients for 0.5 mM and for 2.0 mM protons versus square root of NaCl concentration. Standard errors are calculated from triplicate measurements.
3.3.2 – Oxygen Reduction in High Ionic Strength Saline Media

Oxygen reduction on platinum occurs via a four-electron process (equation 3.4).

\[ O_2(aq) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(aq) \]  \hspace{1cm} [3.4]

The potential at which oxygen reduction occurs is more positive in comparison to the reduction of protons\[^{[29]}\]. The cyclic voltammogram of oxygen reduction (Fig. 3.5(A)), at ambient atmospheric pressure in 4.0 M NaCl containing 3 mM protons, shows a drawn-out shape which is indicative of slow, irreversible electron transfer kinetics\[^{[30]}\].

To ensure a complete reduction of oxygen to water and to avoid any complications with kinetics due to proton transport, a proton concentration of 3 mM was used. Potential steps from 0.4 V to -0.2 V vs. SCE were used in chronoamperometric measurements (Fig. 3.5(B)) and the single parameter standard deviation method mentioned above was used in the data analysis (Fig. 3.5(B) insert) to obtain the diffusion coefficients and equilibrium oxygen data (Fig. 3.5(C)).

With increasing NaCl concentration, the dissolved oxygen concentration varies from the salting out effect and although the results obtained for the equilibrium oxygen concentration are slightly lower than values reported for seawater\[^{[31]}\], the results are in good agreement with literature values that were measured in KOH for example\[^{[32]}\]. Since the optimised diffusion coefficient data for oxygen are slightly higher than values reported in literature (pure water \(D_{O2} = 2 \times 10^{-9} \text{ m}^2 \text{s}^{-1} \) at 25 °C\[^{[33]}\]), this is suggestive of systematic error occurring within the data analysis. The overall trend observed in the diffusion coefficient data for oxygen is similar in comparison to the observed trend of the proton diffusion coefficient data, highlighting that the results confirm with Walden’s law\[^{[34]}\] and are consistent with viscosity affects.

The calculated error bars, from triplicate measurements, are large and this is most likely due to the changes in the platinum surface condition which then alter the oxygen kinetics; it should be noted that such affects are assumed to be absent in the transient data when being analysed.
Figure 3.5. (A) Cyclic voltammogram (at a scan rate of 50 mV s$^{-1}$) for the reduction of ambient oxygen at a 25 μm diameter Pt microwire electrode in the presence of 3 mM protons in aqueous 4.0 M NaCl. (B) Chronoamperometry (potential step from +0.4 to -0.2 V vs. SCE). Insert: The standard deviation optimisation to give the oxygen concentration. (C) Plot of the oxygen diffusion coefficient and a plot of the oxygen concentration as a function of square root of aqueous NaCl concentration. Standard errors are calculated from triplicate measurements.
3.3.3 – Simultaneous Proton, Oxygen and Salinity Determination

As established above, the redox potentials for proton reduction and oxygen reduction occur at different potentials, with their corresponding diffusion coefficients being dependent upon the saline concentration. From this, a simultaneous multi-parameter methodology was employed in electroanalysis issues.

Demonstration of the multi-parameter methodology and its adaptability was achieved in a solution of 1.0 M NaCl containing approximately 3 mM protons. Two defined regions are observed in the cyclic voltammogram (Fig. 3.6(A)), corresponding to first, the reduction of oxygen occurring at +0.1 V vs. SCE and then secondly, the reduction of protons at -0.4 V vs. SCE. In order to obtain the concentration and diffusion coefficient parameter of both redox species, a single double-step chronoamperogram was performed. The reduction of oxygen was the first step, stepping from +0.75 V to -0.25 V vs. SCE, then from -0.25 V to -0.90 V vs. SCE was the next potential step to reduce protons.

The optimised oxygen diffusion coefficient of \( D_{O_2} = 2.2 \times 10^{-9} \text{ m}^2\text{ s}^{-1} \) and a dissolved oxygen concentration of 0.124 mM was obtained from the data fitting process of the chronoamperogram (Fig. 3.6(B)) in a solution of 1 M NaCl; these values are in good agreement with previous data obtained (Fig. 3.5).

Following this, data fitting for the proton diffusion coefficient was first performed, and ignoring the simultaneous oxygen reduction, a value of \( D_{H^+} = 7.25 \times 10^{-9} \text{ m}^2\text{ s}^{-1} \) and a concentration of 2.49 mM was acquired. This value for the proton concentration, however, does not take into account that protons are consumed from the oxygen reduction occurring at the same time. For every mole of oxygen, four protons are consumed, thus approximately \( 4 \times 0.124 \text{ mM} = 0.5 \text{ mM} \) protons are unaccounted for from the measurement, meaning the calculated proton concentration is then corrected to 2.99 mM, which is in excellent agreement with the nominal proton concentration in the solution of 3 mM.

If the oxygen concentration and diffusion coefficient is known, then it is possible to incorporate the proton reduction with the oxygen reduction happening at the same time, into one full single simulation assuming the consumption of protons during the oxygen reduction is fast and the reduction of oxygen is a direct four-electron process.
Using this method, values for proton concentration value of \( c_{H^+} = 3.0 \) mM and diffusion coefficient of \( D_{H^+} = 7.27 \times 10^{-9} \) m\(^2\) s\(^{-1}\) (Fig. 3.6(D)) are generated, in excellent agreement with result above.

**Figure 3.6.** (A) Cyclic voltammogram (scan rate of 50 mV s\(^{-1}\)) for the reduction of ambient oxygen at a 25 \( \mu \)m diameter Pt microwire electrode in the presence of 3 mM protons in aqueous 1.0 M NaCl. (B) Data for minimisation of error for chronoamperometry (potential step from 0.75 to -0.25 V vs. SCE) to give the oxygen concentration 0.12 mM. (C) Data for minimisation of error for chronoamperometry (potential step from -0.25 to -0.90 V vs. SCE) to give the proton concentration 2.5 mM. (D) As in C but with oxygen reduction accounted for to give a proton concentration of 3.0 mM (see text).

Accounting for the loss of protons and the parallel processes of oxygen reduction, digital simulation has allowed the simultaneous determination of proton concentration, proton diffusion coefficient, oxygen concentration, oxygen diffusion coefficient and salinity to be achieved via a numerical fitting analysis coupled with a double-step chronoamperogram, as shown above. Results achieved using this methodology are in good agreement with each other and with the literature values reported. This methodology could be used directly *in situ* in a solution of unknown salinity, where the oxygen and proton concentrations need to be determined. The use of a calibrated electrode is important in order to obtain consistent results, while the
use of an automated data fitting system would enable faster deployment in the industry sector.

3.4 – Summary and Conclusion

A multi-parameter methodology has been developed which employs the use of a microwire electrode, to determine the concentration and diffusion coefficients from transient data in saline media, which when coupled with a numerical digital simulation package, DigiElch, provides a powerful electroanalytical tool.

Use of the microwire electrode avoids effects relating to viscosity at high saline content, as well as being insensitive to mounting imperfections commonly associated with microdisc electrodes, where cracks between the platinum and glass sheath allow ions to penetrate and cause capacitance charging within the transient data.

The information obtained from using the methodology discussed in this chapter allows the concentration of protons and the concentration of oxygen to be determined in solutions containing high NaCl content, through performing a double-step chronoamperogram.

The salinity of a solution can be estimated using data corresponding to the concentration and diffusion coefficient for oxygen, however, the experimental precision for this needs improvement. Extraction of kinetic rate data and co-reactant information could be achieved in the future, with the analytical process being developed for online monitoring systems in remote locations.
3.5 – References

Chapter 4

Oxygen Reduction at Platinum Microwire Electrodes in High Saline Media: Effects of Oxygen Concentration versus Oxygen Activity

Chapter Abstract

Platinum microwire electrodes, with a diameter of 25 µm, were fabricated to investigate the reduction of oxygen in increasing saline media due to their ability of achieving quasi-steady state limiting currents. In this chapter, electrokinetic data such as Tafel gradients, transfer coefficients and standard heterogeneous rate constants were calculated from experimental data in increasing chloride concentration. Tafel analysis showed little difference as the chloride concentration increased from 0.1 M to 4 M NaCl and showed that the first electron transfer was the rate determining step. Calculated standard heterogeneous rate constants were found to remain constant and would suggest that the concentration of oxygen is the important factor, rather than the oxygen activity in solution.

The effect of elevated oxygen pressure on the oxygen reduction reaction is also investigated in this chapter, oxygen concentration and diffusivity data were simultaneously determined using chronoamperometric data at 2 and 4 bar oxygen pressure which was fitted to simulated data using the commercial simulation software package, DigiElch. Tafel analysis was also carried out and showed little difference compared to the Tafel data at ambient pressure. The calculated standard heterogeneous rate constants at elevated pressure were found to vary in contrast to data at ambient pressure and were a likely result of slow equilibration within the pressure cell before running the electrochemical measurements. However, the pressure cell and the data collected at elevated pressures are a proof-of-principle experiment.

Special thanks go to Paul Frith in Mechanical Engineering for designing and manufacturing the pressure cell used in this chapter.

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4 – Oxygen Reduction at Platinum Microwire Electrodes in High Saline Media: Effects of Oxygen Concentration versus Oxygen Activity

4.1 – Oxygen Reduction on Platinum

Oxygen reduction is one of the most important redox processes occurring in corrosion, in fuel cells, and in sensors. Oxygen reduction kinetics are complex and catalyst dependant, with platinum being the most effective catalyst material. In the presence of salt (saline media) oxygen reduction can be suppressed and it is interesting to ask whether oxygen reduction kinetics are affected by the oxygen activity (as a function of salt concentration) or by the actual oxygen concentration.

The overall electrokinetics of reducing oxygen are slow on most materials resulting in considerable overpotentials, with a standard potential of +1.23 V vs. SHE, at pH 0, required to reduce oxygen\(^1\). Platinum is currently the most widely used material that can catalyse the reduction of oxygen under extreme corrosive conditions\(^2\), which makes it attractive for use in Proton Exchange Membrane Fuel Cells (PEMFCs)\(^3\)\(^4\)\(^5\)\(^6\). Underlying the catalyst performance of platinum is the ability to adsorb oxygen for reduction and release of the products without binding too strongly/too weakly to the surface\(^1\)\(^2\).

While there are many intermediate steps that occur on the platinum surface in order for oxygen to be reduced to its products\(^1\)\(^2\)\(^7\)\(^8\)\(^9\), the simplest scheme that describes the reduction of oxygen via two pathways is that suggested by Wroblowa et al.\(^10\), described below\(^11\) (Scheme 4.1).
Scheme. 4.1. Proposed reaction pathways by Wroblowa\textsuperscript{[10]} for the reduction of oxygen, leading to the formation of either hydrogen peroxide (2 electron route) or to water (4 electron route).

Of the two reaction routes, one is a direct four electron reduction whereby oxygen is directly reduced to form water (equation 4.1).

\[
O_2 + 4 e^- + 4 H^+ \rightarrow 2 H_2O \tag{4.1}
\]

The second route is a two electron reduction where hydrogen peroxide is formed first (equation 4.2).

\[
O_2 + 2 e^- + 2 H^+ \rightarrow H_2O_2 \tag{4.2}
\]

The hydrogen peroxide formed can then either be further reduced to give water (equation 4.3), desorb from the electrode surface into the bulk solution or be oxidised back to oxygen.

\[
H_2O_2 + 2 e^- + 2 H^+ \rightarrow 2 H_2O \tag{4.3}
\]

However, in order to reduce oxygen, sites on the platinum surface must be available for oxygen to adsorb on. Anions such as chloride\textsuperscript{[12]}, (bi)sulphate\textsuperscript{[13]} and perchloric ions\textsuperscript{[14]} have been shown to preferentially adsorb onto specific platinum planes and thereby block the reduction of oxygen taking place\textsuperscript{[15]}. 

---

\[O_2 \rightarrow O_{2,ad} \xrightleftharpoons[k_2]{k_1} \xrightarrow[k_3]{k_4} H_2O_{2,ad} \rightarrow H_2O \]

\[H_2O_2 \xrightleftharpoons[k_5]{k_4} \]

\[H_2O \]

\[H_2O_{2,ad} \]
In media containing perchloric anions, Markovic et al.\cite{16} found that platinum facets with an orientation of (100) had a lower activity towards reducing oxygen due to the adsorption of perchloric anions, compared to the (110) orientations. Similarly, Feliu et al.\cite{17} found that the adsorption of bi(sulphate) anions on platinum formed an adsorbed layer on platinum facets with the (111) orientations, and as such had a lower activity towards oxygen reduction, whilst the (100) orientation had a higher activity towards reducing oxygen.

However, the adsorption of hydrogen on platinum (111) was reported to cause the reduction of oxygen to occur \textit{via} the two electron route to produce hydrogen peroxide instead. The cause for the change in electron routes was due to the orientation of the diatomic oxygen, switching from adsorbing side-on to adsorbing end-on at the platinum surface\cite{18}. The observation of spectator ions altering pathway reactions was also reported by Kastounaros \textit{et al.}\cite{19}. It was found that at low surface coverages, oxygen reduced to hydrogen peroxide remained adsorbed on the electrode surface and continued to be reduced to water. But at high surface coverages, the hydrogen peroxide desorbed into solution without undergoing further reduction.

In this chapter, the electrokinetics of oxygen reduction are investigated in increasing saline media ranging from 0.1 M to 4 M NaCl at pH 2 using a platinum microwire electrode to achieve quasi-steady state currents similar to those observed with hydrodynamic techniques (with enhanced mass transport). High pressure electrochemical measurements, coupled with digital simulations were performed to simultaneously determine the concentration of oxygen at increasing pressures in a sodium chloride solution of similar concentration to seawater. The effect of oxygen concentration is contrasted to the effect of oxygen activity and the former is shown to be more relevant.

### 4.2 – Experimental

#### 4.2.1 – Chemical Reagents

Sodium chloride (NaCl, > 99.5 %), hydrochloric acid (HCl, stabilised at a concentration of 1 M) and sulphuric acid (H₂SO₄, 95-98 %) were purchased from
Sigma Aldrich UK and were used without further purification. Commercial platinum wire of 25 µm diameter was purchased from Advent Materials UK. Solutions of NaCl ranging from 0.1 M to 4 M were prepared using purified water with a resistivity of not less than 18 MΩ at 22 °C (Millipore) and were adjusted to pH 2 using HCl. Nitrogen gas (N₂) and oxygen gas (O₂) were purchased from BOC UK.

4.2.2 – Instrumentation

Electrochemical measurements were carried out in a thermo-jacketed electrochemical cell connected to a water bath (Haake) maintained at 25 ± 0.5 °C. Electrochemical measurements were performed using a microAutolab III potentiostat system (Eco Chemie, Netherlands). A standard three-electrode set-up was used using a platinum wire counter electrode, a KCl-saturated calomel reference (SCE) electrode and a 25 µm diameter platinum microwire of 3.08 cm length as the working electrode, prepared as reported previously[20].

4.2.3 – Procedure for Oxygen Reduction Measurements

Electrochemical cleaning of the platinum microwire electrode was achieved by potential cycling at a scan rate of 0.5 V s⁻¹ from -0.3 V to +1.3 V vs. SCE for 35 cycles in aqueous 0.5 M H₂SO₄ under a N₂ atmosphere. After electrochemical cleaning, the microwire electrode was rinsed with deionised water before use. The reduction of oxygen was performed in saline media where the electrochemical cell was open to the ambient air atmosphere for approximately ten minutes before potential cycling at a scan rate of 2 mV s⁻¹ was performed. Measurements were repeated three times for the calculation of statistical errors.

4.2.4 – Procedure for Determining the Concentration and Diffusion Coefficient of Oxygen at Ambient/High Pressures in Saline Media

A smaller platinum microwire was fabricated in order to fit into the pressure chamber. Chronoamperometry was employed in conjunction with digital simulation and fitting
as previously reported\textsuperscript{[20]} (see Chapter 3) to calibrate the length of the platinum microwire electrode to 1.05 cm and was used in digital simulations. Chronoamperometric data obtained at elevated pressures, coupled with digital simulations, were used to simultaneously determine the concentration and diffusion coefficients of oxygen at increasing pressures simultaneously in a solution of 0.5 M NaCl containing 10 mM protons. A pressure cell constructed out of stainless steel was specifically designed for electrochemical measurements to be performed up to pressures of 6 bars (Fig. 4.1).

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure4_1.png}
\caption{Pressure cell used for investigating the reduction of oxygen at elevated pressures. (A) Chamber. (B) Oxygen gas inlet. (C) Electrical connections. (D) Pressure gauge. (E) Oxygen gas outlet. (F) Gas safety value.}
\end{figure}
All metal connections were covered in parafilm to prevent electrical contact to the inside of the pressure cell and to prevent short circuiting of the electrochemical cell. The cell was then closed and secured before pressurising with O₂ gas which was left 5 min to equilibrate (Note: a much longer equilibration time would have been preferable as can be concluded from the data). Cyclic voltammograms were recorded for the reduction of oxygen at each pressure, which then provided the basis for the potential steps for chronoamperometric measurements to be selected.

4.3 – Results and Discussion

4.3.1 – Reduction of Oxygen in High Ionic Strength Saline Media

In chloride containing media, oxygen can be reduced by four electrons to produce water on platinum surfaces only at high overpotentials, with the first electron transfer being the rate determining step (equation 4.4)[21].

\[
O_2 + 4 e^- + 4 H^+ \rightarrow 2 H_2O \tag{4.4}
\]

The reduction of oxygen at pH 0 occurs at a standard potential of +1.23 V vs. SHE, or +0.99 V vs. SCE. At low ionic strength, in the presence of 10 mM proton concentration the pH is approximately 2.0. However, the pH varies at 4 M NaCl and the data reported by Jiang[22] can be calculated using equation 4.5.

\[
\log \gamma_{H^+} = \log \gamma_{H^+}^0 - \alpha_{AB} I_B \tag{4.5}
\]

Here, \( \log \gamma_{H^+} \), the activity coefficient of protons is given by, \( \log \gamma_{H^+}^0 \), the ideal mean activity coefficient of protons at 4 M NaCl (equal to 0.24267), \( \alpha_{AB} \), the Harned interaction coefficient for 4 M NaCl (equal to 0.02997) and \( I_b \), the ionic strength at 4 M NaCl (equal to 4) (see equation 4.6 for calculation).

\[
\log \gamma_{H^+} = 0.24267 - (0.02997 \times 4) = 0.12279 \tag{4.6}
\]

The pH at 4 M NaCl is then calculated using the value of \( \log \gamma_{H^+} \) obtained from equation 4.6, with \( c_{H^+} = 10 \text{ mM} \) (equation 4.7).

\[
pH = -\log(c_{H^+} \gamma_{H^+}) \tag{4.7}
\]
A pH of 1.88 at 4 M NaCl is obtained and therefore, the saline solutions used in this study are typically consistent with pH 2 (within the error of pH probes at high salt concentrations). The standard electrode potential for the reduction of oxygen is shifted towards more negative potentials at low pH, and equation 4.8 can be used to determine the standard electrode potential at pH 2 as +0.872 V vs. SCE.

\[ E_{\text{pH}}^0 = (E^0 - r_p) - (\text{pH} \times 0.059) \]  

[4.8]

Here, \( E_{\text{pH}}^0 \) is the calculated standard electrode potential at a set pH, \( E^0 \) is the standard electrode potential at pH 0 and \( r_p \) is the reference electrode potential (in this case for a saturated calomel electrode it is +0.24 V).

The cyclic voltammograms of the reduction of oxygen in increasing saline media, at pH 2, are shown in Fig. 4.2. The quasi-steady state mass transport limited currents for oxygen reduction can be seen to decrease with increasing chloride concentration (Table 4.1). The overall shapes of the cyclic voltammograms at ambient atmospheric pressure in increasing concentrations of NaCl in the presence of 10 mM protons are drawn out, which is suggestive of slow electron transfer kinetics.

Furthermore, a significant hysteresis effect is observed when comparing forward potential scan and backward potential scan. This is due to a change on the platinum surface that occurs in the hydrogen underpotential deposition region (ca. -0.3 V vs. SCE). The forward scan was used in the analysis of electron transfer kinetic effects. Data from the backward scan have not been further analysed. Also, an excess concentration of 10 mM protons was used to ensure the complete reduction of oxygen to water as well as avoiding any complications from proton concentration polarisation and from related effects on the kinetics resulting from proton consumption at the electrode surface during oxygen reduction at high chloride concentrations.
Figure 4.2. Cyclic voltammograms at a scan rate of 2 mV s$^{-1}$ of the reduction of ambient oxygen at a 25 µm diameter platinum microwire of length 3.08 cm in (i) 0.1 M NaCl, (ii) 0.5 M NaCl, (iii) 2 M NaCl and (iv) 4 M NaCl, at pH 2.

The half-wave potentials, $E_{1/2}$ (evaluated at half the limiting current), are significantly lower than the standard electrode potential of +0.872 V vs. SCE (Table 4.1) and therefore a large overpotential is needed to reduce oxygen, even at low saline concentrations, due to the presence of chloride as reported previously$^{[23]}$. The additional peaks observed at ca. +1.0 V vs. SCE is most likely a result of additional contaminants in the NaCl, such as bromide.
Table 4.1. Values of the calculated dissolved oxygen concentration, the limiting current, \( I_{\text{lim}} \), the half-wave potential, \( E_{1/2} \), and the onset potential, \( E_{\text{onset}} \), in increasing saline concentrations for the reduction of oxygen at a 25 µm diameter platinum microwire electrode of length 3.08 cm, at 25 °C.

<table>
<thead>
<tr>
<th>[NaCl] / mol dm(^{-3})</th>
<th>Calculated ([O_2] / x 10^{-3}) mol dm(^{-3})</th>
<th>Limiting Current at -0.1 V vs. SCE ( I_{\text{lim}} / \mu A)</th>
<th>Half-wave Potential ( E_{1/2} / V) vs. SCE</th>
<th>Onset Potential ( E_{\text{onset}} / V) vs. SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.19</td>
<td>-8.80</td>
<td>0.213</td>
<td>0.328</td>
</tr>
<tr>
<td>0.5</td>
<td>0.17</td>
<td>-7.39</td>
<td>0.175</td>
<td>0.287</td>
</tr>
<tr>
<td>2.0</td>
<td>0.12</td>
<td>-4.37</td>
<td>0.180</td>
<td>0.276</td>
</tr>
<tr>
<td>4.0</td>
<td>0.073</td>
<td>-2.28</td>
<td>0.178</td>
<td>0.269</td>
</tr>
</tbody>
</table>

Dissolved oxygen concentration values were calculated using equation 4.9 and the limiting currents listed above with literature diffusion coefficients from literature values\(^{[20]}\).

\[
I_{\text{lim}} = nFAC\sqrt{D} \times \frac{1}{\sqrt{\pi}} \quad [4.9]
\]

Here, \( I_{\text{lim}} \) is the limiting current (A), \( n \) is the number of electrons, in this case 4, \( F \) is Faraday’s constant (96485 C mol\(^{-1}\)), \( A \) is the area of the microwire (0.024 cm\(^2\)), \( C \) is the oxygen concentration (mol cm\(^{-3}\)) and \( D \) is the diffusion coefficient (cm\(^2\) s\(^{-1}\)). The calculated oxygen concentrations values in Table 4.1 are in shown to be in good agreement with experimentally determined oxygen values reported previously\(^{[20]}\).

The onset potential for the reduction of oxygen was determined by taking the tangent of the background current, between a potential range of +0.45 V and +0.9 V vs. SCE, and the tangent of the forward sweep for the oxygen reduction. Where the intersection of these two tangents met, provided the onset potential at each chloride concentration\(^{[24]}\) (Table 4.1) (Fig. 4.3). The decrease in the limiting current observed is a result of the viscosity effects at high chloride concentration decreasing the diffusion of oxygen to the electrode surface\(^{[20]}\).
Taking the tangents of the background current and of the forward sweep current gives the $E_{onset}$ potential where the two tangents intersect. The cyclic-voltammogram is the reduction of oxygen in 0.1 M NaCl at pH 2 using a platinum microwire of 25 µm diameter and a length of 3.08 cm.

The platinum microwire used in this study is polycrystalline and as such contains a mixture of platinum (110), (111) and (100) orientations, as well as steps and imperfections. Chloride ions can adsorb on to all three orientations\cite{12, 23}, and it has been reported by Stamenkovic et al.\cite{25} that due to the chloride ions having a stronger interaction on platinum (100), the reduction of oxygen is inhibited the most. The platinum (100) sites are blocked preferentially due to the strong adsorption interaction with the chloride ions, and with increasing chloride concentration the remaining platinum sites are also blocked, but not as strongly compared to platinum (100). As a result, there is an associated time effect where a chloride ion desorbs from a platinum orientation to allow oxygen to adsorb and be reduced. But as the amount of platinum orientations decreases with increasing chloride concentration, a larger overpotential is required and causes the onset potential to decrease\cite{12} (Table 4.1). The rate of oxygen reduction is reduced even further in the presence of increasing chloride concentration, as shown in the exchange currents calculated from the Tafel plots.
The Tafel plots on the forward scan of the cyclic voltammograms were plotted for each saline concentration in order to determine the gradient of the Tafel plot as well as calculating the transfer coefficient, α (equation 4.10) (Fig. 4.4).

\[
m = -\frac{\alpha n F}{2.303RT}
\]

[4.10]

Here, \(m\) is the gradient of the Tafel slope (mV dec\(^{-1}\)), \(R\) is the molar gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), \(T\) is the absolute temperature (298 K), \(n\) is the number of electrons transferred and \(F\) is Faraday’s constant (96485 C mol\(^{-1}\)).

Figure. 4.6. Tafel Plots for the reduction of ambient oxygen in (i) 0.1 M NaCl, (ii) 0.5 M NaCl, (iii) 2 M NaCl and (iv) 4 M NaCl at a platinum microwire electrode of 25 µm diameter and length 3.08 cm.

Using the Tafel slope and the number of electrons transferred as 1\(^8\), the transfer coefficients were calculated for each chloride concentration (Table 4.2). It can be seen that all the transfer coefficients are in close agreement with the expected value of 0.5, which shows that the transition state at each chloride concentration retains a 50:50 combination of reactant and product character. The calculated Tafel slopes for each chloride concentration are also in close agreement with the expected value of 120 mV dec\(^{-1}\) for an irreversible one electron transfer and imply that the first electron transfer is the rate determining step for the reduction of oxygen in the presence of
chloride. The slight variations in the calculated Tafel slopes are most likely a result from curvature in the experimental data.

The exchange current, $I_o$, at each increase in chloride concentration is displaced by the concentration of dissolved oxygen in solution, which is a result from the “salting out” effect. At high salt concentrations, a large proportion of the ions in solution are solvated by the water molecules and this causes a change in the solvent-solute interaction for oxygen that then causes the concentration of dissolved oxygen in solution to decrease. Note that the activity of oxygen remains constant due to a constant gas pressure of ambient oxygen\[^{26}\].

The exchange current, $I_o$, gives an indication of the individual anode/cathode currents at zero overpotential when both the anodic and cathodic currents are balanced. The exchange current of the reduction of oxygen can be expressed in regards to the rate constant for electron transfer, $k_0$ (equation 4.11).

$$I_o = nFk_0[O_2]$$ \[4.11\]

Here, $n$ is the number of electrons transferred, $F$ is Faraday’s constant (96485 C mol\(^{-1}\)), $k_0$ is the standard heterogeneous rate constant for electron transfer (cm s\(^{-1}\)) and $[O_2]$ is the dissolved oxygen concentration (mol cm\(^{-3}\)).

**Table. 4.2.** Calculated Tafel slopes for each saline concentration at a 25 µm platinum microwire electrode of length 3.08 cm. Errors were calculated from three repeat measurements.

<table>
<thead>
<tr>
<th>[NaCl] / mol dm(^{-3})</th>
<th>Calculated Tafel Slope / mV dec(^{-1})</th>
<th>Calculated Transfer Coefficient, $n_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>112 ± 0.7</td>
<td>0.52 ± 0.015</td>
</tr>
<tr>
<td>0.5</td>
<td>114 ± 0.4</td>
<td>0.52 ± 0.018</td>
</tr>
<tr>
<td>2.0</td>
<td>114 ± 0.5</td>
<td>0.52 ± 0.012</td>
</tr>
<tr>
<td>4.0</td>
<td>118 ± 0.6</td>
<td>0.51 ± 0.019</td>
</tr>
</tbody>
</table>

The extrapolation of the exchange current is largely dependent on the gradient of the Tafel slope and so any change in the gradient of the Tafel slope is magnified when
extrapolating back. It is therefore assumed that when extrapolating to the exchange current, the standard electrode potential calculated for the reduction of oxygen at pH 2 remains constant at +0.871 V vs. SCE. The exchange current is directly proportional to the rate of electron transfer and so when looking at the exchange current, it is possible to understand the overall electrokinetics of the reduction of oxygen (Fig 4.7).

![Graph](image)

**Figure. 4.7.** Calculated exchange currents, $I_o$, at increasing chloride concentration for the reduction of oxygen at a platinum microwire electrode of 25 µm diameter and length 3.08 cm. Standard errors were calculated over three repeat measurements.

A clear decrease in the calculated exchange currents is observed with increasing saline concentration. The values for the standard heterogeneous rate constant for electron transfer (Table 4.3) were calculated using oxygen concentration values from literature\cite{20}.

It can be seen that standard heterogeneous rate constant remains constant with increasing chloride concentration. This would suggest that the increase in chloride concentration has no overall effect on the rate constant for electron transfer for the reduction of oxygen (within this range of chloride concentrations), with the dissolved oxygen concentration being the main factor influencing the exchange current. This result also suggests that chloride desorption is not a pre-equilibrium reaction step, as this would have impacted on the exchange current data in a different manner. Either, oxygen reduction (leading up to the rate determining step) does not require chloride
desorption (which seems unlikely), or there is a number of Pt sites that is available irrespective of chloride concentration (this also seems unlikely), or the chloride desorption is not required in the run-up to the transition state for electron transfer (e.g. chloride can offer a spot for binding without desorption).

Considering that the rate constant was determined from the exchange current, the “apparent” value of the rate constant should be used as a guide only since the true reversible equilibrium potential for the reduction of oxygen is not experimentally verified at +0.872 V vs. SCE at pH 2.

Table 4.3. Calculated heterogeneous rate constants, $k_0$, at increasing chloride concentration for the reduction of oxygen.

<table>
<thead>
<tr>
<th>[NaCl] / mol dm$^{-3}$</th>
<th>Standard Heterogeneous Rate Constant Log ($k_0$) / cm s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-8.30 ± 0.08</td>
</tr>
<tr>
<td>0.5</td>
<td>-8.42 ± 0.05</td>
</tr>
<tr>
<td>2.0</td>
<td>-8.39 ± 0.09</td>
</tr>
<tr>
<td>4.0</td>
<td>-8.38 ± 0.07</td>
</tr>
</tbody>
</table>

Electrokinetic data were extracted from a report published by Li et al.$^{[27]}$ on the reduction of oxygen at a platinum electrode in 3.5 % (approximately equal to 0.6 M) NaCl solution (Table 4.4) for comparison against the calculated logarithmic standard heterogeneous rate constant at 0.5 M NaCl calculated in Table 4.3.
Table. 4.4. Extracted electrokinetic parameters for the reduction of oxygen in aqueous 3.5 % NaCl solution, using a platinum dis electrode with an area of 0.2 cm².

<table>
<thead>
<tr>
<th>Electrokinetic Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tafel gradient / mv dec⁻¹</td>
<td>126</td>
</tr>
<tr>
<td>Transfer Coefficient, nα</td>
<td>0.47</td>
</tr>
<tr>
<td>Exchange current</td>
<td></td>
</tr>
<tr>
<td>Log (Iₒ / A)</td>
<td>-10.01</td>
</tr>
<tr>
<td>Standard Heterogeneous Rate Constant at 0.6 M NaCl</td>
<td>-8.86</td>
</tr>
<tr>
<td>Log (kₒ / cm s⁻¹)</td>
<td></td>
</tr>
<tr>
<td>Standard Heterogeneous Rate Constant at 0.5 M NaCl</td>
<td>-8.42</td>
</tr>
<tr>
<td>Log (kₒ / cm s⁻¹)</td>
<td></td>
</tr>
</tbody>
</table>

When calculating the standard electrode potential from the data by Li et al., it is assumed that the pH of the solution is approximately 5²⁸, giving a calculated standard electrode potential, Eₒ, to be +0.695 V vs. SCE.

The report states the solution was saturated with dissolved oxygen and as such the concentration of dissolved oxygen is higher at 0.93 mM, compared to around the nominal ambient value of 0.15 mM as reported previously²⁰ (see Chapter 3), and explains the higher extracted exchange current value in Table 4.4, in comparison to the lower values seen in Fig. 4.2. The two values of the logarithmic rate constant are in the same order of magnitude at 0.6 M NaCl and at 0.5 M NaCl, however, the difference between the two calculated values is a result of the difference in chloride concentrations in solution. It is expected that at similar chloride concentrations, the calculated logarithmic rate constants would then be in close agreement with each other.

The extracted Tafel gradient and transfer coefficient are also in good agreement with data calculated above in Fig. 4.2 and Table 4.2, and therefore confirms that the reduction of oxygen is a four electron reduction pathway to give water, as reported by Li et al.
In conclusion, the reduction of oxygen on platinum in high chloride concentrations is affected due to the adsorption of chloride ions on the platinum surface. This effect is likely due to the random desorption of chloride ions giving rise to areas of free platinum sites available for oxygen reduction. It has been observed that the rate of electron transfer is not affected by the chloride concentration, but it is affected by the concentration of oxygen dissolved in solution. The effect of increased pressure and oxygen concentration on the standard heterogeneous rate constant is investigated next.

4.3.2 – Reduction of Oxygen in High Ionic Strength Saline Media at Elevated Pressures

The concentration of oxygen (as well as activity) turned out to be important parameters in the study of the rate of oxygen reduction in the presence of chloride and therefore attempts have been made to vary the oxygen concentration via applied pressure in a special custom-made reactor (Fig. 4.1, pg. 90).

Additional cyclic voltammograms for the reduction of oxygen in 0.5 M NaCl with 10 mM protons were recorded at oxygen pressures of 2 bar and 4 bar (Fig. 4.8(A) (i) and (ii)). Under these conditions an additional prominent signal is observed at +0.8 V vs. SCE, probably corresponding the onset of chloride oxidation[29]. The fact that this prominent (but unwanted) oxidation of chloride is shifted towards more negative potential with increasing pressure can be rationalised based on the higher chlorine concentration (Cl₂ also is more soluble at elevated pressure).

A reduction step at +0.04 V vs. SCE (Fig. 4.8(B)) is observed which corresponds to the reduction of oxygen. The currents are seen to increase with increasing pressure and therefore suggest that the concentration of dissolved oxygen increases.
Figure 4.8. (A) Cyclic voltammograms (scan rate 2 mV s\(^{-1}\)) for the reduction of oxygen at 0.5 M NaCl with 10 mM protons at (i) 2 bars and (ii) 4 bars pressure of oxygen, using a 25 µm diameter platinum microwire of length 1.05 cm. (B) Magnified region of the reduction of oxygen.

The standard electrode potential for the reduction of oxygen at elevated pressures can be calculated by adapting the Nernst equation (see Chapter 2) (equation 4.12).

\[
E_{(cell)} = E^0 + \frac{RT}{4F} \ln \left( \frac{[Ox]}{[Re \cdot d]} \right)
\]

[4.12]
From the standard four electron reduction of oxygen to water in equation 4.1 above, the Nernst equation can be expressed in respect to the partial pressure of oxygen (equation 4.13).

$$E_{(cell)} = E^0 + \frac{RT}{4F} \ln \left( \frac{P_{O_2} \times [H^+]^4}{[H_2O]^2} \right)$$ \hspace{1cm} [4.13]

Given that water is the liquid surrounding phase, the corresponding activity (or concentration) can be set equal to 1 (effectively removing the water activity and placing it into the corresponding standard potential), the Nernst equation is then written as (equation 4.14).

$$E_{(cell)} = E^0 + \frac{RT}{4F} \ln \left( \frac{P_{O_2} \times [H^+]^4}{1} \right)$$ \hspace{1cm} [4.14]

Table 4.5 below shows the calculated standard electrode potentials at 2 and 4 bar pressure. It can be seen that even at high pressures of 4 bar, the difference between the standard electrode potentials at elevated pressures to the standard electrode potential at atmospheric pressure is negligible and therefore it is likely that this small change in the electrode potential will have little effect on the extrapolated exchange current, $I_o$, and calculated rate constants, $k_o$.

**Table. 4.5.** Calculated standard electrode potentials at 2 and 4 bar pressure at pH 2 for the reduction of oxygen.

<table>
<thead>
<tr>
<th>Pressure / bar</th>
<th>Calculated $E_{(cell)}$ at elevated pressure / V vs. SCE</th>
<th>$E^0$ at atmospheric pressure / V vs. SCE</th>
<th>Difference / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.876</td>
<td>0.872</td>
<td>0.004</td>
</tr>
<tr>
<td>4</td>
<td>0.880</td>
<td>0.872</td>
<td>0.008</td>
</tr>
</tbody>
</table>

The cause for the small differences between the atmospheric standard electrode potential and the cell potential at elevated pressures is due to the shift in the equilibrium which is pushed to the right to produce more water as more oxygen is
dissolved into solution. Using the cyclic voltammograms, the potential steps were selected \((E_{\text{initial}} = +0.4 \, \text{V vs. SCE and } E_{\text{final}} = -0.3 \, \text{V vs. SCE})\) for chronoamperometry for simultaneously determining the concentration and diffusion coefficients of the dissolved oxygen at increasing pressures using digital simulation. Chronoamperometry was performed by stepping the potential from +0.4 V to -0.3 V vs. SCE (Fig. 4.9).

The oxygen concentration and oxygen diffusion coefficients were simultaneously obtained from the chronoamperometric data. The diffusion coefficient parameter in DigiElch was allowed to be iterated by the software whilst the oxygen concentration was varied between 0.1 mM and 1 mM. The resulting parabolic standard deviation plot (see inserts in Fig. 4.9) allows the concentration to be obtained.
As the pressure of oxygen increases, the concentration of dissolved oxygen is seen to increase. An apparent dissolved oxygen concentration of 0.46 mM was obtained at 2 bars pressure and an apparent dissolved oxygen concentration of 0.74 mM was obtained at 4 bars. The diffusion coefficients were found to decrease slightly in
comparison to the optimised value of $D_{O_2} = 2.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at atmospheric pressure$^{20}$ (Fig. 4.10).

![Figure 4.10. Plot of the dissolved oxygen concentration and the oxygen diffusion coefficients as a function of oxygen pressure. Errors are calculated from three repeat measurements. Note that solutions were not fully equilibrated and therefore measured concentrations are too low and errors on diffusion coefficients may be increased.](image)

The error bars based on triplicate measurements are seen to increase with increasing pressure and are mainly due to variations in the electrokinetics of oxygen reduction resulting from the presence of chloride ions changing the surface. The optimised diffusion coefficients are seen to decrease slightly with increasing pressure and this is could be related to the temperature variation within the not fully-equilibrated pressure cell.

Figure 4.11 shows the cyclic voltammograms with increasing current for the reduction of oxygen at increasing scan rates. During these experiments the current response for the oxygen reduction appears to become more prominent, which is likely due to the effect of additional oxygen diffusing into the solution with time rather than a direct
scan rate effect. In fact, all of the data are likely to be associated with oxygen concentration levels lower that those expected for equilibrium.

Figure 4.11. Cyclic voltammograms of the reduction of oxygen (in 0.5 M NaCl) at a 25 µm diameter platinum microwire of length 1.05 cm at a scan rate of (i) 2 mV s$^{-1}$, (ii) 10 mV s$^{-1}$, (iii) 20 mV s$^{-1}$, (iv) 50 mV s$^{-1}$ and (v) 100 mV s$^{-1}$ at (A) 2 bars pressure and (B) 4 bars pressure.

For a solution containing 0.5 M NaCl under ambient conditions in a previous chapter (see Chapter 3) a plateau current for the reduction of oxygen was observed to be approximately 3 µA at a similar electrode. When considering the higher partial pressure for pure 1 bar O$_2$, one would expect this current to increase to approximately 15 µA. This can be compared to current at 2 bars O$_2$ (approximately 18 µA) and at 4 bars O$_2$ (approximately 30 µA) as shown in Figure 4.8. These cyclic voltammograms
were performed slightly later compared to the chronoamperometry experiments (see Fig. 4.9) and therefore the saturation with oxygen under pressure might have been further advanced towards equilibrium. From the data it is apparent that complete equilibrium was still not attained.

Taking the baseline of cyclic voltammogram at a scan rate of 2 mV s\(^{-1}\) at both 2 bars and 4 bars pressure, Tafel plots were constructed to determine the slope of the gradient as well as the transfer coefficient (Fig. 4.12). The electrokinetic parameters for 2 and 4 bar pressures are summarised in the table below (Table 4.6).

![Tafel plots](image)

**Figure. 4.12.** Tafel plots (in 0.5 M NaCl aqueous solution) of the reduction of oxygen at (i) 2 bars and (ii) 4 bars pressure.
Table. 4.6. Calculated electrokinetic parameters for the reduction of oxygen at 2 bar and 4 bar pressure in 0.5 M NaCl aqueous solution at pH 2, using a microwire electrode of 25 µm diameter and length of 1.05 cm.

<table>
<thead>
<tr>
<th>Pressure / bar</th>
<th>Calculated Tafel Slope / mV dec(^{-1})</th>
<th>Calculated Transfer Coefficient, (n_a)</th>
<th>Calculated Exchange Current, Log ((I_o) / A)</th>
<th>Calculated Standard Heterogeneous Rate Constant, Log ((k_o) / cm s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>123</td>
<td>0.48</td>
<td>-14.91</td>
<td>-11.99</td>
</tr>
<tr>
<td>4</td>
<td>128</td>
<td>0.47</td>
<td>-13.95</td>
<td>-11.32</td>
</tr>
</tbody>
</table>

At both pressures, the Tafel slopes show that the reduction of oxygen is limited by the rate of the first electron transfer, along with the calculated transfer coefficients being in close agreement to the expected 0.5 value, implying that the transition state is an equal combination of both reactants and products. With the assumption that the standard potential for the reduction of oxygen at pH 2 does not change with pressure, the exchange currents show that with increasing pressure, the exchange currents move to more positive values. Taking into account the oxygen concentration data from Fig. 4.12, the extrapolation leads to \(k_0\) values which are significantly lower than with previous data obtained at ambient pressures.

The large difference observed in the rate constant data at elevated pressures compared to data at ambient pressures is likely a result of the system did fully reaching equilibrium before running the electrochemical measurements. The calculated values of the exchange currents are based on an estimate of oxygen concentration dissolved in solution at the time of pressurising. Leaving the system to equilibrate for a longer time period will change the values of the exchange currents and the concentration of dissolved oxygen, as noted above, and as such will also change the calculated rate constants. More work will be needed in future in order to calculate more accurate rate constants at elevated pressures.
4.4 – Summary and Conclusion

Electrokinetic parameters such as Tafel gradients, transfer coefficients and standard heterogeneous rate constants have been calculated for the reduction of oxygen in increasing saline solutions at ambient pressures.

Tafel plots in increasing saline solutions have shown little deviation from the expected 120 mV dec$^{-1}$ which imply that the first electron transfer is the rate determining step and the calculated transfer coefficients, α, remain consistent around the 0.5 value. The standard heterogeneous rate constants have shown that the concentration of dissolved oxygen is the important factor compared to the activity of oxygen, with the calculated values showing little variation between them.

It has been shown that high pressure experiments with a platinum microwire electrode allow simultaneous determination of the diffusivity and the concentration of oxygen in saline media.

The values extracted from the experimental data suggest that the diffusivity is (as expected) close to constant (from 1 bar to 4 bars) with the variation arising probably due to the temperature of the pressure cell. The oxygen concentration scales with pressure, but full equilibrium conditions were not achieved.

Experimental problems using the pressure cell arose due to (i) slow equilibration of the oxygen concentration in the experimental system (leading to gradual increase in currents), (ii) unexpected temperature fluctuations, and (iii) damage to the reference electrode which when compressed and decompressed lost the frit separating the internal and external saline electrolyte. Nevertheless, initial chronoamperometry data and cyclic voltammetry data at elevated pressures have been obtained and analysed as proof-of-principle experiment.

Most importantly, it has been shown that the standard rate constant for oxygen reduction is clearly associated with oxygen concentration and not with oxygen activity.
4.5 – References


Chapter 5

Effect of a Polymer of Intrinsic Microporosity on Oxygen Reduction Processes in Saline Media

Chapter Abstract

Microwire electrodes can achieve quasi-steady state currents without the need to use forced convection, unlike hydrodynamic techniques such as the rotating disc electrode. In this chapter, a 25 µm diameter platinum microwire electrode was used to investigate the effect of a polymer of intrinsic microporosity (PIM-EA-TB) on the reduction of oxygen in increasingly saline media. Quasi-steady currents in the cyclic voltammograms for the reduction of oxygen showed little difference with and without a PIM-EA-TB coating. The Tafel analysis showed that the first electron transfer was the rate determining step with and without the microporous PIM-EA-TB coating.

Next, the effect of scan rate on the reduction of oxygen was explored with and without a PIM-EA-TB. Data are explained with capacitance current contributions at high scan rates and with kinetic current contributions at low scan rates. The electrode surface capacitance with/without PIM-EA-TB coating immersed in the saline solution, and independent of chloride concentration, was calculated. PIM-EA-TB is therefore sufficiently permeable for both oxygen and ions to not affect surface reactivity for small molecules and ions.
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5 – Effect of a Polymer of Intrinsic Microporosity on Oxygen Reduction Processes in Saline Media

5.1 – Introduction to Polymers of Intrinsic Microporosity (PIMs)

Polymers of intrinsic microporosity, commonly referred to as PIMs, are a specific classification of polymers that contain a rigid backbone structure. With this structural feature, the polymers pack in an inefficient manner thereby generating a high surface area (in the order of $10^3$ m$^2$ g$^{-1}$ and higher) as well as behaving as molecular sieves, making them highly attractive towards gas separation\cite{1}\cite{2}\cite{3}. Furthermore, various applications of using PIMs have been reported in literature such as in membrane separations between water and oil\cite{4}, desalination devices\cite{5}, organic solvent nanofiltration\cite{6} and recently increasing the stability of fuel cell anode catalysts\cite{7}.

The key feature for an intrinsically microporous polymer is having one unit that contains a site of contortion such as a non-planar rigid backbone\cite{8}. It has recently been shown that these PIMs can be electrospun to produce fibres for adsorbing organic contaminants from non-aqueous solutions using PIM-1\cite{9}. The hydrophobicity of PIM-1 as well as the ease for solution-based processing in various organic solvent made it an attractive polymer for use. However, over time, PIM-1 can age physically leading to a decrease in the performance of separation. Shin et al. demonstrated that combining PIM-1 with graphene flakes, and through using Raman and SEM characterisation, the ageing effect could be slowed down depending on the ratio of PIM to graphene used\cite{2}. Likewise, blending PIM-1 with commercially available compounds such as Matrimid, Metal Organic Frameworks (MOFs) or bulk metals can enhance the gas separation properties for next generation membrane devices\cite{3}\cite{10}.

PIMs can be employed to stabilise catalysts, for example platinum catalysts. Platinum is a highly active catalyst, one which is commonly used in fuel cells such as proton exchange membrane (PEM) fuel cells\cite{11}, for the reduction of oxygen. Use of platinum nanoparticles can enhance the catalytic properties over using conventional bulk platinum\cite{12}, however, the stability of platinum nanoparticles (typically between 3-5 nm size) on the anode can be low due to corrosion during potential cycling. It has been reported that use of PIM-EA-TB, which is synthesised via polymerisation using Tröger’s base (Fig. 5.1), as a coating can prevent the corrosion of the platinum
nanoparticles when investigating the oxidation of methanol\textsuperscript{[7]} as well as facilitating rapid ion transport\textsuperscript{[13]}.

![Chemical structure of a polymer of intrinsic microporosity, PIM-EA-TB.](image)

**Figure. 5.1.** Chemical structure of a polymer of intrinsic microporosity, PIM-EA-TB.

Gases such as oxygen are able to pass through the PIM-EA-TB coating easily to reach the electrode due to the overall large porosity of the PIM which is important for fuel cells where the reduction of oxygen on platinum takes place. The surface of the platinum is typically polycrystalline, although synthesis of platinum nanoparticles can be tailored to produce specific surface planes\textsuperscript{[14]}. Depending on the solution used, the counter ions may preferentially adsorb onto anyone of the planes thereby inhibiting the reduction of oxygen. For example, the reduction of oxygen in perchloric acid is inhibited\textsuperscript{[15]}, and other anions, such as chloride ions can also poison the catalytic platinum surface\textsuperscript{[16]}\textsuperscript{[17]}. Hydrodynamic techniques such as the Rotating Disc Electrode (RDE) are typically used when investigating the electrokinetics of oxygen reduction, generating steady state currents through varying the rotation speed of the electrode on various electrode substrates. However, quasi-steady state currents can be achieved through using microwire electrodes, which are quick and easy to fabricate\textsuperscript{[18]}.

In this chapter, the use of the PIM polymer, PIM-EA-TB, as a film-coating on platinum electrodes is investigated using a microwire electrode for the reduction of oxygen in highly saline media with NaCl concentration ranging from 0.1 M to 4 M at pH 2. The open porosity of the PIM-EA-TB and the rigid molecular structure on the electrode surface prevent significant catalyst-site blocking to occur. PIM coatings therefore protect catalysts without affecting reactivity, which has potential applications in catalyst protection in the presence of bigger molecules such as proteins or enzymes.
5.2 – Experimental

5.2.1 – Chemical Reagents

Sodium chloride (NaCl, > 99.5 %), hydrochloric acid (HCl, stabilised at a concentration of 1 mol dm$^{-3}$), chloroform (CHCl$_3$, 99.5 %), and sulphuric acid (H$_2$SO$_4$, 95-98 %) were purchased from Sigma Aldrich UK and were used without further purification. PIM-EA-TB was prepared from a literature method$^{[1]}$. Commercial platinum wire of 25 µm diameter was purchased from Advent Materials UK. All solutions were prepared using purified water with a resistivity of not less than 18 MΩ at 22 °C (Millipore) and were adjusted to pH 2 using HCl. Nitrogen gas (N$_2$) and Argon gas (Ar) were purchased from BOC UK.

5.2.2 – Instrumentation

Electrochemical measurements were carried out in a thermo-jacketed electrochemical cell connected to a water bath (Haake) maintained at 25 ± 0.5 °C. Electrochemical measurements were performed using a microAutolab III potentiostat system (Eco Chemie, Netherlands). A standard three-electrode configuration was used using a Pt wire counter electrode, a KCl-saturated calomel reference (SCE) electrode and a 25 µm diameter platinum microwire, prepared as reported previously$^{[18]}$, as the working electrode (Fig. 5.2). The length of the exposed microwire was previously calibrated (see Chapter 4, pg. 89) at 1.05 cm and was used in all the experimental measurements.
Figure 5.2. Schematic drawing of the assembly of the platinum microwire using lamination foil to allow a 1 cm long section to be exposed to solution.

5.2.3 – Procedure for Modifying the Platinum Microwire Electrode with PIM-EA-TB

Electrochemical cleaning was achieved by potential cycling at a scan rate of 0.5 V s\(^{-1}\) from -0.5 to +1.3 V vs. SCE for 35 cycles in aqueous 0.5 M H\(_2\)SO\(_4\) under a N\(_2\) atmosphere for the platinum wire electrode. After electrochemical cleaning the electrode was rinsed with deionised water first before being immersed into a solution of PIM-EA-TB:CHCl\(_3\) of a 1 mg to 1 mL ratio for approximately 1 s. The modified electrode was then air dried for 5 min before being rinsed with deionised water. Electrochemical measurements were performed after the modified electrode was air dried for 5 min.

5.3 – Results and Discussion

5.3.1 – Effect of PIM-EA-TB Coating on Platinum Electrodes I: Oxygen Reduction in Increasingly Saline Solutions

The reduction of oxygen typically proceeds via a four electron pathway to produce water (equation 5.1)

\[
O_2(aq) + 4H^+ + 4e^- \rightarrow 2H_2O(aq)
\]  

[5.1]

This reaction occurs at pH 0, where the standard electrode potential, \(E^0\), is +1.23 V vs. SHE. When using a saturated calomel reference electrode (SCE) the \(E^0\) is shifted to
+0.99 V vs. SCE. Adjusting the solutions to pH 2 causes the $E^0$ to be further shifted towards more negative potentials. For each change in pH unit, the voltage changes by 0.059 V (as expressed by the Nernst equation, see Chapter 2). A change from pH 0 to pH 2 is therefore equivalent to 0.118 V shift towards negative potentials and so the estimated $E^0$ for the reduction of oxygen at pH 2 is +1.11 V vs. SHE, or +0.872 V vs. SCE (see Chapter 4).

To avoid any complications with proton transport to the electrode surface, a proton concentration of 10 mM was used to ensure a complete reduction to water. The experimental observation of the oxygen reduction in saline media occurs at much more negative potential due to kinetic overpotential.

Cyclic voltammetric data for the reduction of oxygen with a PIM-EA-TB coating and without a PIM-EA-TB coating clearly show the reduction of oxygen at around +0.21 vs. SCE (Fig. 5.3).
Figure. 5.3. Cyclic voltammograms of the reduction of oxygen (saturated at 1 bar pure oxygen) at a scan rate of 2 mVs$^{-1}$ using a platinum microwire electrode of 1.05 cm length and of 25 µm diameter with (i) PIM-EA-TB coating and (ii) without PIM-EA-TB coating in (A) 0.1 M NaCl, (B) 0.5 M NaCl, (C) 2 M NaCl and (D) 4 M aqueous NaCl solution.
At low chloride concentrations the cyclic voltammograms (Fig. 5.1(A) and (B)) show no additional redox peaks at high potentials. However, at a chloride concentration of 2 M (Fig. 5.1(C)), an additional redox peak is seen at around +1.0 V vs. SCE, which also increases when the chloride concentration is increased to 4M (Fig. 5.1(D)). These additional redox peaks are likely from bromide contamination in the sodium chloride. The oxygen concentration at 2 M NaCl and 4 M NaCl solutions is low, at around 0.1 mM\cite{18}, and as such a low levels of contaminants will therefore be noticeable at high electrode potentials. With the standard electrode potential, $E^0$, calculated at pH 2 to be +0.872 V vs. SCE, the half-wave potentials are significantly lower and so a large overpotential is required in order to reduce oxygen (Table 5.1).

**Table. 5.1.** Values of the half-wave potential and the limiting currents with and without a PIM-EA-TB coating in increasing saline solutions for the reduction of oxygen at a platinum microwire electrode with a diameter of 25 µm and length of 1.05 cm.

<table>
<thead>
<tr>
<th>[NaCl] / mol dm$^{-3}$</th>
<th>With PIM-EA-TB Coating</th>
<th>Without PIM-EA-TB Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Half-wave potential $E_{1/2}$/ V vs. SCE</td>
<td>Limiting Current $I_{(lim)}$/ µA $^a$</td>
</tr>
<tr>
<td>0.1</td>
<td>0.221</td>
<td>-2.90</td>
</tr>
<tr>
<td>0.5</td>
<td>0.188</td>
<td>-2.53</td>
</tr>
<tr>
<td>2.0</td>
<td>0.185</td>
<td>-1.45</td>
</tr>
<tr>
<td>4.0</td>
<td>0.181</td>
<td>-0.81</td>
</tr>
</tbody>
</table>

$^a$ Limiting current at -0.1 V vs. SCE.

The two data sets in Table 5.1, show very little difference when comparing the limiting currents and the half-wave potentials with and without a PIM-EA-TB coating. This suggests that the PIM-EA-TB coating has no effect on the reduction of oxygen and the transport of oxygen to the electrode surface is not affected by the PIM-EA-TB coating. The slight variation between the two data sets is likely due to small thermal gradients, vibrations or density differences in solution. Tangents of the
background current, between a potential range of +0.45 V and +0.9 V vs. SCE, and of the reduction current were taken. The intersection of the two tangents (Fig. 5.4(A)) allows the onset potential for oxygen reduction, \( E_{\text{onset}} \), to be established with increasing chloride concentration (Fig. 5.4(B))\(^{[19]} \).

**Figure. 5.4.** (A) Taking the tangents of the background current and forward scan current gives the \( E_{\text{onset}} \) potential determination for a PIM-EA-TB coated platinum wire of 25 \( \mu \)m diameter and length 1.05 cm in 0.5 M NaCl. (B) A plot of the \( E_{\text{onset}} \) potential with increasing NaCl concentration (i) with a PIM-EA-TB coating and (ii) without a PIM-EA-TB coating.

Overall, the onset potentials are shown to decrease with increasingly saline concentration in Fig. 5.4. The onset potentials using aPIM-EA-TB coating are shifted towards higher potentials by around +10 mV and this small increase in the onset
potential can be explained by the local disruption of water and chloride ions on the platinum surface by the rigid molecular structure of the PIM-EA-TB, generating small local regions that are not blocked by chloride ions allowing oxygen to be reduced \(^{(20)(21)}\) (Fig. 5.5). The PIM-EA-TB structure has lone pairs of electrons on the nitrogen groups which can be protonated, with the pH for protonation of PIM-EA-TB occurring at 4\(^{[5]}\). As such, the PIM-EA-TB is fully protonated when immersed into a NaCl / HCl solution at pH 2. The protonation generates a positive charge that attracts the chloride ions to the PIM-EA-TB structure and with small regions of the electrode surface being in close contact with the PIM-EA-TB coating, the protonated PIM may slightly enhance the reduction of oxygen and varying the pH of the saline solution will likely have an effect on the reduction of oxygen. With the nitrogen groups becoming less protonated at higher pH values the number of regions free from chloride blocking will decrease thereby affecting the amount of oxygen reduced.

\[ RT \frac{1}{F} \frac{m}{n} = 2.303RT \]

\[ \alpha = \frac{m}{2.303RT} \]

Here, \( m \) is the gradient of Tafel slope, \( R \) is the molar gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), \( T \) is the absolute temperature (298 K), \( n \) is the number of electrons transferred and \( F \) is Faraday’s constant (96485 C mol\(^{-1}\)).
The extrapolation of the exchange current, $I_{o}$, is largely dependent upon the gradient of the Tafel slope. Any change in the Tafel slope would be amplified when extrapolating back to the exchange current. Therefore, the calculated standard electrode potential at pH 2 for the reduction of oxygen is assumed to be constant at +0.871 V vs. SCE and that there is no change throughout the electrochemical measurement.

**Figure. 5.6.** Tafel plots for the reduction of oxygen in increasing saline media using (A) a bare 25 µm diameter platinum wire and (B) a 25 µm diameter platinum wire coated with PIM-EA-TB in (i) 0.1 M NaCl, (ii) 0.5 M NaCl, (iii) 2 M NaCl and (iv) 4 M NaCl solutions.
Both sets of Tafel plots show that with increasing chloride concentration, the slopes are displaced as concentration of oxygen decreases, an effect known as “salting out”. This decrease in the concentration of oxygen with increasing chloride concentration is in agreement with previously reported literature[18].

The rate limiting step for the reduction of oxygen is the first electron transfer, giving a Tafel slope of 120 mV dec$^{-1}$ and a transfer coefficient of 0.5[22]. The calculated Tafel slopes and transfer coefficients are listed below, using the number of electrons transferred as 1 (Table 5.2).

Table. 5.2. Calculated Tafel slopes and transfer coefficients values in increasing saline media with and without PIM-EA-TB coating. Standard errors are calculated from three repeat measurements.

<table>
<thead>
<tr>
<th>[NaCl] / mol dm$^{-3}$</th>
<th>With PIM-EA-TB Coating</th>
<th>Without PIM-EA-TB Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated Tafel Slope / mV dec$^{-1}$</td>
<td>Calculated Transfer Coefficient, $n_a$</td>
</tr>
<tr>
<td>0.1</td>
<td>119 ± 0.6</td>
<td>0.53 ± 0.012</td>
</tr>
<tr>
<td>0.5</td>
<td>122 ± 0.4</td>
<td>0.50 ± 0.016</td>
</tr>
<tr>
<td>2.0</td>
<td>123 ± 0.7</td>
<td>0.52 ± 0.018</td>
</tr>
<tr>
<td>4.0</td>
<td>124 ± 0.6</td>
<td>0.49 ± 0.017</td>
</tr>
</tbody>
</table>

It can be seen between the two data sets that the transfer coefficients calculated are around 0.5 indicating that the transition state at the electrode surface consists of both the reactants and products. The calculated Tafel slopes of the two data sets are in close agreement with the expected value of 120 mV dec$^{-1}$ and so the first electron transfer is the rate determining step for the reduction of oxygen.

The exchange currents, $I_o$, were calculated from the gradient of the Tafel slopes with increasingly saline concentration and give an idea of the overall current at zero overpotential when both the cathodic and anodic currents are balanced. It can be seen that the with increasing saline concentration, the exchange current decreases.
From the calculated exchange currents, there is little difference with and without a PIM-EA-TB coating and would imply that the difference falls within the associated errors (Fig. 5.7).

**Figure. 5.7.** A plot of the exchange current, $I_0$, for the reduction of oxygen with increasingly saline concentration at a 25 µm platinum wire of length 1.05 cm (i) with a PIM-EA-TB coating and (ii) without a PIM-EA-TB coating.

The exchange current is a measure of the electrokinetics of a reaction, where the exchange current is directly proportional to the rate constant of electron transfer, $k_0$, (equation 5.3).

$$I_0 = nFk_0[O_2]$$  \[5.3\]

The calculated rate constants for both sets of data are shown below (Table 5.3) using the values for the concentration of oxygen in increasing chloride concentration taken from literature$^{[18]}$. 
Table. 5.3. Calculated logarithmic values of the heterogeneous rate constant for electron transfer, $k_0$, with a PIM-EA-TB coating and without a PIM-EA-TB coating for the reduction of oxygen in increasing saline concentrations. Standard errors calculated from three repeat measurements.

<table>
<thead>
<tr>
<th>[NaCl] / mol dm$^{-3}$</th>
<th>Standard Heterogeneous Rate Constant with PIM-EA-TB Coating Log ($k_o$) / cm s$^{-1}$</th>
<th>Standard Heterogeneous Rate Constant without PIM-EA-TB Coating Log ($k_o$) / cm s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-8.17 ± 0.07</td>
<td>-8.19 ± 0.08</td>
</tr>
<tr>
<td>0.5</td>
<td>-8.30 ± 0.09</td>
<td>-8.34 ± 0.05</td>
</tr>
<tr>
<td>2.0</td>
<td>-8.23 ± 0.06</td>
<td>-8.30 ± 0.09</td>
</tr>
<tr>
<td>4.0</td>
<td>-8.20 ± 0.07</td>
<td>-8.28 ± 0.07</td>
</tr>
</tbody>
</table>

From Table 5.3, it can be seen that both sets of data (with/without PIM) are very similar. The observed effects are insignificant and the calculated rate constants should be considered as the “apparent” rate constants (the reversible potential is not experimentally verified). The reason for this is that the reduction of oxygen is irreversible and the true equilibrium potential for the oxygen reduction at pH 2 is not known – it is possible that the equilibrium potential for the reduction of oxygen, at pH 2, changes at higher saline media and therefore the values listed of the rate constants should be used as guide only.

In conclusion there are no significant effects of the porous PIM-EA-TB polymer on the electrochemical oxygen reduction reaction and this suggests that the polymer does not strongly bind to the platinum surface. Even when charged due to protonation, the porosity is sufficient to avoid double layer effects to be observed at slow scan rates. Small effects may appear for onset potentials and possibly at higher scan rates, which are investigated next. Cross sectional SEM images of the PIM coating on the platinum microwire are required in order to measure the thickness of the coating and determine if a uniform distribution of the coating is present.
5.3.2 – Effect of PIM-EA-TB Coating on Platinum Electrodes II.: Effect of Scan Rate on the Reduction of Oxygen in Increasingly Saline Solutions

The effect of increasing scan rates was explored on the reduction of oxygen, using a PIM-EA-TB coated platinum microwire and a bare platinum microwire without any PIM-EA-TB coating. The cyclic voltammograms with a PIM-EA-TB coating and without a PIM-EA-TB at increasing scan rates are shown in 0.1 M NaCl solution at pH 2 (Fig. 5.8). It can be seen that there is a clear step feature at around +0.25 V vs. SCE, corresponding to the reduction of oxygen.

**Figure. 5.8.** Cyclic voltammograms of the reduction of oxygen in 0.1 M NaCl at pH 2 using (A) a bare 25 μm platinum wire and (B) a PIM-EA-TB coated 25 μm platinum wire, at a scan rate of (i) 10 mVs⁻¹, (ii) 20 mVs⁻¹, (iii) 50 mVs⁻¹ and (iv) 100 mVs⁻¹.
With increasing scan rate, an additional redox couple is observed at high potentials centred around $+0.7 \text{ V vs. SCE}$ (Process 1), possibly related to the oxidation and reduction of platinum (equation 5.4).

$$\text{Pt}^{II} + 2e^- \rightarrow \text{Pt}^0$$  \hspace{1cm} [5.4]

At negative potentials around $-0.2 \text{ V vs. SCE}$, the hydrogen underpotential deposition (HUPD) is observed with the peaks becoming more prominent at a scan rate of 100 mVs$^{-1}$. The presence of the HUPD peaks is characteristic when platinum undergoes potential cycling in acidic conditions at negative potentials.

The exchange current for oxygen reduction was estimated from the corresponding Tafel plots (not shown) with increasingly saline concentration for each increase in scan rate, with and without the PIM coating. With increasing scan rate, the effect of electrode surface capacitance also increases, as seen in the cyclic voltammograms (Fig. 5.8). Using the increasing scan rate and the capacitance current, it is possible to calculate the overall capacitance. The capacitance current, $I_{\text{CAP}}$, is directly proportional to the scan rate, $\nu$ (equation 5.5).

$$I_{\text{CAP}} \propto \nu$$  \hspace{1cm} [5.5]

The kinetic current, $I_{\text{KIN}}$, is independent of the scan rate and the total current, $I_{\text{total}}$, observed is the addition of the kinetic current and the capacitance current (equation 5.6).

$$I_{\text{total}} = I_{\text{CAP}} + I_{\text{KIN}}$$  \hspace{1cm} [5.6]

In logarithmic form (equation 5.7).

$$\log I_{\text{total}} = \log(I_{\text{CAP}} + I_{\text{KIN}})$$  \hspace{1cm} [5.7]

At low scan rates, the capacitance current is extremely small and so the kinetic current should therefore dominate, but at higher scan rates the capacitance current becomes larger than the kinetic current. In a Tafel plot the resulting linear region will systematically shift with scan rate. From equation 5.7, the value of the capacitance can be extracted.
It is assumed that the limiting exchange current at zero scan rate is the kinetic current with no contribution from the capacitance current. In the calculation of the capacitance, the calculated $I_o$ value at a scan rate of 2 mV s$^{-1}$ is used as the kinetic current with the assumption that the capacitance current is negligible. The total capacitance of the system can be fitted to the data (Fig. 5.9) with the calculated values given below (Table 5.4).

Table 5.4. The calculated capacitance values from the exchange currents, $I_o$, for the reduction of oxygen in increasing chloride concentrations. The calculated area of the 25 µm diameter platinum microwire electrode, of a length of 1.05 cm, was 0.0078 cm$^2$.

<table>
<thead>
<tr>
<th>[NaCl] / mol dm$^{-3}$</th>
<th>Calculated Capacitance / µF cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.64</td>
</tr>
<tr>
<td>0.5</td>
<td>0.59</td>
</tr>
<tr>
<td>2.0</td>
<td>0.61</td>
</tr>
<tr>
<td>4.0</td>
<td>0.60</td>
</tr>
</tbody>
</table>
Figure 5.9. Calculated exchange currents and calculated capacitance at increasing scan rates with (i) PIM-EA-TB coating and (ii) without PIM-EA-TB coating, using a 25 μm diameter platinum wire in (A) 0.1 M NaCl, (B) 0.5 M NaCl, (C) 2 M NaCl and (D) 4 M aqueous NaCl solutions.
A general linear trend is observed as the scan rates increases for each chloride concentration, with the exchange current increasing at higher scan rates (Fig. 5.9). The calculated capacitance is seen to vary little with saline concentration and overall remains constant at around 0.61 ± 0.08 μF cm⁻². Compared to a literature value of approximately 20 μF cm⁻²[23], the calculated capacitance value is significantly lower. This suggests that the RC time constant is larger with the PIM-film on the surface of the microwire electrode and this effect is observed at higher scan rates. A similar situation was also observed in Chapter 6 when calculating the electrochemically active surface area of the platinum microwire[23].

5.4 – Summary and Conclusion

The presence of a polymer of intrinsic microporosity, PIM-EA-TB, on a platinum microwire electrode has been shown to have little effect on the reduction of oxygen in increasingly saline media. Using a microwire electrode allows quasi-steady state currents to be achieved and avoids viscosity effects in comparison to using hydrodynamic techniques, such as the rotating disc electrode.

The onset potentials for oxygen reduction at platinum were found to be shifted towards positive potentials by around +10 mV in the presence of a PIM-EA-TB coating (for all chloride concentrations) possibly resulting from the localised displacement of chloride ions and water molecules by the rigid structure of the PIM-EA-TB on the platinum surface thereby allowing easier access for oxygen to be reduced. However, this effect is in the error margin and it would need additional experimental work to confirm. Cross sectional SEM images would be required to measure the thickness of the coating as well as the distribution of the coating on the microwire surface.

Tafel analysis carried out for the reduction of oxygen with a PIM-EA-TB coating and without a PIM-EA-TB coating in different salt levels were found to be in close agreement with each other, as well as being in agreement with the 120 mV dec⁻¹ slope for an irreversible one electron transfer that is the rate determining step.
The effect of capacitance on the Tafel analysis was revealed. For each chloride solution, the capacitance was calculated for increasing scan rates and was shown to follow a common trend, with the calculated capacitance being on average at $0.61 \pm 0.08 \, \mu\text{F cm}^{-2}$. The low value of the capacitance is most likely a result of the potentiostat rejecting a large amount of the capacitance current being recorded in the cyclic voltammograms at high scan rates.

In summary, data presented in this chapter suggest that the application of a PIM-EA-TB coating to platinum has only insignificant effects on the kinetics for the reduction of small molecules like oxygen in increasingly saline solutions. This result is consistent with the PIM-EA-TB pore size of typically 2 nm and the rigid nature of the molecular structure preventing catalyst blocking. This polymer film coating could be particularly useful in stabilising platinum nanocatalysts for oxygen reduction catalysts for applications in fuel cells.
5.5 – References


Chapter 6

Electrothermal Annealing of Catalytic Platinum Microwire Electrodes: Towards Membrane-Free pH 7 Glucose Microfuel Cells

Chapter Abstract

Cleaning and surface activation of platinum microwires, of 25 μm diameter, has been achieved by a short one-second electrothermal annealing treatment in air at 0.3 A (an orange glow). Data from cyclic voltammograms suggest a decrease in the electrochemically active surface area with annealing time, along with a change in surface structure towards the Pt(100) crystalline face.

Investigation of the impact of electrothermal annealing on the electrocatalytic activity towards (i) oxygen reduction and (ii) glucose oxidation in pH 7 phosphate buffered aqueous solutions was carried out. Electrothermally annealed platinum produces an electrocatalytic response towards glucose oxidation with increasing glucose concentration in contrast to as-received commercial platinum. An annealing step of one-second is just as effective in enhancing catalysis as prolonged electrochemical cleaning in sulphuric acid.

Combination of a non-annealed and an annealed microwire electrode, a simple membrane-free micro-fuel cell system is devised, operating in phosphate buffer at pH 7 with linearly increasing power output reaching 2.2 nW cm$^{-2}$ at high glucose levels of 0.5 M.

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6 – Electrothermal Annealing of Catalytic Platinum Microwire Electrodes: Towards Membrane-Free pH 7 Glucose Microfuel Cells

6.1 – Micro-Fuel Cells

Platinum has a wide range of applications within electrochemistry and in particular, areas involving sensing and catalytic energy conversion. The generation of power electrochemically from “bio-fuels” such as glucose\(^1\), ammonia\(^2\), alcohols\(^3\) or cellulose\(^4\) plays an important role in sensing applications or in micro-power sources to supply electrical energy to implantable devices\(^5\) and micro-devices\(^6\). Physiological levels of glucose in normal, healthy human blood fall into the range of 4 to 6 mM and at lower levels glucose is also present in tissue and other bio-fluids\(^7\). The generation of power by electrochemical oxidation of this concentration of glucose to carbon dioxide (associated with the 4-electron reduction of oxygen to water) should deliver theoretically in the order of 1 mW cm\(^{-2}\) power, but the experimentally achieved values are highly dependent on suitable enzyme catalysts and device design\(^8\). Often enzymes are employed to allow effective and selective reactions at anode and cathode to occur. With highly specialised bio-catalysts or well-engineered mass transport conditions membrane-free micro-fuel cells are possible with very limited fuel cross-over\(^9\). However, incorporation of bio-catalysts into devices remains problematic and simple catalytic surfaces may offer a desirable alternative.

Platinum microwire electrodes have been widely studied\(^10\),\(^11\),\(^12\) and employed, for example, in sensing\(^13\). The diffusion to mirowire electrodes is cylindrical and rapidly approaches quasi-steady state\(^14\), which helps in stabilising sensor responses. Hence, the application of microwires as fuel cell electrodes has potential benefits in terms of stability of power output and has been employed, for example, in PtCu alloy electrocatalyst testing\(^15\). In this report, we present a rapid method of cleaning and annealing commercial platinum microwires using electrothermal treatment. It is shown that platinum can be made more active towards the oxidation of glucose in pH 7 phosphate buffer media and that a combination of two microwires, one annealed and one not, immersed into the same solution can be employed to generate power.
6.2 – Experimental

6.2.1 – Chemical Reagents

Phosphoric acid (H₃PO₄, 85 %), sulphuric acid (H₂SO₄, 95-98 %), sodium hydroxide (NaOH, 98 %), D-(+)-glucose and hydrochloric acid (HCl, stabilised at a concentration of 1 mol dm⁻³) were obtained from Sigma Aldrich UK. Commercial platinum wire of 25 µm diameter was purchased from Advent Materials UK. All chemicals were used as received without further purification. Solutions were prepared using purified water with a resistivity of not less than 18 MΩ cm at 22 °C. Aqueous 0.1 M phosphate buffer solutions were prepared to pH 7. Argon gas was purchased from BOC UK (Pureshield).

6.2.2 – Instrumentation

Electrochemical experiments were carried out using a conventional three electrode configuration, using a KCl-saturated calomel reference (SCE) electrode, a platinum wire counter electrode and a laminated 25 µm diameter platinum microwire as the working electrode prepared as reported previously[14]. Electrochemical measurements were performed using an Ivium Compactstat (Netherlands) at room temperature, 22 ± 1 °C. Electrothermal annealing of the microwire electrodes were performed using an ISO-Tech IPS1603D power source. Copper tape was applied to the end of wires to improve connections (Fig. 6.1). If not stated otherwise, all solutions were purged for 10 minutes using Ar gas prior to performing electrochemical measurements. Scanning electron micrographs were obtained on a JEOL JSM6310 SEM.

6.2.3 – Procedures I.: Electrode Fabrication and Annealing

Fabrication of the microwire electrodes was carried out according to a previously reported method[14], using 25 µm diameter platinum wire and commercial lamination foil with an individual sheet thickness of 125 µm. Electrothermal annealing of the platinum microwires was achieved by passing a current of 0.3 A (to give orange glow or approximately ~1000 K) through a set length wire of approximately 6 cm for either
1 s, 10 minutes, or 4 h before lamination and use in experiments. Electrochemical cleaning of the platinum microwires was achieved by potential cycling at with a scan rate of 0.5 V s\(^{-1}\) from -0.5 to +1.3 V vs. SCE for 35 cycles in aqueous 0.5 M H\(_2\)SO\(_4\).

**Figure. 6.1.** Schematic drawing of the assembly of the platinum microwire (after annealing) into lamination foil to allow a 3 cm long section to be exposed to solution.

### 6.2.4 – Procedures II.: Glucose Micro-Fuel Cell Fabrication

A glass cylinder of length 3 cm and an internal diameter of approximately 5 mm was prepared from a glass pipette. The as-received platinum microwire and the electrothermally annealed (at 0.3 A for 1 s) platinum microwire were attached to the inside of the glass cylinder at opposite sides using silicone sealant (Ambersil, Silicoset 150). The bottom of the glass cylinder was then was sealed and solution were filled in to 2 cm height. A potentiostat was employed to read out point-by-point the steady state current as a function of applied potential.

### 6.3 – Results and Discussion

#### 6.3.1 – Effects of Electroannealing on Surface Area and Faceting

The characterisation of commercial platinum wire before and after electrothermal annealing was first carried out using scanning electron microscopy imaging (SEM). The commercial platinum wire (Fig. 6.2(A) and 6.2(B)) displays a rough surface morphology with vertical crevices all following the same direction along the wire, that
were likely formed from the mechanical process during production (temper hard, 99.99%). After electrothermal annealing at 0.3 A for 1 s (Fig. 6.2(C) and 6.2(D)), smooth surface features are observed along with crystal outline or “step” like features, indicating the formation of larger atomic terraces of lower surface energy and the progression towards a more monocrystalline structure. This trend is very clear for 4 h annealed samples (Fig. 6.2(E) and 6.2(F)). By comparison, simple electrochemical cleaning by potential cycling did not significantly affect the morphology.

Figure 6.2. Scanning electron micrographs (SEMs) of (A, B) a commercial platinum wire (temper, hard), (C, D) a 1 s electrothermally annealed, and (E, F) a 4 h electrothermally annealed platinum wire (annealing current 0.3 A over 6 cm length).
Electrochemical characterisation of the commercial platinum wire before and after electrothermal annealing at 0.3 A for 1 s was conducted in 0.5 M H$_2$SO$_4$ (Fig. 6.3). Voltammetric data for a platinum wire that has been electrochemically cleaned by voltammetric cycling is also shown. All three wires exhibit characteristic polycrystalline platinum features in acid, with platinum surface oxidation (between ca. +0.40 V and +1.25 V vs. SCE) and the hydrogen underpotential deposition (HUPD) region (between ca. +0.10 V and -0.25 V vs. SCE) clearly observed. The pair of peaks at ca. -0.15 V vs. SCE are associated with Pt (110) sites (or more accurately, defects that are the junction of two (111) planes, i.e. (111)×(111), which is actually equivalent to a "(110)" step), whilst those at ca. -0.10 V vs. SCE indicate Pt (100) (or more accurately, defect sites due to the junction of a (111) and (100) plane, i.e. (111)×(100) steps)$^{[16][17][18]}$.

After electrothermal annealing for 1 s, three observations are evident: (i) the total current associated with HUPD has decreased, (ii) the Pt (111)×(100) signal has become more predominant over the Pt (111)×(111) signal and (iii) there is a feature just positive of the (111)×(100) sites from 0.0 to +0.15 V vs. SCE that can be identified as being associated with (100) sites. The electrochemical cleaning of the as-received wire has the effect of increasing the sharpness of the HUPD peaks, indicative of removal of contaminants. The electrochemically cleaned sample also has a much smaller population of (100) sites but still significant (111)×(100) steps, consistent with all terrace order being disrupted by potential cycling into the oxide region.
Figure 6.3. Cyclic voltammograms (scan rate (i) 20, (ii) 200 and (iii) 500 mV s\(^{-1}\); in 0.5 M H\(_2\)SO\(_4\) under argon) for a 25 µm diameter platinum microwire (A) as received, (B) after electrothermal annealing at 0.3 A for 1 s, and (C) electrochemically cleaned for 35 cycles in 0.5 M H\(_2\)SO\(_4\). (D) Bar graph of the estimated charge from electrochemical measurements of Q\(_{H}\) for Pt(111)×(111) and Q\(_{H}\) Pt (111)×(100) for increasing annealing times.
Integrating the charge under the curve for the HUPD regions associated with the Pt(111)×(111) and Pt(111)×(100) sites, and using the corresponding approximate conversion factors (210 µC cm⁻²¹⁹), it is possible to estimate the active electrochemical area (ESA) of the platinum wire as a function of associated crystallographic plane (Table 6.1; Fig. 6.3(D)).

However, the geometric surface area for a 25 µm diameter wire of 3 cm length is expected to be 2.3 mm², which suggests that values obtained here are somewhat low, possibly due to insufficient time resolution of the digital potentiostat system.

Furthermore, due to the convolution of the adsorption/desorption peaks in the HUPD region the absolute values for charge associated with Pt(111)×(111) and Pt(111)×(100) are not accurate. However, the approximate ratio of Pt(111)×(100) to Pt(111)×(111) charges provides a useful indication of the relative changes in surface structure as a result of the annealing process.
Table 6.1. Estimated electrochemical charge and surface area data (from cyclic voltammetry data at 500 mVs⁻¹ in 0.5 M H₂SO₄; ESA; assuming Hₐds is 210 µC/cm² [19]) for increasing annealing time at 0.3 A of a commercial platinum wire compared to electrochemical cleaning in aqueous 0.5 M H₂SO₄.

<table>
<thead>
<tr>
<th></th>
<th>Charge under Hₐds region / µC</th>
<th>Charge under Pt(111) × (111) / µC</th>
<th>Charge under Pt(111) × (100) / µC</th>
<th>Ratio Q(111) × (100) / Q(111) × (111)</th>
<th>Charge under (PtOₓ/PtOH) / µC</th>
<th>Ratio Q₀/ Qₜ</th>
<th>ESA / mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemically cleaned Pt</td>
<td>1.08</td>
<td>0.44</td>
<td>0.64</td>
<td>1.4</td>
<td>7.1</td>
<td>6.6</td>
<td>0.51</td>
</tr>
<tr>
<td>Pt wire as received</td>
<td>0.90</td>
<td>0.46</td>
<td>0.44</td>
<td>0.96</td>
<td>6.8</td>
<td>7.6</td>
<td>0.43</td>
</tr>
<tr>
<td>0.3 A 1 s</td>
<td>0.30</td>
<td>0.12</td>
<td>0.18</td>
<td>1.5</td>
<td>4.2</td>
<td>14</td>
<td>0.14</td>
</tr>
<tr>
<td>0.3 A 10 min</td>
<td>0.24</td>
<td>0.07</td>
<td>0.17</td>
<td>2.4</td>
<td>4.0</td>
<td>16</td>
<td>0.11</td>
</tr>
<tr>
<td>0.3 A 4 h</td>
<td>0.20</td>
<td>0.04</td>
<td>0.16</td>
<td>4.0</td>
<td>3.8</td>
<td>19</td>
<td>0.09</td>
</tr>
</tbody>
</table>

With increasing annealing time, (i) the ratio of Pt(111)×(100) to Pt(111)×(111) appears to increase and (ii) the total electrochemically active surface area (ESA) appears to decrease. It is evident that applying a high current through the wire (to generate an orange glow) provides enough thermal energy for significant atomic restructuring of the surface (and bulk) and the energetically favoured Pt(100) crystallographic plane to dominate (either as steps or in the form of terraces). With increasing annealing time, single crystalline regions begin to form, resulting in loss of ESA and causing the microwire to become more brittle.
6.3.2 – Effects of Electroannealing on Glucose Oxidation

Voltammetric data for the oxidation of glucose was obtained in 0.1 M phosphate buffer at pH 7 and under argon using (A) an as-received platinum microwire, (B) an electrothermally annealed microwire, and (C) an electrochemically cleaned microwire (Fig. 6.4). The oxidation of glucose is detected as anodic current signal with onset at -0.46 V vs. SCE very close to the hydrogen adsorption region. For the as-received platinum wire there is no significant oxidation for glucose even with increasing glucose concentrations. This indicates that there is little or no catalytic activity, possibly due to adsorbed species blocking the sites required for glucose oxidation.

After electrothermal annealing at 0.3 A for 1 s; a glucose oxidation signal is clearly observed (Fig. 6.4(B)). The action of thermal annealing for 1 s is enough to burn away any contaminants and adsorbed species to leave behind a clean, active surface. Furthermore, it is known that the Pt(100) surface is the most active toward glucose oxidation[20], which is enhanced after electrothermal annealing. A similar effect is observed for the electrochemically cleaned platinum microwire electrode (Fig. 6.4(C)) where a comparable activity for glucose oxidation is observed. This is an interesting observation in that the ESA of the electrothermally annealed wire is approximately four times smaller than the electrochemically cleaned wire, which suggests a trade-off between increasing site-specific activity and decreasing total surface area.

Chloride anions have been shown to compete with the binding of glucose on reactive platinum surfaces. Chloride therefore often acts as inhibitor for glucose oxidation except for processes at some modified platinum materials[21]. Figure 6.4(D) demonstrates the dramatic effect of the addition of 0.1 M NaCl into the solution. The glucose oxidation signal is immediately suppressed and so the oxidation of glucose prevented.
Figure 6.4. (A-C) Cyclic voltammograms (scan rate 200 mV s$^{-1}$) for oxidation of 4 mM glucose in 0.1 M phosphate buffer pH 7 using (A) an as-received platinum microwire (B) an electrothermally annealed platinum microwire (0.3 A, 1 s), (C) an electro-chemically cleaned platinum microwire (after 35 cycles at 500 mV s$^{-1}$ in 0.5 M $\text{H}_2\text{SO}_4$). (D) Comparison of cyclic voltammograms (scan rate 20 mV s$^{-1}$) for oxidation of 4 mM glucose at an electrothermally annealed platinum microwire (0.3 A, 1 s) in (i) the absence, and (ii) in the presence of 0.1 M NaCl. (E) Plot of glucose oxidation peak current (scan rate 200 mV s$^{-1}$) versus glucose concentration for two types of electrodes (error bars calculated from an average of three repeats).
When using a SCE reference electrode in neutral phosphate buffer, small traces of chloride leak into solution and over time will “fully poison” the surface of the platinum electrode. This can be observed at low scan rates where the signal for glucose oxidation is reduced. The inhibition effects of slow chloride poisoning can be partially avoided by increasing the scan rate to 200 mV s⁻¹, where an increase in the glucose oxidation signal is achieved as the platinum oxide later is removed and “fresh” platinum, free from chloride poisoning, is formed when scanning from positive to negative potentials. The similarity in reactivity of the 1 s electrothermally annealed electrode and the electrochemically cleaned electrode can be demonstrated when comparing the glucose oxidation current as a function of glucose concentration. Figure 6.4(E) shows a plot with both types of electrodes showing increasing current versus glucose concentration and beginning to plateau at approximately 10 mM. Although it is clear that electrochemical cleaning and electrothermal annealing are equally beneficial in terms of improving the catalytic activity of as-received Pt microwires, the protocol for the electroannealing process is fast and convenient when compared to the electrochemical cleaning process in sulfuric acid.

6.3.3 – Effects of Electroannealing on Oxygen Reduction

The reduction peak signal at +0.02 V vs. SCE (Fig. 6.4) is associated mainly with the conversion of surface oxidised platinum species back to platinum metal. However, at similar potentials the reduction of oxygen can also be observed. Figure 6.5 shows voltammetric data comparing (A) an as-received platinum microwire, (B) an electrothermally annealed, and (C) an electrochemically cleaned microwire electrode in 0.1 M phosphate buffer with ambient levels of oxygen (ca. 0.2 mM). The reduction peak appears increased when compared to data in Figure 6.4 and for voltammetric signals recorded at slower scan rate a clear step-feature consistent with the steady reduction response for oxygen are observed. All three electrodes show similar peak features and mass transport-limited currents for oxygen reduction although the oxide reduction peak feature for the electrothermally annealed electrode appears to be most pronounced. Whilst a full analysis of the oxygen reduction kinetics is beyond the scope of this paper, it can be concluded that all three electrodes are similarly active towards oxygen reduction.
Figure 6.5. Cyclic voltammograms (scan rates of (i) 20 (ii) 50 (iii) 100 and (iv) 200 mV s$^{-1}$) for reduction of ambient oxygen in 0.1 M phosphate buffer pH 7 using (A) an as-received platinum microwire, (B) an electrothermally annealed platinum microwire (0.3 A, 1 s), and (C) an electrochemically cleaned platinum microwire (35 cycles at 500 mV s$^{-1}$ in 0.5 M H$_2$SO$_4$).
6.3.4 – Membrane-less Oxygen-Glucose Micro-Fuel Cell

In order exploit the differences in reactivity observed for the electrothermally annealed *versus* the as-received platinum microwire electrode, we investigate the spontaneous power generation of the two microwires immersed in 0.1 M phosphate buffer at pH 7 in the presence of glucose. As concluded from section 6.3.2, the as-received platinum electrode is not able to oxidise glucose, whilst electrothermal annealing clearly activates the electrode towards this reaction. This catalytic asymmetry coupled with the oxygen reduction activity of both electrodes results in a measurable potential difference and in practice a zero current potential of typically 90 mV is observed (Fig. 6.6(A)).

When varying the potential applied between the two electrodes away from the equilibrium value currents are observed. Fig. 6.6(A) summarises the point-by-point measured current data and three reaction zones are clearly distinguished. At all negative potentials and at potential positive of +90 mV, current and potential exhibit opposite signs and therefore energy is consumed. Only in the middle section from 0 mV to 90 mV is a zone of energy production observed.
Figure 6.6. (A) Current versus potential plot for two platinum microwires (one as-received and one electroannealed for 1 s) immersed into (i) 0.125 M and (ii) 1.0 M glucose in 0.01 M phosphate buffer at pH 7 (average taken over three readings). (B) The associated power output for (i) 0.125 M and (ii) 1.0 M glucose in 0.01 M phosphate buffer at pH 7 (error bars for three repeats). Line (iii) shows a theory line based on the assumption that simple Tafel behaviour prevails (see text). (C) Schematic drawing of Tafel lines for the two platinum microwire electrodes to demonstrate the fundamental origin of the power output. (D) Variation of maximum power output at 50 mV with increasing glucose concentration in 0.01 M phosphate buffer pH 7. The inset shows a schematic drawing of the two proposed electrode reactions.

Plots of power output are shown in Figure 6.6(B), which exhibit a maximum at approximately +50 mV. The schematic Tafel plot in Figure 6.6(C) can be used to better explain the observed behaviour. Zero current points $\eta_1$ and $\eta_2$ are indicated for the two types of electrodes (assuming similar reactivity to oxygen). The Tafel lines
for oxygen reduction at electrode 1 and 2 are denoted \( O_1 \) and \( O_2 \), and those for glucose oxidation are denoted \( G_1 \) and \( G_2 \). Current flow during power generation is indicated by two arrows associated with a change in overpotential \( \Delta \eta_1 \) and \( \Delta \eta_2 \). The magnitude of oxygen reduction current (at the as-received electrode) and the glucose oxidation current (at the electrothermally annealed electrode) need to be equal and therefore the oxygen reduction process associated with \( \Delta \eta_2 \) is the dominating process.

In order to compare theory and experiment more quantitatively the relevant processes indicated here as \( O_1/O_2 \) and \( G_1/G_2 \) (see Fig. 6.6(D)) can be expressed under open circuit conditions in terms of the corresponding Tafel laws (equations 6.1 – 6.4).

\[
\log I_{O_1} = a_{O_1}(\eta_1) + b_{O_1} \quad [6.1]
\]

\[
\log I_{O_2} = a_{O_2}(\eta_1) + b_{O_2} \quad [6.2]
\]

\[
\log I_{G_1} = a_{G_1}(\eta_1) + b_{G_1} \quad [6.3]
\]

\[
\log I_{G_2} = a_{G_2}(\eta_1) + b_{G_2} \quad [6.4]
\]

The symbols \( a \) and \( b \) denote Tafel parameters. Values for \( \eta_1 = \frac{b_{G_1} - b_{O_1}}{a_{O_1} - a_{G_1}} \) and \( \eta_2 = \frac{b_{G_2} - b_{O_2}}{a_{O_2} - a_{G_2}} \) can be obtained from the Tafel parameters. Under conditions of power output, the currents \( I_{O_2} \) and \( I_{G_1} \) are directly associated with oxygen reduction at the as received electrode and glucose oxidation at the electrothermally annealed electrode (equations 6.5 and 6.6).

\[
\log I_{O_2} = a_{O_2}(\eta_2 - \Delta \eta_2) + b_{O_2} \quad [6.5]
\]

\[
\log I_{G_1} = a_{G_1}(\eta_1 - \Delta \eta_1) + b_{G_1} \quad [6.6]
\]

The balance of currents between anode and cathode can now be expressed as \( I_{O_2} - I_{O_2}^0 = I_{G_1} - I_{G_1}^0 \). where the superscript 0 is used to indicate zero net current conditions with \( \Delta \eta_1 = \Delta \eta_2 = 0 \). Although the resulting equation cannot be solved analytically, it is possible to express \( \Delta \eta_1 \) as a function of \( \Delta \eta_2 \) (equation 6.7).
\[ \Delta \eta_1 = \frac{1}{a_{o1}} \log[10^m - 10^j + 10^q] \quad [6.7] \]

Here, \( m = a_G (\eta_2 - \Delta \eta_2) + b_G, \quad j = b_G, \quad q = b_{o1}. \)

It is then possible to calculate the potential difference between anode and cathode as \( \Delta E = (\eta_2 - \Delta \eta_2) - (\eta_1 + \Delta \eta_1). \) The corresponding current is obtained either from equation 6.5 or 6.6. The behaviour of the theoretical output is dominated by the oxygen reduction kinetics (as shown in Fig. 6.6(C)) and \( \Delta \eta_2 \) has to be significantly higher compared to \( \Delta \eta_1. \)

With realistic values (i.e. a Tafel slope of 118 mV for all processes) and adjusting the \( b \) constants to match the experimentally observed 90 mV open circuit potential, a very good match of theory and experiment is achieved (see power plot in Fig. 6.6(B)). From this it can be concluded that in aqueous 1.0 M glucose in 10 mM phosphate buffer pH 7 the rate for glucose oxidation at “as received” platinum is 33 times slower compared to that at electroannealed platinum. This result is consistent with data observed with voltammetry (see Fig. 6.4(A) and 6.4(B)).

Figure 6.6(D) shows the maximum power output as a function of glucose concentration and it can be observed that a plateau is reached with 2 nW cm\(^{-2}\) at \( ca. \) 0.5 M glucose probably indicative of saturation of the catalyst surface. Improvements of this system may be possible by changing the relative area of anode and cathode and by further modifying the catalytic behaviour (e.g. Tafel parameters). For realistic devices the effects of catalyst poisoning would also need to be considered.
6.4 – Summary and Conclusion

A simple electro-annealing cleaning procedure has been devised to rapidly clean a platinum microwire. Based on voltammetric data, a one-second treatment has been shown to be as effective as prolonged potential cycling in sulfuric acid, although the electrochemically active surface area (ESA) and surface structure also changed significantly during electrothermal treatment.

Nevertheless, good electrocatalytic activity towards glucose oxidation in pH 7 phosphate buffer is observed and a very simple “membrane-free” micro-fuel cell concept has been proposed based on a combination of an as-received and an electro-annealed platinum microwire. Differences in reactivity cause a net glucose oxidation process at the electro-annealed microwire anode and a net oxygen reduction process at the as-received platinum microwire cathode. Due to excess glucose in the solution the energy penalty of removing oxygen at the anode can be accepted and the energy output can be shown to be proportional to glucose levels.

The power versus potential profile has been shown to be dominated by the oxygen reduction kinetics. Realistically, for practical applications better catalysts are required and poisoning of the platinum (for example by chloride and proteins) would have to be taken care of and the power output would have to be significantly improved.
6.5 – References

Chapter 7

Residual Porosity of 3D-LAM-Printed (Laser Additive Manufacturing) Stainless-Steel Electrodes Allows Galvanic Exchange of Platinisation

Chapter Abstract

Laser additive manufacturing (LAM, and also commonly referred to as “3D-printing”) was used to produce stainless steel (316L) rods from a powder precursor composition. Particles of an average diameter between 20–40 μm in the powder precursor were fused together using the laser additive manufacturing method of “powder bed fusion”, producing stainless steel rods of 3 mm diameter.

In this chapter, the stainless steel rods were investigated electrochemically and compared to conventional stainless steel. When immersed in neutral aqueous phosphate buffer solution, the 3D-printed steel electrodes exhibited voltammetric features that were similar to the conventional bulk stainless steel (316L), with Fe(II/III) phosphate and Cr(II/III) phosphate observed as two reversible surface processes. Small crevices on the surface of the 3D-printed electrodes allowed galvanic exchange of platinum with greater growth and adhesion to the surface, in contrast to the conventional stainless steel (316L) electrodes.

After galvanic exchange, a porous platinum deposit was formed on the 3D-printed stainless steel electrode, which displayed high activity, mechanical robustness and good catalytic activity towards methanol oxidation.

Chapter Publications

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7 – Residual Porosity of 3D-LAM-Printed (Laser Additive Manufacturing) Stainless-Steel Electrodes Allow Galvanic Exchange of Platinisation

7.1 – Laser Additive Manufacturing (LAM)

Laser additive manufacturing, LAM\textsuperscript{[1][2]} (a type of 3D-printing\textsuperscript{[3]}), is a useful tool for the ability to manufacture prototype devices on a small scale production with complex, high precision using novel composite materials. 3D parts are fabricated by a laser beam which melt and solidifies plastic, ceramic, metallic or composite powder materials in a layer-by-layer growth fashion (Fig. 7.1\textsuperscript{[4]}), with alloys and highly novel composites (e.g. metal-diamond) being used in the LAM manufacturing\textsuperscript{[5]}.

![Figure 7.1. Schematic drawing of the laser additive manufacturing (LAM) process based on a powder flow (median diameter 31 μm) through a delivery nozzle with a laser (200 W continuous wave yttrium fibre laser source operating at 1070 nm wavelength) producing film deposits under nitrogen atmosphere.](image)
The production scale of LAM technologies range from; individual prototypes up to thousands of pieces. Products made using LAM technology are used in industrial applications due to the ability to manufacture items at an intricate level with high precision. Complex channel networks designed for heating, mixing and cooling, have been fabricated using LAM processes since the cost for conventional manufacturing of the complex structures is considerably more expensive than using LAM technologies\[6\].

There is a growing interest in the use of 3D-printing techniques in chemistry\[7\], as well as in electrochemistry\[8\]. Where conventional lithography allows ease of access to produce planar structures, such as generator-collector electrode pattern\[9\], 3D-printing allows the ability to produce highly complex structures with complete control over the third spatial dimension, leading to the printing of complete devices. Over recent years, many forms of 3D-printing have been developed, for example on hot nozzle extrusion\[10\], “bio-printing”\[11\], ink jetting\[12\], and on laser-aided techniques\[13\]. Recently, a stainless steel micro-fuel cell (MFC) was made by LAM as reported by Scotti et al.\[14\]. The outcome of the report was that the performance of the micro-fuel cell can scale with the lengthening/optimisation of the flow field, which is important in micro-fuel cell applications intended to power mobile devices. Structures with sub-millimetre flow channels were shown to be converted from computer-aided design to a practical device quickly. Although the potential for the application of LAM (and 3D-printing\[15\]) within the electrochemical sciences is apparent, relatively few examples of the fabrication of novel electrode materials actually exist\[16\].

Stainless steel (316L), composed mostly of Fe (62 wt%), Cr (17-19 wt%), (Ni 13-15 wt%), and smaller amounts of Mo, Mn, Si, and Cu, has been used in industrial applications for oil and gas pipelines, as a material for counter electrodes\[17\] as well as being tested for applications in photo-electrochemical water splitting\[18\]. As the surface of stainless steel is not electrochemically active, modification of the surface can be achieved using catalytic materials such as platinum group metals. While this enhances the catalytic reactivity of the surface, for example in fuel cell applications, the interaction of catalytic materials with stainless steel surfaces has been of interest, for example also in corrosion protection\[19\].
Galvanic replacement has been used previously as a route to noble metal catalyst deposition to produce core-shell iron-rich Fe-Pt nanoparticles for heterogeneous catalysis\cite{20} as well as platinum nano-materials for fuel cell catalysis\cite{21}. Formation of the more noble Pt drives the deposition process, whilst dissolving Fe. Pt nanocatalysts have been produced by using galvanic exchange deposition of metallic iron nanoparticles in carbon nanotubes\cite{22}. Cu and Pb surfaces have also been used in galvanic replacement\cite{23}, however, there are currently no reports for the galvanic exchange to deposit catalytic platinum directly onto stainless steel (316L) electrode surface.

The electrochemical properties of 3D-printed stainless steel and its facile surface modification with a platinum catalyst via galvanic replacement are reported in this chapter. Promoted adhesion of the platinum deposit to the stainless steel substrate is shown to be a result of residual porosity in 3D-printed steel and the method of galvanic replacement offers a simple route to platinum-coated stainless steel (3D-printed) electrodes. The modified stainless steel electrodes show good reactivity towards the oxidation of methanol for potential applications in direct methanol micro-fuel cell devices.

7.2 – Experimental Details

7.2.1 – Chemical Reagents

Hexachloroplatinic(IV) acid (H$_2$PtCl$_6$) and methanol (MeOH, 99.8 %) were obtained from Fisher Scientific and were used without further purification. Hydrochloric acid (HCl, stabilised at a concentration of 1 mol dm$^{-3}$) and sulphuric acid (H$_2$SO$_4$, 95-98 %) were obtained from Sigma Aldrich UK and were used as received. Stainless steel (316L), nickel, and nickel-chromium 20-80 metal rods of 2 or 3 mm diameter were obtained from Advent UK. Purified water, with a resistivity of not less than 18 MΩ cm at 22°C, was used for the preparation of solutions. Argon gas (Ar) and nitrogen gas (N$_2$) were purchased from BOC UK (Pureshield).
7.2.2 – 3D-LAM of Stainless Steel (316L) Rods

The laser additive manufacturing (LAM) method employed here for stainless steel 316L has been reported in detail recently[14]. Stainless steel powder (with typically 20-40 μm diameter particles) are supplied layer-by-layer via recoater and a 200 W laser (near-IR 1070 nm) is applied to melt material under an atmosphere of nitrogen (Fig. 5.1). A custom-built positioning system is employed to translate computer aided design structures into printed objects.

7.2.3 – Instrumentation

A conventional three electrode cell set-up was employed for electrochemical measurements, using a KCl-saturated calomel reference (SCE) electrode, a Pt wire counter electrode and a 3D-printed stainless steel rod (316L grade) as the 3 mm diameter working electrode. Electrochemical experiments were carried out at room temperature, 22 ± 2 °C, using an Ivium Compactstat (Ivium, Netherlands). All solutions were purged for 10 minutes using argon prior to performing electrochemical measurements.

7.2.4 – Procedure for Galvanic Exchange Deposition of Platinum on Stainless Steel

One end of the stainless steel rod was polished using P600 grade silicon carbide paper (Buehler) to produce a clean and slightly roughened surface, which was then rinsed with deionised water. Silicone sealant (Ambersil, Silicoset 150) was applied to the sides of the stainless steel rod to define a 3 mm diameter disc electrode. Galvanic exchange of platinum was achieved by immersion of the electrode into a solution of 2 mM hexachloroplatinic(IV) acid in 1 M HCl for 24 h at room temperature. After this treatment, the electrode was rinsed with deionised water and dried under N₂ gas. The process was repeated with a conventional 3 mm diameter stainless steel rod (316L) (Advent UK) for comparison.
7.3 – Results and Discussion

7.3.1 – Characterisation of 3D-LAM-Printed Stainless Steel

Scanning electron microscopy (SEM) was carried out to characterise the surface of the 3D-printed stainless steel electrode (Fig. 7.2). The SEM image shows the surface morphology to be dense and compact and the appearance is similar to conventional stainless steel, with scratch-like features observed resulting from the polishing treatment carried out. Dark areas are seen in the SEM image (Fig. 7.2(A)) which are not seen on the conventional stainless steel and indicate minor crevices that were likely formed from the laser annealing process and resulting in residual porosity.

Figure 7.2. SEM images of 3D-printed stainless steel after polishing. Images recorded at (A) 1000 × and (B) 10000 × magnification.
Using the 3 mm diameter 3D-printed stainless steel electrodes, cyclic voltammetry experiments were carried out in argon-purged 0.1 M phosphate buffer solution at pH 7 (Fig. 7.3). Two prominent redox processes are observed, with oxidation and reduction peaks that are indicative of chemical reversibility.

Figure 7.3. (A) Cyclic voltammograms (scan rate (i) 10, (ii) 20, (iii) 50, (iv) 100, and (v) 200 mVs⁻¹) for a bare 3 mm diameter 3D-printed stainless steel electrode immersed in 0.1 M phosphate buffer at pH 7 under argon. (B) As above, but (i) under argon, (ii) in ambient air, (iii) with 6 mM H₂O₂. (C) As above, with 6 mM H₂O₂ and with a scan rate of (i) 10, (ii) 20, (iii) 50, (iv) 100, and (v) 200 mVs⁻¹).

Process 1 is centred around -0.4 V vs. SCE (with a peak-to-peak separation of ca. 200 mV at scan rate 200 mVs⁻¹) and can be identified (by comparison with literature data
as a Fe(II)/Fe(III) type process associated with the iron phosphate material at the stainless steel – solution interface (equation 7.1).

\[ \text{Process 1: } \text{Fe(II)} \leftrightarrow \text{Fe(III)} + e^- \quad [7.1] \]

Process 2 is centred around +0.4 V vs. SCE (with a larger peak-to-peak separation of \( \text{ca.} \ 600 \ \text{mV} \)) and is likely to be associated with Cr(II)/Cr(III)\(^{25}\) (equation 7.2), rather than the presence of nickel phosphate material at the stainless steel | solution interface (see for example ref\(^{26}\)). To confirm the tentative assignment of process 2 as Cr(II)/(III) instead of Ni(II/III), additional experiments using nickel and nickel-chromium metal electrodes under the same experimental conditions were performed (not shown).

\[ \text{Process 2: } \text{Cr(II)} \leftrightarrow \text{Cr(III)} + e^- \quad [7.2] \]

The peak currents of both redox couples increased approximately linearly with scan rate, consistent with surface immobilised redox processes (or with a thin film of redox active phosphate-based material). The reduction of oxygen only occurs at very negative potentials, beyond of the potential for the formation of Fe(II) when comparing the voltammetric responses under argon, and in the presence of ambient air (Figure 7.3(Bi) and 7.3(Bii)). Upon the addition of hydrogen peroxide, the Fe(II)/Fe(III) redox system acts as a catalyst (Fig. 7.3(Biii)). The Fe(II)-catalytic reduction occurs at mildly negative potential and before the reduction of oxygen. This process is indicative of a two-electron reduction reaction of hydrogen peroxide to water at the surface of the stainless steel electrode.

The effect of scan rate in the presence of 6 mM H\(_2\)O\(_2\) (Fig. 7.3(C)) was investigated. It was observed that the chemically reversible response for Fe(II)/Fe(III) is enhanced in comparison to Cr(II)/Cr(III). Using a conventional 3 mm diameter stainless steel electrode, the same electrochemical measurements were performed and it was found that identical voltammetric responses were observed (not shown). This confirmed that the 3D-printed stainless steel electrode could be used instead of conventional stainless steel for electrochemical measurements.
7.3.2 – Surface Reactivity of 3D-Printed Stainless Steel After Galvanic Exchange Platinisation

Under galvanic conditions, formation of catalytically active platinum occurred spontaneously on the surface of the 3D-printed stainless steel electrode\(^{[20][21]}\). Since iron is the most electropositive metal component within stainless steel, a reaction linking the dissolution of iron to platinum deposition occurs, with chloro complexes of these species formed (equation 7.3).

\[
2 \text{Fe}(0) + \text{Pt}(IV) \rightleftharpoons 2 \text{Fe}(II) + \text{Pt}(0) \quad [7.3]
\]

The scanning electron micrograph (Fig. 7.4(A)) of platinum deposit using the galvanic replacement show a uniform nano-sized cauliflower-shaped platinum growth over the stainless steel surface. After 24 h growth, the estimated thickness of the film from crevices (Fig. 7.4(B)) was in the order of 10 \(\mu\)m.

Platinum films were also obtained at conventional stainless steel surfaces, but with poor adhesion. These films delaminate and disconnect from the electrode surface when rinsing with water, or transferring into other electrolyte media. In contrast, platinum films on 3D-printed stainless steel substrates are mechanically robust (presumably due to the residual porosity in 3D-printed stainless steel) and can be used in electrochemical applications.
Figure 7.4. (A) Scanning electron optical image for pristine 3D-printed stainless steel after 24 h galvanic replacement with platinum. (B,C) Scanning electron optical images for “aged” 3D-printed stainless steel after galvanic replacement with platinum and 150 potential cycles in 0.5 M H₂SO₄. Images recorded at (B) 1000 × and (C) 10000 × magnification.
The electrochemical behaviour of the 3D-printed stainless steel surface changes significantly in the presence of the platinum deposit. Voltammetric data (Fig. 7.5) shows the characteristic platinum surface signals in 0.5 M H₂SO₄. The platinum surface oxidation region (ca. +0.4 V to +1.1 V vs. SCE) and the hydrogen underpotential deposition region (ca. +0.1 V to -0.3 V vs. SCE) are clearly recognised.

![Cyclic voltammogram](image)

**Figure. 7.5.** (A) Cyclic voltammogram (scan rate 20 mVs⁻¹) for a platinum coated 3 mm diameter 3D-printed stainless steel electrode immersed in argon-purged 0.5 M H₂SO₄ with oxide and hydrogen adsorption regions indicated. (B) As above, but with a scan rate of (i) 10, (ii) 20, (iii) 50, (iv) 100, and (v) 200 mVs⁻¹.

The electrochemical surface area (ESA) for the active platinum was calculated at 0.52 cm², using the charge under the oxide region (Qₒ = 0.15 mC) or the hydrogen region (Qₕ = 0.11 mC) and using the corresponding conversion factors (0.21 mC cm⁻² was used as the conversion factor²⁷²⁸). A roughness factor of 7.4 is calculated and is consistent with the appearance of the scanning electron micrographs.
Comparison with data obtained with a 3 mm platinum disk electrode (Table 7.1) demonstrates the similarity between galvanically exchanged and pure platinum.

**Table. 7.1.** Measured electrochemical properties of platinised stainless steel electrode in aqueous 0.5 M H₂SO₄ (scan rate 20 mVs⁻¹). For comparison, data obtained for a 3 mm diameter Pt disk electrode (*) under the same conditions are shown in the second row.

<table>
<thead>
<tr>
<th>Q₉₇[a] / mC</th>
<th></th>
<th>Q₀[b] / mC</th>
<th>Electrochemically Active Surface Area (ESA) / cm²</th>
<th>Current Density for MeOH oxidation / mA cm⁻²</th>
<th>Roughness Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td></td>
<td>0.15</td>
<td>1.4</td>
<td>0.52</td>
<td>13.40</td>
</tr>
<tr>
<td>0.08*</td>
<td></td>
<td>0.10*</td>
<td>1.3*</td>
<td>0.38*</td>
<td>0.08*</td>
</tr>
</tbody>
</table>

[a] Charge under H₉adsorption.  [b] Charge under (PtOₓ/PtOH)₉desorption.

A slow degradation of the platinum signal is observed (not shown), when the platinised stainless steel electrode was cycled for prolonged periods of time, at 200 mVs⁻¹ for 150 cycles, with approximately 20 % loss of active area. The mechanism for this slow decay could be linked to changes at the underlying stainless steel electrode. SEM images of the “aged” platinum surface after continuous cycling shows stress arising in the platinum coating (Fig. 7.4(B) and 7.4(C)) resulting in cracking and fracturing of the film which is indicative of effects from some corrosion of stainless steel underneath the platinum film. For future applications of platinum-coated 3D-printed stainless steel electrodes, more milder conditions are required on order to minimise the rate of steel corrosion under the platinum film.
7.3.3 – Catalytic Activity of 3D-Printed Stainless Steel After Galvanic Exchange Platinisation for Methanol Oxidation

Utilising the conditions for galvanic replacement to deposit platinum, the platinum-coated 3D-printed stainless steel electrode can be employed in electrocatalysis, for example the oxidation of methanol to carbon dioxide (equation 7.5), which is a challenging test system relevant to fuel cell applications\[29][30].

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 6 \text{H}^+ + 6 e^- \quad [7.5]
\]

The iron “impurities” within the 3D-printed stainless steel electrodes provide a beneficial role in methanol fuel cells and has recently been highlighted by Antolini\[31]. Voltammetric data for a bare 3D-printed stainless steel electrode immersed in 0.5 M H\textsubscript{2}SO\textsubscript{4} containing 0.2 M methanol (Fig. 7.6(A)) shows no obvious anodic signal associated with the methanol oxidation process. This indicates that the unmodified steel electrode does not exhibit catalytic properties.

In the presence of the platinum coating, significant anodic currents are obtained (Fig. 7.6(B)), with peak features at +0.6 V vs. SCE (on the forward scan) and at +0.4 V vs. SCE (on the reverse scan) are observed and are associated with the oxidation of methanol\[32]. With increasing scan rates, the anodic peak current is relatively independent of the scan rate and is characteristic of a catalytic process with surface-kinetic rate limiting processes. While polishing of the steel electrode removes the platinum and a large majority of the catalytic response is also removed, some platinum remains within the crevices. For complete removal of platinum, very rigorous and sustained polishing is required.
Figure 7.6. (A) Cyclic voltammogram (scan rate (i) 20, (ii) 50, (iii) 100, and (iv) 200 mVs$^{-1}$) for a bare 3 mm diameter 3D-printed stainless steel electrode immersed in 0.5 M H$_2$SO$_4$ containing 0.2 M methanol. (B) As above, but for a platinum-coated 3D-printed stainless steel electrode and scan rates of (i) 10, (ii) 20, (iii) 50, (iv) 100, and (v) 200 mVs$^{-1}$. (C) As above, but for platinum-coated steel at a scan rate of 20 mVs$^{-1}$ and with (i) 0.1, (ii) 0.2, (iii) 0.4, (iv) 0.8, (v) 1.0 M methanol. (D) Plot of methanol oxidation peak current versus methanol concentration (error bars calculated from triplicate measurements).
Well-defined signals are observed at higher methanol concentrations (Fig. 7.6(C)), which are found to increase almost linearly with increasing methanol concentration (Fig. 7.6(D)) and the absence of a peak current plateauing at higher methanol concentrations is indicative of a highly active catalyst.

When normalised to the catalytic current density (by dividing the peak current by the electrochemically active surface area, vide supra), typical catalytic current densities (or specific activities) of 13.4 mA cm\(^{-2}\) are obtained for a 1 M methanol solution (Fig. 7.6(D)). While this value is relatively high, it compares well to typical values reported for good platinum alloy-based methanol oxidation catalysts\(^{[33]}\) (under the same or similar experimental conditions), the specific activity values for bare platinum disc electrodes have been reported to an order of magnitude lower\(^{[27]}\). When employing a 3 mm diameter platinum electrode under the same experimental conditions, a specific activity of only 0.08 mA cm\(^{-2}\) is achieved (Table 7.1).

It is proposed that the good catalytic current observed using the platinised 3D-printed stainless steel is linked to the presence of “iron purities” incorporated during corrosion of the underlying stainless steel electrode. It has been reported previously that the presence of iron as a “dopant” in platinum nanoparticle catalysis can enhance the catalytic activity for ethanol oxidation\(^{[34]}\) and for methanol oxidation\(^{[35]}\). Enhancing the oxidation of formic acid has been achieved using a high level of 50 atom\% in FePt nanoparticles\(^{[36]}\).

The galvanic replacement reaction appears to be driven by iron dissolution as well as some incorporation into the platinum film which leads to enhancement of catalytic activity and a more systematic study of this phenomenon is needed in the future.
7.4 – Summary and Conclusion

The process of 3D-printing stainless steel electrodes allows complex shapes to be manufactured as either patterned surfaces or as compact cells which can be employed for applications in energy generation or sensing. The 3D-printed stainless steel has been shown to be electrochemically active and is consistent with conventional stainless steel (316L) without significant catalytic reactivity towards methanol oxidation.

The galvanic replacement of platinum for iron at the 3D-printed stainless steel surface produces a compact platinum layer that is highly active towards catalysis. The platinum film is relatively robust to prolonged cycling in aqueous acidic solution due to the residual porosity in the 3D-printed steel material increasing the adhesion between the electrode surface and the platinum film (when compared to similar films on conventional stainless steel).

The reactivity of the platinum towards methanol oxidation is good when compared to platinum alloy catalysts and enhanced when compared to conventional platinum catalyst materials. This enhancement is likely to be associated with the presence of mainly iron metal impurities (originating from the stainless steel during galvanic replacement). Further study and exploration of this observation is required for a wider range of catalytic processes.

The 3D-printing and galvanic deposition method described herein has the potential to allow construction of electrochemical devices without the need for complex manufacturing steps. Controlling the residual porosity at the 3D-printed stainless steel surface and adding new components for composite materials and alloys opens up a wide range of new electrode systems to be designed. The use of 3D-printed stainless steel as a low cost electrode substrate could be commercially attractive.
7.5 – References


Chapter 8

Conclusions and Future Work

Platinum is a highly active catalyst for the reduction of oxygen, however, it is susceptible towards poisoning from ions in the electrolyte solution and at high concentrations of electrolyte, the effects of poisoning at more pronounced. The reduction of oxygen is dependent upon its dissolved concentration and its ability to diffuse towards the electrode surface. The electrokinetics of the reduction of oxygen is related to the concentration of dissolved oxygen rather than the activity as is shown here.

For the investigation of oxygen reduction processes, platinum microwire electrodes were fabricated to develop a multi-parameter chronoamperometric method coupled with digital simulation to simultaneously determine the concentration and diffusivity of protons and oxygen in increasing chloride electrolyte concentrations. Data from the digital fitting showed optimised proton concentrations to be within a $\pm 5\%$ error range of the nominal concentration added with the optimised proton diffusion coefficients to be in good agreement with literature values. Slow electron transfer kinetics for the reduction of oxygen was observed due to changes by chloride adsorption at the platinum surface and corresponded to the large errors when optimising the concentration and diffusion coefficients of oxygen at high saline concentrations. A potential area for future work is exploring the effects of coatings on the electrode surface to prevent surface changes by chloride adsorption which could help in reducing the errors for oxygen optimisation. Likewise, increasing the number of repeat measurements to increase the sample size for statistical analysis would further refine the analysis.

The use of a platinum microwire electrode and the ability to achieve quasi-steady state currents was further employed in the analysis of the electrokinetics of catalytically reducing oxygen in high chloride electrolyte concentrations at ambient and high
pressures. Tafel analysis was carried out and showed that the slope of the Tafel region for the reduction of oxygen at increasing chloride concentrations was in close agreement to the literature value of 120 mV dec\(^{-1}\) signifying a characteristic irreversible one-electron transfer. The calculated electron transfer coefficients were found to be consistent at around 0.5 and the exchange currents were found to decrease with increasing salinity. Taking into consideration the concentration of dissolved oxygen in saline solutions, the calculated values for the standard heterogeneous rate constant with increasing chloride concentration were found to remain constant. As the electrokinetics of oxygen reduction is dependent upon the concentration of dissolved oxygen, and the activity of the electrolyte must also remain constant, the concentration of dissolved oxygen must therefore increase. At elevated pressures of 2 and 4 bar oxygen pressure, it was found that the reduction response varied. Significant improvements can be made to the experiment, such as (i) allowing the system to reach full equilibration at pressurising before running the electrochemical measurements, (ii) using a reference electrode specifically designed to withstand high pressures and (iii) maintaining a constant temperature within the pressure cell, which will need to be considered in future experiments.

The effects of polymer of intrinsic microporosity (PIM) coatings on the catalytic reduction of oxygen were investigated on a platinum microwire electrode in increasing chloride electrolyte solutions. Local disruption of chloride ions and water molecules by the PIM coating generated areas suitable for oxygen reduction to take place on the platinum surface causing the onset potential for the reduction of oxygen to be shifted around towards positive potentials in the presence of the PIM coating for increasing chloride concentrations. Through Tafel analysis of the reduction of oxygen, it was found that the PIM coating has no effect on the reduction of oxygen due to the high porosity and rigid molecular structure of the PIM not blocking platinum sites. Cross sectional SEM images of the PIM coating on the platinum microwire are required in order to measure the thickness of the coating and determine if a uniform distribution of the coating is present. Capacitance values with and without PIM coatings were calculated with increasing scan rate in increasing chloride concentration. However, the obtained capacitance values were one order of magnitude smaller than reported literature values and this is likely a result from the
potentiostat rejecting a large amount of the capacitance current during recording of the cyclic voltammograms at high scan rates. By adding a filter between the potentiostat and the electrodes may be able to overcome the large loss of the capacitance current. The PIM coating makes it suitable for applications in stabilising nanocatalyst composites without effecting any electrochemical reactions.

Highly active catalytic platinum microwires were produced using a simple and quick electro-thermal annealing cleaning methodology. The active catalytic electrodes were found to be capable of oxidising glucose in varying concentrations of phosphate buffer. Voltammetric data in sulphuric acid showed that with increasing annealing time, the electrochemically active surface area (ESA) and surface structure significantly changed. It was observed that the calculated ESA was significantly smaller than the geometric area, and was explained by the inability of the potentiostat to sample the current quick enough at high scan rates. Tafel analysis of both the oxidation of glucose and the reduction of oxygen showed that without electro-thermal annealing, the rate of glucose oxidation was 33 times slower. From this, a microfuel cell was constructed using an electro-annealed platinum microwire to oxidise glucose and an as received platinum microwire to reduce oxygen, which produced a power output of 2.2 nW cm\(^{-2}\) in a glucose concentration of 0.5 M. Optimisation of the microfuel cell could be achieved by use of different concentrations of phosphate buffer solutions and varying diameters of platinum microwires used.

Producing electrodes using low-cost manufacturing methods is of great interest and 3D-LAM printing electrochemically active electrodes can be a cost effective way of producing various devices for a wide range of applications. 3D-printed stainless steel electrodes were found to behave as conventional stainless steel electrodes in neutral phosphate buffer solutions. Due to the 3D-LAM printing, residual porosity of the 3D-printed electrodes provided good adhesion of platinum films to the surface when undergoing a simple galvanic exchange between the iron in the stainless steel and a solution of 2 mM platinum. The platinised 3D-LAM printed stainless steel electrodes were found to exhibit high catalytic activity towards the oxidation of methanol in acidic electrolyte solutions, making the methodology of platinisation highly attractive.
for fuel cell applications. Controlling the residual porosity of the 3D-printed stainless steel surface and using various alloys or composite materials allows a wide range of electrodes to be printed easily.

In summary, the electrocatalysis of oxygen in increasingly saline solutions have been investigated to further understand the electrokinetics behind the reduction of oxygen and the effects of high chloride electrolyte solutions. It has been shown that the concentration of oxygen is an important factor in the electrokinetics of reducing oxygen. Platinum microwires have been shown to be effective against viscosity effects at high chloride concentrations, in comparison to conventional hydrodynamic techniques, in achieving quasi-steady state currents during electrochemical measurements. The simple electrode design allows surface modification by dip-coating to be carried out easily in small quantities of solution. A simple two-electrode microfuel cell was fabricated using platinum microwires modified by electro-thermal annealing, which was able to catalyse glucose in neutral buffer solution, producing a small amount of power. A method to producing highly catalytic platinum electrodes was developed, utilising the residual porosity of 3D-LAM-printed stainless steel electrodes. After 24 h immersed in a platinum solution, the modified 3D-LAM-printed electrodes were found to be highly catalytic towards methanol oxidation. The simple galvanic exchange could be used to manufacture methanol fuel cells with high current outputs and a variety of composites and deposits can be investigated.
Appendix A - Postgraduate Record

Papers published


Conferences, Events and Demonstrations

- ESEAC 2016 – 16th Annual Conference (June 2016), Assembly Rooms, Bath. UK. (Talk)
- PG Symposium (May 2016), University of Bath. UK. (Talk)
- Bath Electrochemistry Winter School (January 2016), University of Bath. UK. (Demonstrator)
- ECHEMS (June 2015), Bad Zwischenahn, Germany. (Poster)
- Bath Electrochemistry Winter School (January 2015), University of Bath. UK. (Demonstrator)
- Electrochem (September 2014), Loughborough University. UK. (Poster)
- ECHEMS (July 2014), Wells, Bath. UK. (Poster)
- PG Symposium (May 2014), University of Bath. UK. (Poster)
- MEG Meeting (April 2014), Loughborough University. UK. (Talk)
- Bath Electrochemistry Winter School (January 2014), University of Bath. UK. (Demonstrator)